NSF/DOE Solar Hydrogen Fuel

Engineering Surfaces, Interfaces, and Bulk Materials for Unassisted Solar Photoelectrochemical (PEC) Water Splitting

Professor Thomas Jaramillo

Stanford University

June 7, 2017

Project ID#: PD119

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*: $685,000 (as of 3/31/15)

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

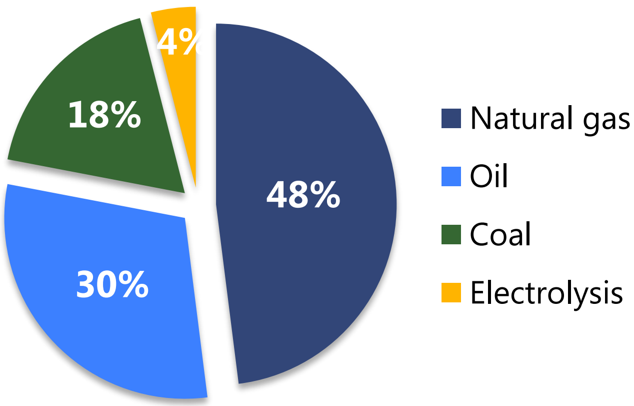
Partners

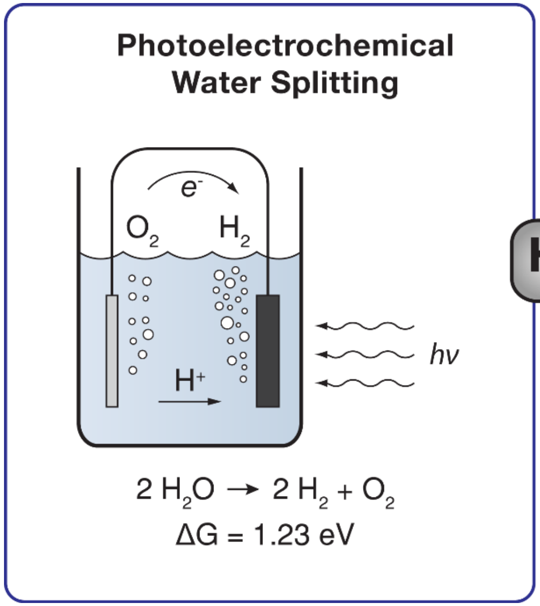
- National Renewable Energy Laboratory (NREL)
- PEC Working Group

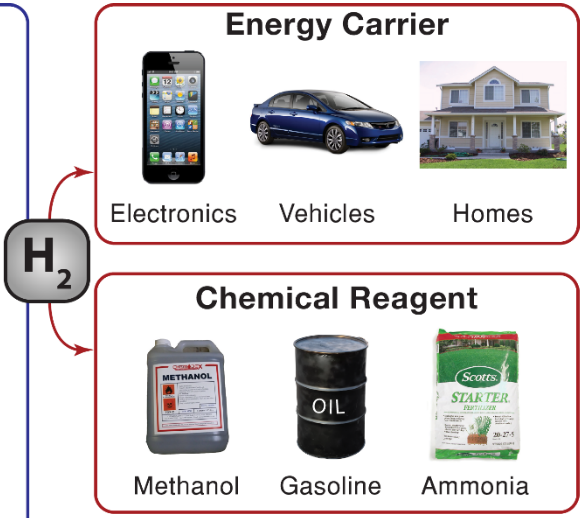
Relevance and Impact

H_2 Production via Photoelectrochemical Water Splitting

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

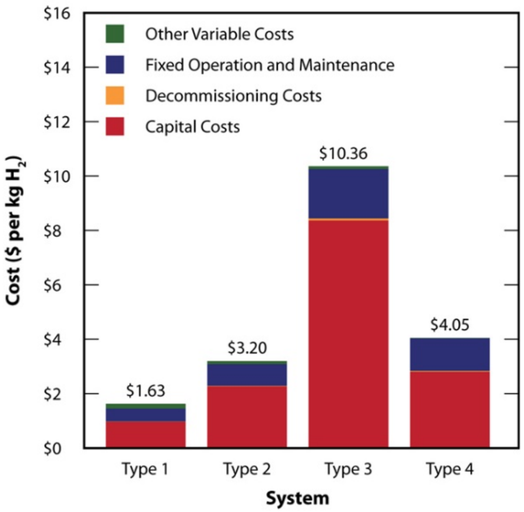






iPhone 5 image: http://static.ibnlive.in.com/ibnlive/pix/sitepix/09_2012/iphone-5-b-130912.jpg
Car image: cdnedge.vinsolutions.com/dealerimages/Dealer 3294 Images/2011-honda-civic-si.jpg
House image: http://www.plu.edu/~allenka/img/House_Front.jpg
Methanol image: http://www.chemodex.co.uk/store/images/methanol.jpg
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
B.A. Pinaud, J.D. Benck, L.C. Seitz, A.J. Forman, Z. Chen, T.G. Deutsch, B.D. James, K.N. Baum, G.N. Baum, S. Ardo, H. Wang, E. Miller, and T.F. Jaramillo. *Energy & Environmental Science*, 2013. **6** (7): 1983-2002.

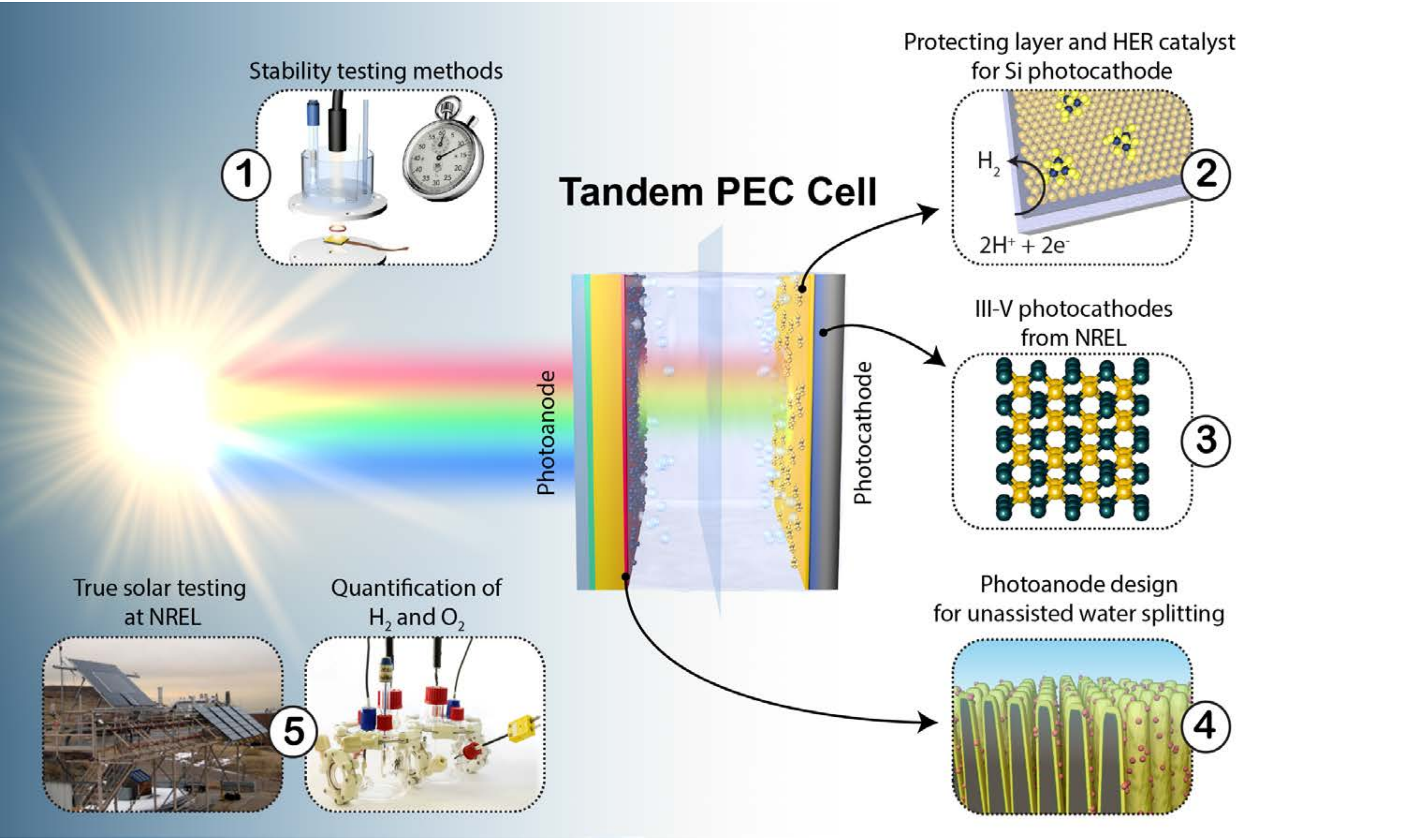
Relevance and Impact

Objectives

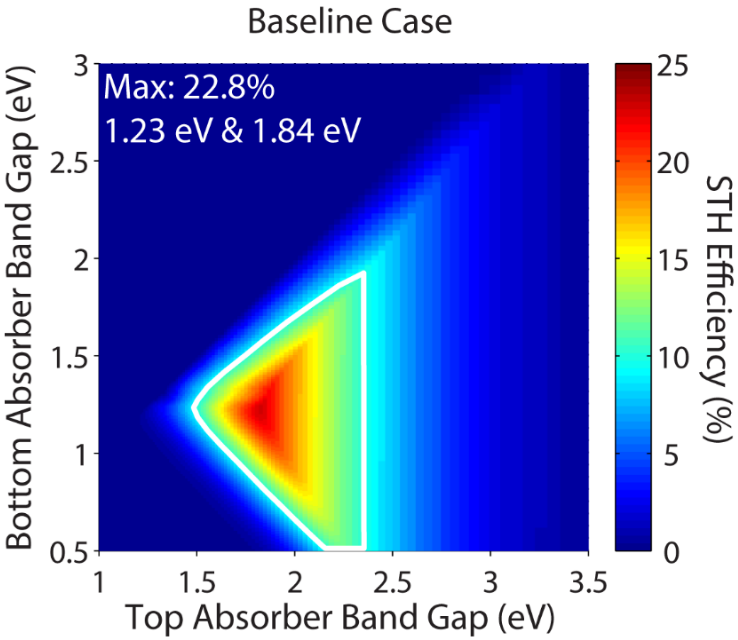
- Method and protocol development to understand photoelectrode corrosion *in acid*.
- Interfacial engineering of the Si surface to provide enhanced catalytic activity and corrosion resistance *in acid* by means of molybdenum sulfide nanomaterials.
- Interfacial engineering of III-V photocathode surfaces with similar approaches, in collaboration with Dr. Todd Deutsch at the National Renewable Energy Laboratory (NREL).
- Integration of $BiVO_4$ to Si to make a tandem photoelectrochemical cell capable of unassisted water splitting.
- Quantification of H_2 and O_2 and true solar testing at NREL.
- Study the mechanistic degradation of PEC water splitting devices by developing an *operando* electrochemical flow cell coupled to both an optical and confocal Raman microscope to inform new strategies for improving our catalysts and protection layers.

Technical Targets from DOE Fuel Cell Technologies Office MYRDD Plan:
10% STH Efficiency
100 J/s per m^2 of Hydrogen Production

Approach
Testing Design and Tandem Device Engineering

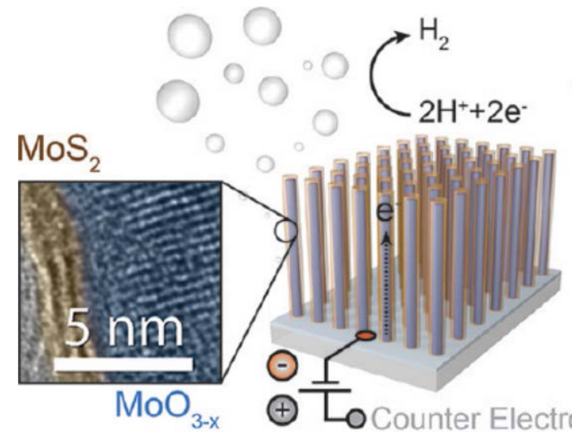


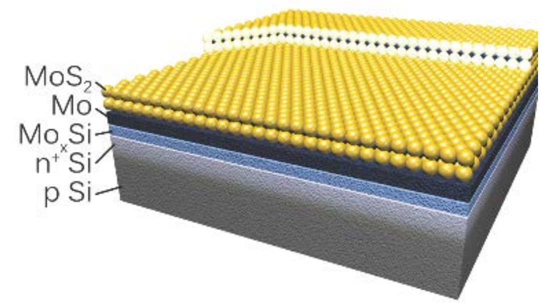
Photoabsorber materials



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.

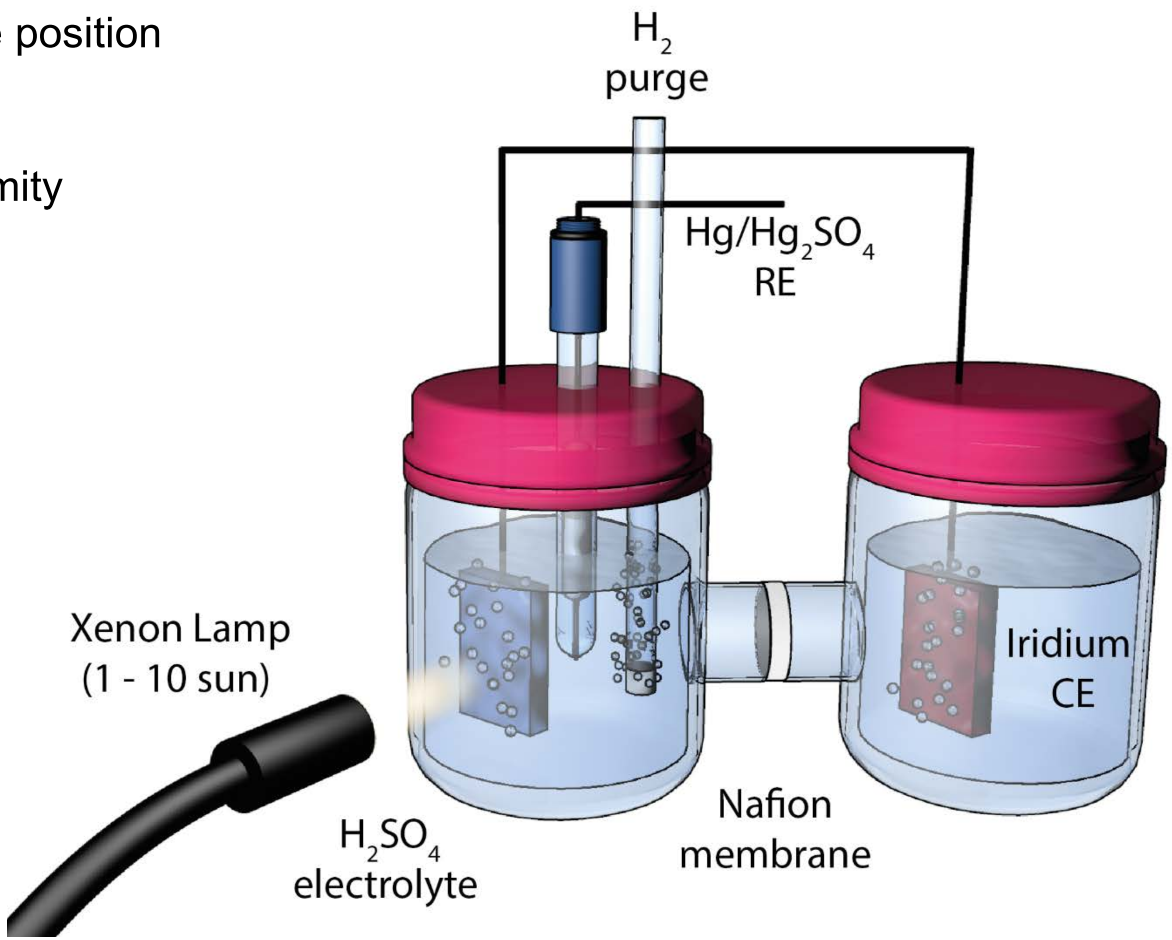
Seitz, L. C.; Chen, Z.; Forman, A. J.; Pinaud, B. A.; Benck, J. D.; Jaramillo, T. F. *ChemSusChem* **2014,** *7* (5), 1372-1385.
Zhebo Chen, Dustin Cummins, Benjamin N. Reinecke, Ezra Clark, Mahendra K. Sunkara, and Thomas F. Jaramillo. *Nano Letters* **2011** *11* (10), 4168-4175
J.D. Benck, S.C. Lee, K.D. Fong, J. Kibsgaard, R. Sinclair, & T.F. Jaramillo. *Advanced Energy Materials* 4 (18) 2014. p. 1400739

Approach

Stability measurement setup

The photoelectrochemical setup improves the reliability of our long term stability measurements

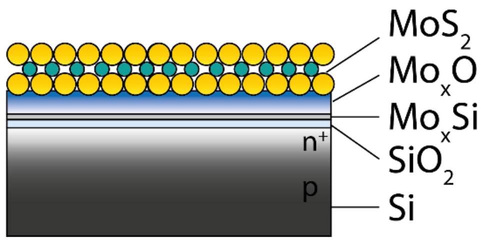
- Precise control over the position of the electrode
- High illumination uniformity
- 1 – 10 sun intensity



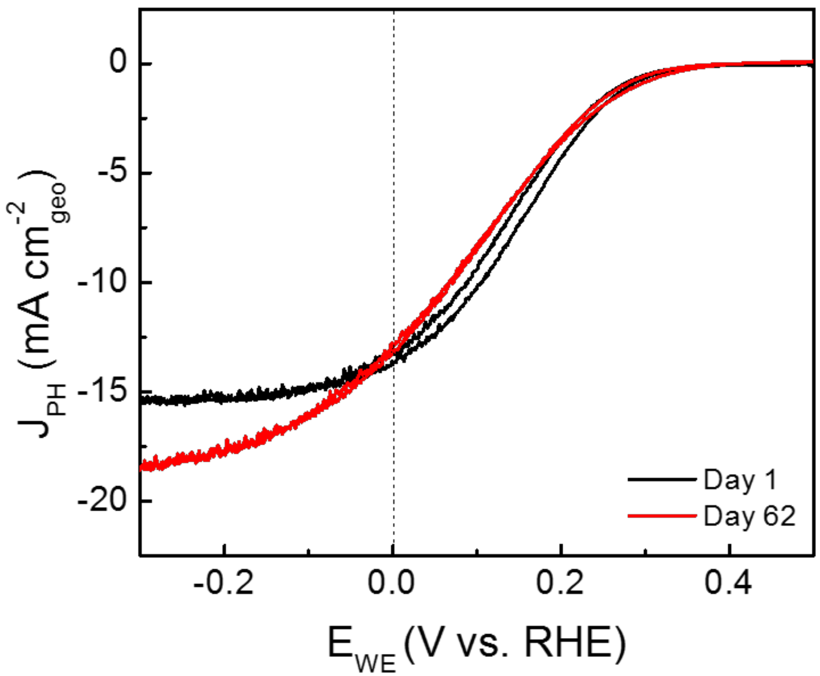
Accomplishments and Progress

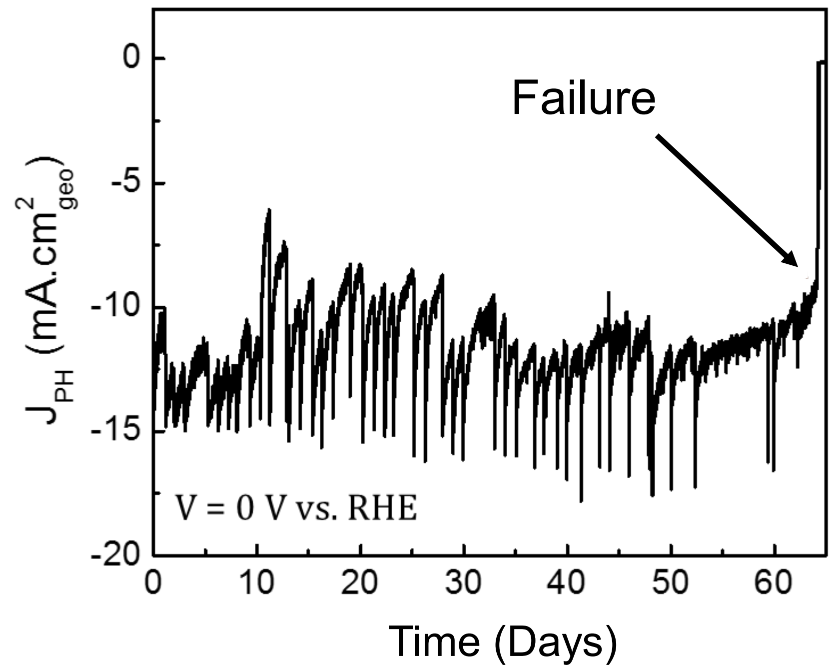
Demonstrated Stability of MoS_2-Si

(1) Mo Sputtering
(2) H_2 anneal 550 °C
(3) H_2S anneal 250 °C



Silicon photocathodes were prepared with MoS_2 protection layers. Stability testing in 0.5 M sulfuric acid found that ***the samples were stable for 64 days*** of continuous 1 sun illumination. The electrode subsequently failed catastrophically.



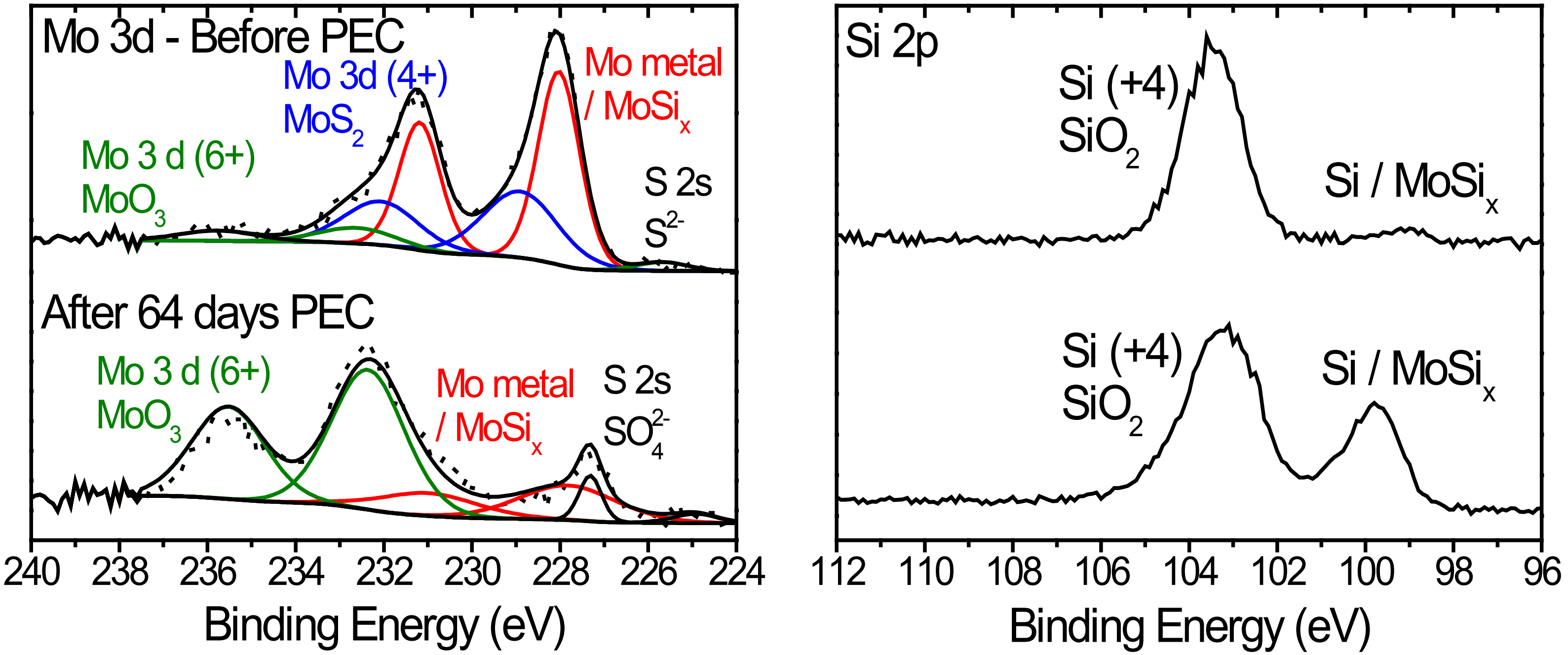


Laurie A King, T. Hellstern, S. Park, R. Sinclair and T. F. Jaramillo *Submitted 2016*

Accomplishments and Progress

Understanding the Failure Mechanism of MoS_2-Si

Comparison pre and post PEC stability testing

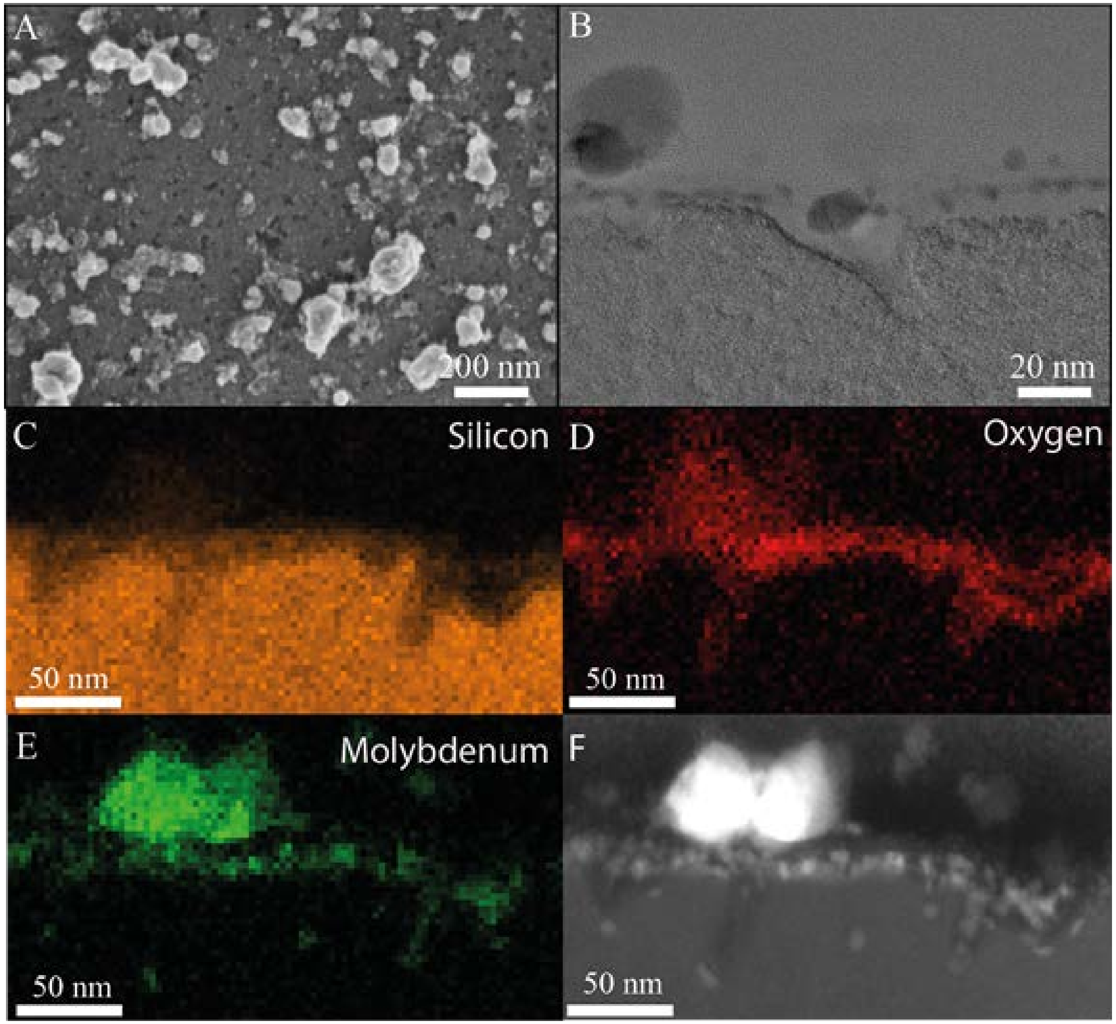


After the 64 days of PEC testing and catastrophic failure, XPS characterisation reveals a drastic transformation in the chemical oxidation states of the elements present. Specifically, the proportion of oxidized molybdenum increased from 10 % to 75 %.

Accomplishments and Progress

Understanding the Failure Mechanism of MoS_2-Si

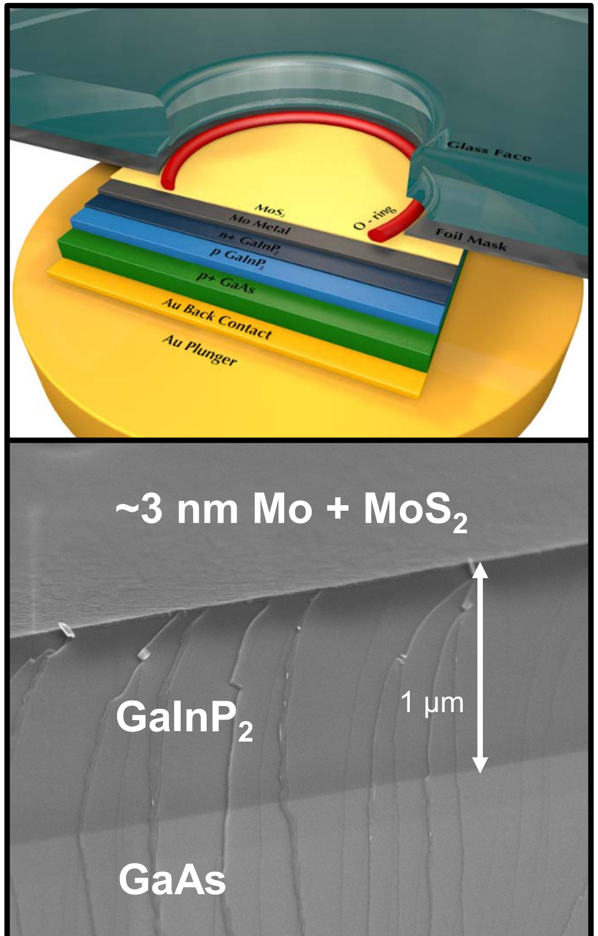
Microscopy post PEC stability testing

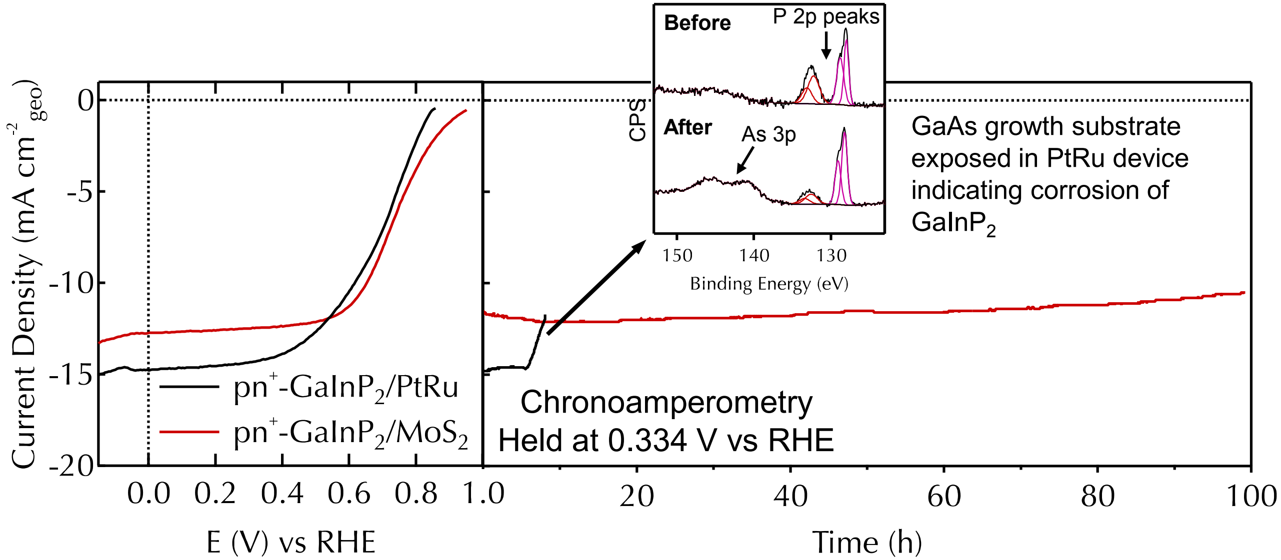


After the 64 days of PEC testing and catastrophic failure, SEM reveals a highly roughened surface with both pits and agglomerates across the surface. TEM of the same sample reveal significant roughening with pits of up to 30 nm deep. By STEM-EDS mapping, it is clear that the pits extend through the protective molybdenum layers into the silicon and that silicon has been etched away.

Accomplishments and Progress

Protecting the surface of $GaInP_2$





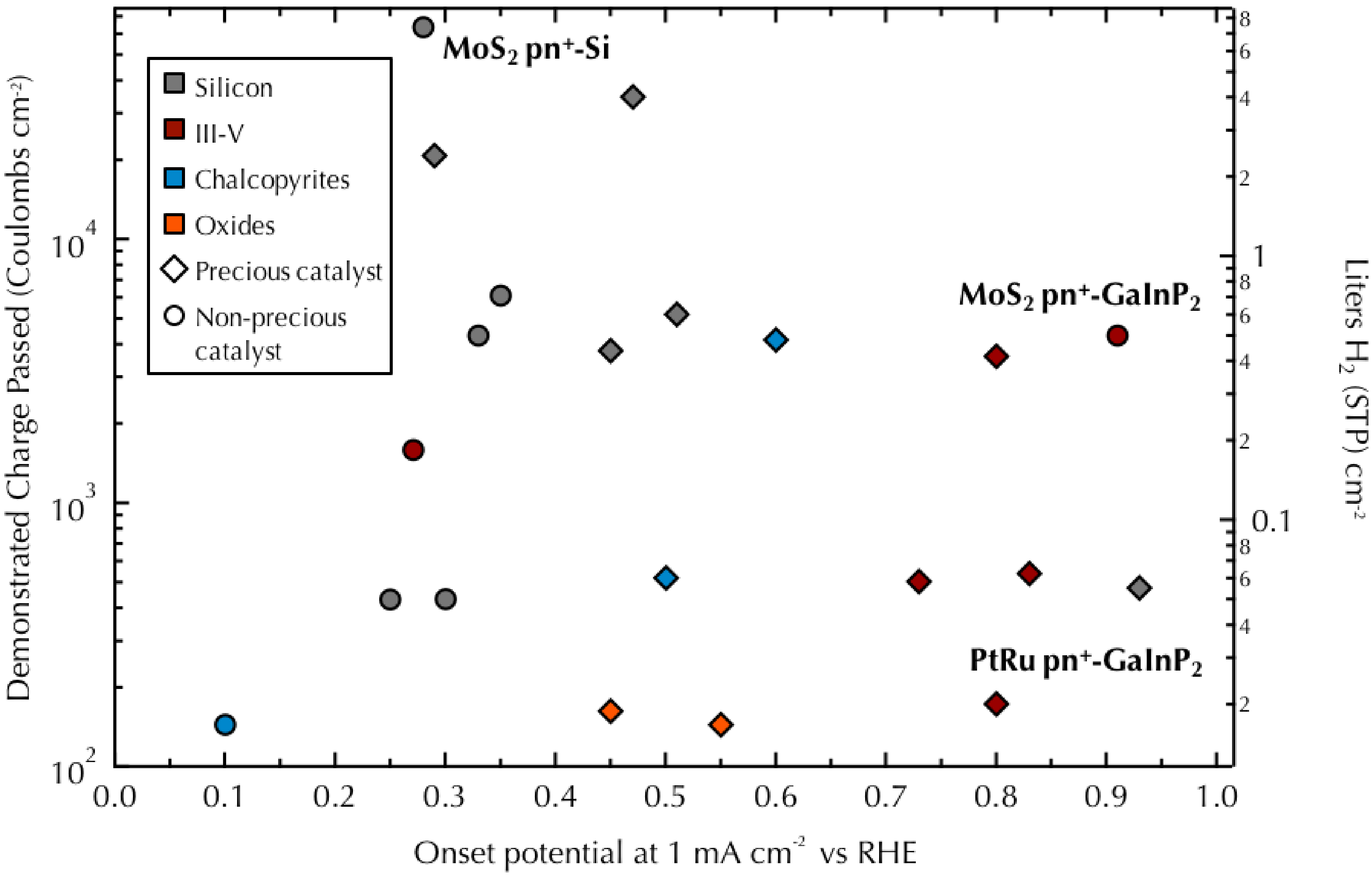
MoS_2 was used to protect pn+ $GaInP_2$ for >100 hrs in 3M sulfuric acid.

The MoS_2 further functioned as a catalyst for the hydrogen evolution reaction with an earlier onset potential than a platinum-modified pn+ $GaInP_2$ photocathode.

Reuben J. Britto, Jesse D. Benck, James L. Young, Christopher Hahn, Todd G. Deutsch, and Thomas F. Jaramillo. *The Journal of Physical Chemistry Letters* **2016** 7 (11), 2044-2049
Reuben J. Britto, James L. Young, Ye Yang, Miles Steiner, David LaFehr, Mathew Beard, Todd G. Deutsch, and Thomas F. Jaramillo. *In Prep.*

Accomplishments and Progress

Protecting the surface of $GaInP_2$



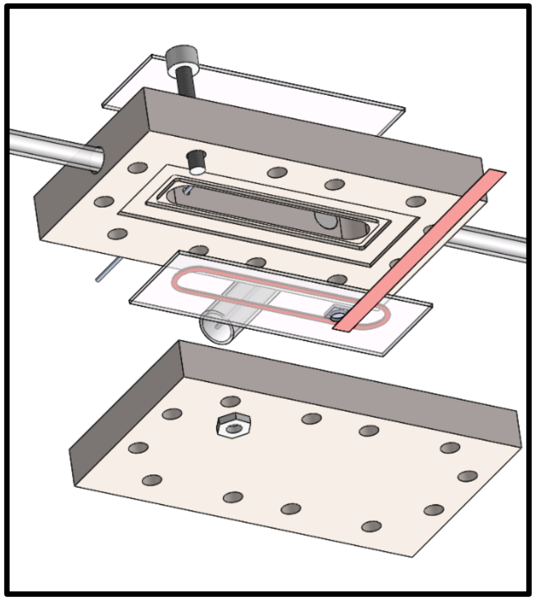
Reuben J. Britto, Jesse D. Benck, James L. Young, Christopher Hahn, Todd G. Deutsch, and Thomas F. Jaramillo. *The Journal of Physical Chemistry Letters* **2016** 7 (11), 2044-2049

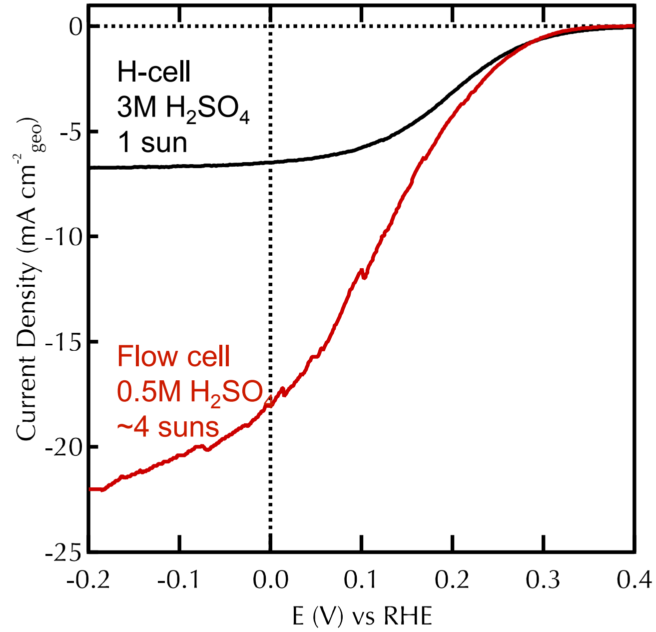
Reuben J. Britto, James L. Young, Ye Yang, Miles Steiner, David LaFehr, Mathew Beard, Todd G. Deutsch, and Thomas F. Jaramillo. *In Prep.*

Laurie A King, T. Hellstern, S. Park, R. Sinclair and T. F. Jaramillo *Submitted 2017*

Accomplishments and Progress

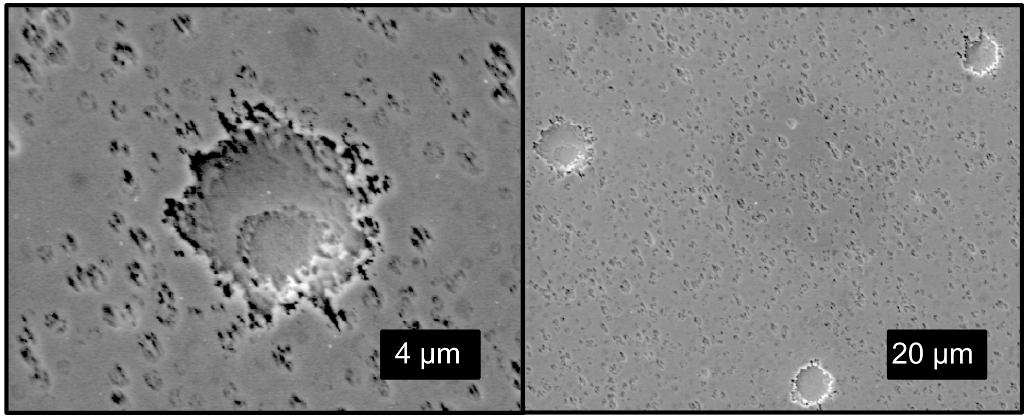
Operando flow cell development





Preliminary *operando* data collection from a p-$GaInP_2$/MoS_2 photocathode in our flow cell.

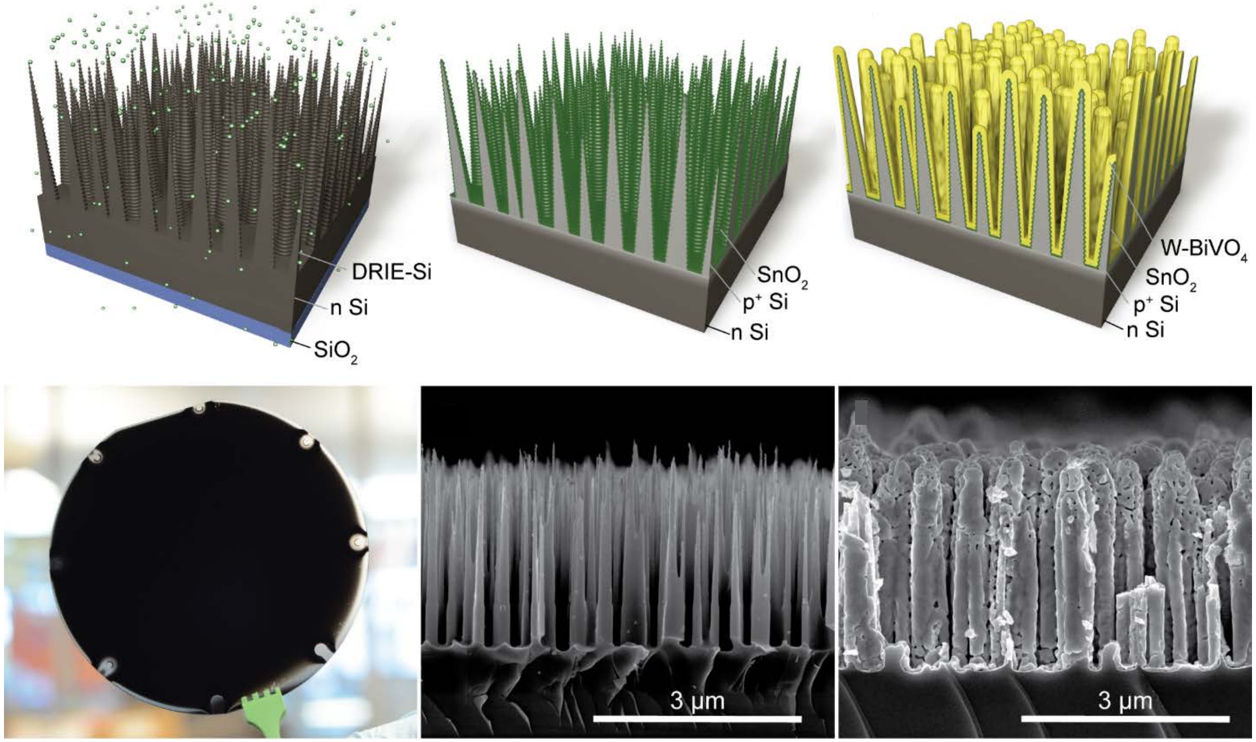
Once in operation, we can investigate pinhole formation as it occurs.

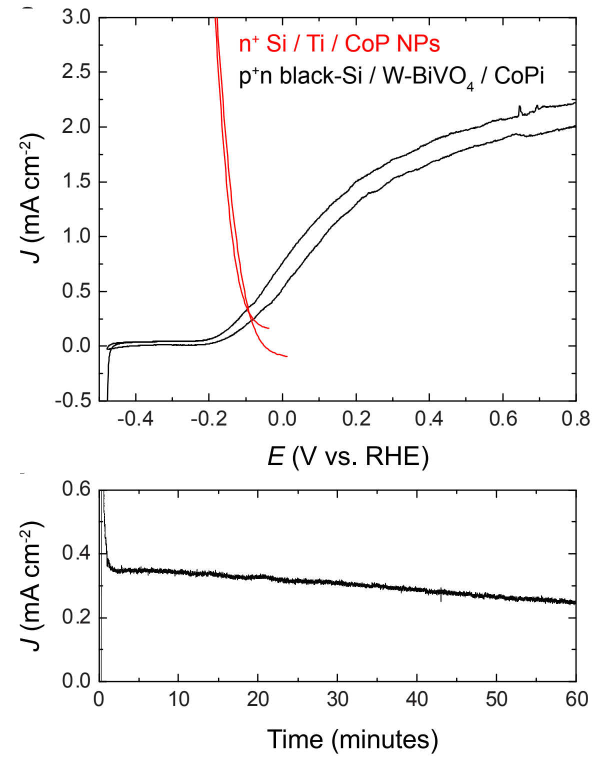


SEM of p-$GaInP_2$/MoS_2 after 100 h of testing in 3 M H_2SO_4

Unassisted Tandem Photoelectrochemical Water Splitting Cell

We developed a device design and a scalable fabrication scheme of a tandem heterojunction photoanode structure: $p^{+}n$ black-Si core/SnO_2 interface/W-doped $BiVO_4$ shell/CoPi catalyst. When coupled with CoP NPs, the device demonstrates a unassisted water splitting without any precious metal.



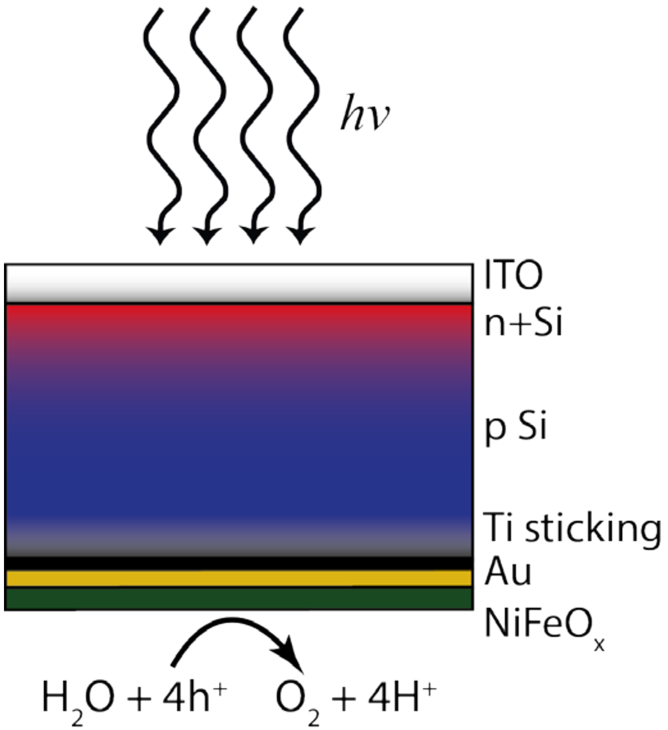


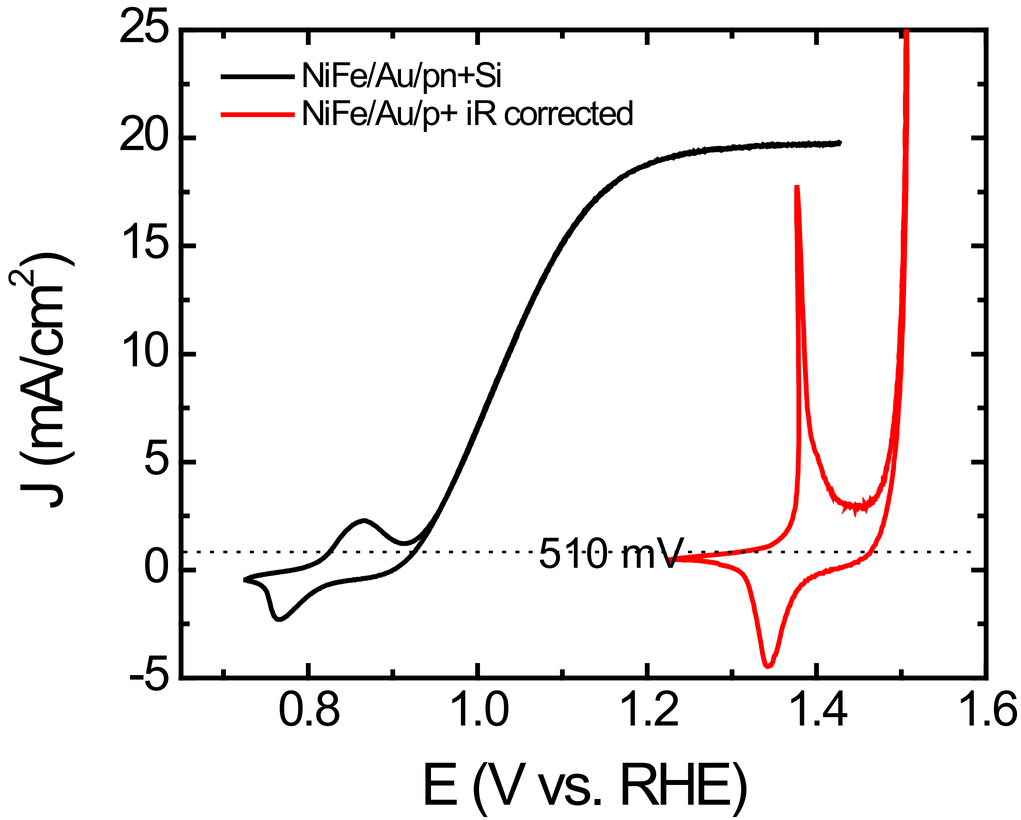
Chakthranont, P., Hellstern T. R., McEnaney, J. M., and Jaramillo T. F. *In Preparation*

Accomplishments and Progress

Backside Illuminated Silicon Photoanode

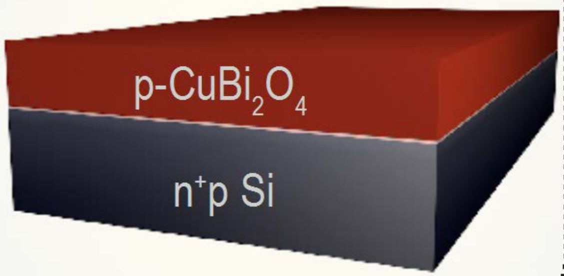
Towards the development of a monolithic device we designed and fabricated a backside illuminated silicon photoanode with approximately 510 mV photovoltage.





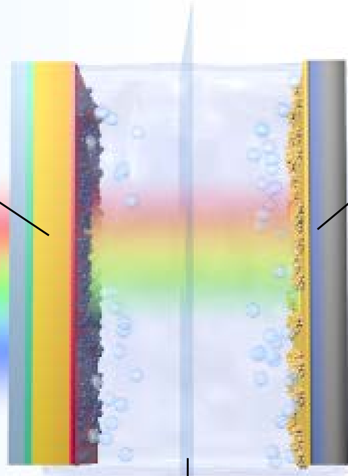
Proposed Future Work

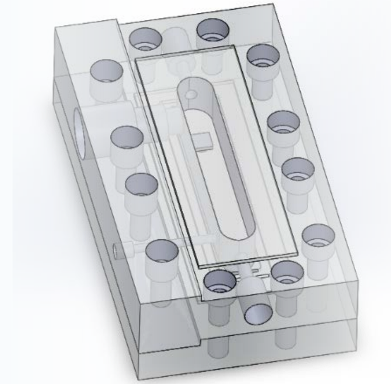
Continuing work



$CuBi_2O_4$/Si heterojunction

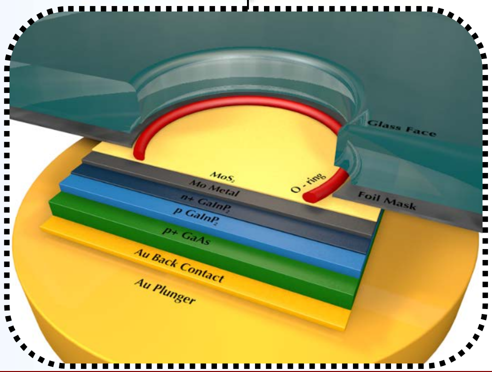
Explore different materials for tandem device to enable higher efficiency and stability





Further *in situ* investigation of MoS_2 failure mechanisms to improve $GaInP_2$ stability using a flow combined with microscopy

Combining current and future innovations to make a non-precious metal unassisted water splitting device with high stability



Further work into stabilization strategies for III-V photo-absorbers for unassisted water splitting devices with NREL

Collaborations

National Renewable Energy Laboratory (NREL)

We work with Todd Deutsch and James Young on the $GaInP_2$ stability project. Our collaboration involves:

- Fabrication
- Sample exchange
- Parallel testing
- Discussion and idea sharing
- Process optimization

James and Todd

Manuscript published together:

Reuben J. Britto, Jesse D. Benck, James L. Young, Christopher Hahn, Todd G. Deutsch, and Thomas F. Jaramillo. Molybdenum Disulfide as a Protection Layer and Catalyst for Gallium Indium Phosphide Solar Water Splitting Photocathodes. *J. Phys. Chem. Lett.* **2016** *7* (11), 2044-2049

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

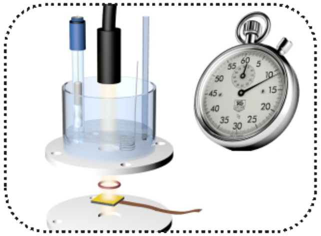
Consortium that will accelerate the research, development and deployment of advanced water splitting technologies for renewable hydrogen production. Scientific experts in these technology areas will come together to identify key materials, metrics, and targets essential to commercial viability.

EMN Workshop at Stanford (2016)

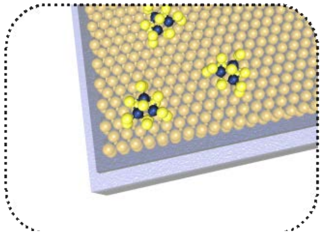
Summary

Approach

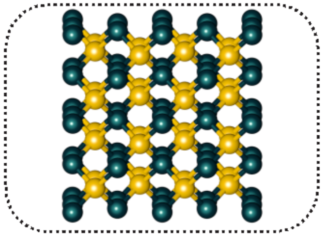
- We are developing protection layers for addressing stability and activity of both the photoanode and photocathode in acid



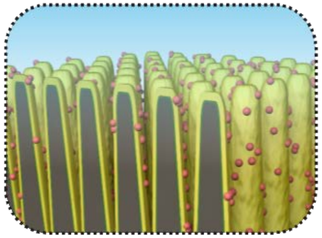
Stability testing design



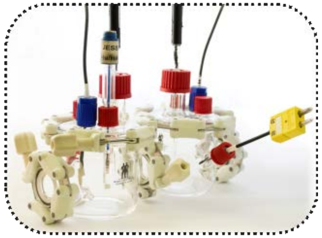
Si protection



III-V protection

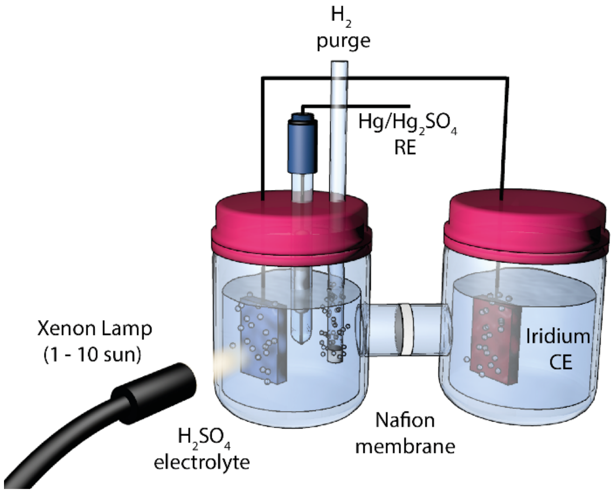


Photoanode design



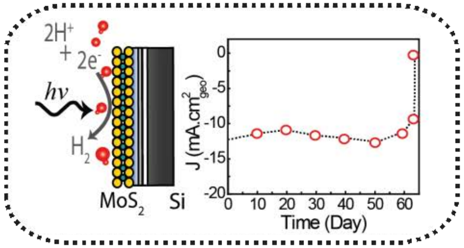
Unassisted PEC device

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



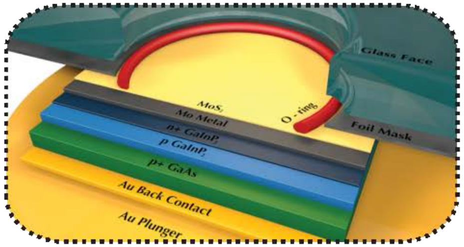
Summary

Accomplishments



- Achieved long-term stability of MoS_2-Si photocathode in acid for 64 days

  Laurie A King, T. Hellstern, S. Park, R. Sinclair and T. F. Jaramillo *Submitted 2017*

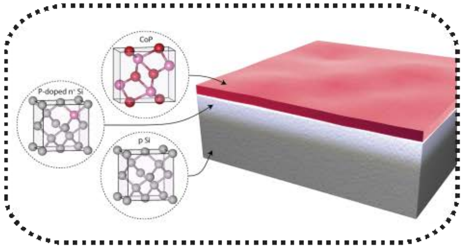


- Protected $GaInP_2$ in acid for over 100 hours with MoS_2

  Reuben J. Britto, Jesse D. Benck, James L. Young, Christopher Hahn, Todd G. Deutsch, and Thomas F. Jaramillo. *The Journal of Physical Chemistry Letters* **2016** *7* (11), 2044-2049

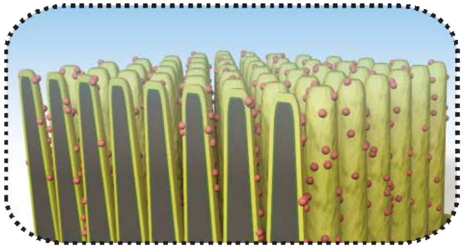
  Reuben J. Britto, James L. Young, Ye Yang, Miles Steiner, David LaFehr, Mathew Beard, Todd G. Deutsch, and Thomas F. Jaramillo. *In Prep.*

  Reuben J. Britto, Laurie A. King, Pongkarn Chakthranont, James L. Young, Todd G. Deutsch, and Thomas F. Jaramillo. *In Prep.*



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

  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. *In Prep*