Novel Chalcopyrites\# for Advanced Photoelectrochemical Water-Splitting

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HydroGEN Projects Kick-Off Meeting

\#: CuX(S,Se) material class, typically identified by its most popular alloy Cu(In,Ga)Se\textsubscript{2}
HydroGEN Kick-Off Meeting

Novel Chalcopryrites for Advanced Photoelectrochemical Water-Splitting
- Lead PI: Nicolas Gaillard (University of Hawaii)
- Co-PIs: Clemens Heske (UNLV)
  Thomas Jaramillo (Stanford)

Project Vision
Strengthen theory, synthesis and advanced characterization “loop” to accelerate development of efficient materials for PEC H₂ 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
   - AM1.5a: 28 mA/cm²

2. Low-cost processes available for CIGS
   - PV module cost $100-150/m²

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

Solar cell vs. Photoelectrode
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 \( \text{STH}>10\% \).

**Technical background**

**Fundamental steps in PEC \( \text{H}_2 \) production**

- **#1**: light absorp. and electron generation (**photocurrent**)
- **#2**: charge separation with junction (**voltage**)
- **#3**: \( \text{H}_2 \) evolution (**catalysis and durability**)

This project goal: \( \text{Cu(In,X)}(\text{S,Se})_2 \)

**Existing PV drivers**: \( \text{CuInGaSe}_2, \text{Si}, \text{Perovskites} \)
Innovation and Objectives

Project history
- UH/UNLV/Stanford + NREL/LLNL funded by EERE (2014) to identify promising chalcopyrites for PEC H₂.
- 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)
Cu(In,Ga)S₂
Bandgap tunable chalcopyrite electrodes (J>10mA/cm²)

Interface (voltage)
Energetics at the CdS/CIGS₂ interface

Surface (catalysis and durability)
350 hrs at 8 mA/cm² with MoS₂

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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

<table>
<thead>
<tr>
<th>Metric</th>
<th>State of the Art</th>
<th>Proposed</th>
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<tbody>
<tr>
<td>Photo-voltage</td>
<td>0.7-0.8 V</td>
<td>&gt; 1 V</td>
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<tr>
<td>STH efficiency</td>
<td>4%</td>
<td>&gt;10%</td>
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<tr>
<td>Durability</td>
<td>350 hrs</td>
<td>&gt;1,000 hrs</td>
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**Modeling of band offsets (LLNL)**

**Durability of MoS$_2$/Si (Stanford)**

MoS$_2$/Si in H$_2$SO$_4$

1,500 hrs @ 11.5 mA/cm$^2$
Technology Innovation

1. “Printing” techniques to synthesize chalcopyrites
   - Lower manufacturing costs and enable synthesis of new chalcopyrites (e.g. Cu(B,In)Se₂)

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: 
\( \text{CuGa}(S,\text{Se})_2 \)

- color can be tuned with 
\( S/\text{Se} \) ratio.

→ 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 CuGa₃Se₅) and bottom PV driver (1.1 eV CuInGaSe₂)

- **Corrosion Analysis of Materials (T. Deutsch)**
  - Support development of surface passivation and validate device durability/efficiency