Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Novel Chalcopyrites# for Advanced Photoelectrochemical Water-Splitting

Nicolas Gaillard

November 14th 2017

HydroGEN Projects Kick-Off Meeting

#: CuX(S,Se) material class, typically identified by its most popular alloy $Cu(In,Ga)Se_2$

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

HydroGEN Kick-Off Meeting

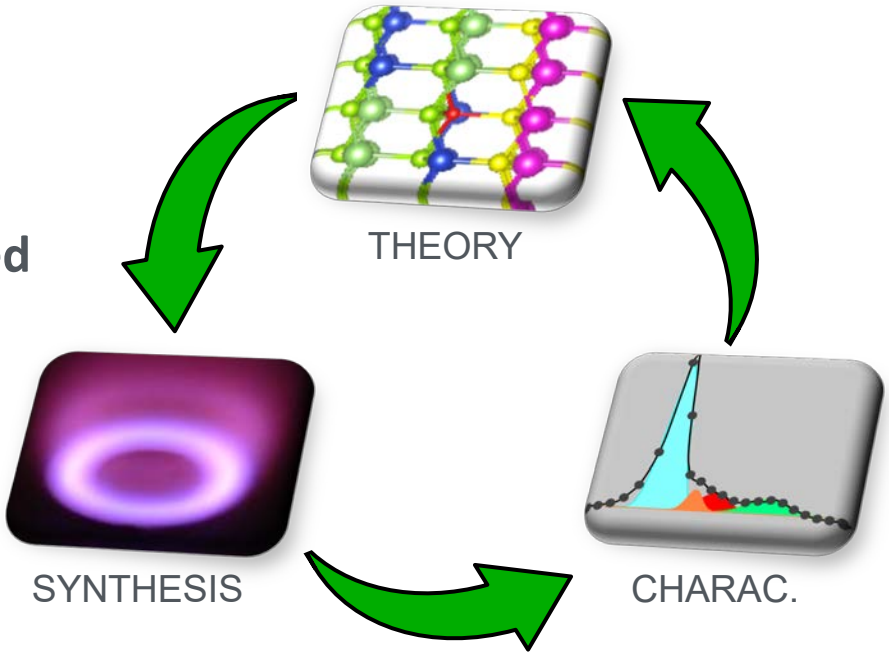
Novel Chalcopyrites for Advanced Photoelectrochemical Water-Splitting

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

Award #	EE0008085
Year 1 Funding	$280,172

Project Vision

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

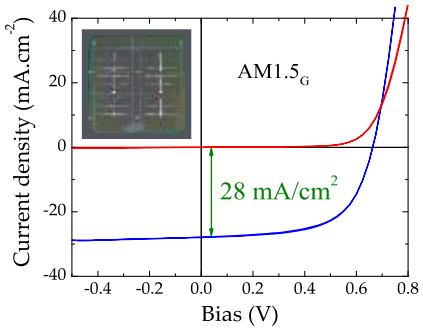


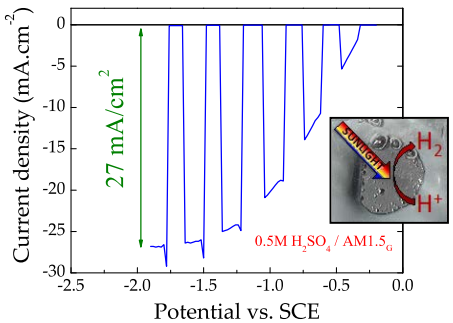
Project Impact

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

Technical background

1. CIGS can generate high photocurrent density





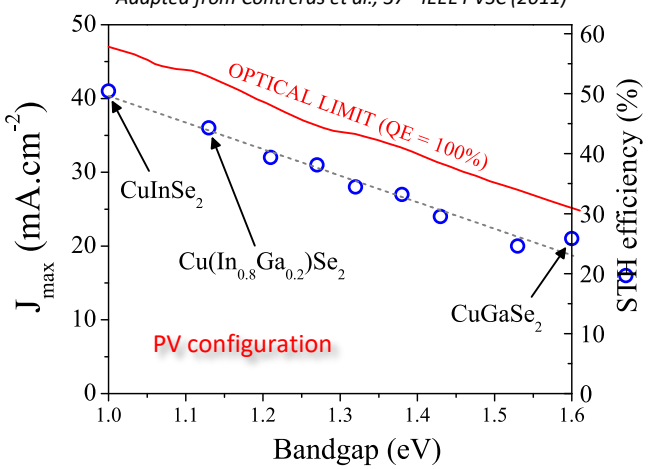
Solar cell vs. Photoelectrode

2. Low-cost processes available for CIGS

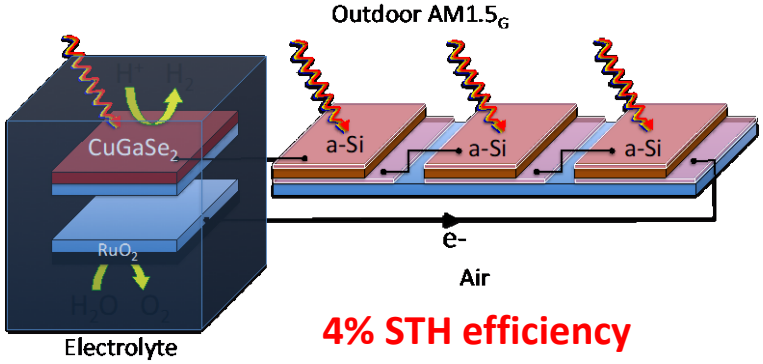
PV module cost $100-150/m^2

3. CIGS are bandgap (color) tunable

Adapted from Contreras et al., 37th IEEE PVSC (2011)



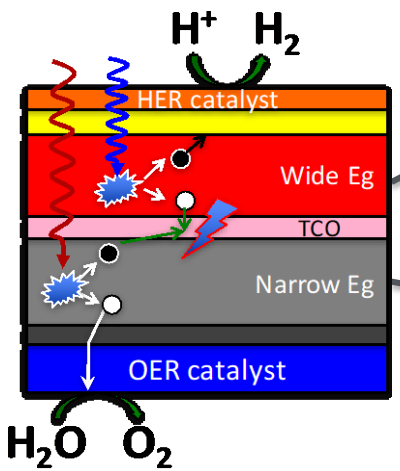
4. Demonstrated water splitting with co-planar CIGS



4% STH efficiency

Technical background

→ Our goal: combine a **new wide bandgap (E_G) chalcopyrite** photo-electrode with an **existing narrow bandgap PV driver** to create a tandem PEC device with STH>10%.



This project goal: $Cu(In,X)(S,Se)_2$
X: Ga, Al, B

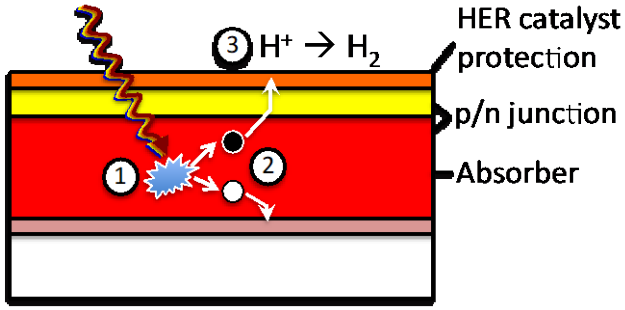
Existing PV drivers: $CuInGaSe_2$, Si, Perovskites

Fundamental steps in PEC H_2 production

#1: light absorp. and electron generation (**photocurrent**)

#2: charge separation with junction (**voltage**)

#3: H_2 evolution (**catalysis and durability**)



PEC cell

Innovation and Objectives

Project history

- 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.
- Issues identified with these systems will be addressed in this new project.

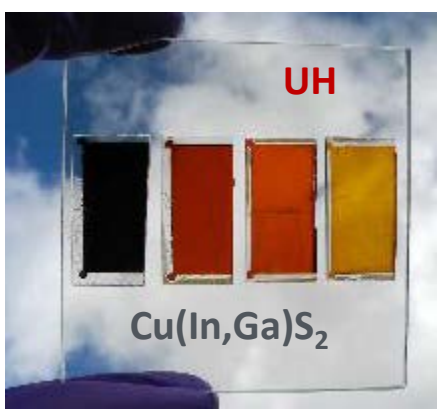
Partnerships

- UH (N. Gaillard)
→ Absorbers and junctions synthesis

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

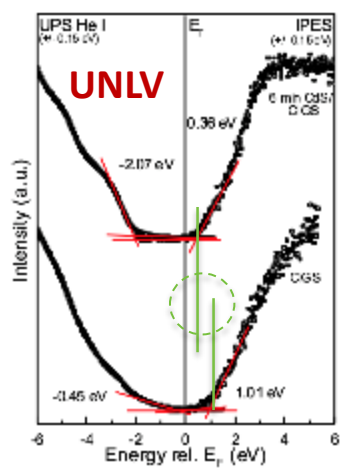
- Stanford (T. Jaramillo)
→ Surface catalysis and corrosion protection

Absorber (photocurrent)



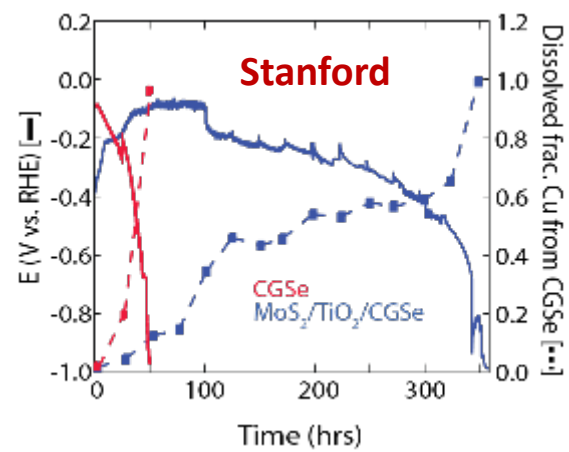
Bandgap tunable chalcopyrite electrodes (J>10mA/cm²)

Interface (voltage)



Energetics at the CdS/CIGS$_2$ interface

Surface (catalysis and durability)



350 hrs at 8 mA/cm² with MoS_2

Innovation and Objectives

Barriers

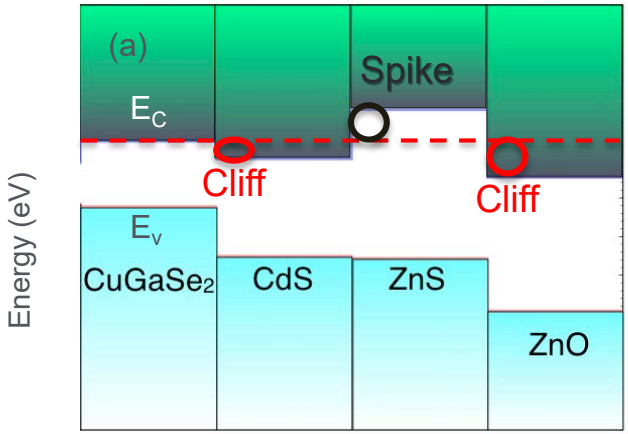
Efficiency: the photo-voltage generated by wide E_G CIGS is too low.
→ Identify alternative buffers with tunable energetics (ZnOS, ZnMgO).

Durability: coating a 20 nm thick MoS_2 film on rough CIGS is challenging.
→ Improve MoS_2 coverage with ALD techniques.

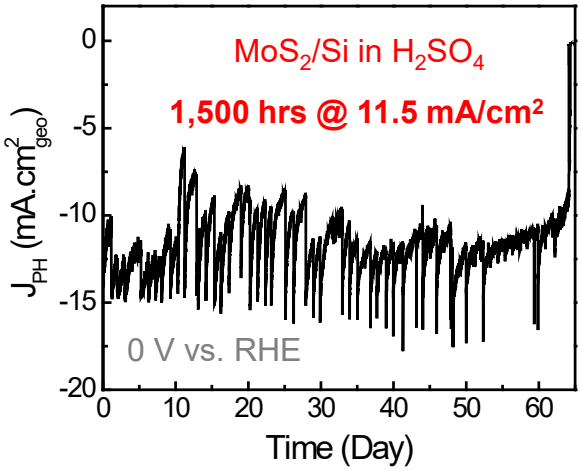
Proposed targets

Metric	State of the Art	Proposed
Photo-voltage	*0.7-0.8 V*	*> 1 V*
STH efficiency	*4%*	*>10%*
Durability	*350 hrs*	*>1,000 hrs*

Modeling of band offsets (LLNL)

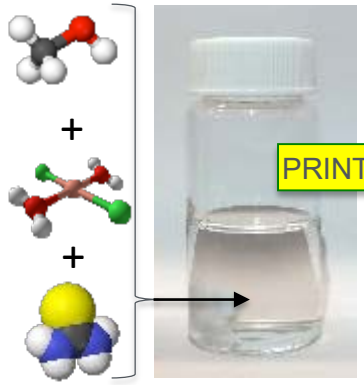


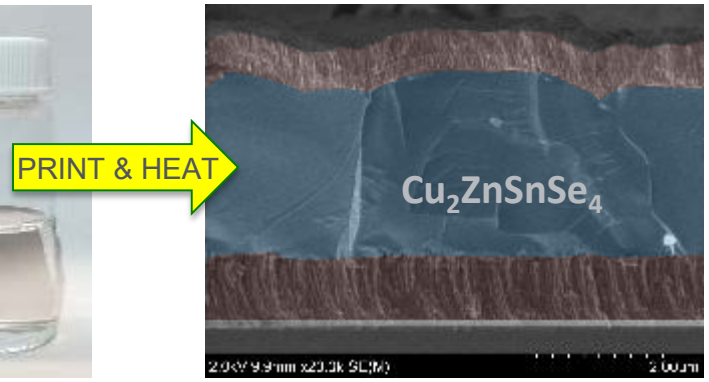
Durability of MoS_2 / Si (Stanford)

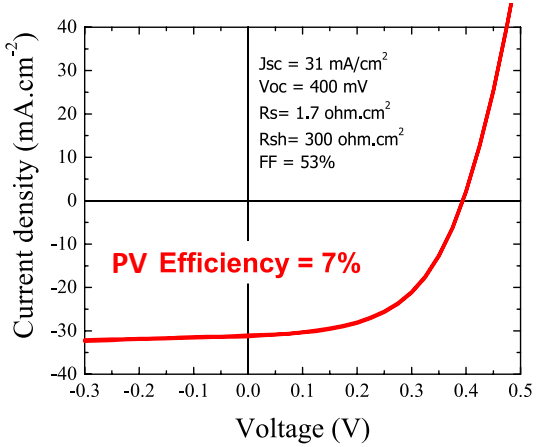


Technology Innovation

1. "Printing" techniques to synthesize chalcopyrites

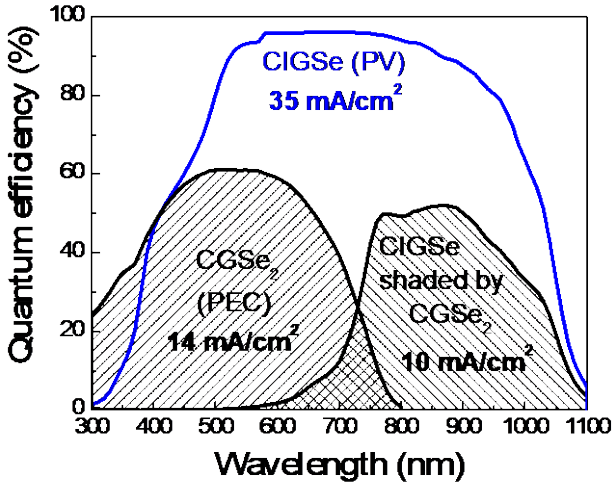


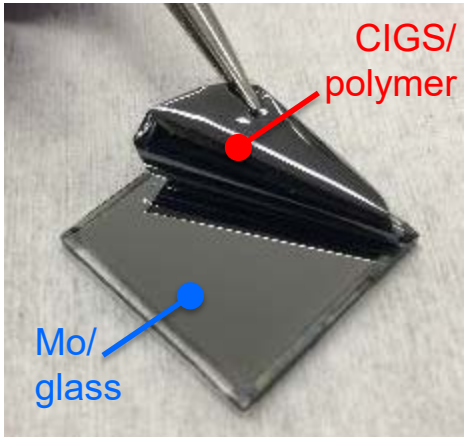


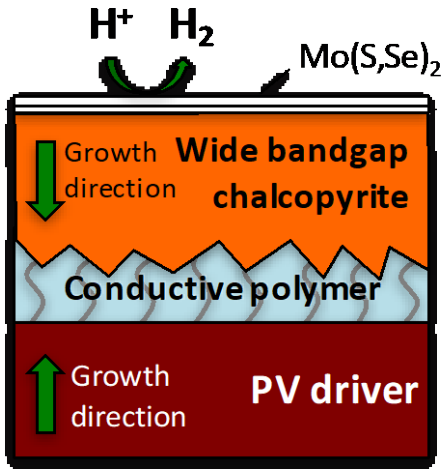


→ **Lower manufacturing costs and enable synthesis of new chalcopyrites (e.g. $Cu(B,In)Se_2$)**

2) Innovative tandem device integration schemes







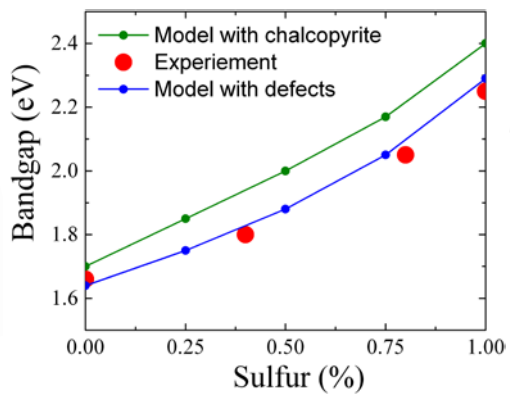
→ **"Transferable" PEC onto fully integrated PV cell to solve process compatibility issues**

Effective Leveraging of the EMN Resource Nodes

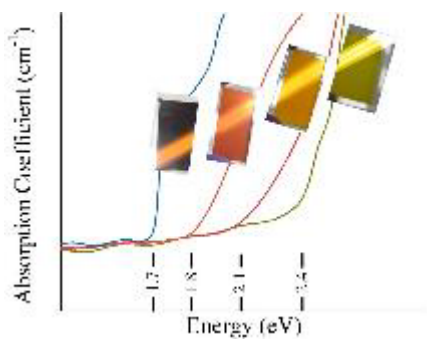
- **Computational Materials Diagnostics and Optimization of PEC Devices (T. Ogitsu).**

Example of past LLNL/UH work:
$CuGa(S,Se)_2$
color can be tuned with S/Se ratio.

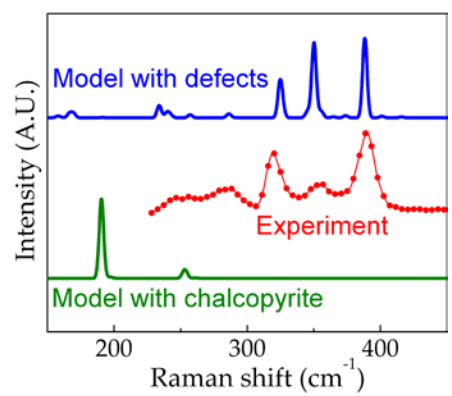
THEORY



SYNTHESIS



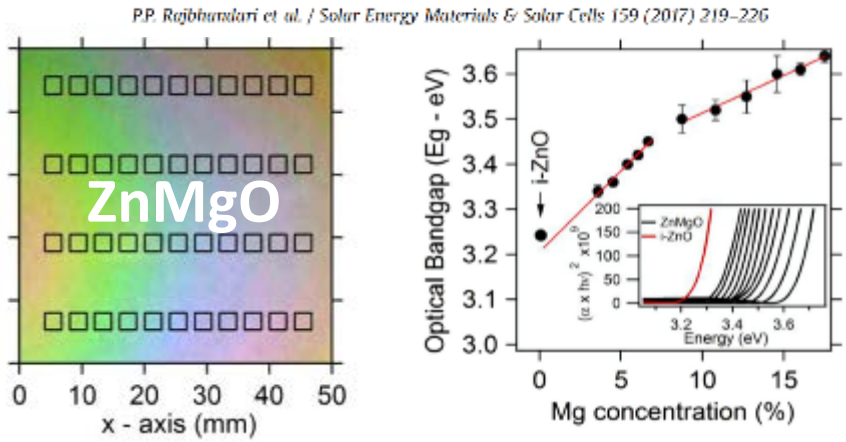
CHARACTERIZATION



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

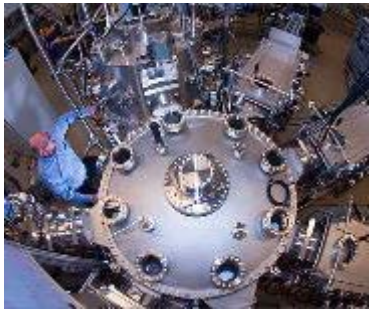
Effective Leveraging of the EMN Resource Nodes

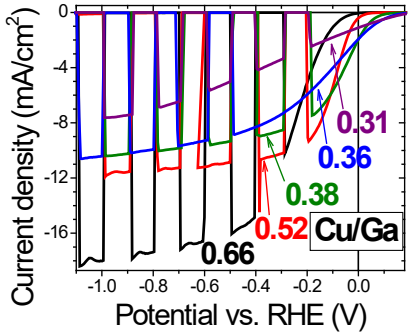
- **High-Throughput Thin Film Combinatorial Capabilities (A. Zakutayev)**



→ Rapid screening of a graded buffer (>40 different chemical compositions) on a single CIGS sample

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





→ High purity absorbers for top PEC (1.8 eV $CuGa_3Se_5$) and bottom PV driver (1.1 eV $CuInGaSe_2$)

- **Corrosion Analysis of Materials (T. Deutsch)**

→ Support development of surface passivation and validate device durability/efficiency