Novel Chalcopyrites for Advanced Photoelectrochemical Water-Splitting

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University of Hawaii
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P162

Project Overview

Novel Chalcopyrites for Advanced Photoelectrochemical Water-Splitting

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- Co-PIs: Clemens Heske (UNLV)
  Thomas Jaramillo (Stanford)

Award #	EE0008085
Start/End Date	10/01/2017 – 09/30/2020
Year 1 Funding* Year 2 Funding*	$280,172 $430,570

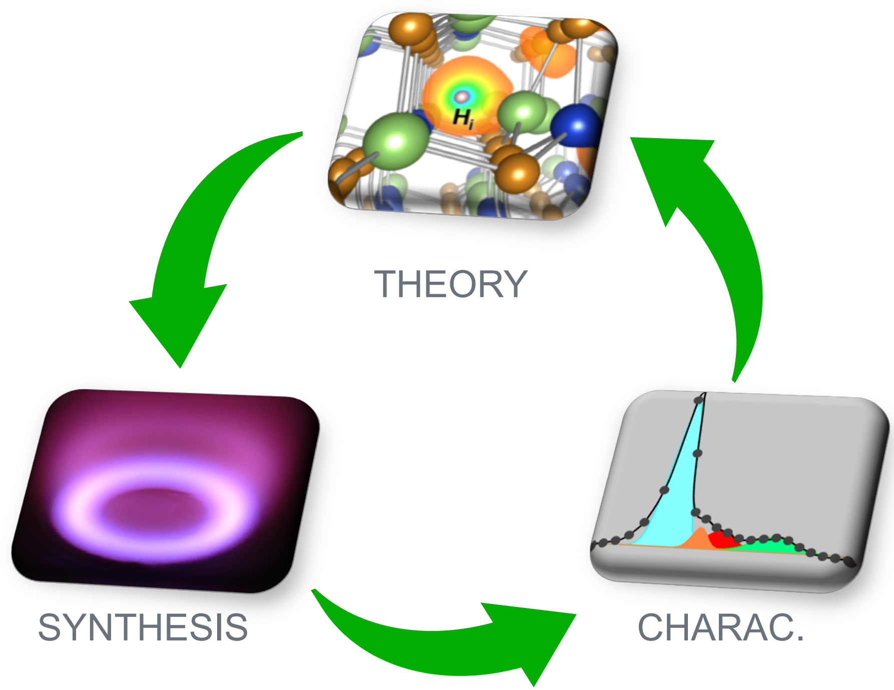
** this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Project Vision

We accelerate the development of new PEC water splitting materials through **integrated theory, synthesis and advanced characterization**.

Project Impact

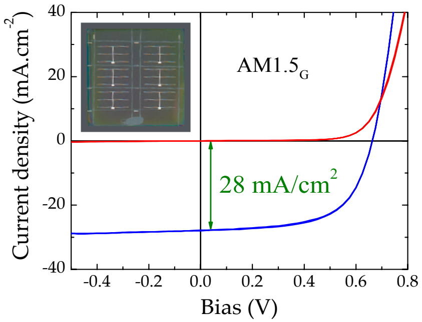
We develop innovative techniques to fabricate chalcopyrite-based water splitting devices that can meet DOE's cost target of $2/kg H_2.

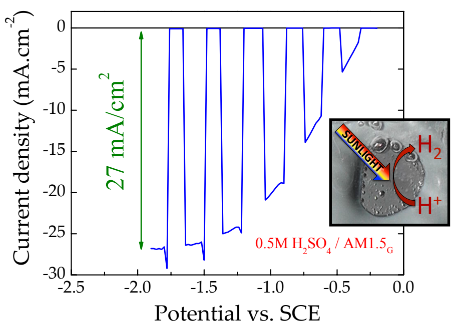


Approach – Technical background

The promise of chalcopyrite-based PEC systems

1. Chalcopyrites can generate high photocurrent density



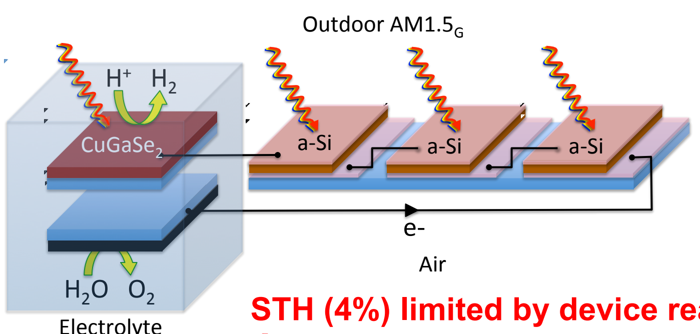


Solar cell vs. **Photoelectrode**

2. Low-cost processes available

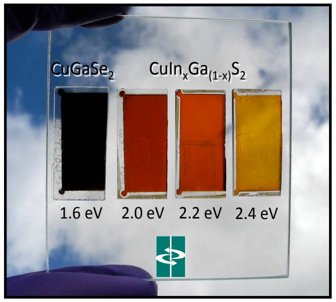
Chalcopyrite PV module cost: $100/m^2$

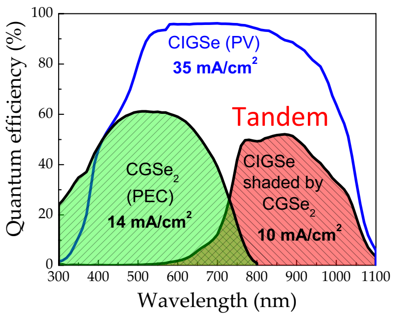
3. Demonstrated water splitting with co-planar devices



STH (4%) limited by device real-estate:
→ tandem integration required.

ap (E_G) tunable





Chalcopyrites compatible with tandem architecture

Take home message: chalcopyrites are excellent candidates for PEC water splitting. Novel wide bandgap (E_g) absorbers with improved optoelectronic properties needed for high efficiency **tandem cells**.

Approach – Summary

Project motivation

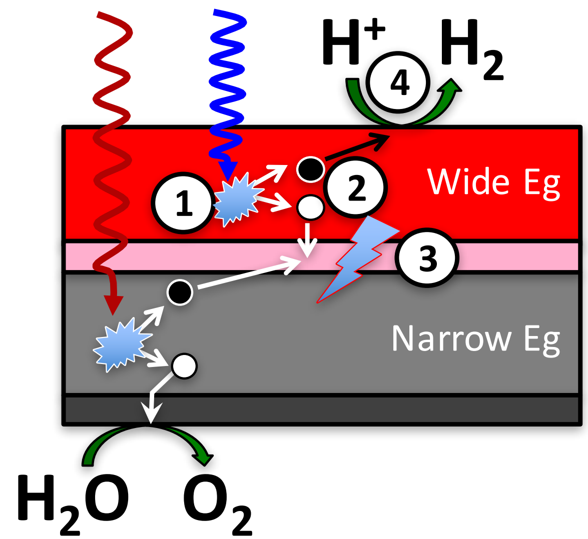
- UH/UNLV/Stanford/NREL/LLNL funded by EERE (2014) to identify promising chalcopyrites for water splitting H_2 production.
- New absorbers, interfaces and surface protection schemes were evaluated.
- Key barriers identified with these systems will be addressed in this new project.

Key Impact

Metric	State of the Art	Proposed
STH Efficiency	*4%*	*>10%*
Durability	*350 hrs*	*>1,000 hrs*

Technical barriers addressed in this project

1. **Synthesis and Manufacturing barrier (AJ)**: wide bandgap chalcopyrites are difficult to make with vacuum-based processes.
2. **Materials Efficiency barrier (AE)**: chalcopyrites interface energetics are not ideal for PEC water splitting.
3. **Integrated device configuration barrier (AG)**: there is no known method to make efficient chalcopyrite-based tandems.
4. **Materials Durability barrier (AF)**: coating ultra-thin protective layers on ‘rough’ polycrystalline chalcopyrites is challenging.



Approach – Partnerships / Scope

Task 1 - Modeling and Synthesis of Chalcopyrite Photocathodes

To address **Synthesis and Manufacturing (AJ)** and **Materials Efficiency (AE)** barriers, we model and develop new alloying and doping techniques to improve chalcopyrites efficiency.

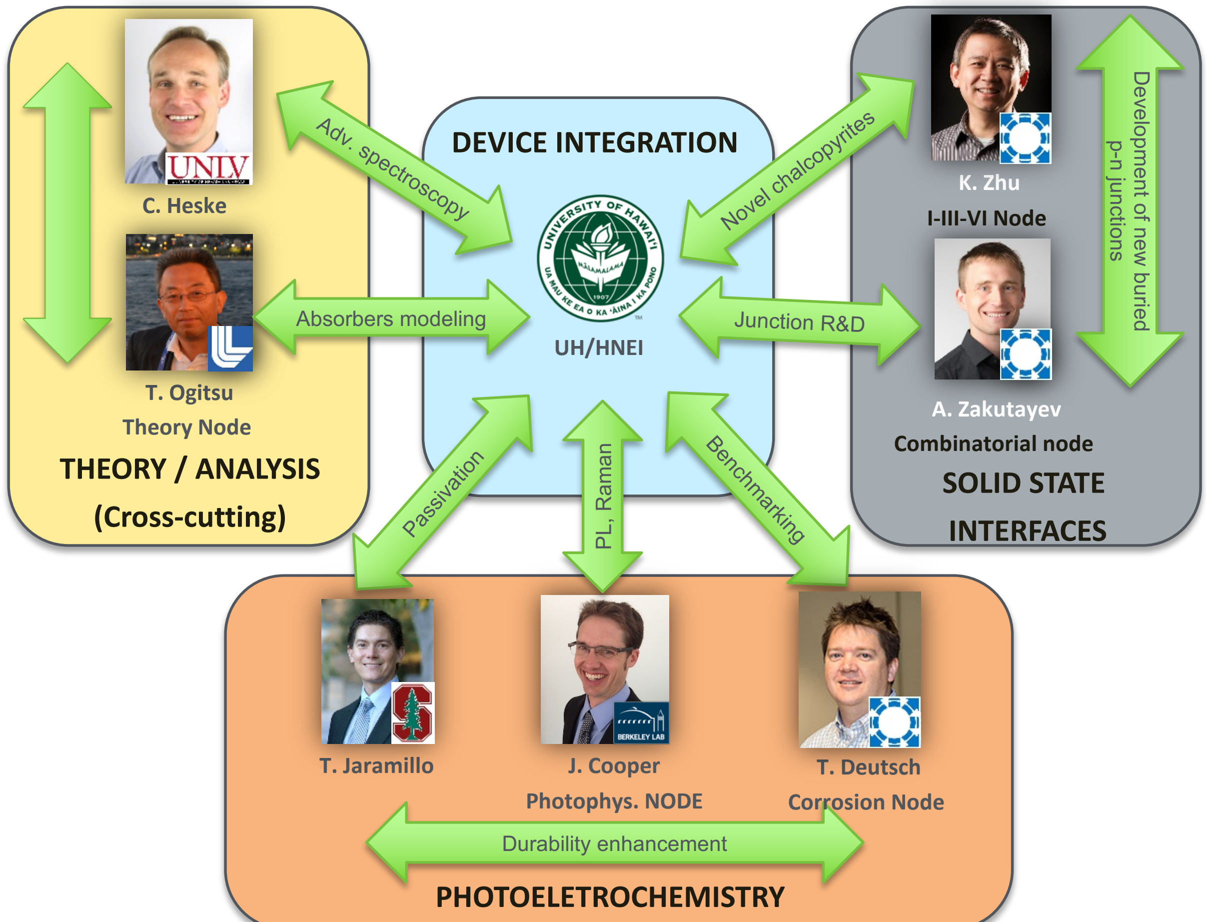
Task 2 - Interfaces Engineering for Enhanced Efficiency and Durability

To address **Materials Efficiency (AE)** and **Materials Durability (AF) barriers**, we develop new interfaces to tune chalcopyrite "energetics" and improve their stabilities during PEC water splitting.

Task 3 - Hybrid Photoelectrode Device Integration

To address **Integrated device configuration barrier (AG)**, we develop a unique "transfer" method to create semi-monolithic chalcopyrite-based tandem devices.

Integrated Theory, Analysis, Synthesis and Testing

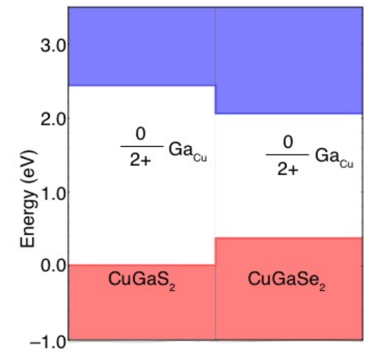


Take home message: our program is developing materials, methods and models addressing all fundamentals of photoelectrochemistry to accelerate the development of water splitting materials.

Approach – Innovation highlight #1

1) Novel chalcopyrites alloying using printing techniques

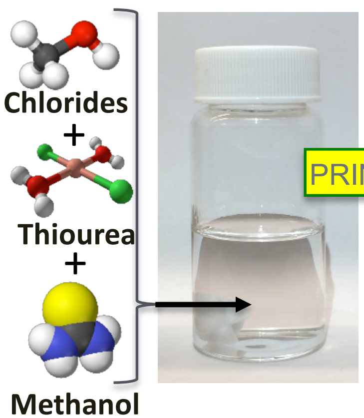
Synthesis and Manufacturing barrier (AJ): our models revealed that low photo-voltage in $CuInGaS_2$ originates from Ga_{Cu} defects. Alternative Ga-free wide bandgap Cu(In,**Al**)Se_2, Cu(In,**B**)Se_2 identified by theory. However, these materials are too challenging to make by co-evaporation.



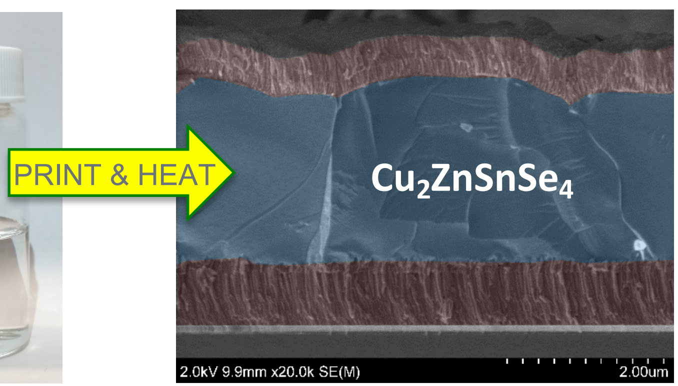
Proposed innovation: replace evaporation with "printing" technique to synthesize Cu(In,Al,B)Se_2 using molecular inks containing all necessary constituents (e.g. CuCl, $InCl_2$, $AlCl_3$/BCl_3).

→ **Proof of concept:** solution processed $Cu_2ZnSnSe_4$ solar cells (funding agency: ONR)

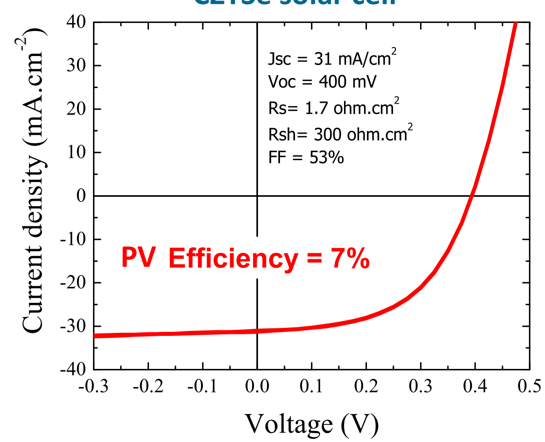
Molecular ink (stable over 12 months)



Cross-section of a printed CZTSe solar absorber



Current vs. voltage of a printed CZTSe solar cell



→ **This approach lowers material cost and provides a viable path to meet DOE's target of $60/m².**

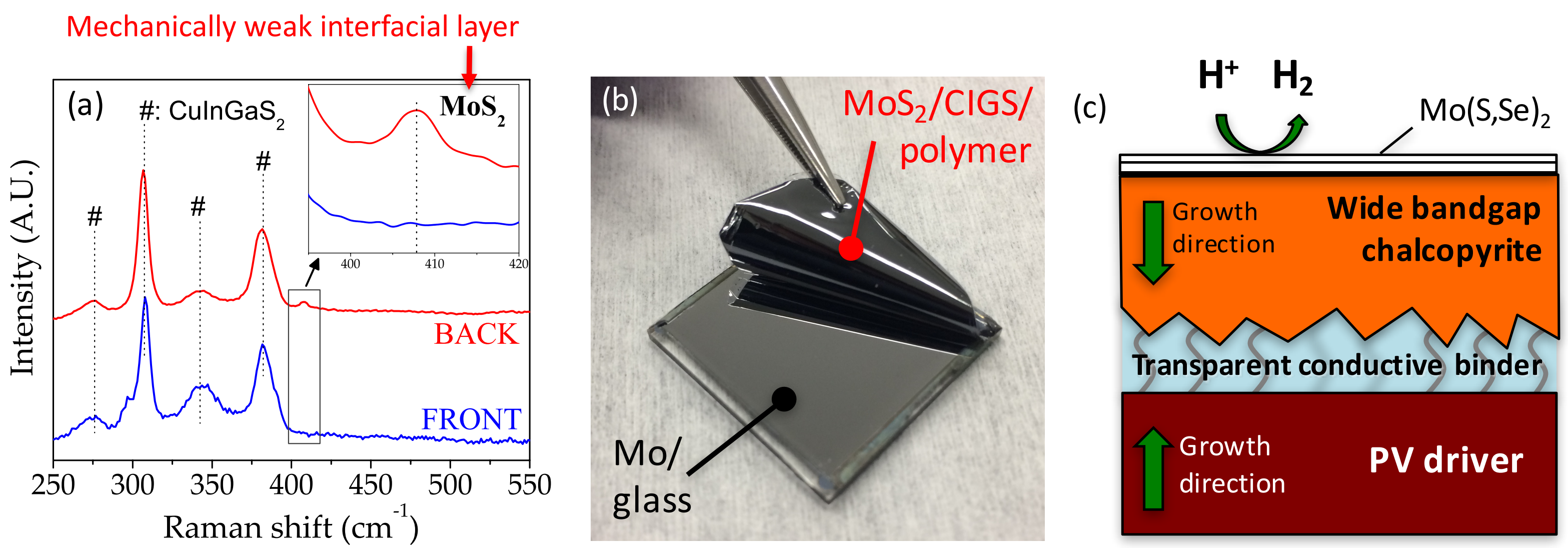
Approach – Innovation highlight #2

2) Innovative tandem device integration schemes

Integrated Device Configurations barrier (AG): materials compatibility (e.g. temperature) is the biggest challenge in multi-junction device integration. With current chalcopyrite PV technology, it is impossible to fabricate high efficiency monolithic multi-junction devices by directly depositing a wide-bandgap photocathode onto a narrow bandgap PV driver.

Proposed innovation: exfoliation of finished PEC cells and bonding onto fully processed PV drivers to create a semi-monolithic tandem device.

→ **Proof of concept:** 1 μm thick CIGS layer successfully "peeled" from substrate using polymer

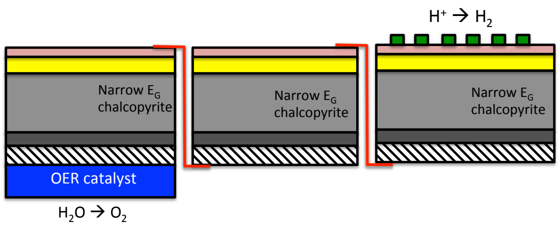


→ **Enable integration of chalcopyrites into low-cost tandem water splitting devices**

Relevance & Impact – Techno-economics of chalcopyrite-based PEC systems

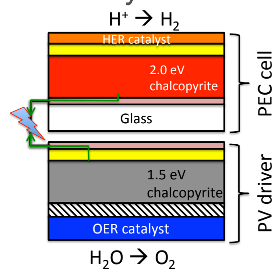
Current technology

Co-planar architecture



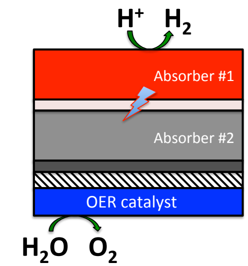
Intermediate goal

Stacked hybrid device

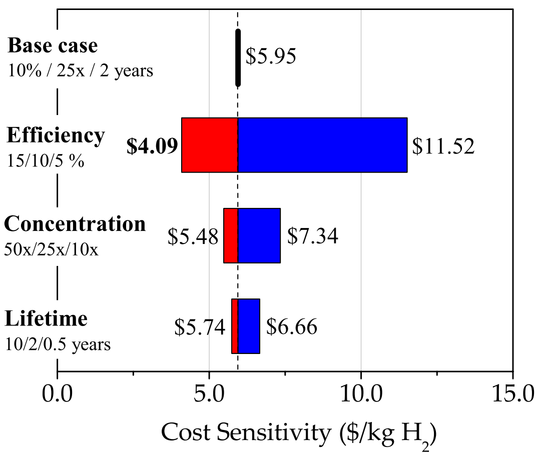


Ultimate goal

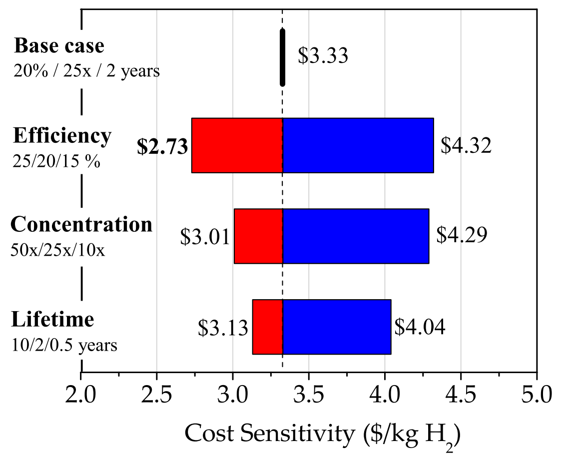
(Semi) Monolithic hybrid device



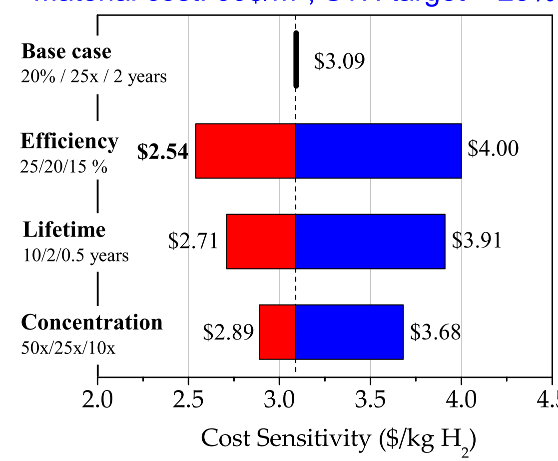
Material cost: 100$/m², STH 5-10%



Material cost: 200$/m², STH target > 15%



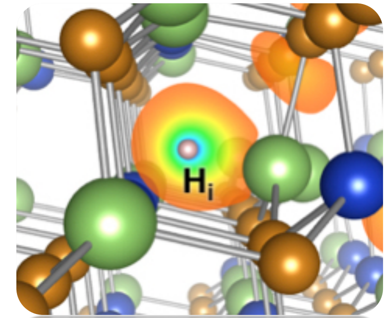
Material cost: 60$/m², STH target = 25%

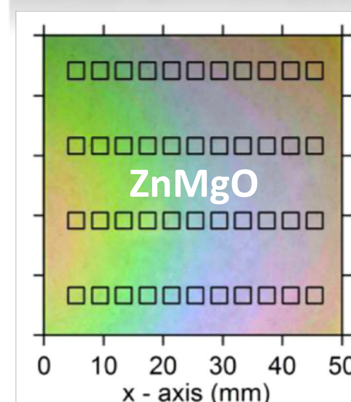


Note: $1.95 $/kg H_2 achievable with both 25% STH and 10-year lifetime

Take home message: the wide E_g chalcopyrites developed under this program are compatible with the tandem approach and can meet the efficiency requirements for PEC H_2 production at a cost < 2$/kg H_2.

Relevance & Impact – Leveraging EMN capability nodes





- **Computational Materials Diagnostics and Optimization (T. Ogitsu).**
  - → **Role:** modeling of materials optoelectronic properties (Eg vs composition, defects chemistry…etc).
  - → **Benefit to this program:** defines synthesis conditions and thermodynamic stability of novel chalcopyrites.
  - → **Broader impact for HydroGEN:** LLNL models can be used to predict bulk/interfaces of future materials for PEC water splitting and other H_2 production pathways.

- **I-III-VI Compound Semiconductors for Water-Splitting (K. Zhu)**
  - → **Role:** synthesis of high-purity PEC and PV chalcopyrite materials ($CuGa_3Se_5$ and $CuInGaSe_2$).
  - → **Benefit to this program:** "reference" vacuum-based chalcopyrites to evaluate new strategies (Na doping).
  - → **Broader impact for HydroGEN:** materials developed could be used for other H_2 production pathways (i.e. PV/electrolysis).

- **High-Throughput Thin Film Combinatorial Capabilities (A. Zakutayev)**
  - → **Role:** screening of n-type buffer materials (e.g. graded MgZnO: 40 ≠ compositions on 1 CIGS sample).
  - → **Benefit to this program:** accelerates material discovery for improved interface energetics (buried junction).
  - → **Broader impact for HydroGEN:** comprehensive library of optical, electronic and microstructural properties of new multi-compound materials made available to the scientific community via the HydroGEN Datahub.

- **Corrosion Analysis of Materials (T. Deutsch)**
  - → **Role:** supports development of surface passivation against photo-corrosion.
  - → **Benefit to this program:** provide access to unique instrumentation (e.g. ICPMS).
  - → **Broader impact for HydroGEN:** assessment of durability test protocols (e.g. fixed current vs. fixed potential).

- **Photophysical Characterization of PEC Materials and Assemblies (J. Cooper)**
  - → **Role:** supports development of novel wide-bandgap absorbers.
  - → **Benefit to this program:** provide new insights into charge carrier dynamics at Solid/Solid and Solid/Liquid interfaces.
  - → **Broader impact for HydroGEN:** identify corrosion mechanisms and potential pitfalls of protection strategies.

Accomplishments – Milestones and Go/No-Go criteria for budget period 1

→ All milestones and Go/NoGo decision points met for Y1

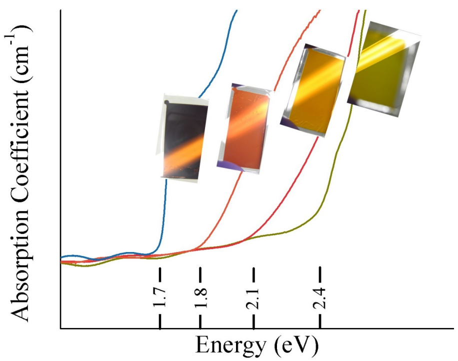
Milestone ID	Task #	Subtask Title	Description	Significance to Project	Anticipated Quarter	Status
Milestone #1	1	1.1-Defects passivation	A printed polycrystalline chalcopyrite thin film material made of grains at least 500 nm across and with impurity concentration less than 15%.	Demonstrates viability of the "printing" technique to fabricate chalcopyrite materials.	Q1	**100%**
Milestone #2	3	3.1-Conductive Polymer	Produce a nanowire-based composite demonstrating a sheet resistance below 200 Ω/sq and transparency > 70%.	Transparent conductive binder required to create semi-monolithic tandem device.	Q2	**100%**
Milestone #3	2	2.1-Interface: durability	Stabilized chalcopyrite photocathode that retains 90% of its copper content after 100 hrs of continuous operation to achieve an initial photocurrent density of 8 mA/cm^2 under simulated AM1.5G illumination.	This study will provide insights into the degradation mechanism of chalcopyrites photoelectrodes.	Q3	**100%**
Go/No-Go #1/2	**1**	**1.2-Printed Chalcopyrites**	**A solution-processed $CuIn(S,Se)_2$-based PV device with a short-circuit photocurrent density corresponding to at least 70% of the absorber's theoretical limit and free-electron losses (Eg – Voc.q) less than 600 mV.**	**Further validates the feasibility of the proposed "printing" technique. Ternary $CuInSe_2$ serves as baseline materials for quaternary $CuInBSe_2$ and $CuInAlSe_2$.**	Q4	**100%**
Go/No-Go #2/2	**2**	**2.1-Interface: durability**	**Demonstrate 500 hrs stability in a photoelectrode operating under simulated AM1.5G illumination at a fixed potential that achieves an initial photocurrent of 8mA/cm2 and does not drop below 5mA/cm2 over the duration of the test.**	**Validates the proposed protection strategy (e.g. TiO_2/MoS_2) for durable PEC H_2 production**	Q4	**100%**

Accomplishments – Task 1: Modeling and Synthesis of Chalcopyrite Photocathodes

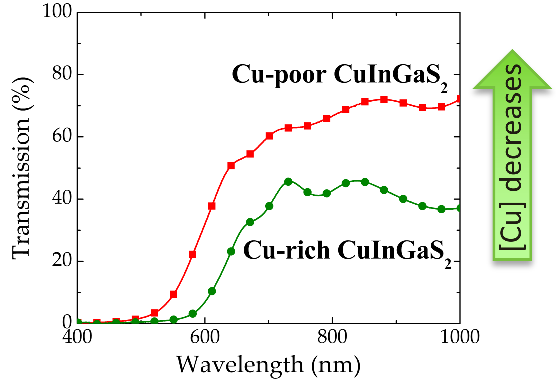
Material barrier (AJ)

1.1) Theoretical modeling (LLNL theory node)

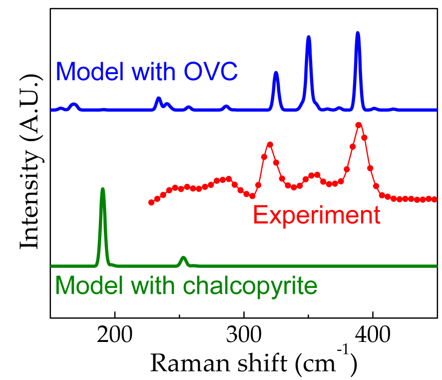
Bandgap tunable $Cu(In,Ga)(S,Se)_2$



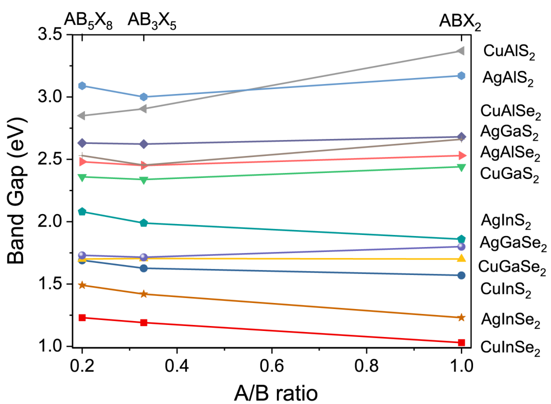
The lower the [Cu], the higher the optical transmission



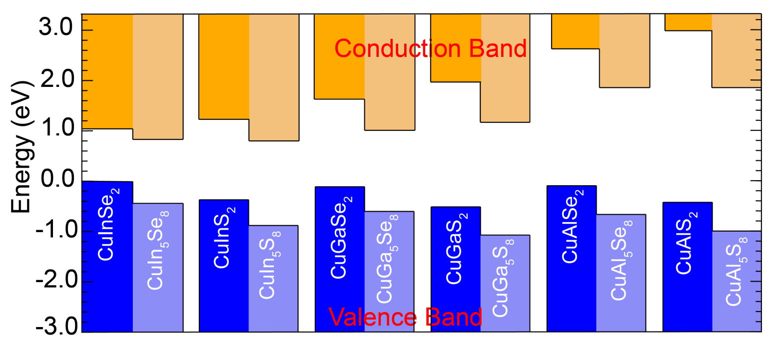
Theory identified Cu-poor films as "ordered vacancy compounds" (OVC)



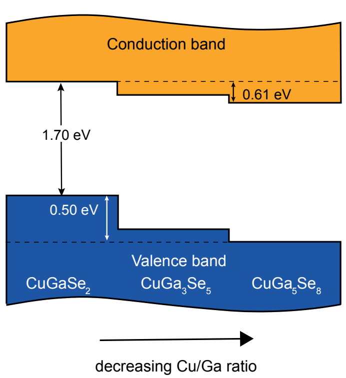
Bandgap modeling of OVC candidates



Modeling of energetics in chalcopyrites vs OVCs



$CuGaSe_2$ (HNEI baseline) vs. $CuGa_3Se_5$ (NREL baseline)



Broader impact to community: modeling provides critical information on absorber's thermodynamic stability, defect chemistry and help identify promising new material candidates.

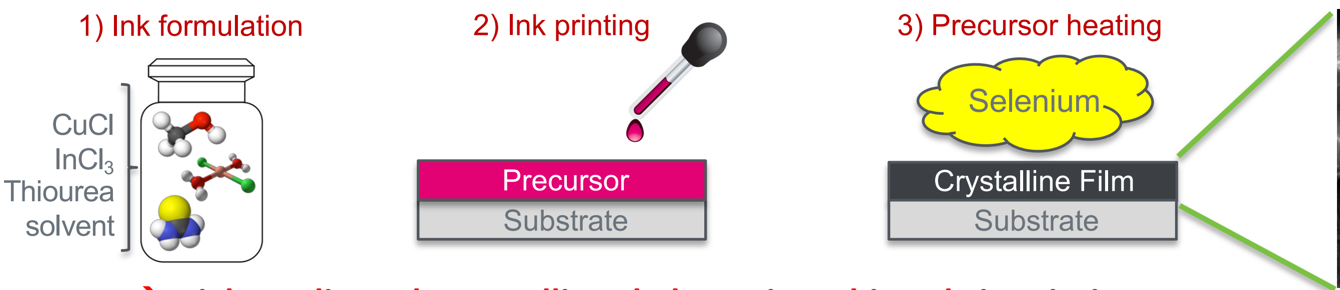
Accomplishments – Task 1: Modeling and Synthesis of Chalcopyrite Photocathodes

Material barrier (AJ)

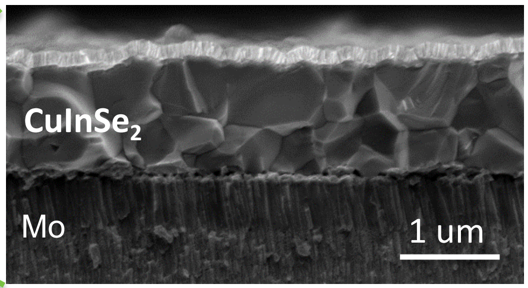
1.2) Chalcopyrites "printing" using molecular inks

Milestone #1: 100%

a. Process development (UH)

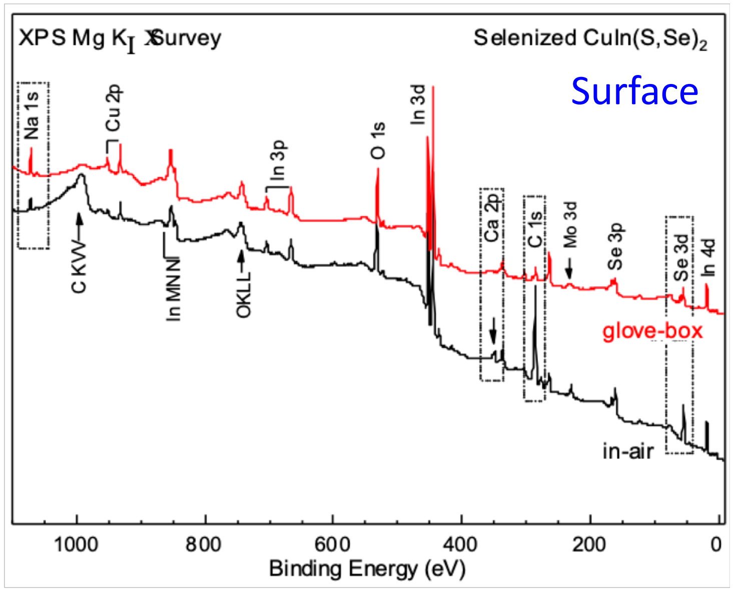


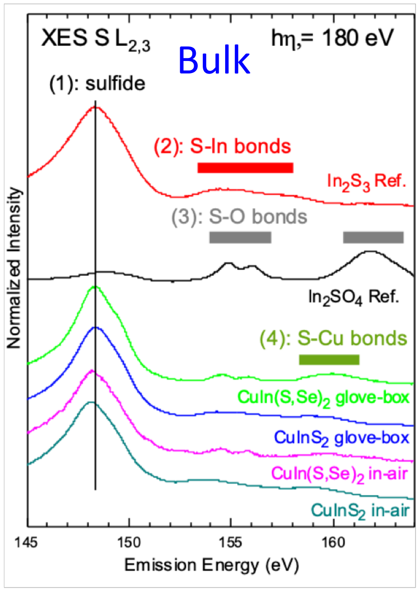
Cross-section of printed chalcopyrite absorber



→ **High-quality poly-crystalline chalcopyrite achieved via printing**

b. Spectroscopic analysis of printed $CuInSe_2$ (UNLV/ALS)





Case study: effect of ink formulation conditions (in-air vs. in glovebox) on absorber chemistry (doping vs. contamination)

→ (XPS) Formulating ink in glovebox significantly reduces carbon contamination,

→ (XPS) Higher sodium (beneficial for chalcopyrites) signal observed when ink formulated in air,

→ (XPS) Difference in Se environment: SeO_2 or $NaSe_xO_y$ (glovebox) vs. pure Se (air),

→ (XES) Regardless of ink preparation conditions, no significant presence of S-O bonds in absorber bulk.

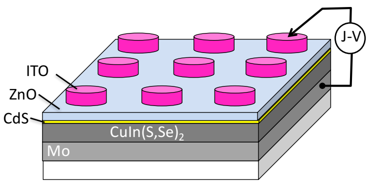
Accomplishments – Task 1: Modeling and Synthesis of Chalcopyrite Photocathodes

Material barrier (AJ)

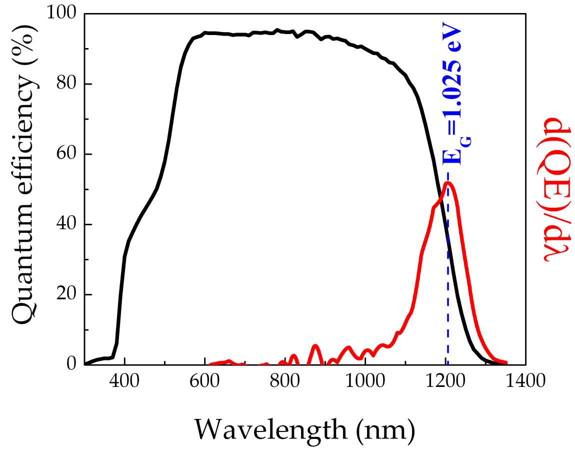
1.2) Chalcopyrites "printing" using molecular inks

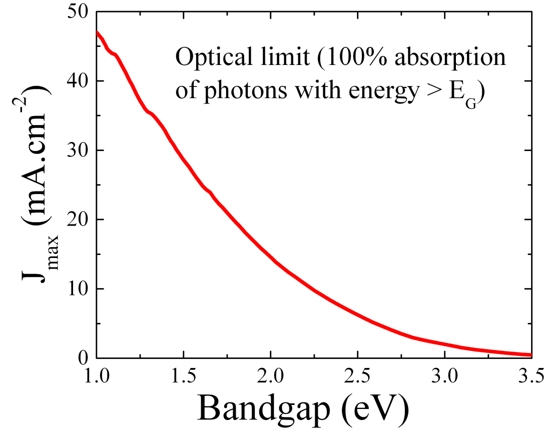
GNG 1/2: 100%

c. Absorber photo-conversion efficiency validation (UH-NREL CIGSe node)



Printed $CuIn(S,Se)_2$ solar cells





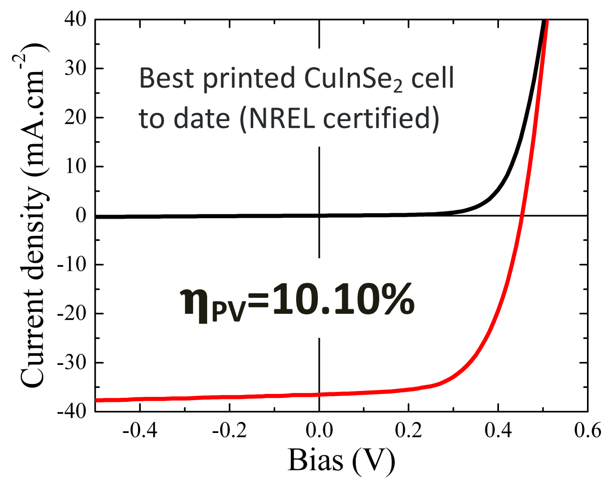
GNG requirements for a 1.025 eV bandgap chalcopyrite:

- Jsc = 70% of Jsc max (46.2 mA/cm2) = 32.34 mA/cm2

- Voc = 1.025-0.6= 0.425V

Solid-state data measured at NREL on HNEI's printed $CuInSe_2$

Device ID		Eff (%)	FF(%)	Jsc (mA/cm2)	Voc (mV)	% Jsc achieved	% Voc achieved	PASS GNG
H1810-03	2	8.33	47.37	34.02	517	>100%	>100%	Y
H1810-03	3	7.57	45.10	33.68	498	>100%	>100%	Y
H1810-03	1	7.52	45.64	33.12	498	>100%	>100%	Y
H1810-03	3	5.33	35.25	32.72	462	>100%	>100%	Y
H1810-03	3	5.82	36.91	32.57	484	>100%	>100%	Y
H1810-03	4	6.27	44.73	32.95	425	>100%	>100%	Y
H1810-03	4	6.76	44.35	32.03	476	99%	>100%	N
H1810-03	2	5.83	38.96	32.07	467	99%	>100%	N
H1810-03	1	7.29	46.32	32.20	489	99%	>100%	N
H1810-03	3	7.54	52.22	32.14	449	99%	>100%	N
H1810-03	4	7.06	51.68	30.90	442	96%	>100%	N
H1810-01	3	8.03	65.72	27.75	440	86%	>100%	N
H1810-01	3	7.41	61.77	27.54	436	85%	>100%	N
H1810-01	4	7.31	59.01	28.57	434	88%	>100%	N
H1810-01	2	7.20	60.85	27.61	429	85%	>100%	N
H1810-01	4	7.37	60.30	29.24	418	90%	98%	N

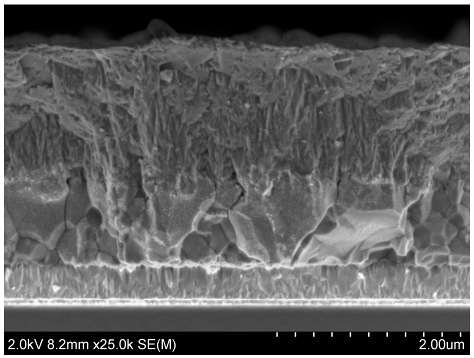


Go-No-Go Achieved: six solid-state devices made of printed $CuInSe_2$ passed the Jsc and Voc requirements for GNG Y1

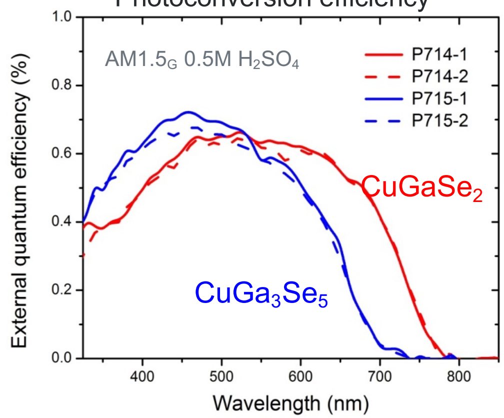
2.1) Surface treatment of $CuGa_3Se_5$ photocathodes (NREL CIGSe node)

a. PEC characteristics of $CuGa_3Se_5$ OVC absorbers (AMR 2017)

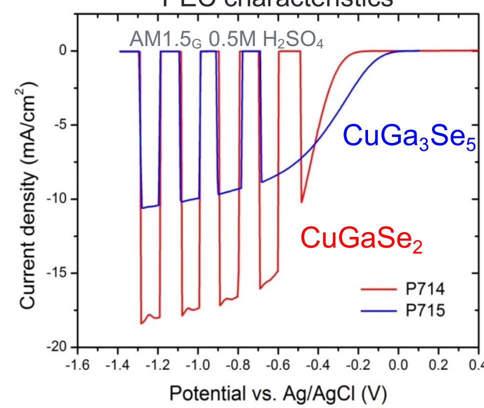
Cross section of vacuum-processed $CuGa_3Se_5$



Photoconversion efficiency

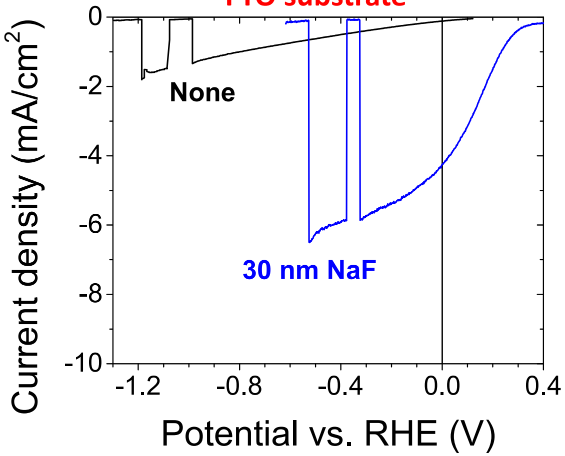


PEC characteristics

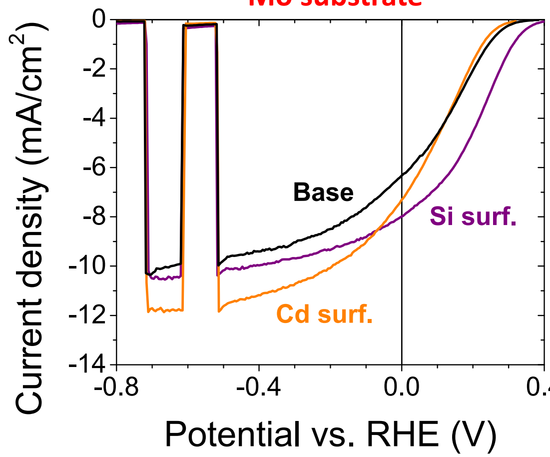


b. Surface passivation with Na, Cd or Si

FTO substrate



Mo substrate



Surface treatments tested so far:

- NaF: 30 nm (evaporated)
- Si: 6 nm (evaporated)
- Cd2+: partial electrolyte (PE) treatment

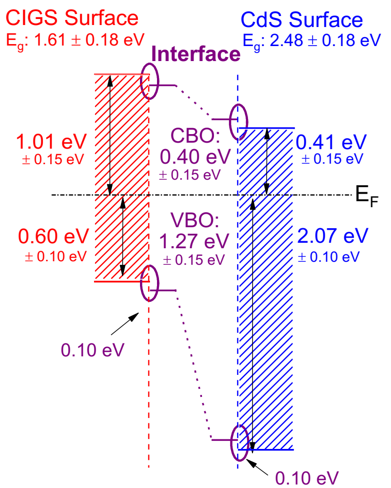
→ Significant improvements in photoconversion (Na, Cd) and/or charge separation (Na, Si) achieved via surface treatment.

Accomplishments – Task 2: Interfaces for Enhanced Efficiency & Durability

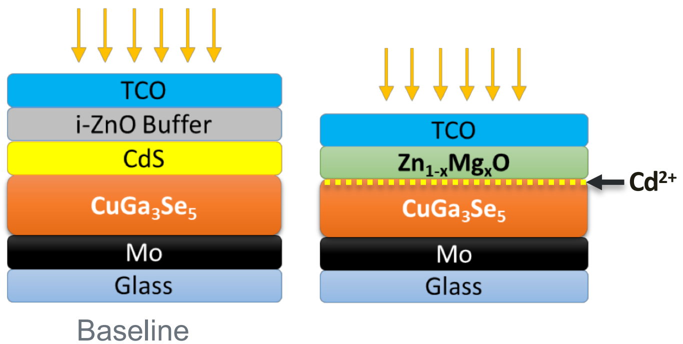
Efficiency barrier (AE)

2.2) Combinatorial development of tunable "buffers" (NREL Combinatorial Node)

Non-ideal energetics at wide-E_G chalcopyrite/CdS interface (non-zero CBO) evidenced by spectroscopy (UNLV)

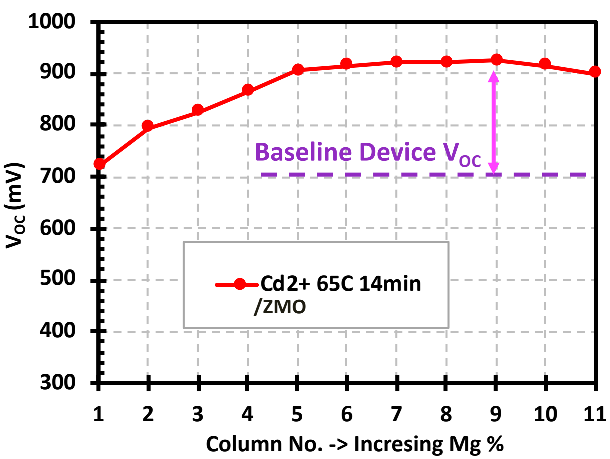


- Cd^{2+} solution treatment of $CuGa_3Se_5$ surface
- CdS layer for $CuGa_3Se_5$ PV device substituted with bandgap tunable $Zn_{1-x}Mg_xO$
- Combinatorial sputtering of $Zn_{1-x}Mg_xO$ for optimizing conduction band offset

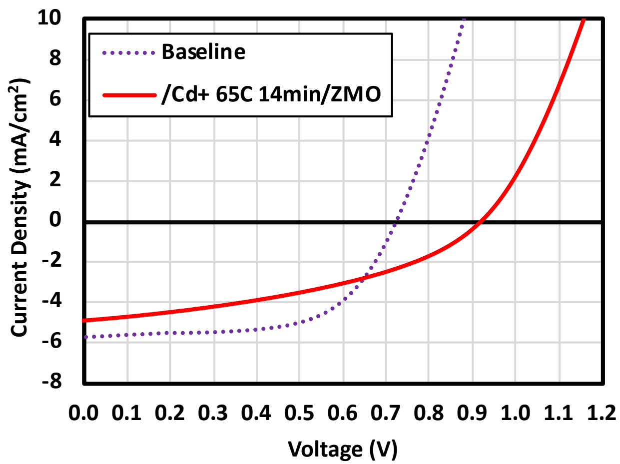


Increasing Mg Conc.

44 solid-state cells with graded buffer integrated over a $CuGa_3Se_5$ sample with uniform composition (25mm x 25mm)



7.0% ← Mg Composition → 15.0%



- **V_{OC} up to 925 mV** with Cd^{2+} PE treatment of the absorber and $Zn_{1-x}Mg_xO$ buffer layer.

- With $Cd^{2+}/Zn_{1-x}Mg_xO$ devices exhibit higher V_{OC} but slightly reduced current compared to baseline (CdS-treated) device.

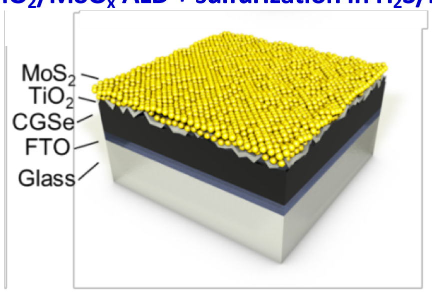
Accomplishments – Task 2: Interfaces for Enhanced Efficiency & Durability

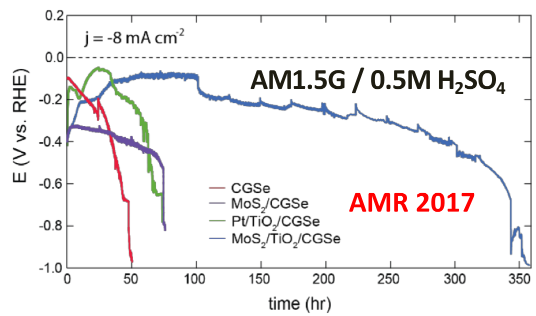
Durability barrier (AF)

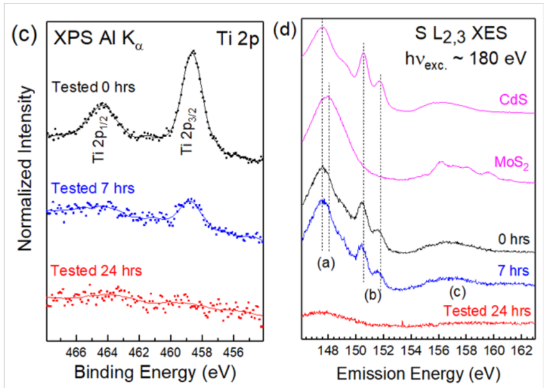
2.3) Protection against photo-corrosion (Stanford-UNLV-NREL)

a. Protecting $CuGaSe_2$ with TiO_2/MoS_2

TiO_2/MoO_x ALD + sulfurization in H_2S/H_2







Molybdenum Disulfide Catalytic Coatings via Atomic Layer Deposition for Solar Hydrogen Production from Copper Gallium Diselenide Photocathodes, T. R. Hellstern, D. W. Palm, J. Carter, A. D DeAngelis, K. Horsley, L. Weinhardt, W. Yang, M. Blum, N. Gaillard, C. Heske, and T. F Jaramillo, **ACS Appl. Energy Mater. 2** (2), 1060 (2019).

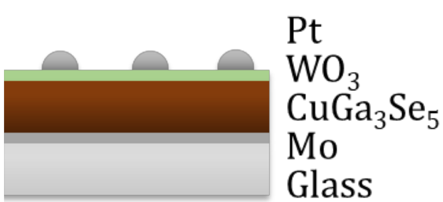
$CuGaSe_2$ durability enhanced with MoS_2/TiO_2 from 50 to 350 hrs

Post durability testing XPS/XES analyses of $MoS_2/TiO_2/CuGaSe_2$

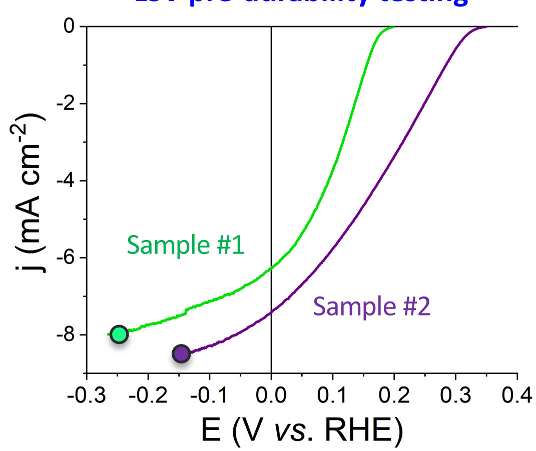
b. Protecting $CuGa_3Se_5$ with WO_3/Pt

GNG 2/2: 100%

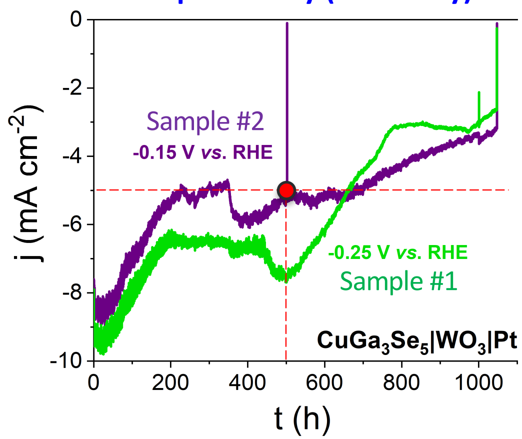
1) 600 cycles of WO_3 ALD (approx. 3 nm)
2) '1 nm' of Pt nanoparticulate catalyst via e-beam evaporation



LSV pre-durability testing



Chronoamperometry (durability) testing



$J>5$ mA/cm^2 after 500 hrs of testing

Broader impact to community: strategies identified to protect chalcopyrites from photo-corrosion applicable to other material classes. Provides experimental starting points to '2B benchmarking' team to establish future durability protocols.

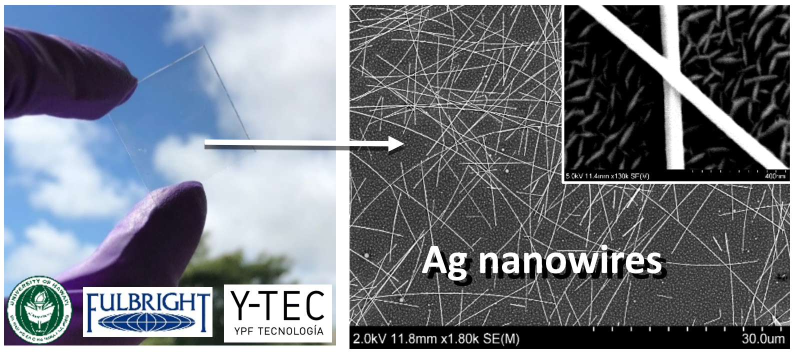
Accomplishments – Task 3: Hybrid Photoelectrode Device Integration

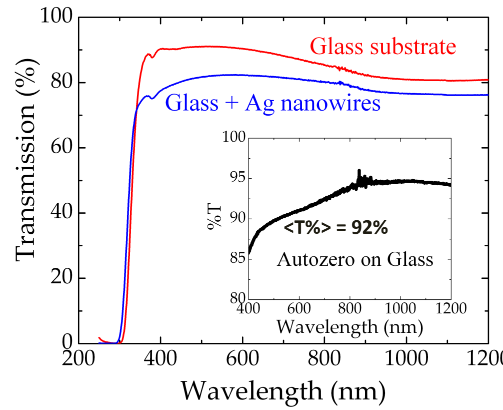
Device barrier (AG)

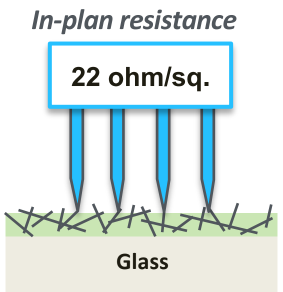
3.1) Transparent conductive (TC) binder for semi-monolithic tandem (UH)

a. AgNW/polyester resin TC binder (AMR2018)

Milestone #2: 100%

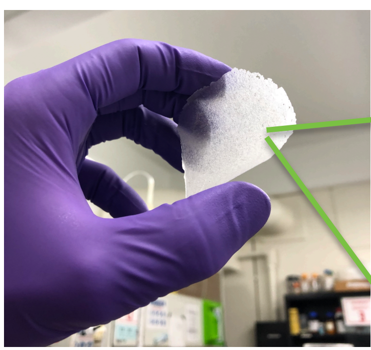




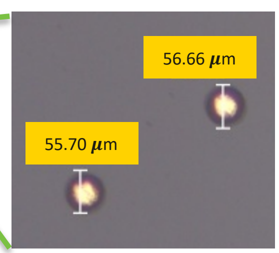


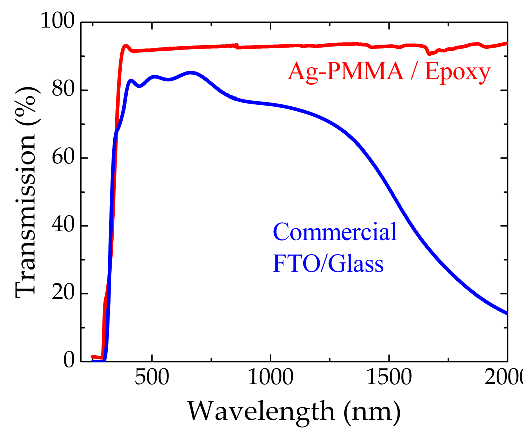
As conductive & transparent as commercial FTO.

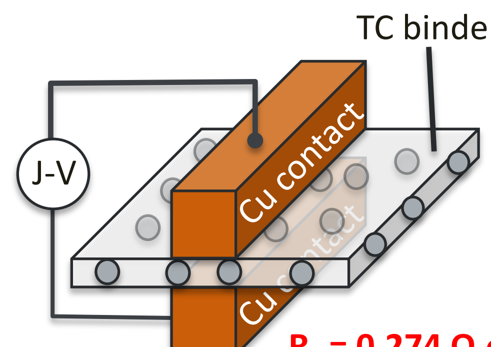
b. Ag-coated PMMA beads/epoxy resin TC binder



Free-standing 20 μm thick TC binder (1 wt.% sphere to epoxy)







R_S = 0.274 Ω.cm^2
(~ R_S in solar cells)

Broader impact to community: provides a technique to integrate dissimilar material systems as well as a viable path towards a device that can meet DOE's cost target of \$2/kg H_2 or less.

Collaboration – Interactions with EMN project node experts to date

→ Active interactions between academic teams and EMN nodes with regular communication regarding samples exchange and collected data.

Task #	Academia-Nodes Interactions	Specific activity	Goal	Impact to Project	Barrier
1	UH - LLNL theory Node	**Data exchange** (XRD spectra, optical data, low temperature conductivity measurements).	Model the effect of [Cu] on OVCs optical transmission.	This work provides guidance for novel chalcopyrite candidates selection.	AE
1	UH - NREL I-III-VI Node	**Sample exchange** ($CuInSe_2$ solid state devices).	Measure photo-conversion properties of printed $CuInSe_2$	Validates the printing method to be used to create quaternary chalcopyrites (Y1 GNG #1/2).	AE, AJ
1	UH - NREL Corrosion Node	**Sample exchange** (1.8eV $GaInP_2$ preference photodiode).	Calibrate UH solar simulator for wide E_G chalcopyrite PEC testing	In line with benchmarking efforts, this ensure proper characterization of the proposed chalcopyrite systems.	AE
2	Stanford - NREL I-III-VI Node	**Sample exchange** ($CuGa_3Se_5$).	Test WO_3 ALD nano-coating for protection against photocorrosion.	Extend chalcopyrite photocathodes durability beyond 500 hrs (GNG #2/2).	AF
2	UH - LBNL Photophys. Node	**Sample exchange** (Cu-poor $CuInGaS_2$).	Characterize electrical defects with photoluminescence	Identify chemical/structural defects responsible for the low photovoltage measured in some chalcopyrites.	AF
2	NREL I-III-VI Node - NREL Combinatorial Node	**Sample exchange** ($CuGa_3Se_5$).	Deposition of composition graded MgZnO buffer (optimization)	Increase the photovoltage produced by chalcopyrite photocathodes (700 to 925 mV as of March 2019).	AE

Collaboration – Collaboration with cross-cutting ‘2b’ benchmarking team

- N. Gaillard, C. Heske, T. Jaramillo, T. Ogitsu and T. Deutsch have been participating in the development of PEC standards since 2008.
- Inputs for the next round of methods and protocols shared with PEC “2b benchmarking” team through the provided questionnaires.
- Participation to HydroGEN AWSM Benchmarking Meeting (organized in conjunction to ECS conference), Seattle, May 13th, 2018.
- Participation to “Advanced Water Splitting Technology Pathways Benchmarking & Protocols Workshop” held in Phoenix on October 24th & 25th 2018.

REVIEW

This section of Journal of Materials Research is reserved for papers that are reviews of literature in a given area.

Accelerating materials development for photoelectrochemical hydrogen production: Standards for methods, definitions, and reporting protocols

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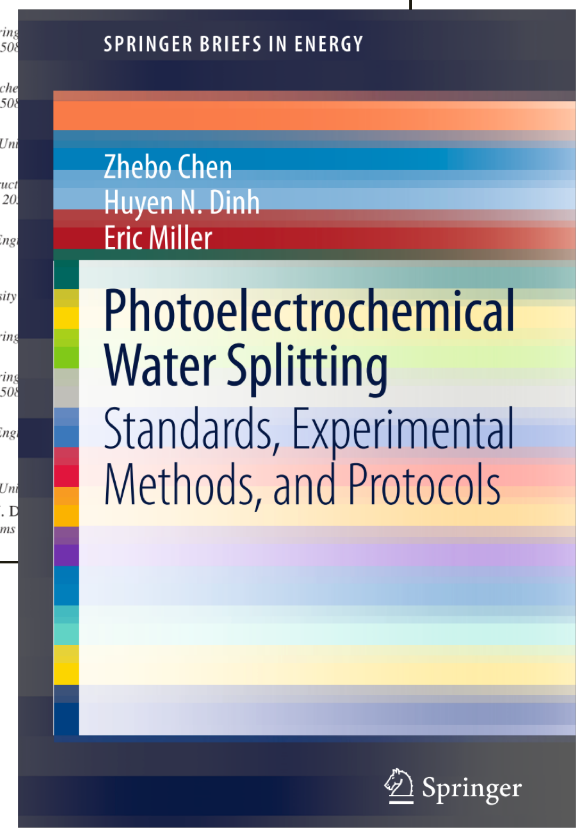


Planned Future Work(#)

Estimated budget: ~$430K

Task 1 - Modeling and Synthesis of Chalcopyrite Photocathodes

Sub-task 1.1 – defects passivation (known Ga-based materials): validate Theory Node predictions on alkali passivation with standard vacuum-processed wide bandgap chalcopyrite.
Sub-task 1.2 – printed chalcopyrites (new systems): synthesize Cu(In,Al)Se_2 and/or Cu(In,B)Se_2, report on their optical and PEC properties.

→ Intended outcomes: wide E_g chalcopyrites with photocurrent density greater than **80% of their theoretical limit.**
→ **IMPACT: have materials capable of 20% STH efficiency or higher.**

Task 2 - Interfaces Engineering for Enhanced Efficiency and Durability

Sub-task 2.1 – interface energetics: establish MgZnO composition with best energetics for $CuGa_3Se_5$.
Sub-task 2.2 – interface durability: further improve the deposition of WO_3 protective layers.

→ Intended outcomes: wide E_g chalcopyrites with **photo-voltage over 1V** capable of water splitting for **750 hrs**.
→ **IMPACT: establish a path for un-assisted and durable PEC water splitting.**

Task 3 - Hybrid Photoelectrode Device Integration

Sub-task 3.1 – conductive polymers: further develop the concept of transparent/conductive (TC) binder.
Sub-task 3.2 – semi-monolithic HPE device: test sub-components of semi-monolithic device, using TC binder as top contact of PV drivers or back contact of PEC electrodes.

→ Intended outcomes: **proof of concept of semi-monolithic device** with functional sub-components.
→ **IMPACT: develop an efficient chalcopyrite-based tandem device with potential to meet DOE's $2/kg H_2 cost target.**

#: Any proposed future work is subject to change based on funding levels

Y2 Milestones and GNG table

Milestone Summary Table-Y2							
Recipient Name:	University of Hawaii / Hawaii Natural Energy Institute						
Project Title:	Novel Chalcopyrites for Advanced Photoelectrochemical Water-Splitting						
Task #	Task or Subtask	Milestone Type	Milestone Number*	Milestone Description (Go/No-Go Decision Criteria)	Milestone Verification Process (What, How, Who, Where)	Anticipated Date	Anticipated Quarter
2.1	Interface: energetics	Milestone	2.1-1	Determine the factors contributing to increased open circuit voltage of at least 900 mV with a MgZnO:Ga-coated and surface-treated wide bandgap chalcopyrite absorbers under simulated AM1.5G illumination, with a stretch goal of demonstrating over 200 mV improvement over the baseline by the end of year 2.	Voc will be recorded at NREL via J-V analysis and reported in quarterly report	18	Q6
2.2	Synthesis of chalcopyrite	Milestone	1.2-2	A printed polycrystalline $Cu(In,Al,B)Se_2$ thin film material losing less that 50% of photocurrent and photovoltage after exfoliation/transfer.	Current density and bandgap will be measured at HNEI via quantum efficiency analysis and reported in quarterly report	21	Q7
2.2	Interface: durability	Milestone	2.2-2	Retain 90% of metal content in a thin, transparent protective coating over the course of 100 hrs of electrocatalytic HER testing at -10 mA/cm^2.	To be measured at Stanford via ICPMS	24	Q8
2.2	Interface: durability	Go/No-Go	GNG#1	Using a chalcopyrite photocathode, sustain hydrogen production (initially exceeding -8 mA/cm^2) at 90% of initial photocurrent density for 200 hours.	To be measured at Stanford via chronoamperometry or potentiometry.	27	Q9
3.2	HPE integration	Go/No-Go	GNG#2	Create a semi-monolithic tandem device exhibiting a Voc that is at least 50% of the sum of the Voc's of the individual tandems.	To be measured at HNEI or NREL via current-voltage analysis	30	Q9

Project Summary

<u>High-level project goal:</u> Strengthen **theory, synthesis and advanced characterization "feedback loop"** to accelerate development of chalcopyrites for efficient PEC H_2 production.

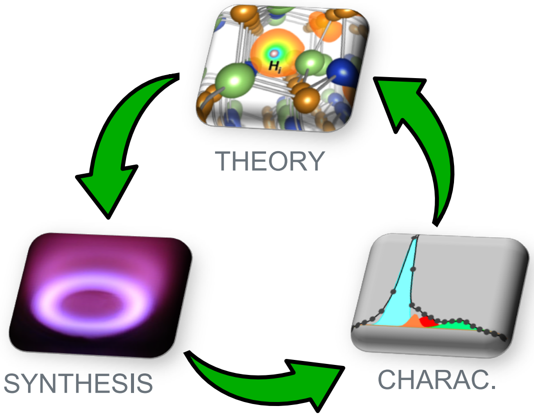
<u>Technical objectives:</u>

- To address **Synthesis and Manufacturing (AJ)** and **Materials Efficiency (AE)** barriers, we model and develop new alloying and doping techniques to enhance chalcopyrites efficiency.

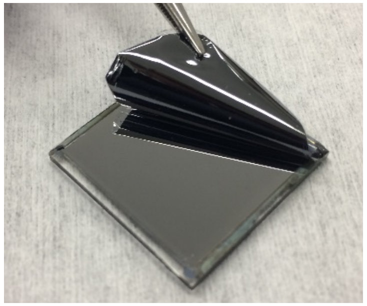
- To address **Materials Efficiency (AE)** and **Materials Durability (AF)** barriers, we develop new interfaces to improve chalcopyrites surface energetics and chemical stability during PEC operation.

- To address **Integrated device configuration (AG)** barrier, we develop a unique method with "transferable" PEC films to create semi-monolithic chalcopyrite-based tandems.

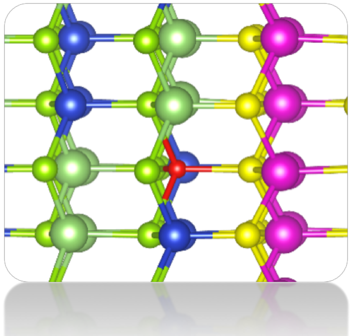
<u>Benefits for HydroGEN and scientific community:</u> our models can be used to predict the properties of future materials (optical absorption, thermodynamic stability, defect chemistry) and interfaces (band-edges offsets).



Transferable PEC thin films



Interface modelling



Technical Back-Up Slides

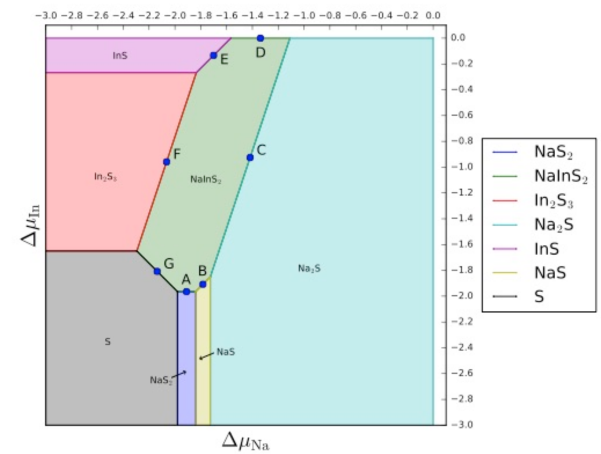
Collaboration – Benefits of information provided into the HydroGEN data-hub

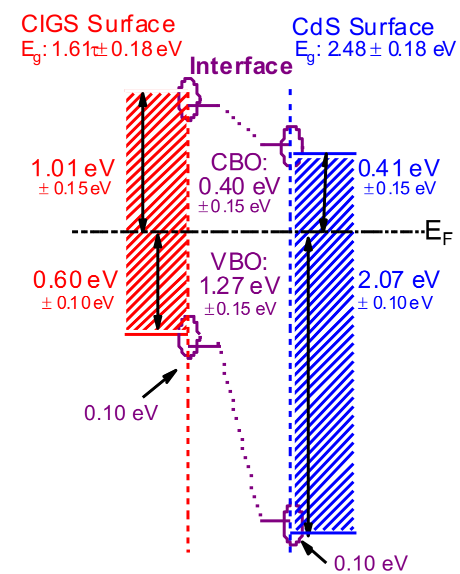
Following our "**theory, synthesis and advanced characterization feedback loop**" philosophy, we aim at developing material and interface models that will accelerate development of renewable H_2 production technologies.

During phase 1, data uploaded on the HydroGEN-hub included primarily bulk properties of chalcopyrite absorbers and n-type buffers, providing the community with useful information regarding:

- Theoretical predictions related to defect chemistry and possible passivation strategies of other absorbers.
- Fundamental properties of multi-compound buffers, including optical spectra (bandgap) and microstructure (crystallographic).
- Surface and bulk spectroscopy techniques and gathering data on the purity and chemical nature of water splitting materials.

During phase 2(#), we will focus our efforts on interface properties and further develop our phase 1 models to predict conduction and valence band alignment (a.k.a. "energetics"), compare them against spectroscopic measurements and ultimately PEC water splitting device performance.



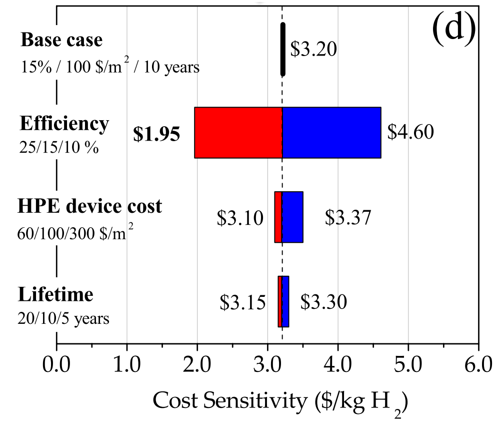


#: Any proposed future work is subject to change based on funding levels

Critical Assumptions

To meet DoE's cost target on renewable hydrogen production, a PEC device must:
- operate at an STH efficiency of 25%,
- be made using materials costing less than $100/m²
- have a lifetime of 10 years or better.

We present how the chalcopyrite material class has the potential to meet these three important requirements.



1. PEC operation at 25% STH efficiency: to date, the highest STH efficiency reported with chalcopyrite-based PEC devices is 10% (Angstrom Lab). This efficiency was achieved using a co-planar device, in which each CIGSe sub-cell shared a fraction of the total device area. By increasing chalcopyrites' bandgap, we plan to relocate the PV driver under the PEC cell, increasing the overall efficiency of the device. Our load line analysis shows that an STH efficiency of 25% is theoretically achievable with a new PV-grade 1.7eV CIGS cell (this program's main goal) and an existing 1.1eV CIGSe device (NREL). It is worth mentioning that our program will benefit from advances on chalcopyrites made by other research teams with the support of DoE.

2. Materials costs of $100/m²: First Solar already produces CdTe panels at $82/m² (14% module at 59¢/W in 2013). Also, Solar Frontier fabricates 13.9% CISe modules at 63¢/W in 2013, equivalent to a manufacturing cost of $90/m². These production costs are expected to be reduced further with emerging solution-based synthesis technologies.

3. Lifetime of 10 years or better: advanced surface analysis pointed out the formation of Ga_2O_3 at the surface of the copper chalcopyrites during PEC operation. This oxide, unstable in acid, is one possible cause for photocorrosion. Meeting the durability targets will thus require the development of efficient protection coating to prevent Ga_2O_3 growth. In this project, we plan to use WO_3 as a protective layer, a low-cost material that is highly stable in acidic solutions. If necessary, the protective layer could be periodically etched and re-deposited at moderate cost.