Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

# Novel Chalcopyrites for Advanced Photoelectrochemical Water-Splitting

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**University of Hawaii**

# P162

NREL BERKELEY LAB Sandia National Laboratories INL Idaho National Laboratory Lawrence Livermore National Laboratory SRNL

# Project Overview

## Novel Chalcopyrites for Advanced Photoelectrochemical Water-Splitting

- Lead PI: Nicolas Gaillard (University of Hawaii)
- Co-PIs: Clemens Heske (UNLV)
  Thomas Jaramillo (Stanford)

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

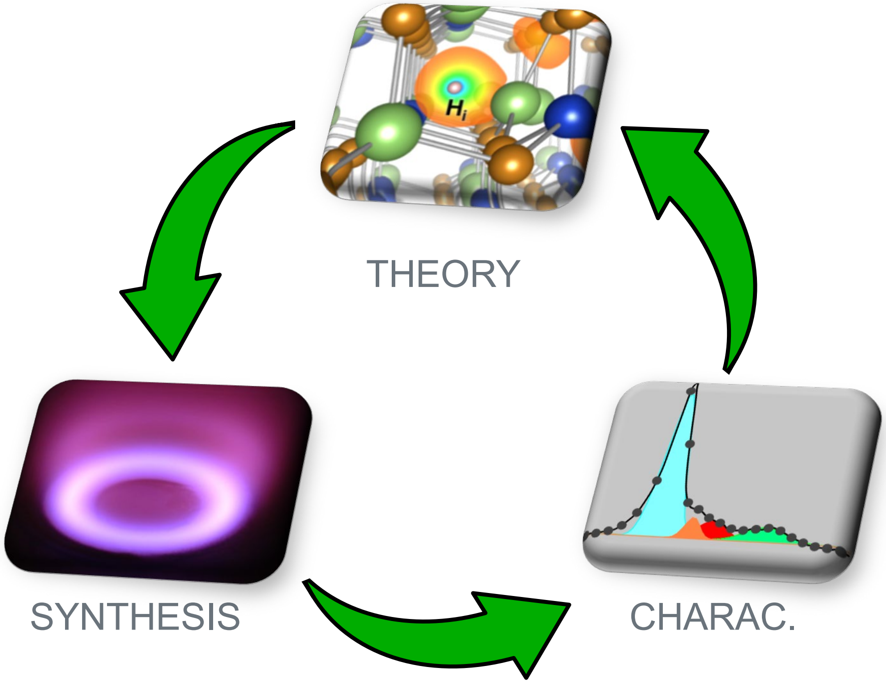
** this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

### Project Vision

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

### Project Impact

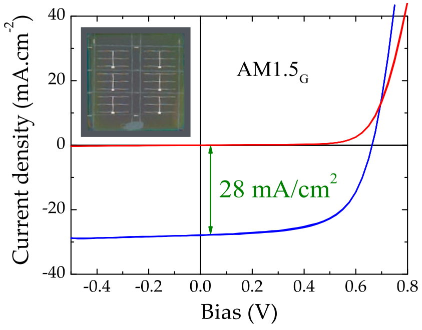
We develop innovative techniques to fabricate chalcopyrite-based water splitting devices that can meet DOE's cost target of $2/kg $H_2$.



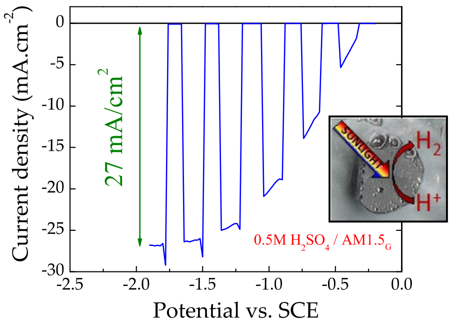
# Approach – Technical background

## The promise of chalcopyrite-based PEC systems

### 1. Chalcopyrites can generate high photocurrent density



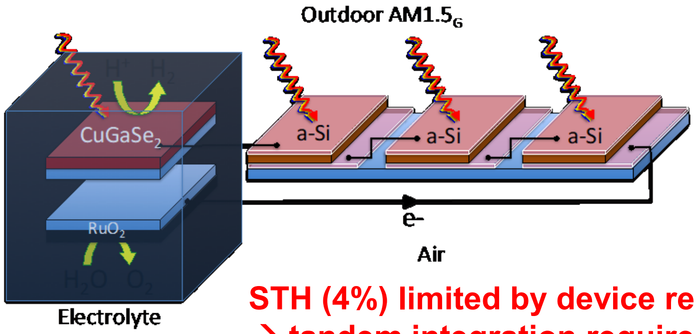
**Solar cell** **vs.** **Photoelectrode**



### 2. Low-cost processes available

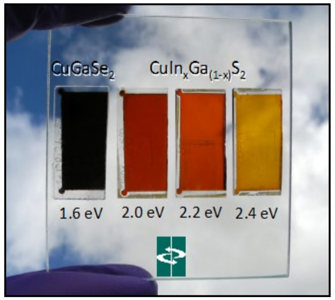
**Chalcopyrite PV module cost: \$100/m²**

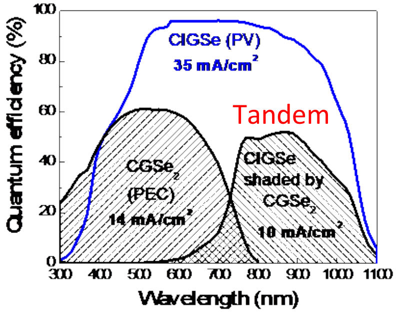
### 3. Demonstrated water splitting with co-planar devices



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

### 4. Chalcopyrites are bandgap ($E_G$) 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* |

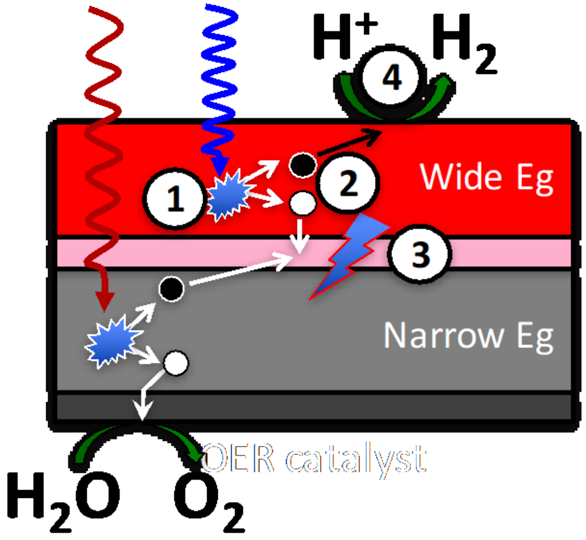
## Technical barriers addressed in this project

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.

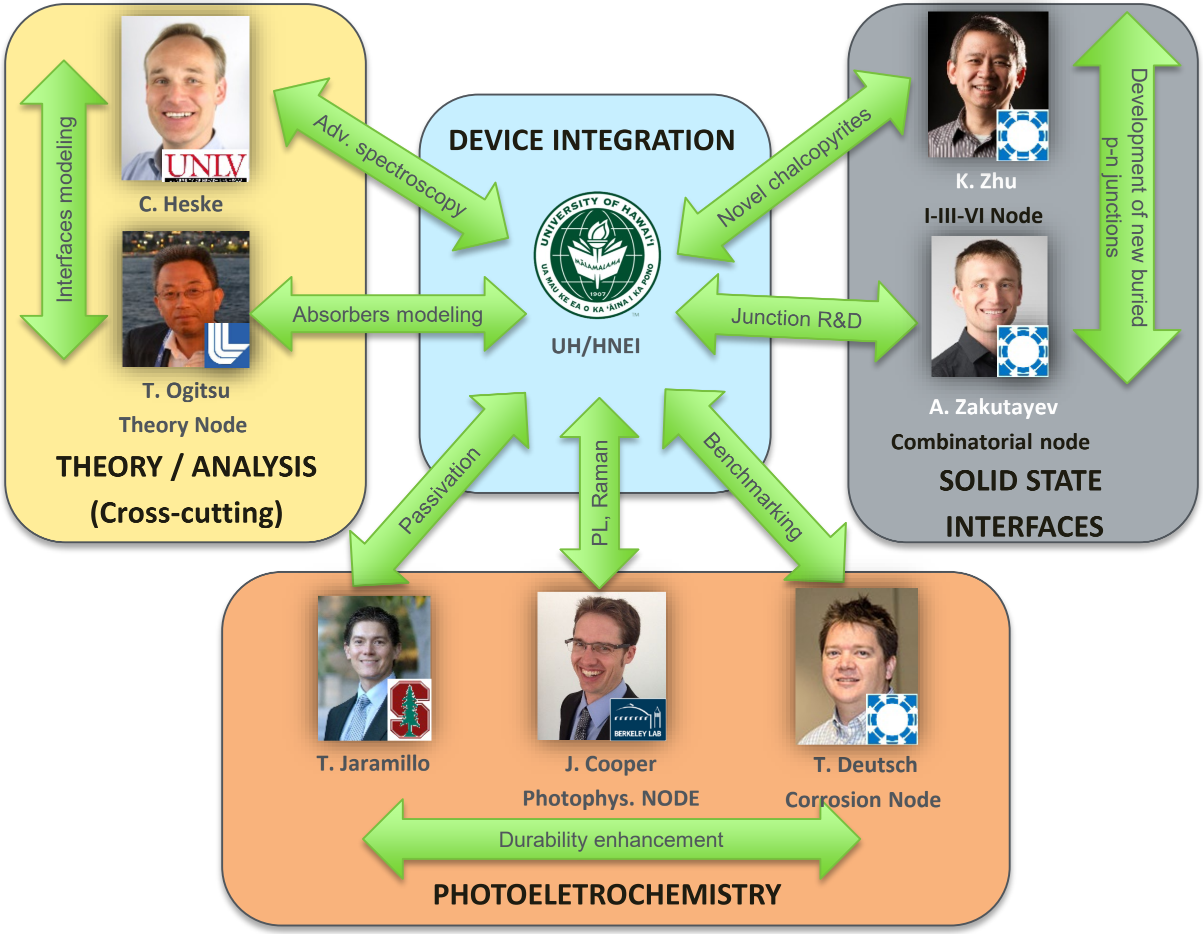
### Task 2 - Interfaces Engineering for Enhanced Efficiency and Durability

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***



Interfaces modeling

C. Heske

T. Ogitsu

Theory Node

**THEORY / ANALYSIS**

**(Cross-cutting)**

Adv. spectroscopy

Absorbers modeling

**DEVICE INTEGRATION**

UH/HNEI

Novel chalcopyrites

Junction R&D

K. Zhu

I-III-VI Node

A. Zakutayev

Combinatorial node

Development of new buried p-n junctions

**SOLID STATE INTERFACES**

Passivation

PL, Raman

Benchmarking

T. Jaramillo

J. Cooper

Photophys. NODE

T. Deutsch

Corrosion Node

Durability enhancement

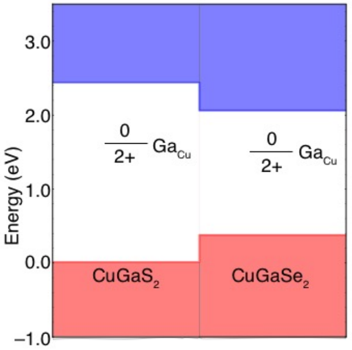
**PHOTOELETROCHEMISTRY**

**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

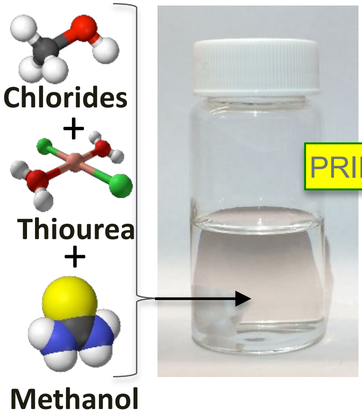
**Synthesis and Manufacturing barrier (AJ):** our models revealed that low photo-voltage in $CuInGaS_2$ originates from $Ga_{Cu}$ defects. Alternative Ga-free wide bandgap Cu(In,**Al**)$Se_2$, Cu(In,**B**)$Se_2$ identified by theory. However, these materials are too challenging to make by co-evaporation.



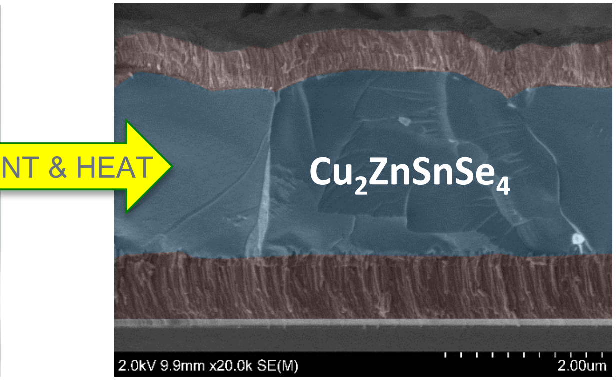
**Proposed innovation:** replace evaporation with “printing” technique to synthesize Cu(In,Al,B)$Se_2$ using molecular inks containing all necessary constituents (e.g. CuCl, $InCl_2$, $AlCl_3$/$BCl_3$).

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

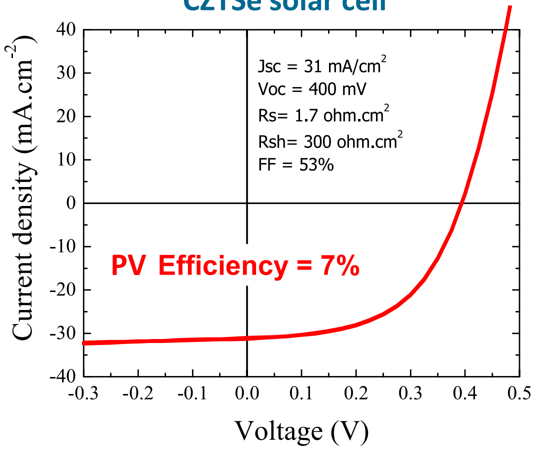
**Molecular ink**
**(stable over 12 months)**



**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/m$^2$.**

# Approach – Innovation highlight #2

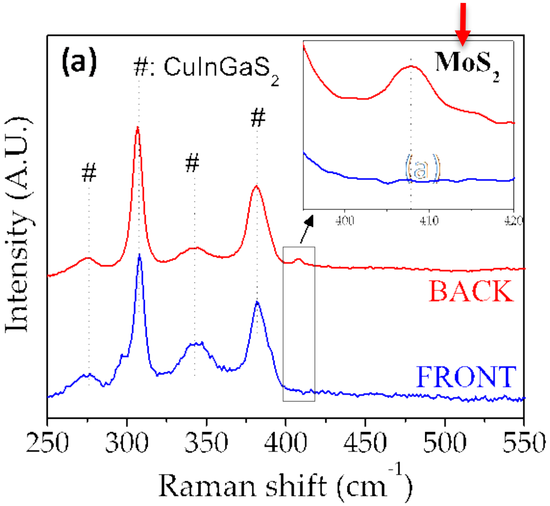
## 2) Innovative tandem device integration schemes

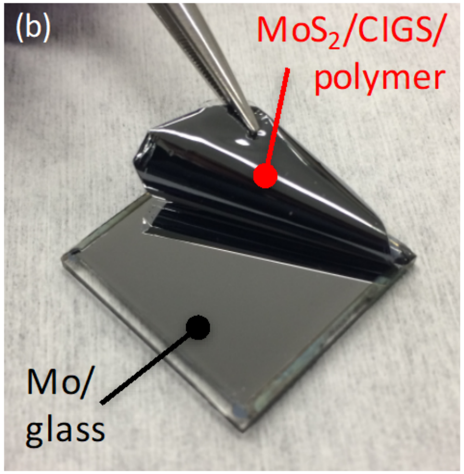
**Integrated Device Configurations barrier (AG):** materials compatibility (e.g. temperature) is the biggest challenge in multi-junction device integration. With current chalcopyrite PV technology, it is impossible to fabricate high efficiency monolithic multi-junction devices by directly depositing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

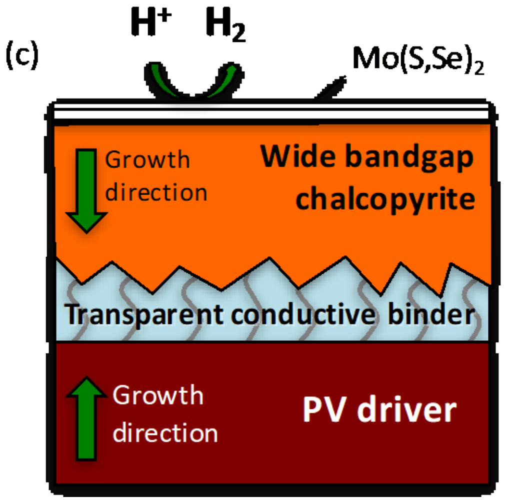
**Proposed innovation:** exfoliation of finished PEC cells and bonding onto fully processed PV drivers to create a semi-monolithic tandem device.

→ **Proof of concept:** 1 $\mu$m thick CIGS layer successfully “peeled” from substrate using polymer

Mechanically weak interfacial layer





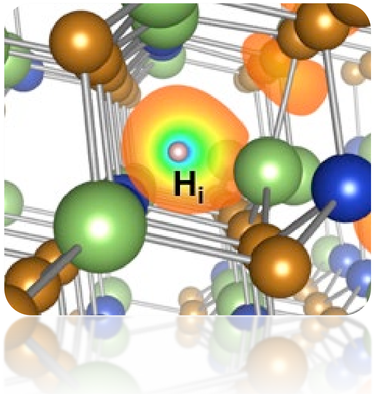


→ **Enable integration of chalcopyrites into low-cost tandem water splitting devices**

# Relevance & Impact – Leveraging EMN capability nodes

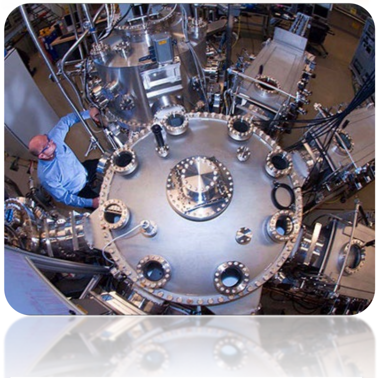
### Computational Materials Diagnostics and Optimization (T. Ogitsu).

- **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.



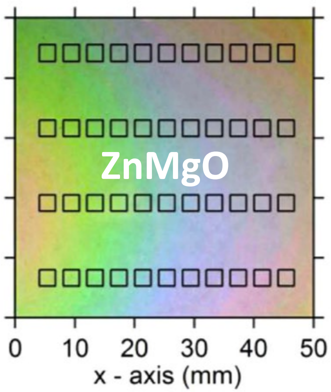
### I-III-VI Compound Semiconductors for Water-Splitting (K. Zhu)

- **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 2

→ Milestones and Go/NoGo decision points met or on track for Y2

| Task # | Subtask Title | Milestone ID | Description | Anticipated Quarter | Status |
|---|---|---|---|---|---|
| **2.1** | Interface: energetics | Milestone #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. | Q1 | **100%** |
| **2.2** | Synthesis of chalcopyrite | Milestone #2 | A printed polycrystalline $Cu(In,Al,B)Se_2$ thin film material losing less that 50% of photocurrent and photovoltage after exfoliation/transfer. | Q2 | **100%** |
| **2.2** | Interface: durability | Milestone #3 | 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. | Q3 | **90%** |
| **2.2** | **Interface: durability** | **Go/No-Go #1/2** | **Using a chalcopyrite photocathode, sustain hydrogen production (initially exceeding -8 mA/cm^2) at 90% of initial photocurrent density for 200 hours.** | **Q4** | **100%** |
| **3.2** | **HPE integration** | **Go/No-Go #2/2** | **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.** | **Q4** | **100%** |

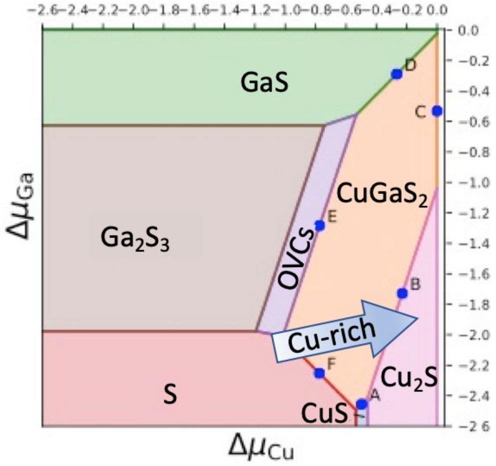
# Accomplishments – Task 1: Modeling and Synthesis of Chalcopyrite Photocathodes

**Material barrier (AJ)**

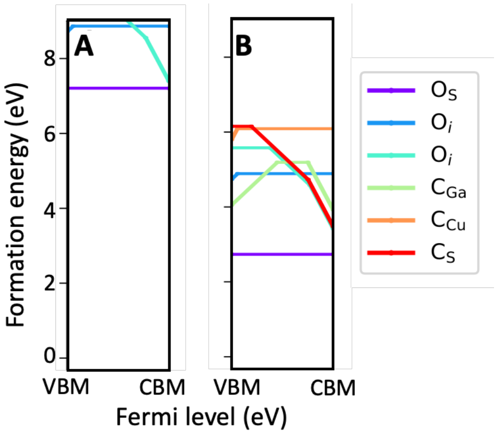
## 1.1) Theoretical modeling (LLNL theory node)

**This year's focus: understanding influence of impurities on absorbers optical absorption losses**

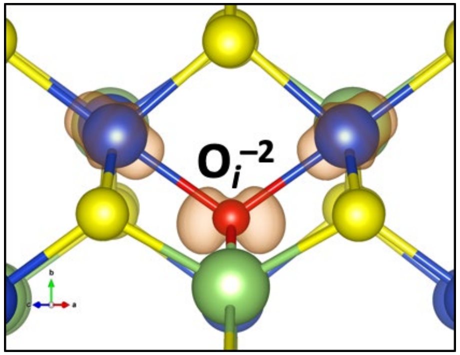
*Higher O and C incorporation predicted in certain Cu-rich growth conditions*



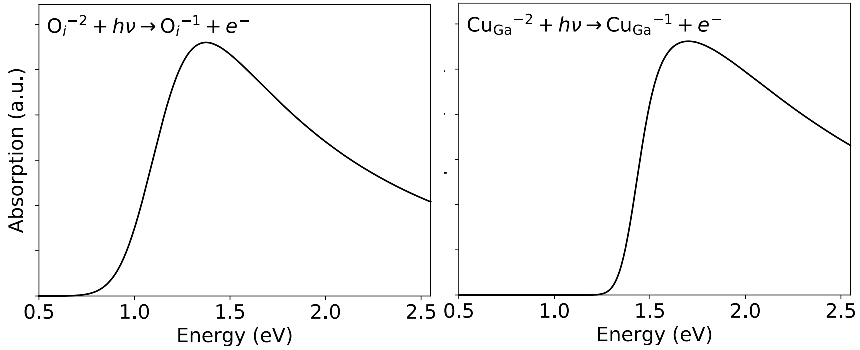
*Illumination and interfacial band bending can influence the favorable defect populations*



*Charge density isosurface associated with localize state of Oi acceptors*



*Identifying (intrisinic and extrinsic) sources for sub-bandgap absorption losses*



**Broader impact to community:** modeling provides critical information on absorbers thermodynamic stability, defect chemistry and helps identify promising new material candidates.

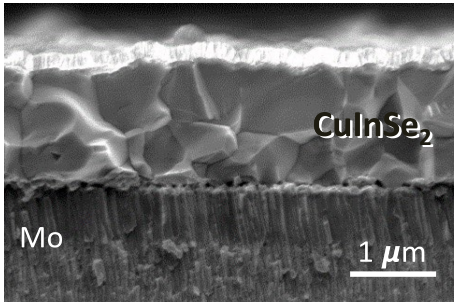
# Accomplishments – Task 1: Modeling and Synthesis of Chalcopyrite Photocathodes

**Material barrier (AJ)**

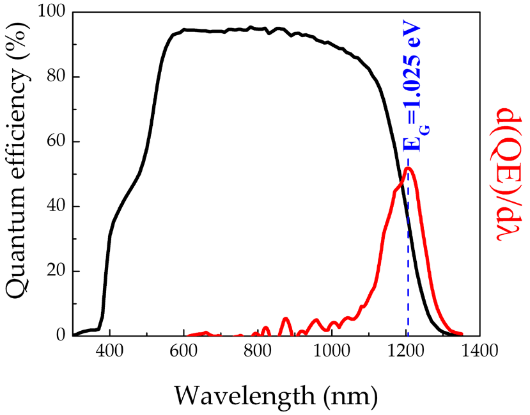
## 1.2) Chalcopyrites “printing” using molecular inks

### a. Narrow bandgap $CuInSe_2$ (AMR 2019)

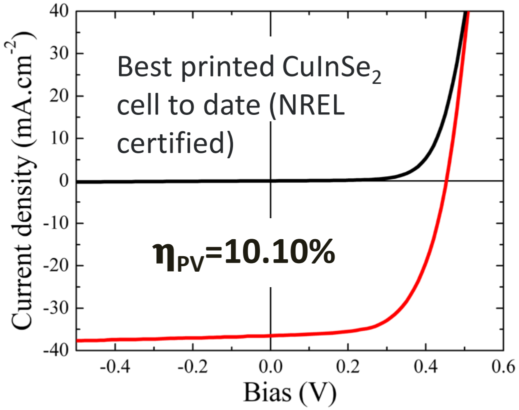
*Highly crystalline printed $CuInSe_2$ absorber*



*Quantum efficiency >90% demonstrated*



*PCE>10% validated on PV cells by NREL*

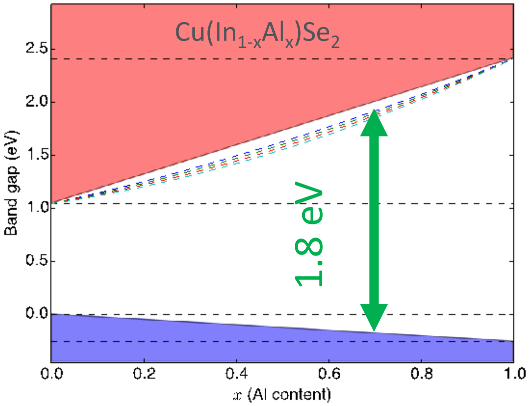


Best printed $CuInSe_2$ cell to date (NREL certified)

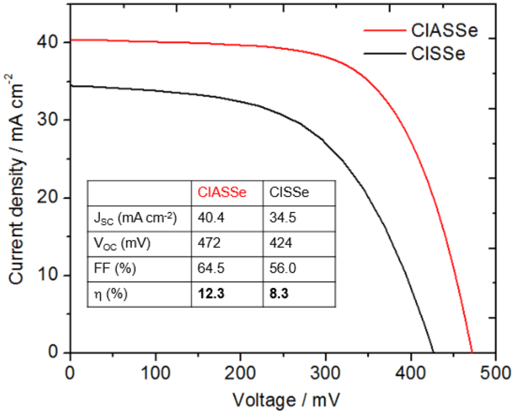
**$\eta_{PV}$=10.10%**

### b. Wide bandgap $CuInAlSe_2$

*Modeling of CIASe Eg vs. [Al] (LLNL)*

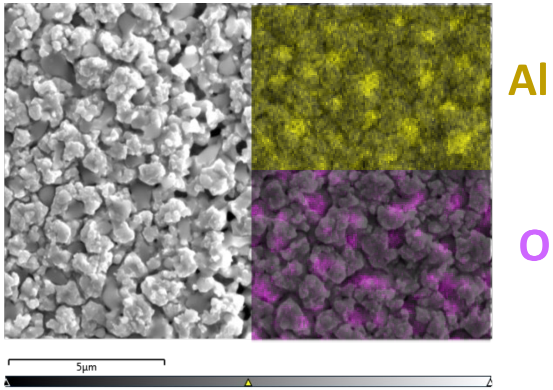


*PCE>12% with $CuInAlSe_2$ ([Al]=10%)*



| | CIASSe | CISSe |
|---|---|---|
| $J_{SC}$ (mA cm$^{-2}$) | 40.4 | 34.5 |
| $V_{OC}$ (mV) | 472 | 424 |
| FF (%) | 64.5 | 56.0 |
| η (%) | **12.3** | **8.3** |

*Challenge: Increasing [Al] beyond 30% leads to segregation (formation of $Al_2O_3$)*



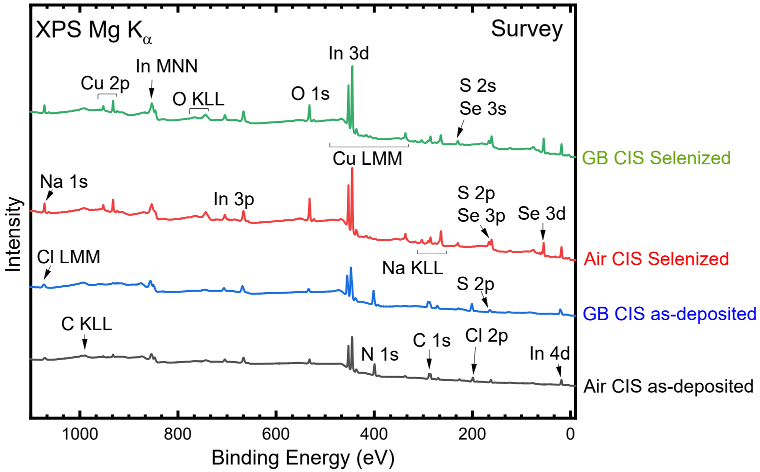
*SEM top view / EDX map of $CuInAlSe_2$*

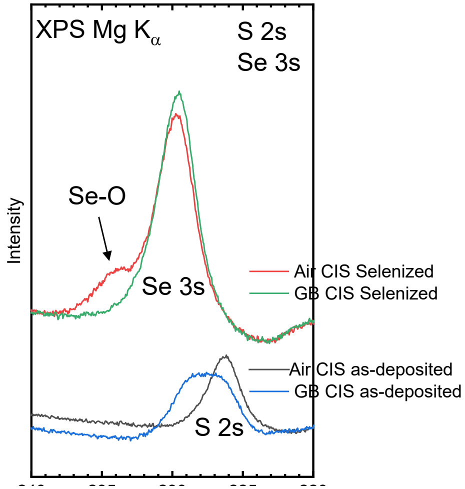
# Accomplishments – Task 1: Modeling and Synthesis of Chalcopyrite Photocathodes

**Material barrier (AJ)**

## 1.2) Effect of synthesis and coating environments: air and glovebox (GB)

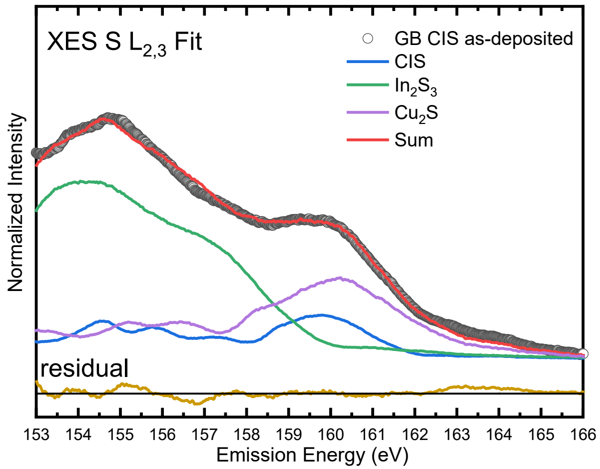
### X-ray Photoelectron Spectroscopy (XPS) @ UNLV



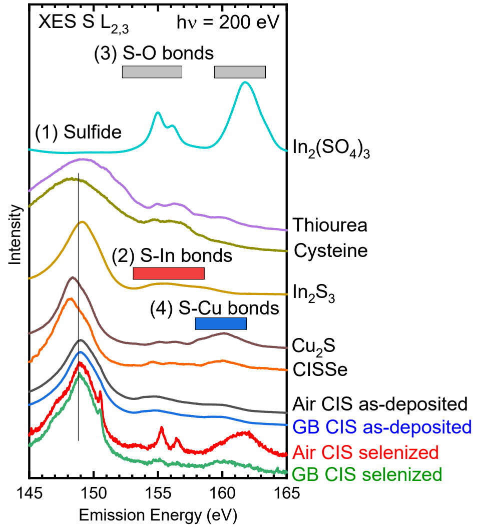


- Synthesis and spin-coating **in air**: more pronounced surface oxidation
- Synthesis and spin-coating **in GB**: less homogeneous, different chemical environments
- Selenization replaces majority of S atoms by Se
- Selenization also removes N and Cl, leads to presence of Na and increase of O

### X-ray Emission Spectroscopy (XES) @ ALS



*Fit analysis of glove-box (GB) $CuIn(S,Se)_2$ sample using $In_2S_3$, $Cu_2S$, and $CuInS_2$ (CIS) references: provides insights into the chemical impact of deposition and processing steps*



- Local chemical environment of S at/near the surface
- As-deposited samples show a variety of local chemical bonding environments
- Increase in S-O bonds in absorber synthesized and spin-coated in air

# Accomplishments – Task 2: Interfaces for Enhanced Efficiency & Durability

Efficiency barrier (AE)

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

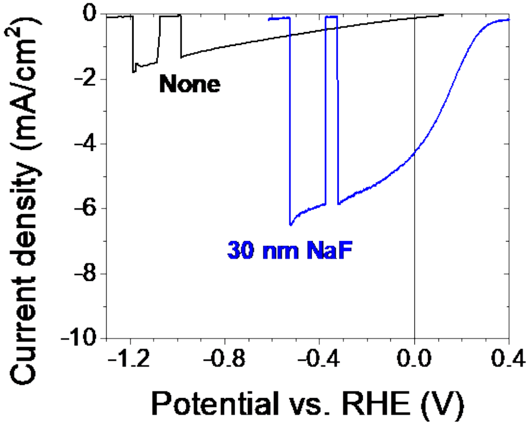
### a. Surface passivation with Na, Cd or Si (AMR 2019)

**Surface treatments tested so far:**

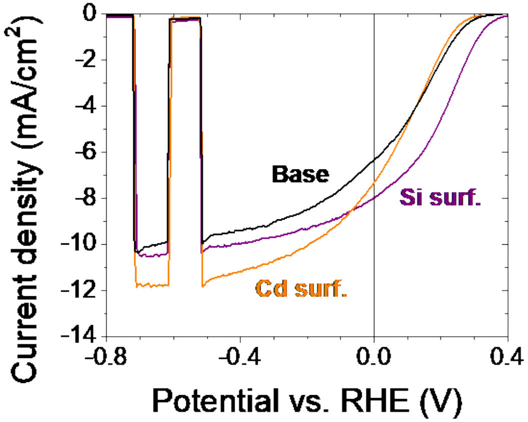
- NaF: 30 nm (evaporated)
- Si: 6 nm (evaporated)
- Cd2+: partial electrolyte (PE) treatment

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

FTO substrate

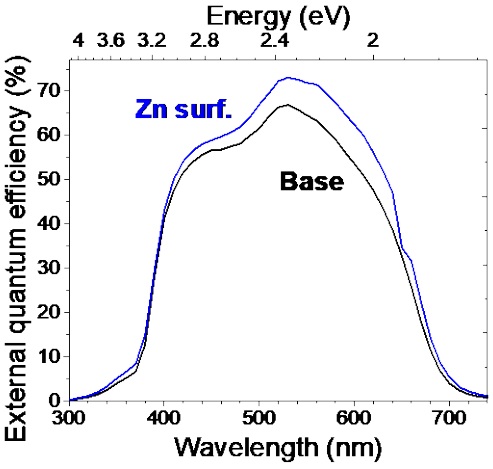


Mo substrate

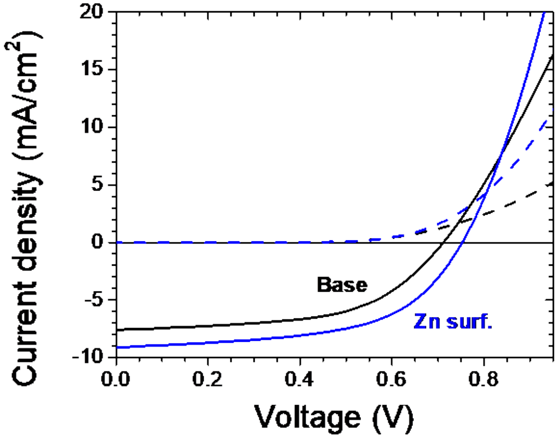


### b. Surface passivation with Zn

- In situ Zn + Se co-evaporation at the end of $CuGa_3Se_5$ co-evaporation
- Zn surface treatment increases solar cell efficiency from 3.0 to 3.8%
- Improvements possibly due to surface passivation
  - $CuGa_3Se_5$/CdS lattice mismatch is 5.3%
  - $CuGa_3Se_5$/ZnSe lattice mismatch is 2.7%
- PEC photocathode performance degraded in $H_2SO_4$ electrolyte. Future tests to include higher pH.



Mo substrate



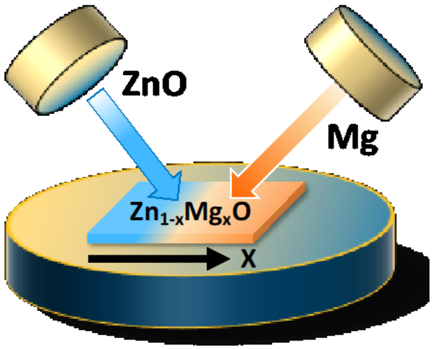
# Accomplishments – Task 2: Interfaces for Enhanced Efficiency & Durability

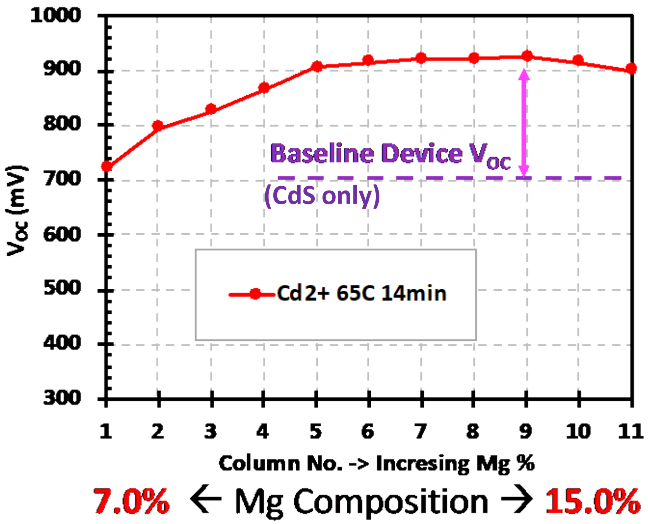
**Efficiency barrier (AE)**

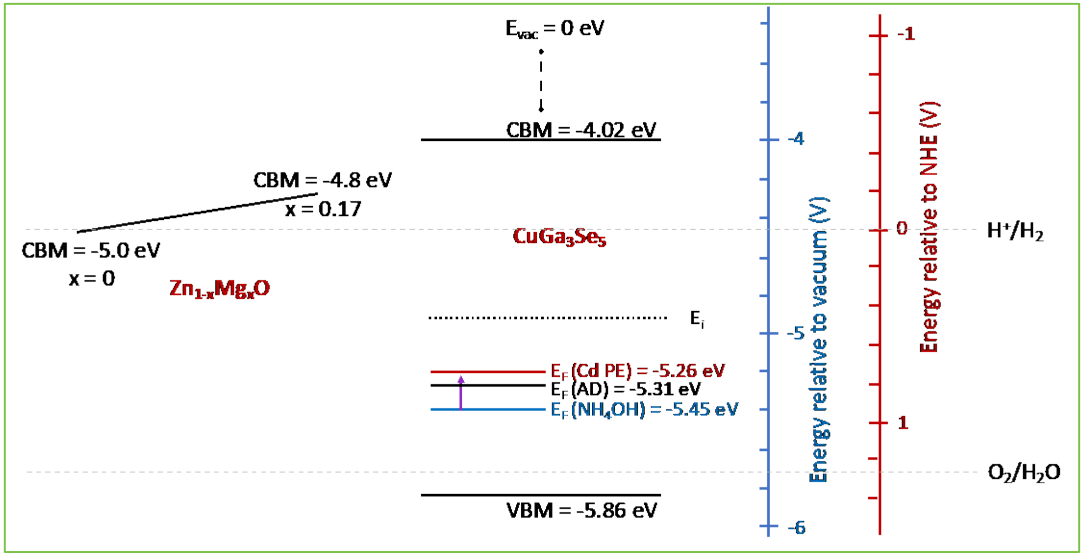
## 2.2) Combinatorial development of tunable "buffers" (NREL Combi./CIGSe Nodes)

**Factors contributing to increased $V_{OC}$ up to 925 mV with MZO and surface-treated $CuGa_3Se_5$ absorbers:**

- ❑ $Cd^{2+}$ partial electrolyte treatment
  - removes surface O and Na
  - Ion exchange of Cu and Ga with Cd; possibly create compensating defect(s)
  - Change of absorber surface conductivity type to either intrinsic or n-type ('p-i-n' junction)
- ❑ Improved CB alignment with higher bandgap $Mg_xZn_{1-x}O$







**Energy band positions for $CuGa_3Se_5$ absorber with different surface treatments, in comparison with the CBM position in $Mg_xZn_{1-x}O$.**
(based on XPS, Kelvin probe, hall effect and UV-Vis spectroscopy data, all measured at NREL)

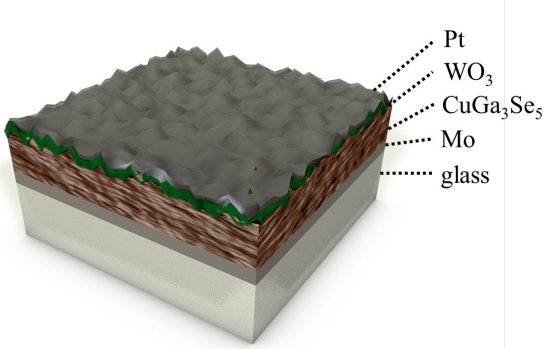
# Accomplishments – Task 2: Interfaces for Enhanced Efficiency & Durability

**Durability barrier (AF)**

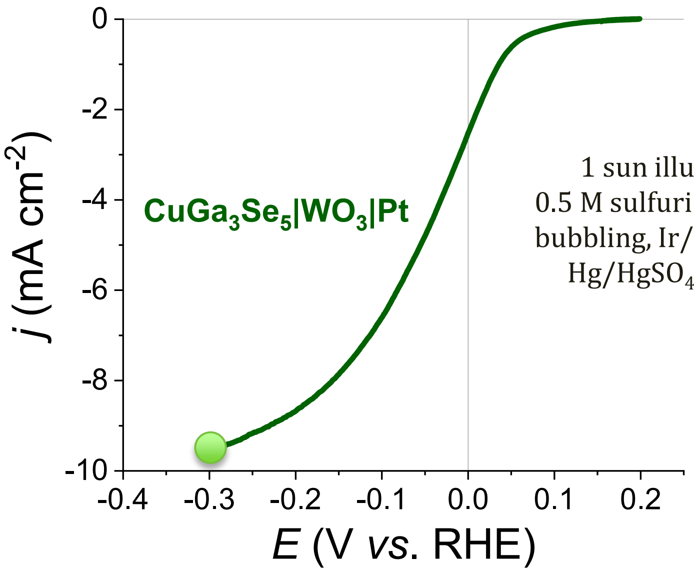
## 2.3) Protection against photo-corrosion (Stanford-NREL CIGSe Node)

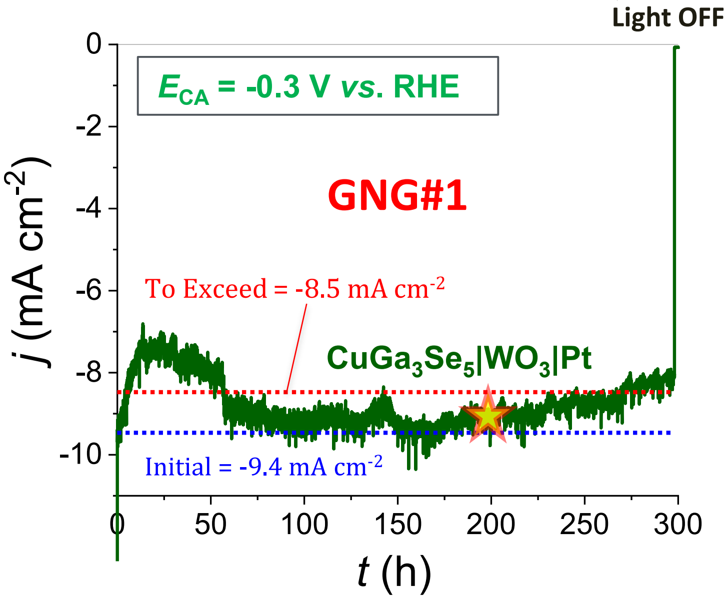
### Sample preparation

- $CuGa_3Se_5$ thin film co-evaporated on Mo at NREL,
- $CuGa_3Se_5$ sample coated at Stanford with 3.3 nm $WO_3$ (sputtered) coating and 1 nm Pt (e-beam evaporated) catalyst



### PEC testing





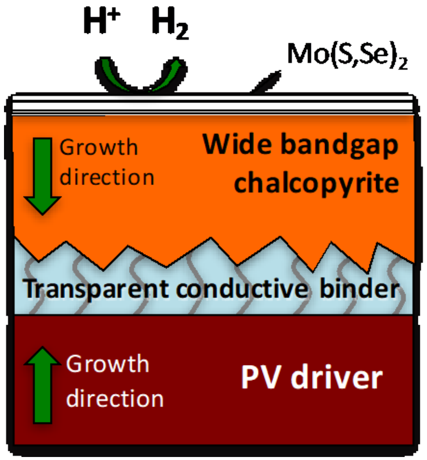
**→ Generate > 90% of initial photocurrent density for more than 270 h of continuous testing**

# Accomplishments – Task 3: Hybrid Photoelectrode Device Integration

**Device barrier (AG)**

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

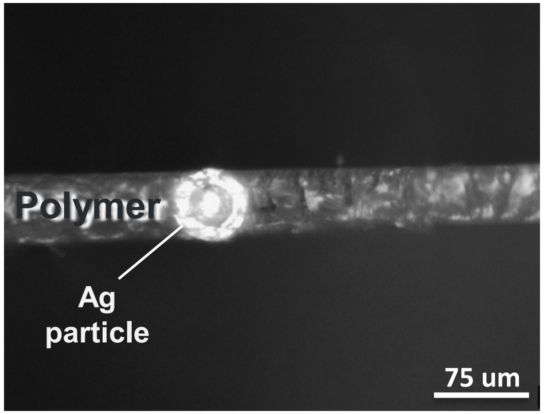
**Transparent conductive flexible composites (TCFC) to "glue" top cells onto fully integrated bottom cells**



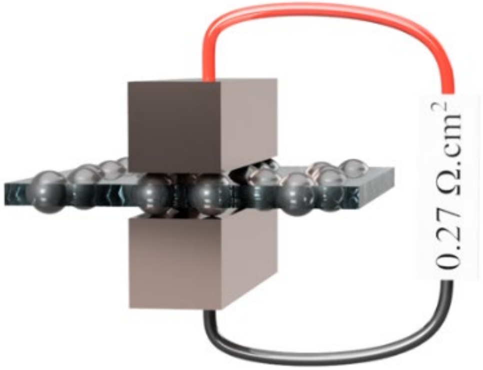
*Concept image of UH's TCFC comprising conductive spheres protruding out of a polymeric film*

*Image of UH's free-standing TCFC*

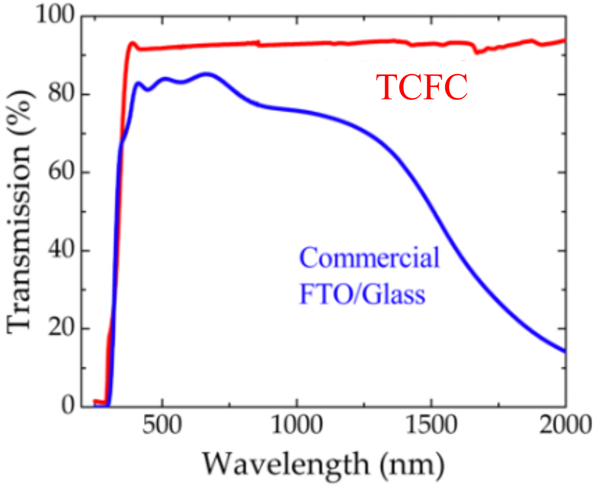
*Optical cross-sectional view of TCFC*



*Resistance as low as 0.2 ohm.cm²*



*Optical transparence as high as 90%*



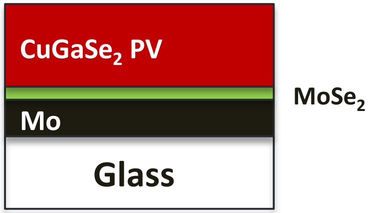
# Accomplishments – Task 3: Hybrid Photoelectrode Device Integration

**Device barrier (AG)**

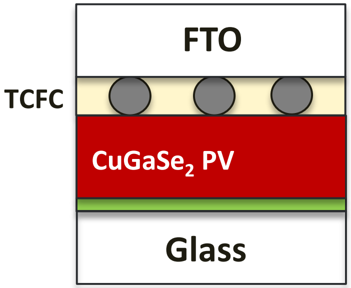
## 3.2) Semi-monolithic tandem integration (UH-NREL CIGSe Node)

**→ Approach: semi-monolithic devices were created by exfoliating and bonding wide bandgap (1.7 eV) $CuGaSe_2$ solar cells onto narrow bandgap (1.1 eV) silicon devices using HNEI's transparent conductive flexible composites (TCFC).**

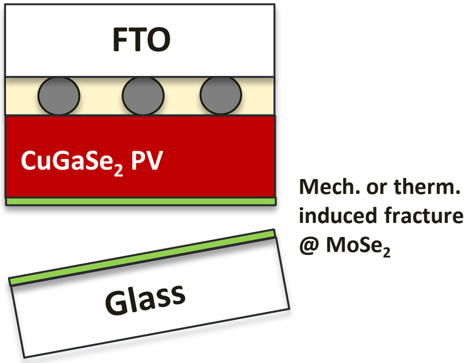
**1. Top cell integration (NREL)**



**2. Bonding onto FTO handle with TCFC**

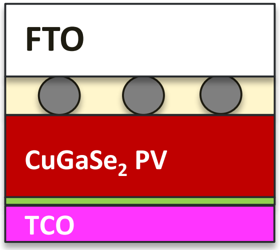


**3. Exfoliation**



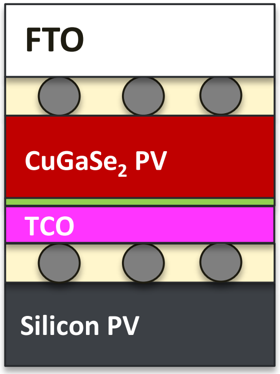
Mech. or therm. induced fracture @ $MoSe_2$

**4. TCO deposition**



TCO layer improves lateral charge collection

**5. Final bonding onto Si bottom cell with TCFC**



Our concept of semi-monolithic tandem could be extended to combine chalcopyrites with other "incompatible" low-temp. PV classes (a-Si, organic absorbers, Perovskites…etc.)

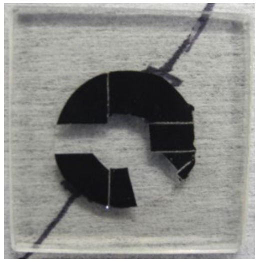
# Accomplishments – Task 3: Hybrid Photoelectrode Device Integration

**Device barrier (AG)**

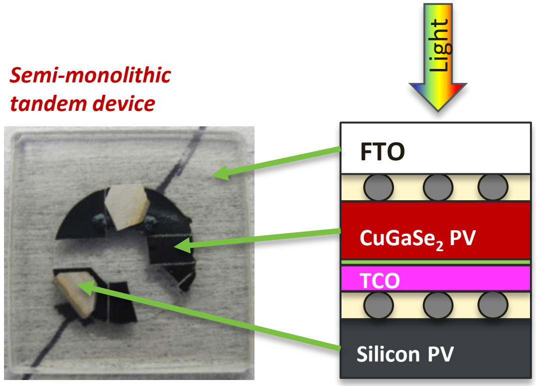
## 3.2) Semi-monolithic tandem integration (UH-NREL CIGSe Node)

→ **Validation using NREL's 1.6 eV $CuGaSe_2$ device and Si solar cells.**

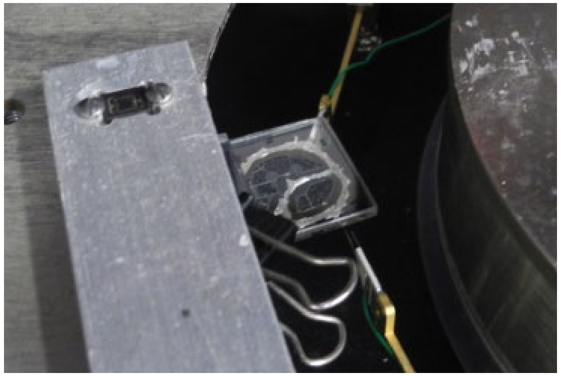
*CGSe cell transferred onto FTO*

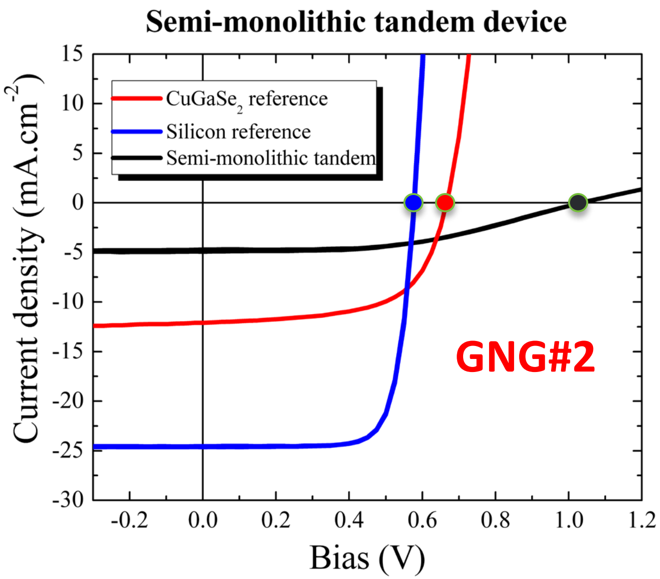


*Semi-monolithic tandem device*



*Test setup (inverted config.)*





| Device | Voc (mV) |
|---|---|
| CGSe reference cell | 660 |
| Si reference cell | 580 |
| Semi-monolithic tandem | 1,035 |

$$\frac{V_{oc-tandem}}{V_{oc-Si}+V_{vo-CGSe}} = \frac{1,035}{660+580} = 83\% \gg \text{GNG\#2 (50\%)}$$

- → Semi-monolithic concept successfully demonstrated.
- → Future work to include integration of chalcopyrites with wider bandgaps (1.8-2.0 eV).

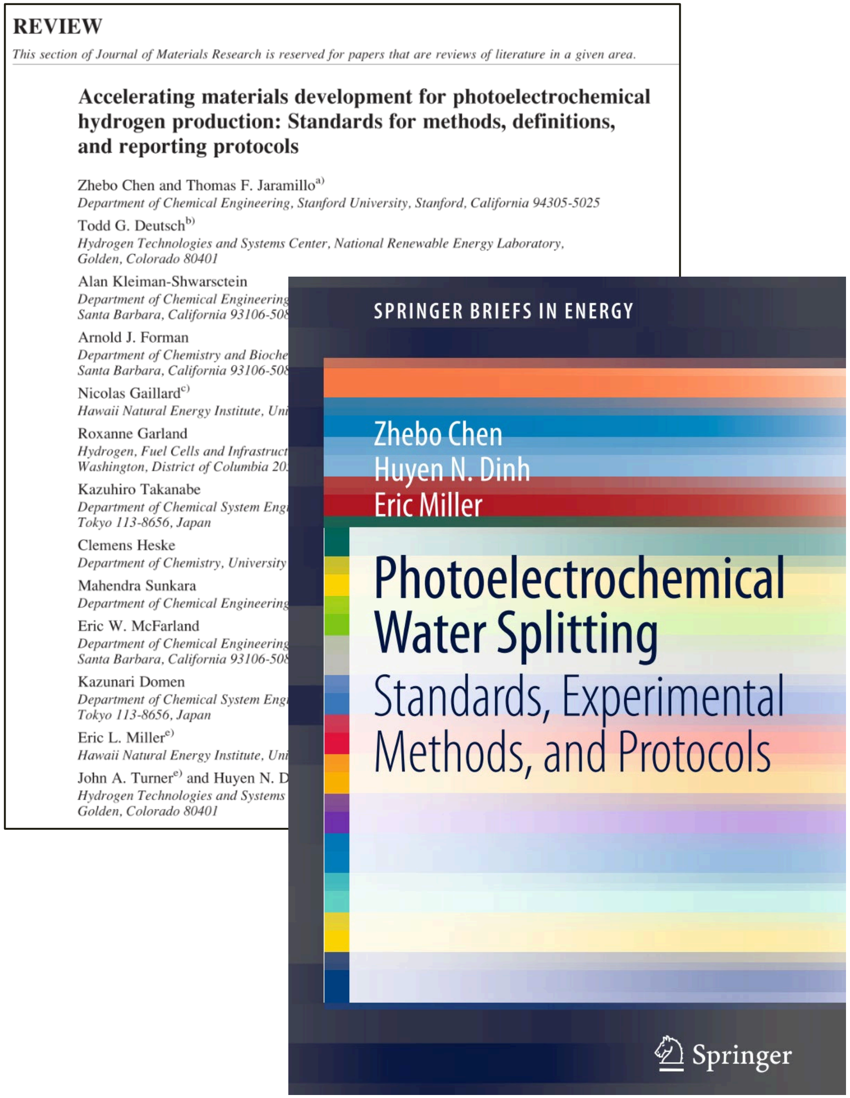
# Collaboration – Interactions with EMN project node experts to date

**→ 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 [O] and [C] impurities on OVCs optical transmission. | This work provides guidance for novel chalcopyrite candidates selection. | AE |
| 1 | UH - NREL I-III-VI Node | **Sample exchange** ($CuInAlSe_2$ solid state devices). | Measure photo-conversion properties of printed $CuInAlSe_2$ | Validates the printing method to be used to create quaternary chalcopyrites. | 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 (Y2 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.
- Participation to “2nd Annual Advanced Water Splitting Technology Pathways: Benchmarking & Protocols Workshop” held in Scottsdale on October 28th & 31st 2019.



**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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SPRINGER BRIEFS IN ENERGY

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Huyen N. Dinh
Eric Miller

Photoelectrochemical Water Splitting
Standards, Experimental Methods, and Protocols

Springer

# Planned Future Work[#]

**Estimated budget: ~$410K**

## Task 1 - Modeling and Synthesis of Chalcopyrite Photocathodes

**Sub-task 1.1 – defect passivation:** with help from Theory Node (LLNL) and Photophysical Node (LBNL), further elucidate the impact of [Cu] on wide bandgap chalcopyrite sub-$E_G$ transmission properties (e.g. Cu-rich $CuGaSe_2$ vs. Cu-poor $CuGa_3Se_5$).
**Sub-task 1.2 – printed chalcopyrites**: understand and solve Al segregation in $Cu(In,Al)Se_2$ to improve optoelectronic characteristics.

→ **IMPACT: produce materials compatible with 20% STH efficiency or higher.**

## Task 2 - Interfaces Engineering for Enhanced Efficiency and Durability

**Sub-task 2.1 – interface energetics**: combine new surface treatments with MgZnO to create top cells with $V_{oc}$ >1V.
**Sub-task 2.2 – interface durability**: further improve the deposition of $WO_3$ protective layers and finalize milestone #3.

→ **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 conductive binder and test alternative media.
**Sub-task 3.2 – semi-monolithic HPE device**: pair wide bandgap chalcopyrite photocathodes with other PV drivers aiming for total photovoltage >1.6V.

→ **IMPACT: create the first efficient chalcopyrite-based tandem device.**

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

# Y3 Milestones and project deliverable table

**Milestone Summary Table-Y3**

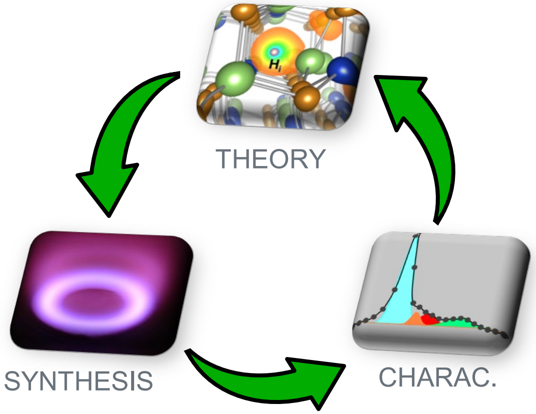
**Recipient Name:** University of Hawaii / Hawaii Natural Energy Institute

**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 |
|---|---|---|---|---|---|---|---|
| **1.2** | Synthesis of chalcopyrite | Milestone | 1.2-3 | A printed single-phase polycrystalline $Cu(In,Al,B)(S,Se)_2$ thin film material showing photovoltage greater than 700 mV. | Voc will be recorded at NREL via J-V analysis and reported in quarterly report | 30 | Q10 |
| **2.1** | Interface: energetics | Milestone | 2.1-3 | Demonstrate an open circuit voltage greater than 1,000 mV on at least 10 MgZnO:Ga-coated wide bandgap chalcopyrite absorbers integrated on a Mo substrate under simulated AM1.5 G illumination. | Voc will be recorded at NREL via J-V analysis and reported in quarterly report | 33 | Q11 |
| **2.2** | Interface: durability | Milestone | 2.2-4 | Retain 90% of metal content in a thin, transparent protective coating over the course of 300 hrs of electrocatalytic HER testing at -10 mA/cm^2. | To be measured at Stanford via chronoamperometry | 36 | Q12 |
| **3** | HPE integration | Project deliverable | | A standalone semi-monolithic chalcopyrite-based device capable of producing renewable hydrogen with an STH efficiency of at least 5%, with a stretch goal of 10%. | To be measured at HNEI or NREL via current-voltage analysis | 39 | Q13 |

# Project Summary

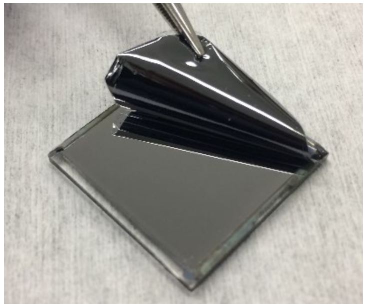
High-level project goal: Strengthen **theory, synthesis and advanced characterization “feedback loop”** to accelerate development of chalcopyrites for efficient PEC $H_2$ production.



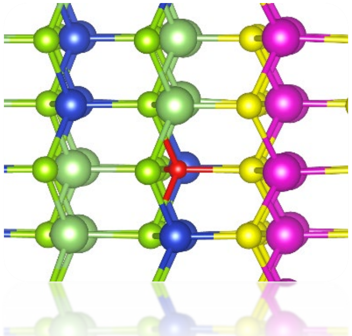
Technical objectives:

- 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.

**Transferable PEC thin films**



**Interface modelling**



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