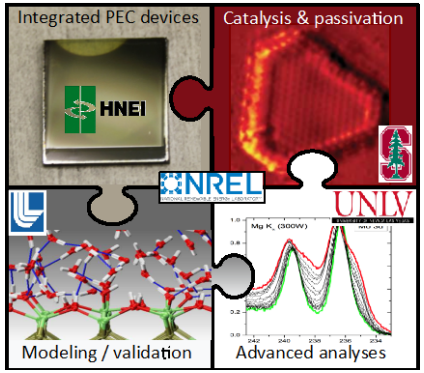
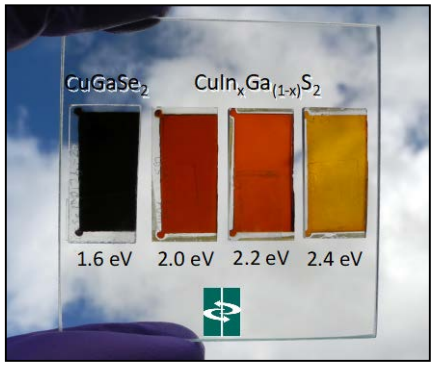
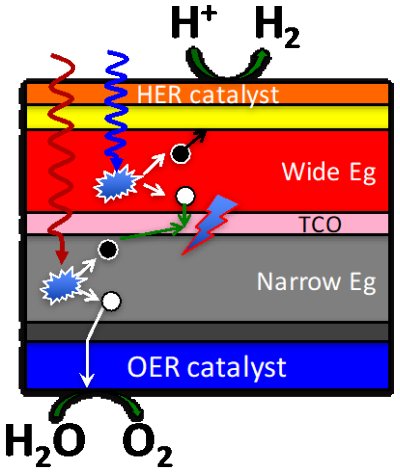






Wide Bandgap Chalcopyrite Photoelectrodes for Direct Solar Water Splitting

PI: Nicolas Gaillard

University of Hawaii

Hawaii Natural Energy Institute

2018 DoE Annual Merit Review

June 14th 2017

Project ID#: PD116

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date: 10/1/2014
- Passed GNG#1: 10/6/2015
- Passed GNG#2: 10/5/2016
- Project end date: 9/30/2018 (1-yr NCE)

Budget

- Total budget funding: $3,050,000
  - DoE share: 100%
  - Contractor share: 0%
- Total DoE funds spent: $2,900,000

(as of 04/2018, including Nat. Labs).

Barriers

Challenges for PEC H_2 production technology:

– Materials Efficiency (AE)
– Materials Durability (AF)
– Integrated device configuration (AG)
– Synthesis and Manufacturing (AJ)

Partners / primary role

- HNEI (N. Gaillard)
→ Absorber / p-n junction fabrication

- Stanford (T. Jaramillo)
→ Surface catalysis and corrosion protection

- UNLV (C. Heske)
→ Bulk/sub-surface/surface characterization

- LLNL (T. Ogitsu)
→ Absorber/interface theoretical modeling

- NREL PEC team (T. Deutsch)
→ Device validation and PEC reactor design

- NREL CIGS group (K. Zhu)
→ New chalcopyrites and buffers

Relevance - Objectives

- **Long-term goal**: identify efficient and durable copper chalcopyrite-based materials which can operate under moderate solar concentration and capable of generating hydrogen via PEC water splitting at a cost of $2/kg or less.

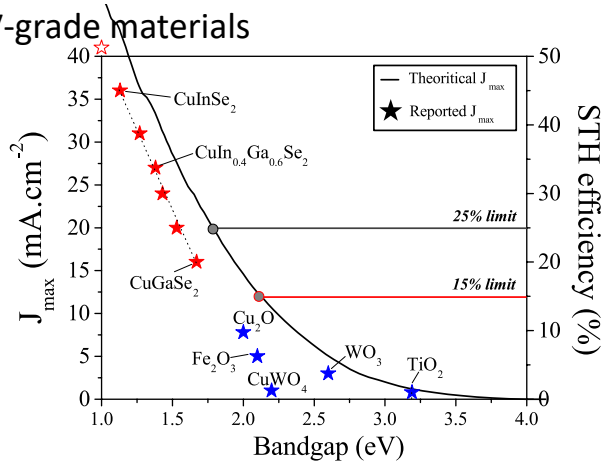
- **This project**: (1) develop new wide bandgap (>1.7 eV) copper chalcopyrites compatible with the hybrid photoelectrode (HPE) design, (2) demonstrate at least 15% STH efficiency and (3) generate 3L of H_2 under 10x concentration ("Type 4" PEC reactor) in 8 hours.

Table 3.1.8 Technical Targets: Photoelectrochemical Hydrogen Production: Photoelectrode System with Solar Concentration [a]

Characteristics	Units	2011 Status	2015 Target	2020 Target	Ultimate Target
Photoelectrochemical Hydrogen Cost [b]	$/kg	NA	17.30	5.70	2.10
Capital cost of Concentrator & PEC Receiver (non-installed, no electrode) [c]	$/m^2	NA	200	124	63
Annual Electrode Cost per TPD H_2 [d]	$/ yr-TPD$H_2$	NA	2.0M	255k	14k
Solar to Hydrogen (STH) Energy Conversion Ratio [e, f]	%	4 to 12%	15	20	25
1-Sun Hydrogen Production Rate [g]	kg/s per m^2	3.3E-7	1.2E-6	1.6E-6	2.0E-6

Relevance – Benefits of copper chalcopyrites for PEC H_2 production

1. PV-grade materials

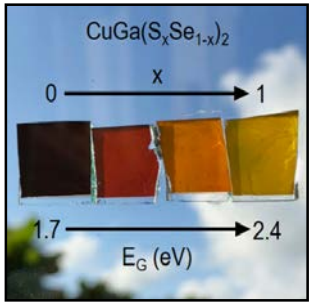


Photocurrent densities in line with DoE targets

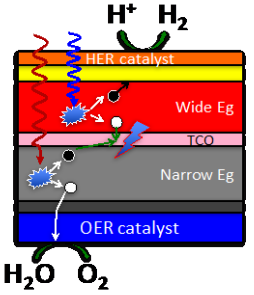
2. Bandgap tunable

$Cu(In,Ga)S_2$

$CuGa(S,Se)_2$



Hybrid photoelectrode

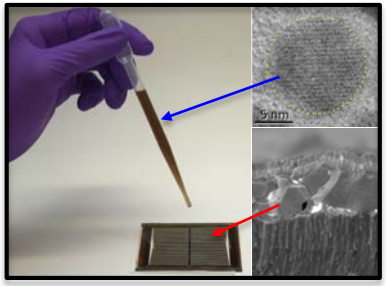


PV driver and PEC electrode can be stacked for efficient PEC H_2 production

3. Cost-effective processes developed

Production

R&D

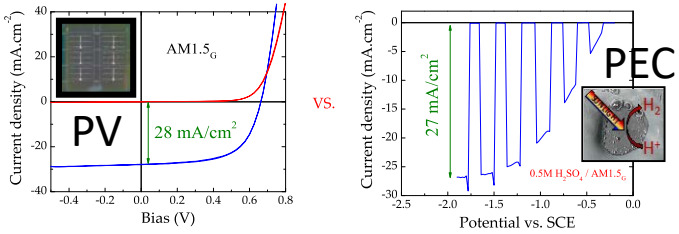


Solution processed chalcogenide material (ONR funding)

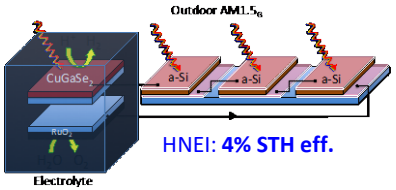
The CIGSSe class can meet DoE's material target cost of $60/m^2$.

4. Efficient PEC water splitting demonstrated with CIGSSe

Electrodes

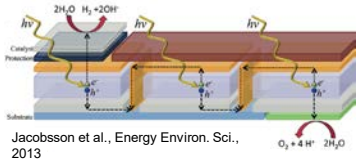


Devices



HNEI: **4% STH eff.**

Angstrom Lab.: **10% STH eff.**



Jacobsson et al., Energy Environ. Sci., 2013

Take home message: copper chalcopyrites are excellent candidates for PEC water splitting. New materials with wider bandgaps are needed to relocate PV driver(s) under the photocathode (HPE structure) in order to achieve STH efficiencies > 10%.

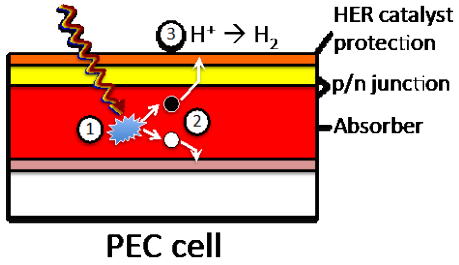
Approach – Milestones

Task 1. PV-grade wide bandgap absorbers: **AE and AJ barriers**

Task 2. Sub-surface energetics improvement (p/n junction): **AE and AG barriers**

Task 3. Surface catalysis and corrosion resistance: **AE and AF barriers**

Task 4. Device certification and efficiency benchmarking: **AG barrier**



PEC cell

Task#	FY15 Milestones	Due Date	Status
1	Synthesize a $CuInGaS_2$ thin film material with controlled stoichiometry & microstructure	12/2014	Complete
2	Fabricate $Cu(In,Ga)S_2$ cells with Voc> 600 mV	03/2015	Complete
3	Durability > 500 hrs at 8 mA/cm^2 with a chalcorpyrite photoelectrode	06/2015	25%
4	Chalcopyrite photoelectrode with bandgap > 1.7eV that generates at least 10-12 mA/cm2	09/2015	Complete
Go/No-Go decision criteria: Demonstrate a chalcopyrite photoelectrode material with bandgap > 1.7eV that generates a photocurrent density of at least 10-12 mA/cm^2			

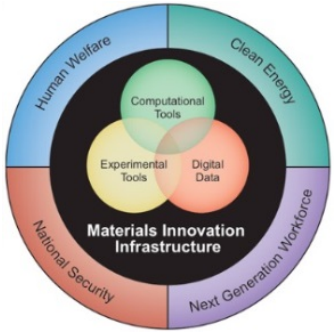
Task#	FY16 Milestones		
1	$Cu(In,Ga)S_2$ solar cells with a photoconversion efficiency > 6%	12/2015	Complete
4	Photocurrent density relevant to 15-16% STH with chalcorpyrite 12-13 mA/cm^2	03/2016	Complete
3	Durability > 750 hrs at 8 mA/cm^2, with a stretch goal of 1,000 hrs	06/2016	45%
2	Fabricate $Cu(In,Ga)S_2$ cells with Voc> 750 mV	09/2016	Complete
Go/No-Go decision criteria: Demonstrate a wide bandgap chalcopyrite-based heterojunction with an open circuit potential of at least 750 mV			

Task#	FY17 Milestones		
1	Photocurrent density relevant to 16-17% STH with a chalcopyrite 13-14 mA/cm2	12/2017	92%
2	Fabricate $Cu(In,Ga)S_2$ cells with Voc> 900 mV	03/2018	94%
3	Durability > 1,000 hrs at 8 mA/cm^2, with a stretch goal of 2,000 hrs	06/2018	
4	HPE PEC device with a standalone STH of >15% generting at least 3L of H2 in 8 hrs.	09/2018	

Barriers list : AE: Materials Efficiency, AF: Materials Durability, AG: Integrated device configuration, AJ: Synthesis/Manufacturing.

Approach – Integrated experiment, computation and theory

Materials Genome initiative (MGI) / Energy Materials Network (EMN)



Innovative materials discovery and development for faster product development. Key elements include:

- Integrating experiment, computation, and theory
- Making digital data accessible
- Creating a world-class materials workforce
- Leading a culture shift in materials research

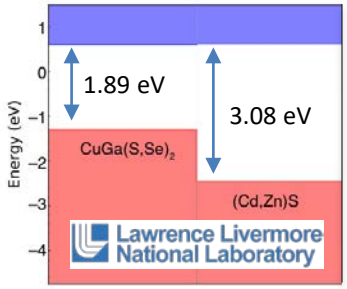
Accelerating materials development using integrated modeling, synthesis and advanced characterizations:

1. New wide bandgap materials discovery using theoretical modeling: bandgap, conductivity type and defect density.

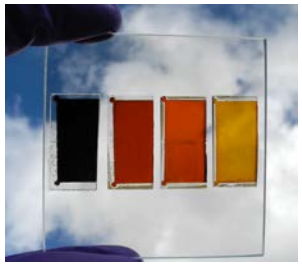
2. Theory-guided synthesis of wide bandgap chalcopyrites using state-of-the-art vacuum-based deposition tools.

3. Advanced surface and interface spectroscopy analyses of newly formed materials to validate modeling and refine synthesis.

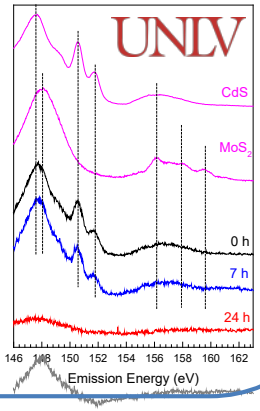
Modeling



Synthesis



Advanced analysis

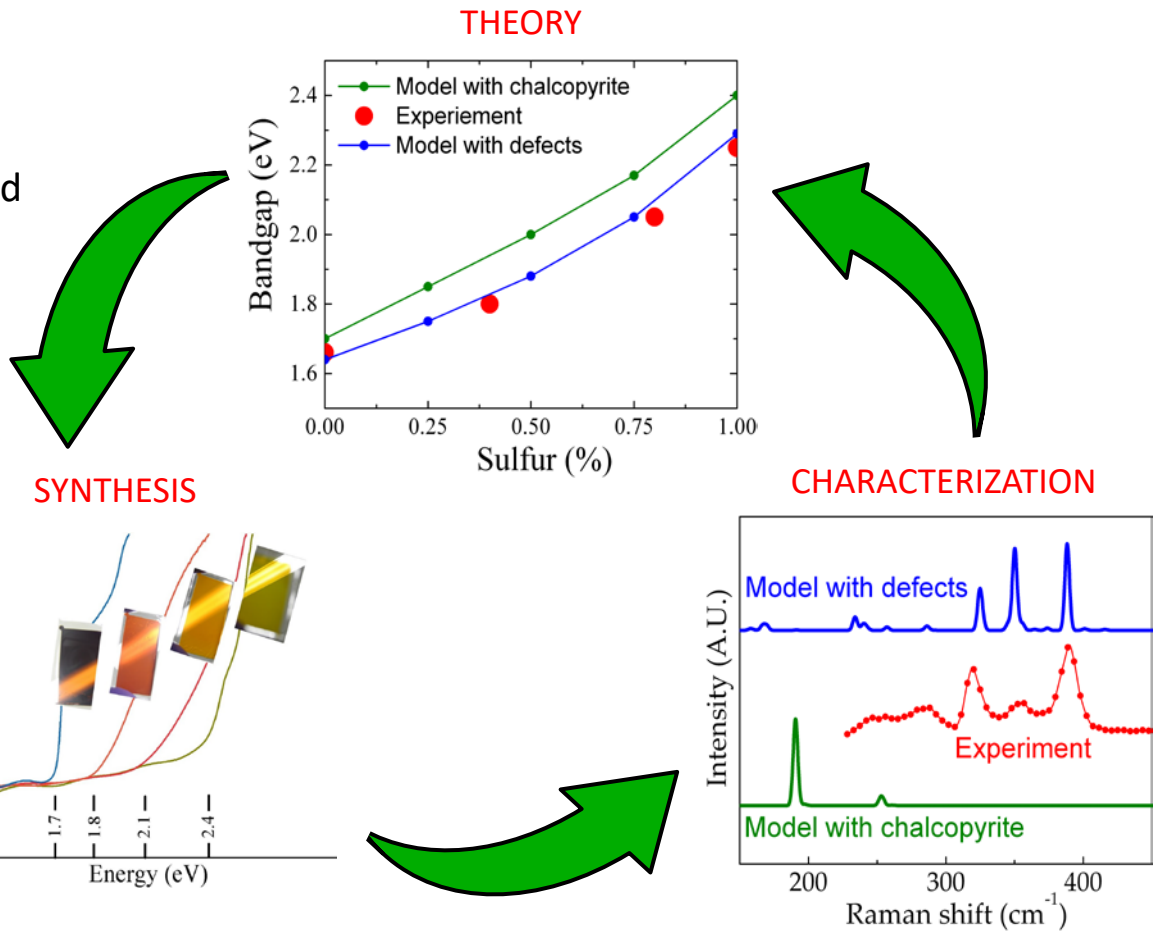


NREL

Accomplishments – Task 1: PV-grade absorbers

1. Materials development through integrated **Theory**-**Synthesis**-**Characterization**

e.g. $CuGa(S,Se)_2$
→ E_G can be tuned by the S/Se ratio.



Each round of testing improves the accuracy of the theoretical model.

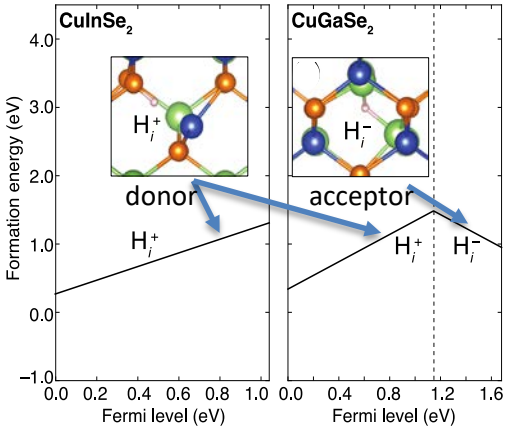
→ Successful integration of **theory**, **synthesis** and **characterization** in the development of chalcopyrite materials.

Accomplishments – Task 1: PV-grade absorbers

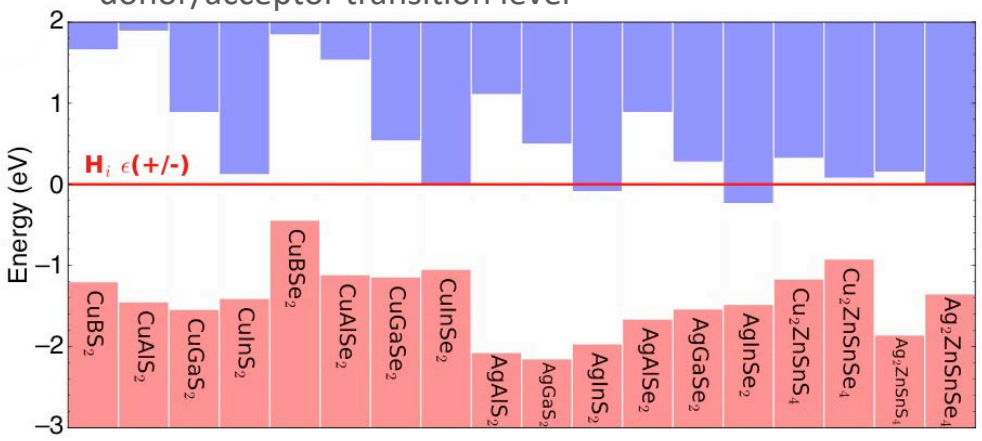
2. Theoretical modelling of hydrogen-related defects in chalcopyrites

Hydrogen interstitials (H_i)

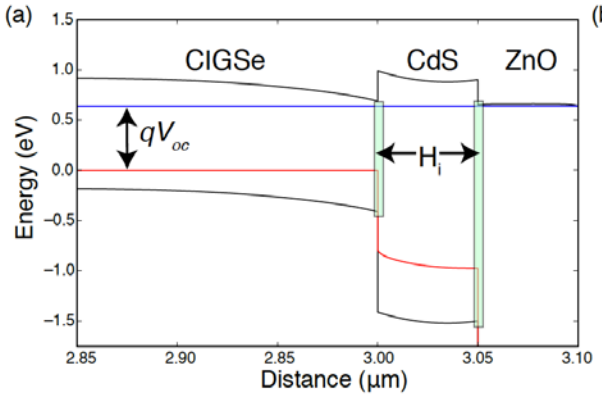
- Common impurities from vacuum or liquid processing.
- Predominantly donors in Ag, In-containing absorbers.
- Can act as compensating acceptors in larger-gap absorbers.

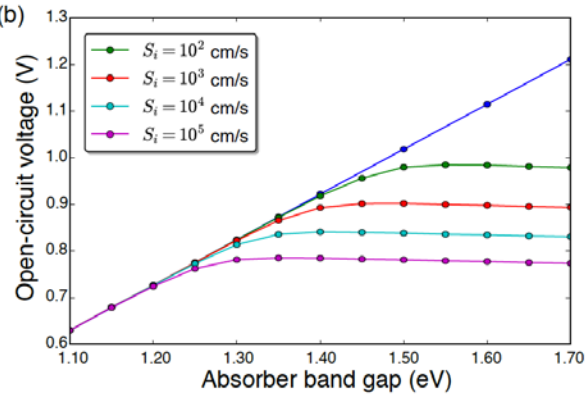


Impurities may pin interfacial Fermi levels at the donor/acceptor transition level



J.B. Varley *et al.* J. Appl. Phys. **123,** 161408 (2018).





Theory-guided insights into origins of reduced efficiencies

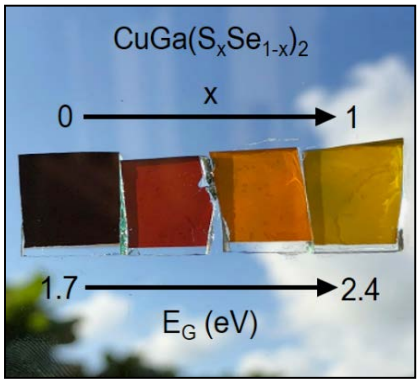
Accomplishments – Task 1: PV-grade absorbers

3. Bandgap tunable $CuGa(S,Se)_2$ absorbers

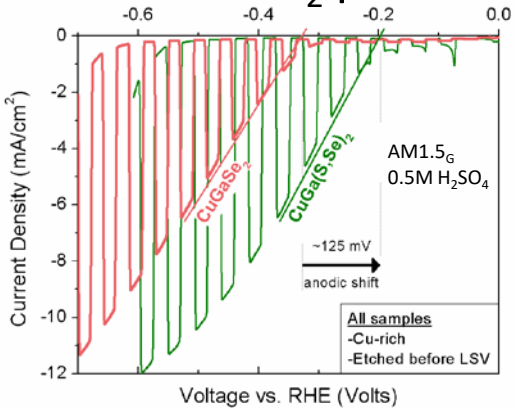
a. Synthesis

2-step annealing protects $F:SnO_2$ from damage

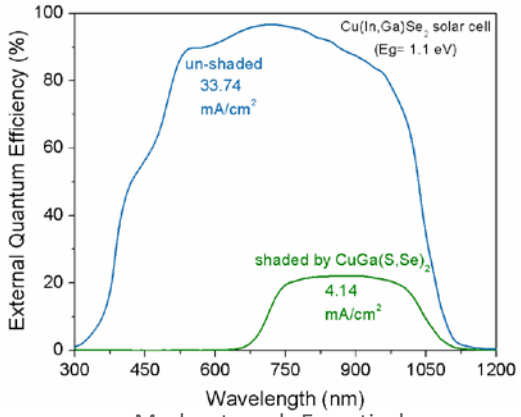
Sulfurization only works when $CuGaSe_2$ is grown Cu-rich



b. $CuGaSSe_2$ photocathode Performance

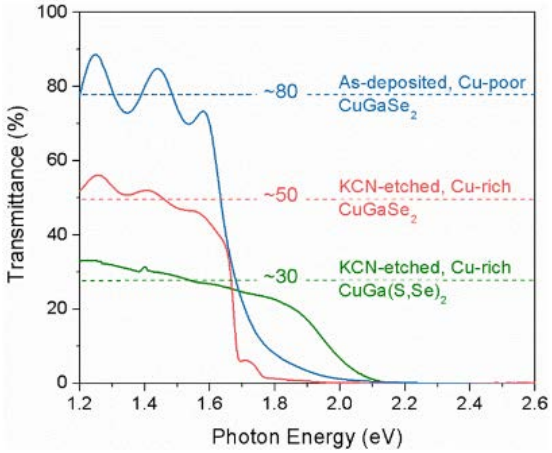


>10 mA/cm² current output in 3-electrode linear sweep voltammetry

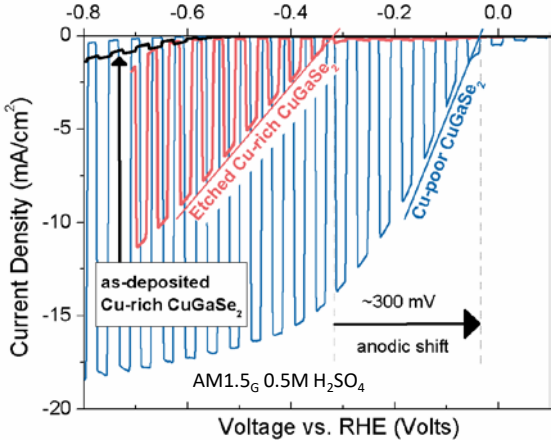


Moderate sub-E_G optical transmittance for $CuGa(S,Se)_2$

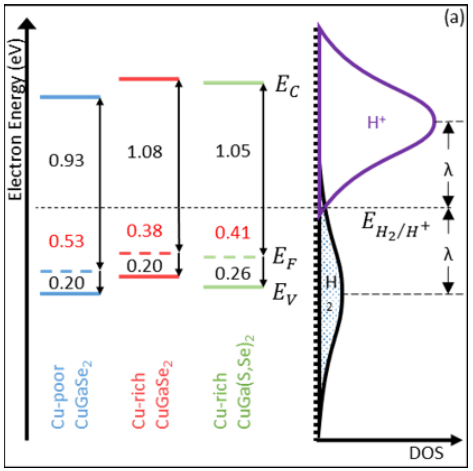
c. Copper Impacts Performance



Sub-E_G transmittance is reduced when $CuGaSe_2$ is Cu-rich



Lower current and more cathodic onset voltage when $CuGaSe_2$ is Cu-rich



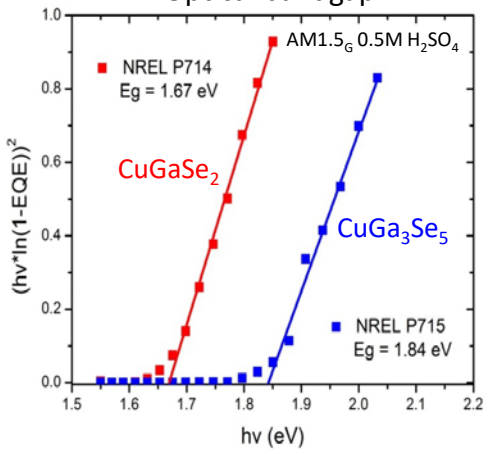
Cu changes energy bands such that current "turns on" at lower applied bias, explaining why V_{ONSET} of Cu-rich $CuGaSe_2$ is more cathodic

Accomplishments – Task 1: PV-grade absorbers

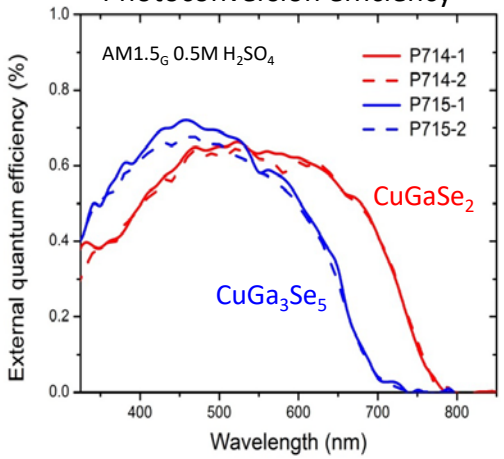
4. Ordered defect $CuGa_3Se_5$ absorbers (NREL)

a. Material development using Mo back contact AMR 2017

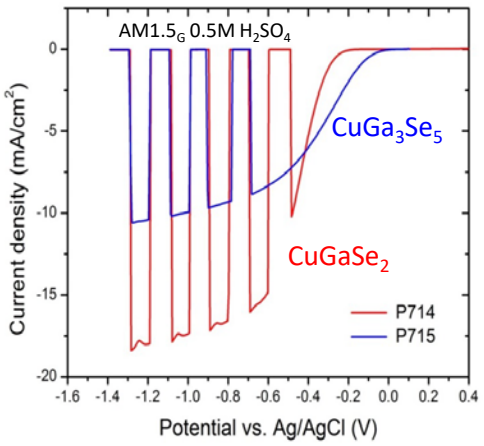
Optical bandgap



Photoconversion efficiency



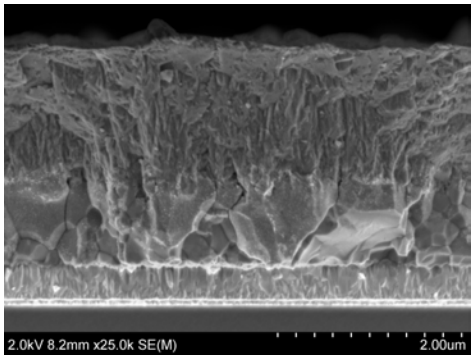
PEC characteristics

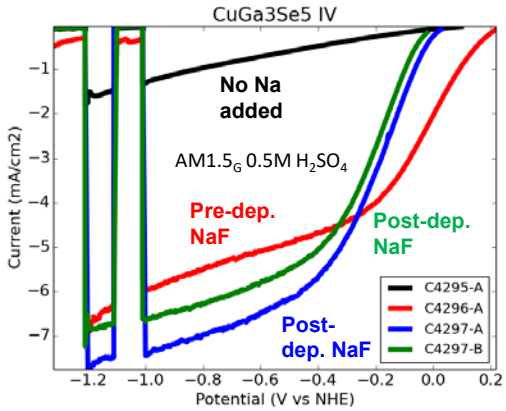


b. $CuGa_3Se_5$ integration on transparent conductive FTO substrates

→ Challenge: FTO acts as a natural barrier to sodium diffusion, an element known to improve chalcopyrite electronic properties

Cross section of $CuGa_3Se_5$ with NaF post treatment



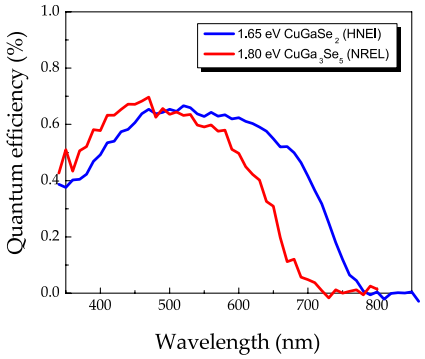


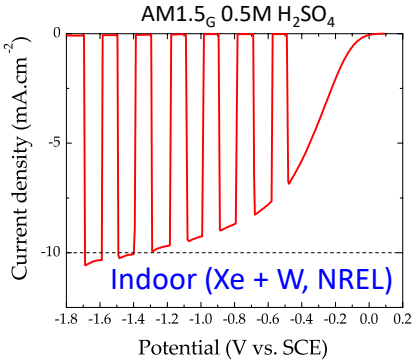
- Photo-conversion recovered with use of NaF treatment.
- Significant effect of deposition order (NaF pre vs. post treatment) on photocurrent onset potential.

Accomplishments – Task 1: PV-grade absorbers

Summary of research performed on wide bandgap chalcopyrites

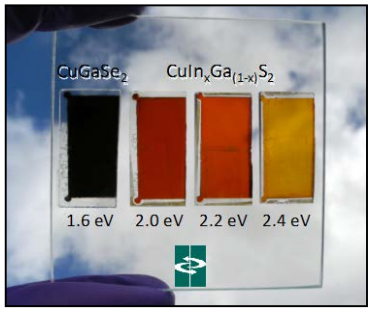
Approach 1: $CuGa_3Se_5$ (1.80 eV)



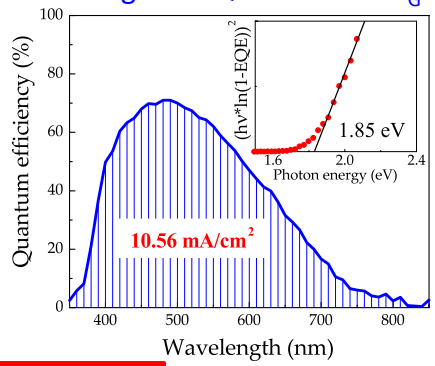


10.0 mA/cm²

Approach 2: $Cu(In,Ga)S_2$ from $Cu(In,Ga)Se_2$

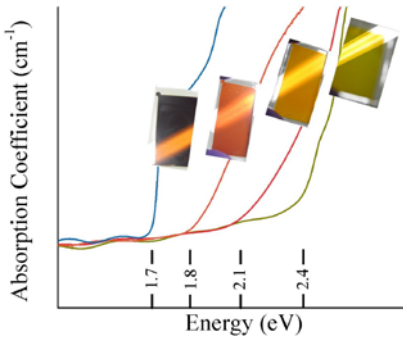


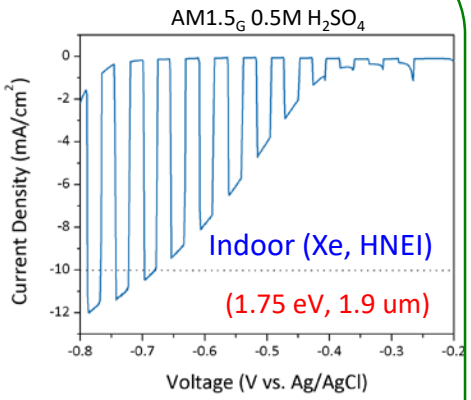
Integrated QE over $AM1.5_G$



10.5 mA/cm²

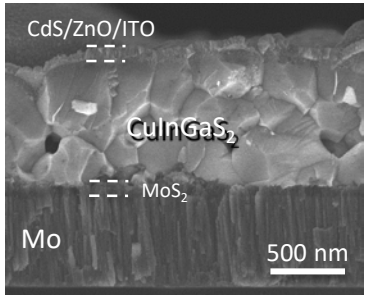
Approach 3: $CuGa(S,Se)_2$ from $CuGaSe_2$

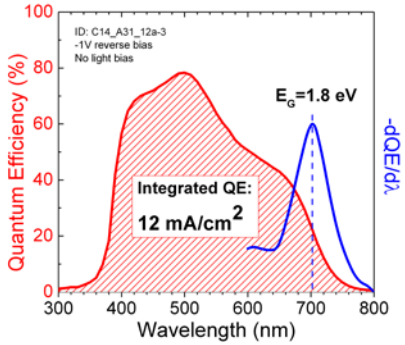




11.0 mA/cm²

Approach 4: $Cu(In,Ga)S_2$ from CuInGa metal alloys



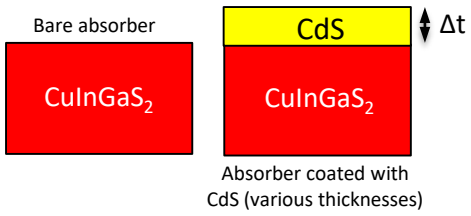


12 mA/cm²

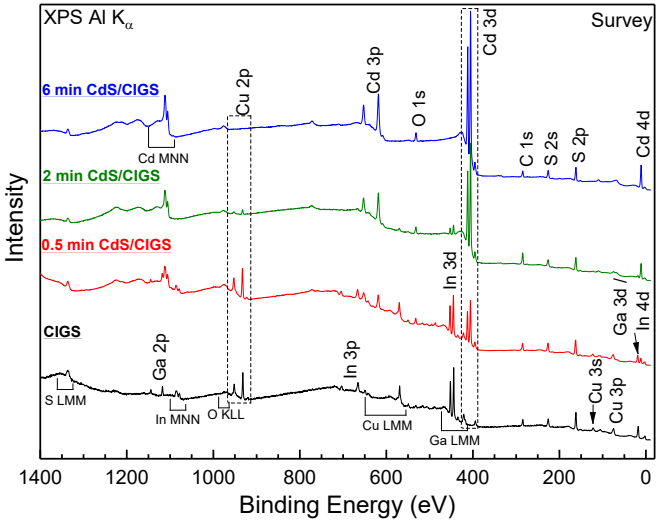
Accomplishments – Task 2: Sub-surface energetics

1. Determination of the band alignment at the CdS/CIGS$_2$ (1.8 eV bulk E_G) interface

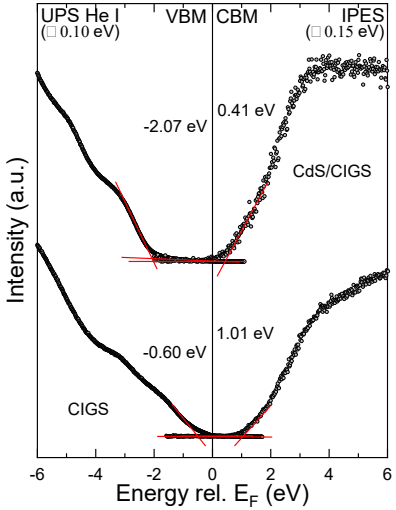
First sample set provided by HNEI to UNLV for spectroscopic analysis

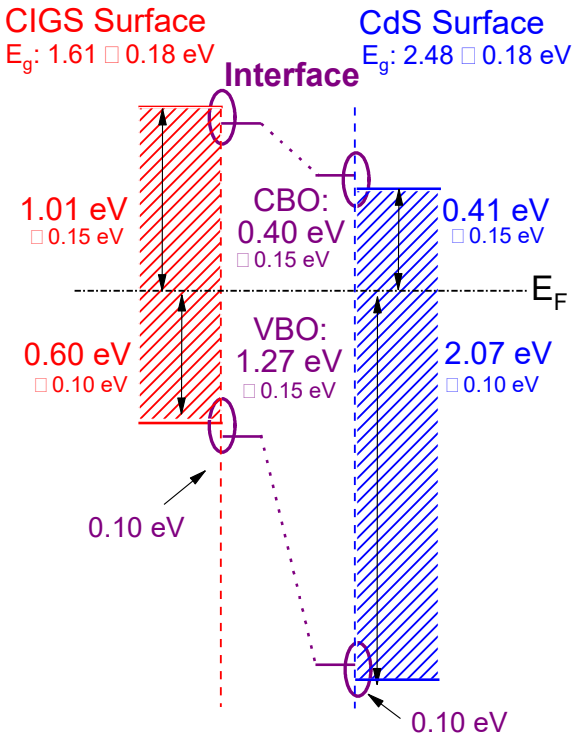


XPS survey scans



UPS and IPES spectra





Used UPS & IPES to derive the electronic surface band gap for CIGS absorber (1.61 eV) and CdS buffer (2.48 eV).

Determined interface-induced band bending with XPS.

Derived full electronic interface structure, including a "cliff" of 0.40 eV in the conduction band.

Accomplishments – Task 2: Sub-surface energetics

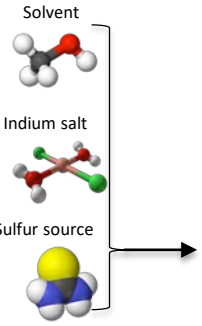
2. n-type buffer engineering

a. Development of printable In_2S_3 process

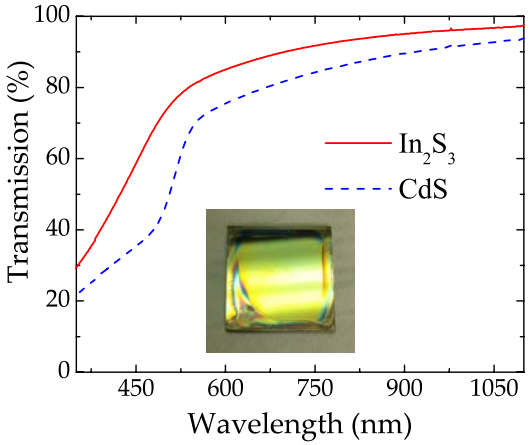
Conventional CdS process

Vol/CdS layer: **100 mL**

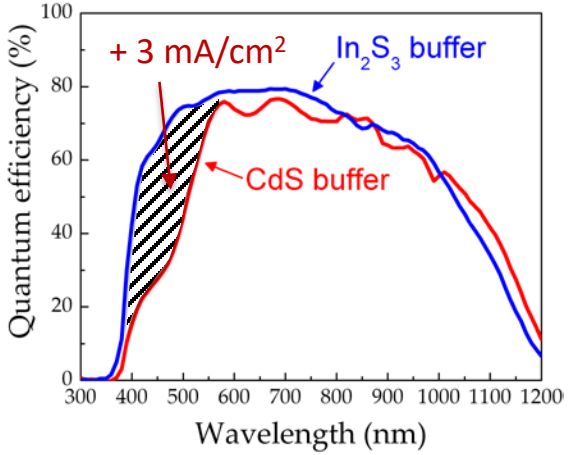
New printable In_2S_3 ink



Vol/In_2S_3 layer: **100 µL**

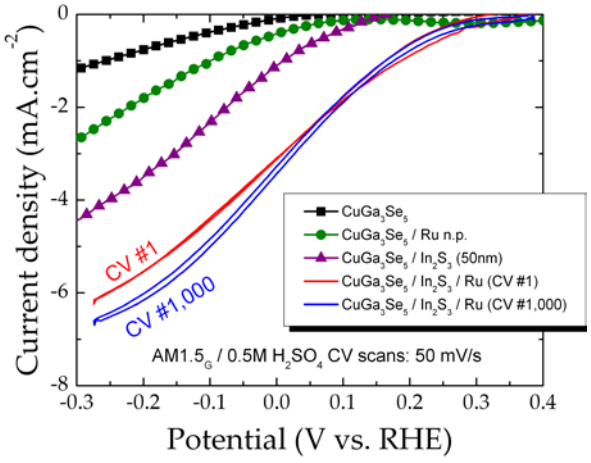


PV test with 1.1 eV $CuInGaSe_2$

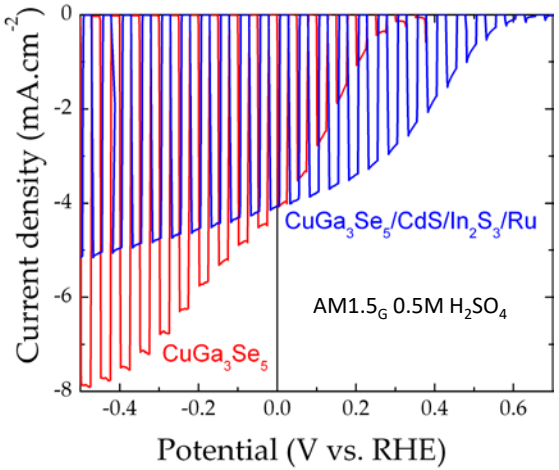


b. $CuGa_3Se_5$ (1.8 eV)/In_2S_3 hetero-junctions

Test #1: $CuGa_3Se_5$/**Mo**



Test #2: $CuGa_3Se_5$/**FTO**



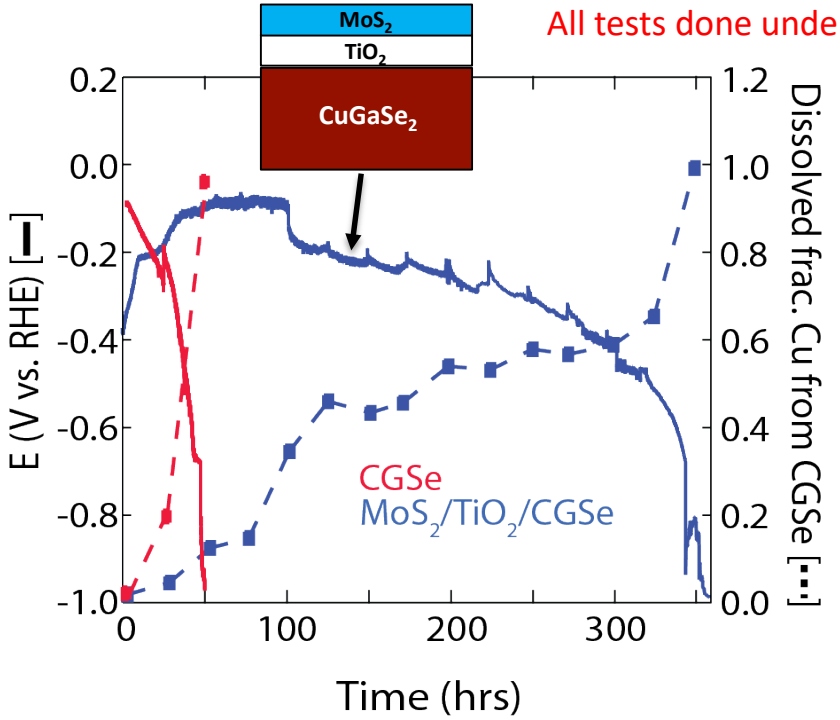
- Successful development of printable In_2S_3 process.
- Short-term stability of In_2S_3 in pH0.5 demonstrated.
- 0.6 V vs. RHE onset obtained by combining CdS with In_2S_3.

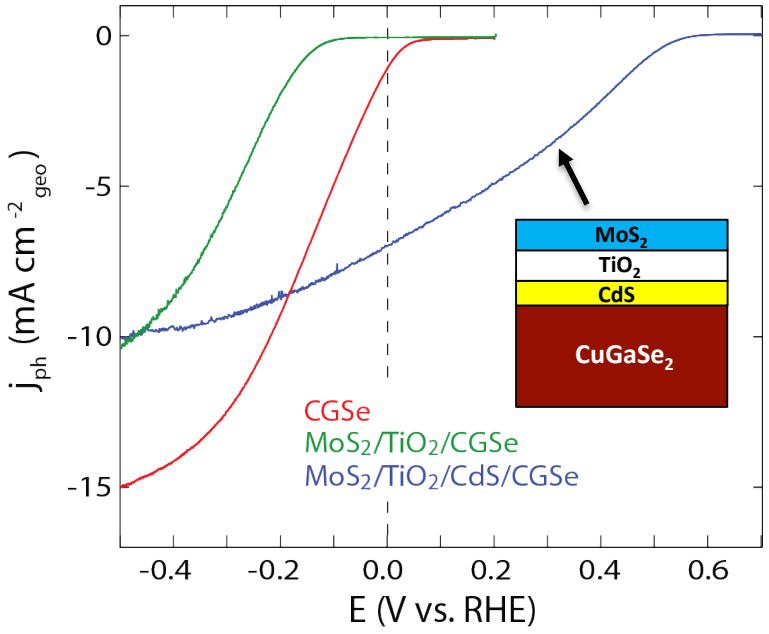
Accomplishments – Task 3: Surface catalysis/corrosion resistance

1. Corrosion resistance enhancement using MoS_2 – TiO_2 films AMR 2017

1. Deposit 5 nm TiO_2 and 4 nm MoO_x on CGSe by ALD
2. Convert MoO_x to MoS_2 using H_2S
3. Conduct CP tests at – 8 mA cm^{-2} with one LSV every 25 hrs to determine stability
4. Probe degradation mechanism using ICP-MS of electrolyte

All tests done under $AM1.5_G$ in 0.5M H_2SO_4





MoS_2/TiO_2 protective scheme extends the life of CGSe electrodes for **~350 hrs** (vs. 250 hrs in AMR2016).

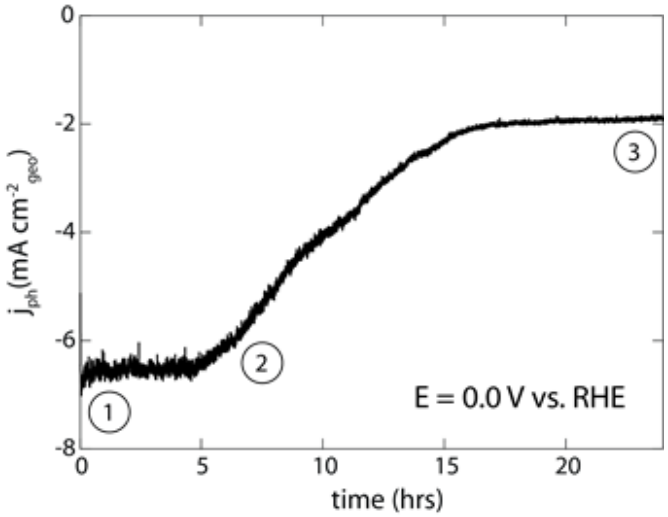
CdS buffer layer improves the onset of CGSe photocathodes.

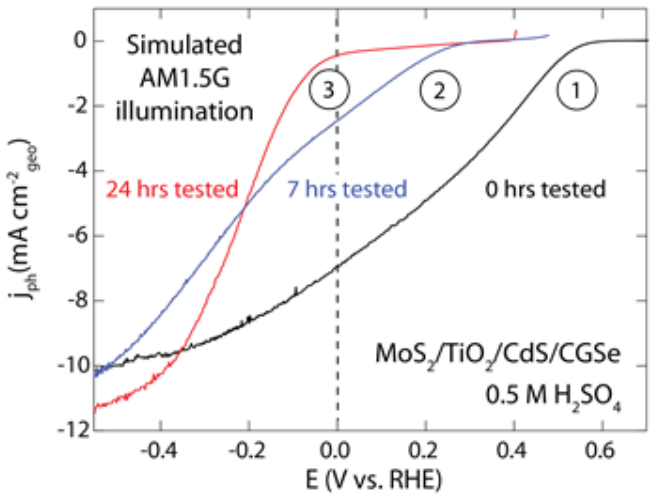
T.R. Hellstern, A. D. DeAngelis, L.A. King, N. Gaillard, T.J. Jaramillo. *In Preparation*

Accomplishments – Task 3: Surface catalysis/corrosion resistance

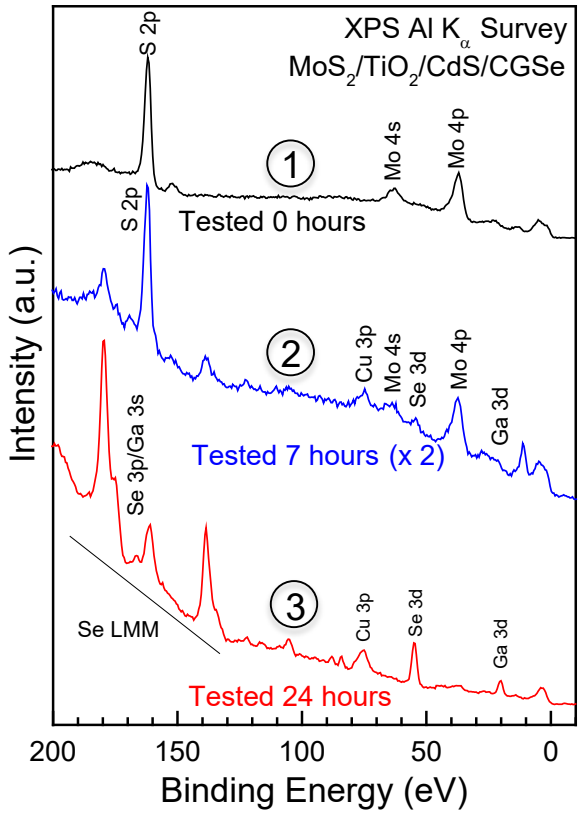
2. Electrochemical and spectroscopic characterization of CdS/CGSe photoelectrodes AMR 2017

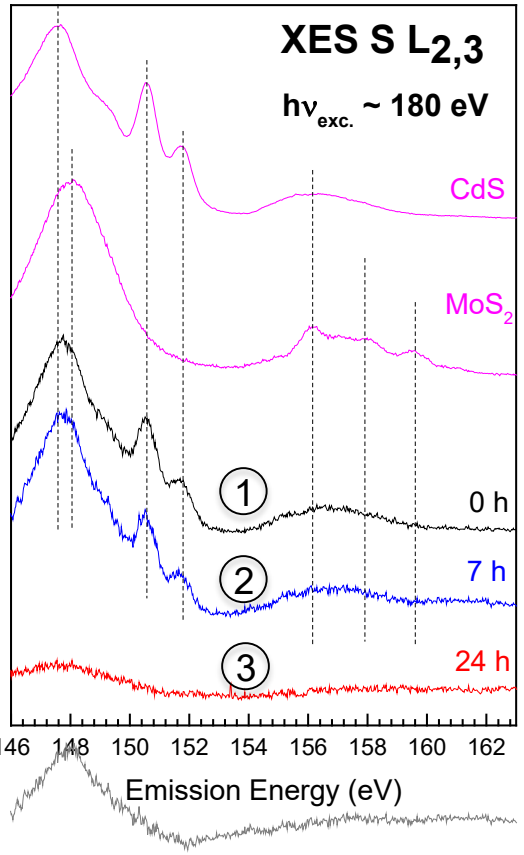
Electrochemical Characterization (Stanford)





Spectroscopic Characterization (UNLV)



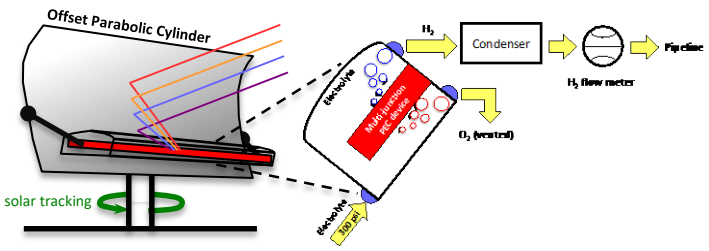


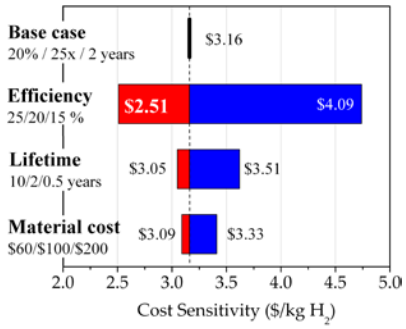
Combination of electrochemical and spectroscopic characterization leads to deeper understanding of degradation mechanisms.

T.R. Hellstern, D. Palm, J. Carter, A. D. DeAngelis, M. Blum, N. Gaillard, C. Heske, T.J. Jaramillo. *In preparation*

Accomplishments – Task 4: CIGS-based PEC device

1. Co-planar vs. Tandem PEC system: techno-economic considerations





→ STH efficiency is the parameter with the largest leverage on H2 production costs.

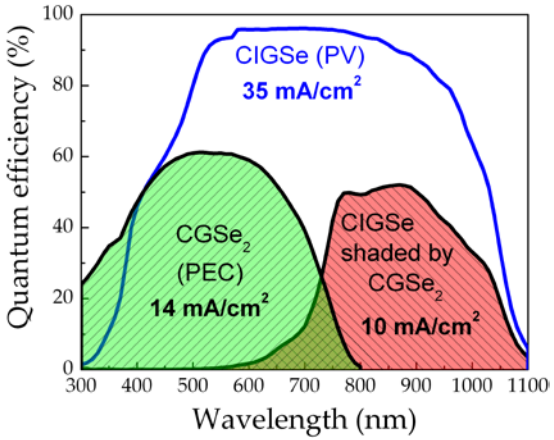
→ Co-planar: STH_{max}=15%, **H_2 @ $4.09/kg**

→ Tandem: STH_{max}=25%, **H_2 @ $2.51/kg**

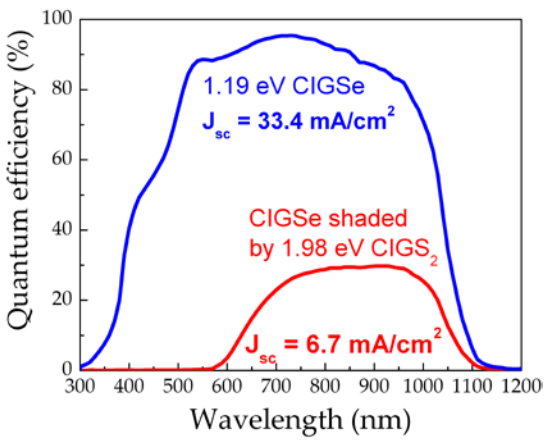
→ Tandem devices make better use of real estate and offer superior efficiency.

2. Paths toward chalcopyrite-based tandem PEC devices

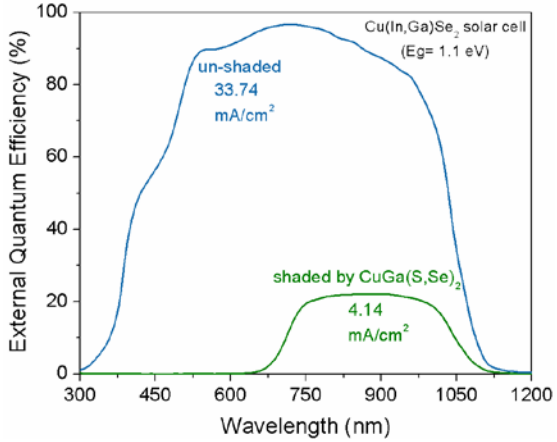
CIGSe PV and CGSe photocathode



CIGSe PV and $CIGS_2$ photocathode



CIGSe PV and CG(S,Se) photocathode



→ Optical balance demonstrate a good match between CIGSe PV driver and CGSe photocathode: J > 10 mA/cm².
→ Better photocathode energetics (higher photo-voltage) required to achieve unassisted water splitting.

Accomplishments - Response to reviewers' comments

"The fill factor and photocurrents of the chalcopyrites being made thus far will very likely make the top cell the limiting component in a tandem device."

→ The statement regarding the (wide bandgap) chalcopyrite materials made thus far being the limiting component of a tandem device is correct. Indeed, optical balance analyses revealed that the transmittance of some systems (e.g. $CuGa(S,Se)_2$) is not sufficient to ensure high photocurrent in a complete device. We have learned recently that copper plays an important role in optical transmission (the higher [Cu] the lower %T). Reducing [Cu] in wide bandgap chalcopyrites will be our priority in future work (see EMN PD162).

"It is not clear that the chalcopyrites demonstrated thus far provide enough photovoltage for successful demonstration."

→ The photovoltage produced by our wide bandgap chalcopyrites is indeed still too low to ensure spontaneous water splitting. Achieving high photovoltage with such systems has been a challenge faced also by the PV community for many years, and very few alternatives to CdS buffer have been found. The best surface treatment used so far in our project (In_2S_3) has led to V_{onset} of about 0.6 V_{RHE}. Buffers with tunable bandedges must be identified such that they can be matched with the energetics of the proposed wide bandgap chalcopyrites (see EMN PD162).

Collaborations

- US DoE PEC working group: white papers (metal oxides and chalcopyrites) and standardized test protocols,

- International Energy Agency/HIA/Annex 26: collaboration with international institutes and universities including the Institute for Solar fuels (HZB), Delft University, University of Warsaw (Poland).

Project-specific collaborations:

- Stanford, UNLV, LLNL and NREL: partners in this project (**ALL TASKS**),

- Y-TEC, Argentina (C. Dos Santo Claro): PEC testing, supported through the Fulbright scholarship (**TASK 1**),

- University of Louisville (M. Sunkara): photoluminescence on $CuGaSe_2$ materials (**TASK 1**),

- Jozef Stefan Institute-Slovenia (M. Mozetic): U.S./European project on sulfides ($CIGS_2$) (**TASK 1**),

- University of Los Andes-Colombia (S. Barney): reactive sputtering of ZnOS buffers (**TASK 2**),

- University of Bordeaux-France (A. Rougier): development of temperature-resistant TCOs as intermediate layers for multi-junction CIGSSe solar cells and PEC devices (**TASK 4**).

Remaining challenges / Lesson learned / Future Work

Task 1. PV-grade wide bandgap absorbers

Remaining challenges: the optical transmittance of most wide bandgap chalcopyrites too low to ensure high STH efficiency

Lesson learned: [Cu] has a profound impact on opto-electronic properties.

Future work: re-focus effort on best candidates for final tandem PEC structure: Cu-poor $CuGaSe_2$ and $CuGa_3Se_5$.

Task 2. Sub-surface energetics improvement (p/n junction)

Remaining challenges: best open circuit potential are 50mV lower than project final goal (900mV).

Lesson learned: Buffers with tunable energetics are key for maximum charge separation.

Future work: focus on most promising chalcopyrites and finalize sub-surface doping: Cd^{2+}, Na^{+} and K^{+}.

Task 3. Surface catalysis and corrosion resistance

Remaining challenges: new MoS_2 and TiO_2 ALD process successfully developed, yet durability limited to 350 hours.

Lesson learned: degradation mechanisms must be better understood such that issues can be adequately targeted.

Future work: focus on most promising chalcopyrites and finalize sub-surface doping: Cd^{2+}, Na^{+} and K^{+}.

Task 4. Device certification and efficiency benchmarking

Remaining challenges: create the first chalcopyrite-based tandem PEC device.

Lesson learned: moving to FTO substrates early in project was the right choice. Yet, the mechanical stack approach has its limits

Future work: Build the tandem device with best chances to meet project goal (most likely $CuGa_3Se_5$/GaAs) and perform outdoor testing.

*Any proposed future work is subject to change based on funding level

Project summary

Relevance	Create the first chalcopyrite-based HPE device with low-cost, PV-grade and durable thin film materials to meet DoE's efficiency and durability targets.
Approach	Focus on the development of wide bandgap chalcopyrite PEC materials, identify compatible buffers to improve energetics (p-n junction), evaluate Earth-abundant materials for both HER catalysis and corrosion protection and assess the STH efficiency of the complete HPE device.
Accomplishments	(1) Modelled and synthesized multiple wide bandgap chalcopyrites systems capable of generating over 10 mA/cm^2 with open circuit voltage up to 850 mV, (2) identified origins of low optical transmission and low photovoltage in some specific absorbers, (3) improved chalcopyrites durability with MoS_2/TiO_2 coating up to 350 hrs and (5) establish the non-ideal interface energetics between wide bandgap chalcopyrites and conventional CdS buffers.
Collaborations	Project-specific collaboration with U.S. and international teams to address barriers in each of the 4 technical tasks.
Proposed future work	(1) Focus on candidates with proven opto-electronic properties ($CuGaSe_2$, $CuGa_3Se_5$), (2) continue to improve sub-surface treatments (NaF) to meet the 900mV V_{oc} target, (3) continue development of conformal MoS_2 and TiO_2 coatings using ALD to meet 1,000-hour durability targets and (4) benchmark the STH efficiency of $CuGa_xSe_y$/GaAs tandems.