Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Novel Chalcopyrites for Advanced Photoelectrochemical Water-Splitting

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PD162

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*	$280,172

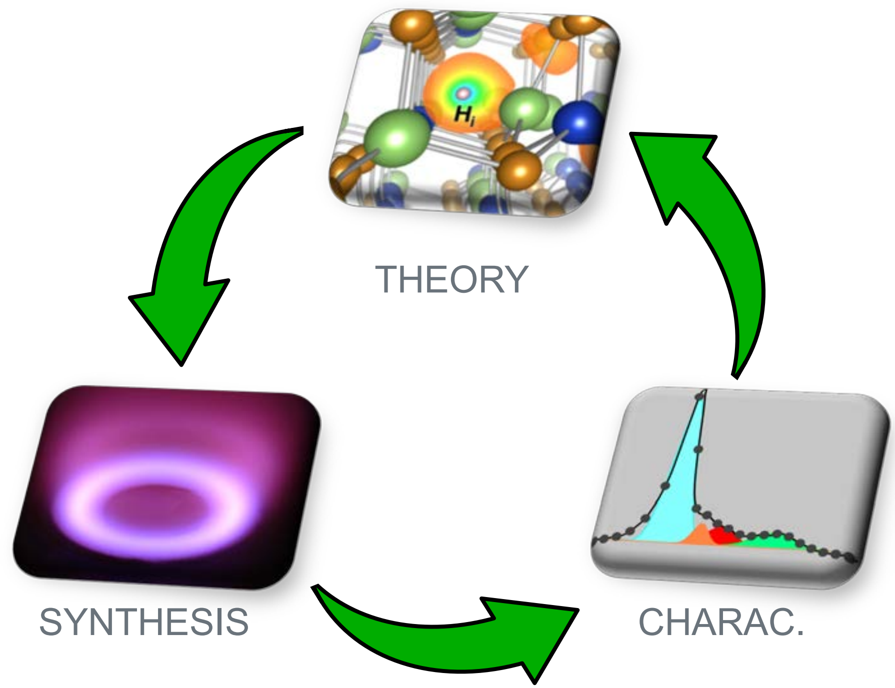
** this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Project Vision

Strengthen **theory, synthesis and advanced characterization "loop"** to accelerate development of efficient materials for PEC H_2 production.

Project Impact

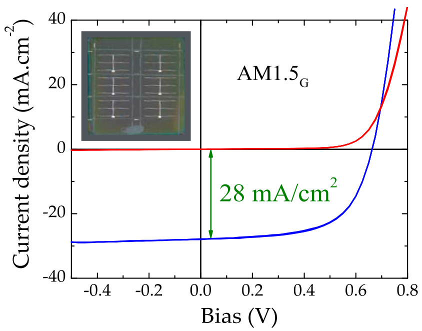
Innovative technologies to synthesize and integrate existing or exploratory chalcopyrites into low-cost PEC devices. These techniques could be extended to other material classes.



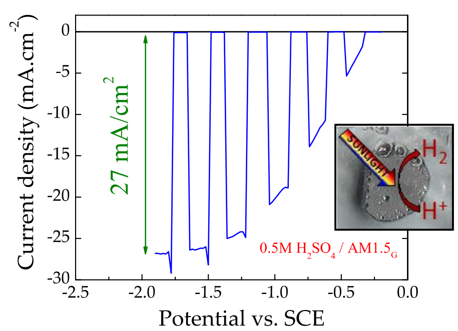
Approach – Technical background

The promise of chalcopyrite-based PEC systems

1. Chalcopyrites can generate high photocurrent density



Solar cell **vs.**

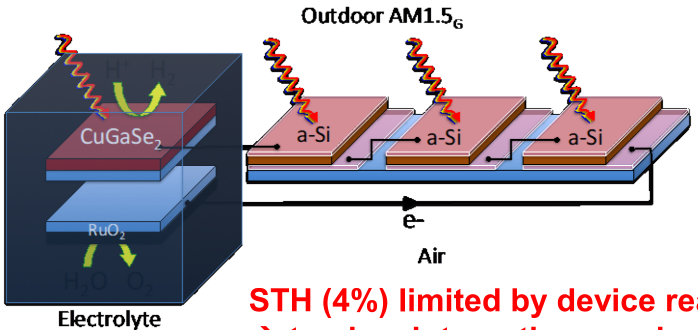


Photoelectrode

2. Low-cost processes available

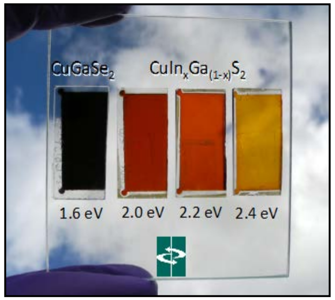
Chalcopyrite PV module cost: \$150/m²

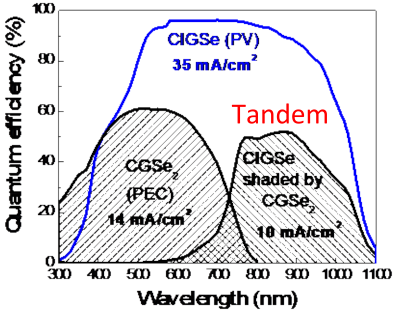
3. Demonstrated water splitting with co-planar devices



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 PEC H_2.
- 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*

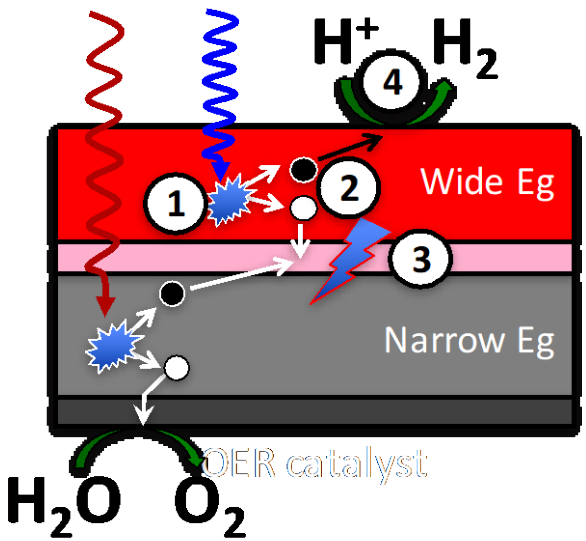
Technical barriers addressed in this project

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 – Scope of work for budget period 1

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.

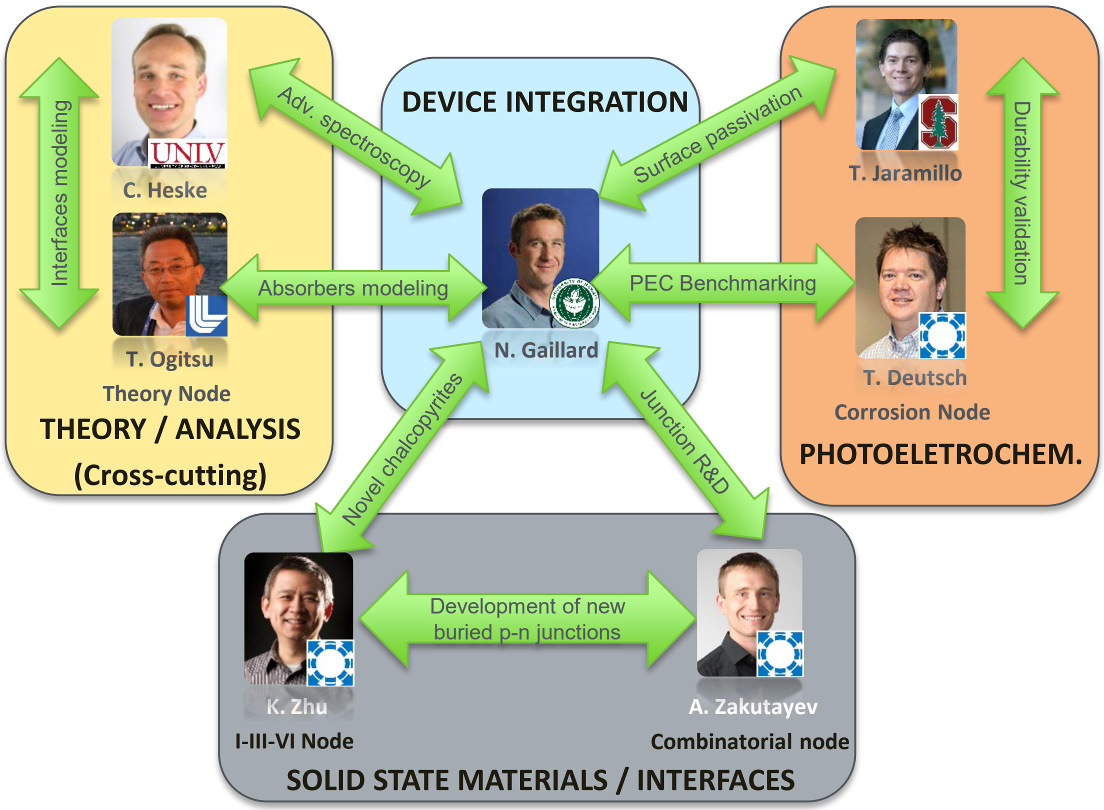
Task 2 - Interfaces Engineering for Enhanced Efficiency and Durability

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

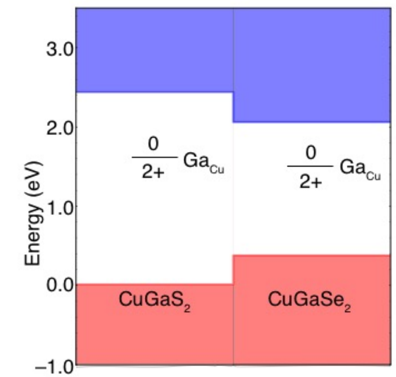


Take home message: our program is developing materials, methods and models addressing all fundamentals of photoelectrochemistry to accelerate the development of water splitting materials.

Approach – Innovation highlight #1

1) Novel chalcopyrites alloying using printing techniques

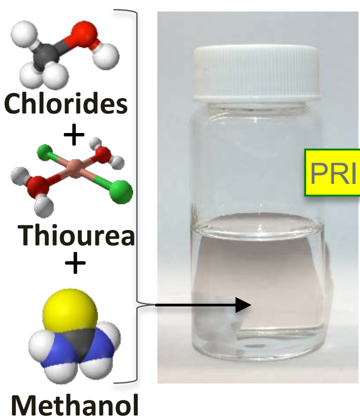
Synthesis and Manufacturing barrier (AJ): our models revealed that low photo-voltage in $CuInGaS_2$ originates from Ga_{Cu} defects. Alternative Ga-free wide bandgap Cu(In,**Al**)Se_2, Cu(In,**B**)Se_2 identified by theory. However, these materials are too challenging to make by co-evaporation (aluminum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



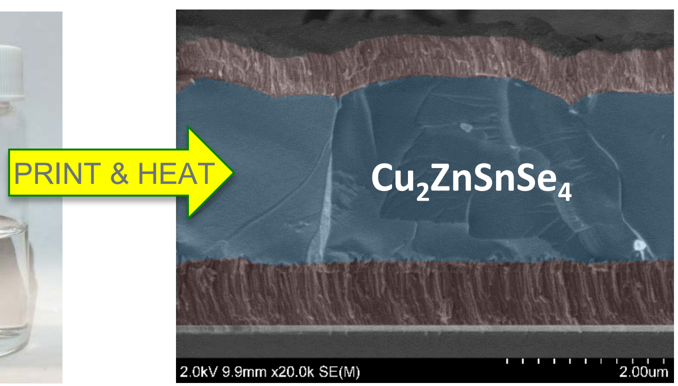
Proposed innovation: replace evaporation with "printing" technique to synthesize Cu(In,Al,B)Se_2 using molecular inks containing all necessary constituents (CuCl, $InCl_2$, $AlCl_3$/BCl_3).

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

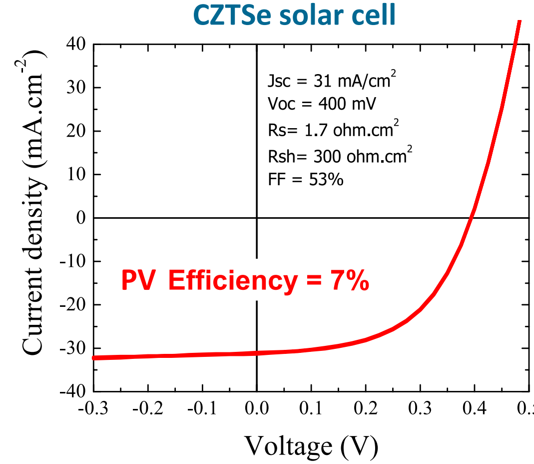
Molecular ink (stable over 12 months)



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.**

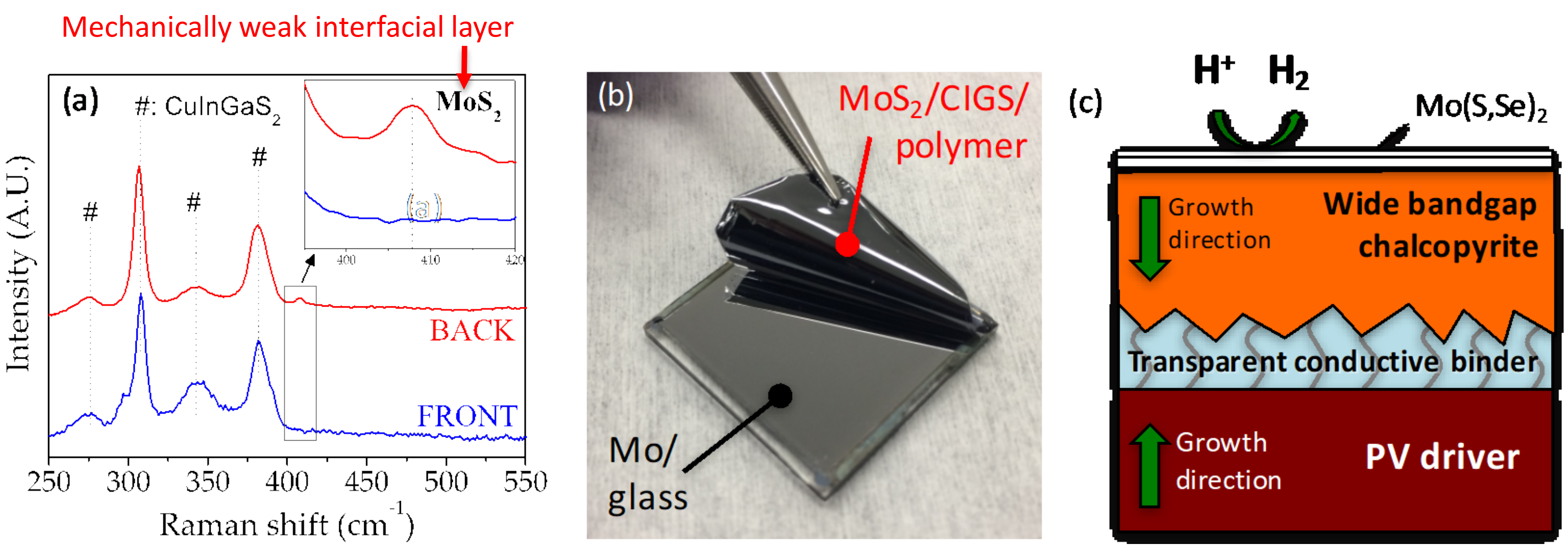
Approach – Innovation highlight #2

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

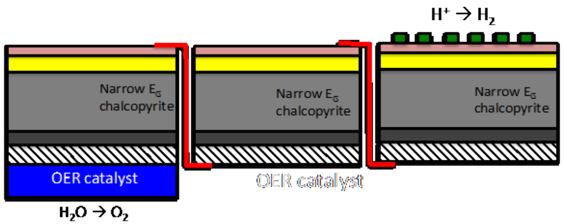


→ **This concept could be extended to other low-temp. PV classes (e.g. a-Si, Perovskites)**

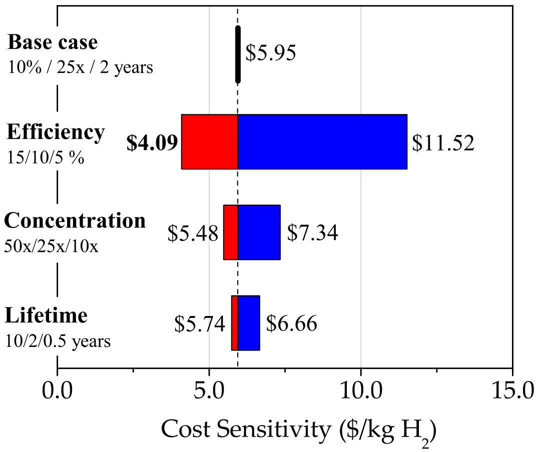
Relevance & Impact – Techno-economics of chalcopyrite-based PEC systems

Current technology

Co-planar architecture

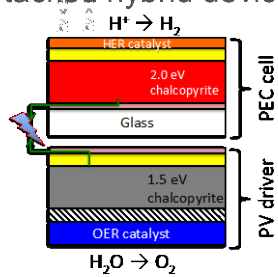


Material cost: 100\$/m², STH 5-10%

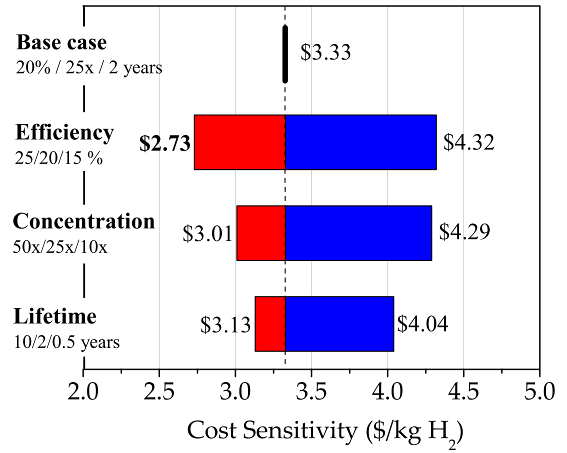


Intermediate goal

Stacked hybrid device

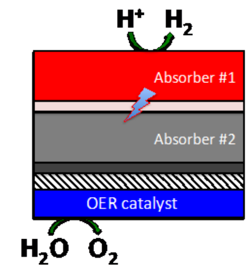


Material cost: 200\$/m², STH target > 15%

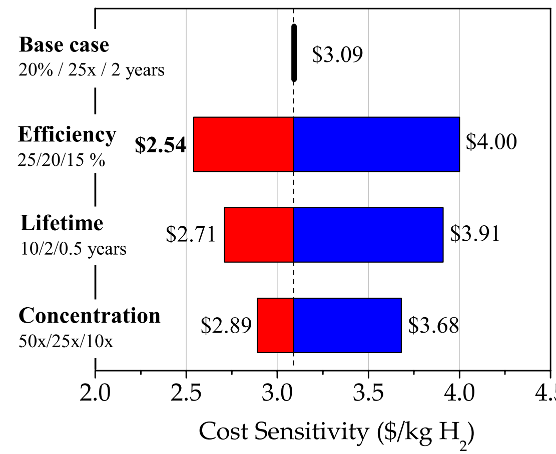


Ultimate goal

(Semi) Monolithic hybrid device



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



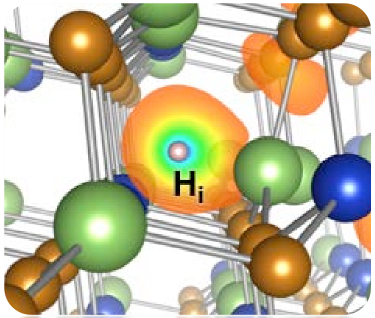
Note: \$1.95 \$/kg H_2 achievable with both 25% STH and 10-year lifetime

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

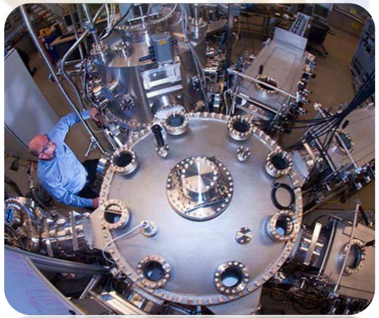
Computational Materials Diagnostics and Optimization (T. Ogitsu).

- **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)

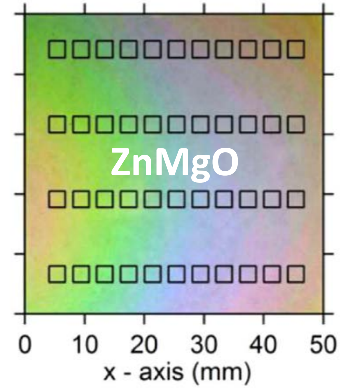
- **Role:** synthesis of high-purity PEC and PV chalcopyrite materials ($CuGa_3Se_5$ and $CuInGaSe_2$).
- **Benefit to this program:** “ideal” vacuum-based chalcopyrites to evaluate new strategies (Na doping).
- **Broader impact for HydroGEN:** materials developed could be used for other H_2 production 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.

P.P. Rajbhandari, Sol. Energ. Mat. & Sol. Cells 159 (2017)



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).

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

→ **All milestones timely met and project well on track to meet all Go/NoGo decision points for Y1**

Task #	Subtask Title	Milestone ID	Description	Significance to Project	Anticipated Quarter	Status
1	1.1-Defects passivation	Milestone #1	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%**
3	3.1-Conductive Polymer	Milestone #2	Produce a nanowire-based composite demonstrating a sheet resistance below 200 Ω/sq and transparency > 70%.	Transparent conductive binder required in the PEC layer exfoliation/transfer concept (semi-monolithic tandem).	Q2	**100%**
2	2.1-Interface: durability	Milestone #3	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	In progress
1	**1.2-Printed Chalcopyrites**	**Go/No-Go #1/2**	**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$_2$ (Y2$^{(\#)}$).**	**Q4**	**97%**
2	**2.1-Interface: durability**	**Go/No-Go #2/2**	**Demonstrate 500 hrs stability in a photoelectrode operating under simulated AM1.5G illumination at a fixed potential that achieves an initial photocurrent of 8 mA/cm2 and does not drop below 5 mA/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**	**80%**

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

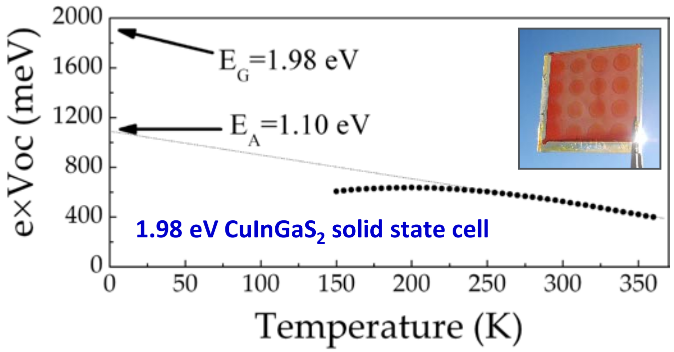
Accomplishments – Task 1: Modeling and Synthesis of Chalcopyrite Photocathodes

Material barrier (AJ)

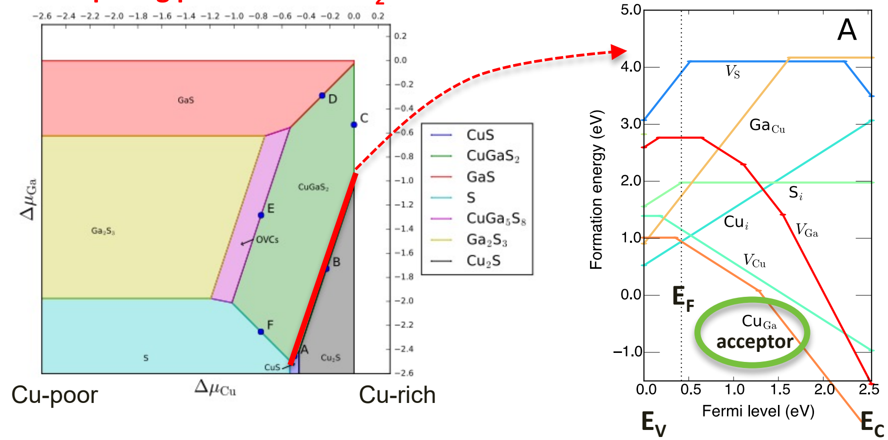
1.1) Theoretical modeling (LLNL node)

a. Defect identification in known gallium-based wide E_g chalcopyrites (e.g. $CuInGaS_2$)

Low photovoltage in Cu-rich wide E_g chalcopyrites could originate from mid-gap defects.

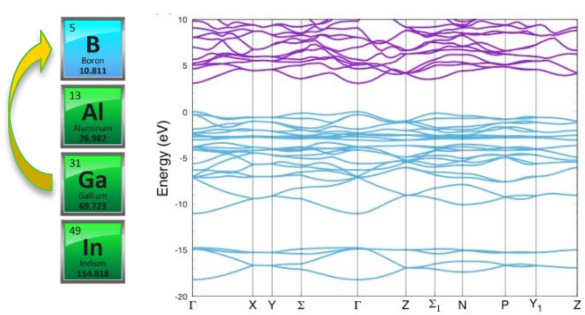


Competing phases in $CuGaS_2$ | **(Ga,Cu) defects in Cu-rich $CuGaS_2$**

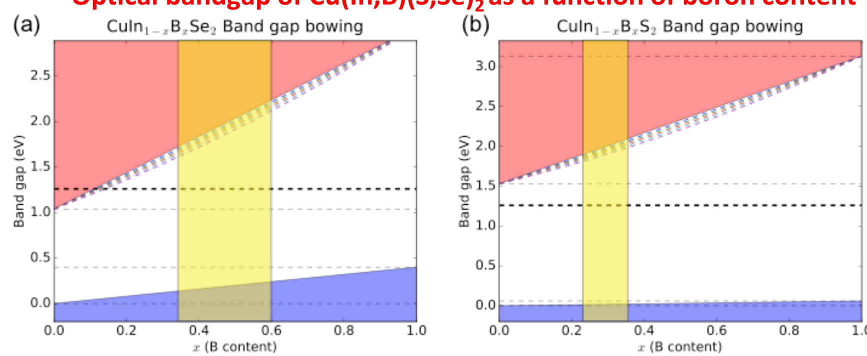


b. Identifying new gallium-free wide E_g chalcopyrites

Electronic band structure of $CuBSe_2$



Optical bandgap of $Cu(In,B)(S,Se)_2$ as a function of boron content



Broader impact to community: LLNL's modeling provides critical information on absorber's thermodynamic stability, defect chemistry and establish the optoelectronic properties of new material candidates.

Accomplishments – Task 1: Modeling and Synthesis of Chalcopyrite Photocathodes

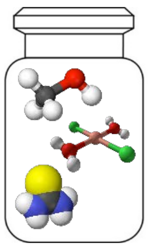
Material barrier (AJ)

1.2) Chalcopyrites "printing" using molecular inks

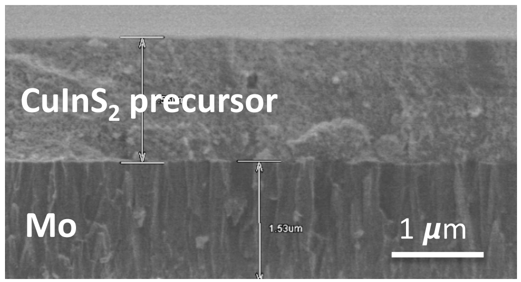
Milestone #1: 100%

a. Process development (UH)

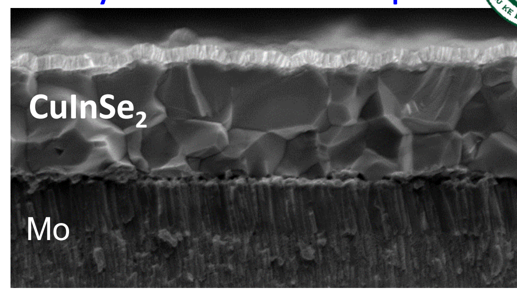
CuCl
$InCl_3$
Thiourea
MeOH



Spin coating + air annealing



Crystallization in Se atmosphere

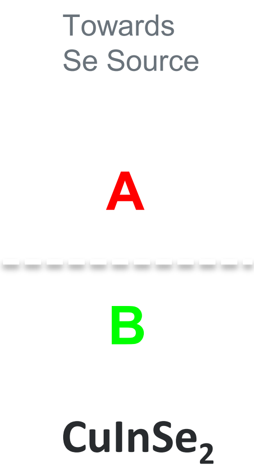


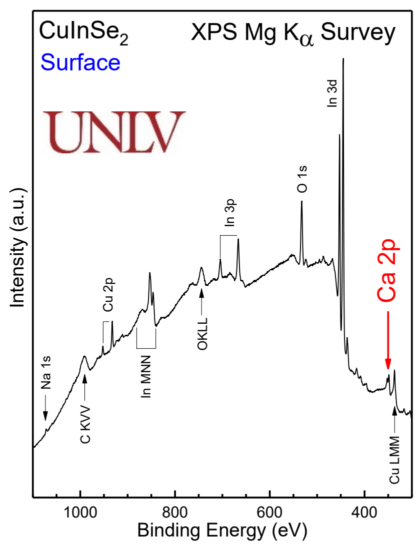
EDX analysis

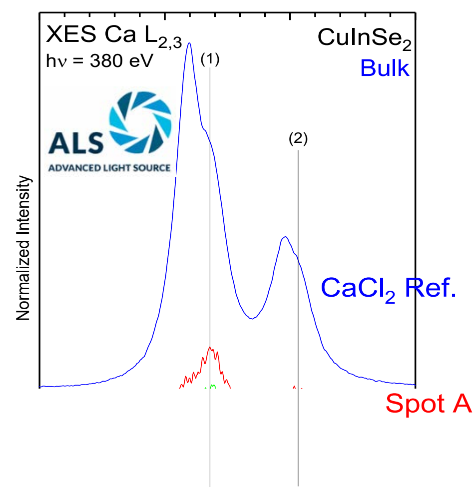
	Element	Precursor	Absorber
Main constituents	Cu	22.7%	31.7%
	In	21.7%	28.4%
	S	39%	3.7%
	Se	0%	29.6%
Impurities	Cl	5.7%	**0%**
	N	1.9%	**0%**
	O	7.8%	**6.2%**

→ High-quality poly-crystalline chalcopyrite achieved via printing

b. Spectroscopic analysis of printed $CuInSe_2$ (UNLV, cross-cutting activity)







Unusual calcium detected both at $CuInSe_2$ surface and in bulk!

Next step: identify if the origin of this foreign element and assess its impact on printed chalcopyrites.

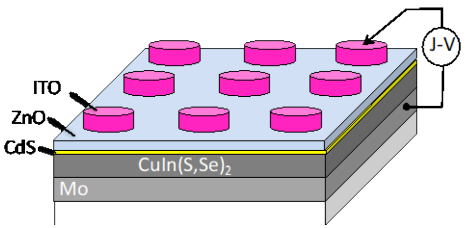
Accomplishments – Task 1: Modeling and Synthesis of Chalcopyrite Photocathodes

Efficiency barrier (AE)

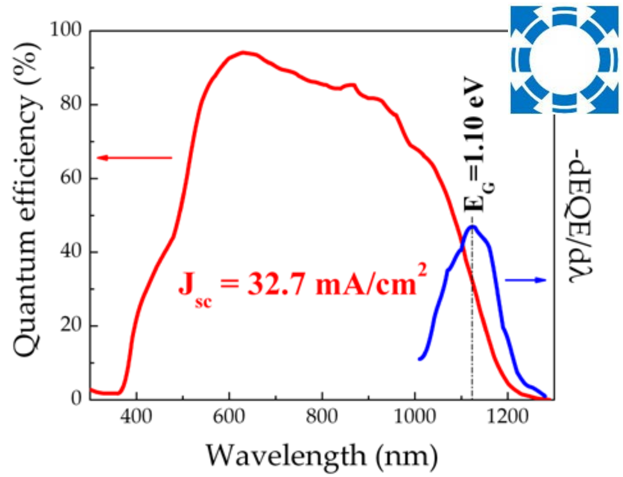
1.2) Chalcopyrite "printing" using molecular inks

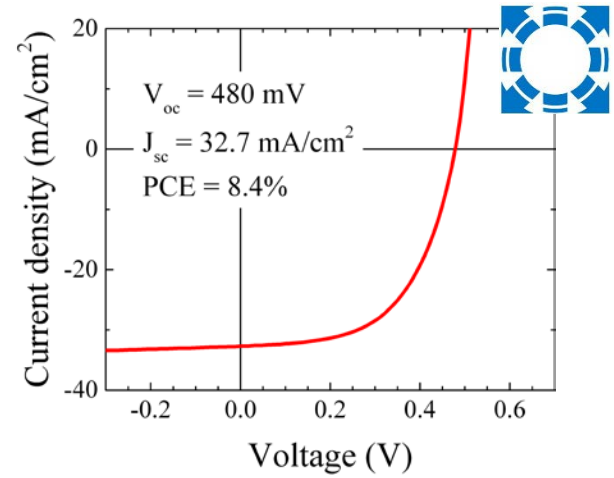
GNG 1/2: 97%

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



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





Device ID	Voc (mV)	Jsc (mA/cm^2)	FF (%)	Eff. (%)
A1-1	406	28.6	53.1	6.2
A1-2	439	31.7	59.4	8.3
A1-3	443	32.1	57.6	8.2
A1-4	**480**	**32.7**	**55.7**	**8.5**
A2-1	386	23.5	42.2	3.8
A2-2	416	31	53.2	6.8
A2-3	395	30.1	52.6	6.3
A2-4	361	19.8	42.1	3.0
A2-5	417	27.6	52.2	6.0
A2-6	427	31.5	59.6	8.0
A2-7	416	31.3	59.4	7.7
A2-8	396	29.2	53.7	6.2
Average	415.2	29.1	53.4	6.6
Std dev	30.7	3.9	5.9	1.8
Rel. err.	0.07	0.13	0.11	0.27

Solid-state analyses validate "printing" approach:

- J_{sc} of best cell (A1-4) > 70% J_{max} of 1.1eV absorber.

→ 100% of GNG criteria on photocurrent

- Free-electron losses of best cell cell (A1-4) = 620 mV.

→ 97% of GNG criteria on open-circuit voltage

Broader impact to community: the "printing" approach offers a simpler method to develop multi-compound materials that are normally challenging to synthesize by vacuum-based techniques.

Accomplishments – Task 2: Interfaces for Enhanced Efficiency & Durability

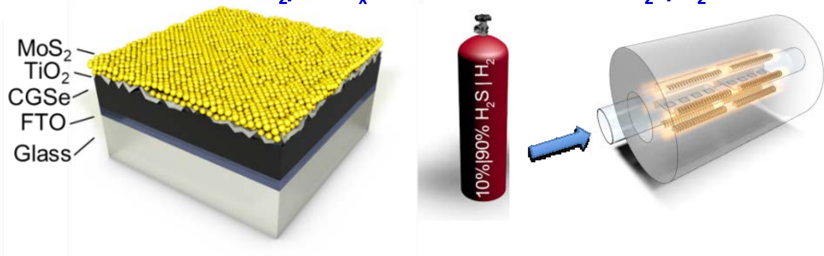
Durability barrier (AF)

2.2) Protection against photo-corrosion (Stanford-NREL's Corrosion)

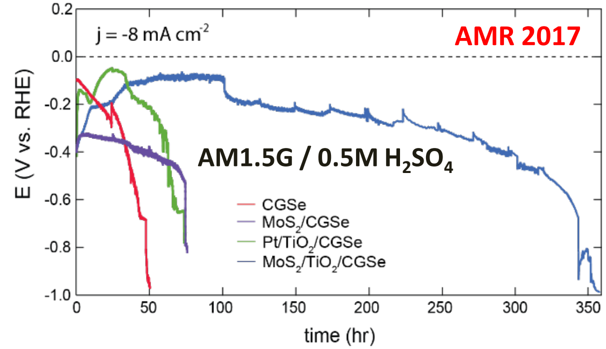
GNG 2/2: 80%

a. Protecting $CuGaSe_2$ in acidic solution with TiO_2/MoS_2

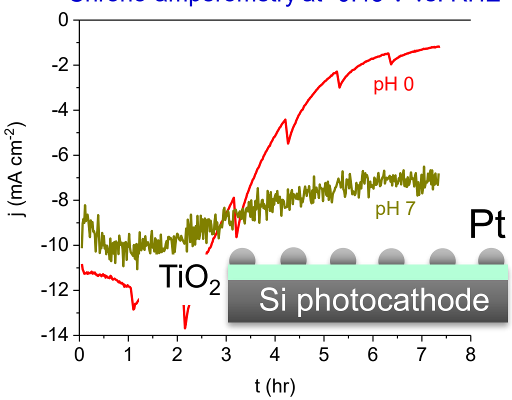
TiO_2/MoO_x ALD + sulfurization in H_2S/H_2

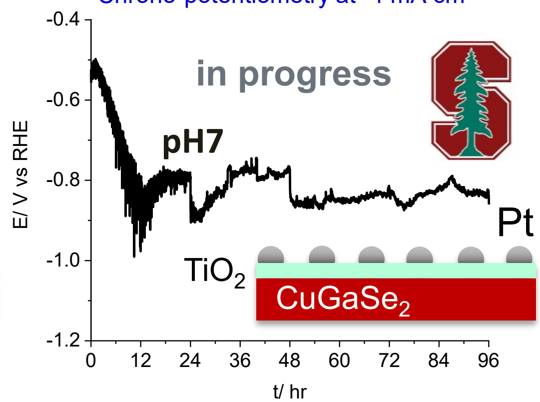


$CuGaSe_2$ durability enhanced with TiO_2/MoS_2 from 50 to 350 hrs

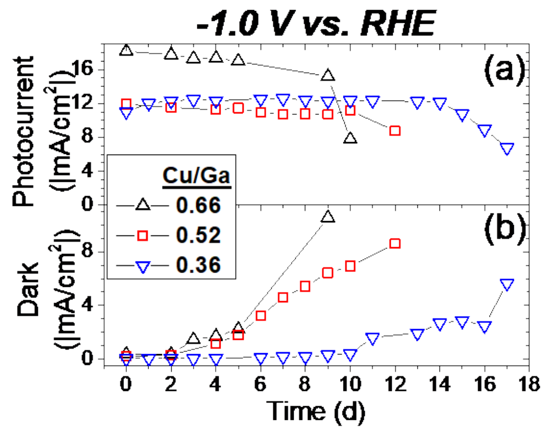


b. Effect of electrolyte pH on durability





c. Effect of Cu/Ga on durability



I-III-VI Node

400 hrs achieved on bare $CuGa_3Se_5$

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.

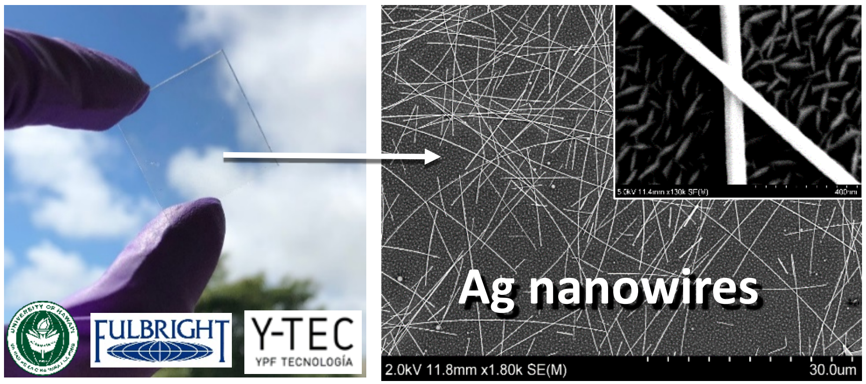
Accomplishments – Task 3: Hybrid Photoelectrode Device Integration

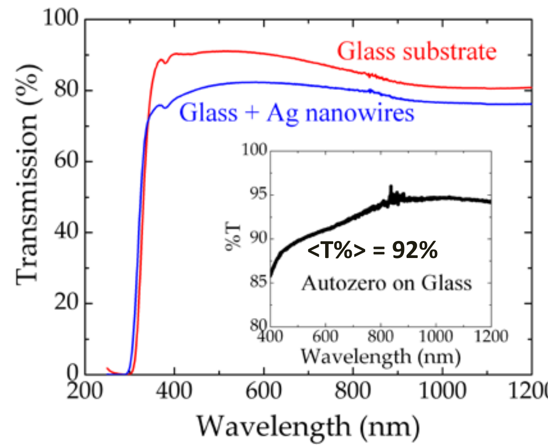
Device barrier (AG)

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

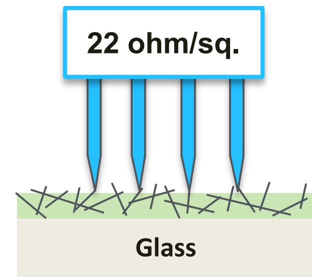
a. Intrinsic properties of binder-less TC layer

Milestone #2: 100%





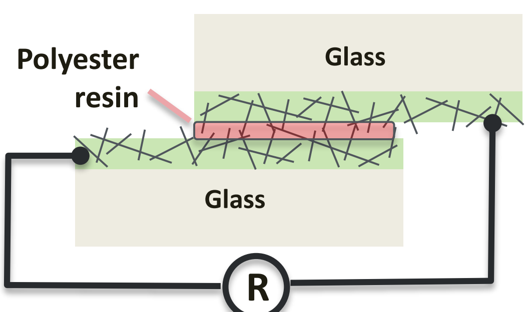
In-plan resistance



As conductive & transparent as commercial FTO.

b. Properties of AgNW/polyester resin TC binder

Stacked architecture



Stack (contact area ≃ 4 cm²)	R (ohm)
FTO/FTO (for reference)	*32*
Glass/AgNW/AgNW/Glass	*50*
Glass/AgNW/**resin**/AgNW/Glass	*150*

Interconnectivity between AgNW in a stacked configuration using polyester resin demonstrated.

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.

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

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.

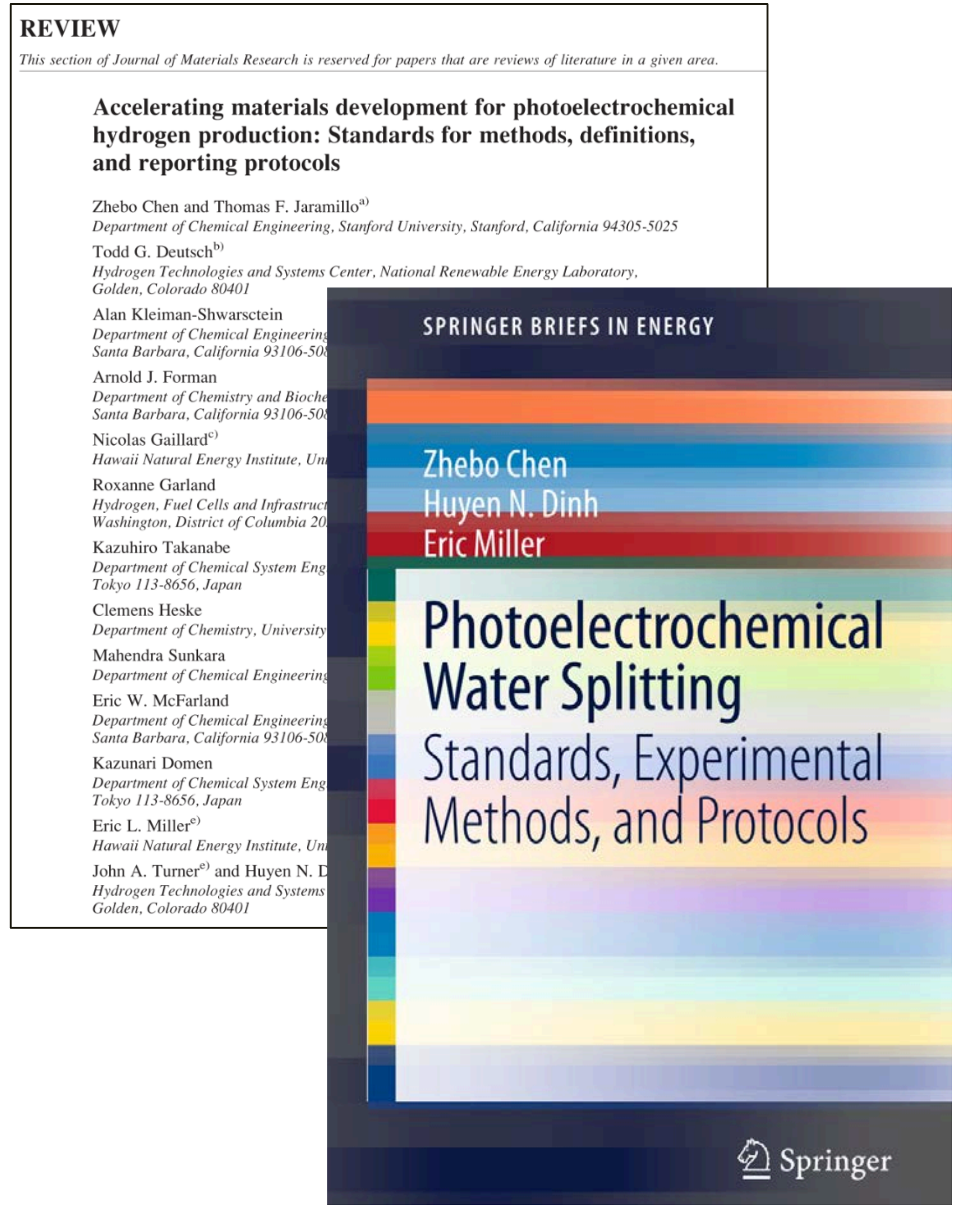
Task #	Academia-Nodes Interactions	Specific activity	Goal	Impact to Project	Barrier
1	UH - LLNL theory Node	**Data exchange** (Raman spectra, solid state electrical measurements, phase diagrams and defects energy mappings).	Calculate the energy and prevalence of point defects.	This work provides guidance for future passivation strategies (i.e. Alkali doping).	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.	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** ($CuGa_3Se_5$).	Evaluate intrinsic stability of Cu-poor chalcopyrites	Clarify the role of chalcopyrites composition on durability.	AF
2	Stanford - NREL Corrosion Node	**Sample exchange** ($CuGa_xSe_y$).	Measure fraction of Cu dissolved in electrolyte during PEC testing (ICPMS)	Elucidate the primary mechanism of photocorrosion in chalcopyrites.	AF
2	NREL I-III-VI Node - NREL Combinatorial Node	**Sample exchange** ($CuGa_3Se_5$).	First combinatorial study: Deposition of composition graded MgZnO buffer	Identify the optimum energetics an n-type buffer should have for a given wide E_G chalcopyrite in order to increase the photovoltage.	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.

- Our team will be participating to the upcoming “benchmarking” workshops to be held in conjunctions to the ECS Seattle and MRS Boston 2018 meetings.



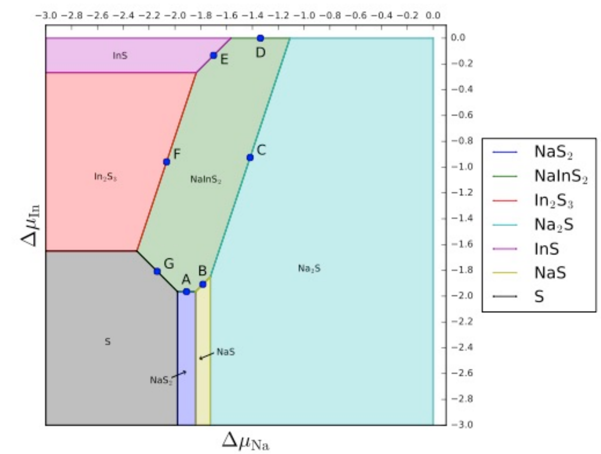
Collaboration – Benefits of information provided into the HydroGEN data-hub

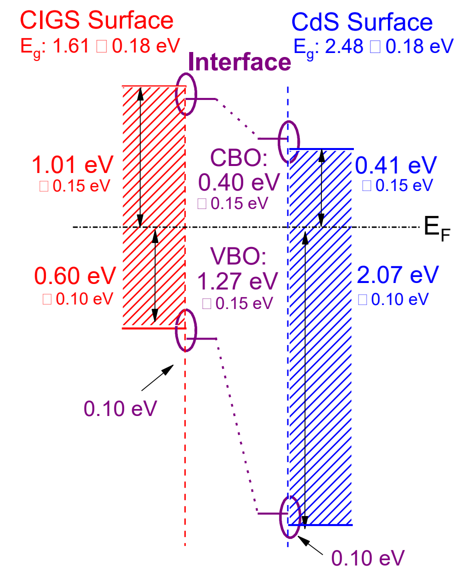
Following our "**theory, synthesis and advanced characterization feedback loop**" philosophy, we aim at developing material and interface models that will accelerate development of renewable H_2 production technologies.

During phase 1, data uploaded on the HydroGEN-hub include 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.





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Proposed Future Work

Estimated budget: $425,000

Task 1 - Modeling and Synthesis of Chalcopyrite Photocathodes

Sub-task 1.1 – defect passivation (known Ga-based materials): test 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: produce materials compatible with 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 MoS_2/TiO_2 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 conductive binder and test alternative media.
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: create the first efficient chalcopyrite-based tandem device.**

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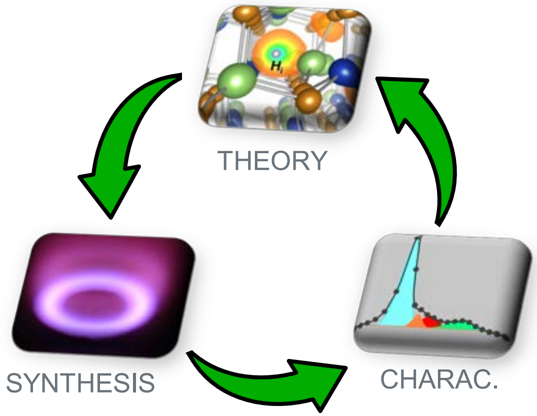
Project Summary

<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.



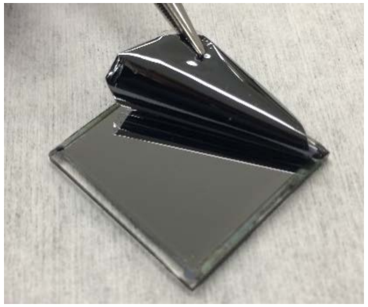
<u>Technical objectives:</u>

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

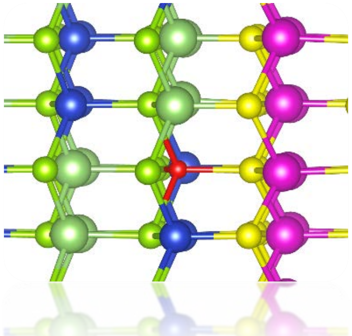
- To address **Materials Efficiency** and **Materials Durability** barriers, we develop new interfaces to improve chalcopyrites surface energetics and chemical stability during PEC operation.

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

Transferable PEC thin films



Interface modelling



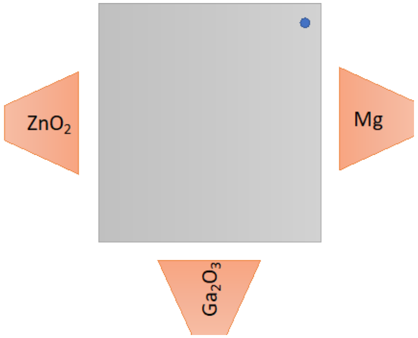
<u>Benefits for HydroGEN and scientific community:</u> our models can be used to predict the properties of future PEC bulk (optical absorption, thermodynamic stability, defect chemistry) and interface (band-edges offsets) properties.

Technical Back-Up Slides

Accomplishments - Task 2: Interfaces Engineering for Enhanced Efficiency and Durability

2.1 Improving chalcopyrites energetics (UH-NREL's Combinatorial and I-III-VI nodes)

Combinatorial deposition of (Zn,Mg)O:Ga thin films



Synthesis

- (Zn,Mg)O:Ga thin films deposited from ZnO, Mg, Ga_2O_3 targets in Ar/O_2.
- Substrates: SiO_2 heated to 100C or 200C.

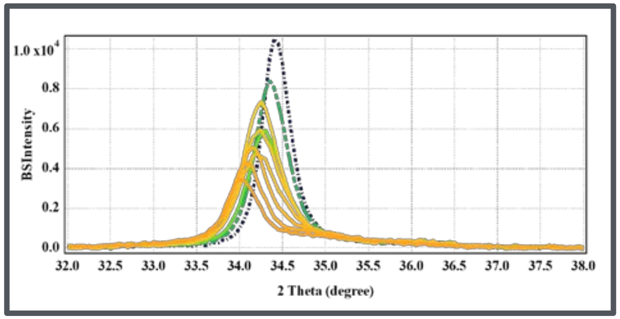
Characterization

- XRD patters are all (0002) oriented wurtzite ZnO, no MgO or Ga_2O_3 peaks observed.
- With increasing Ga/(Ga+Zn) atomic ratio
  - the ZnO (0002) peak intensity reduces and shifts towards lower angle.
  - Conductivity decreases, indicating that there may be too much Ga in the film.

Next steps

- Quantify Mg content using RBS
- Determine conduction band shift
- Deposit on $CuGa_3Se_5$ wide bandgap absorbers

XRD mapping



Conductivity mapping