

Nano-architectures for 3rd generation PEC devices: A study of MoS₂, fundamental investigations and applied research

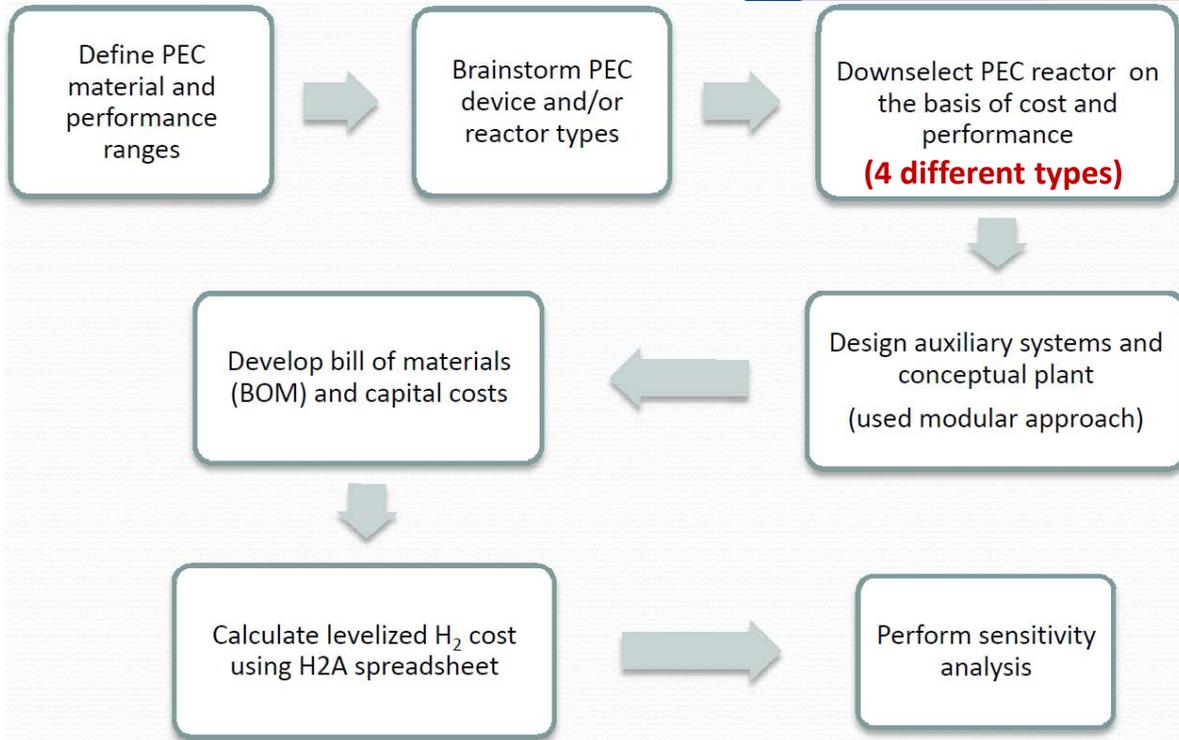
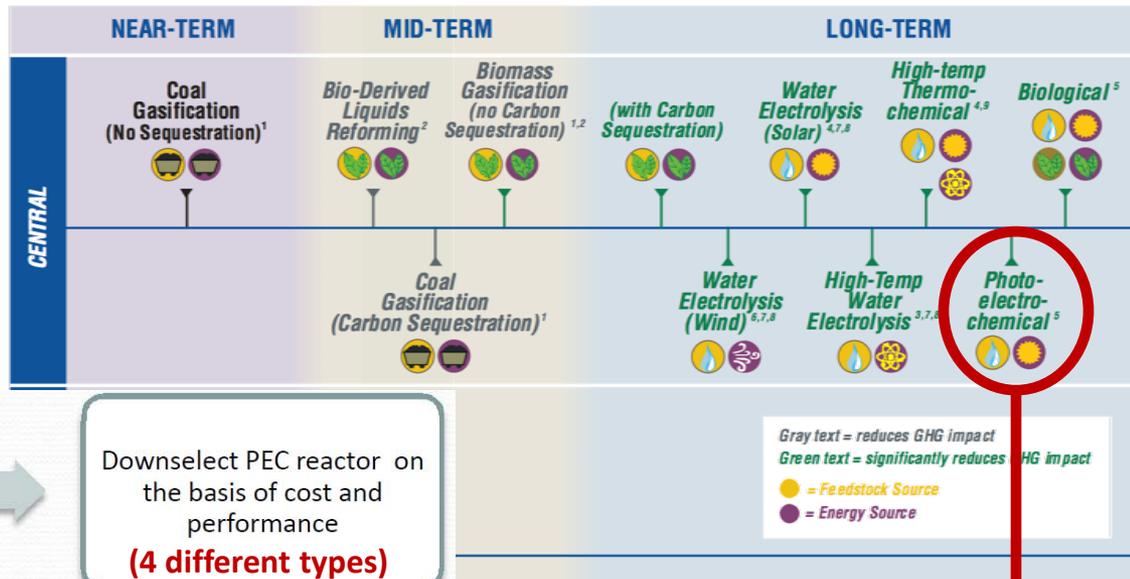
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Stanford University

Project ID: PD033

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The importance of PEC H₂ production

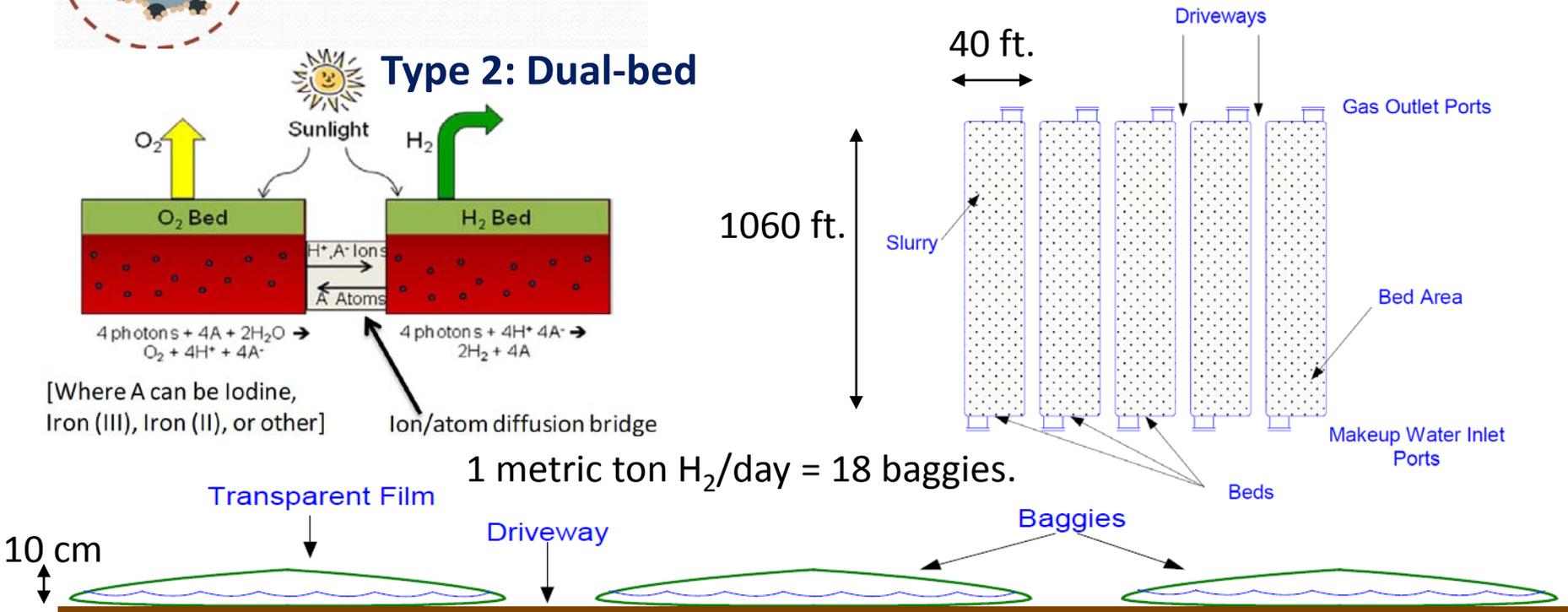
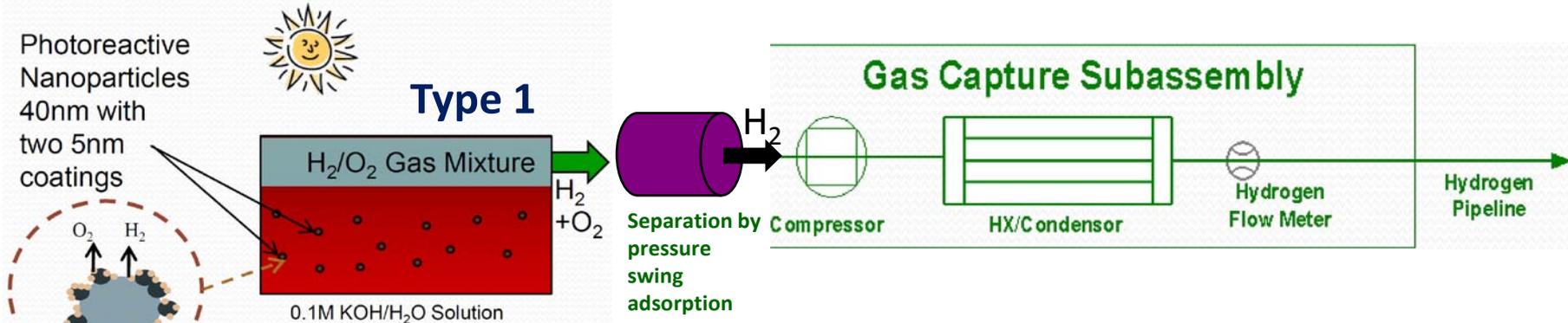
DOE Hydrogen Production Roadmap
http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/h2_production_roadmap.pdf



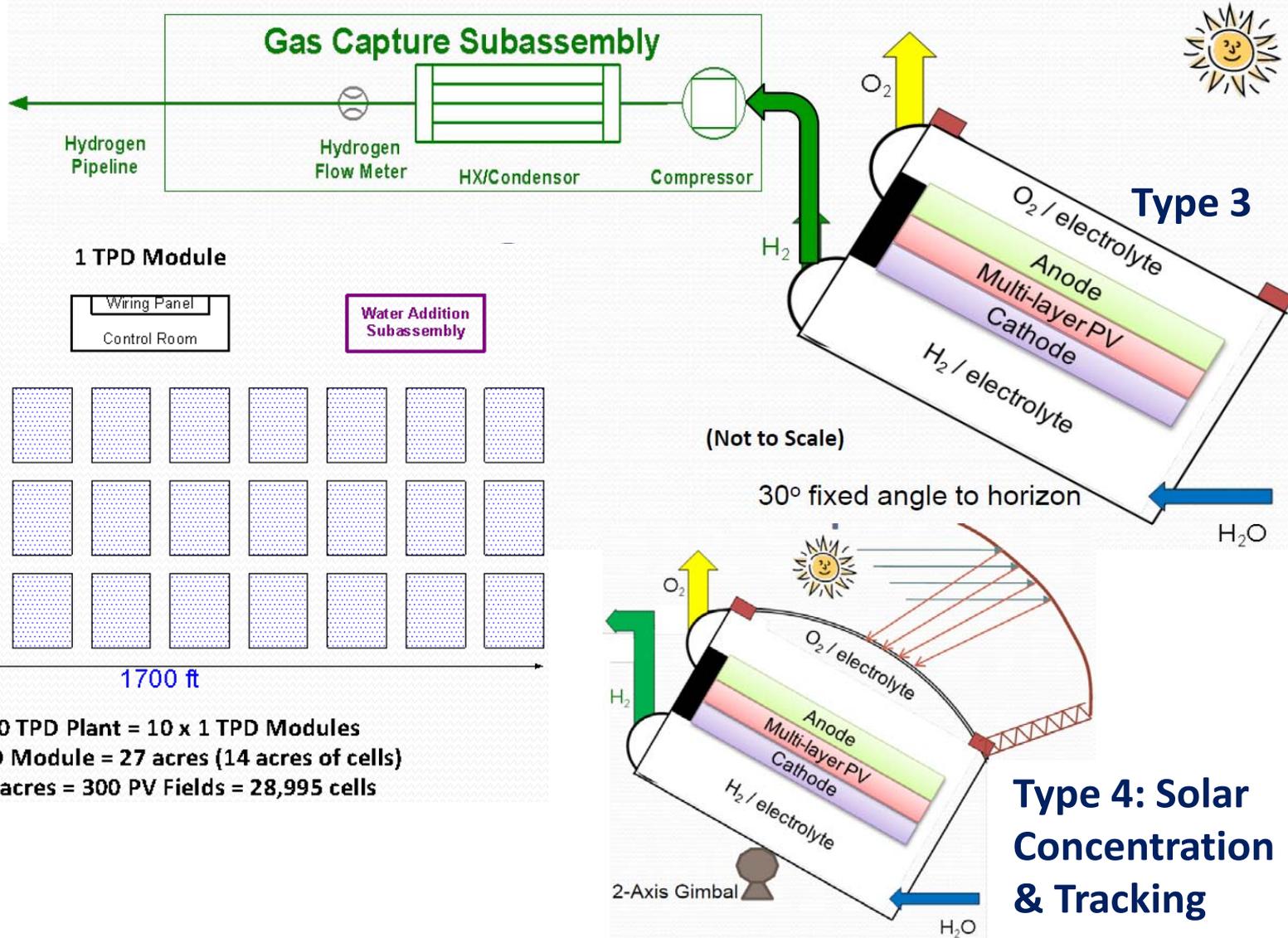
PEC

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



Reactor Types 3 & 4: Planar PEC Array



The Bottom Line: Costs of PEC-derived H₂

Recall that 1 kg H₂ 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

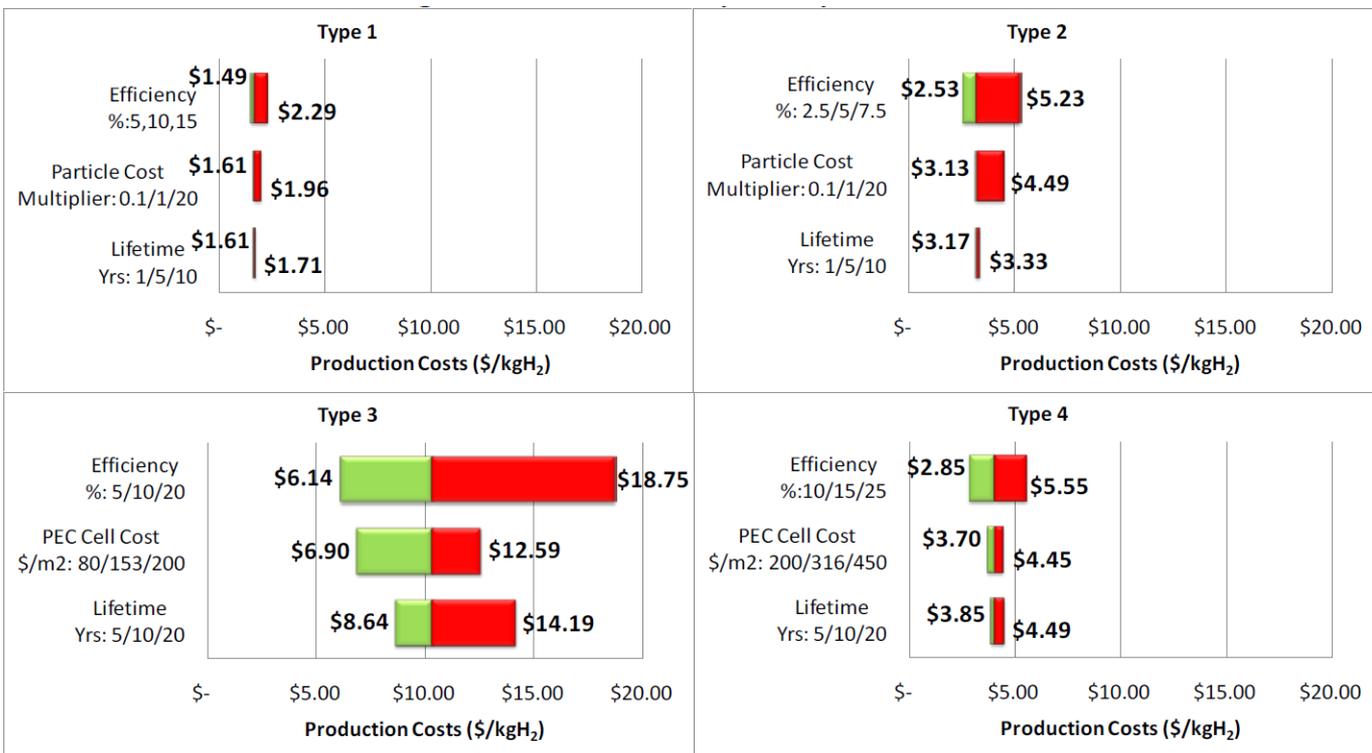
| Efficiency | Particle Cost | Particle Lifetime |
|------------|---------------|-------------------|
| 2.5% | 0.1x | 1 Year |
| 5% | 1x | 5 Year |
| 7.5% | 20x | 10 Year |

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 |

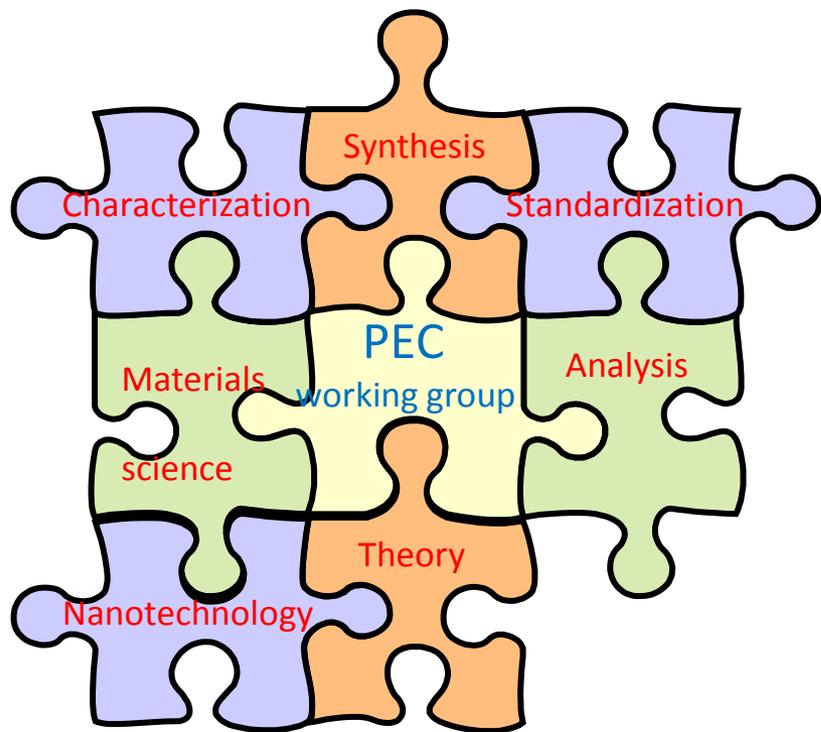
Type 4 Sensitivity Analysis Parameters

| 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 H₂ (\$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.



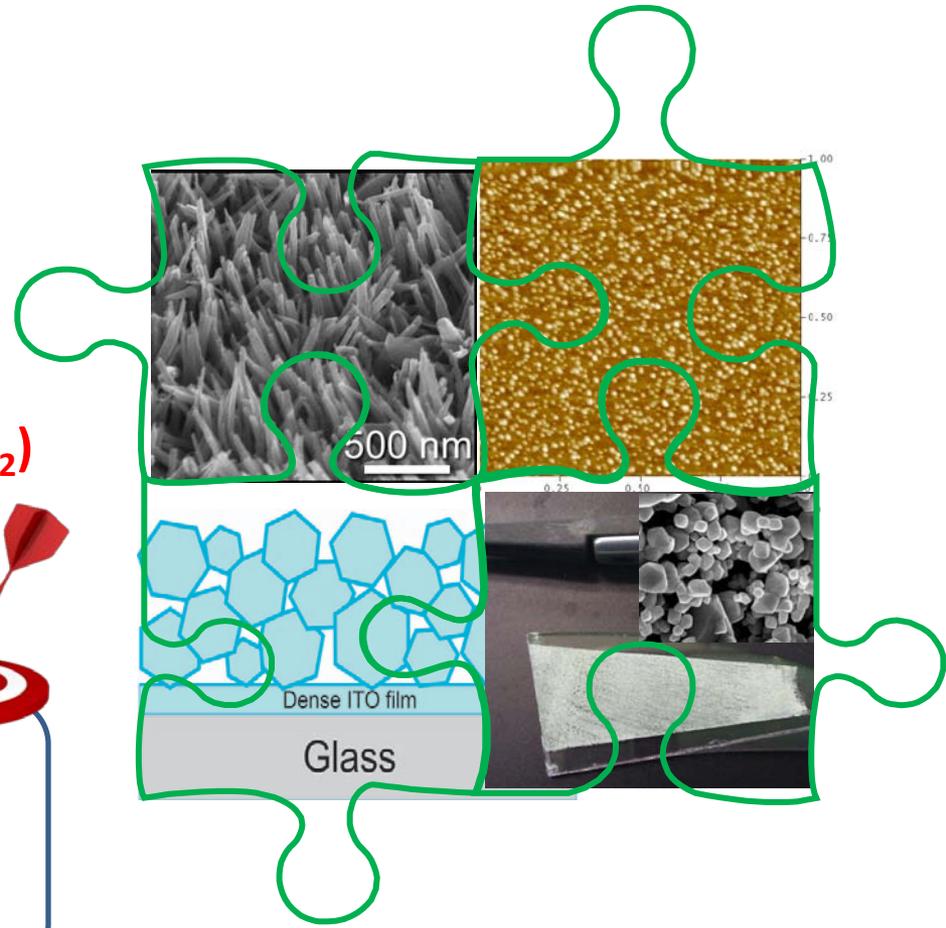
PEC Working Group:
 Evaluating working directions
 Sharing and building-up knowledge
 Accelerating research progress

➤ **3rd Generation PEC materials (nano-MoS₂)**

➤ **Transparent conducting oxide (TCO) scaffolds/substrates for PEC**



DOE Targets: >1000h @STH > 8% (2013)
 \$2 - 4/kg H₂ projected PEC cost
 (beating >\$10/kg H₂ for PV-electrolysis)



Overview

Timeline

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

Budget

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

Barriers

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

Targets

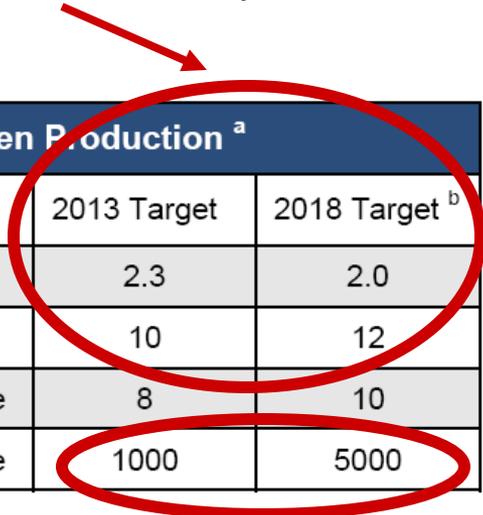
| Semiconductor | 2006 | 2013 | 2018 |
|---------------|--------|----------|----------|
| Bandgap | 2.8 eV | 2.3 eV | 2.0 eV |
| Efficiency | 4 % | 10 % | 12 % |
| Durability | N/A | 1000 hrs | 5000 hrs |

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.



| 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 MoS₂ and WS₂.

| Barrier | Challenges | Strengths |
|--|---|---|
| Y. Materials Efficiency | <ul style="list-style-type: none"> - Bandgap is too small at 1.2 eV - Indirect bandgap - C. Band 0.4 eV too low w.r.t. $E^0_{H^+/H_2}$ - Relatively low charge mobility along the c-axis ($0.1 \text{ cm}^2/\text{V}\cdot\text{sec}$) | <ul style="list-style-type: none"> - Absorbs large fraction of solar photons. - Nanostructuring can improve both bandgap problem and mismatched CB - High charge mobility along the basal plane ($> 100 \text{ cm}^2/\text{V}\cdot\text{sec}$) - Excellent hydrogen evolution catalysis |
| Z. Materials Durability | <ul style="list-style-type: none"> - n-type materials are unstable due to photo-oxidation of the sulfide surface. | <ul style="list-style-type: none"> - p-type materials have demonstrated long-term photo-stability ($\sim 1000 \text{ hrs}$) |
| AA. PEC Device and System Auxiliary Material | <ul style="list-style-type: none"> - Need a transparent, conducting, high surface area scaffold for nanomaterials. | <ul style="list-style-type: none"> - Such a photoelectrochemical substrate could be applicable to a wide range of PEC materials. |

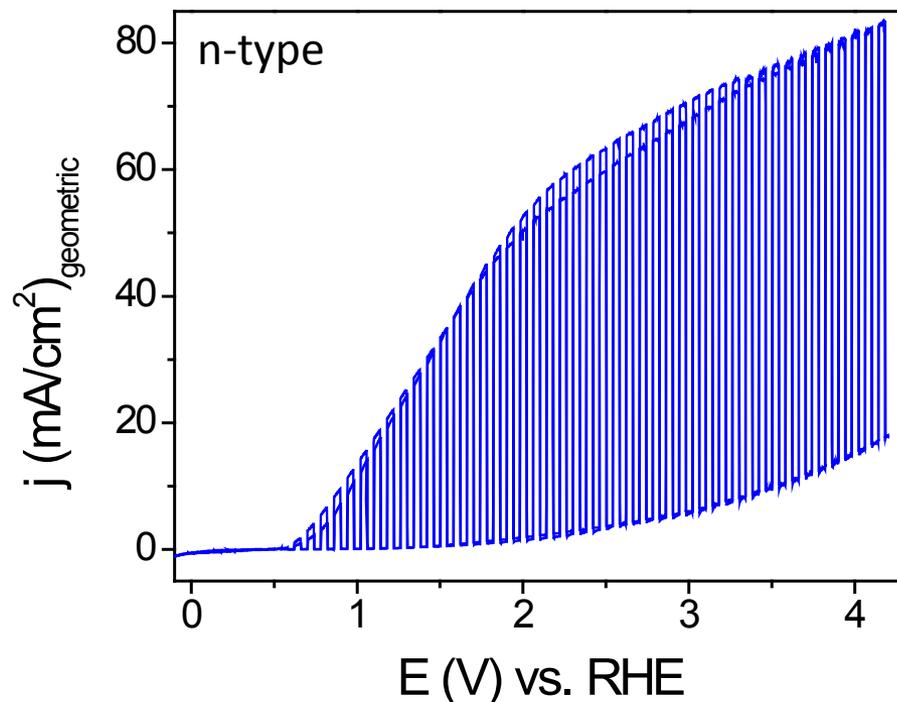
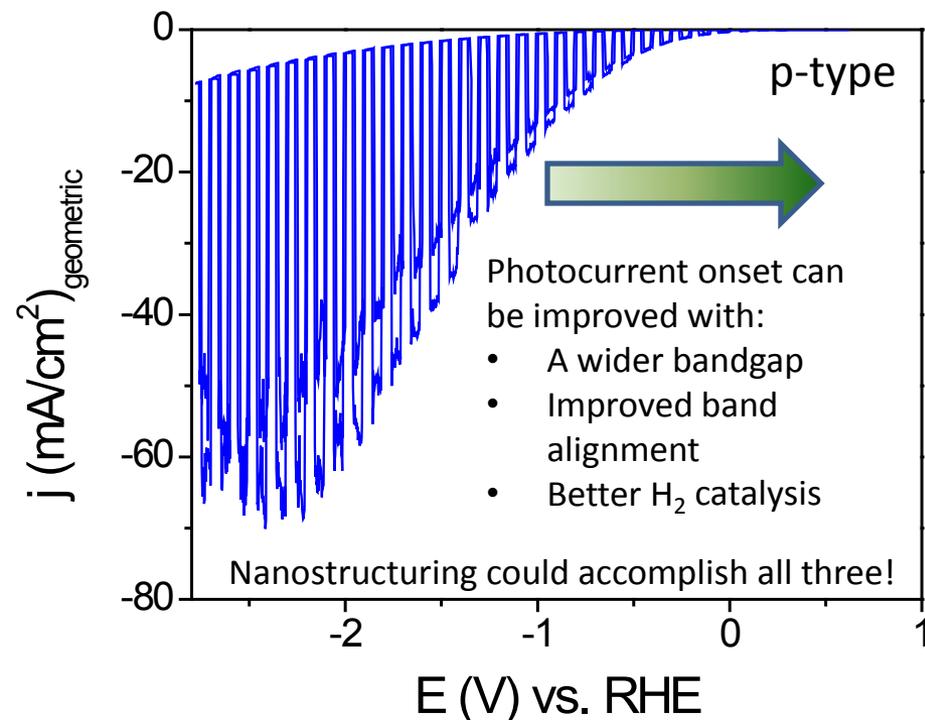
Relevance: Project Objectives

1. Fundamental Science of MoS₂ (primarily funded through DOE BES as part of an EFRC @ Stanford “CNEEC”)
 - Barrier Y. To develop **efficient** PEC materials consisting of nanostructured MoS₂ with:
 - a wider bandgap
 - improved band alignment with respect to H₂ and O₂ evolution potentials
 - improved surface catalytic properties
 - Barrier Z. To develop **durable** MoS₂ 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 (MoS₂)

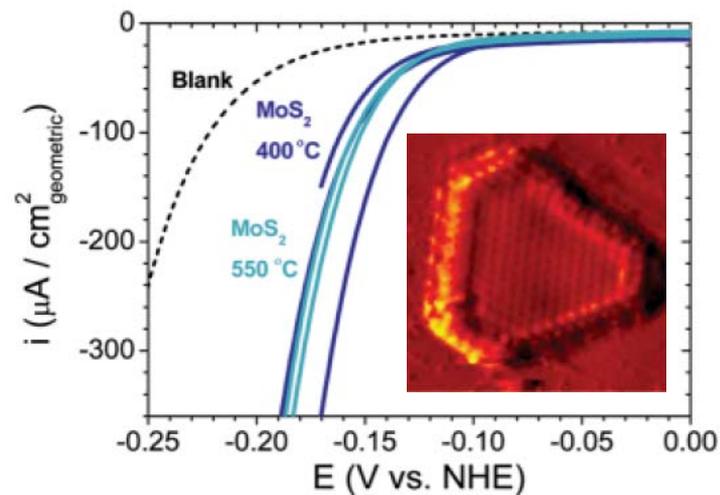
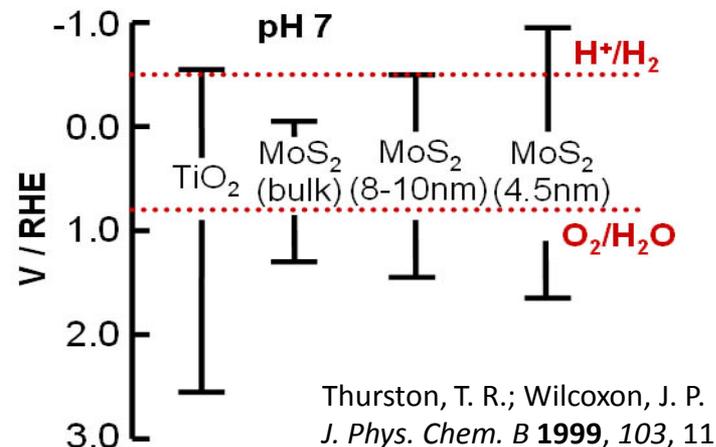
PEC measurements of bulk MoS₂ crystals

- Up to ~ 60 mA/cm² under ~ 10 suns illumination
- However, a large bias is required!
- Different types of MoS₂ conductivity
 - p-type: photo-cathodic H₂ evolution.
 - n-type: photo-anodic corrosion.



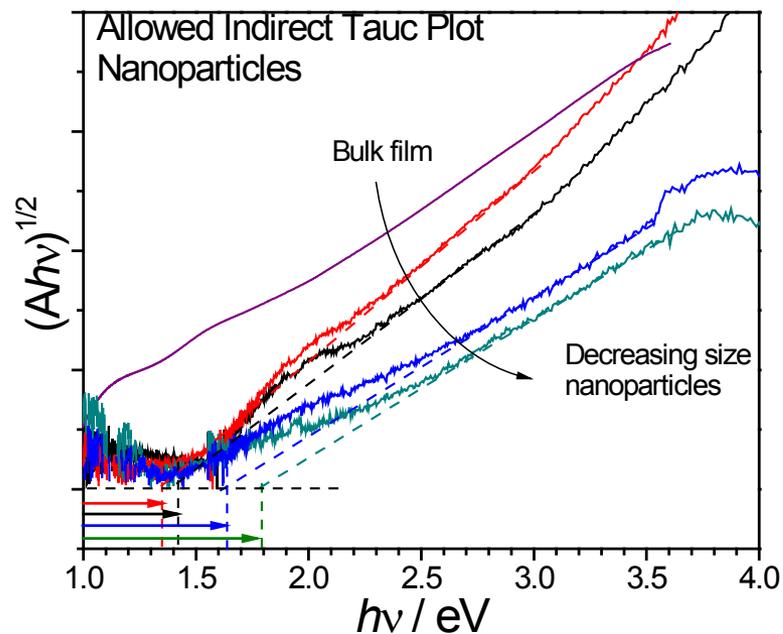
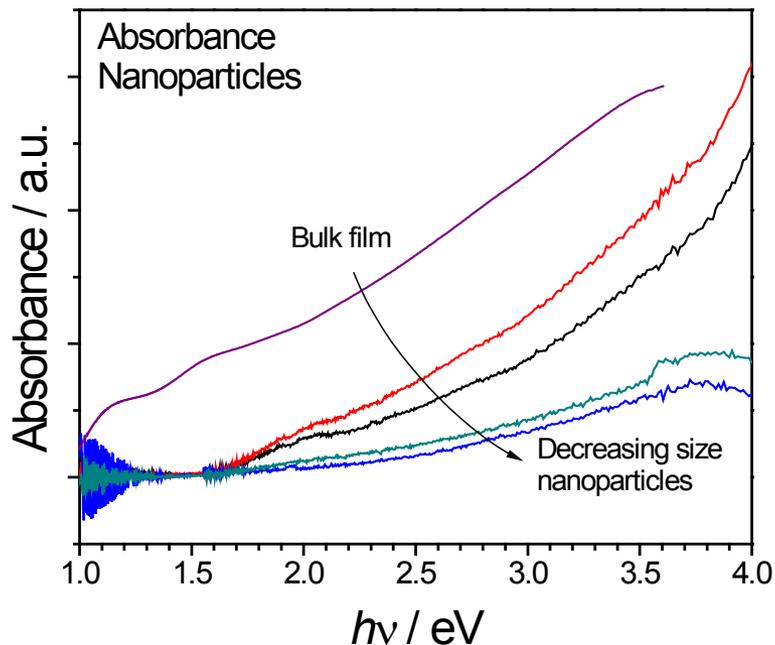
Approach: Bulk MoS₂ vs. Nano MoS₂

- Bulk MoS₂
 - Mismatched bands
 - Poor charge transport
 - Poor catalytic activity
- Nano-MoS₂
 - Bands straddle water splitting
 - Shorter charge transport distances
 - High catalytic activity



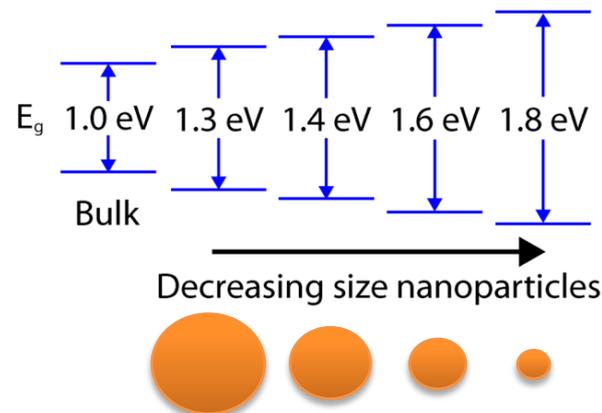
Jaramillo, et al. *Science* **2007**, 317, 100

Technical Accomplishments: Previous Work on Bandgap Engineering of MoS₂ 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.

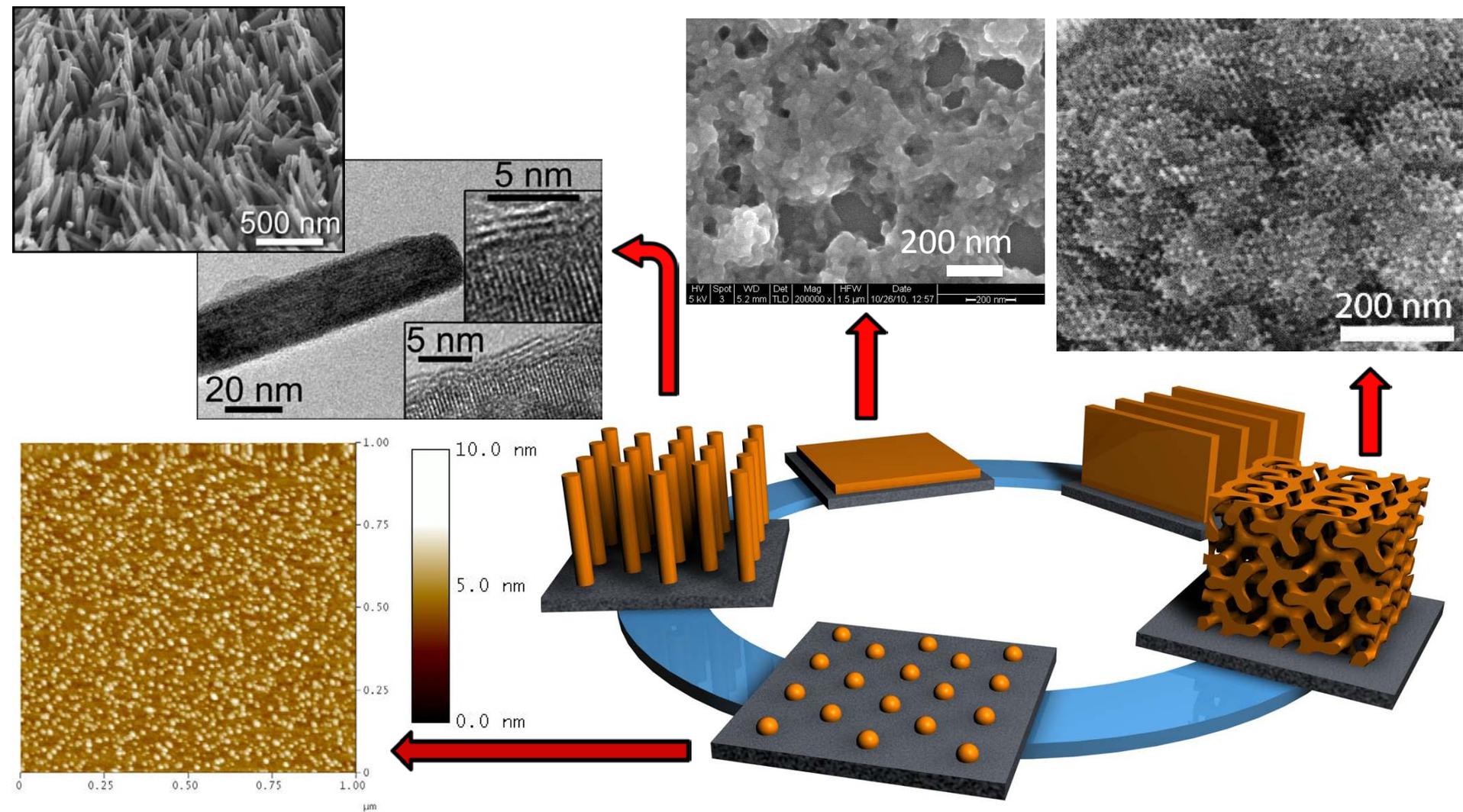


Blueshift in bandgap with decreasing size.

Approach: Milestones

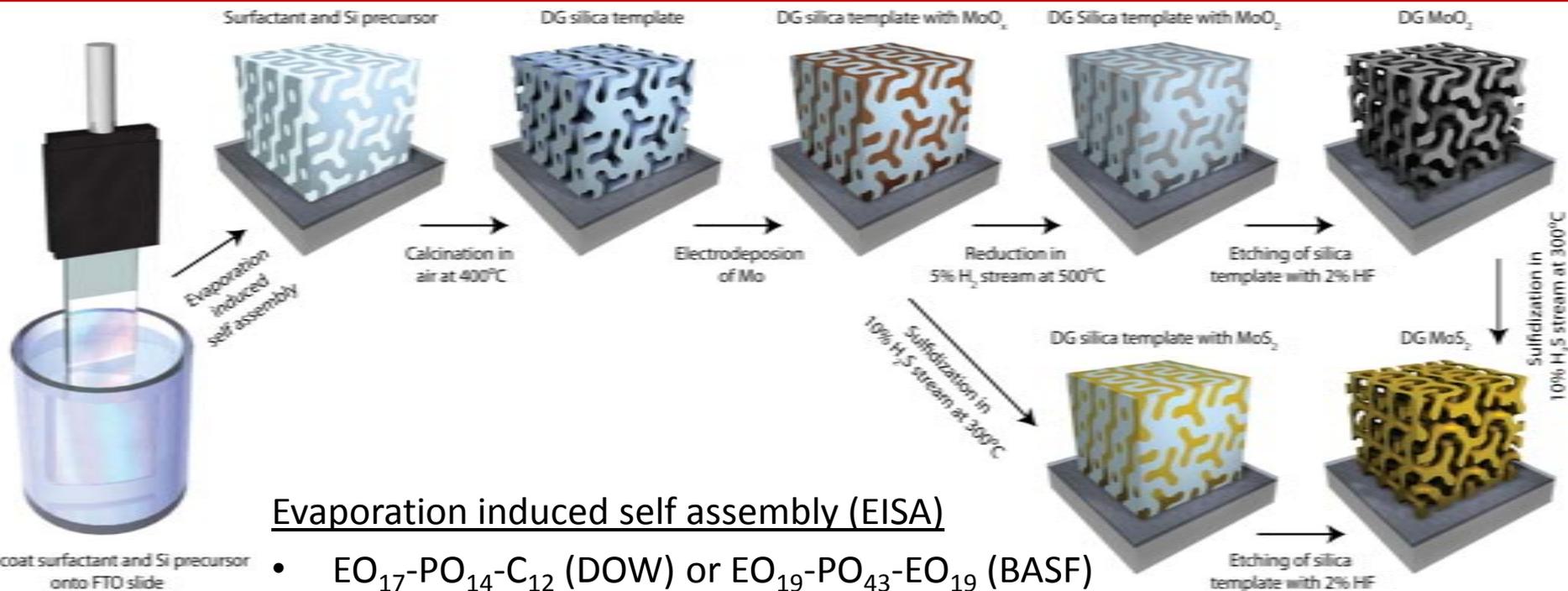
| Milestones | Progress Notes | Comments | % Comp. |
|---|--|---|---------|
| Develop a transparent conducting oxide (TCO) 3-D scaffold upon which MoS ₂ and WS ₂ nanostructures can be deposited, and characterize resulting devices. | A high surface area 3-D TCO scaffold has been developed. | Next step 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 MoS₂ Nanostructures



Take-home message: We have synthesized and studied a wide range of MoS₂ nanostructures.

Technical Accomplishment: Synthesis of a nano-structured MoS₂ Double Gyroid



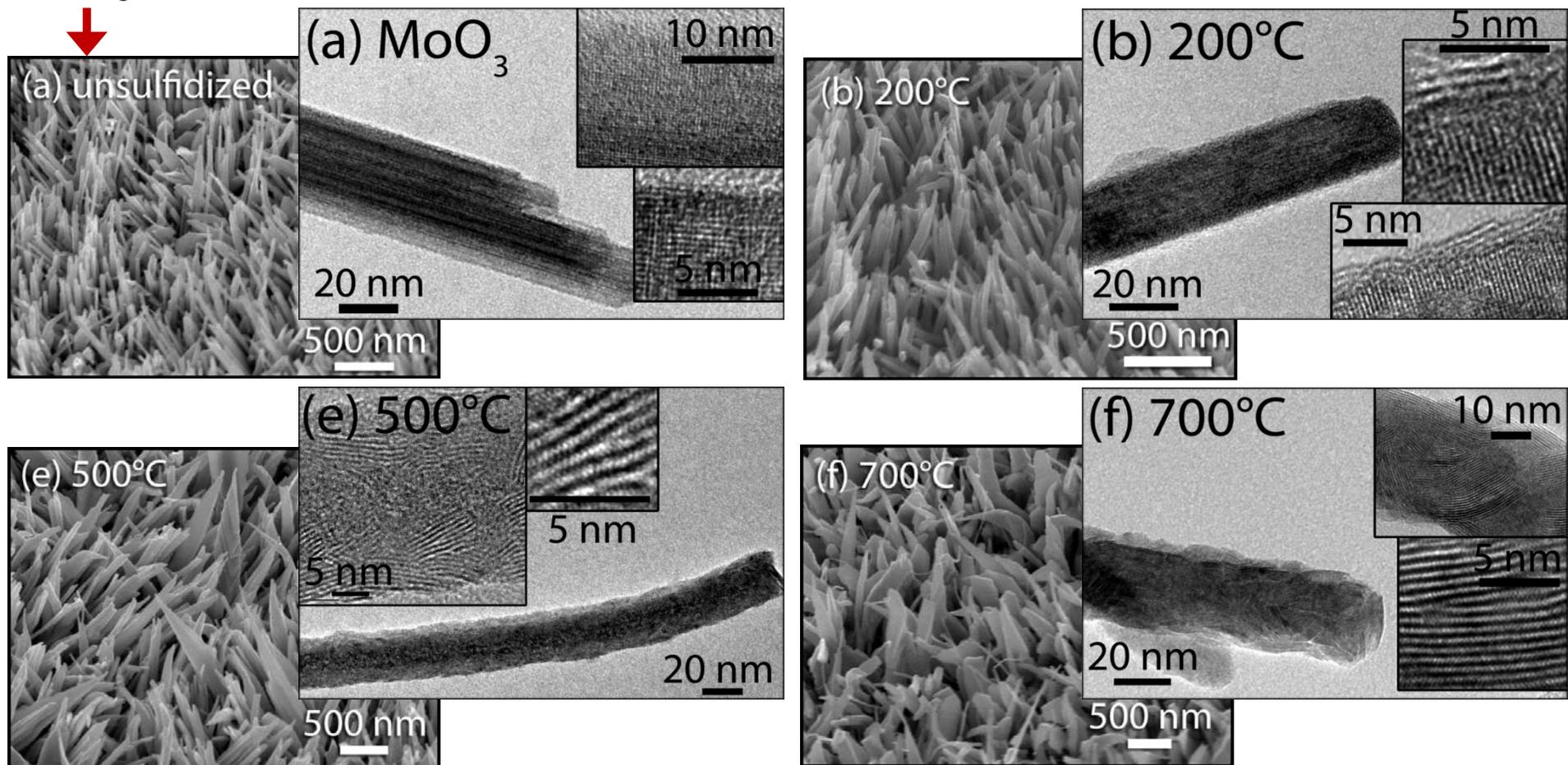
Evaporation induced self assembly (EISA)

- EO₁₇-PO₁₄-C₁₂ (DOW) or EO₁₉-PO₄₃-EO₁₉ (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 MoS₂.

Technical Accomplishment: Synthesis of $\text{MoO}_3\text{-MoS}_2$ 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).

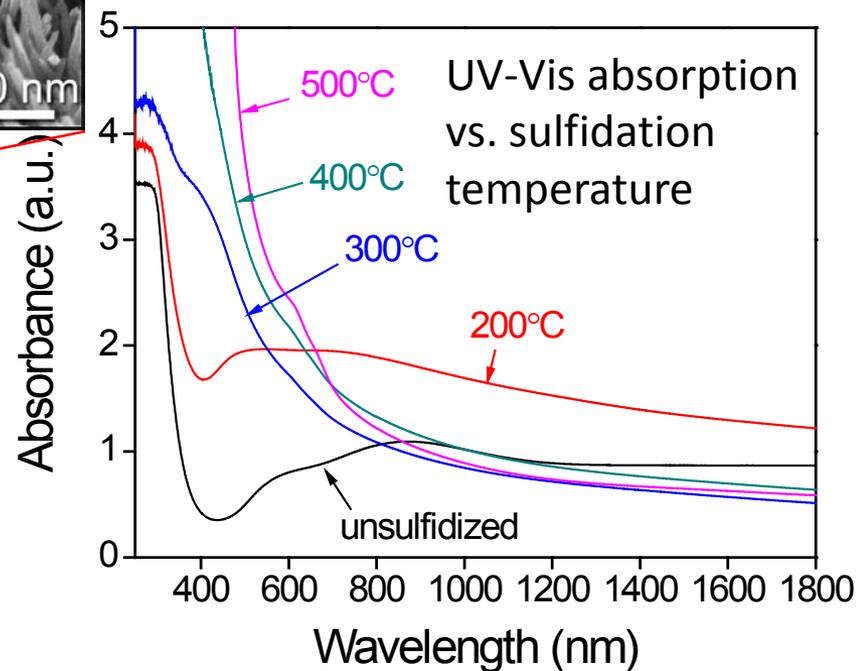
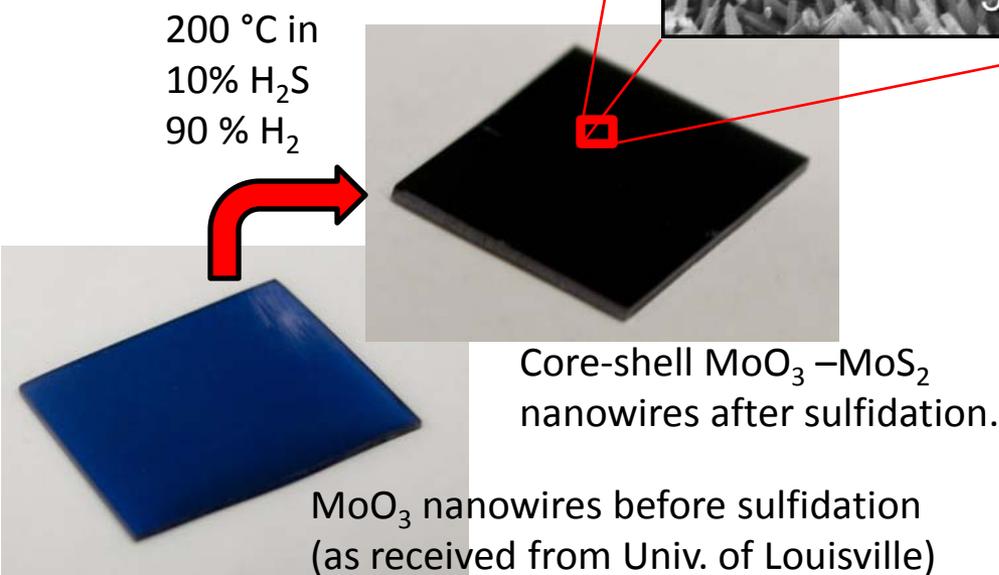


Take-home message: We developed a route to synthesize nanowires consisting of an MoO_3 core and an MoS_2 shell, with exquisite control of the shell thickness via sulfidation temp.

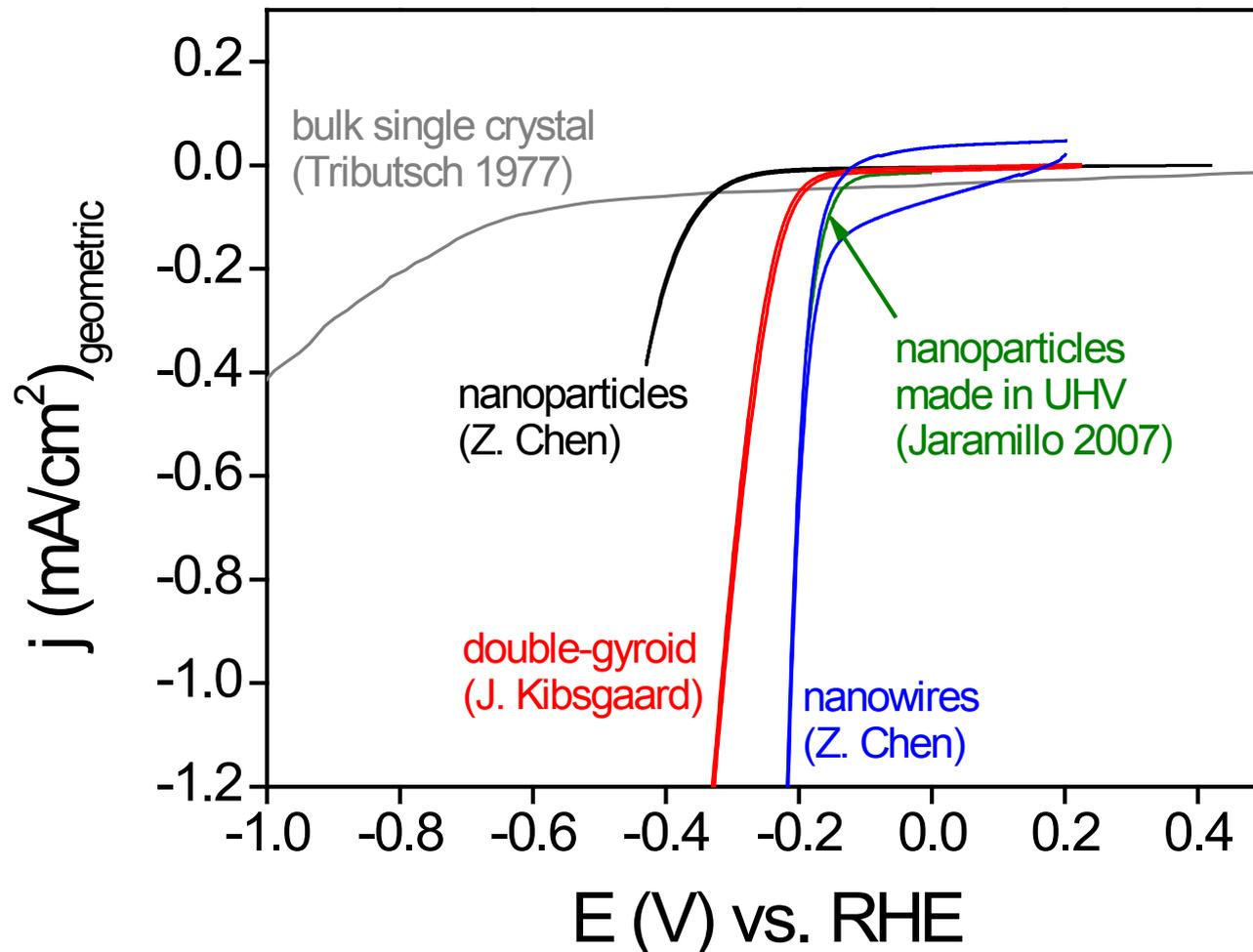
Technical Accomplishment: Excellent Photon Absorption by core-shell MoO_3 - MoS_2 Nanowires

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.

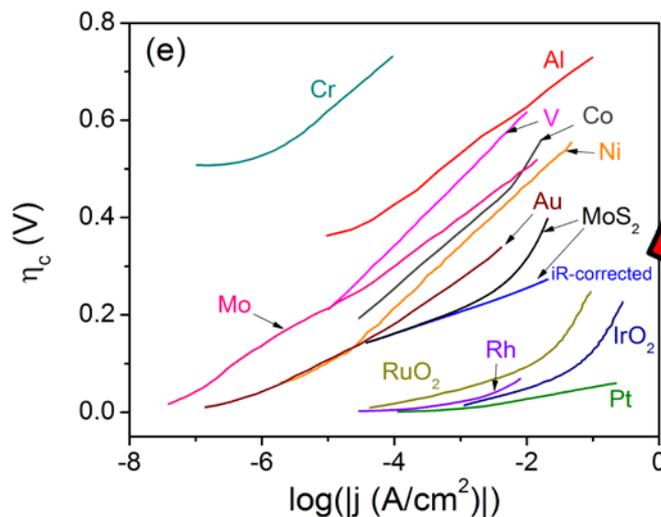
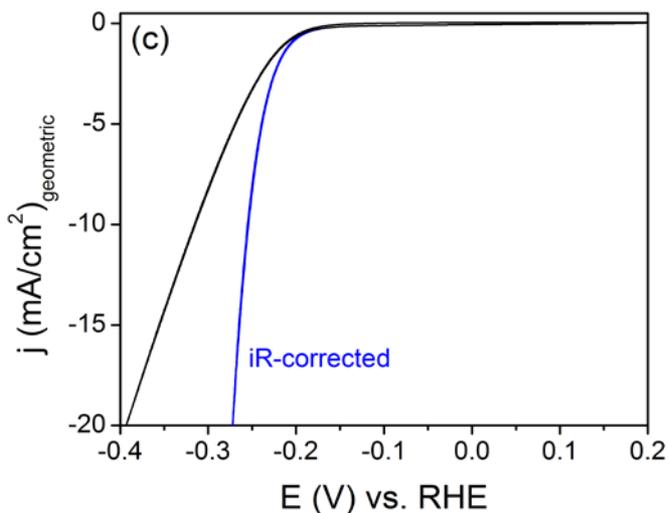


Technical Accomplishment: Excellent electrocatalytic H₂ evolution by nano-MoS₂

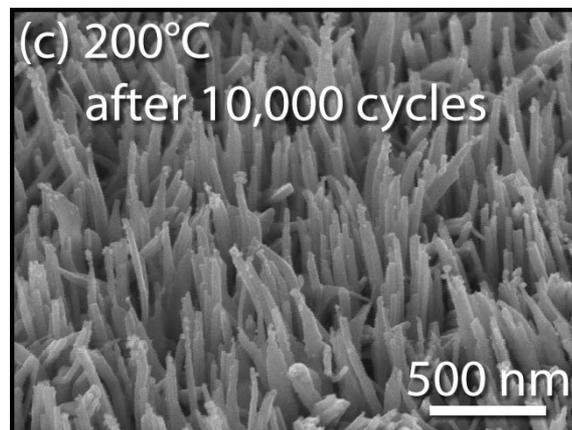
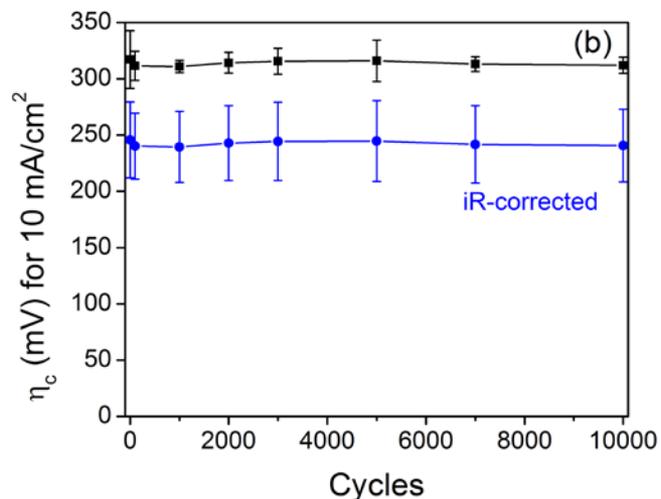


Take-home message: The MoS₂ nanostructures that we have developed are all active H₂ electrocatalysts.

Technical Accomplishment: Highly active, highly stable H₂ evolution electrocatalysis by core-shell MoO₃-MoS₂ Nanowires

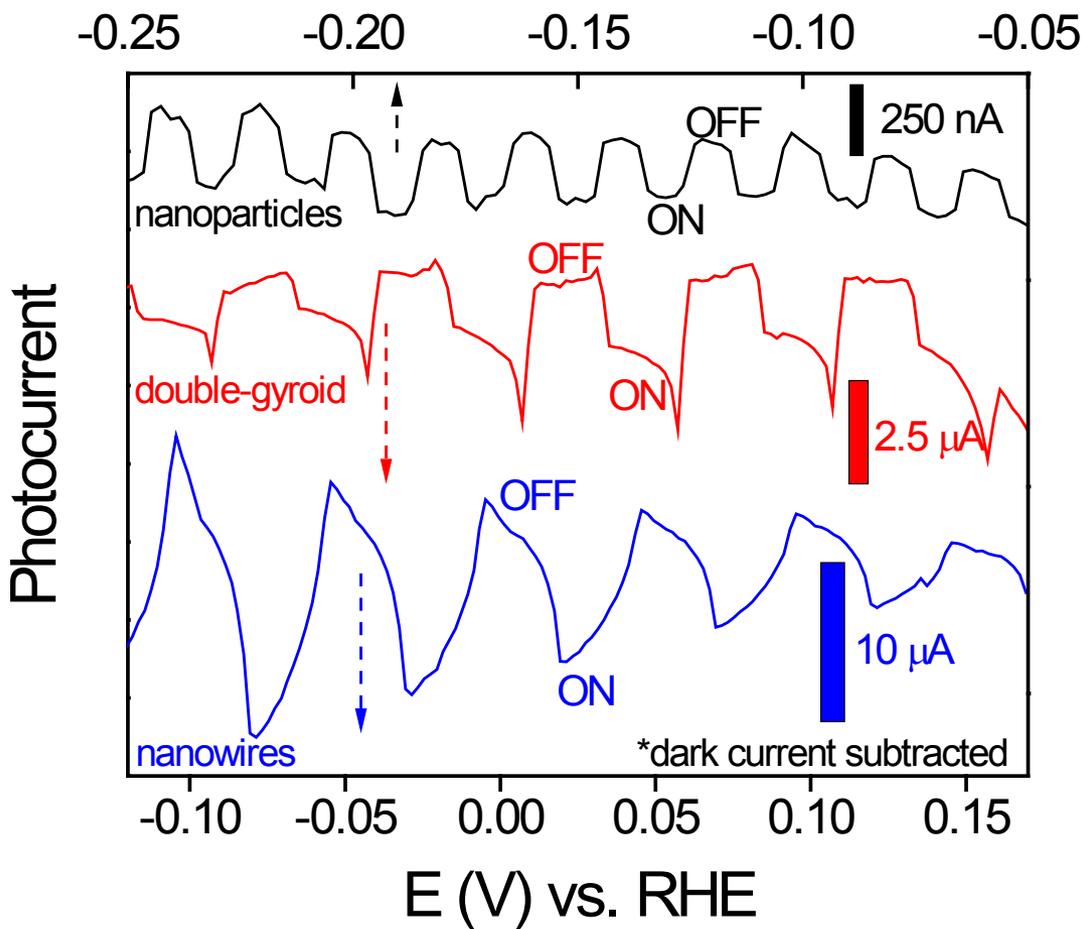


Core-shell
MoO₃-MoS₂
Nanowires

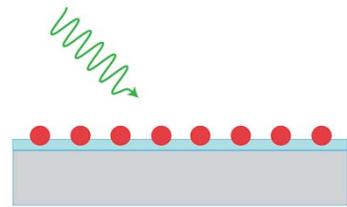


Take-home message: Among non-precious metal catalysts, this is **the most active** H₂ evolution catalyst ever reported in an acidic environment. It is **100% stable** even after 10,000 cycles.

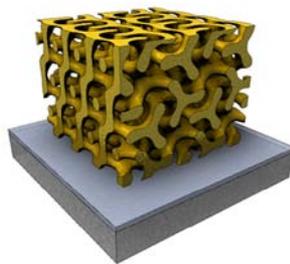
Technical Accomplishments: PEC Characterization of Nanostructured MoS₂



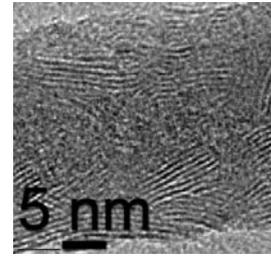
- Absorption limitations in nanoparticle submonolayer



- Charge transport and Diffusion limitations in double-gyroid

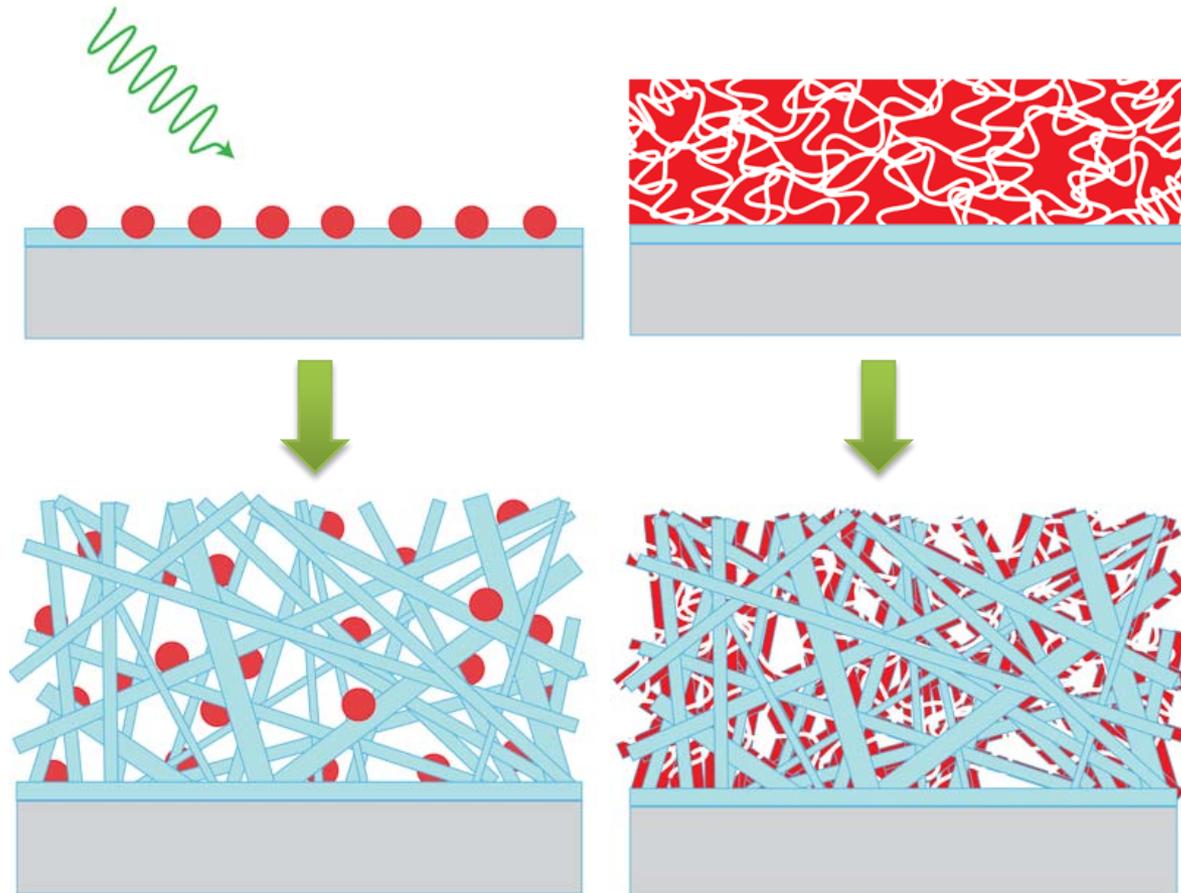


- Hole transport limitations in nanowires



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 MoS₂ can be deposited.

Relevance: Photo-electrochemical Substrate Development

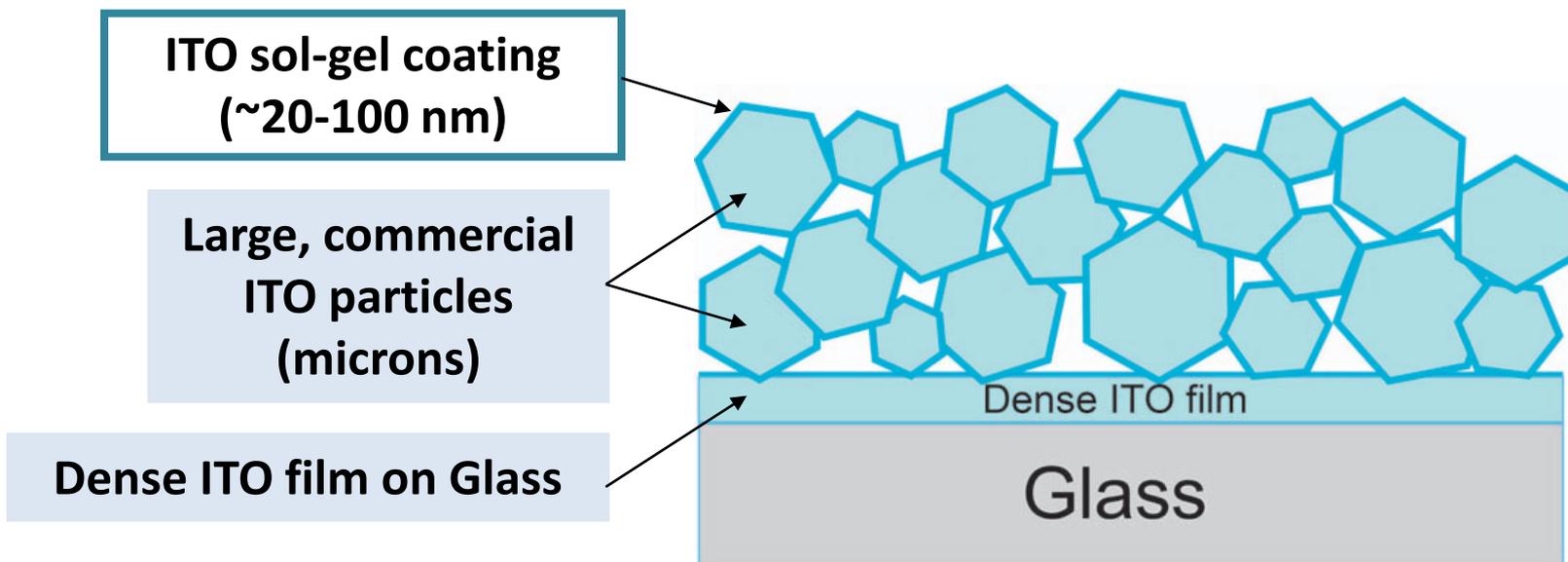


Take-home message: A photo-electrochemical substrate that is transparent, conducting, high surface area, and macroporous would be of significant value to the engineering of PEC materials as it allows for effectively long absorption paths through nanomaterials without requiring charge transport over long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

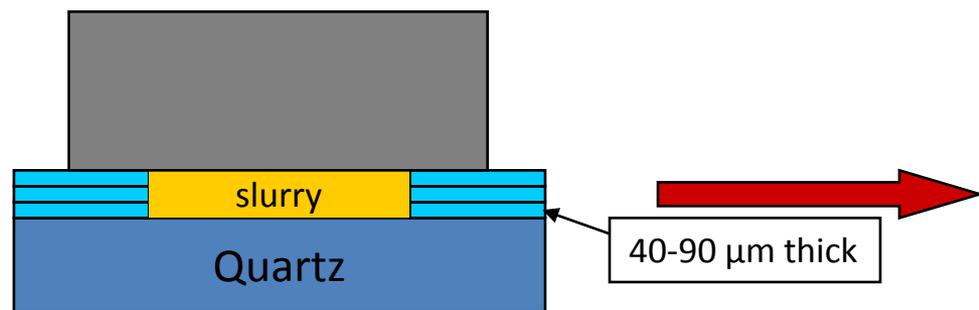
Three different forms of ITO are employed to produce the desired substrate architecture.



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

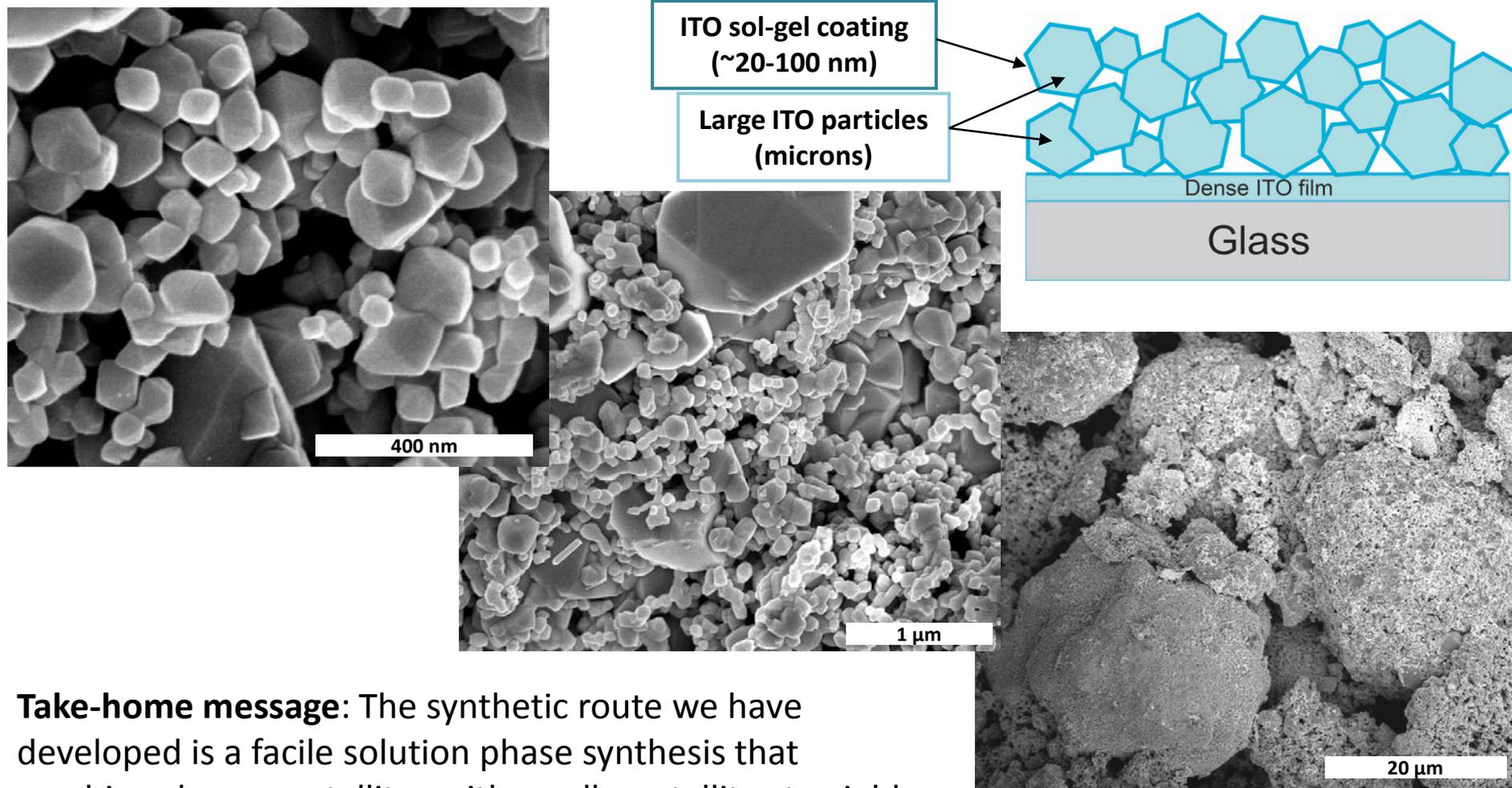
Take-home message: We have developed a scalable synthetic route involving low-cost materials and simple solution processing to produce a thick, macroporous ITO film on top of a thin, dense, commercial ITO film on glass.

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 N₂
 - Create oxygen defects to increase conductivity

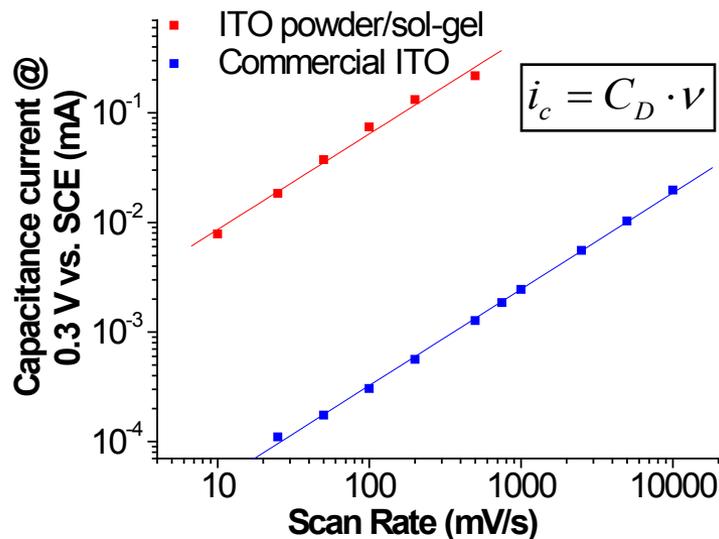
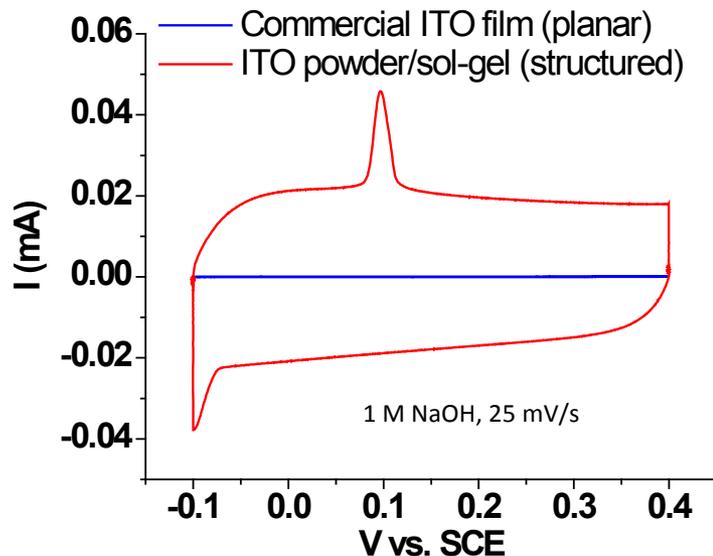


Technical Accomplishment: Physical characterization of the Photoelectrochemical Substrate

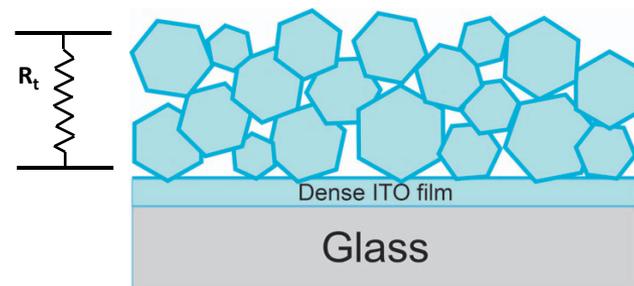


Take-home message: The synthetic route we have developed is a facile solution phase synthesis that combines large crystallites with small crystallites to yield a film with high conductivity, tunable film thickness, tunable surface area, and is scalable to large area PEC device panels

Technical Accomplishment: Achievement of a Milestone for a Photoelectrochemical Substrate



- Sheet resistance on quartz substrate:
 - 0.5 – 2.0 k Ω/\square
- Transverse resistance (R_t)
 - $\sim 1 \Omega/10 \mu\text{m}$



200 fold increase in surface area!

- Thickness (t) = 100 μm ... $R_t = \sim 10 \Omega$

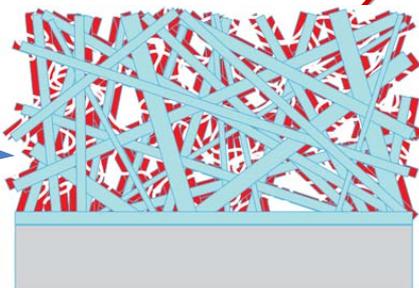
Take-home message: We have hit our target of developing a photo-electrochemical substrate that is transparent, conducting, high surface area, and macroporous.

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

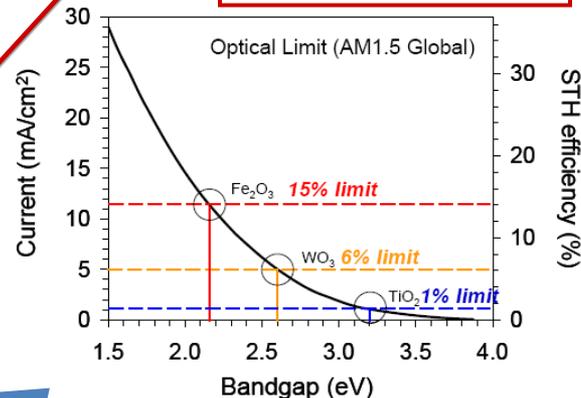
Future Work: To deposit MoS₂ and other PEC materials known to have charge-transport limitations (e.g. Fe₂O₃) onto the recently developed macroporous, high surface area, ITO scaffolds.

MoS₂

Thin MoS₂ film = high resistivity, low *hν* absorption

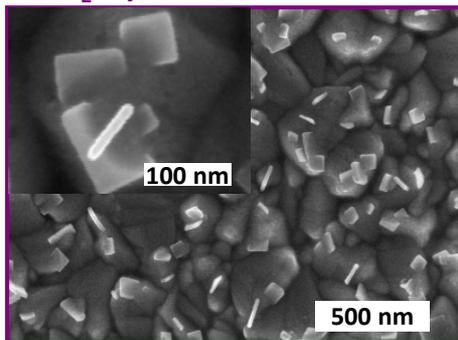


Fe₂O₃ Hematite



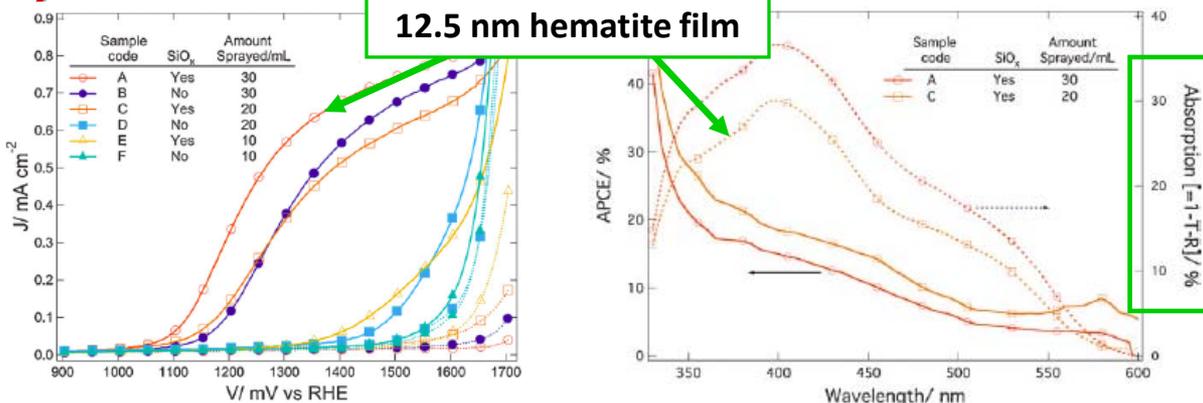
J. Mater. Res., 2010, 25, 3-16

MoS₂ crystals on FTO substrate



Thin hematite film = high performance, low *hν* 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 MoS₂ 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 MoS₂ 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 MoS₂ nanostructures that are highly active H₂ 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 MoS₂ 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 MoS₂ and other PEC materials known to have charge-transport limitations (e.g. Fe₂O₃) onto the recently developed macroporous, high surface area, ITO scaffolds.

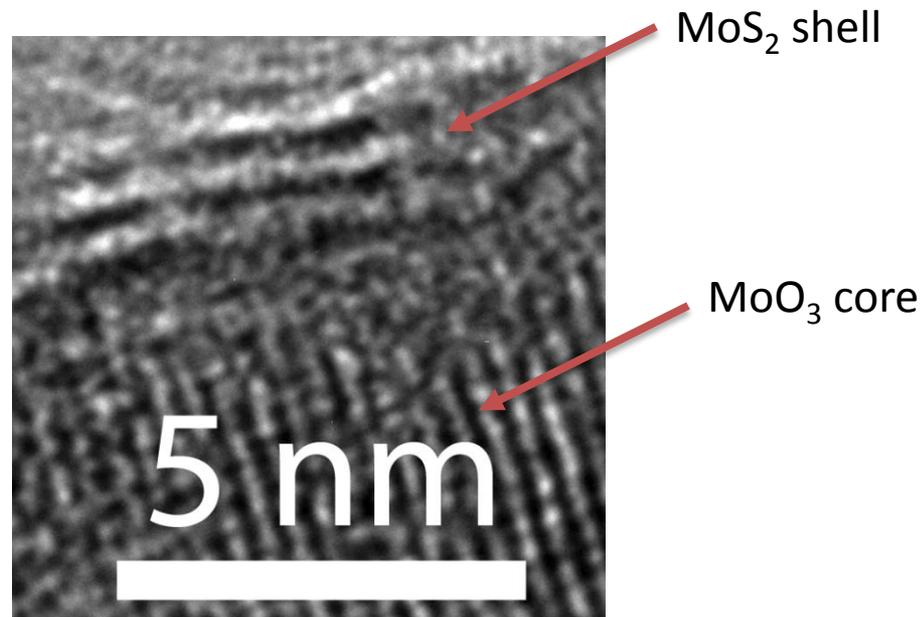
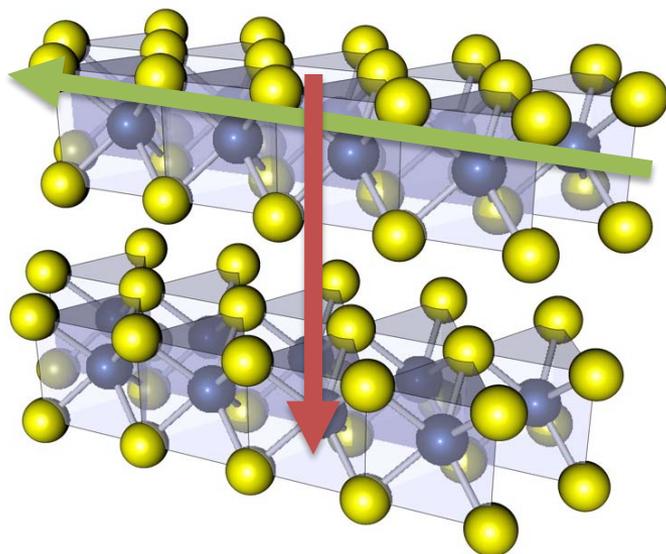
Technical Back-Up Slides

(max of 5)

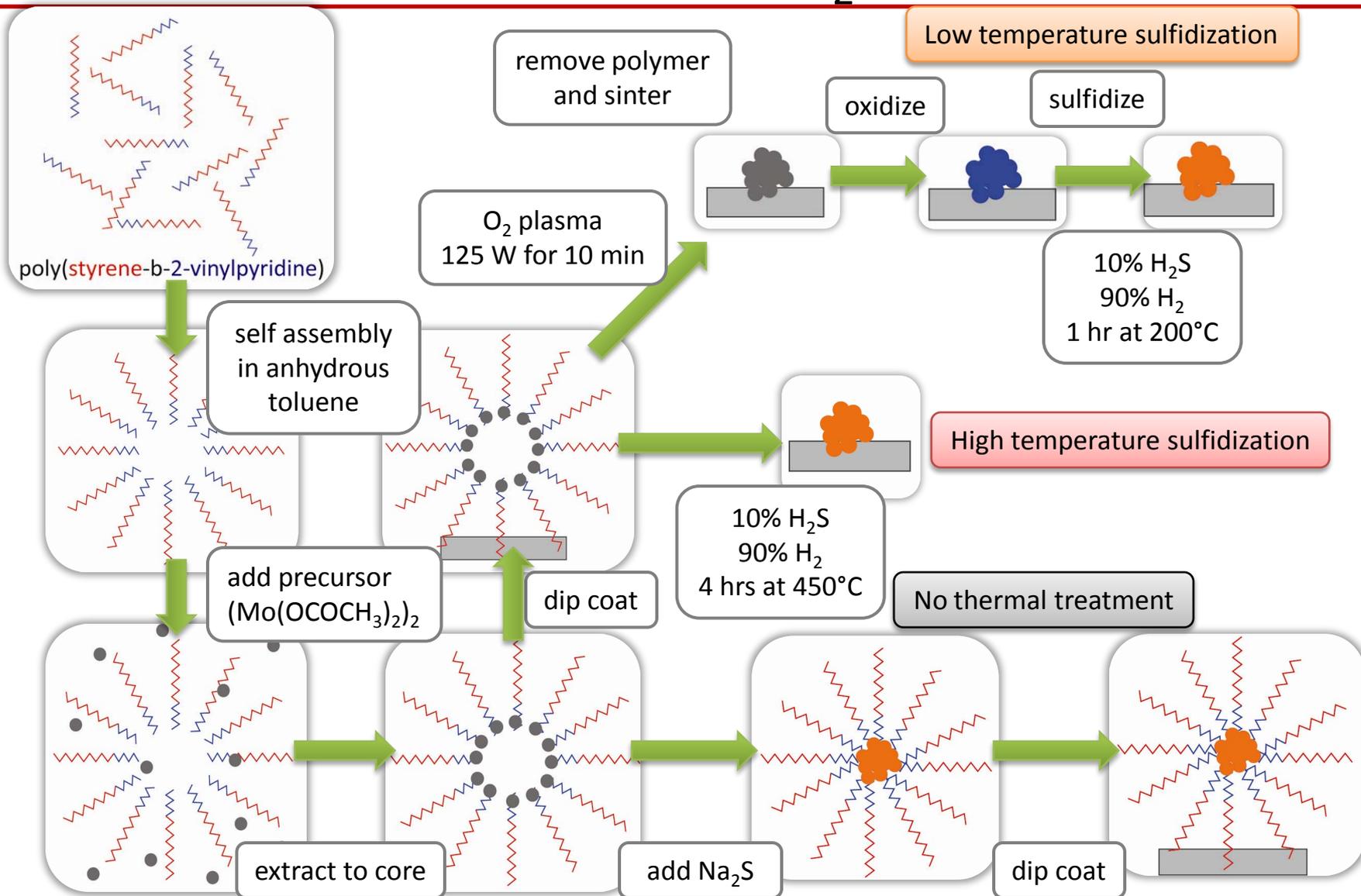
Charge Transport in Nano-MoS₂

- $\mu \sim 100\text{-}260 \text{ cm}^2/\text{Vs}$ within layers, $\sim 0.1 \text{ cm}^2/\text{Vs}$ between¹, usually results in $R_s \sim 100\text{-}200 \Omega$ in bulk
- nanostructuring minimizes distance of e^- and h^+ travel
- $R_s < 1 \Omega$ achieved in thin layers!

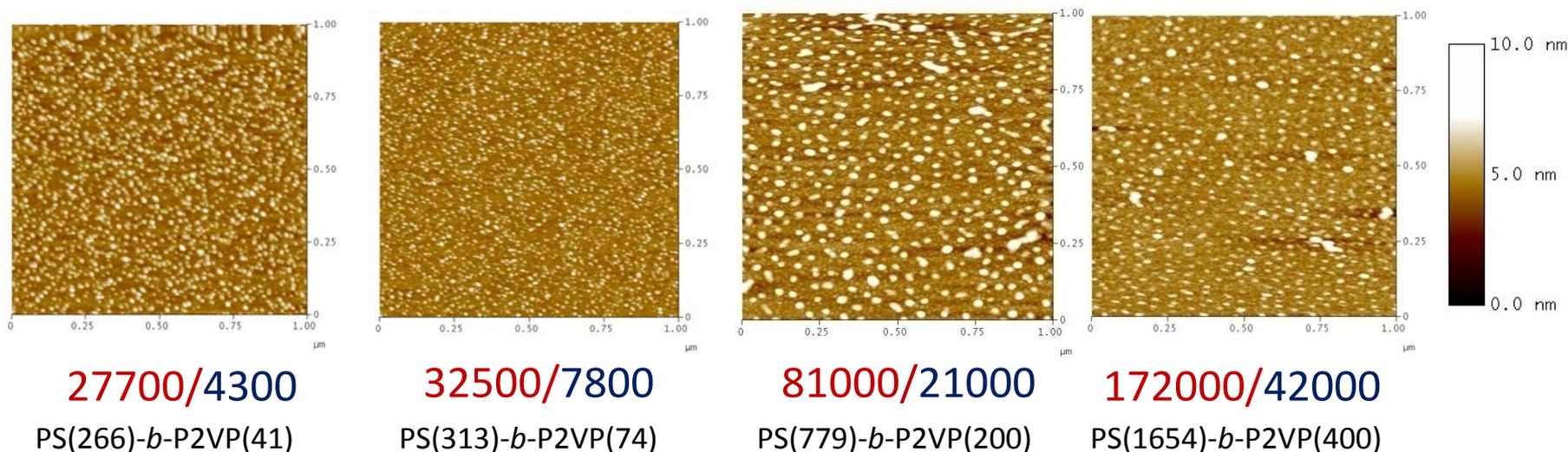
¹Tributsch and Bennett, *J. Electroanal. Chem.*, 1977 **81**, 97



Technical accomplishment: Development of Multiple Routes to MoS₂ Nanoaprticles



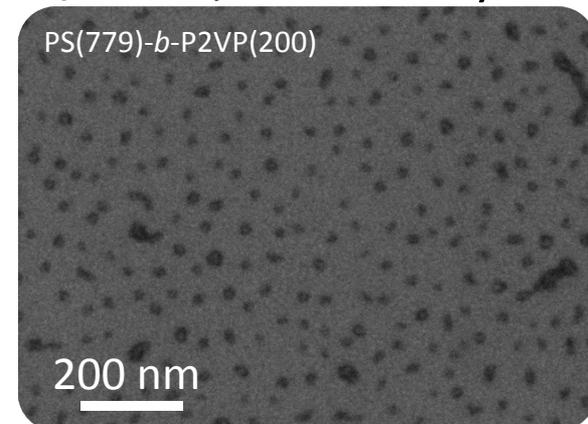
Technical accomplishments: Size-control of MoS₂ nanoparticles



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

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

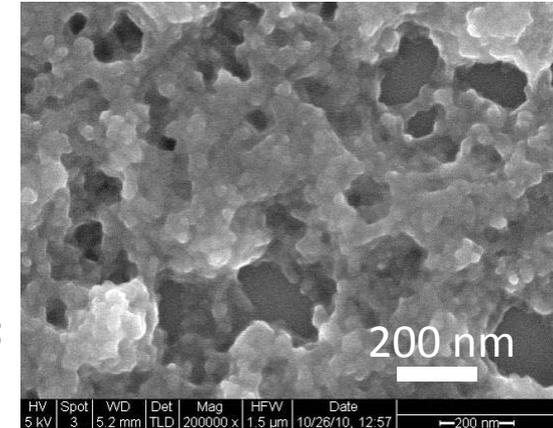
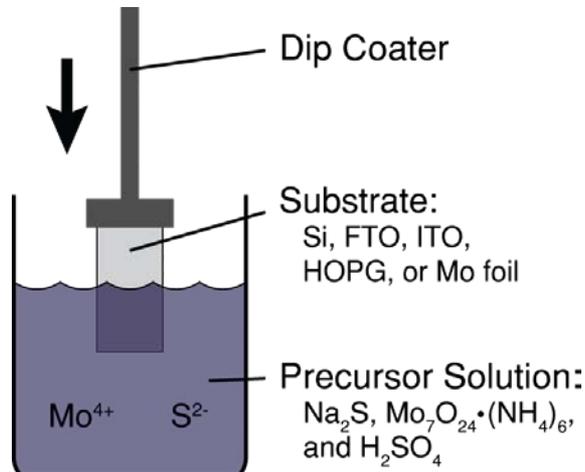
*Measurement limited to microscope resolution



Technical Accomplishment: Development of Ultra-thin MoS₂ films by Chemical Bath Deposition

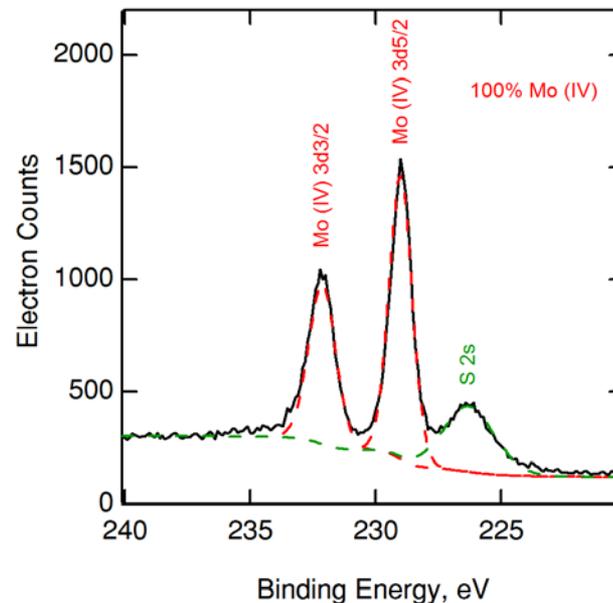
Synthesis:

1. Chemical solution deposition
 - Aqueous, room temperature
2. Post-deposition sulfidization
 - 10% H₂S/90% H₂ at 300 C



XPS Characterization:

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



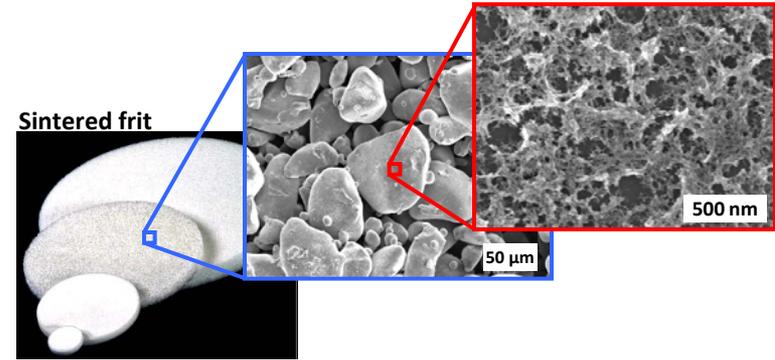
Properties:

- Conformal coating
- Thickness ~10 nm
- XPS confirms Mo (IV) corresponding to MoS₂

Technical Accomplishment: Alternate Approaches to PEC Substrate Development

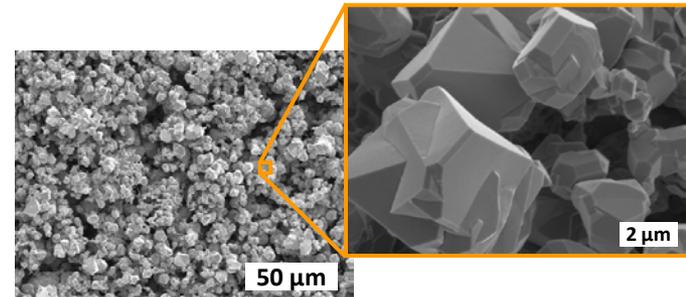
- **ITO Sol-gel on structural glass/quartz frit**

- Physically robust
- Poor crystallinity
- low bulk conductivity
- M Ω sheet resistance



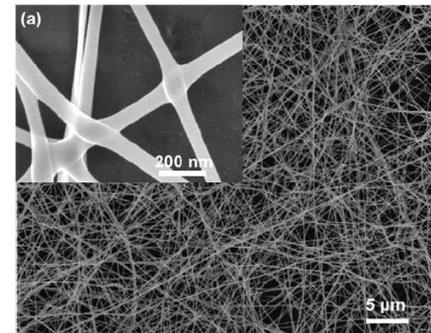
- **High temp sintering of ITO powder**

- ~2600 °C, H₂/O₂ torch
- Superb crystallinity
- Poor cohesion within film
- High k Ω – low M Ω sheet resistance



- **ITO nanofiber films**

- Collaboration with Yi Cui group @ Stanford
- Flexible films
- 10-100 k Ω sheet resistance
- Poor adhesion to substrate
 - Film delamination



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