NSF/DOE Solar Hydrogen Fuel: Engineering Surfaces, Interfaces, and Bulk Materials for Unassisted Solar Photoelectrochemical (PEC) Water Splitting

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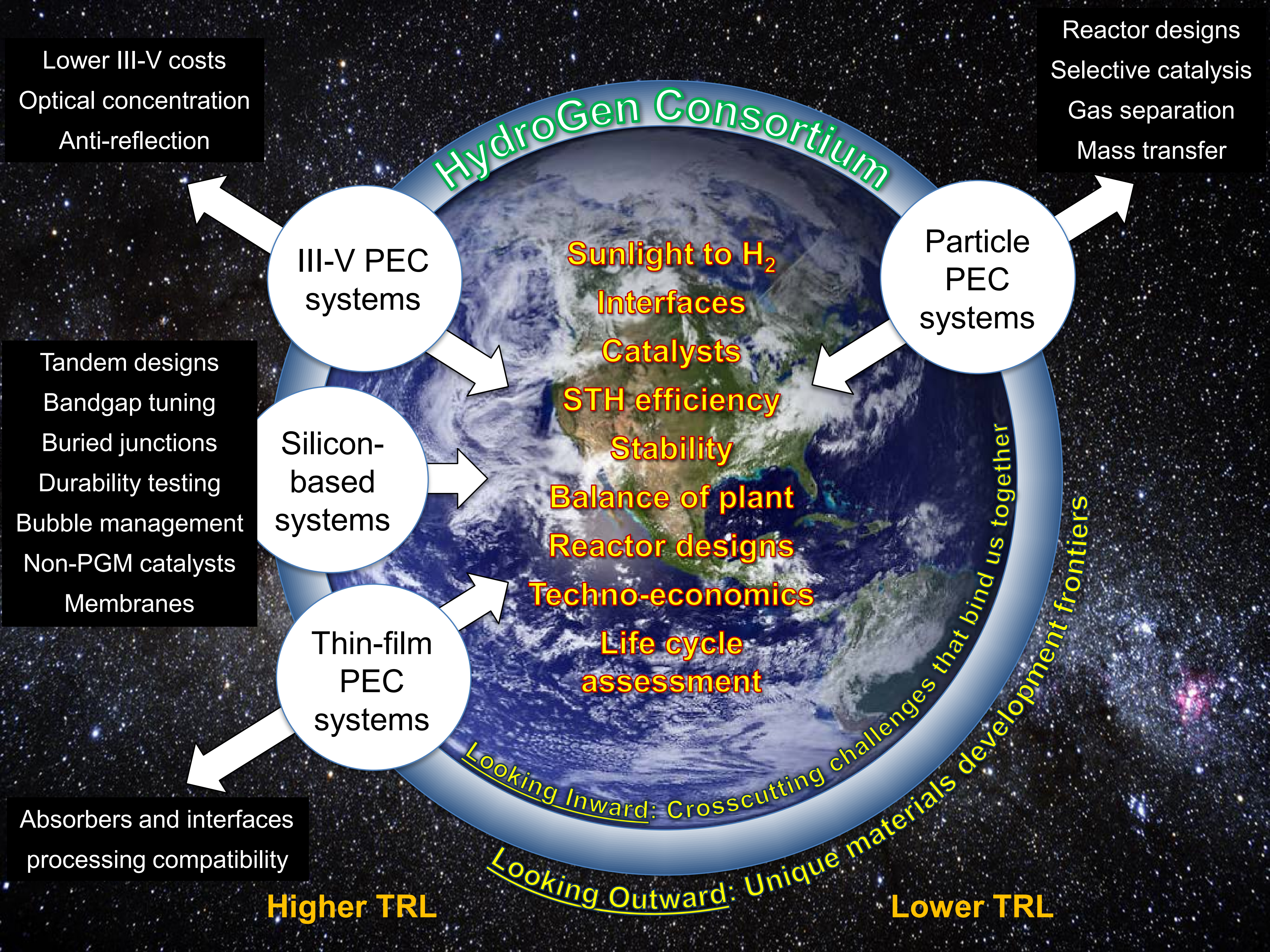
Stanford University

June 8, 2016

Project ID#: PD119


HydroGen Consortium
Lower III-V costs
Optical concentration
Anti-reflection
III-V PEC systems
Reactor designs
Selective catalysis
Gas separation
Mass transfer
Particle PEC systems
Tandem designs
Bandgap tuning
Buried junctions
Durability testing
Bubble management
Non-PGM catalysts
Membranes
Silicon-based systems
Thin-film PEC systems
Absorbers and interfaces
processing compatibility
Sunlight to H_2
Interfaces
Catalysts
STH efficiency
Stability
Balance of plant
Reactor designs
Techno-economics
Life cycle assessment
Looking Inward: Crosscutting challenges that bind us together
Looking Outward: Unique materials development frontiers
Higher TRL
Lower TRL

Overview

Timeline and Budget

- Project Start Date: 1/1/15
- Project End Date: 12/31/2017
- Total Project Budget: $750,000
  - Total Recipient Share: $750,000
  - Total Federal Share: $750,000
  - Total DOE Funds Spent*: $434,826

    * as of 3/31/16

Partners

- National Renewable Energy Laboratory (NREL)
- PEC Working Group

Barriers and Targets

Barriers

- Materials Efficiency – Bulk and Interface (AE)
- Materials Durability – Bulk and Interface (AF)
- Integrated Device Configurations (AG)

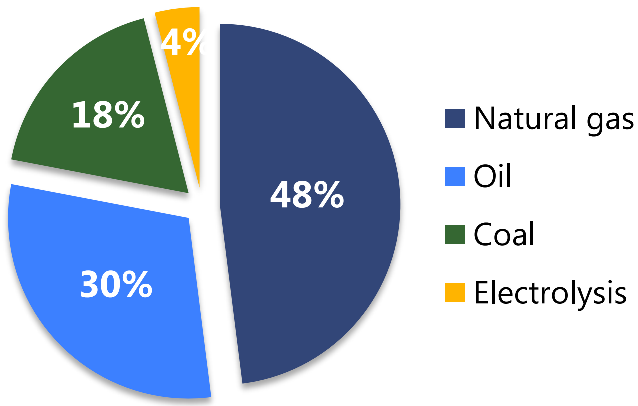
Targets

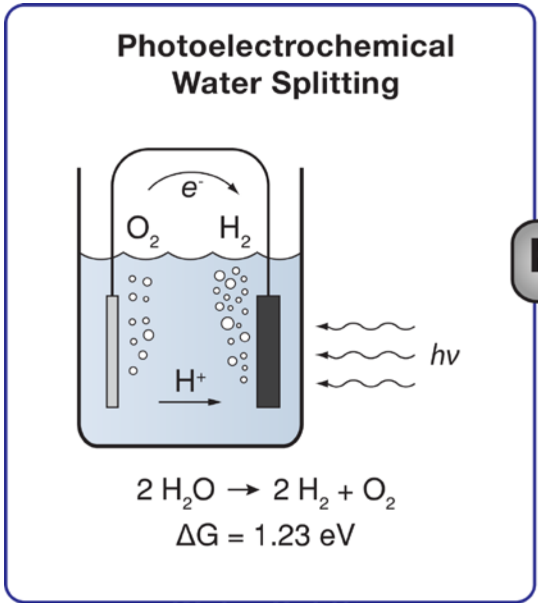
- Photoelectrochemical Hydrogen Cost
- Annual Electrode Cost per TPD H_2
- Solar to Hydrogen (STH) Energy Conversion Ratio
- 1 sun Hydrogen production rate

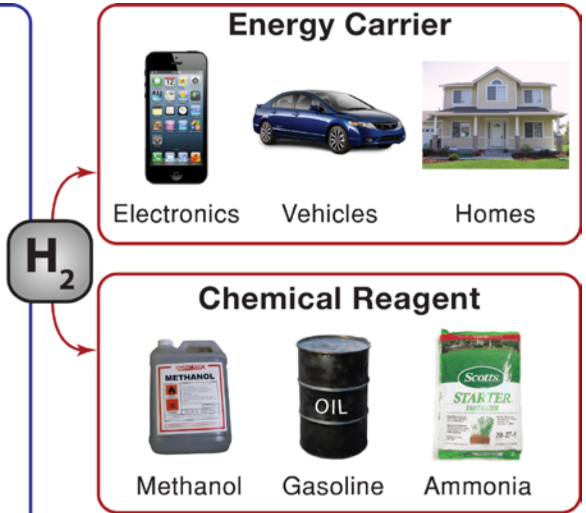
Relevance and Impact

H_2 Production via Photoelectrochemical Water Splitting

Origin of worldwide H_2 production of ~50 billion kg/year

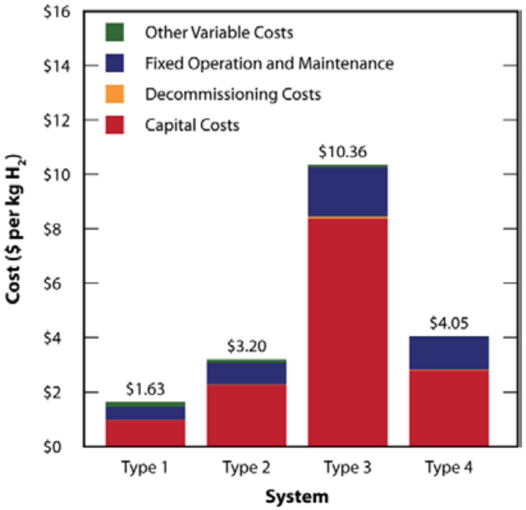






iPhone 5 image: http://static.ibnlive.in.com/ibnlive/pix/sitepix/09_2012/iphone-5-b-130912.jpg
Car image: cdnedge.vinsolutions.com/dealerimages/Dealer 3294 Images/2011-honda-civic-si.jpg
House image: http://www.plu.edu/~allenka/img/House_Front.jpg
Methanol image: http://www.chemodex.co.uk/store/images/methanol.jpg
Oil drum image: http://blog.timesunion.com/opinion/files/2011/11/1121_WVtarsands.jpg
Fertilizer image: http://www.orau.org/ptp/collection/consumer%20products/fertilizer.jpg

Hydrogen is an important industrial chemical and potential future fuel. Photoelectrochemical (PEC) water splitting offers the potential for sustainable H_2 production from sunlight and water. Technoeconomic analysis of centralized PEC H_2 production facilities shows that this process can become economically competitive with further improvements in device efficiency, durability, and cost.



U.S. Department of Energy & National Hydrogen Association.
A. Midilli & I. Dincer. *International Journal of Hydrogen Energy* **2007**, 32, 511
Pinaud, B.A., T.F. Jaramillo, et al. *Energy & Environmental Science*, 2013. **6** (7): 1983-2002.

Relevance and Impact

Objectives

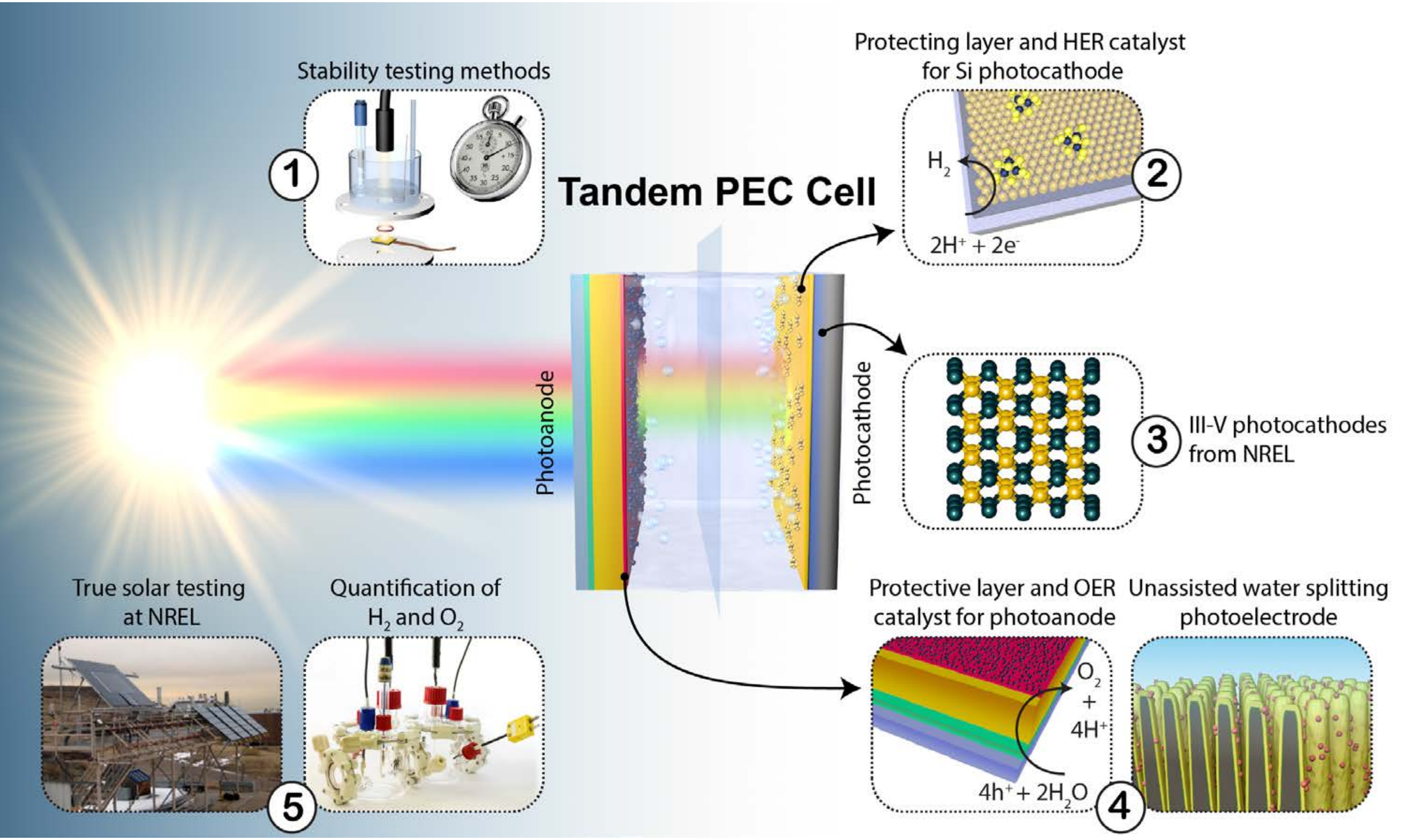
- Method and protocol development to understand photoelectrode corrosion *in acid*.
- Interfacial engineering of the Si surface to provide enhanced catalytic activity and corrosion resistance *in acid* by means of molybdenum sulfide nanomaterials.
- Interfacial engineering of III-V photocathode surfaces with similar approaches, in collaboration with Dr. Todd Deutsch at the National Renewable Energy Laboratory (NREL).
- Interfacial engineering of the $BiVO_4$ surface to provide enhanced electronic properties, catalytic activity and corrosion resistance *in acid* with a series of ultra-thin metal / metal oxide films.
- Quantification of H_2 and O_2 and true solar testing at NREL.

Technical Targets we are aiming to meet:

10% STH Efficiency
100 J/s per m^2 of Hydrogen Production

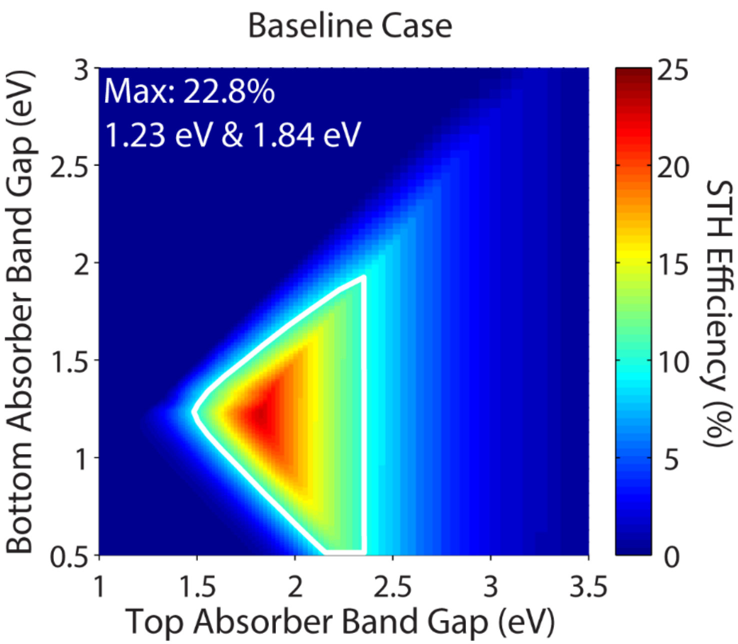
Approach

Testing Design and Tandem Device Engineering



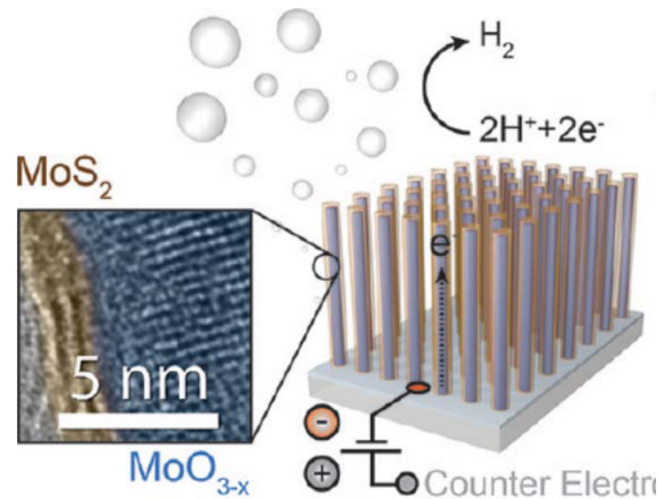
Approach
Material Selection

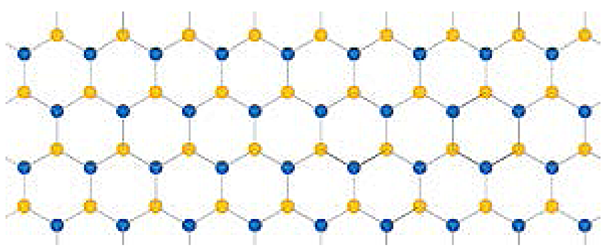
Photoabsorber materials



Modeling of realistic STH efficiency as a function of band gaps for a tandem absorber PEC system shows that 20% STH can be achieved with a tandem device with band gaps of 1.2 and 1.8 eV

Protection layer material





MoS_2 is promising as a protection layer for materials unstable in acid.

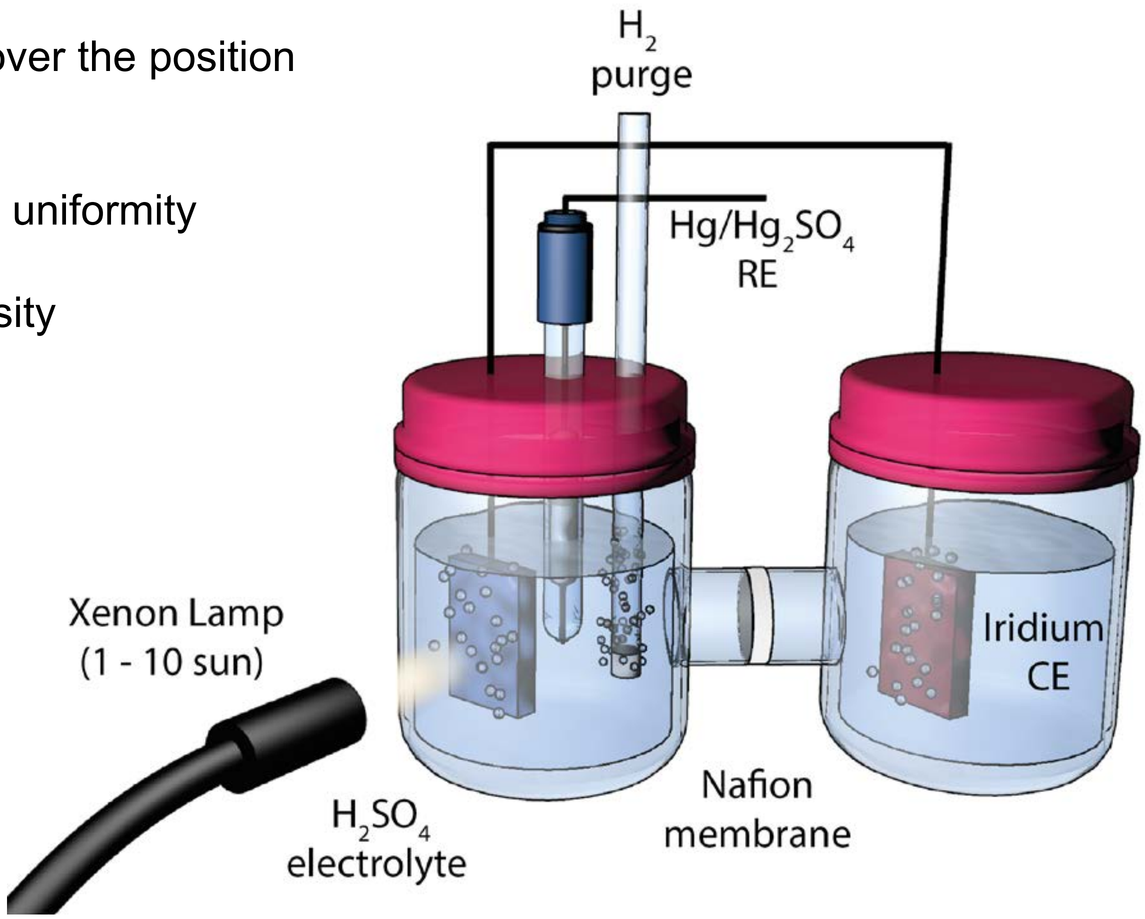
Seitz, L. C.; Chen, Z.; Forman, A. J.; Pinaud, B. A.; Benck, J. D.; Jaramillo, T. F. *ChemSusChem* **2014,** *7* (5), 1372-1385.
Zhebo Chen, Dustin Cummins, Benjamin N. Reinecke, Ezra Clark, Mahendra K. Sunkara, and Thomas F. Jaramillo. *Nano Letters* **2011** *11* (10), 4168-4175

Approach

Stability measurement setup

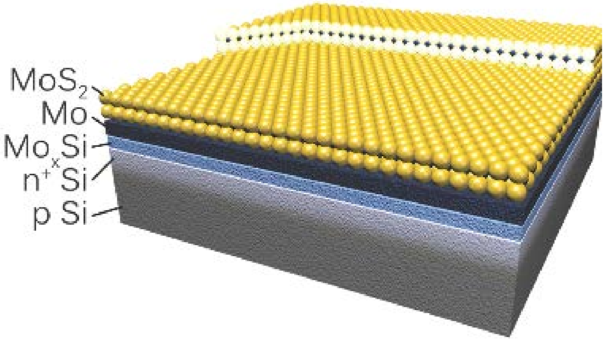
We have developed a photoelectrochemical (PEC) setup improves the reliability of our long term stability measurements

- Precise control over the position of the electrode
- High illumination uniformity
- 1 – 10 sun intensity



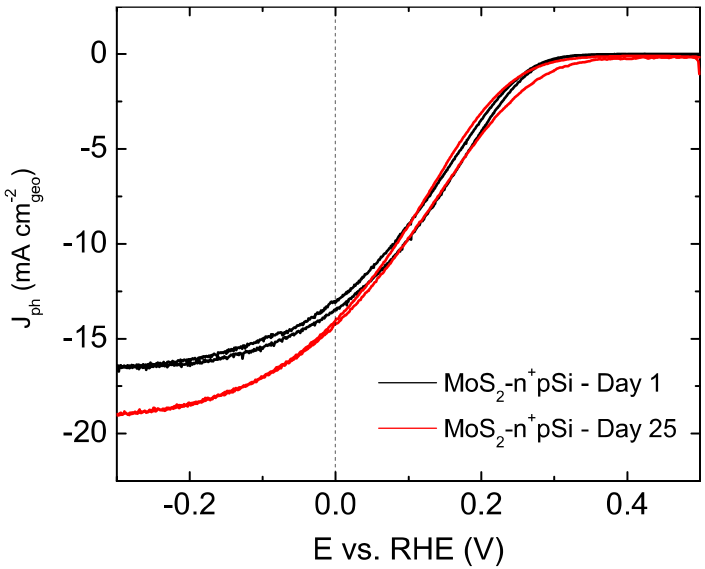
Accomplishments and Progress

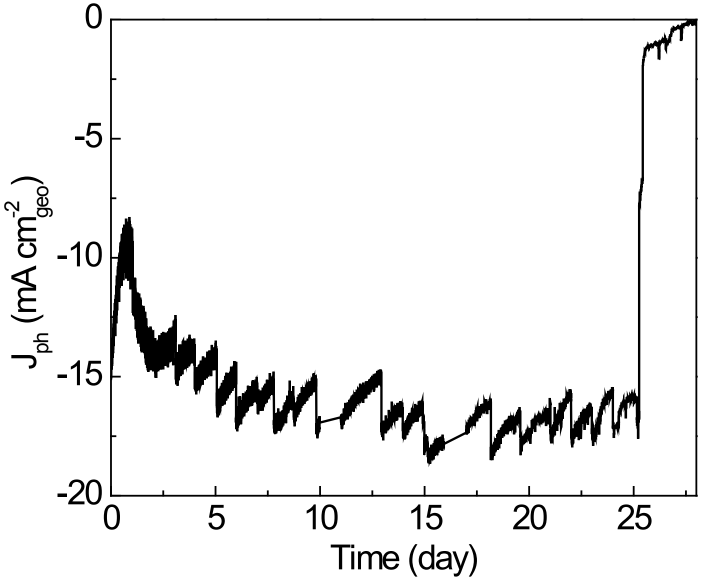
Stability of MoS_2-Si Photocathodes



Benck J. D., Lee S. C., Fong K. D., Kibsgaard J., Sinclair R., Jaramillo T. F. (2014). Adv. Energy Mater., 4: 1400739.

- Silicon photocathodes were prepared with MoS_2 protection layers.
- Stability testing in 0.5 M sulfuric acid, under 1 sun illumination at 0.0 V vs. RHE, found the samples to be stable for 25 days of continuous operation.
- The electrode subsequently failed catastrophically during Day 26.



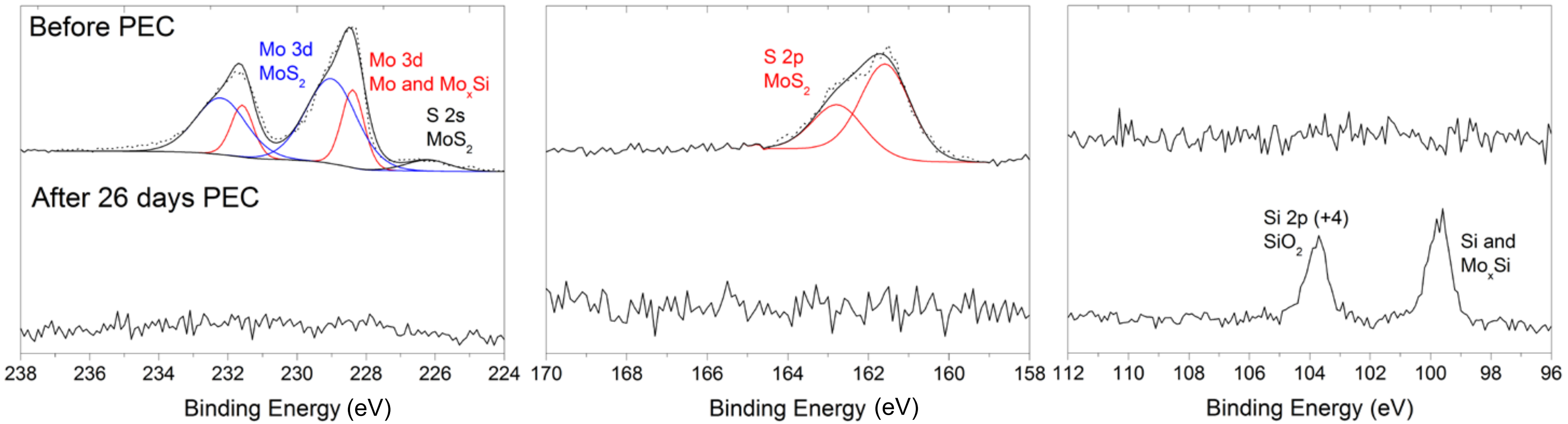


Laurie A. King, Thomas R. Hellstern, and Thomas F. Jaramillo. *Manuscript in Preparation (2016).*

Accomplishments and Progress

Understanding failure mechanisms of MoS_2-Si

Comparison by XPS measurement pre and post PEC stability testing

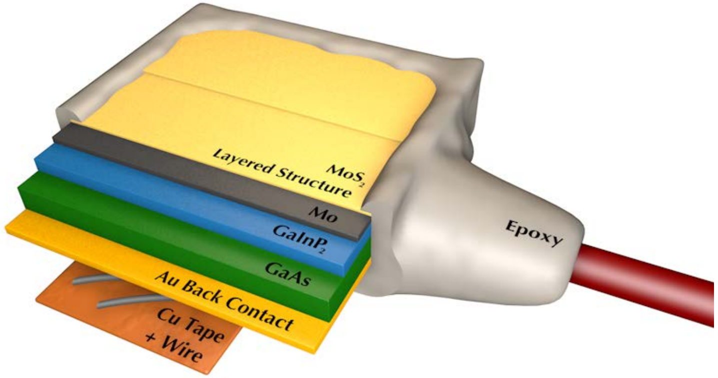


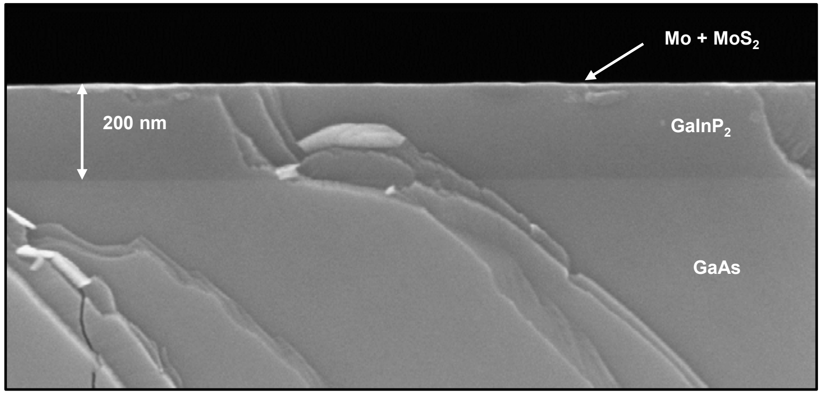
- After the 26 days of PEC testing and catastrophic failure, no molybdenum or sulfur species are detected by XPS evidencing the absence of the MoS_2 protection layer.
- Additionally, silicon is uncovered with evidence of additional silicon dioxide formation.
- Ongoing efforts are aimed at probing failure mechanisms and at increasing stability.

Laurie A. King, Thomas R. Hellstern, and Thomas F. Jaramillo. *Manuscript in Preparation (2016).*

Accomplishments and Progress

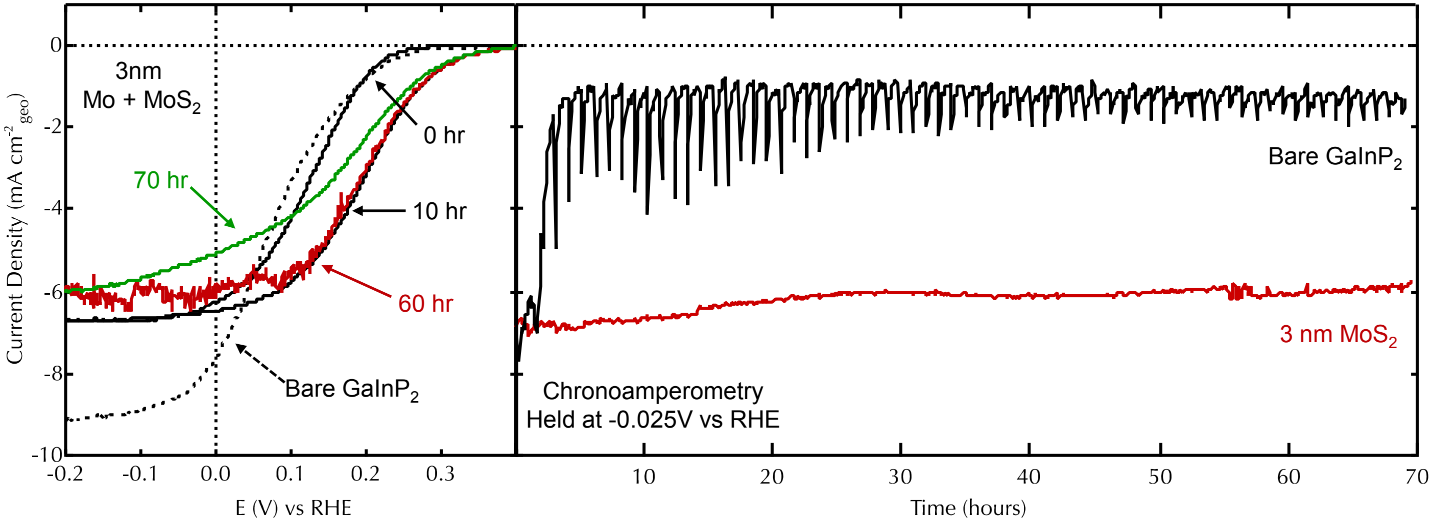
Protecting the surface of $GaInP_2$





We used MoS_2 to protect $GaInP_2$ in acid increasing its stability >500x without losing significant photocurrent density.

The MoS_2 further functions as a catalyst for the Hydrogen Evolution Reaction improving onset potential.

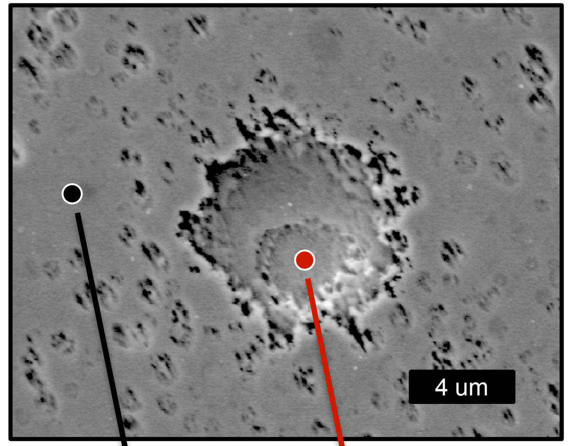


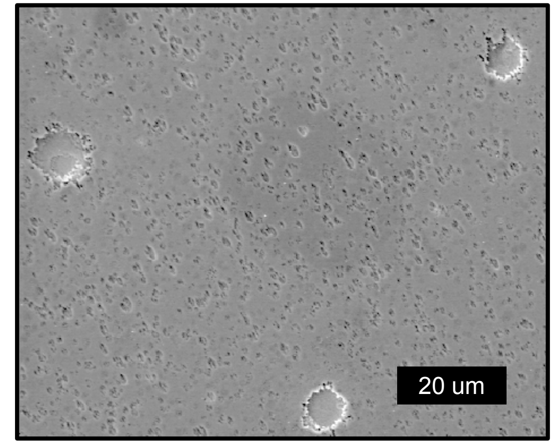
Britto R.J., Benck J.D., Young J.L., Hahn C., Deutsch, T.G., Jaramillo T.F. *Journal of Physical Chemistry Letters* (accepted, 2016)

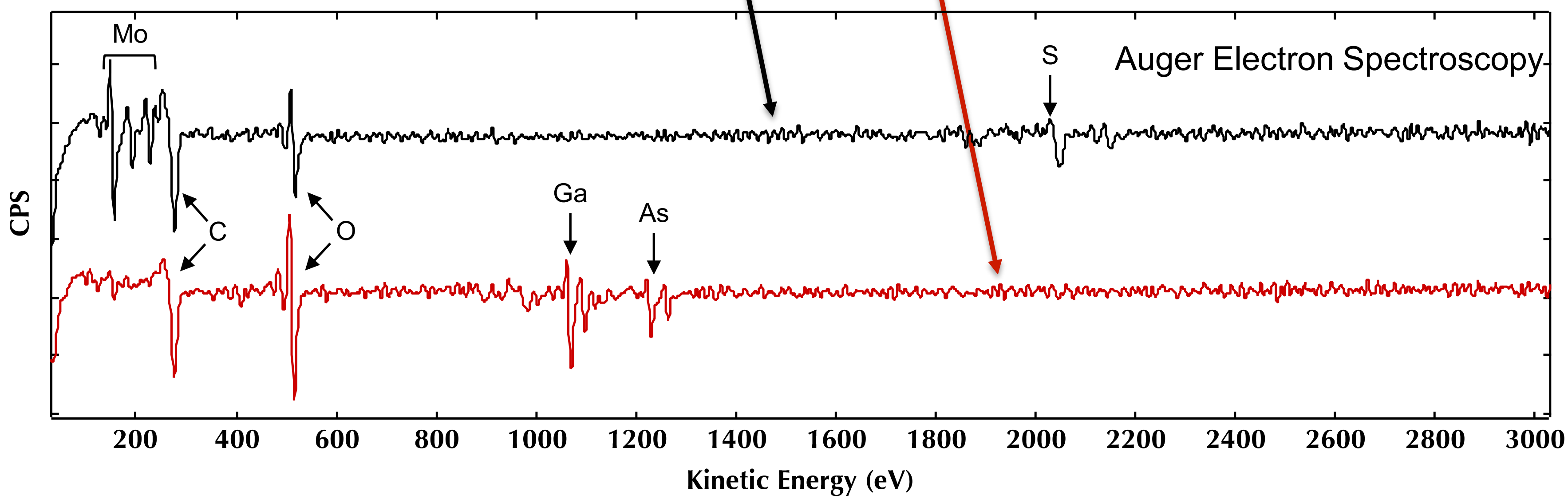
Accomplishments and Progress

Characterizing failure mechanisms of MoS_2-$GaInP_2$

The Auger spectra reveals the failure mechanism for MoS_2 on $GaInP_2$. Pores form in the MoS_2 exposing the $GaInP_2$ underneath. The $GaInP_2$ is then corroded to expose the degenerately doped GaAs substrate.

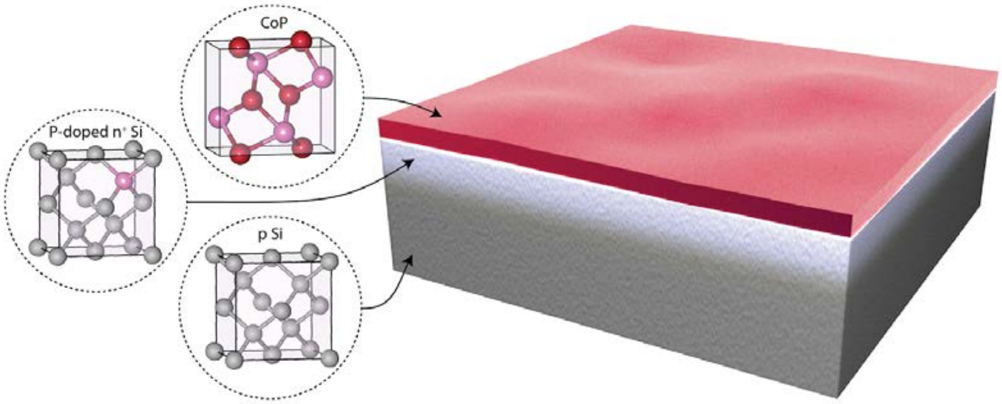




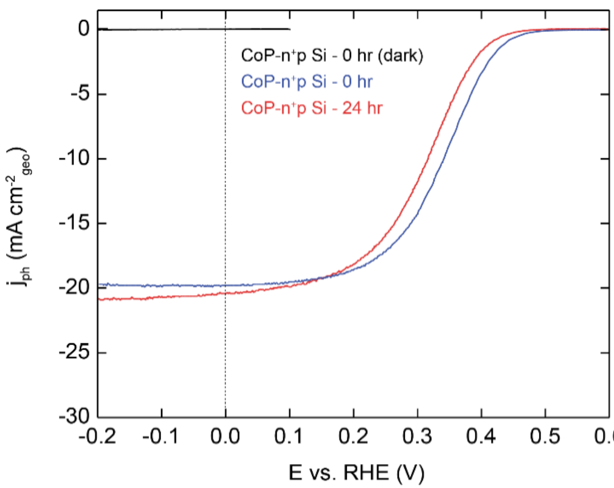


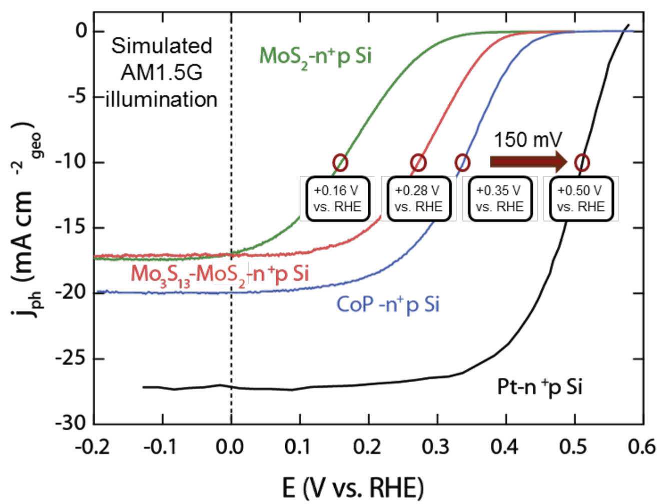
Accomplishments and Progress

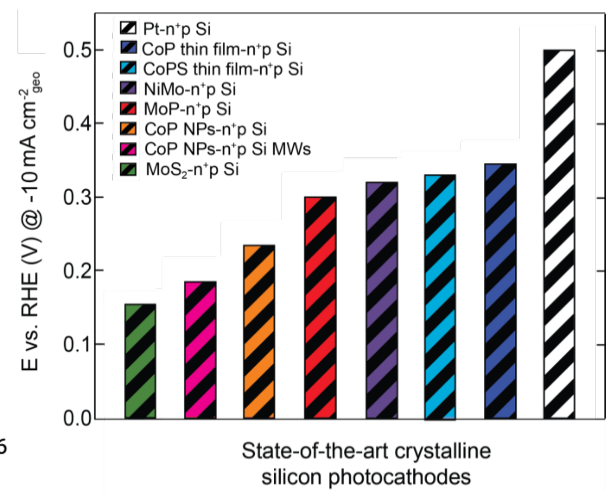
Stability of CoP-n⁺p Si Photocathodes



The CoP catalyst grown on n⁺p Si shows excellent activity and stability. This performance puts it among the best non-precious metal Si photocathodes ever tested in acidic or basic electrolyte.





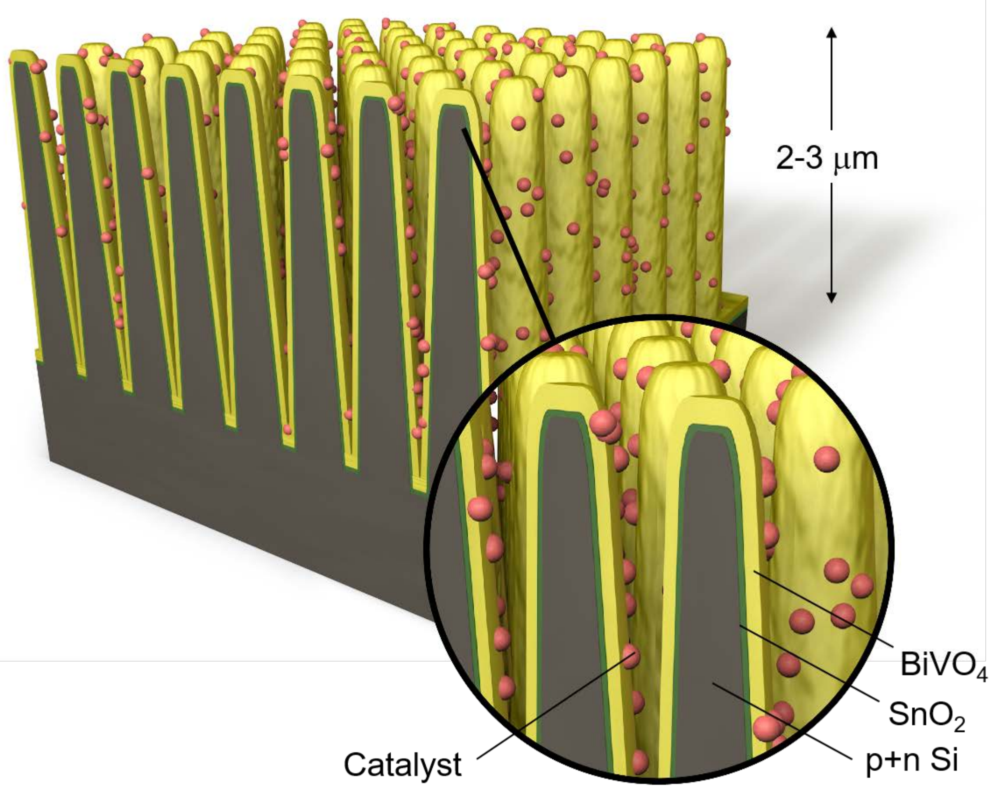


Hellstern T. R., Benck J. D., Kibsgaard J., Hahn C., Jaramillo T. F. et al. Advanced Energy Materials 6 (4) 2016

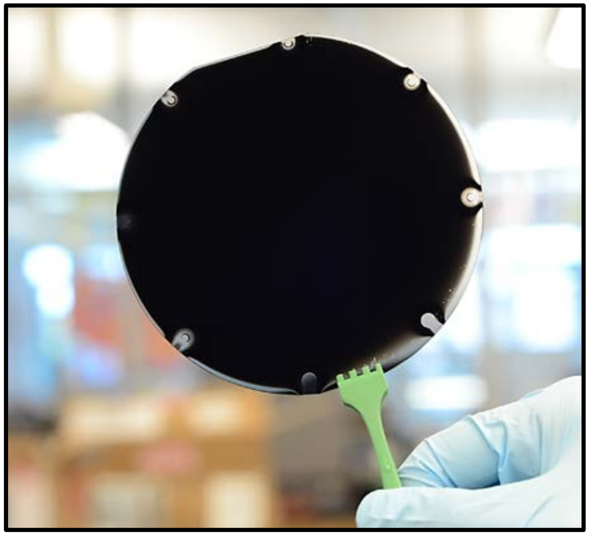
Accomplishments and Progress

Synthesis of nanostructured $BiVO_4$ on Si NWs

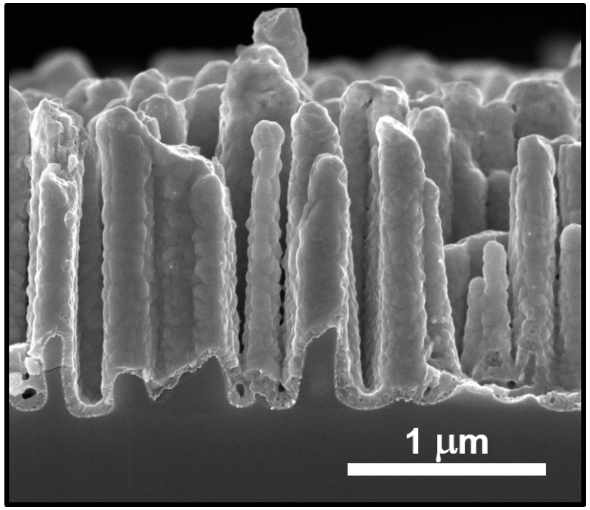
Spray pyrolysis was developed to deposit a thin film of W-doped $BiVO_4$ on a scaffold of Si NWs to improve the charge separation of $BiVO_4$ and increase the photovoltage of the heterojunction photoanode



Pongkarn Chakthranont, Thomas R. Hellstern, Joshua M. McEnaney, and Thomas F. Jaramillo. *Manuscript in preparation* (2016).



Wafer-scale Si NWs

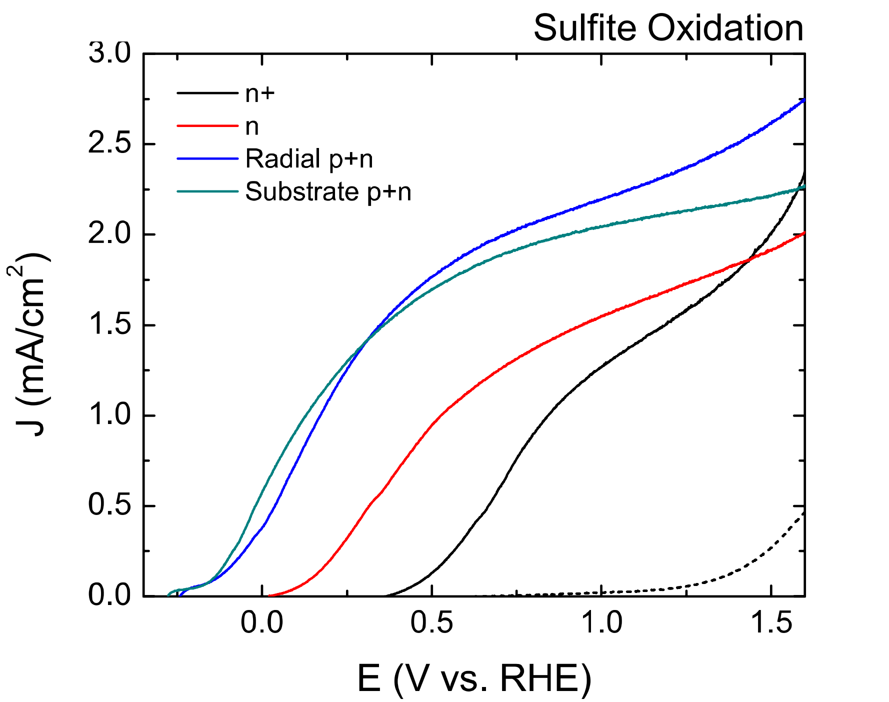


W-doped $BiVO_4$ coated Si NWs

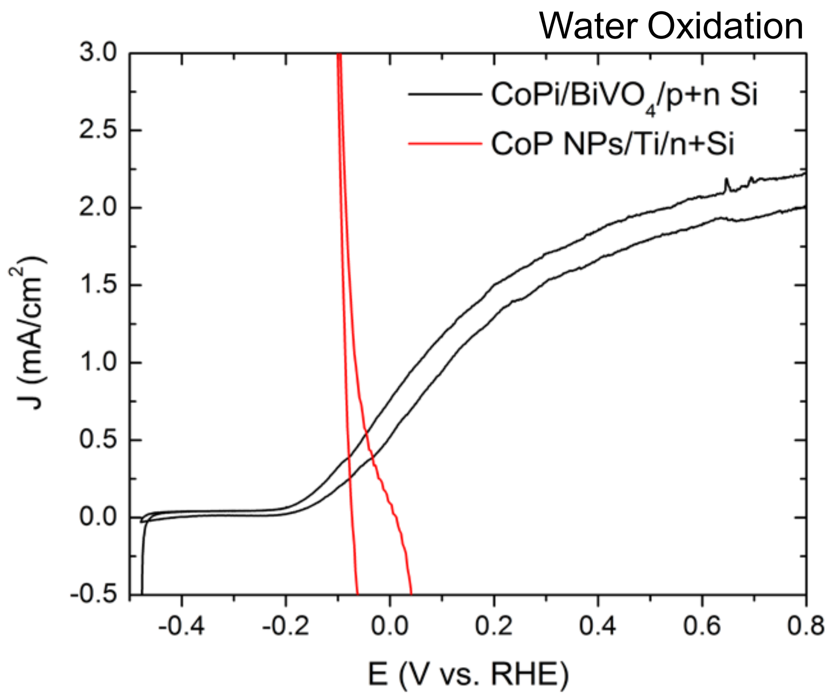
Accomplishments and Progress

Precious metal-free Unassisted Water Splitting Photoelectrode

- By optimizing the doping profile of the Si NWs, a heterojunction $BiVO_4$/Si photoanode can achieve a photocurrent onset as early as -0.2 V vs. RHE
- When paired with a CoP nanoparticle cathode, the device can perform unassisted water splitting at 0.4 mA/cm^2 without any precious metals



Sulfite oxidation I-V curves of W-doped $BiVO_4$/Si heterojunction photoanode with various types of Si p-n junction



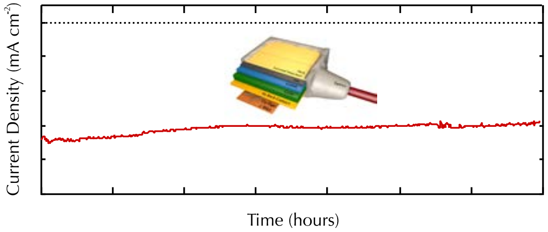
Water oxidation I-V curve of CoPi-decorated $BiVO_4$/Si photoanode paired with CoP nanoparticle cathode

Pongkarn Chakthranont, Thomas R. Hellstern, Joshua M. McEnaney, and Thomas F. Jaramillo. *Manuscript in preparation* (2016).

Collaborations

Manuscript under review

Molybdenum Disulfide as a Protection Layer and Catalyst for Gallium Indium Phosphide Solar Water Splitting Photocathodes
Reuben J. Britto, Jesse D. Benck, James L. Young, Christopher Hahn, Todd G. Deutsch, Thomas F. Jaramillo



National Renewable Energy Laboratory (NREL)
Todd Deutsch, James Young

We work with Todd and James on the $GaInP_2$ stability project. Our collaboration involves:
- Fabrication
- Sample exchange
- Parallel testing
- Discussion and idea sharing
- Process optimization


James and Todd

PEC Working Group
The PEC Working Group meets regularly to review technical progress, develop synergies, and collaboratively develop common tools and processes for PEC water splitting. Organized through the Department of Energy led by Eric Miller.

Energy Materials Network Workshop
Consortium that will accelerate the research, development and deployment of advanced water splitting technologies for renewable hydrogen production. Scientific experts in these technology areas will come together to identify key materials, metrics, and targets essential to commercial viability.

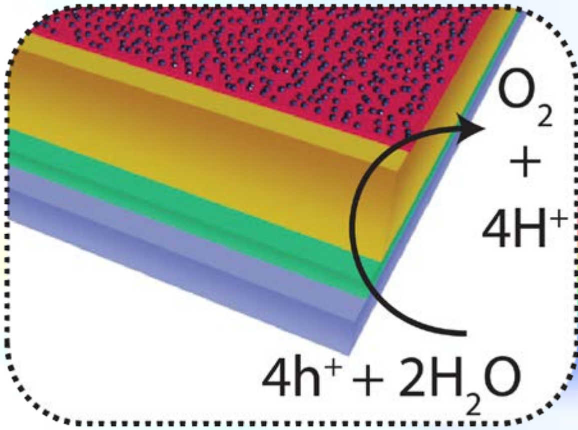

PEC Working Group at Stanford University

Proposed Future Work

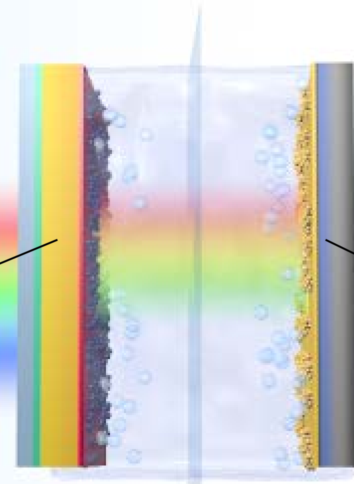
Immediate goals

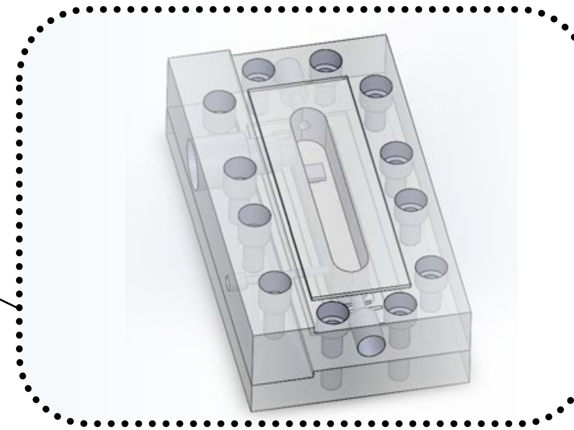
Applying acid stabilization strategies developed for $BiVO_4$ in acid to heterojunction device

Further *in situ* study of MoS_2 failure mechanisms to improve $GaInP_2$ stability



Protection layer on $BiVO_4$/Si heterojunction photoelectrode





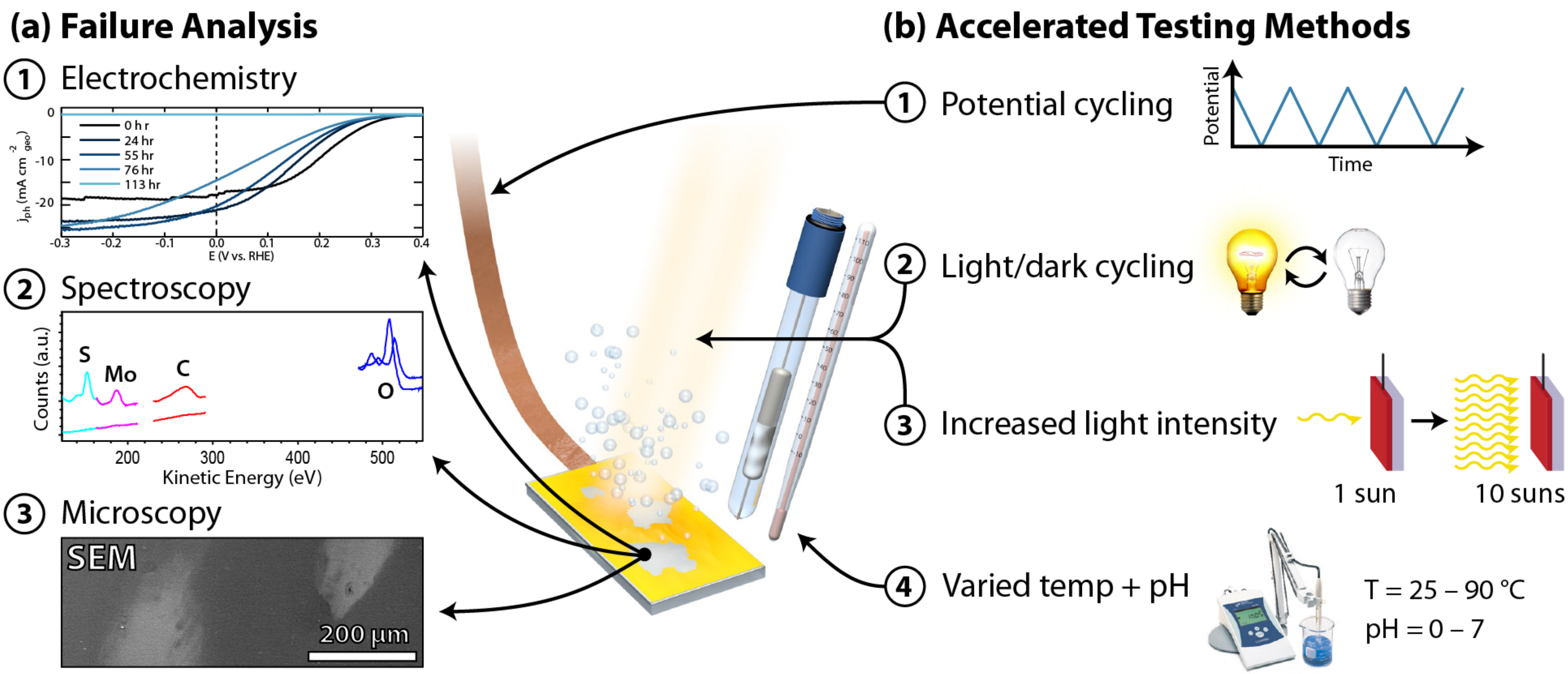
PEC Flow Cell combined with microscopy

Combining current and future innovations to make a non-precious metal unassisted water splitting device that is stable in acid

Proposed Future Work

Long term goals

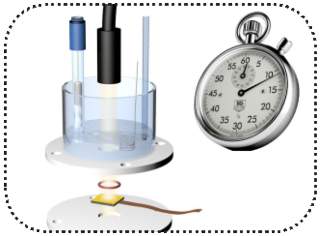
Developing methods to identify photoelectrode failure mechanisms and predict long-term performance using short-term tests



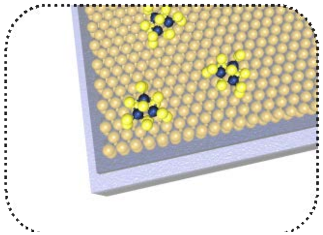
Summary

Approach

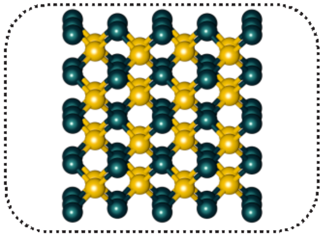
- We are developing protection layers for addressing stability and activity of both the photoanode and photocathode in acid



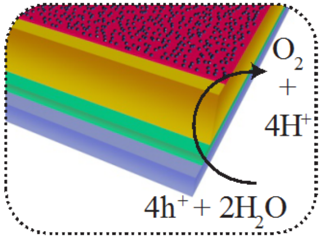
Stability testing design



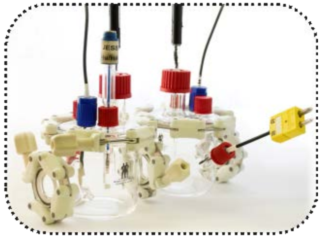
Si protection



III-V protection

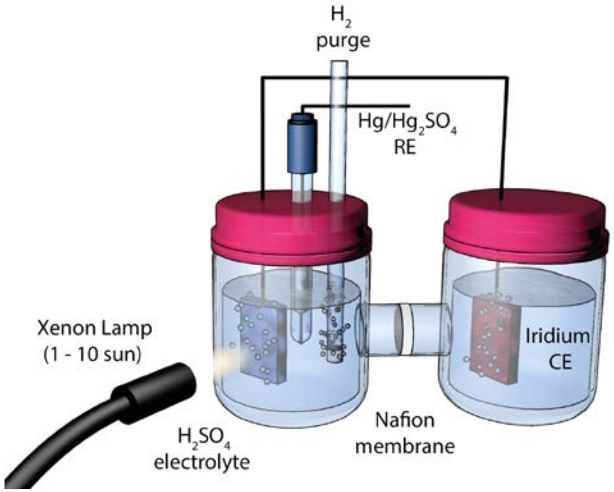


Photoanode design



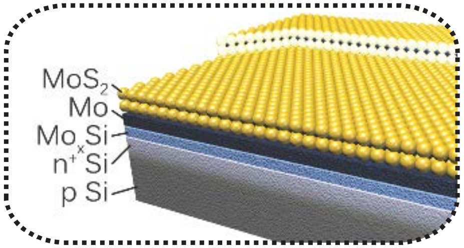
Unassisted PEC device

- The photoelectrochemical setup provides precise control of the electrode illumination, which improves the reliability of our long term stability measurements



Summary

Accomplishments

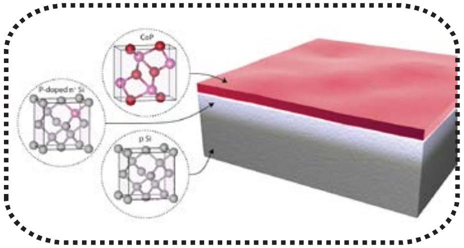


- Achieved long-term stability of MoS_2-Si photocathode in acid for 25 days

  Laurie A. King, Thomas R. Hellstern, and Thomas F. Jaramillo. *Manuscript in Preparation* (2016).

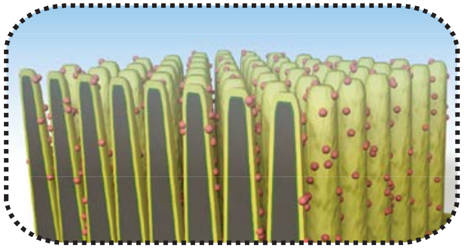
- Protected $GaInP_2$ in acid for over 70 hours with MoS_2

  Britto R.J., Benck J.D., Young J.L., Hahn C., Deutsch, T.G., Jaramillo T.F. *Journal of Physical Chemistry Letters* (accepted, 2016)



- Developed a highly active and stable photocathode consisting of CoP HER catalyst on Si

  Thomas R. Hellstern, Jesse D. Benck, Jakob Kibsgaard, Chris Hahn, Thomas F. Jaramillo. *Advanced Energy Materials* 6 (4) 2016



- Engineered a wafer-scaled nanostructure heterojunction $BiVO_4$/Si photoanode that can perform unassisted water splitting

  Pongkarn Chakthranont, Thomas R. Hellstern, Joshua M. McEnaney, and Thomas F. Jaramillo. *Manuscript in preparation* (2016).