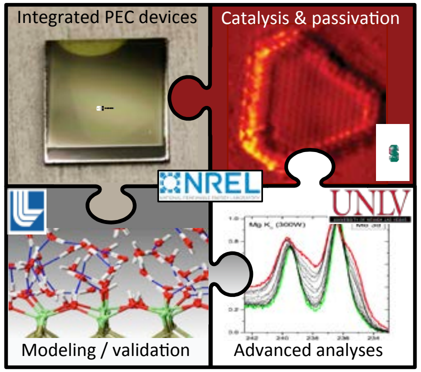
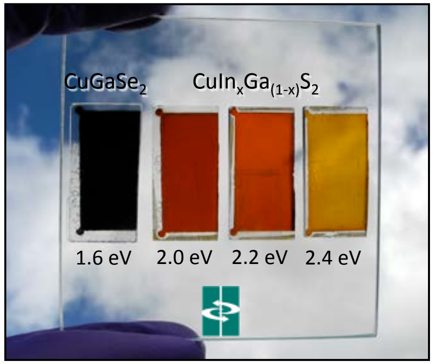
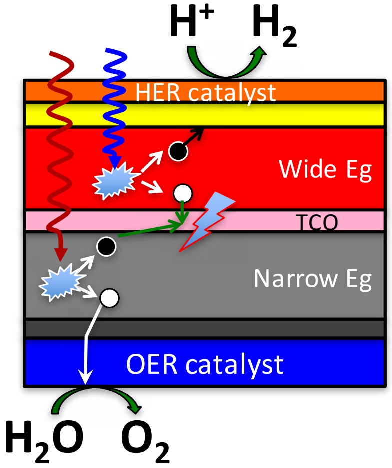






Wide Bandgap Chalcopyrite Photoelectrodes for Direct Solar Water Splitting

PI: Nicolas Gaillard
Hawaii Natural Energy Institute

2017 DoE Annual Merit Review
June 8th 2017

Project ID#: PD116

Overview

Timeline

- Project start date: 10/1/2014

- Passed GNG#1: 10/6/2015

- Passed GNG#2: 10/5/2016

- Project end date: 9/30/2017

Budget

- Total budget funding: $3,050,000
  - DoE share: 100%
  - Contractor share: 0%
- Total DoE funds spent: $2,089,000

(as of 04/2017, including Nat. Labs).

Barriers

Challenges for PEC H2 production technology:

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

Partners / primary role

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

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

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

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

- NREL PEC team (K. Zhu, T. Deutsch, J. Turner)
→ Device validation and PEC reactor design

- NREL CIGS group (C. Muzzillo)
→ New chalcopyrites and buffers

Relevance - Objectives

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

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

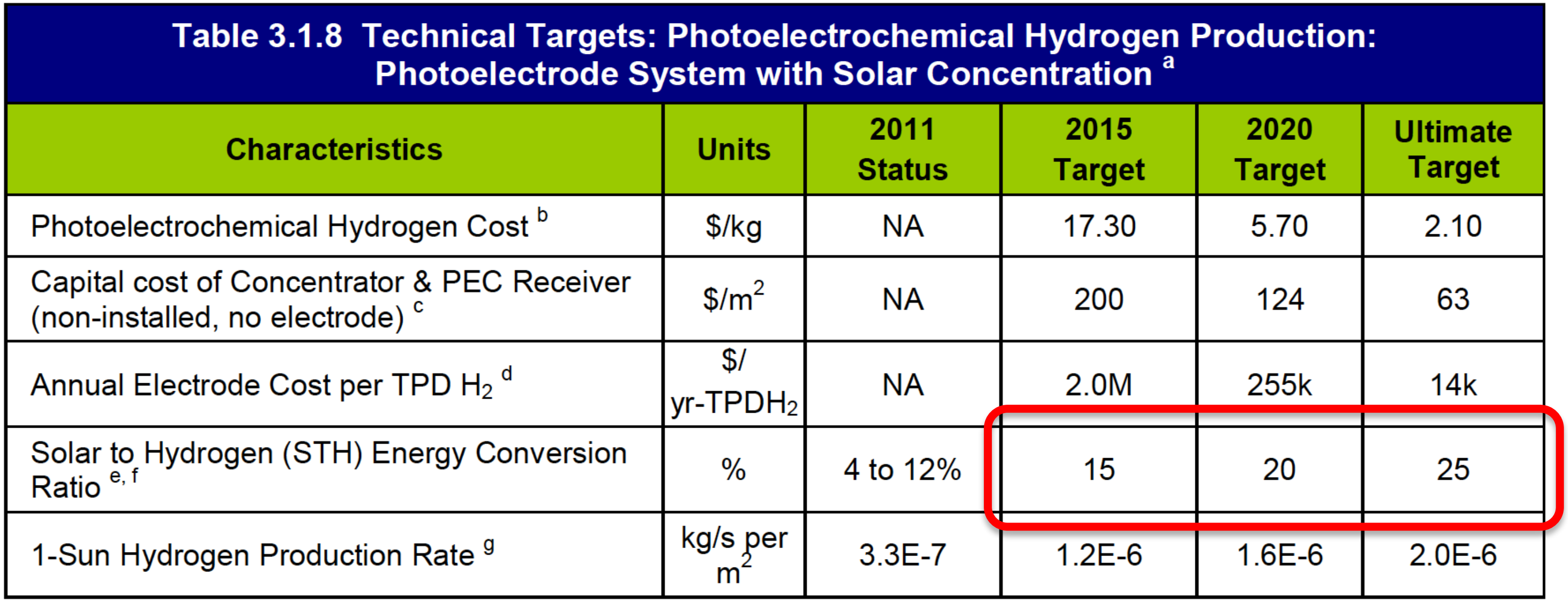
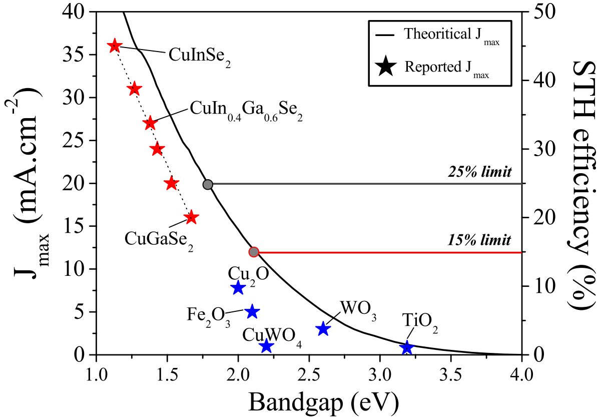


Table 3.1.8 Technical Targets: Photoelectrochemical Hydrogen Production: Photoelectrode System with Solar Concentration [a]

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

Relevance – Benefits of copper chalcopyrites for PEC H_2 production

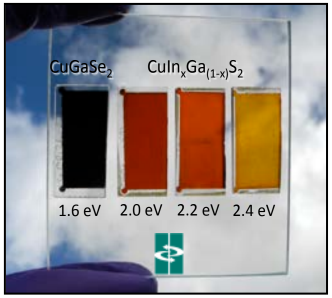
1. PV-grade materials



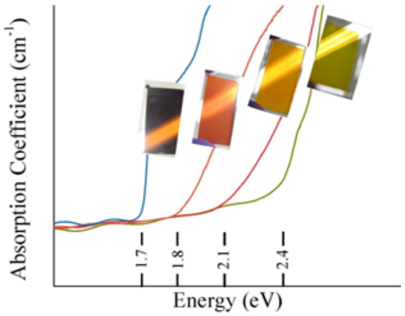
Photocurrent densities in line with DoE targets

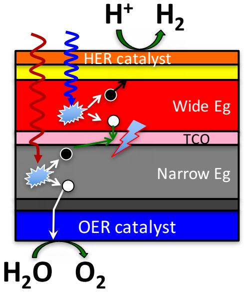
2. Bandgap tunable

Cu(In,Ga)S_2



CuGa(S,Se)$_2$



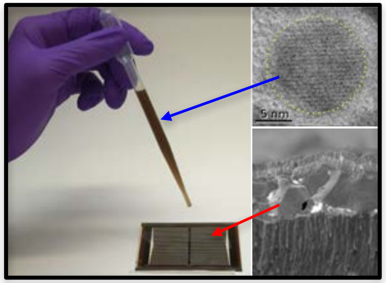


PV driver and PEC electrode can be stacked for efficient PEC H_2 production

3. Cost-effective processes developed

Production

R&D

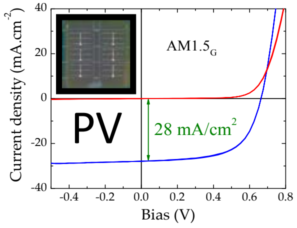


Solution processed chalcogenide material (ONR funding)

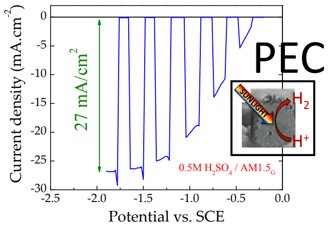
The CIGSSe class can meet DoE's material target cost of $60/m².

4. Efficient PEC water splitting demonstrated with CIGSSe

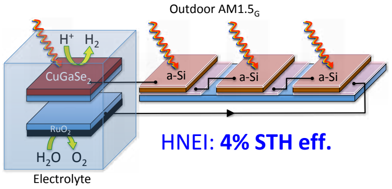
Electrodes



vs.

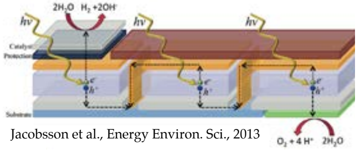


Devices



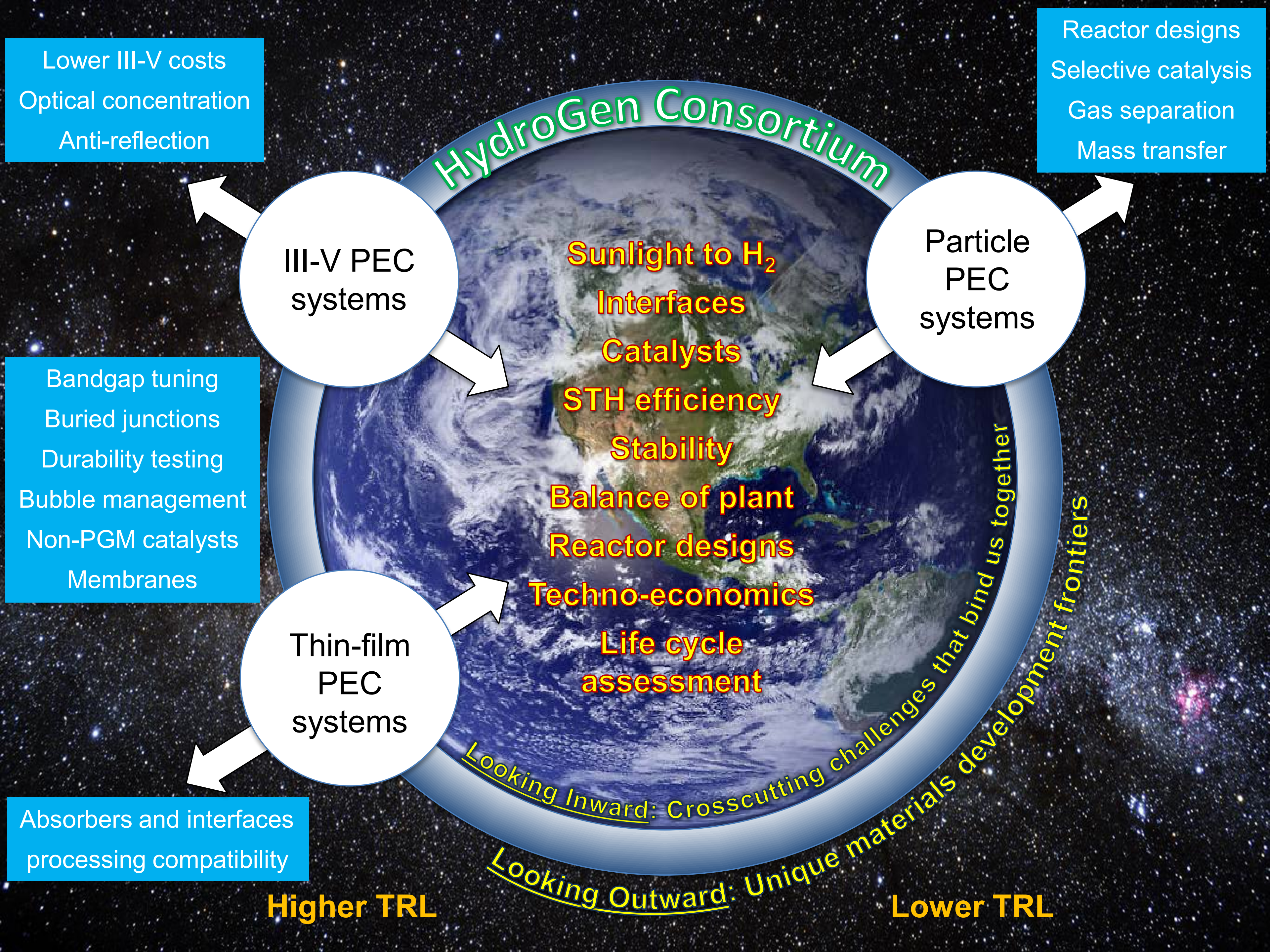
HNEI: **4% STH eff.**

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



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

Take home message: copper chalcopyrites ($CuInGaSe_2$) are excellent candidates for PEC water splitting. New materials with wider bandgaps are needed to relocate PV driver(s) under the photocathode (HPE structure) in order to achieve STH efficiencies >10%.



HydroGen Consortium

Lower III-V costs
Optical concentration
Anti-reflection

Reactor designs
Selective catalysis
Gas separation
Mass transfer

III-V PEC systems

Particle PEC systems

Thin-film PEC systems

Sunlight to H_2
Interfaces
Catalysts
STH efficiency
Stability
Balance of plant
Reactor designs
Techno-economics
Life cycle assessment

Bandgap tuning
Buried junctions
Durability testing
Bubble management
Non-PGM catalysts
Membranes

Absorbers and interfaces
processing compatibility

Looking Inward: Crosscutting challenges that bind us together

Looking Outward: Unique materials development frontiers

Higher TRL

Lower TRL

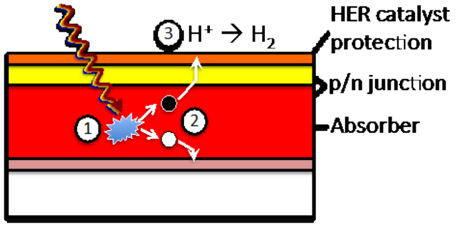
Approach – Milestones

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

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

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

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



PEC cell

Task#	**FY15 Milestones**	Due Date	**Status**
1	Synthesize a CuInGaS_2 thin film material with controlled stoichiometry & microstructure	12/2014	**Complete**
2	Fabricate Cu(In,Ga)S_2 cells with Voc> 600 mV	03/2015	**Complete**
3	Durability > 500 hrs at 8 mA/cm^2 with a chalcorpyrite photoelectrode	06/2015	**25%**
4	Chalcopyrite photoelectrode with bandgap > 1.7eV that generates at least 10-12 mA/cm2	09/2015	**Complete**

Go/No-Go decision criteria: Demonstrate a chalcopyrite photoelectrode material with bandgap > 1.7eV that generates a photocurrent density of at least 10-12 mA/cm^2

Task#	**FY16 Milestones**		
1	Cu(In,Ga)S_2 solar cells with a photoconversion efficiency > 6%	12/2015	**Complete**
4	Photocurrent density relevant to 15-16% STH with chalcorpyrite 12-13 mA/cm^2	03/2016	**Complete**
3	Durability > 750 hrs at 8 mA/cm^2, with a stretch goal of 1,000 hrs	06/2016	**45%**
2	Fabricate Cu(In,Ga)S_2 cells with Voc> 750 mV	09/2016	**Complete**

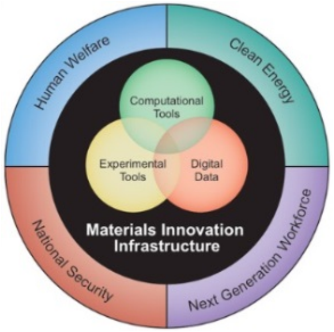
Go/No-Go decision criteria: Demonstrate a wide bandgap chalcopyrite-based heterojunction with an open circuit potential of at least 750 mV

Task#	**FY17 Milestones**		
1	Photocurrent density relevant to 16-17% STH with a chalcopyrite 13-14 mA/cm2	12/2016	**92%**
2	Fabricate Cu(In,Ga)S_2 cells with Voc> 900 mV	03/2017	**88%**
3	Durability > 1,000 hrs at 8 mA/cm^2, with a stretch goal of 2,000 hrs	06/2017	
4	HPE PEC device with a standalone STH of >15% generting at least 3L of H2 in 8 hrs.	09/2017	

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

Approach – Integrating experiment, computation and theory

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



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

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

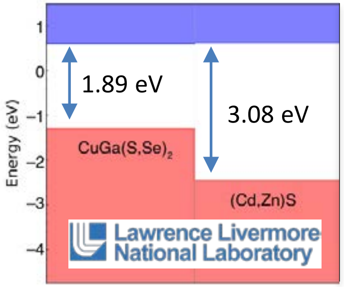
Accelerating materials development using integrated modeling, synthesis and advanced characterizations:

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

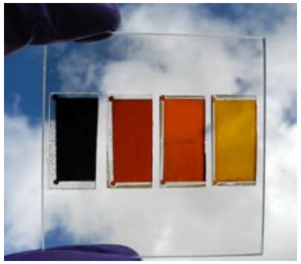
2. Theory-guided synthesis of wide bandgap chalcopyrites using state-of-the-art vacuum-based deposition tools.

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

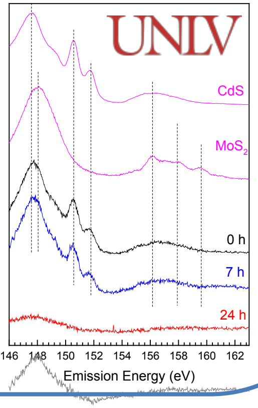
Modeling



Synthesis



Advanced analysis



Accomplishments – Task 1: PV-grade absorbers

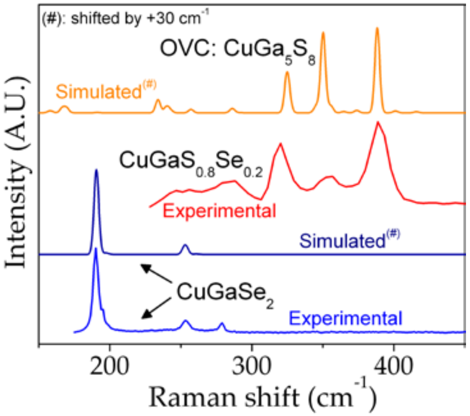
AE / AJ barriers

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

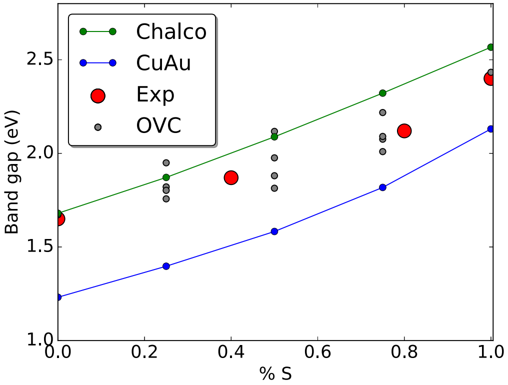
a. Identifying competing crystallographic phases in wide bandgap chalcopyrites

→ Case of $CuGa(S,Se)_2$: calculated bandgap values assuming chalcopyrite phase do not match with experiments.

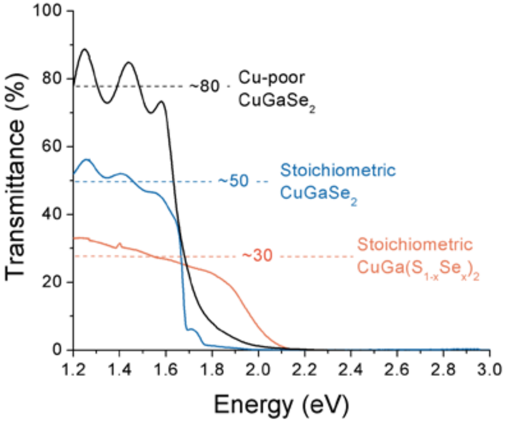
Ordered **V**acancy **C**ompounds (OVC: $CuGa_5S_8$) detected in CGSSe by Raman.



New bandgap calculations show better match between CGSSe and OVC.

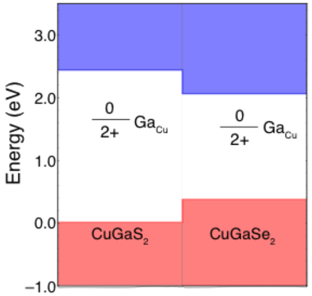


Next step: identify if OCVs are responsible for CGSSe's low transmittance.



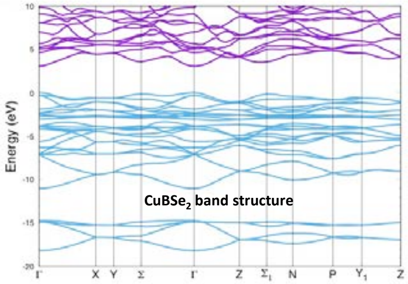
b. Identifying new materials candidate with improved electronic properties

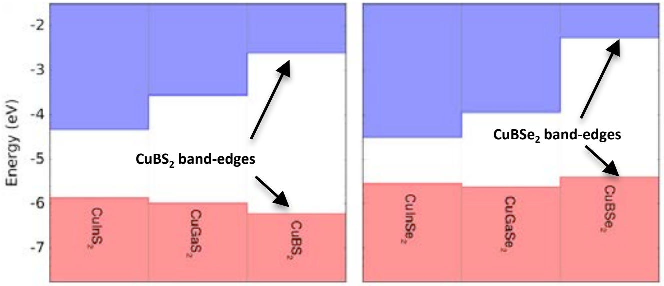
Ga_{Cu} antisites create deep traps (0.5 eV below E_c) in chalcopyrites which deteriorates optoelectronics



Alternative **Ga-free** wide bandgap chalopyrite candidates identified by DFT:

$Cu(In,B)(S,Se)_2$





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

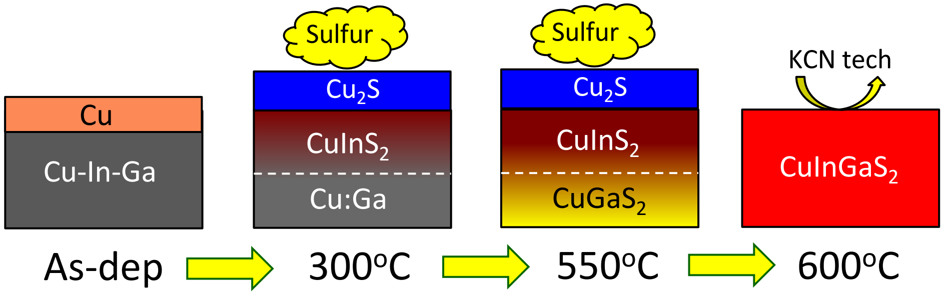
Accomplishments – Task 1: PV-grade absorbers

AE / AJ barriers

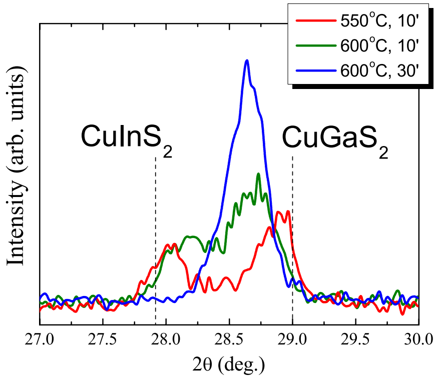
2. Improvement of bandgap tunable CuInGaS_2 absorbers

a. Understanding growth thermodynamics

Close capsule annealing



X-ray diffraction measured on sulfurized CuInGa alloys



→ Sulfurization process successfully developed to create phase-pure wide bandgap $CuInGaS_2$.

b. Solid-state properties of wide bandgap $CuInGaS_2$

SEM cross-section of a CIGS_2-based solar cell

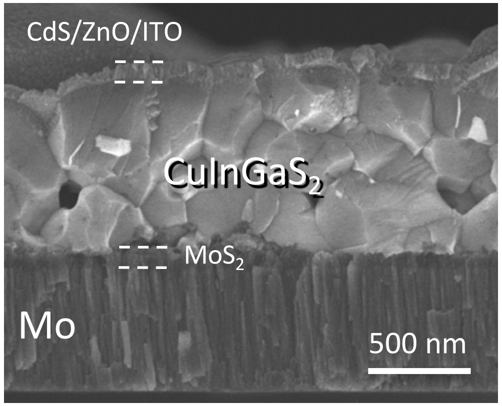
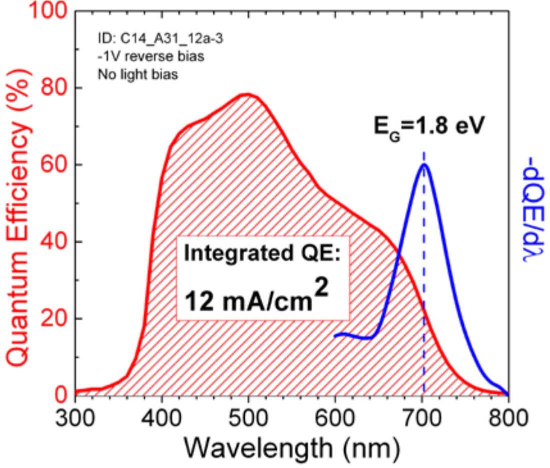
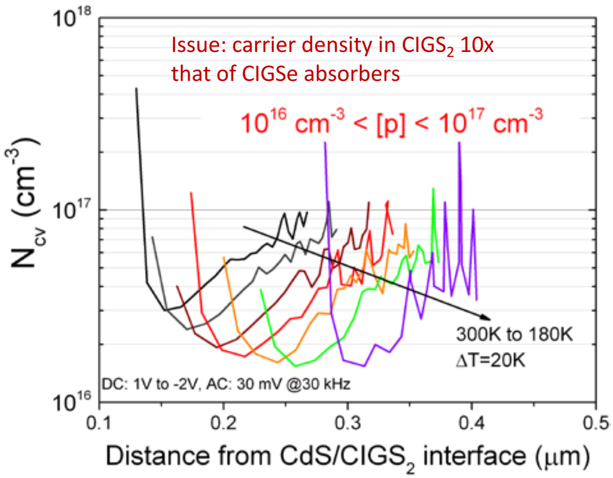


Photo-conversion efficiency



Free carrier profile density



→ Excellent photo-conversion achieved with CIGS_2 (up to 80%), J=12 mA/cm^2 (PV configuration),

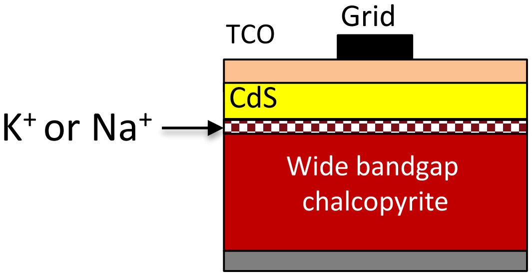
→ High free carrier density can limit performance: to be addressed with sub-surface doping (see next slide).

Accomplishments – Task 2: Sub-surface energetics

AE / AG barriers

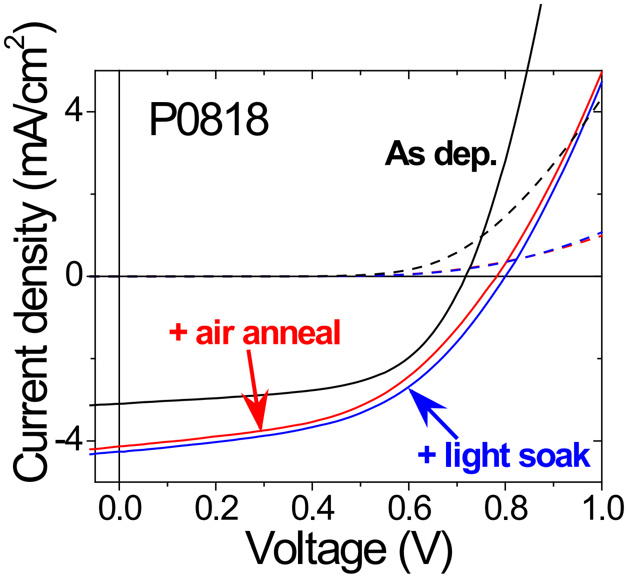
1. Sub-surface treatment for improved energetics

- → $CuGa_3Se_5$ co-evaporation
- → Alkali (K, Na) post treatment
- → n-type CdS buffer treatment
- → Solar cell integration & testing



NREL's CIGSe cluster tool

Treatment	E_g (eV)	V_{OC} (mV)	J_{SC} (mA/cm^2)
$CuGa_3Se_5$	1.93	713	3.3
+ air anneal		789	4.2
+ light soak		800	4.3
$CuGa_3Se_5$ + **K**$GaSe_2$	1.84	718	5.0
+ air anneal		747	5.2
$CuGa_3Se_5$ + **Na**F	1.83	574	5.7
+ air anneal		719	7.1
$CuGa_3Se_5$ + **$Cu(GaIn)_3Se_5$**	1.70	734	8.9
+ air anneal		752	9.7



→ $CuGa_3Se_5$ and $CuGaSe_2$ with Eg> 1.7 eV and open circuit potential > 750 mV successfully fabricated (GNG #2).

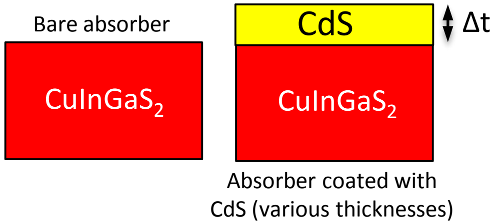
Accomplishments – Task 2: Sub-surface energetics

AE / AG barriers

2. Improving energetics with n-type buffer materials

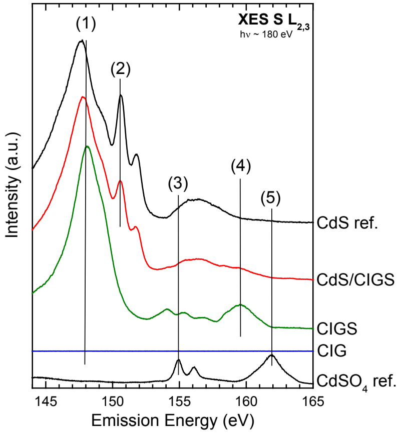
a. 1st round: CdS n-type buffer

First sample set provided by HNEI to UNLV for spectroscopic analysis

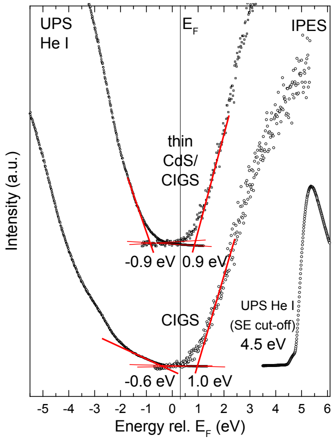


Absorber coated with CdS (various thicknesses)

Composition



Energetics



Electronic and chemical surface structure at each process step:

- Composition and chemical bonding
- Band edges, surface band gap, and work function
- Interface optimization

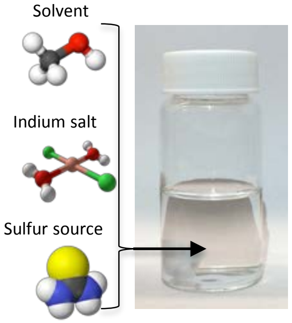
b. 2nd round: In_2S_3 n-type buffer

Conventional CdS process

Vol/CdS layer: **100 mL**

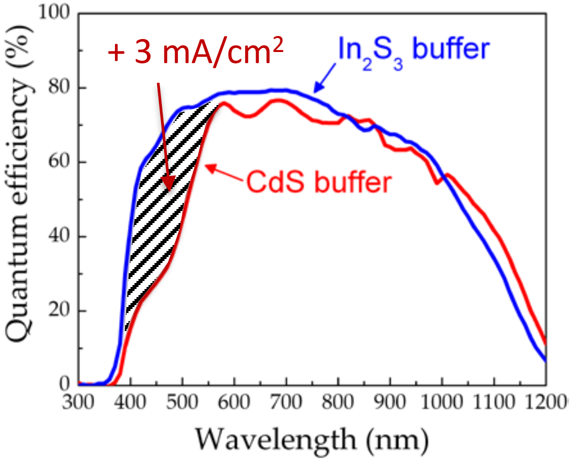
vs.

New printable In_2S_3 ink

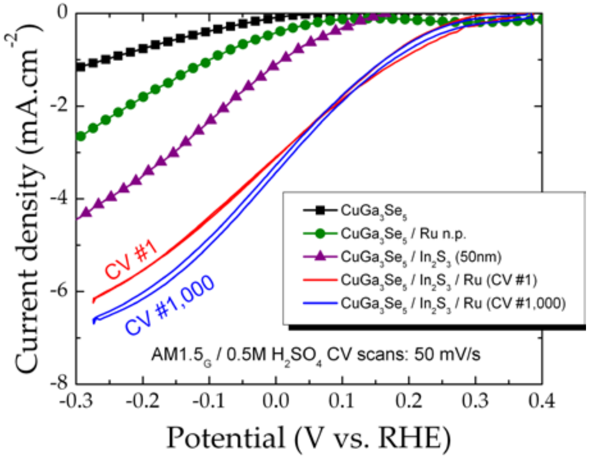


Vol/In_2S_3 layer: **100 µL**

PV test with 1.0 eV $CuInSe_2$



PEC test with 1.8 eV $CuGa_3Se_5$



→ New molecular ink-based process successfully developed to synthesize In_2S_3 buffer,

→ In_2S_3 buffer allows for higher photo-conversion in UV (+3mA/cm²): critical for wide bandgap chalcopyrites,

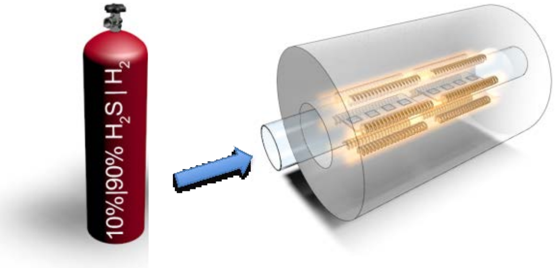
→ Preliminary tests show good durability for In_2S_3 in 0.5M sulfuric acid (pH 0.5).

Accomplishments – Task 3: Surface catalysis/corrosion resistance

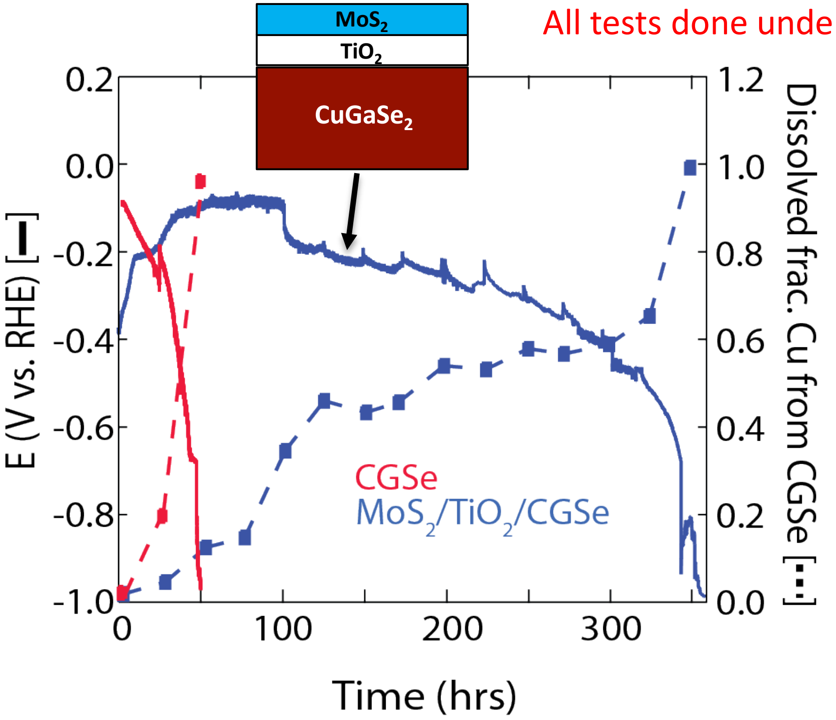
AE / AF barriers

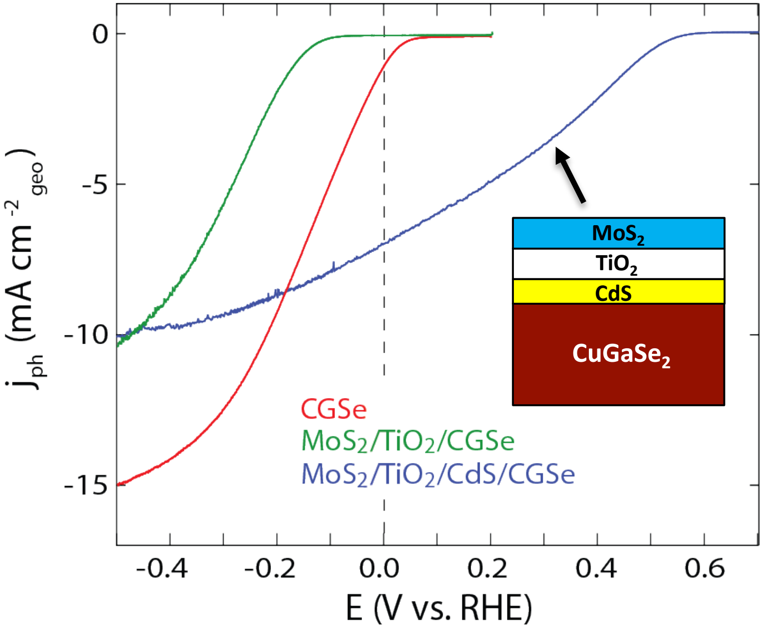
1. Corrosion resistance enhancement using MoS_2 – TiO_2 films

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



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





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

CdS buffer layer improves the onset of CGSe photocathodes.

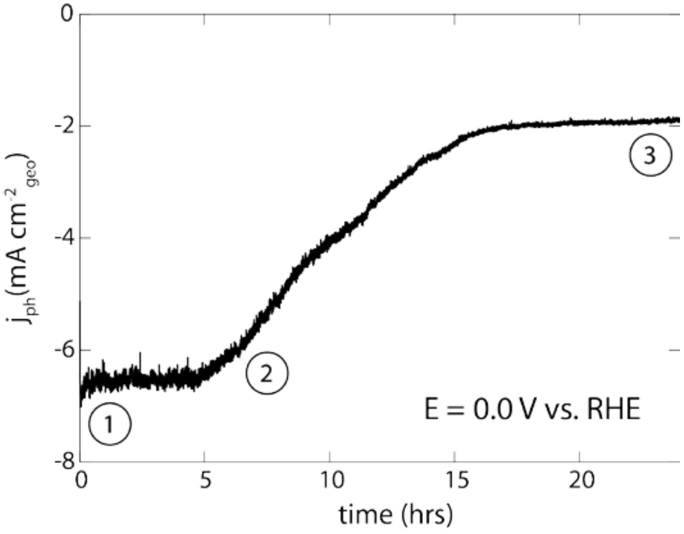
T.R. Hellstern, A. D. DeAngelis, L.A. King, N. Gaillard, T.J. Jaramillo. *In Preparation*

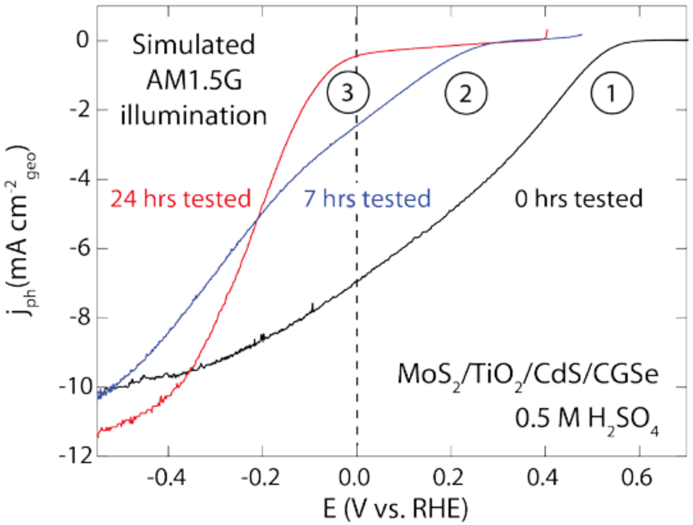
Accomplishments – Task 3: Surface catalysis/corrosion resistance

AE / AF barriers

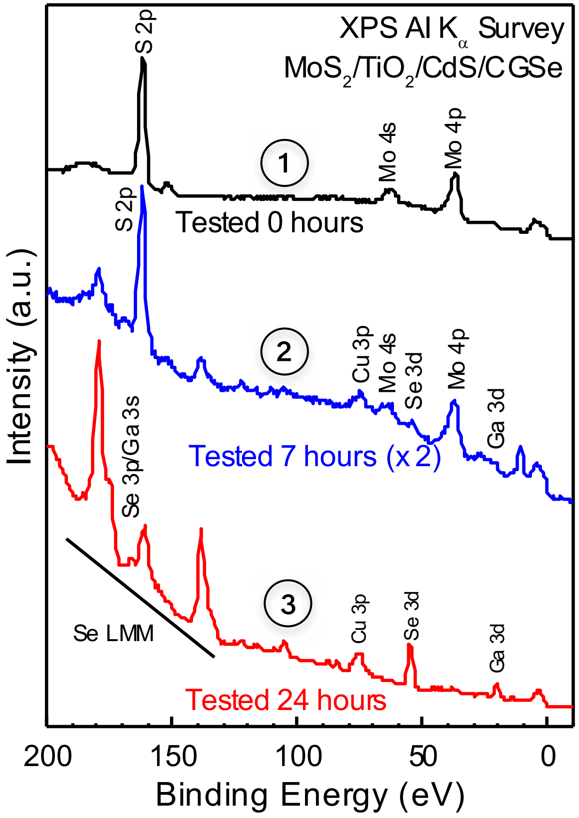
2. Electrochemical and spectroscopic characterization of CdS/CGSe photoelectrodes

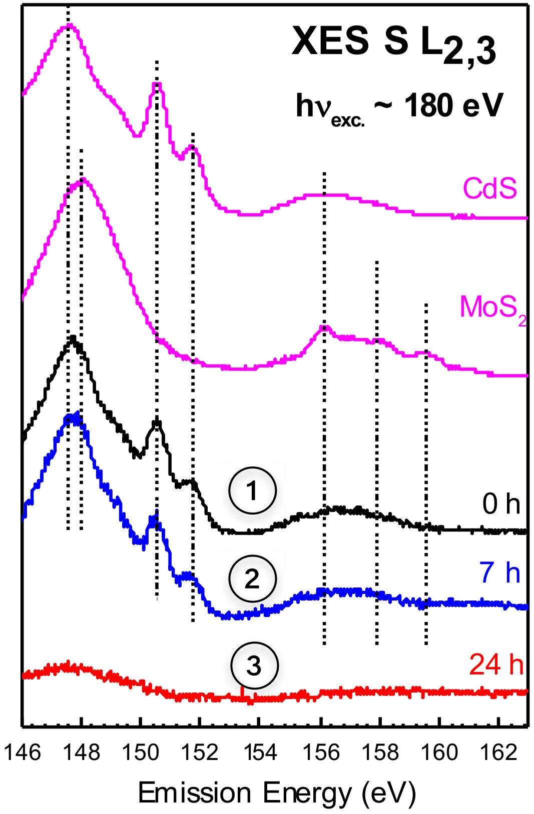
Electrochemical Characterization (Stanford)





Spectroscopic Characterization (UNLV)





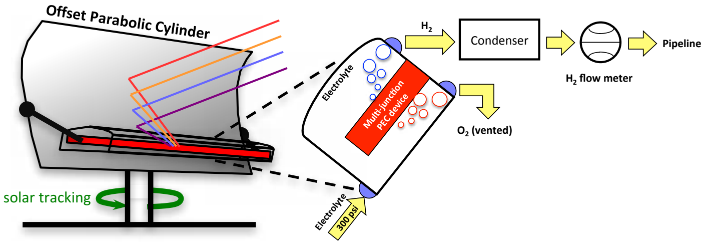
Combination of electrochemical and spectroscopic characterization leads to deeper understanding of degradation mechanisms.

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

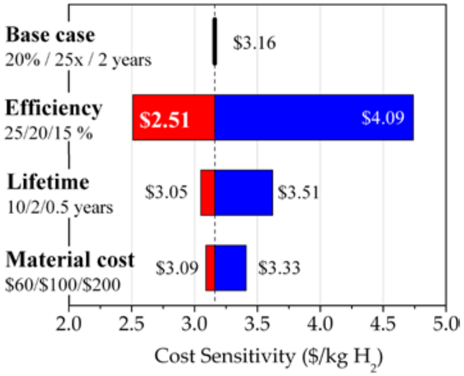
Accomplishments – Task 4: CIGS-based PEC device

AG barriers

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



H2A model parameters:
- 50 TPD centralized plan with 98% operating capacity
- "Type 4" PEC reactor,
- Reactor + optics (25x base case) replaced every 10 yrs.



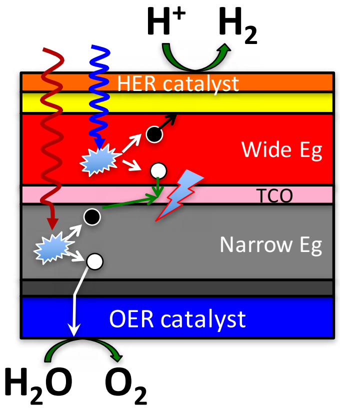
→ STH efficiency is the parameter with the largest leverage on H2 production costs.

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

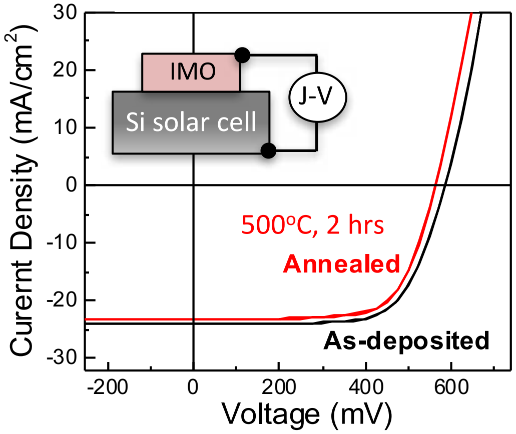
→ Tandem: STH_{max}=25%, **H_2 @ $2.51/kg**

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

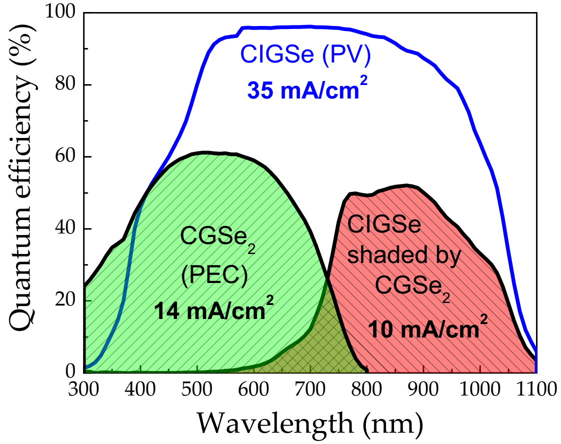
2. Paths for chalcopyrite-based tandem PEC devices



Temperature-resistant TCO (Mo-doped InO_2) tested on Si solar cells



Optical balance between CIGSe PV driver and CGSe photocothode



→ Temperature-resistant transparent conductive oxide (TCO) identified for monolithic tandem: Mo-doped InO_2,

→ Optical analyses demonstrate a good match between CIGSe PV driver and CGSe photocathode: J> 10 mA/cm^2,

→ Upcoming monolithic devices: **Si/IMO/CGSe**, then **GaAs/IMO/CGSe** and finally **CIGSe/IMO/CGSe**.

Accomplishments - Response to reviewers' comments

"The project is mainly focused on PV and its link to hydrogen production is not clear."

- → Testing absorber candidates in PV configuration provides reliable (no photo-corrosion) and statistical data to accelerate their development. For a given chalcopyrite, we find that photocurrent densities measured on both PEC and PV cells are nearly identical,
- → In the final tandem **PEC** device, the transparent conductive oxides (ZnO, ITO) used for solid-state characterization will be replaced with MoS_2/TiO_2 HER/protective layers,
- → We note that all known chalcopyrite PEC candidates suffer from poor surface energetics with respect to water splitting. We have demonstrated that buffer layers (CdS, In_2S_3) improve chalcopyrite photocathodes surface energetics with onset potential anodic shift up to 800mV. With the current state-of-the-art, this surface treatment is a necessary step towards un-biased water-splitting.

"The work has too much emphasis on efficiency. This does not mean a lot if the device can not run for any reasonable period of time."

- → In this project, we have decided to address absorbers, energetics and durability in 3 distinct tasks, such that no single roadblock will hinder the overall progress. Two of these tasks (1 and 2) are focused on efficiency, and one (task 3) on durability,
- → Our buried junction approach offers the possibility to develop both the efficient photo-converter (absorber-buffer) and the protective coating independently,
- → We note that durability over 1,500 hrs has been demonstrated with atomically flat silicon photocathodes protected with MoS_2. Our current effort is to optimize MoS_2 deposition on rough polycrystalline chalcopyrites to meet our 1,000-hr durability target.

Collaborations

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

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

Project-specific collaborations:

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

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

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

- EMPA (A. Braun): in-situ characterization of phase transformation during materials synthesis (**TASK 1**),

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

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

Remaining challenges & barriers / Proposed future work

Task 1. PV-grade wide bandgap absorbers

Challenges/Barriers: chalcopyrites' chemistry (i.e. Cu-poor, S-rich…etc.) can have a profound impact on their opto-electronic properties.

Proposed Future Work:
- finalize our study on CuGaSSe and CuInGaSSe and conclude on the effect of Ordered Vacancy Compounds,
- re-focus effort on best candidates for final tandem PEC structure: Cu-poor $CuGaSe_2$ and $CuGa_3Se_5$.

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

Challenges/Barriers: best open circuit potential are 100mV lower than project final goal (900mV)

Proposed Future Work:
- finalize the development of alternative buffer layers, including In_2S_3 and ZnOS,
- focus on most promising chalcopyrite sub-surface doping: Cd^{2+}, Na^+ and K^+.

Task 3. Surface catalysis and corrosion resistance

Challenges/Barriers: new MoS_2 and TiO_2 ALD process successfully developed, yet durability limited to 350 hours

Proposed Future Work:
- continue to develop ex-situ and in-situ spectroscopic techniques to better understand degradation mechanisms,
- evaluate SiO_2 passivation layer as alternative to TiO_2 to meet the 1,000+ hrs durability goal.

Task 4. Device certification and efficiency benchmarking

Challenges/Barriers: create the first chalcopyrite-based monolithic tandem PEC device.

Proposed Future Work:
- validate tandem structure using CGSe, temperature-resistant TCO ($Mo:InO_2$) and silicon or GaAs model PV drivers,
- benchmark STH efficiency of best performing tandem device and build reactor for PEC H_2 production.

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

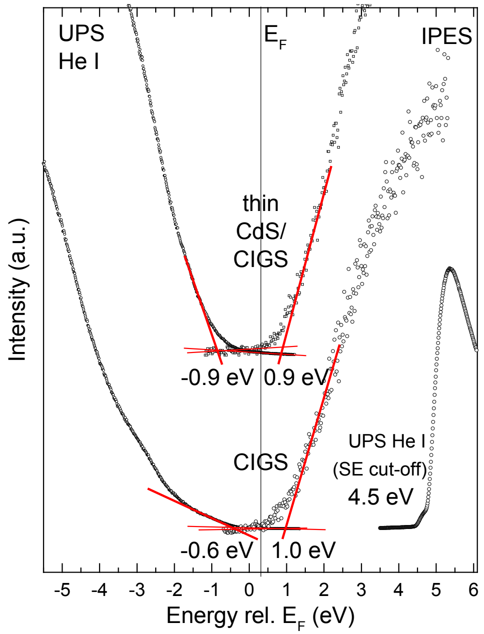
Project summary

Relevance	Create the first chalcopyrite-based HPE device with low-cost, PV-grade and durable thin film materials to meet DoE's efficiency and durability targets.
Approach	Focus on the development of wide bandgap chalcopyrite PEC materials, identify compatible buffers to improve energetics (p-n junction), evaluate Earth-abundant materials for both HER catalysis and corrosion protection and assess the STH efficiency of the complete HPE device.
Accomplishments	(1) Identified two possible causes to explain poor opto-electronic properties of some candidates: Ga-related point defects and Ordered Vacancy Compounds, (2) refined synthesis protocols to create phase-pure 1.8 eV $CuInGaS_2$ absorbers generating 12 mA/cm^2, (3) reached over 750 mV Voc with surface-modified chalcopyrites (GNG#2), (4) improve durability with MoS_2/TiO_2 coating up to 350 hrs (+ 100 hrs compared to FY16) and (5) demonstrated temperature-resistant Mo-doped InO_2 can serve as TCO in monolithic tandem PEC devices.
Collaborations	Project-specific collaboration with U.S. and international teams to address barriers in each of the 4 technical tasks.
Proposed future work	(1) Focus on candidates with proven opto-electronic properties ($CuGaSe_2$, $CuGa_3Se_5$), (2) combine sub-surface treatments with corrosion-resistant In_2S_3 buffers to meet the 900mV V_{oc} target, (3) continue development of conformal MoS_2 and TiO_2 coatings using ALD to meet 1,000-hour durability targets and (4) benchmark the STH efficiency of CGSe/IMO/PV (PV: Si, GaAs or CIGSe).

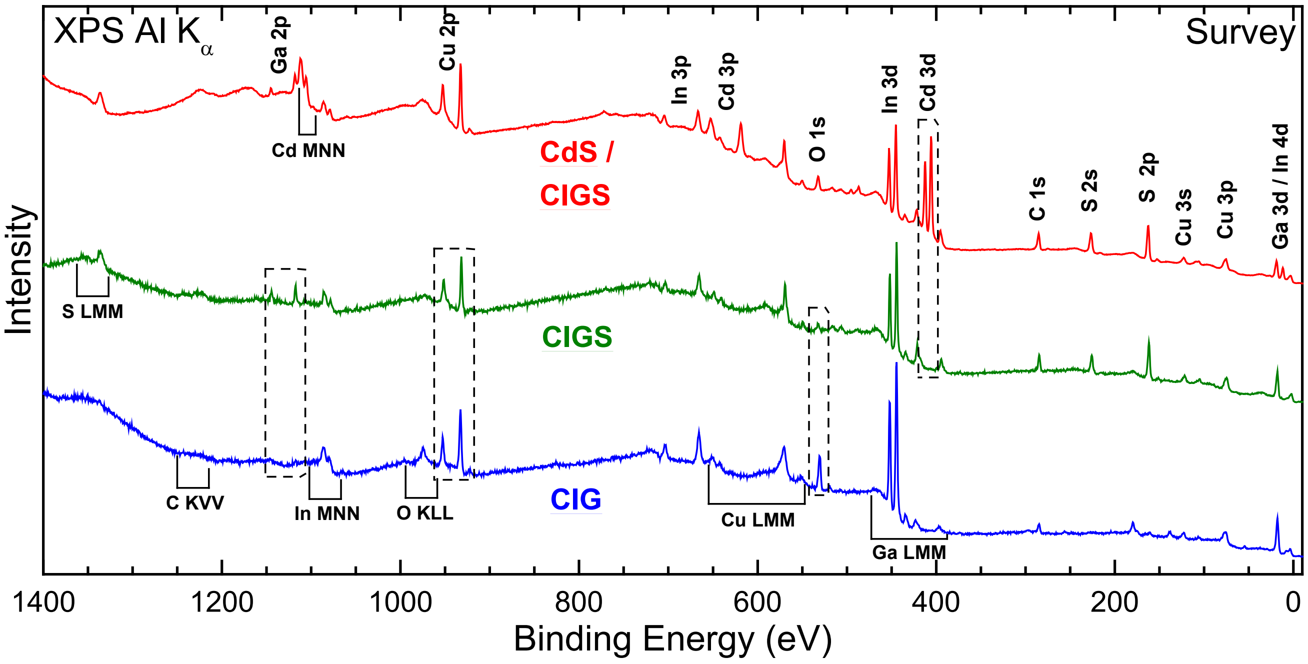
Technical back-up slides

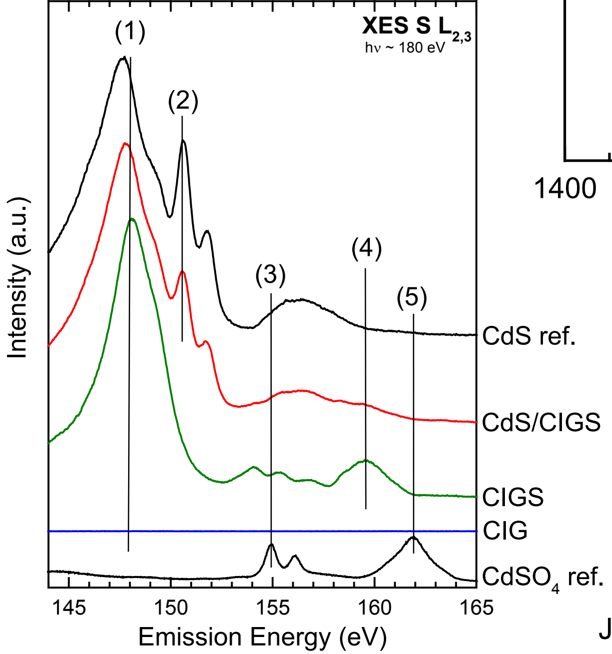
Accomplishments – Task 2: Sub-surface energetics

AE / AG barriers



Analysis of metallic precursors (CIG), after sulfurization (CIGS), and after CdS deposition (CdS/CIGS)





Electronic and chemical surface structure at each process step:

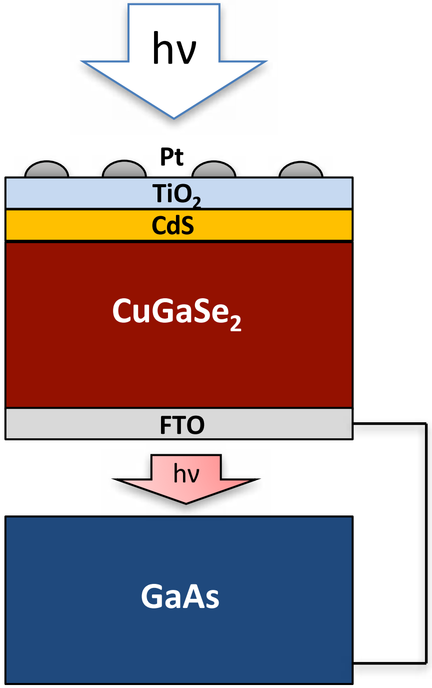
- Composition and chemical bonding
- Band edges, surface band gap, and work function
- Interface optimization

J. Carter, K. Horsley, A. D. DeAngelis, M. Blum, N. Gaillard, C. Heske. *In Preparation*

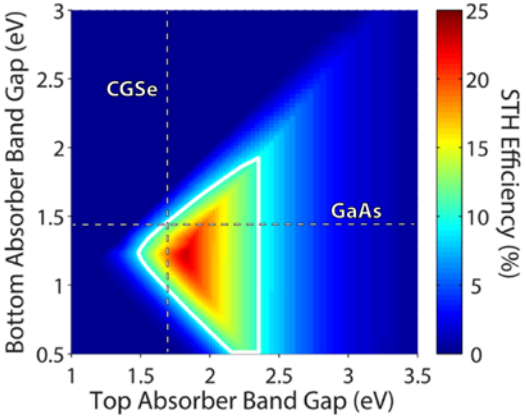
Accomplishments – Task 4: CIGS-based PEC device

AG barriers

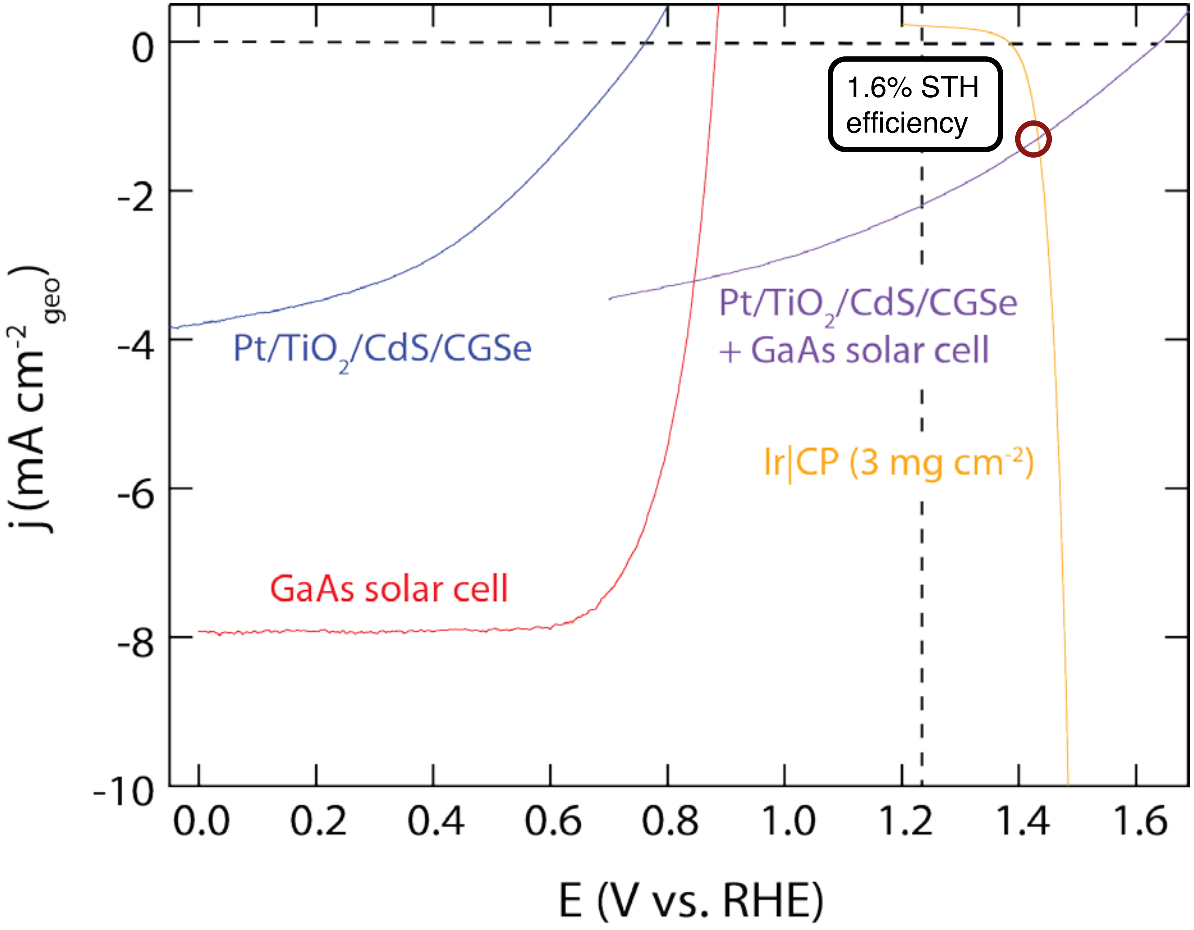
c. PV-biased photoelectrosynthesis of H_2 from water using CdS/CGSe photoelectrode and GaAs PV-driver



Tandem Mechanical Stack



L.C. Seitz, et. Al. *ChemSusChem* 7 (5), 2014, 1372



1.6% STH efficiency provides a baseline to improve by increasing the saturation current density, onset potential, and fill factor

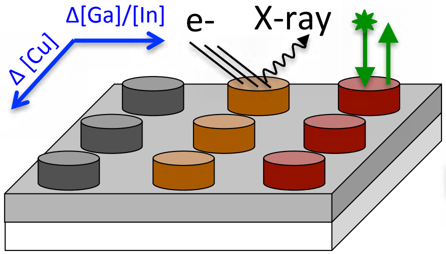
T.R. Hellstern, D. Palm, J. Carter, A. D. DeAngelis, M. Blum, N. Gaillard, C. Heske, T.J. Jaramillo. *In Preparation*

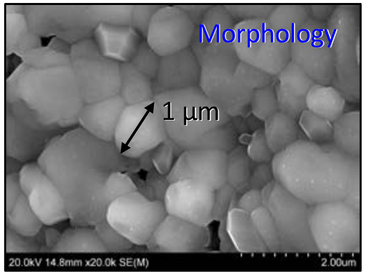
Accomplishments – Task 1: PV-grade absorbers

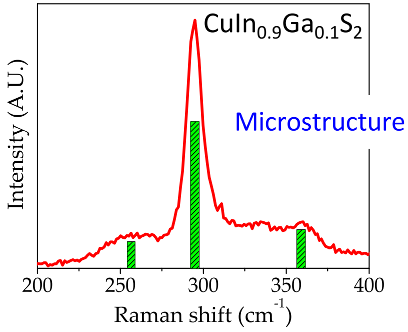
AE / AJ barriers

3. Accelerating PV-grade $Cu(In,Ga)S_2$ material development

Step1: Synthesis and characterization

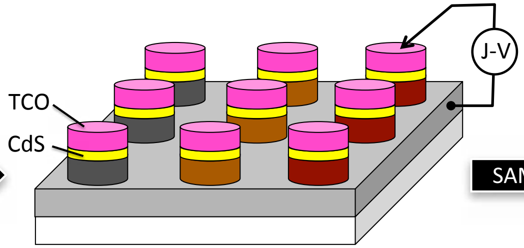


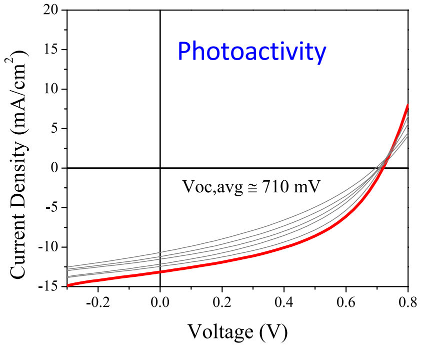


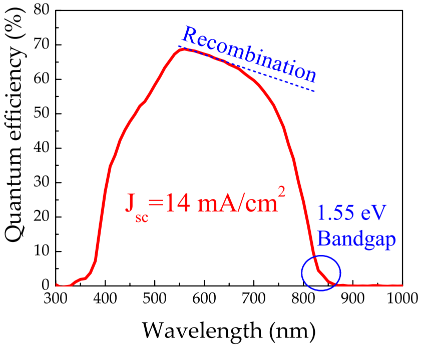


SAME SAMPLE

Step 2: Solid-state properties mapping

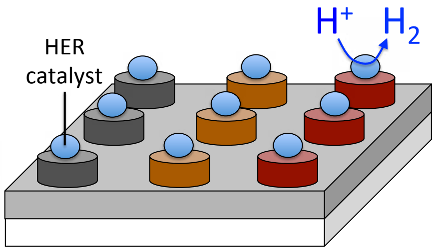


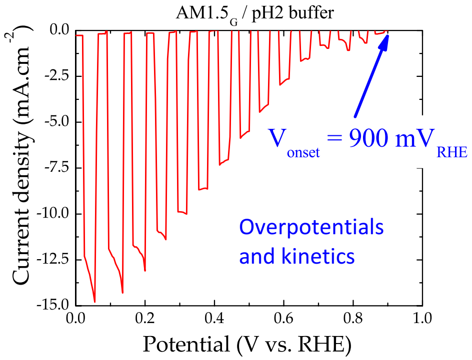


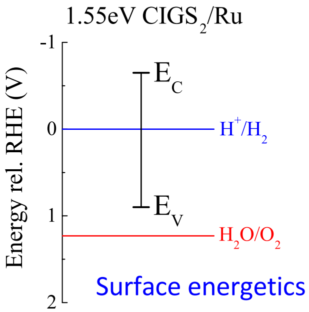


SAME SAMPLE

Step 3: PEC characterization







Take home messages:
- Three chalcopyrite (CIGS, CGSSe, CIASe) alloys identified with optimum bandgap energy for PEC applications,
- New synthesis/testing (<u>solid-state</u> & <u>PEC</u>) strategy developed to accelerate materials discovery,
- 1.55 eV PV-grade CIGS with great potential for PEC H_2 production successfully developed with this approach.