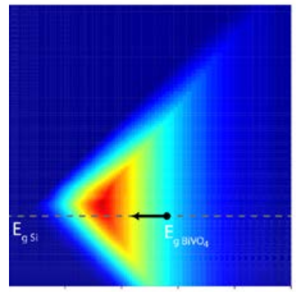
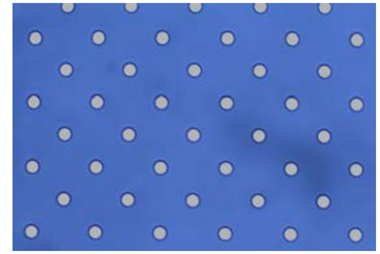
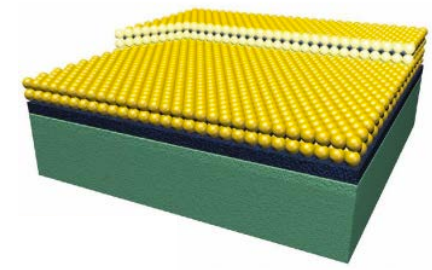



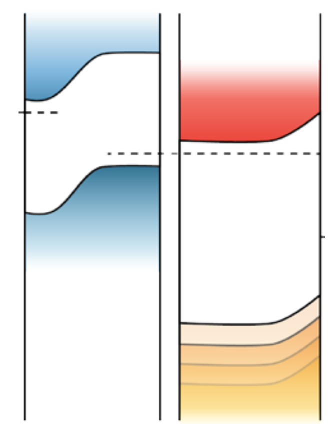
NSF/DOE Solar Hydrogen Fuel

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

Prof. Thomas Jaramillo
Dept. of Chemical Engineering
Stanford University

June 9th, 2015

Project ID#: PD119



Overview

Timeline

- Project Start Date: 1/1/15
- Project End Date: 12/31/2017

Budget

- Total Project Budget: $750,000
  - Total Recipient Share: $750,000
  - Total Federal Share: $750,000
  - Total DOE Funds Spent*: $67,258

    * As of 4/15/15

Partners

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

Barriers

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

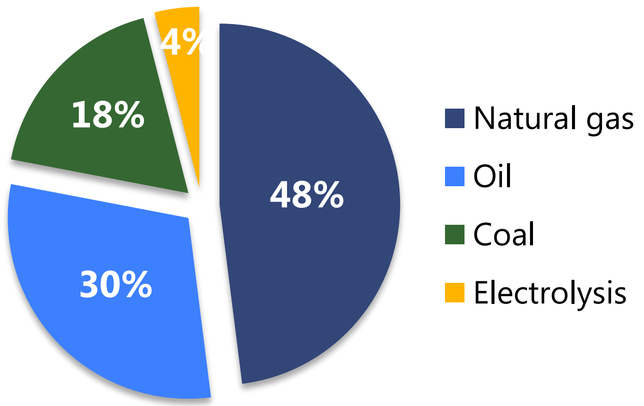
Targets

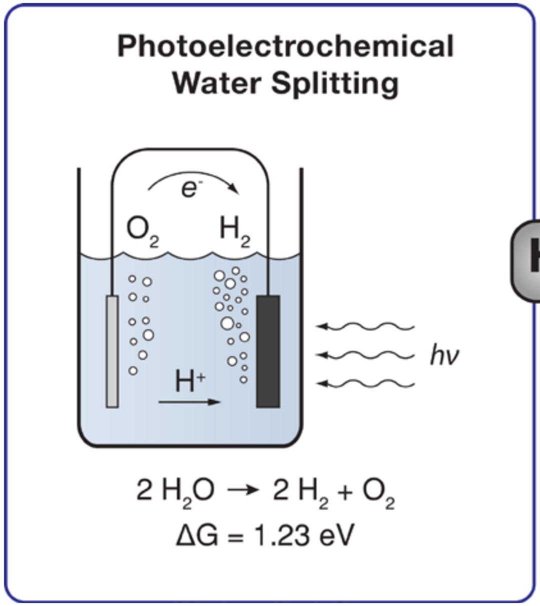
- Photoelectrochemical Hydrogen Cost
- Annual Electrode Cost per TPD H_2
- Solar to Hydrogen (STH) Energy Conversion Ratio
- 1 sun Hydrogen production rate

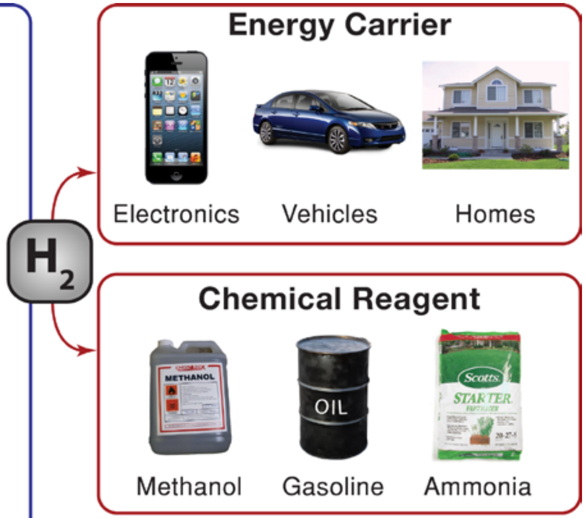
Relevance and Impact

H_2 Production via Photoelectrochemical Water Splitting

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

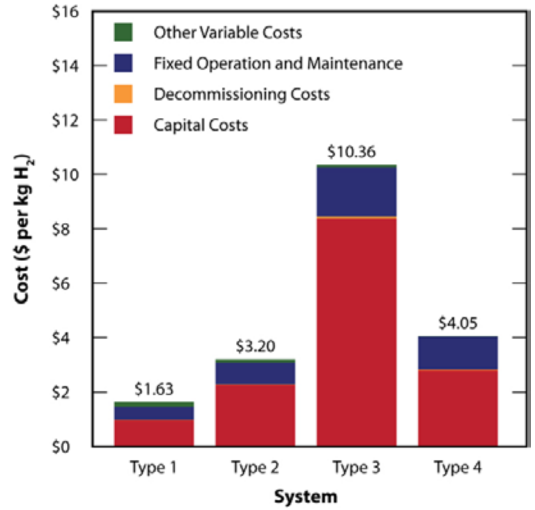






iPhone 5 image: http://static.ibnlive.in.com/ibnlive/pix/sitepix/09_2012/iphone-5-b-130912.jpg
Car image: cdnedge.vinsolutions.com/dealerimages/Dealer 3294 Images/2011-honda-civic-si.jpg
House image: http://www.plu.edu/~allenka/img/House_Front.jpg
Methanol image: http://www.chemodex.co.uk/store/images/methanol.jpg
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 and H_2 production from renewable resources, 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

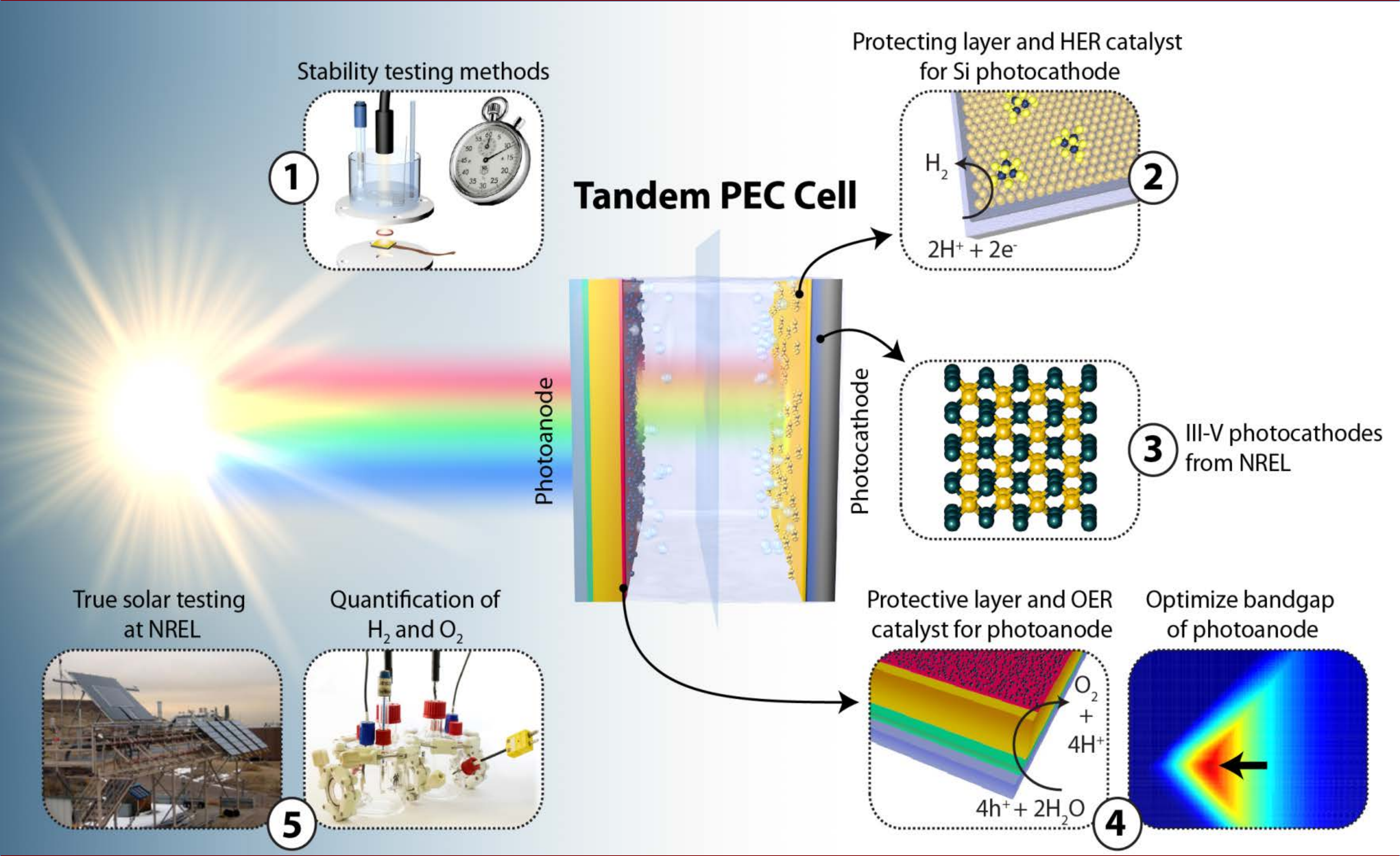
- Method and protocol development to understand photoelectrode corrosion *in acid*.
- Interfacial engineering of the Si surface to provide enhanced catalytic activity and corrosion resistance *in acid* by means of molybdenum sulfide nanomaterials.
- Interfacial engineering of III-V photocathode surfaces 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:

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

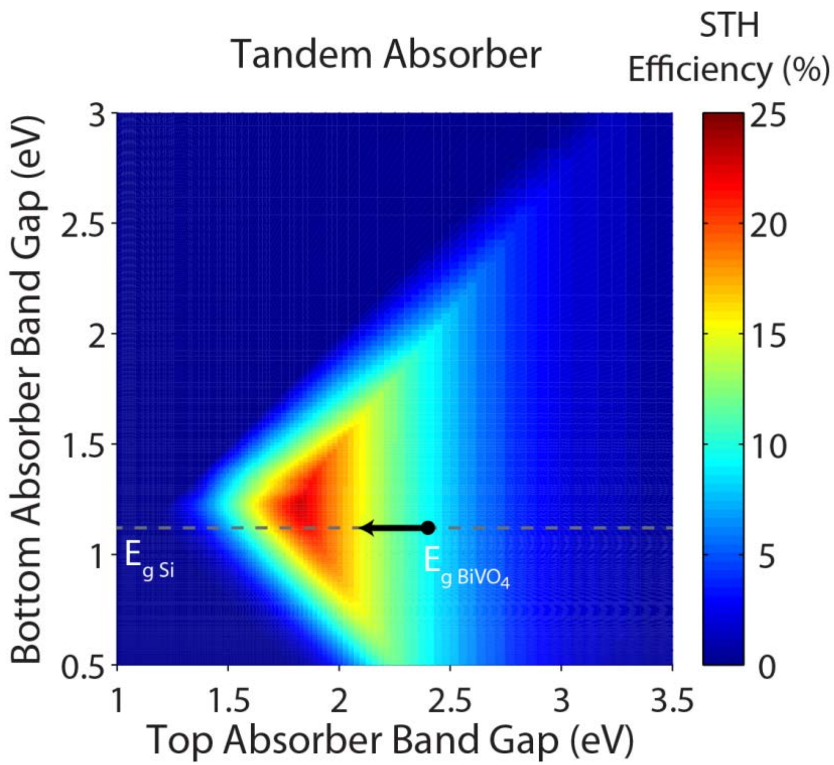
Approach

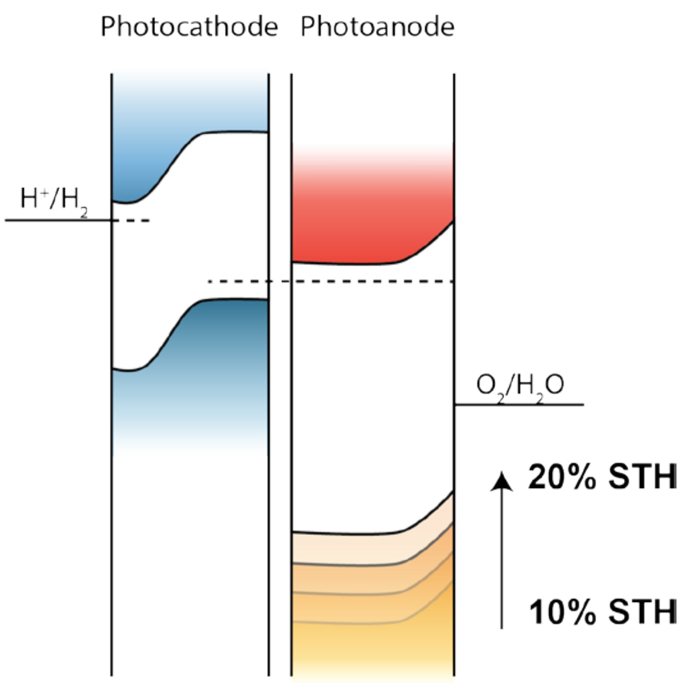
Testing Design and Tandem Device Engineering



Approach

Theory Guided Material Selection





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

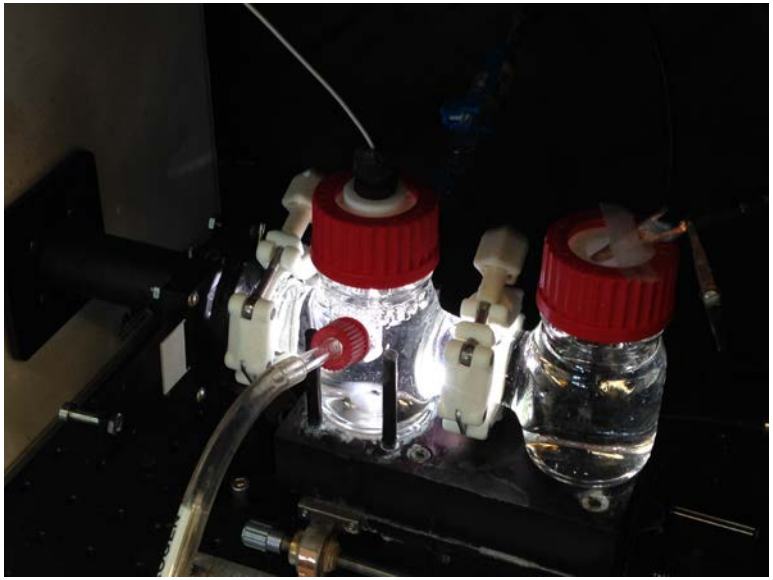
Theoretical model is used to direct material selections and provide realistic goal for STH of each tandem system

Seitz, L. C.; Chen, Z.; Forman, A. J.; Pinaud, B. A.; Benck, J. D.; Jaramillo, T. F. *ChemSusChem* **2014,** *7* (5), 1372-1385.

Accomplishments
Stability measurement setup

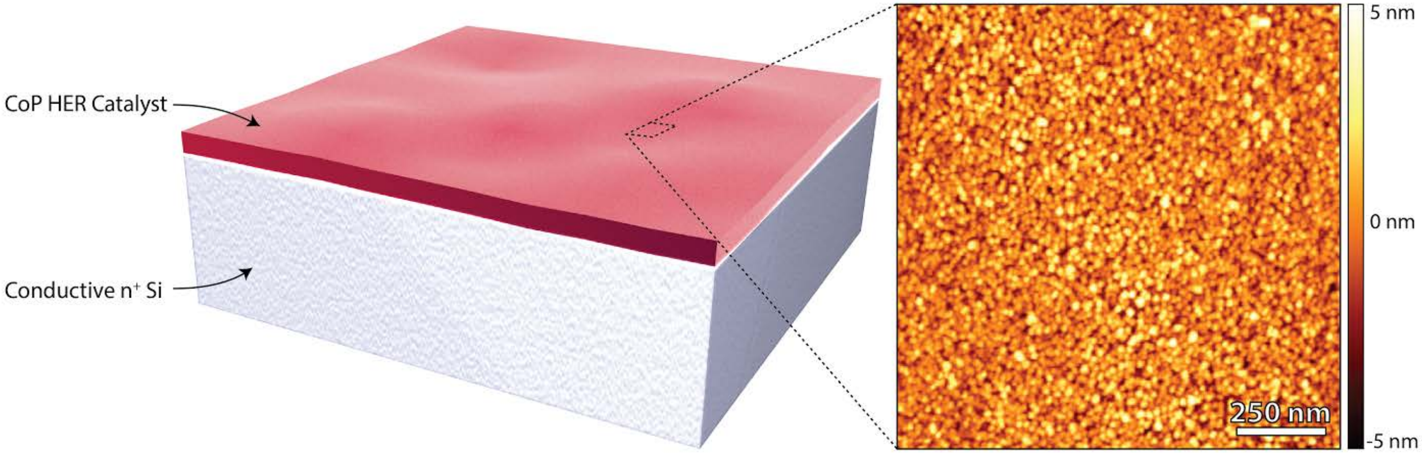
New photoelectrochemical setup improves the reliability of photoelectrochemical measurements

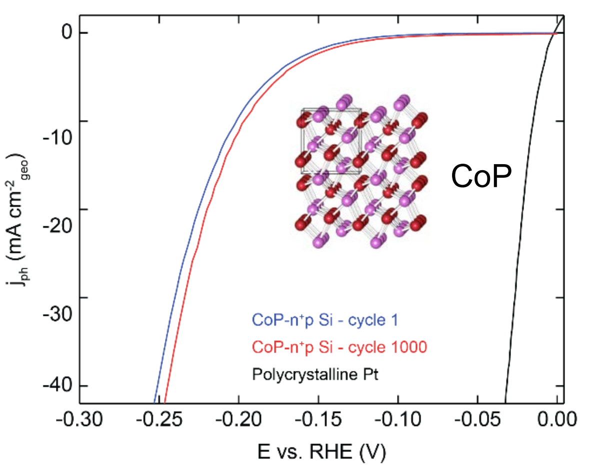
- Precise control over the position of the electrode
- High uniformity in the light spot

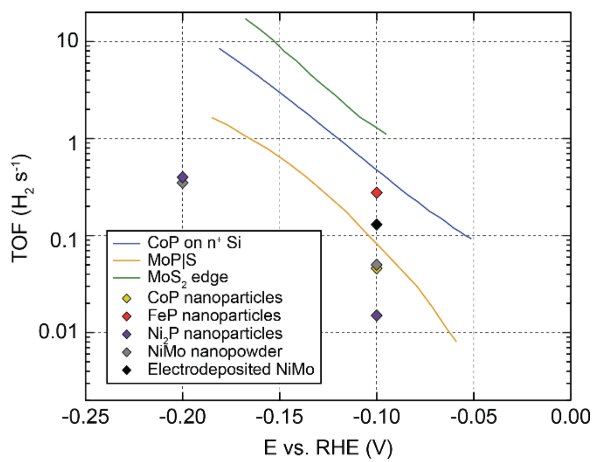


Accomplishments
Cobalt Phosphide HER Catalyst

CoP, a nonprecious metal phosphide, shows very high activity for the HER. We synthesized a flat, thin film CoP catalyst on conductive silicon.





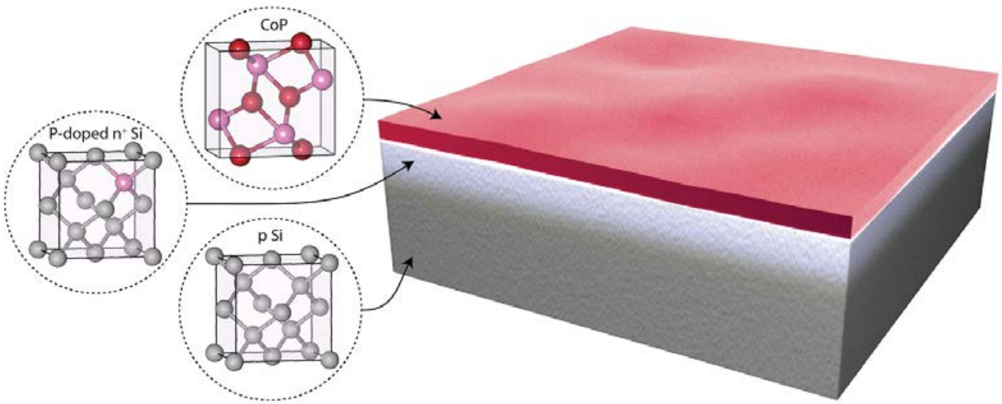


This CoP catalyst shows a remarkable turn over frequency and excellent total electrode activity despite its low surface area, making it an ideal choice to improve the efficiency of Si photocathodes.

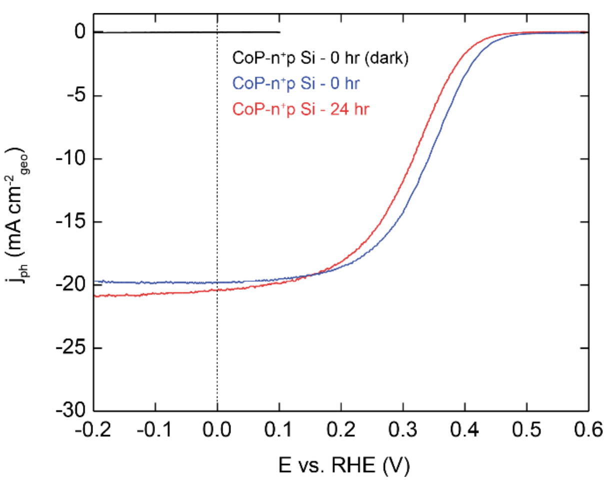
T.R. Hellstern, T.F. Jaramillo, et al. *submitted* (2015)

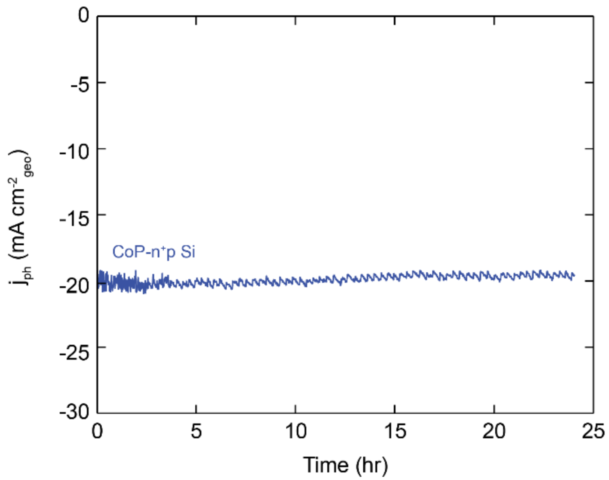
Accomplishments

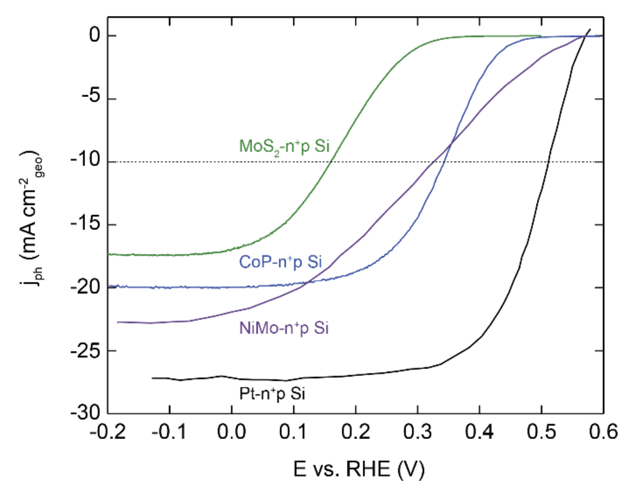
CoP-n$^+$p Si Photocathode



The CoP catalyst incorporated onto photoactive 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.







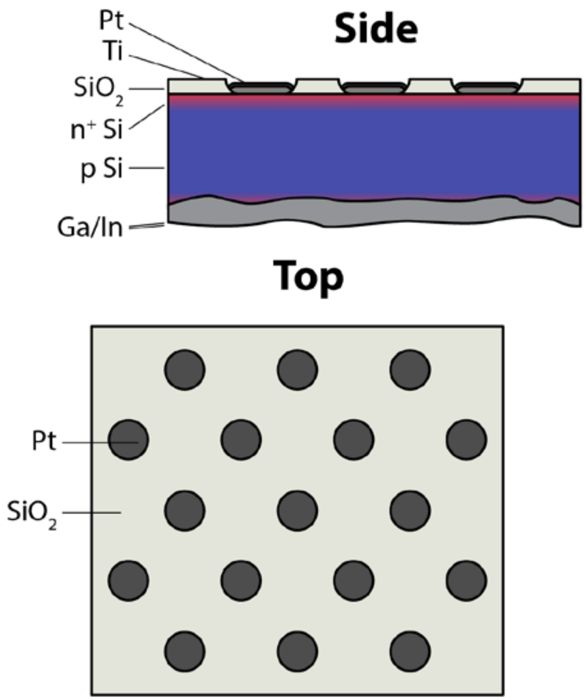
CoP-n$^+$p Si data: T.R. Hellstern, T.F. Jaramillo, et al. *Submitted* (2015)

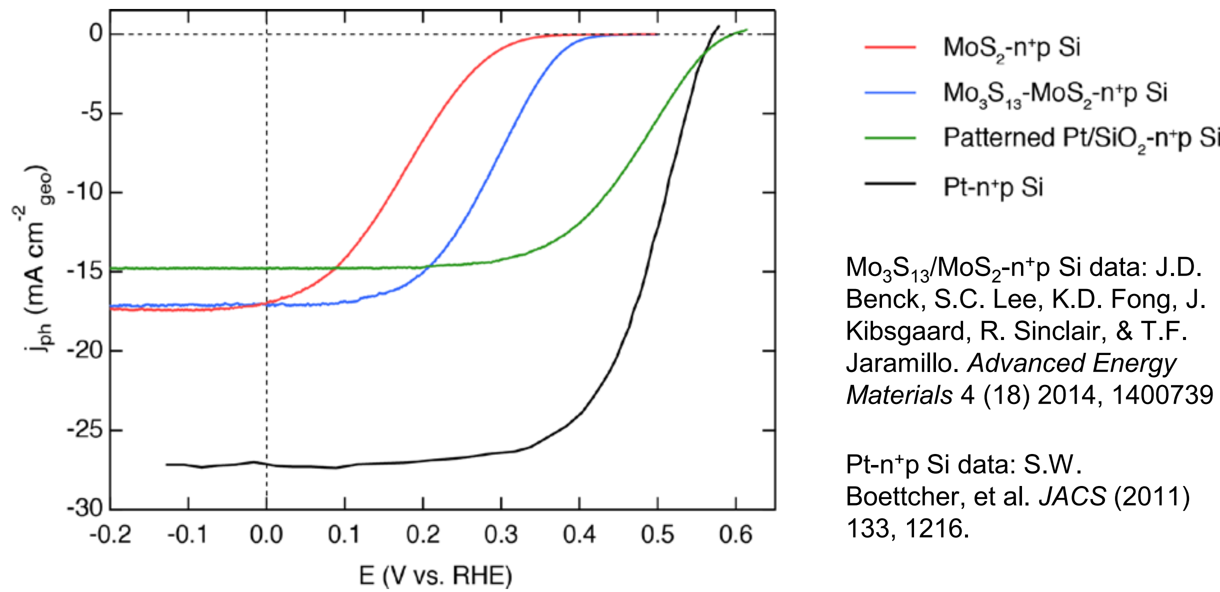
MoS_2-n$^+$p Si data: J.D. Benck, S.C. Lee, K.D. Fong, J. Kibsgaard, R. Sinclair, & T.F. Jaramillo. *Advanced Energy Materials* 4 (18) 2014, 1400739

Pt-n$^+$p Si data: S.W. Boettcher, et al. *JACS* (2011) 133, 1216. NiMo-n$^+$p Si data: E.L. Warren, et al. *E&ES* (2012) 9653-9661.

Accomplishments

Lithographically Patterned Si Photocathode

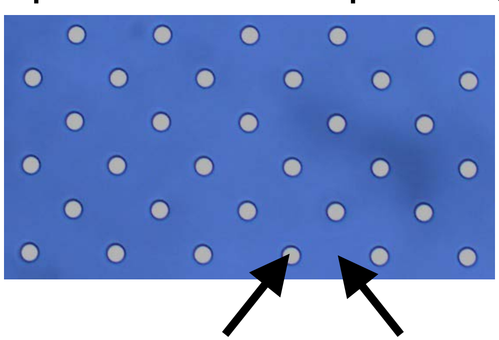




Mo_3S_{13}/MoS_2-n^+p Si data: J.D. Benck, S.C. Lee, K.D. Fong, J. Kibsgaard, R. Sinclair, & T.F. Jaramillo. *Advanced Energy Materials* 4 (18) 2014, 1400739

Pt-n^+p Si data: S.W. Boettcher, et al. *JACS* (2011) 133, 1216.

Optical Microscope Image



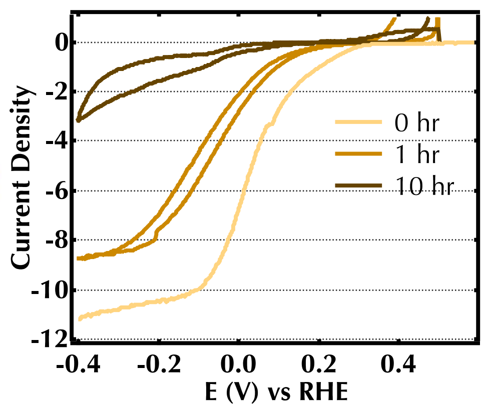
Pt/Ti metal circles Thermal SiO_2

We created a Si photocathode with lithographically patterned surface catalyst to reduce charge carrier recombination inside the semiconductor, improving the photocurrent onset potential. Future work will focus on increasing the saturation photocurrent density and incorporating nonprecious metal HER catalysts into this architecture.

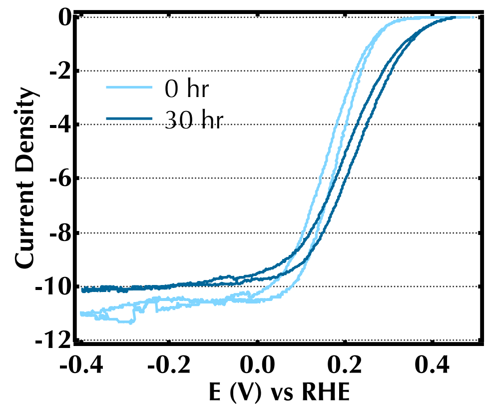
Accomplishments

Protecting the surface of $GaInP_2$

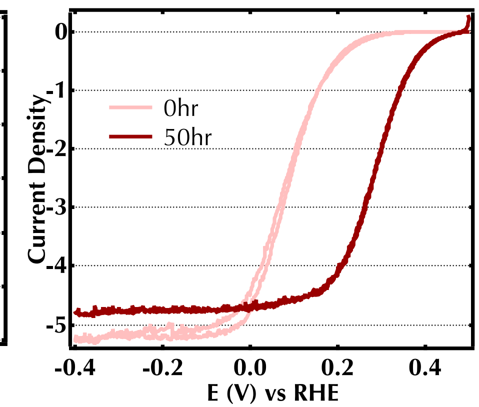
Bare $GaInP_2$



~ 1 nm MoS_2



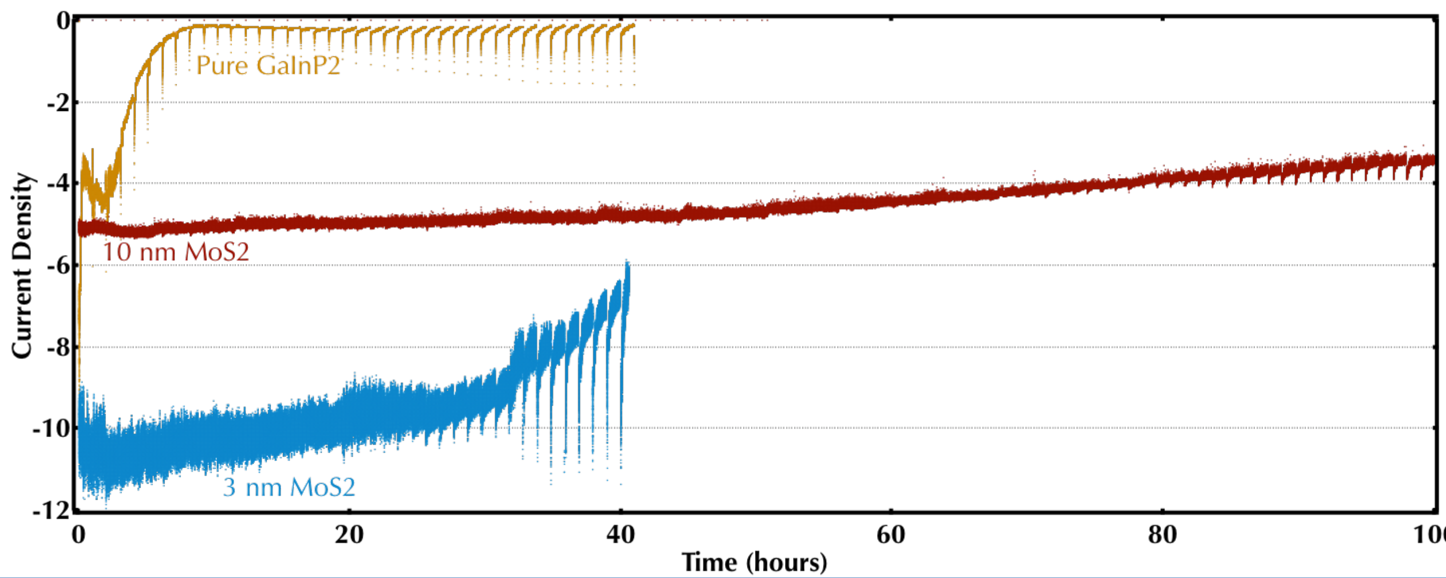
~ 4 nm MoS_2



We used MoS_2 to protect $GaInP_2$ against degradation in acid increasing its stability >30x without losing significant photocurrent density.

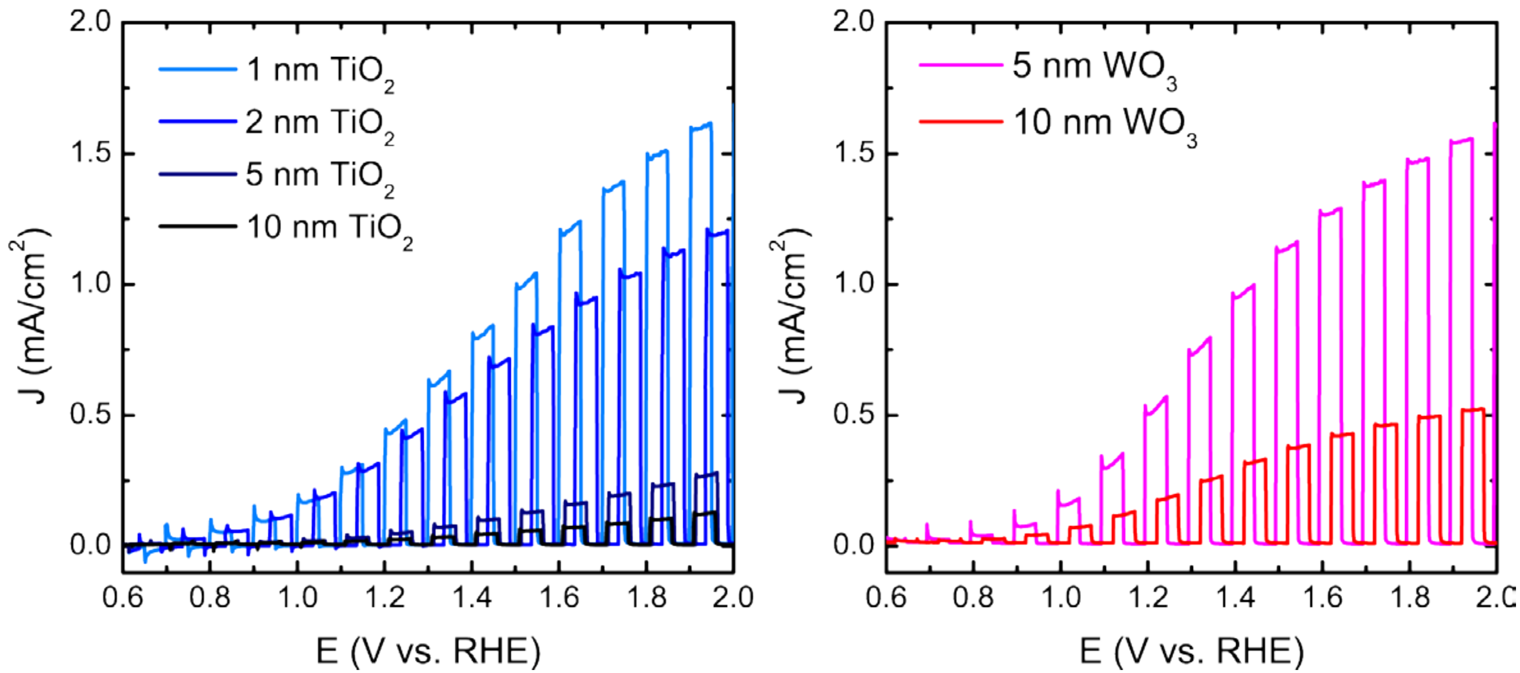
The MoS_2 further functions as a catalyst for the Hydrogen Evolution Reaction improving onset potential.

Chronoamperometry (Held at J_{sc})



Accomplishments

TiO_2 and WO_3 protection layers on a $BiVO_4$ Photoanode



Chopped-illuminated I-V curves of W-doped $BiVO_4$ photoanodes coated by wide band gap oxides with various thickness tested in H_2SO_4 (pH 1)

- Atomic layer deposition (ALD) of Ultrathin TiO_2 and WO_3 protection layers were developed
- Comparing to ALD TiO2, WO_3 layer has lower resistivity. Hence, thicker protection layer to be utilized

Collaborations

National Renewable Energy Laboratory
Todd Deutsch
James Young

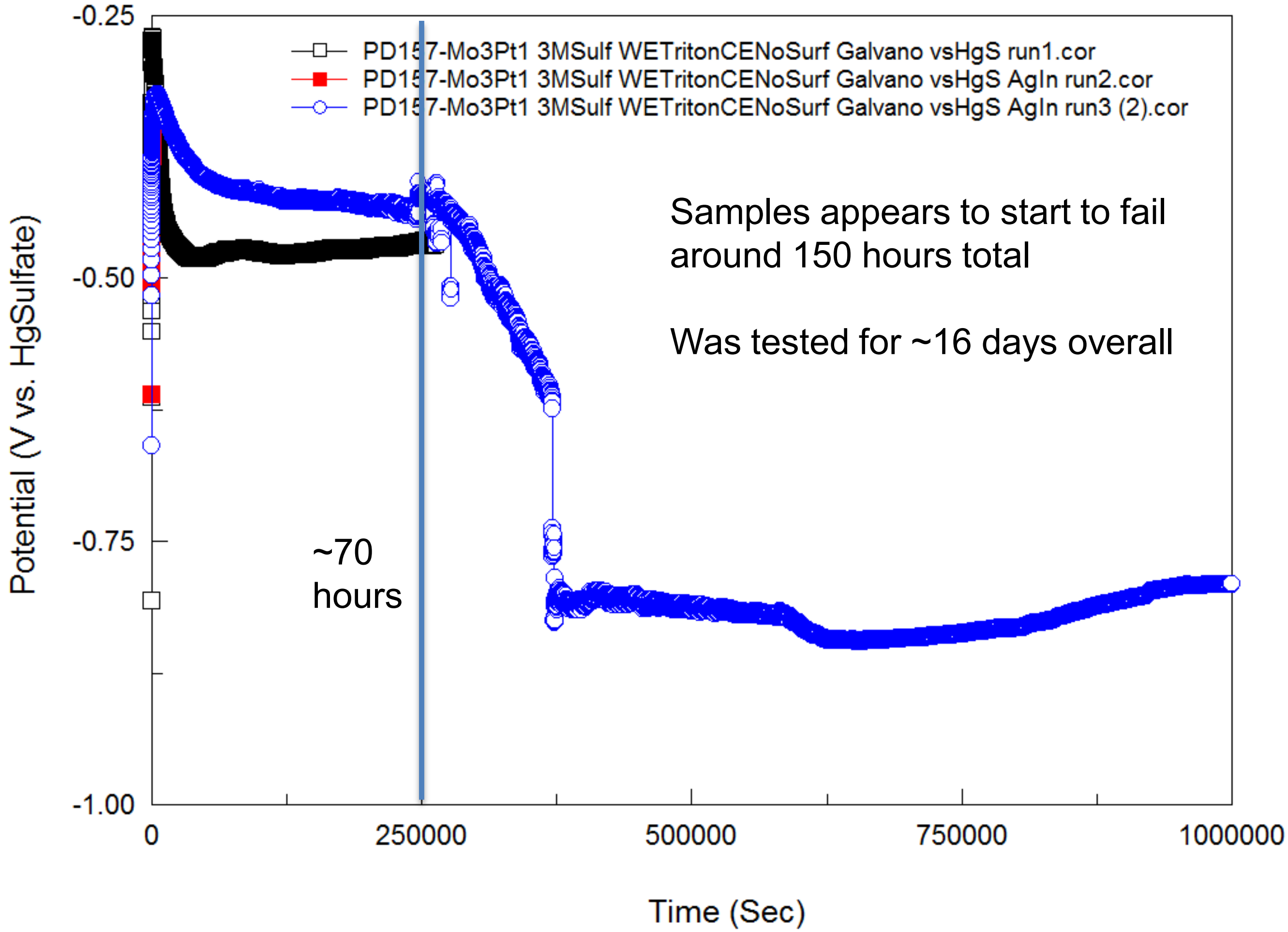
We collaborate together with Todd Deutsch and James Young on stabilizing $GaInP_2$ photocathodes. These III-V semiconductors are fabricated at NREL, while at Stanford we engineer catalysts and surface protection layers.

PEC Working Group

Collaboration among a community of PEC researchers to set standards for device testing and to discuss and address technical challenges in the field. Key organizers include Dr. Eric Miller (DOE), Dr. Heli Wang (NREL), and Prof. Thomas F. Jaramillo (Stanford).

Collaborations - NREL

Sister samples were sent to NREL for chronopentiometry experiments to assess stability, measured at NREL by Todd Deutsch and James Conway to further study the stability of $GaInP_2$

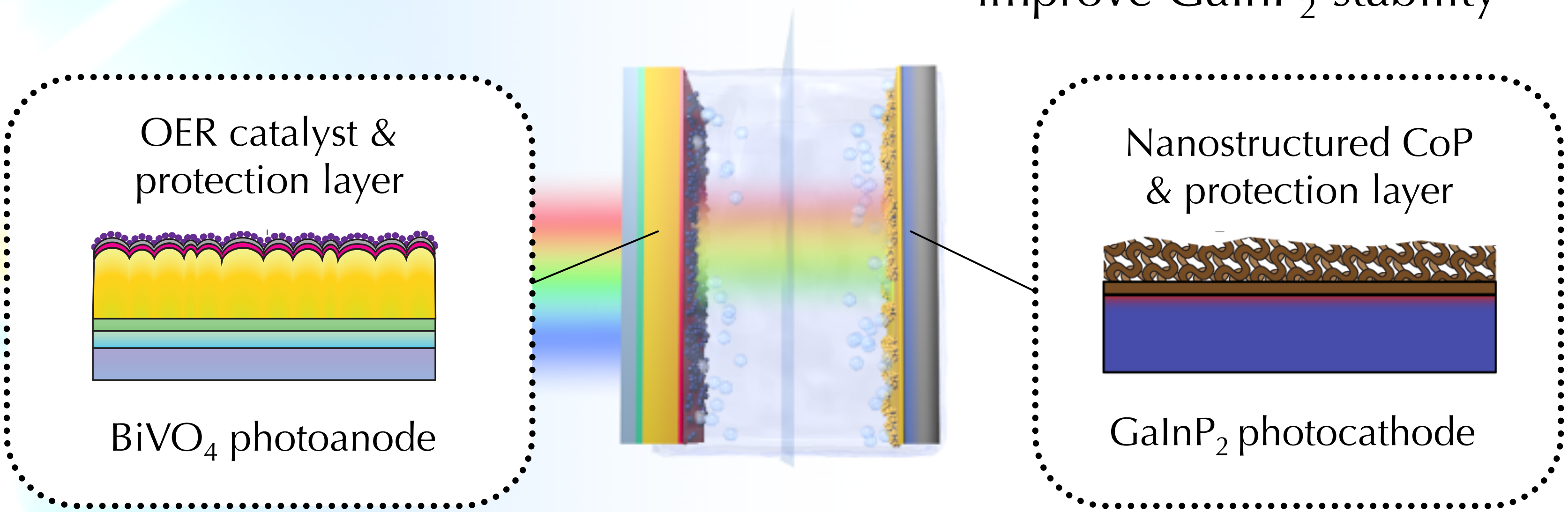


Remaining Challenges & Future Work

Immediate goals

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

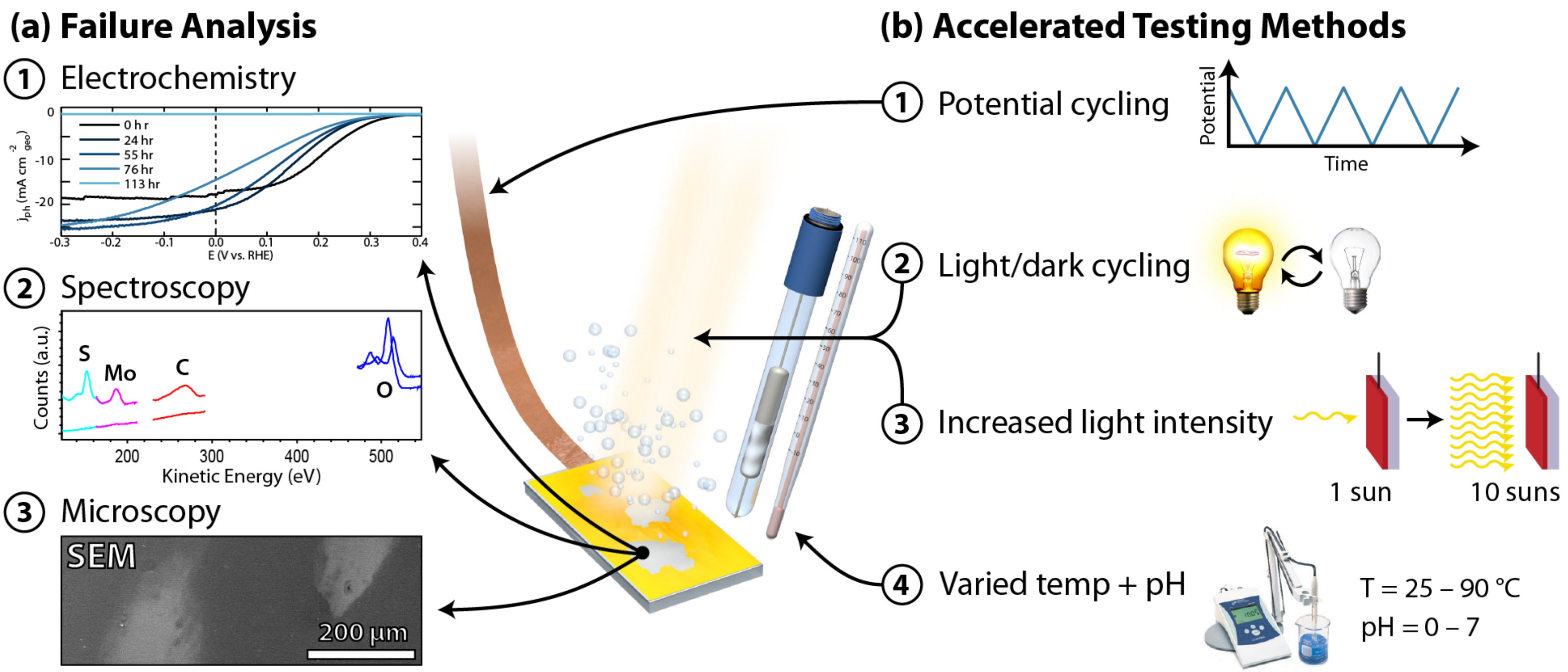
Improving activity of CoP by nanostructuring to increase surface area and further improve $GaInP_2$ stability



Goal: To combine current and future innovations to make a non-precious metal unassisted water splitting device that is stable in acid.

Remaining Challenges & Future Work
Long term goals

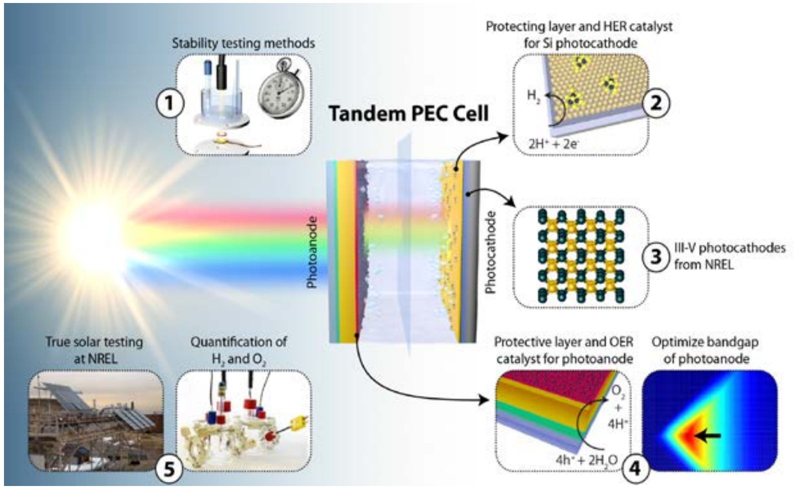
Developing methods to identify photoelectrode failure mechanisms and predict long-term performance using short-term tests



Summary

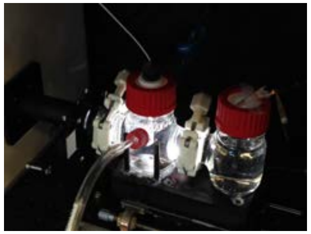
Approach

- We developed a work plan for addressing stability and activity of both the photoanode and photocathode in acid.

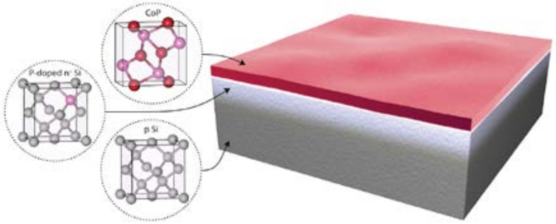


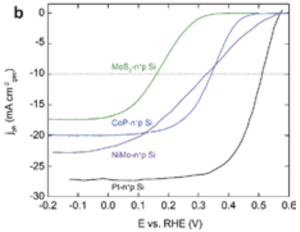
Accomplishments

- Engineered lamp setup for stability testing.



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

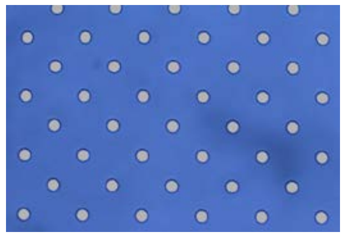


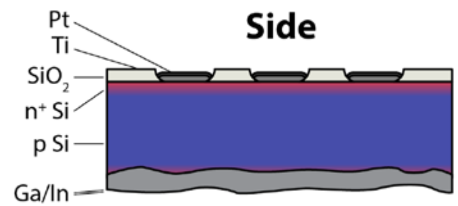


Summary

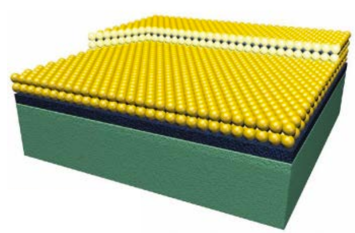
Accomplishments cont.

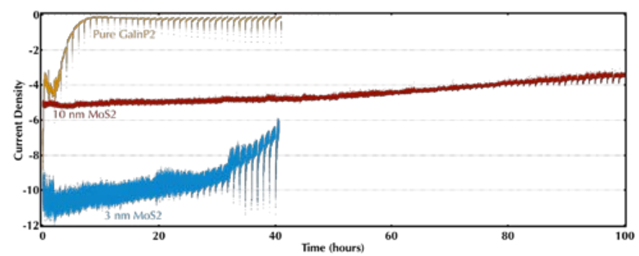
- Interfacial engineering of the Si photocathode





- Improving stability of $GaInP_2$ over 30x using MoS_2 protection layers





- Using ALD of TiO_2 and WO_3 to protect $BiVO_4$ photoanodes