Directed Nano-scale and Macro-scale Architectures for Semiconductor Absorbers and Transparent Conducting Substrates for Photoelectrochemical Water Splitting

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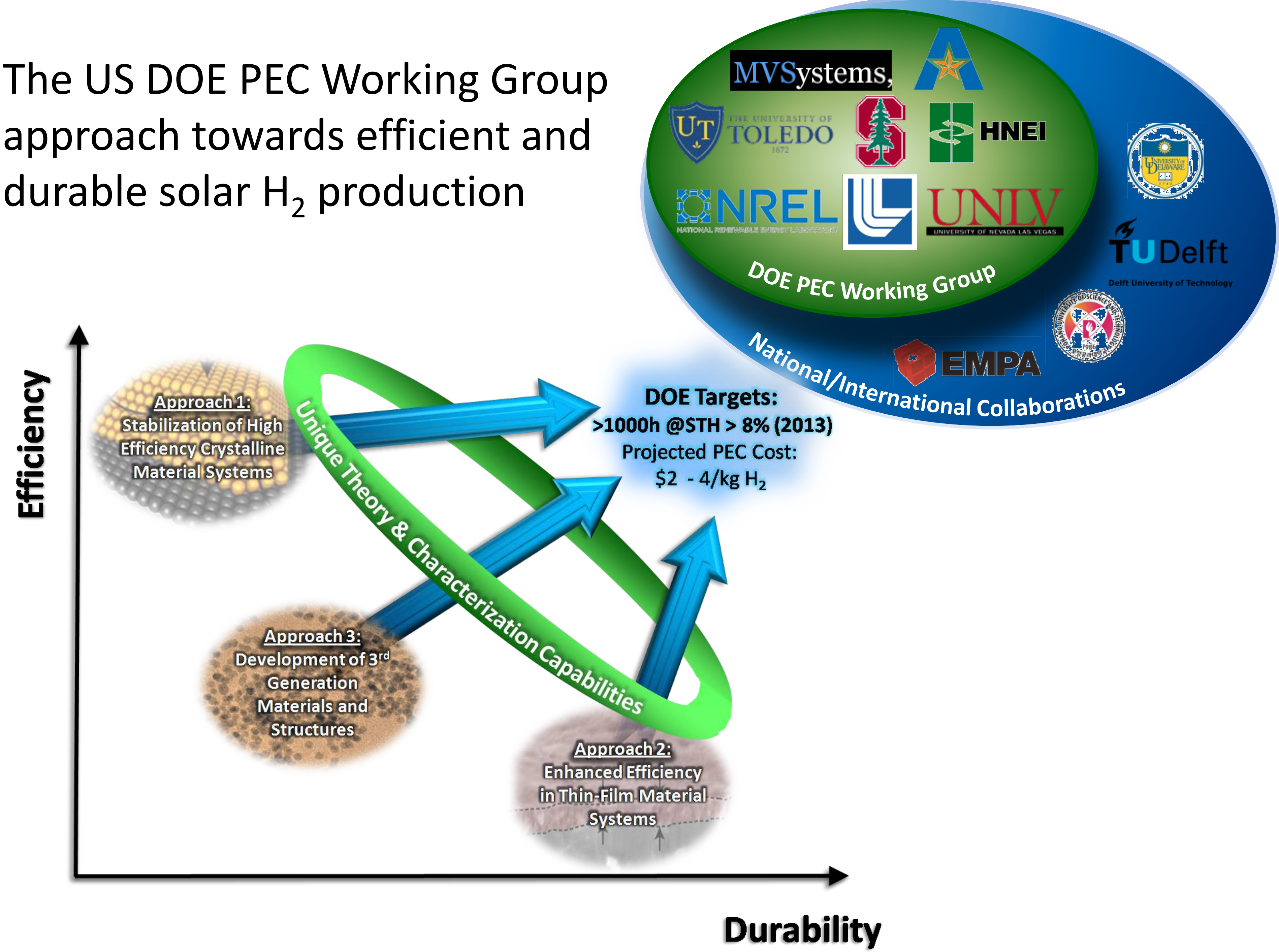
Project ID: PD033

The US DOE PEC Working Group approach towards efficient and durable solar H_2 production



Overview

Timeline

- Start Date: Dec 2008
- End Date: Sep 2012*
- 90% complete

Budget

- Total project funding
  - DOE - $388k
  - Contractor - $64k
- Planned funding in FY12
  - $130k
- Funding for FY13
  - *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 3rd generation materials and structures 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: Project Objectives

1. **HSEs: A Platform Technology with Broad Application to PEC Materials [Applied Science/Engineering → DOE EERE]**
   - **Barrier AA.** To develop and employ **photoelectrode substrates** with:
     - Macro-porosity (> 50 nm),
     - High surface area
     - Optical transparency
     - High electrical conductivity
     - Physical robustness
   - **Barrier Y.** Improve **efficiency** of charge transport limited material
     - Support charge transport limited PEC material (e.g., α-Fe_2O_3) on substrate to demonstrate efficacy

2. **MoS_2: Developing 3rd Generation PEC Materials [Fundamental Science/Engineering → DOE BES EFRC]**
   - **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 catalysis for HER
   - **Barrier Z.** To develop **durable** MoS_2 photo-cathodes

Relevance: PEC Substrate Improvement - High Efficiency Devices

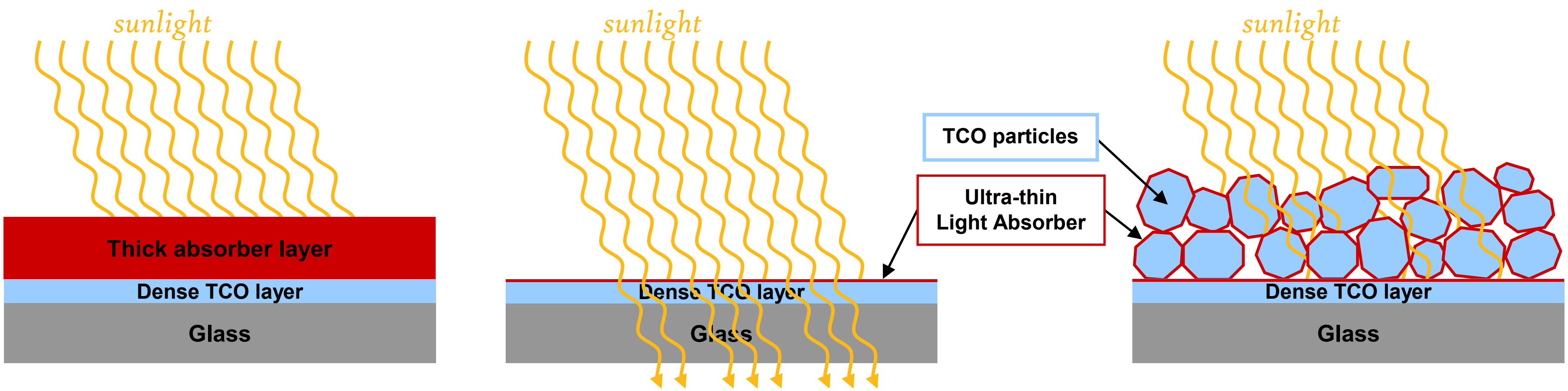
Conventional Devices

Low IQE (long charge trans.)
High loading (high OD)
Low device performance

High IQE (short charge trans.)
Low loading (low OD)
Low device performance

HSE Support

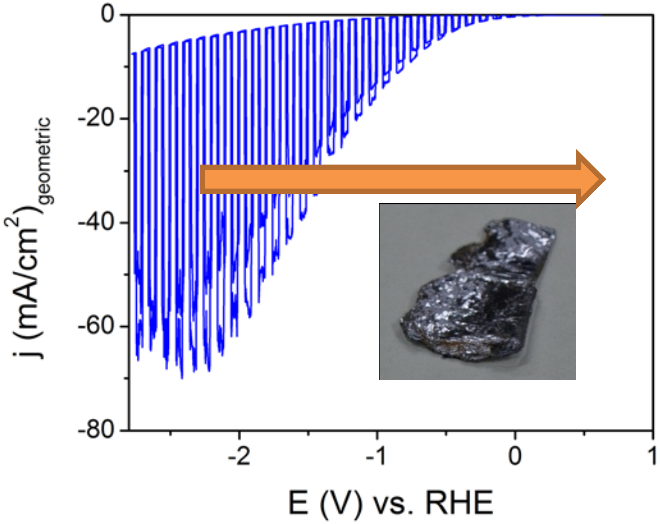
High IQE
High loading (high OD)
High device performance

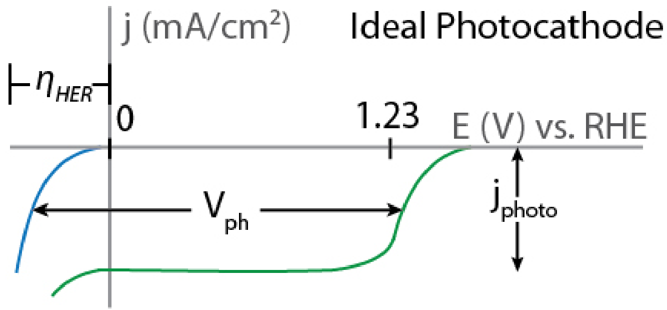


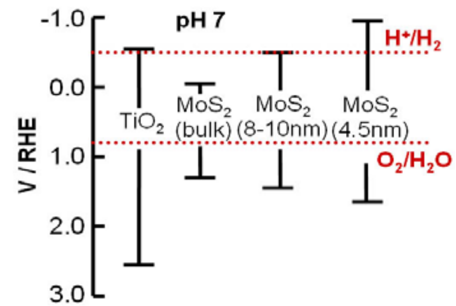
High solar H_2 production rates!

Take-home message: A PEC substrate that is transparent, conducting, high surface area, and macroporous is critical for engineering PEC devices. It allows for increased vertical loading of nanomaterials with minimized semiconductor charge transport distances.

Relevance: Improving PEC Efficiency with Nanostructured MoS_2



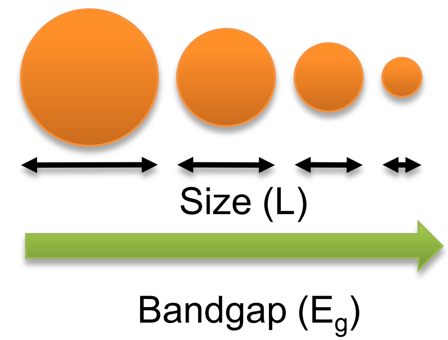




Thurston, T. R.; Wilcoxon, J. P. *J. Phys. Chem. B* **1999**, *103*, 11

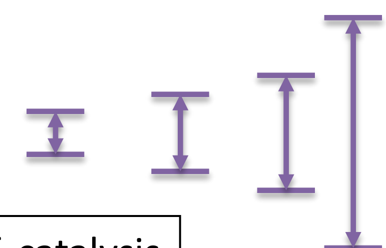
Bulk MoS_2 generates excellent photocurrent, but at high biases

- >60 mA/cm^2 under 10 suns
- Poor catalysis
- Poor photovoltage



Nanostructuring MoS_2

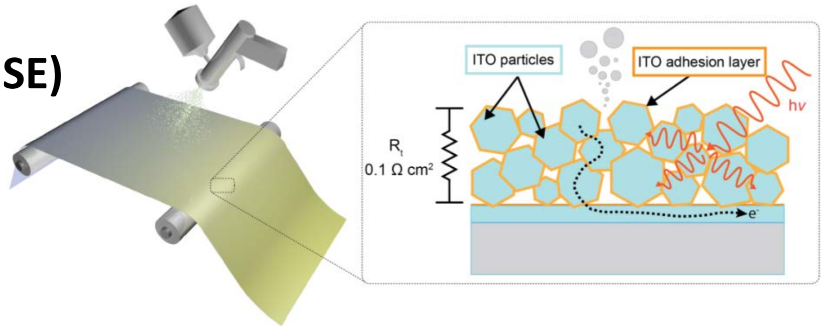
- Excellent catalysis
- Bandgap engineering to increase photovoltage
- Improved band edge alignment



Take-home message: We can nanostructure MoS_2 to address problems of catalysis and photovoltage to improve photocurrent onset and overall efficiency.

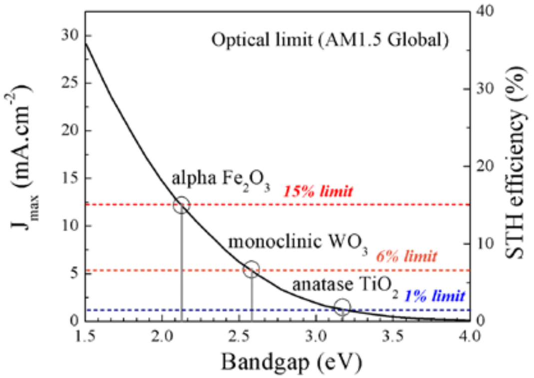
Approach: Fabricate HSE Support, Merge with PEC Nanomaterials

- **Engineer transparent high surface area electrodes (HSE)**
  - Tunable, novel multi-component synthesis



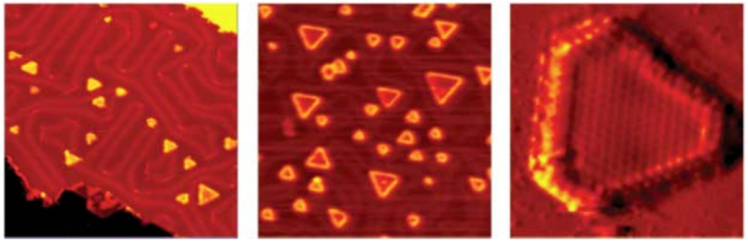
Forman, A.J., et. al., submitted

- **Interface HSE with conventional PEC materials**
  - Charge transport limited oxides (e.g. hematite, Fe_2O_3)



Chen, Z. et. al., J. Mater. Res, **2010**, 25, 3-16

- **Investigate novel PEC active materials**
  - Quantum confined MoS_2



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

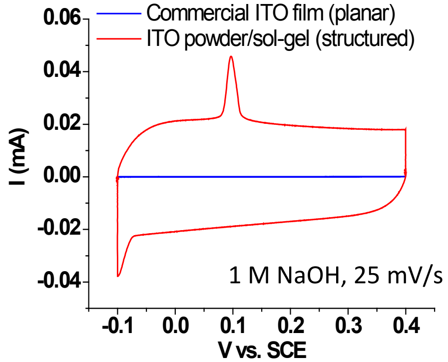
Approach: Milestones

Milestones	Progress Notes	Comments	% Comp.
HSE Design and Synthesis	Novel, template free ITO scaffold has been fabricated	Large area, high throughput synthetic method	100 %
HSE Characterization	RF values synthetically tunable up to ~100	Broad pH, thermal & physical stability	100%
Integrate PEC Materials with HSE	Ti:Fe_2O_3, MnO_x and MoS_2 coatings underway	Interfacial engineering for improved charge transfer	70%
Optimize MoS_2 for PEC Performance & Efficiency	Developed quantum confined MoS_2 nanoparticles	Requires further optimization of ligand chemistry	70%

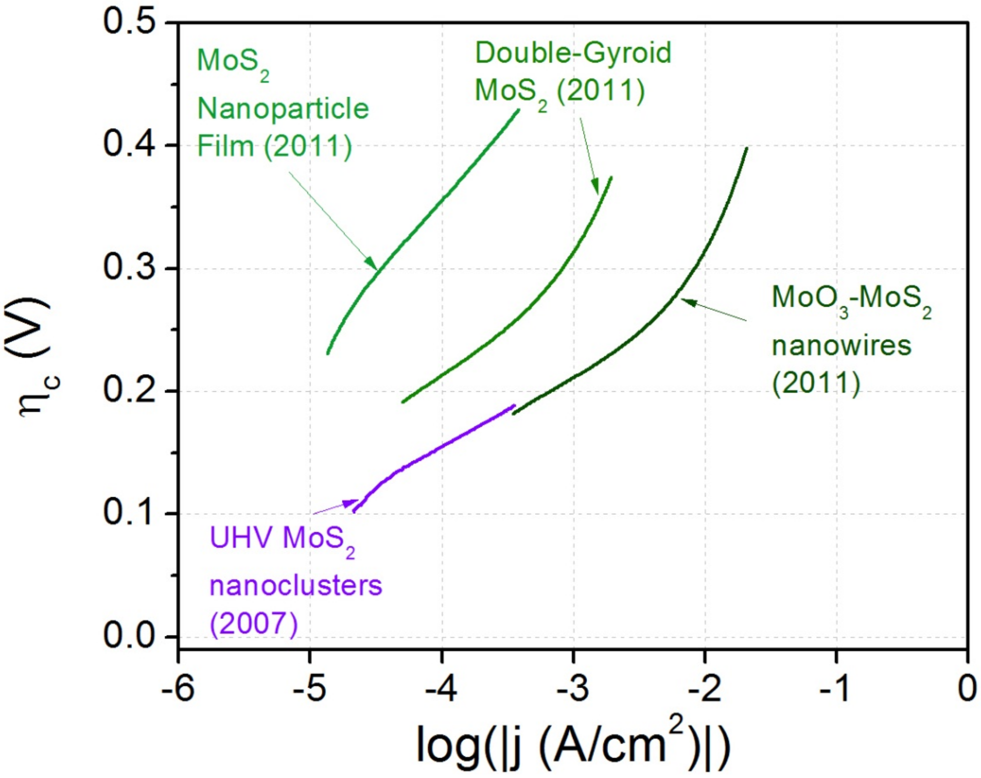
Previous Work: Prototype HSE & Electrocatalytic H_2 Evolution on Nanostructured MoS_2

HSE - Doctor Blade Films

- Novel synthetic method, but limited device area
- Mediocre spatial homogeneity
- Limited e-chem stability window – need for improved device architecture



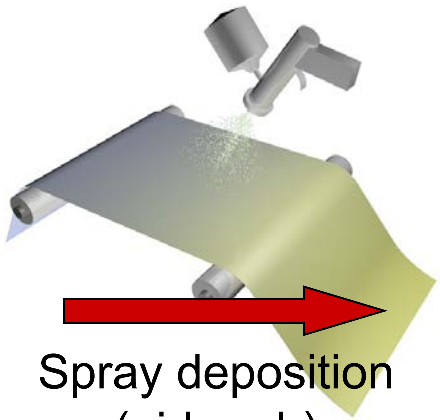
MoS_2 HER Activity



Take-home message: Previously, we demonstrated prototype transparent HSEs as well as promising results on electrocatalytically active MoS_2 nanostructures for H_2 production

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

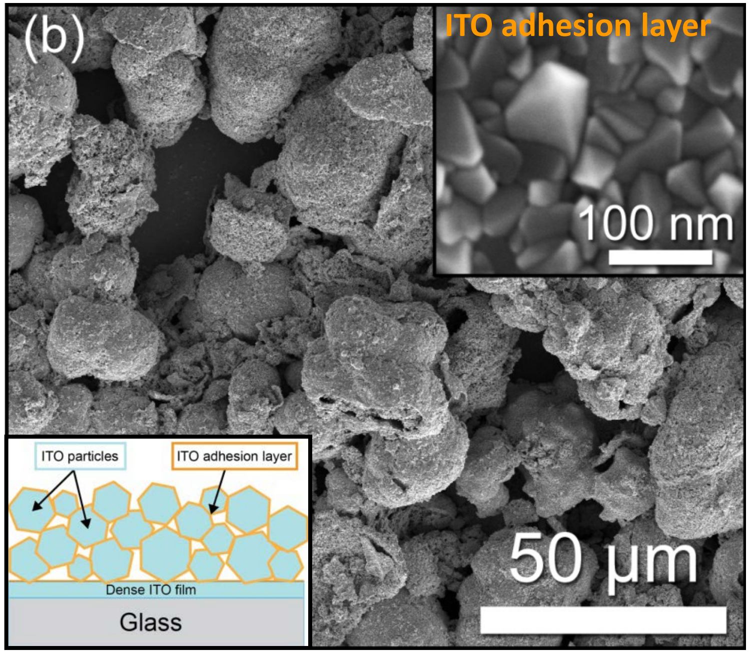
Precursor slurry:
- ITO powder (9:1, In:Sn)
- Indium (III) acetylacetonate
- Tin (IV) chloride
- Sol precursor ratio, 9:1, In:Sn
- HCl
- EtOH



Post-deposition heat treatment

1) 300 °C @ 0.3 °C/min in air
   - Controlled condensation 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

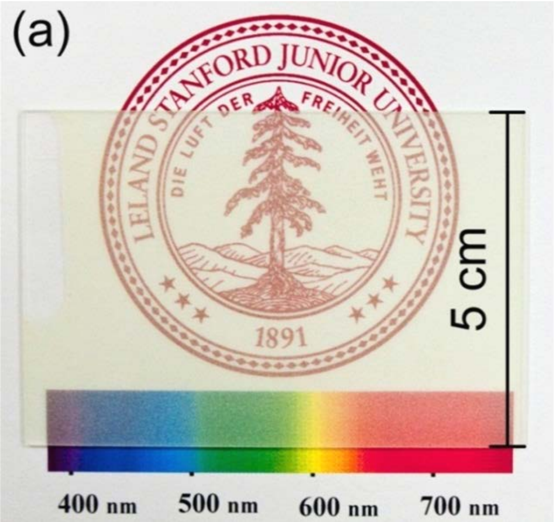
A Novel Synthetic process
- Simple sol-gel prep
- Template-agent free
- Tunable: RF, porosity, light scattering
- Spatially homogeneous
- Scalable to m^2 panels
- Transferable to other TCOs

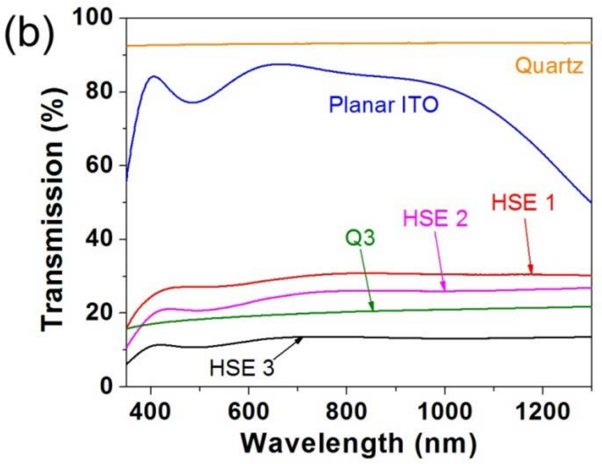


- A.J. Forman, Z. Chen, T.F. Jaramillo,
  "Macro-Structured High Surface Area Transparent Conductive Oxide Electrodes Fabricated via Low Cost, Scalable, Solution Phase Routes"
  - Provisional U.S. Patent filed September 2011.
  - Manuscript submitted, March 2012.

Take-home message: Milestone achieved - Developed a scalable low-cost synthetic route with facile spray processing to produce a fully tunable, high surface area, transparent electrode.

Technical Accomplishment: Highly Conductive &Transparent HSE Devices



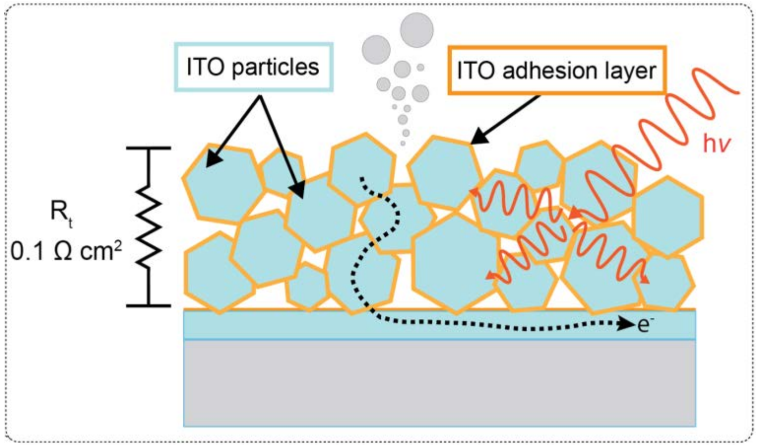


Ideal Optical Performance

- Visible-Near IR Transmission
  - Featureless - no absorption, only scattering
  - Tunable

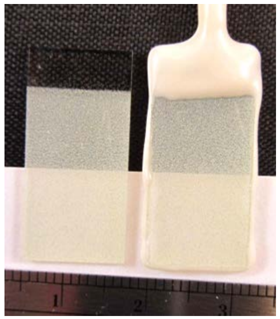
Highly Conductive Scaffolds

- Device sheet resistance:
  - 10-20 Ω/□
- Transverse resistance (R_t)
  - 0.1 Ω/100 μm
- Significant performance increase during past year



Take-home message: HSE structures have conductivities and optical properties that can allow for substantial improvements in PEC efficiency.

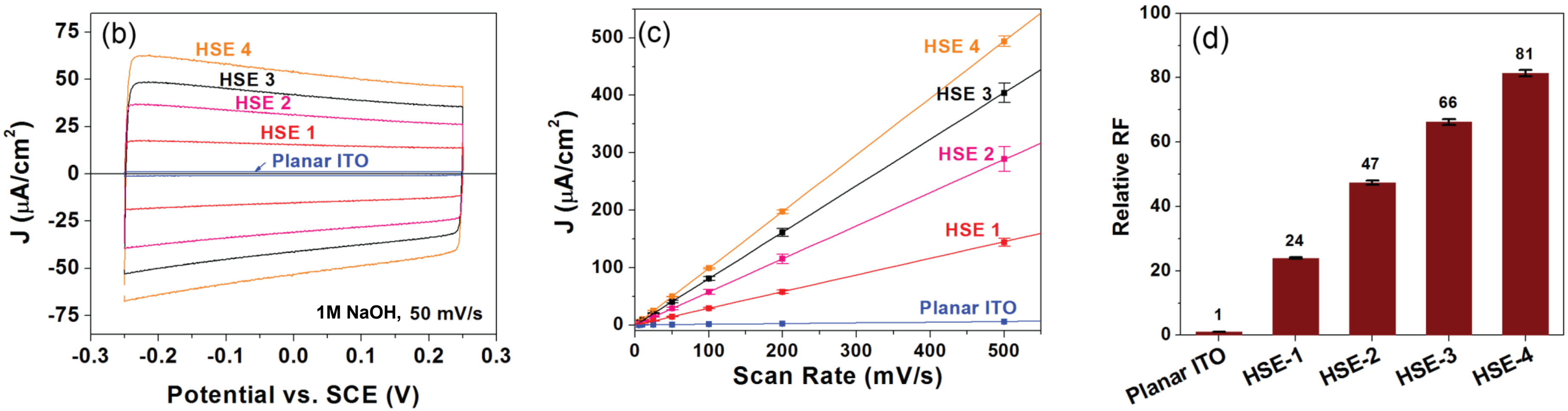
Technical Accomplishment: Quantification of HSE Surface Area



Electrochemical Surface Area Measurements

- Highly tunable RF up to ~100
- Very fast response = *not* diffusion limited

$$\text{Roughness Factor } (\mathbf{RF}) = \frac{\text{cm}^2 \text{ of solid-liquid interface}}{\text{cm}^2 \text{ of device}}$$



~100 fold increase in surface area!

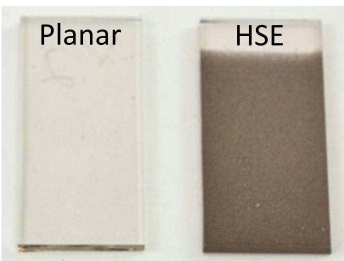
Take-home message: We have hit our target of developing a photo-electrochemical substrate that is transparent, conducting, high surface area, and macroporous.

Technical Accomplishment: HSE for Enhanced Optical Absorption and Electrochemical Accessibility of Ultra-thin Films – MnO_x on the HSE

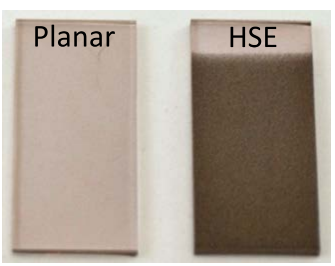
Ultra-thin films by Atomic Layer Deposition (ALD) on the HSE platform

- High IQE ultra-thin layers
- High ionic transport
- High Loading
- High optical density

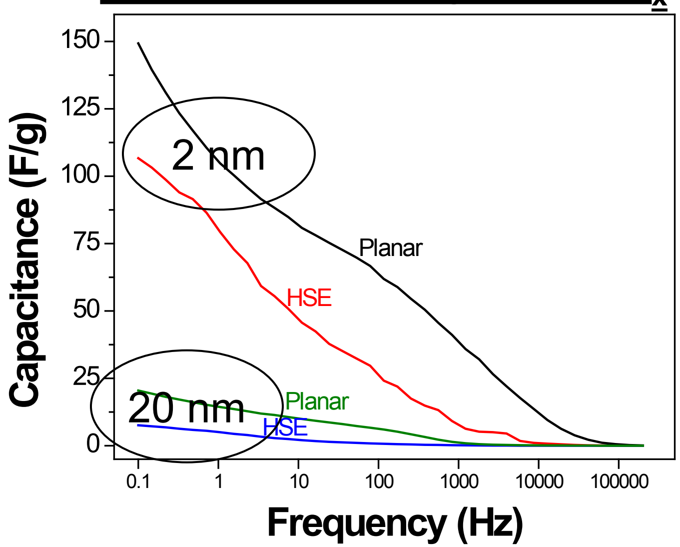
2 nm MnOx



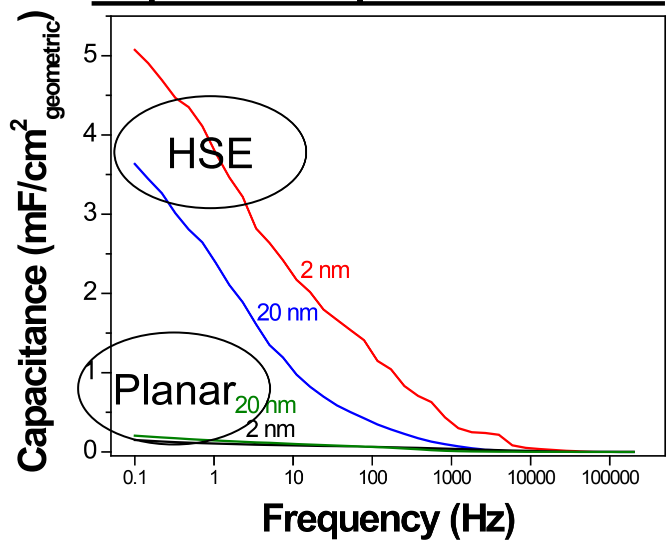
20 nm MnOx



Capacitance per gram MnO_x



Capacitance per device area



In Collaboration with: Prof. Stacey Bent, Katie Pickrahn, Stanford University

Take-home message: HSEs couple high material loading with high IQE to yield superior devices. Simultaneously large RF values, high conductivity, transparency and macro-porosity are uniquely enabling HSE characteristics.

Technical Accomplishment: Validation – using HSE Substrates to Enhance Hematite PEC Device Performance

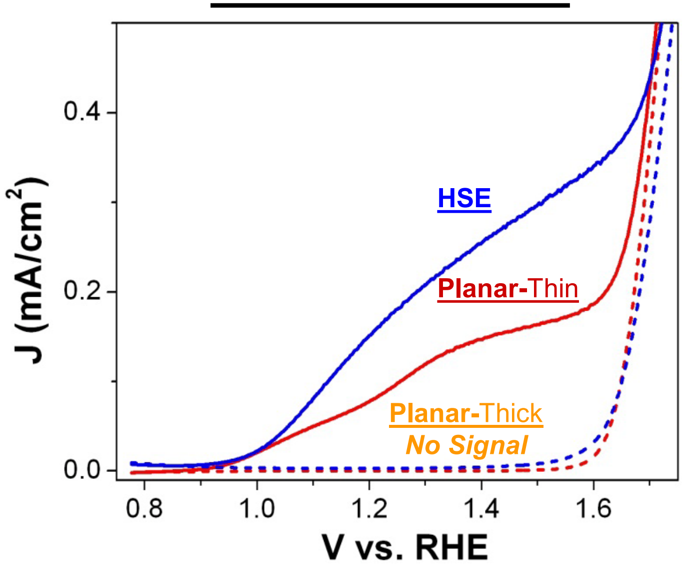
Hematite on HSE: Preliminary Results

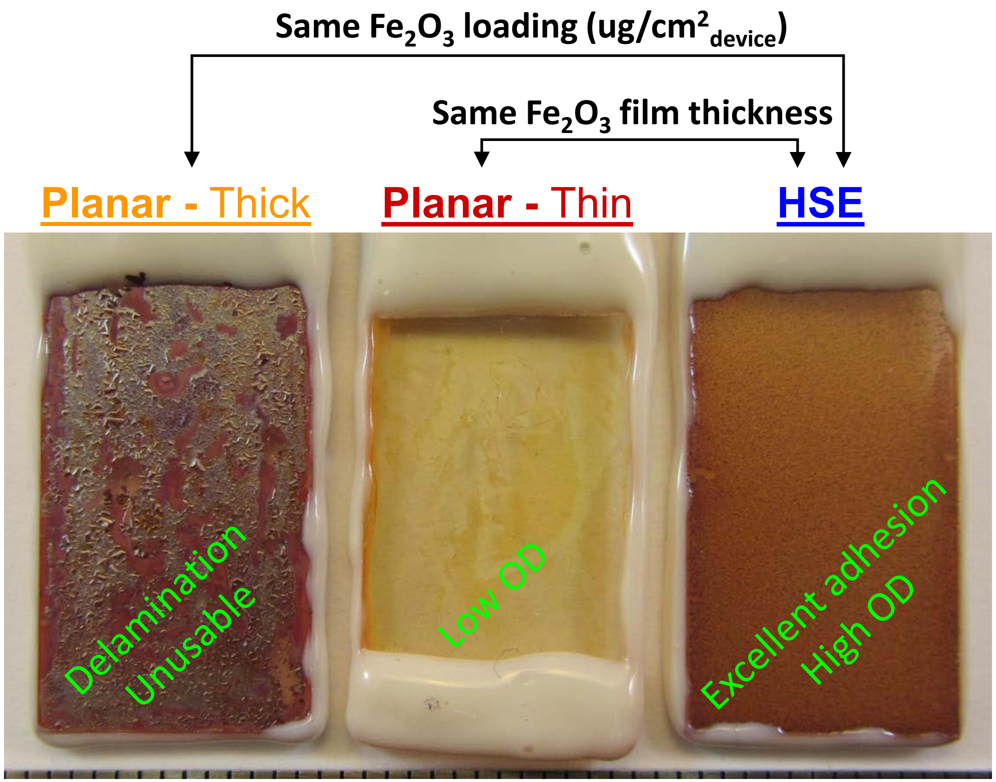
- Performance enhancement vs. planar substrates
- Superior loading → high OD
- Inhibits delamination of thick films

Hematite/ITO interfacial engineering

- Preliminary data on SiO_x, TiO_x layers show photocurrent enhancement

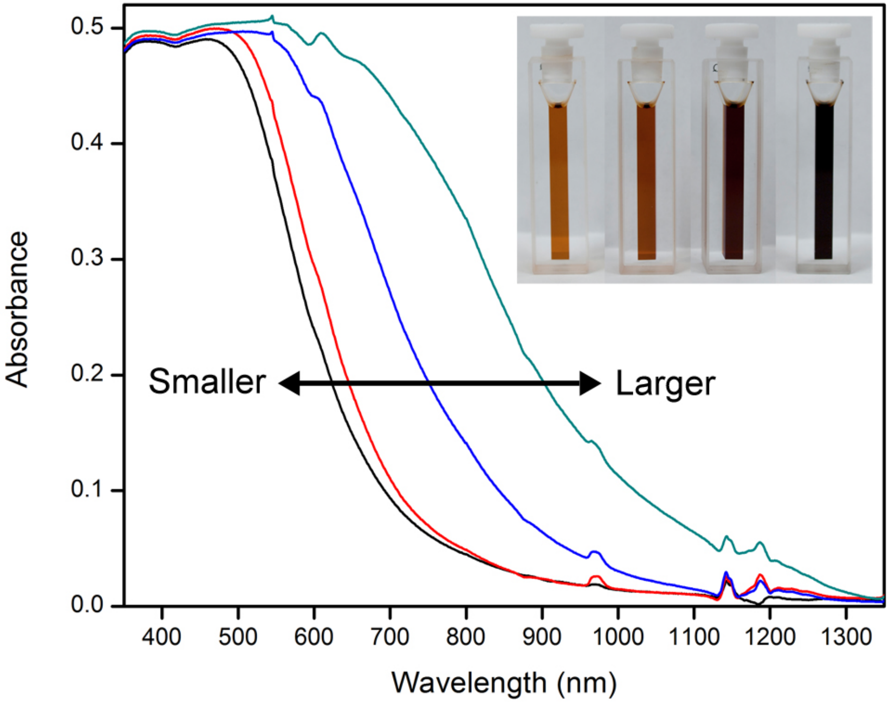
PEC Performance

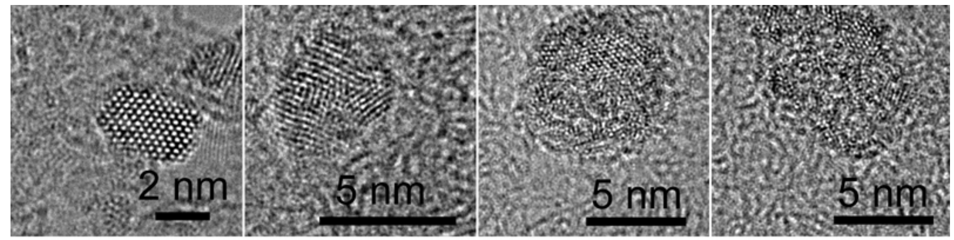




Take-home message: Nanostructured PEC films benefit from HSE support. The HSE permits far higher loadings (OD) of absorber material while preserving electrical contact.

Technical Accomplishments: Bandgap Engineering of MoS_2 nanoparticles





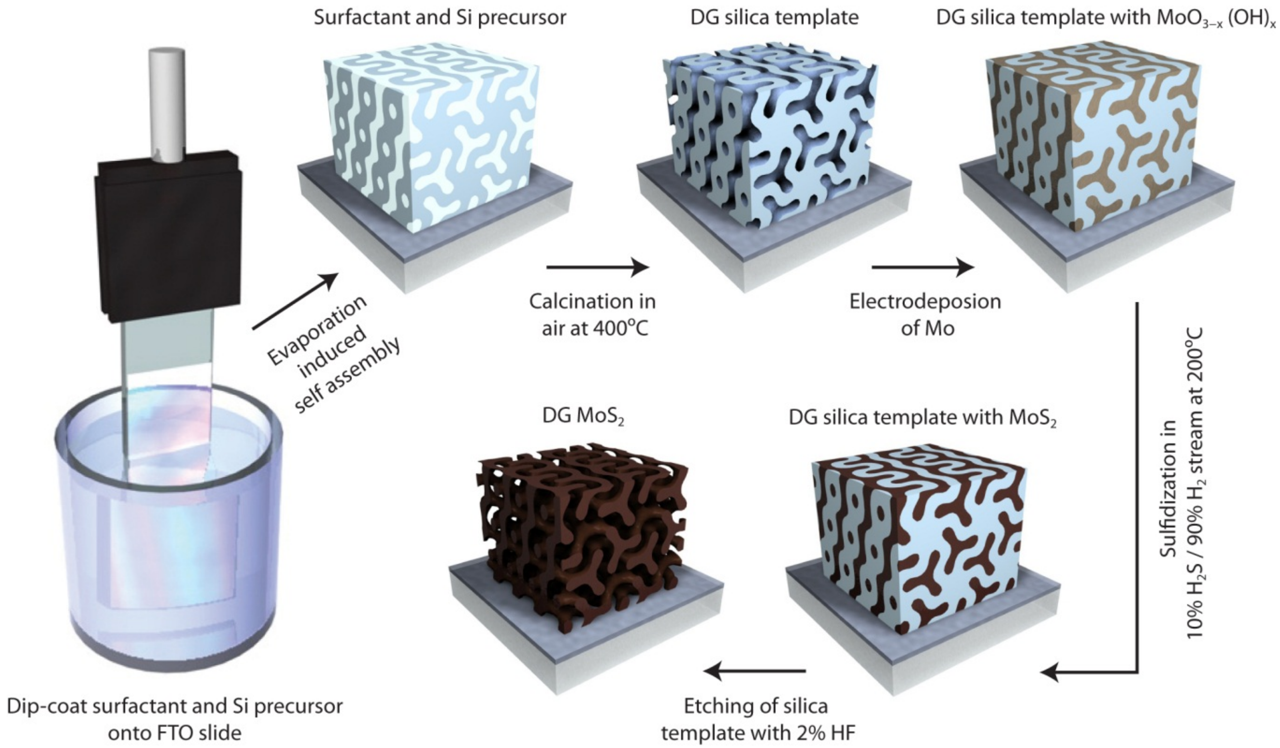
$\bar{x}$ = 2.4 nm	$\bar{x}$ = 4.8 nm	$\bar{x}$ = 7.8 nm	$\bar{x}$ = 8.3 nm
s = 0.7 nm	s = 1.2 nm	s = 2.4 nm	s = 1.7 nm

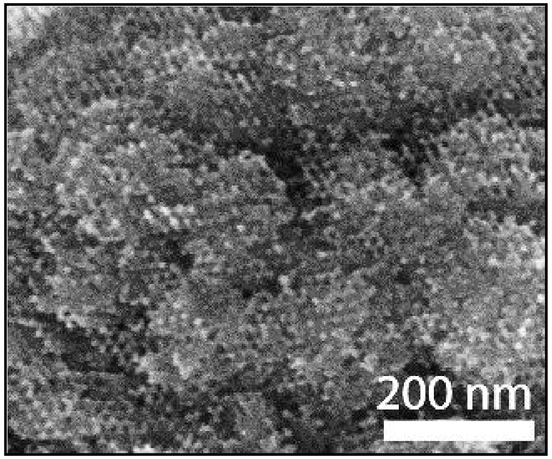
Size by TEM	Absorbance Onset α	Indirect Tauc $(\alpha h\nu)^{1/2}$
2.4 nm	1.8 eV	1.4 eV
4.8 nm	1.7 eV	1.3 eV
7.8 nm	1.5 eV	1.1 eV
8.3 nm	1.2 eV	0.9 eV

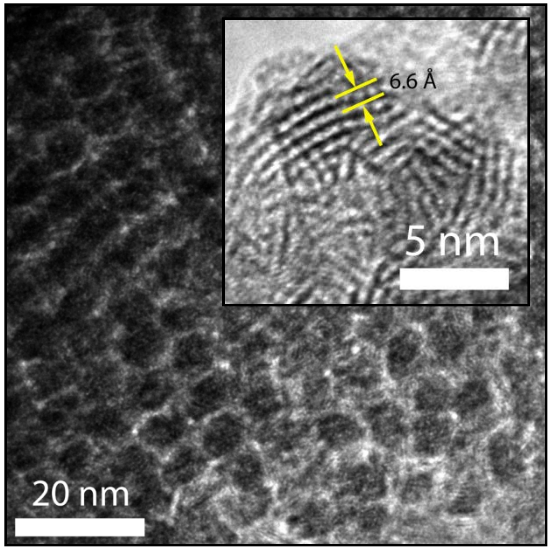
Blueshift in bandgap with decreasing size.

Take-home message: Nanoparticles of approx. 2-3 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.

Technical Accomplishment: Synthesis of a Mesoporous MoS_2 Double Gyroid





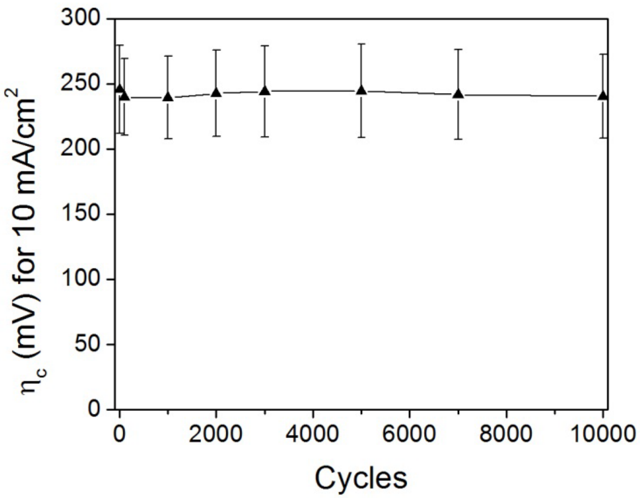


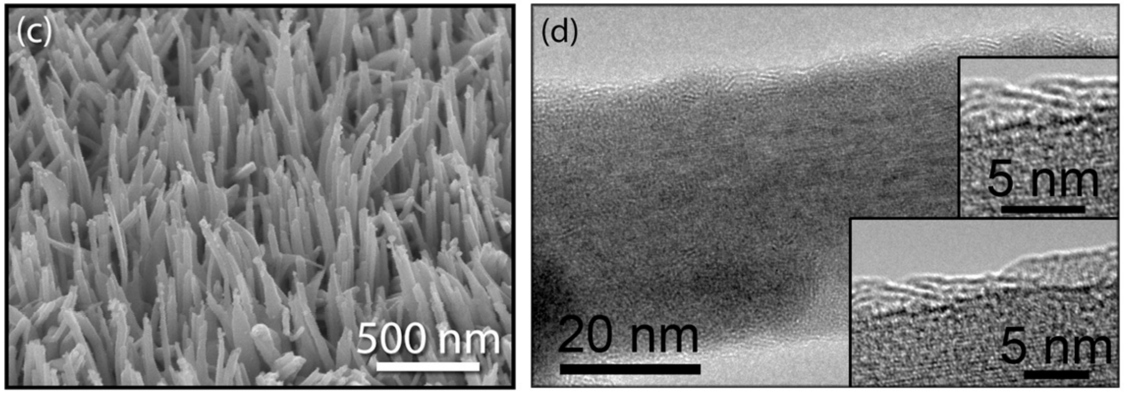
Evaporation induced self assembly (EISA)

- 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: Highly Stable H_2 Evolution Electrocatalysis by Core-shell MoO_3-MoS_2 Nanowires



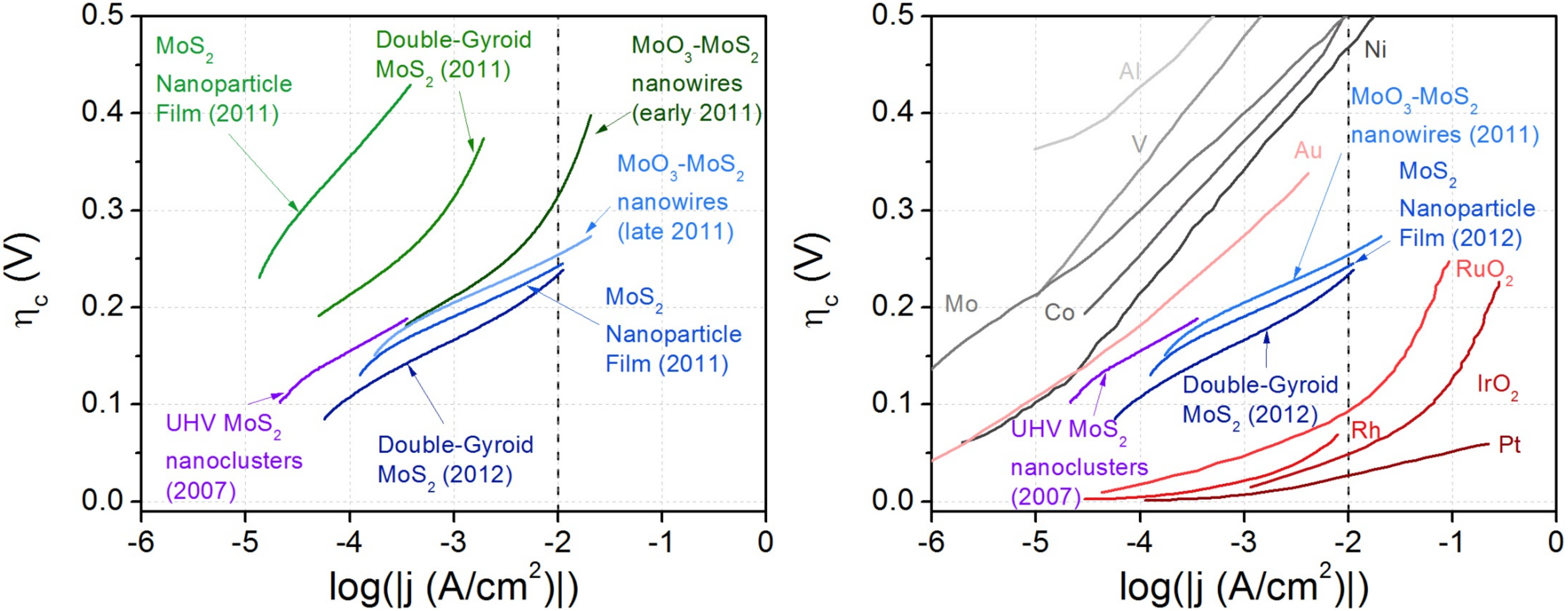


Nanowires after 10,000 cycles in 0.5 H_2SO_4 (aq.)

- Zhebo Chen, Dustin Cummins, Benjamin N. Reinecke, Ezra Clark, Mahendra K. Sunkara, and Thomas F. Jaramillo, "MoS_2 Coated MoO_3 Nanowires: Active, Stable, and Earth-abundant Catalysts for Hydrogen Evolution in Acid" *Nano Letters*, Vol. 11, pp. 4168-4175, 2011.

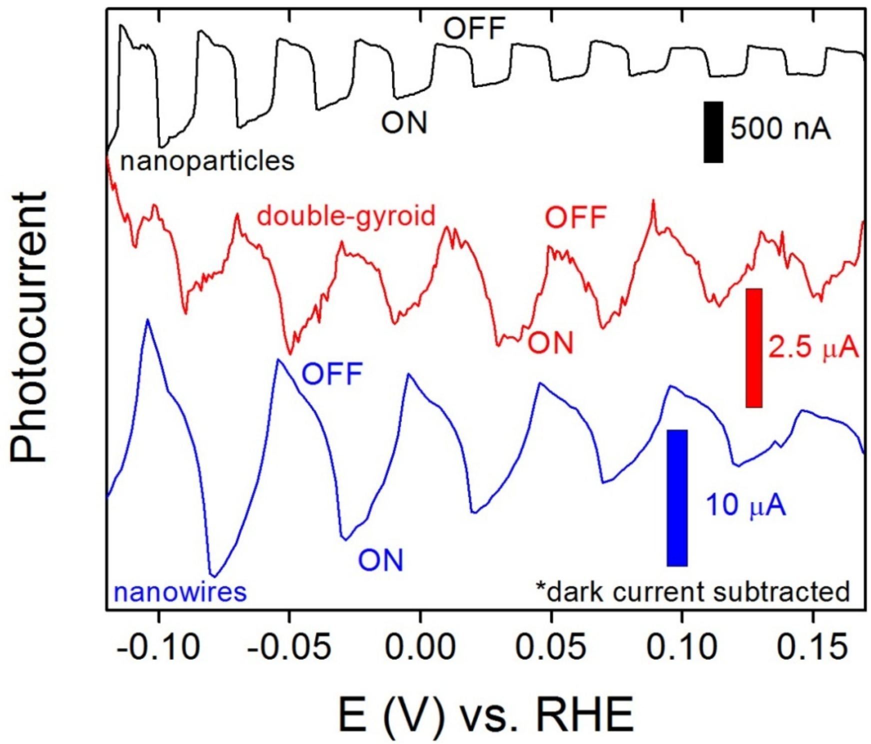
Take-home message: The core-shell nanowires are **100% stable** even after 10,000 cycles in sulfuric acid, and the conformal MoS_2 completely protects the otherwise unstable MoO_3 core.

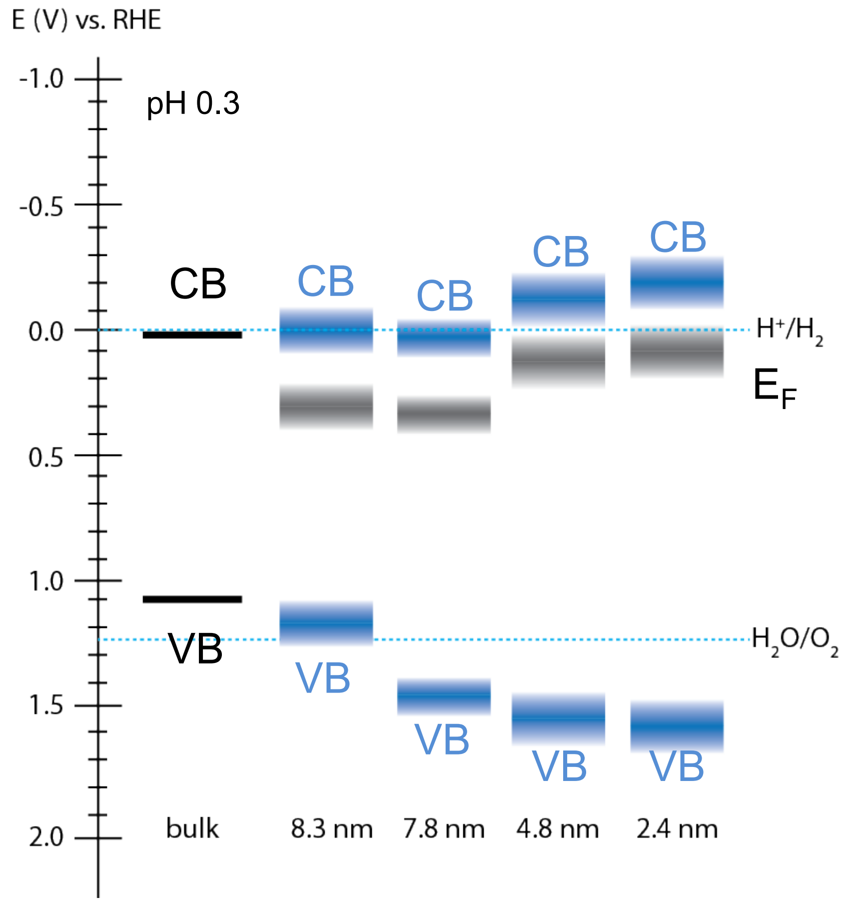
Technical Accomplishments: Significant Enhancement in Electrocatalytic Activity for MoS_2 Nanostructures



Take-home message: Our MoS_2 nanostructures are the most active non-precious metal catalysts for hydrogen evolution in acidic electrolyte ever developed

Technical Accomplishments: PEC Characterization of Nanostructured MoS_2





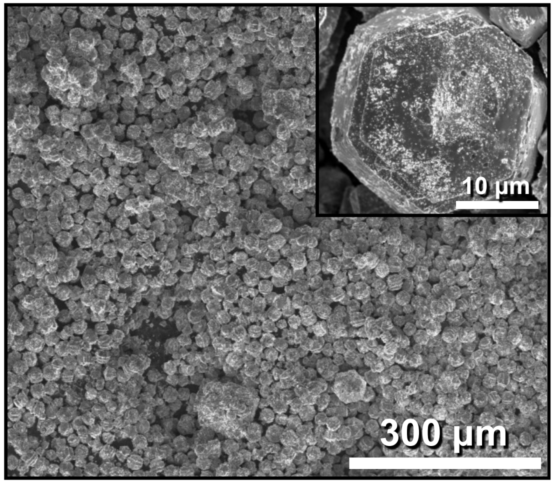
Take-home message: Nano-MoS_2 is PEC active with the correct band structure, and future incorporation into a HSE will allow us to achieve high efficiencies

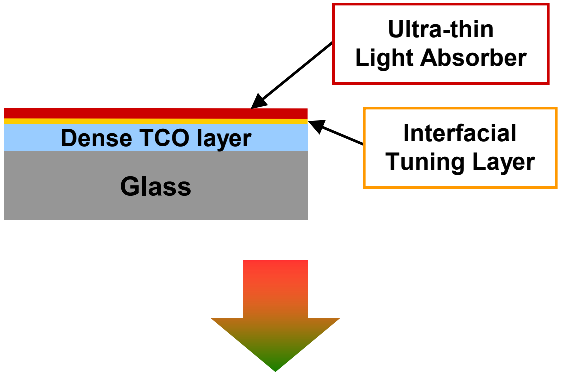
Proposed Future Work: Enabling Performance Gains for Charge-Transport Limited Materials

Future Work

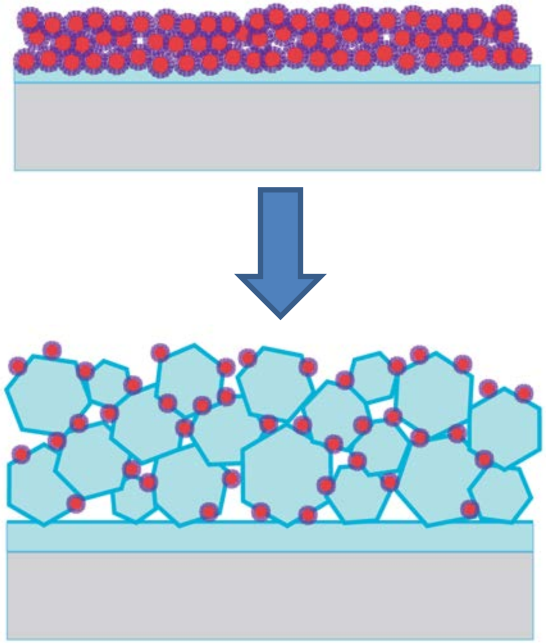
- Expand HSE composition to AZO, FTO and other TCOs
    - Facile spray processing is amenable to many materials
- Perfect HSE/absorber contact via interfacial engineering
    - Monolayers of SiOx, TiOx, etc. to reduce traps and enhance film growth
- Integrate MoS_2 and other nanomaterials with HSE

AZO Particles





Ultra-thin Layer PEC Device Optimization



Take-home message: Future prospects are exciting in integrating PEC materials with the HSE.

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, monthly) 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 **PEC substrates** consisting of macroporous, high surface area, transparent, conducting oxides upon which PEC materials can be loaded.

#2. Develop new **PEC materials** based on nano-structured MoS_2 that can potentially meet DOE performance targets (2013 and 2018).

- **Approach**

#1. The approach is to use scalable, solution-based spray processing to create large area electrodes with porosity on the micron scale.

#2. The approach is to nanostructure MoS_2 in order to tailor its bulk and surface properties for PEC.

- **Technical Accomplishments & Progress**

#1. We developed and characterized a **robust HSE scaffold** that is transparent, conducting and macroporous with a tunable surface area. Initial HSE thin-film device construction shows **significant performance gains**.

#2. We have developed MoS_2 nanostructures that are **highly active H_2 evolution catalysts**, however PEC efficiencies remain low.

- **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**

- Expand HSE composition to AZO, FTO and other TCOs.
- Perfect HSE/absorber contact via interfacial engineering.
- Integrate MoS_2 and other nanomaterials with HSE.

Technical Back-Up Slides

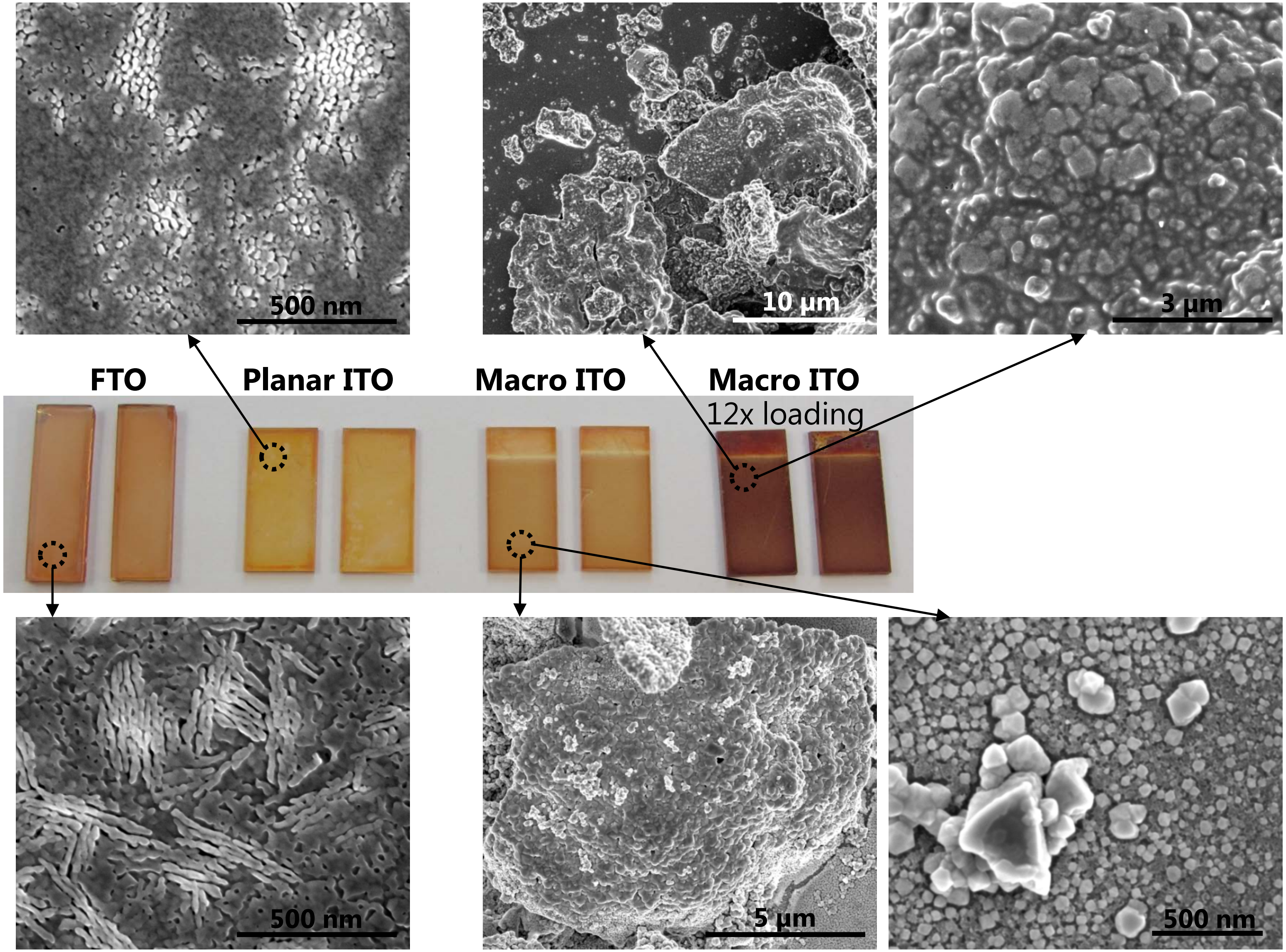
(max of 5)

Relevance: Technology Barriers

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

Barrier	Challenges	Strengths
AA. **PEC Device and System Auxiliary Material**	- Need a transparent, conducting, high surface area scaffold for nanostructured absorbers.	- Enable/enhance charge transport limited PEC materials. - Maximize solar H_2 production: EQE = IQE x OD
Y. **Materials Efficiency**	Oxides for PEC: - Charge transport limitations require thin films - Low absorption coefficients	- Stable, abundant, low cost, synthetically facile - Increased IQE for thin films
	MoS_2 for PEC: - Bandgap is too small at 1.0-1.2 eV - Indirect bandgap - C. Band 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 enlarges bandgap and shifts C. Band above $E^0_{H+/H2}$ - High charge mobility along the basal plane (> 100 $cm^2/V*sec$) - Excellent hydrogen evolution catalysis for nano-MoS_2
Z. **Materials Durability**	- n-MoS_2: unstable photo-oxidation of the sulfide surface	- p-MoS_2: 1000 hrs photostability - nano-MoS_2: Stable H_2 production >10,000 cycles

Backup Slide: Hematite Film Morphology



Backup Slide: Capacitive Behavior of MnO_x