Photoelectrochemical Hydrogen Production: UNLV-SHGR Program Subtask

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This presentation does not contain any proprietary or confidential information
**Timeline**

- **Project start date:** 1 Oct. 2004
- **Project end date:** 31 Dec. 2007
- **Percent complete:** 70%

**Barriers**

- **Barriers for photoelectrochemical (PEC) H₂ production technologies:**
  - Y: Materials Efficiency
  - Z: Materials Durability
  - AB: Bulk Materials Synthesis
  - AC: Device Configuration Designs

**Budget**

- **Total project funding:** $2.81M
  - DOE share: $1,685,861
  - Contractor share: $1,123,361
- **FY06 Funding:** $958k
- **Funding for FY07:** $0

**Collaborators / PIs**

- University of Hawaii at Manoa / Eric L. Miller
- University of Nevada, Las Vegas / Clemens Heske
- University of California, Santa Barbara / Eric McFarland
- National Renewable Energy Laboratory / Mowafak Al-Jassim & John Turner
- MVSystems Incorporated / Arun Madan
- Intematix Corporation / Xiaodong Xiang
- Altair Nanotechnologies Incorporated / Vesco Manev
OBJECTIVES

The primary objective is to assist DOE in the development of hydrogen-production technology utilizing solar energy to photoelectrochemically split water. The primary focus is on low-cost thin film materials (such as metal oxides) and novel multi-junction thin film devices (such as the UH-Hybrid Photoelectrode- HPE).

DOE PEC Program Targets

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2003 Status</th>
<th>2006 Status</th>
<th>2013 Target</th>
<th>2018 Target</th>
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</thead>
<tbody>
<tr>
<td>Usable semiconductor bandgap(^{a})</td>
<td>eV</td>
<td>2.8</td>
<td>2.8</td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Chemical conversion process efficiency (EC)(^{b})</td>
<td>%</td>
<td>4</td>
<td>4</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Plant solar-to-hydrogen efficiency (STH)(^{c})</td>
<td>%</td>
<td>not available</td>
<td>not available</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Plant durability(^{d})</td>
<td>hr</td>
<td>not available</td>
<td>not available</td>
<td>1000</td>
<td>5000</td>
</tr>
</tbody>
</table>

Specific UNLV-SHRG PEC Project Goals

- Identify and develop new PEC film materials compatible with high-efficiency, low-cost H\(_2\) production devices: **Target: 1.6 mA/cm\(^2\) – 6.5 mA/cm\(^2\) AM 1.5 photocurrent**
- Demonstrate functional multi-junction device incorporating best-available PEC film materials: **Target: 2 - 8 % STH efficiency under AM 1.5 illumination**
- Develop avenues, integrating new theoretical, synthesis and analytical techniques, for optimizing future PEC materials and devices
- Explore avenues toward manufacture scaled devices and systems
The main approach of our collaborative network of world-leaders in materials R&D focuses on integrating state-of-the-art theoretical, synthesis and analytical techniques to identify and develop the most promising materials classes to meet the PEC challenges in efficiency, stability and cost.

R&D Feedback Loop:

- **THEORY**: Materials & Interface Modeling
  - Theoretical Calculations of Semiconductor Band Structures

- **SYNTHESIS**: Materials Discovery / Development
  - Physical and Chemical Vapor Deposition
  - Combinatorial & Manufacture Scale Synthesis Techniques

- **ANALYSIS**: Materials & Device Characterization
  - Physical/Solid-State Electronic/Optoelectronic Properties
  - Solid-Solid & Solid-Liquid Interface Characteristics
  - Photoelectrochemical Behavior Analysis

Application to Focus Materials:

- W-compounds
- Zn-compounds
- Fe-compounds
- Si-compounds
- Cu-chalcopyrites
SUMMARY

PROGRESS

➢ **Collaborative Research Team Established:** combining materials theory, synthesis and characterizations, to expedite the materials discovery and development process for improved PEC devices.

➢ **Critical Experience, Protocols, and Infrastructure Developed:**
  ➢ Versatile synthesis tools established for fabricating PEC materials & devices
  ➢ Comprehensive characterization protocols established for PEC materials & devices
  ➢ Rapid-throughput synthesis & screening techniques developed to facilitate discovery
  ➢ Manufacture scale process demonstrated for HPE device fabrication

➢ **Focus Materials Classes Established:** including WO$_3$-, ZnO-, Fe$_2$O$_3$-, silicon-, and copper chalcopyrite-based thin films.

➢ **Key Targets Met in Focus Materials Experiments:**
  ➢ Photocurrents in excess of 3 mA/cm$^2$ in tungsten-based compound films
  ➢ Photocurrents in excess of 6.5 mA/cm$^2$ in Si- and chalcopyrite-based films (with additional bias constraints to be corrected in band edge alignment modifications)
  ➢ STH Device efficiencies in excess of 3% in WO$_3$-based multijunction structures under 1 sun

FUTURE

➢ Continued Development of Research Team Capabilities and Collaboration
➢ Continued Optimization of Performance and Durability in Focus Materials
➢ Continued Discovery of New Materials and Possible Down-Selection of Old Materials
➢ Selection of Best Materials for Incorporation in High-Efficiency PEC Devices
**Approach: Theory**

**Theoretical modeling of PEC materials:**
- To provide theoretical guidance and understanding on materials studied by the PEC team
- To search for new materials and new concepts

**Background of Density-Functional Theory (DFT):**

\[
\frac{-\hbar^2}{8\pi^2 m} \nabla^2 \psi_j(r) + V_{\text{eff}}(r)\psi_j(r) = \varepsilon_j^{KS} \psi_j(r) \quad \text{K-S equation}
\]

\[
V_{\text{eff}}(r) = V_H(r) + V_N(r) + V_{XC}(r)
\]

\[
V_{XC}(r) : \text{ Exchange-correlation potentials: LDA, or GGA}
\]

**Applications:**
- Total energies, Electronic structures such as band structure and density of states, Optical properties such as optical absorption coefficient and transition properties
Approach: Theory

Specific Applications in PEC Materials

Collaboration on $WO_3$ with the PEC team:
- Determined conduction and valence band positions for cation and anion doped $WO_3$
  - Nitrogen incorporation leads to bandgap reduction in $WO_3$
  - Calculated optical absorption coefficient for $WO_3$:N
  - Calculated a minimal shift for the conduction band minimum with molybdenum doping.

Results on ZnO:
- N-incorporation leads to bandgap reduction in ZnO
- Ga-N cluster doping may form intermediate band in ZnO
- Group-IB elements (Cu, Ag, Au) lead to VBM up shift in ZnO
- p-type and gap reduced ZnO is possible by Cu and Ag incorporation
- Ga-N cluster doping may form intermediate band in ZnO

New Materials:
- Theoretical results from $WO_3$ and ZnO to be included in modeling of new PEC material systems
Collectively, our team commands a broad portfolio of thin film synthesis techniques to facilitate the discovery and development of PEC materials and devices for high-performance, low-cost hydrogen production systems, including. Team synthesis capabilities include:

- Physical Vapor Deposition Systems
- Chemical Vapor Deposition Systems
- Spray Pyrolysis Fabrication Systems
- Sol-Gel Fabrication Systems

Reactive sputtering system for compound material films (including oxides, sulfides, etc.)

Co-Evaporation system for copper chalcopyrite films (CIGS, CGS, etc.)

Plasma-enhanced CVD system for low temperature synthesis of metal oxide films
Approach: Synthesis

The team also offers a range of advanced techniques to facilitate rapid discovery of new materials classes and the establishment of large-scale device fabrication. Specific combinatorial synthesis and manufacture-scale equipment includes:

- **Combinatorial Synthesis Systems**
  - Automated Pyrolysis systems
  - Automated Physical-Vapor-Deposition systems

- **Manufacture-Scale Film Technology**
  - Large-scale vacuum-system cluster tools
  - Cassette systems for large sheet depositions

Automated combinatorial pyrolysis system
Automated combinatorial physical-vapor-deposition system
Cluster tool for vacuum-deposition of manufacture scale thin-film devices
Approach: Characterizations

Materials Properties

- **Morphology:** Scanning Electron Microscopy, Atomic Force Microscopy, Spectroscopic Ellipsometry
  
  AFM of WO₃ Films
  
  ← Pure WO₃
  
  N₂-doped WO₃ →

- **Microstructure:** X-Ray Diffractometry, EBSD, Transmission Electron Microscopy

- **Chemistry:** Secondary Ion Mass Spectrometry, X-ray Photoelectron Spectroscopy, Synchrotron X-ray Emission and Absorption Spectroscopy
Approach: Characterizations

Electronic Structure

Electronic Surface Bandgap, Band Edges, Band Alignment, Fermi Energy, Work Function, Electrical Properties

- UV Photoelectron Spectroscopy, Inverse Photoemission
- Impedance Spectroscopy, UV-Vis Spectroscopy
- Conductive Atomic Force Microscopy, Scanning Kelvin Probe Microscopy, Scanning Tunneling Spectroscopy
Approach: Characterizations

Optical and Photoelectrochemical Properties

- Optical-Photoelectrochemical Combinatorial Screening Systems

  Diffuse Reflectance Spectrometry

- Photoluminescence and Cathodoluminescence
Our team utilizes its collective expertise and capabilities in theoretical materials modeling, in materials synthesis, and in materials screening and characterization to identify and develop an expansive set of promising PEC thin-film materials classes. The five classes of “focus materials” currently under investigation include:

- **Tungsten-Based Compound Films (U. Hawaii, Intematix)**
  - Modified Tungsten Oxide Compounds with Anion/Cation Substitutions

- **Zinc-Based Compound Films (NREL)**
  - Modified Zinc Oxide Compounds with Anion/Cation Substitutions

- **Iron-Based Compound Films (UCSB, Altair Nano)**
  - Novel Iron-Based Compound Materials, including Fe$_2$O$_3$ Nanorods

- **Silicon-Based Compound Films (MVSystems)**
  - Amorphous Silicon Carbide Films with p- and n- type Doping

- **Copper Chalcopyrite Compound Films (U. Hawaii)**
  - Copper-Indium-Gallium-Selenium-Sulfur Compounds
**Progress: Tungsten-Based Compound Films**

Tungsten oxide is a model material to study PEC hydrogen generation…

### Promise
- Sufficient absorption to generate modest photocurrents
- Good electron transport properties
- High Stability in Electrolytes
- Thin film process scalable
- Demonstrated in prototype multi-junction devices.

### Challenges
- Non ideal band edge alignment – requires supplemental bias
- Bandgap requires reduction to increase photocurrents
- The photostability over extended time periods and for new tungsten-alloy compositions requires validation

**Hybrid Photoelectrode with pure WO₃ films**

**Load Line Analysis**

**Device Configuration**

**Performance**
**Progress: Tungsten-Based Compound Films**

UV edge plotted as indirect bandgap

- Calculated current density based on UV absorption edge for a 1 μm thick film
  - Shaded region represents absorbed portion of AM1.5G

PEC testing of WO₃:N

- With sufficient nitrogen in the sputtering ambient, bandgap reductions are realized, however this increase in absorption does not correlate with an increase in measured photocurrents . . .
Influence of Nitrogen on Structure

X-ray diffraction pattern shows an initial decrease in crystallinity for monoclinic phase followed by transformation to a stabilized cubic phase for nitrogen partial pressures greater than 3mTorr. The TEM diffraction pattern for nitrogen doping shows smearing, indicating a highly defective lattice.
**Path Forward: Tungsten-Based Films**

**SUMMARY**

- Tungsten oxide has been demonstrated in a multi-junction hybrid phototelectrode configuration.
- Nitrogen is observed to reduce the bandgap to ~2 eV.
- Incorporation of nitrogen results in a highly defective lattice. This degrades the transport properties resulting in poor PEC performance.
- Theory indicates that other dopants can favorably alter band edges.

**FUTURE WORK**

- Elimination of lattice defects for the nitrogen doped WO$_3$
  - by adjusting sputtering parameters
  - by post sputtering annealing
  - by exploring quaternary systems
- Pursue bandgap reduction using different anion/cation species
  - oxy-sulfides (in addition to the oxy-nitrides)
  - by metallic cations
- Based on the need to minimize requisite bias voltage, we will investigate valence band modifications, as well as the effect of composition on conduction band level and its alignment with the hydrogen reduction potential.
**Progress: Zinc-Based Compound Films**

ZnO is inexpensive, nontoxic, and easy to synthesize. It also has a direct bandgap and high electron mobility thereby making it a good candidate for PEC splitting of water.

### Promise
- Conduction band edge only slightly mismatched to drive the hydrogen reaction.
- Impurity doping can shift the valence band edge, providing for bandgap reduction.
- Can also fabricate as P-type ZnO

### Challenges
- Bandgap is too large to effectively utilize the visible light.
- Requires stability improvement against photocorrosion.

### Strategies for PEC Improvement
- **Bandgap reduction**
  - Impurity doping using anion or cation species
- **Explore p-type ZnO**
  - Impurity doping using group 1B metals
**Progress: Zinc-Based Compound Films**

**Structural evolution for RF sputtering of ZnO:N**

- High quality pure ZnO thin films are synthesized
- N-incorporation into ZnO thin films was achieved
- Bandgap reduction in ZnO thin films was achieved by N-incorporation
- Photo-response in ZnO:N thin films was demonstrated

**Optical absorption spectra from ZnO:N samples**

**Photocurrent-voltage curves of the samples under light illumination with the UV/IR filter**

- Solution: Na$_2$SO$_4$
  - pH: 6.8
Progress: Zinc-Based Compound Films

- Bandgap reduction in ZnO thin films was achieved by Cu-incorporation.
- P-type ZnO thin films with reduced bandgaps were achieved by Cu incorporation.
- Photo-response in ZnO:Cu thin films was demonstrated.

Optical absorption spectra from ZnO:Cu samples

Photocurrent-voltage curves of p-type ZnO:Cu samples

Cu increase → Grain size and surface roughness decreased.
**SUMMARY**

- Preliminary work shows that nitrogen can be effectively incorporated into ZnO films to reduce bandgap.
- Need to improve crystallinity for ZnO:N to realize good PEC properties.
- Theoretical calculations show that doping with group 1B transition metals (Cu, Ag) results in bandgap reduction.
- Cu was incorporated into ZnO films with mixed results – bandgap reduction is observed and Cu is found at Zn sites for select films, however the measured photocurrents are low.

**FUTURE WORK**

- The process for RF sputtering of ZnO films requires optimization.
  - Study the film growth as a function of substrate temperature.
  - Incorporation of impurity dopants via co-sputtering will be employed.
- Band gap reduction
  - Impurity band generation by new impurities
  - Acceptor-donor co-doping
- Stability improvement
Iron Oxide, as a commonly-found material with bandgap well-suited for the direct solar water splitting of water, is considered the “Holy Grail” of PEC materials— but its performance has been severely limited by opto-electronic properties...

**Promise**
- Bandgap ~ 2 eV (40% solar light absorption).
- Abundant and inexpensive
- High Stability in Electrolytes (pH>3)

**Challenges**
- Carrier Transport
- Valence Band Edge
- Water Oxidation Kinetics
- Low optical absorption

**Strategies for PEC improvement**
- Photon To Electron Conversion Increase
  - Growth of crystalline oxide
  - Direct growth along the preferred electron conduction paths
  - High Surface Area Materials
- Shift of Band positions
  - Quantum size effects
  - Transition metal doping
- Improve Kinetics of Water Oxidation
  - Identify and deposit optimized surface oxidation electro-catalyst
Progress: Iron-Based Compound Films

Synthesis of nanorod electrodes

FeCl₃ + Salt → β-FeOOH → Thermal treatment → α-Fe₂O₃ → Substrate

Quartz substrate → Ti/Pt → nanorods → Electrocatalyst deposition → RuO₂

Synthetic control of nanorod structure

1) 35 ± 3 nm
2) 21 ± 2 nm
3) 20 ± 3 nm
4) 12 ± 3 nm
Progress: Iron-Based Compound Films

Nanorod characterization & performance

1) Photoelectrochemical performance of 21 and 15 nm nanorods under applied bias showing an efficiency of 1.3% and 1% respectively. (2,3) IPCE of 35nm Fe$_3$O$_4$ nanorods with an applied bias of 100mV and 400mV, graph 2 and 3 respectively, showing the dramatic improvement of the nanorods with the electrodeposition of RuO$_2$ at low applied bias while at high applied bias the oxygen evolution catalyst is not improving the performance of the nanorods. 4) Table of results showing the Efficiency of the nanorods from graph 2 and 3.

* Efficiency from IPCE data

<table>
<thead>
<tr>
<th></th>
<th>Applied Bias</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 mV</td>
</tr>
<tr>
<td><strong>No Catalyst</strong></td>
<td>0.3%</td>
</tr>
<tr>
<td><strong>RuO$_2$</strong></td>
<td>1.6%</td>
</tr>
<tr>
<td><strong>Cobalt</strong></td>
<td>0.2%</td>
</tr>
</tbody>
</table>
SUMMARY

Early stages of research and development on iron oxide nanorods synthesis have shown:
- Control over the size and morphology of the nanostructures
- Improved photoelectrochemical performance as compared with spray pyrolysis deposited films
- Photoelectrochemical efficiencies of ~1%
- This synthesis method is applicable to wide variety of substrates and can be adapted to any size of substrates.

FUTURE WORK

- Control gross structure of photocatalysts
  - Nanorod synthesis conditions (pH, T, electrolyte composition)
  - Explore use of framework templates (deposit in cubic phase nanopores)
- Control opto-electronic properties
  - Nanorod size reduction to increase VB Confinement at d<6nm
  - Nanorod growth to be along (110) plane
  - Nanorod doping by in situ growth or high temperature diffusion
- Control kinetics
  - Selective deposition of surface electrocatalysts (start with Pt, Ni, Au, Ru)
Progress: Silicon-Based Compound Films

Amorphous silicon carbide is an electrochemically stable and photoactive material with tunable bandgap, which would enable the fabrication of “all-silicon” multi-junction water-splitting devices.

**promise**

- Tunable bandgap of 2.0-2.3 eV and good optoelectronic quality
- Large knowledgebase from a-Si technology
- a-SiC shows good corrosion resistance
- Enables “all-silicon multi-junction device” to be fabricated in a “cluster tool” machine

**challenges**

- Non-ideal band edge alignment – requires supplemental bias
- Kinetic limitations apparent for bare a-SiC electrodes
- Long term corrosion and photo-corrosion behavior is not known

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![Graph showing Bandgap tuning by carbon content (Gas flow ratio)](image)

**Bandgap tuning by carbon content (Gas flow ratio)**

<table>
<thead>
<tr>
<th>CH4/(CH4+SiH4) in source gases</th>
<th>Tauc Eg (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.7</td>
</tr>
<tr>
<td>0.1</td>
<td>1.8</td>
</tr>
<tr>
<td>0.2</td>
<td>1.9</td>
</tr>
<tr>
<td>0.3</td>
<td>2.0</td>
</tr>
<tr>
<td>0.4</td>
<td>2.1</td>
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<tr>
<td>0.5</td>
<td>2.2</td>
</tr>
<tr>
<td>0.6</td>
<td>2.3</td>
</tr>
</tbody>
</table>

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**Amorphous Si Panel**
Progress: Silicon-Based Compound Films

All-Silicon Hybrid PEC Device Designs

Device schematic

- Photoactive p-type a-SiC layer
- ohmic interface
- a-Si and/or nc-Si solar cell
- Stainless steel substrate
- O2 evolution catalyst

Band diagram using A-Sic PEC film

- a-SiC: Eg 2.23eV
- a-Si: Eg 1.75eV
- nc-Si: Eg 1.1eV

Cluster-tool fabrication equipment

- large-scale cluster tool design
- reel-to-reel cassette

* US patent #6,258,408B1: MVSystems
Progress: Silicon-Based Compound Films

Optical properties tailored through bandgap and thickness

Photocurrent of >9mA/cm² with a-SiC photocathode

Route to >10% STH Efficiency

<table>
<thead>
<tr>
<th>photo-electrode</th>
<th>photo-electrode bandgap (eV)</th>
<th>current available (mA/cm²)</th>
<th>photovoltaic layer configuration</th>
<th>current available (filtered by top layer) (mA/cm²)</th>
<th>possible STH (%)</th>
<th>achieved STH to date (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO₃</td>
<td>2.6-2.8</td>
<td>4.3-3.3</td>
<td>a-Si/a-Si</td>
<td>8.0</td>
<td>5.3</td>
<td>3.1</td>
</tr>
<tr>
<td>SiC</td>
<td>2</td>
<td>14.4</td>
<td>a-Si/nc-Si</td>
<td>6.0</td>
<td>7.4</td>
<td>~10</td>
</tr>
<tr>
<td>SiC</td>
<td>2.35</td>
<td>8.1</td>
<td>a-Si/nc-Si</td>
<td>7.8</td>
<td>~10</td>
<td>~10</td>
</tr>
<tr>
<td>SiC</td>
<td>~2</td>
<td>~14</td>
<td>nc-Si</td>
<td>~14</td>
<td>~17</td>
<td>~17</td>
</tr>
</tbody>
</table>
**SUMMARY**

- One-sun photocurrent of ~9 mA/cm² demonstrated for a-SiC electrode
- a-SiC films appear stable in cathodic regime (short-term tests)
- Flatband potential and photocurrent onset indicate non-ideal valence band maximum position and kinetic limitations
- a-SiC is compatible with automated fabrication of multijunction devices in cluster tool deposition machine

**FUTURE WORK**

- Optimize optoelectronic quality of a-SiC at \( E_g = 2.0eV-2.3eV \)
  - systematic variation of PECVD process parameters
- Comprehensive PEC characterization a-SiC photoelectrodes
  - band positions, electrode kinetics
  - long term stability
- Fabricate and characterize complete monolithic a-SiC/a-Si multijunction PEC device
Progress: Copper Chalcopyrite Films

Cu(In,Ga)Se$_2$ is proven as an efficient absorber for thin-film solar cells and its optoelectronic properties are equally well suited for photoelectrolysis.

**Promise**
- Direct bandgap and good carrier transport properties
- High PEC photocurrents demonstrated for p-type Cu(In,Ga)Se$_2$ electrodes
- Bandgap and band edges “tunable” by composition
- Synergy with PV CIGS multijunction device research and development

**Challenges**
- Valence band edge of the Cu(In,Ga)Se$_2$ films too high
- Kinetic limitations apparent for bare electrodes
- Long term corrosion and photo-corrosion behavior is not known
- High-temperature fabrication steps

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**Bandgap Bowing Ranges of Cu(In,Ga)Se$_2$ and CuGa(Se,S)$_2$**

S.-H. Wei and A. Zunger, JAP 78, 3846 (1995); H. Matsushita et. al, JJAP 29, 484 (1990)
Electrodes are stable during short-term PEC testing.

Valence band edge too positive in current samples – high bias required.

Photocurrent onset at least 0.3V more cathodic than flatband potential.

Resistance of back contact (high/SnO$_2$:F vs low/Mo) has strong impact on photocurrent curve.
Progress: Copper Chalcopyrite Films

1-Sun Photocurrent: similar in PEC and PV Devices (CuIn$_{0.4}$Ga$_{0.6}$Se$_2$)

**PEC electrode**

- In 0.5M $\text{H}_2\text{SO}_4$
- 28.3 mA/cm$^2$
- AM1.5G

**Solar cell**

- $V_{OC}=663\text{mV}$
- $FF=0.613$
- $\eta=11.3\%$
- 28.0 mA/cm$^2$

**CuGaSe$_2$ deposition conditions, film texture, and photocurrent curves**

**XRD: CGS samples from 2 different recipes**

- CuGaSe$_2$
  - 3-stage process
  - (112)
  - (312)
- CuGaSe$_2$
  - 2-stage process
  - (220)
  - (204)
- SnO$_2$

**Photocurrent 1-sun AM1.5G**

- 3-stage
- in 0.5M $\text{H}_2\text{SO}_4$

Preliminary data shows possible effect of texture [(112)/(220)+(204)] on saturation photocurrent and dark current.
**Path Forward: Copper Chalcopyrite Films**

**SUMMARY**
- 1-sun photocurrents of 21-28 mA/cm² demonstrated for wide-bandgap CIGS and CGS electrodes
- Wide-bandgap CIGS and CGS Films appear stable in cathodic regime
- Flatband potential measurement indicates valence band maximum too high
- Late photocurrent onset indicates kinetic limitations at electrode surface

**FUTURE WORK**
- Assemble comprehensive body of PEC data on existing CIGS electrodes
- Study materials with wider bandgap and lower valence band
  - CuGaSe₂ with Cu-poor surfaces
  - Alloy with sulfur for wider bandgap CuGa(Se,S)₂
- Explore metal nanoparticle deposition on electrode surface for kinetic improvements