PD053

PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

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MVSystems, Inc.
May 16, 2013

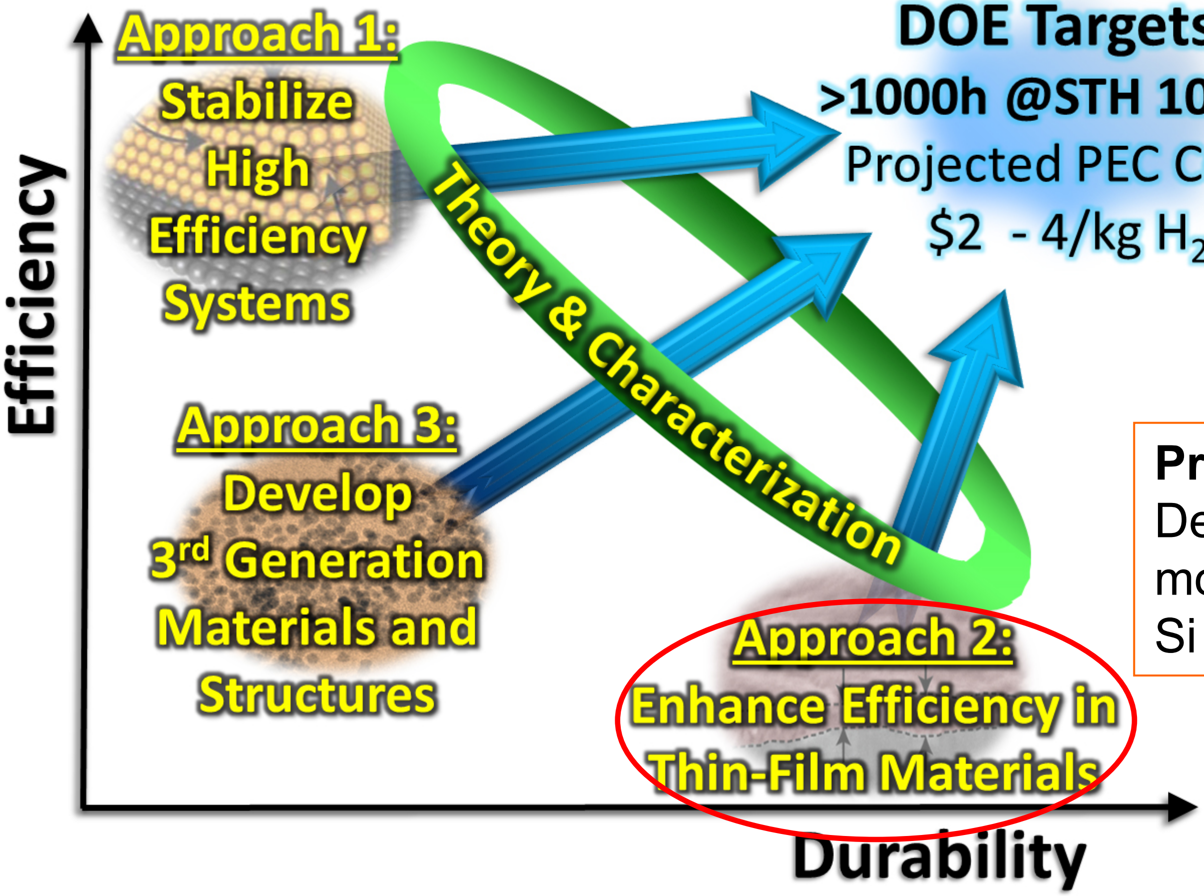
Project ID # DE-FC36-07GO17105, A00

MVSystems, UT THE UNIVERSITY OF TOLEDO 1872 HNEI NREL NATIONAL RENEWABLE ENERGY LABORATORY UNLV UNIVERSITY OF NEVADA LAS VEGAS

DOE PEC Working Group

TUDelft Delft University of Technology EMPA

National/International Collaborations



Approach 1: Stabilize High Efficiency Systems

Approach 3: Develop 3rd Generation Materials and Structures

Approach 2: Enhance Efficiency in Thin-Film Materials

Theory & Characterization

DOE Targets:
>1000h @STH 10-25%
Projected PEC Cost:
\$2 - 4/kg H_2

Project focus (Approach 2): Develop low-cost thin-film based monolithic hybrid devices with a-Si PV cells as engine

Overview

Timeline

Phase 1:

- Project start date: 9/1/2007
- Project end date: 12/31/2010

Passed go/no go evaluation in Nov, 2010

Phase 2:

- Project start date: 1/1/2011
- Project end date: 12/31/2012

No-cost extension: 1/1-9/30/2013

Budget

- Total project funding

  - DOE share: 2,543,415.65
  - MVSystems share: 628,952.40

Barriers

- Challenges for photoelectrochemical hydrogen production technologies:

–Y: Materials Efficiency
–Z: Materials Durability
–AB: Bulk Materials Synthesis
–AC: Device Configuration Designs

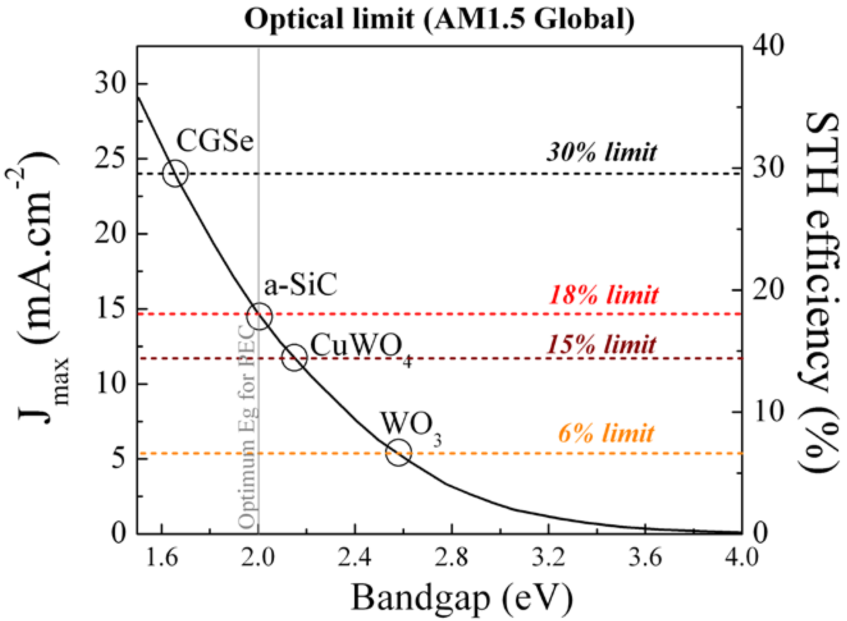
Partners

- Collaborators:
  Hawaii Natural Energy Institute (HNEI)
  National Renewable Energy Laboratory (NREL)
  University of Nevada at Las Vegas (UNLV)
- Project Lead: MVSystems, Inc.

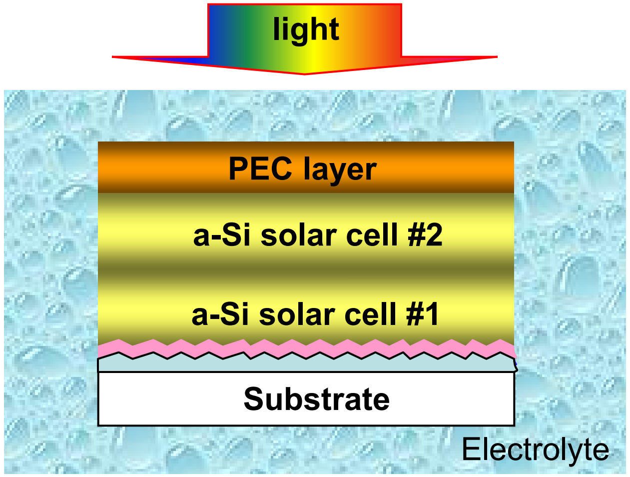
Relevance - Objectives

3 material classes covered in this project:

- Amorphous silicon carbide (a-SiC)
  (performed by MVS) MVSystems, Inc.
- New metal oxides (i.e. $CuWO_4$)
  (performed by HNEI) HNEI
- I-III-VI_2 (Copper Chalcopyrite-based)
  (performed by HNEI) HNEI



Our goal: Develop a monolithic hybrid PEC device powered by MVS' low-cost a-Si-based tandem solar cell.



Project Objectives: (by the end of 9/30/13)

- Solar-to-hydrogen efficiency: 5%
- Durability: 500-hrs

Relevance -Milestones

Goal ->	Material Photocurrent 4mA/cm^2	Material/Device Durability* 500hrs	Device Efficiency (STH) 5%
Amorphous Silicon Carbide (a-SiC)	8mA/cm2 *>100% Achieved*	310hrs @ 1mA/cm^2 *62% Achieved*	6.1%STH *>100% Achieved*
Tungsten Oxide (WO_3)	3.6mA/cm^2 *90% Achieved*	600hrs @ 1.5mA/cm^2 *>>100% Achieved*	3.1%STH *62% Achieved*
I-III-VI_2 (Copper Chalcopyrite-based)	20mA/cm^2 *>>100% Achieved*	420hrs @ 4mA/cm^2 *84% Achieved*	4.34%STH *87% Achieved*

*** Test conditions in slide #26.**

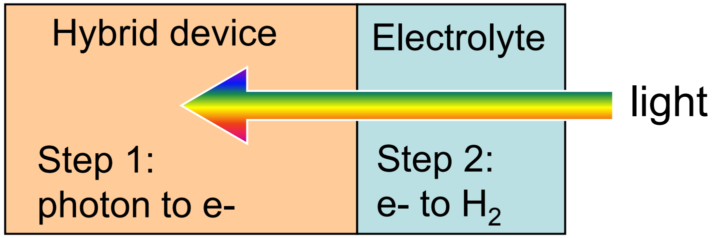
Relevance – Barriers

	a-SiC	Metal oxides	I-III-VI$_2$ (Copper Chalcopyrite-based)
AB: Synthesis	Entire PEC device fabricated with low-cost PECVD in a cluster tool identical to those used in PV industries.	Best performance achieved with conventional sputtering methods	CGSe films synthesized with co-evaporation methods. Synergy with PV industry (CIGSe)
AC: Device design - Achieved: **- Barriers:**	Monolithic device **No barriers**	Hybrid PEC device concept demonstrated with mechanical stack **Current deposition temperature requires innovative integration scheme**	Hybrid PEC device concept demonstrated with co-planar PV/PEC **Current deposition temperature requires innovative integration scheme**
Z: Durability - Achieved: (so far tested)	310-hrs **Need to test the durability at high photocurrent**	600-hrs	420-hrs
Y: Efficiency - Achieved: **- Barriers:**	6.10% STH efficiency **Need to modify surface to lower overpotential**	3.1% STH with pure WO_3 (2.6 eV). **Need to discover metal oxides with appropriate band-gap**	4.34% STH achieved with co-planar integration. **Need to modify band alignment to lower onset potentials**

Approaches

Strategy for achieving STH efficiency > 5%

Basic view of PEC H_2 production:



Solar-to-hydrogen efficiency:

$$STH\ efficiency = \eta_{solid-state} \times \eta_{energetics} \times \eta_{kinetics}$$

Step 1: solid state process:
Engine: how well solar cell performance is

Step 2: interfacial process with two components:

a. *Energetics: how well electrons reach /pass the interface (overpotential)*

b. *Kinetics: how well electrons participate to H_2 reaction*

a-SiC: improve interface energetics and kinetics with appropriate surface treatment - *decrease overpotential*

Metal oxides: identify stable compounds with appropriate band gap (2.0-2.2 eV) - *improve transport properties with elemental doping*

I-III-VI_2: lower valence band edge via Cu and Se (partial) substitution - *decrease overpotentials and increase bandgap from 1.6 to 1.9 eV*

Part I

Amorphous Silicon Carbide (a-SiC)

Part II

Metal Oxide Compounds

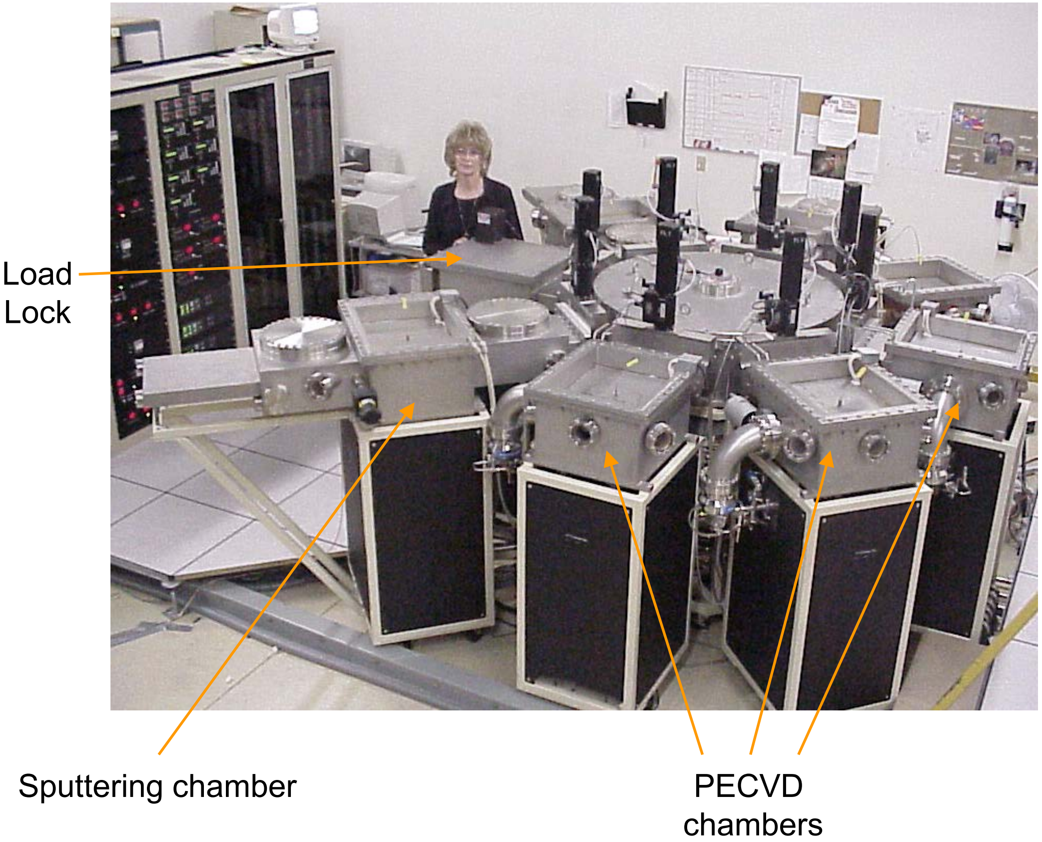
Part III

I-III-VI_2 (Copper Chalcopyrite-based)

a-SiC: Cluster Tool PECVD/Sputtering System

Addressing “Synthesis”

All a-SiC films, photoelectrodes, solar cells and the PEC hybrid devices were fabricated in the cluster tool PECVD/Sputtering System, designed and manufactured by MVSystems, Inc.



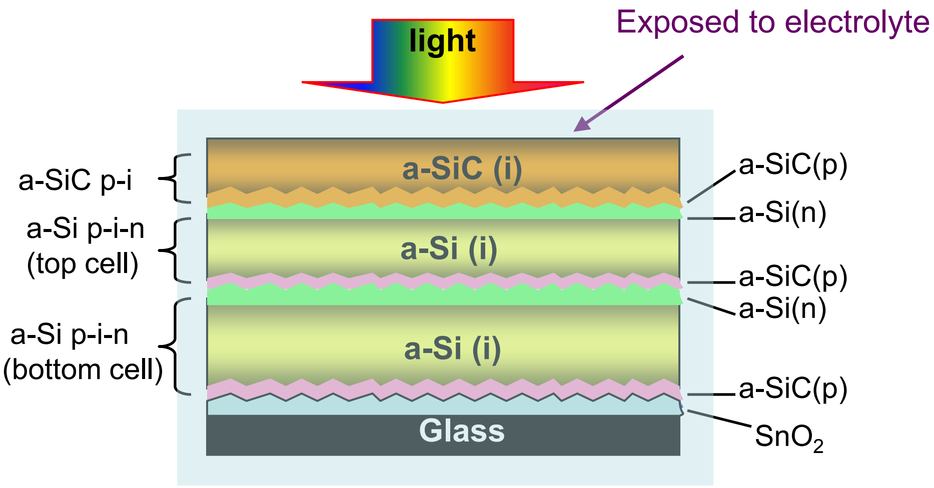
Main deposition parameters:

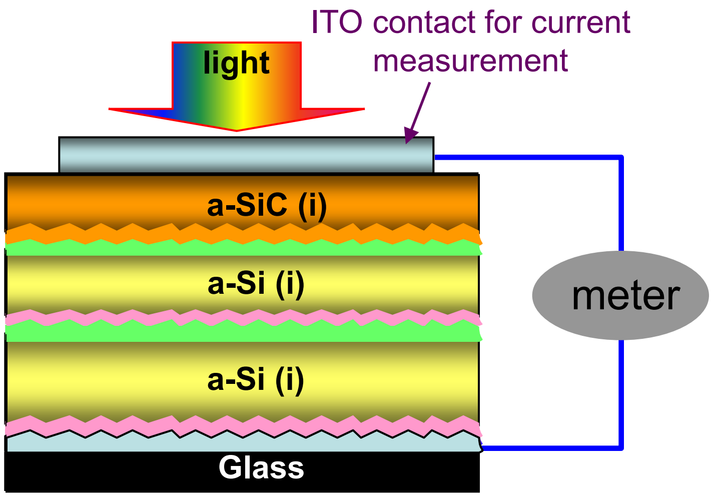
RF power:	**10-20 W**
Excitation frequency:	**13.56 MHz**
Pressure:	**300-550 mTorr**
SiH_4 flow rate:	**20 sccm**
CH_4 flow rate:	**0-20 sccm**
H_2 flow rate:	**0-100 sccm**
Substrate temperature:	**200° C**

http://www.mvsystemsinc.com

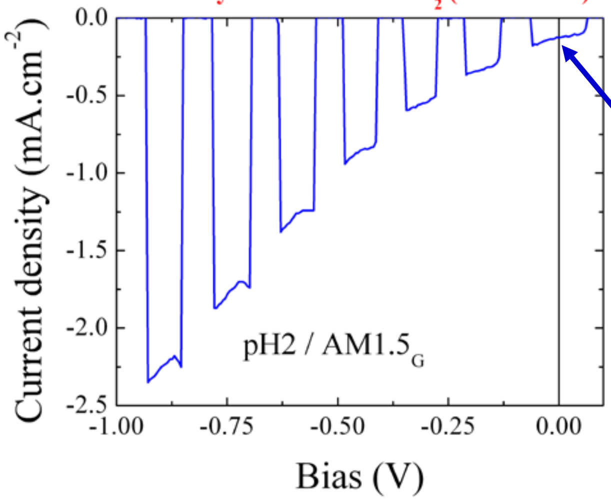
Amorphous and/or nano-crystalline Si solar cells in conjunction with the photo-electrode as the driver for a-SiC, WO3 and I-III-VI_2 PEC.

Progress: Comparison with a Solid-State Configuration





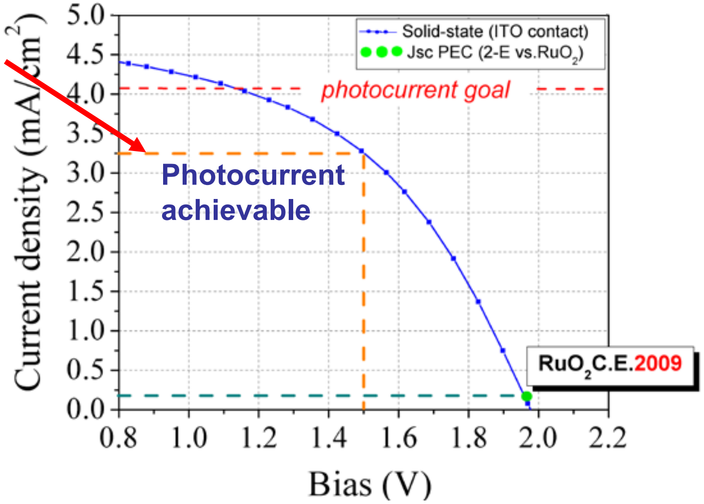
a-SiC hybrid PEC vs. RuO$_2$ (2-electrode)



0.25 mA/cm^2
in electrolyte

>3.2 mA/cm^2
as a solid-state device
assuming 0.3V
overpotential

Solid-state version with ITO contact

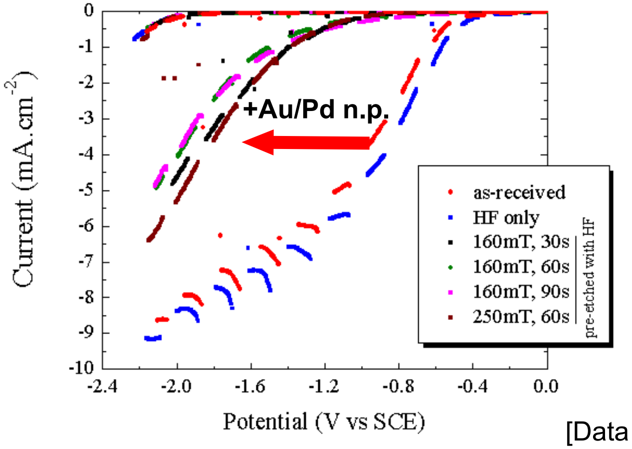


- STH efficiency of hybrid PV/a-SiC device should be >4% base on solid state version (right)
- Low current in hybrid PV/a-SiC device (left)
- <u>Charge carrier extraction problem at the a-SiC/electrolyte interface</u>

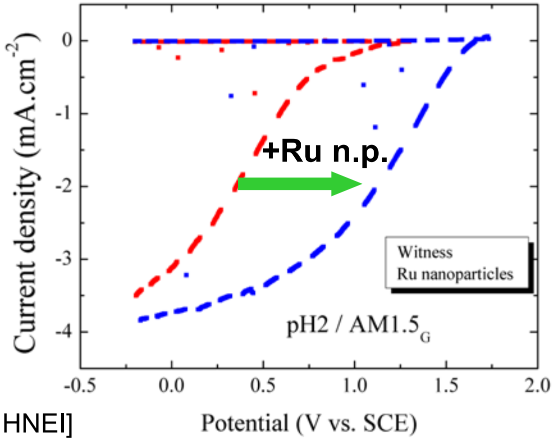
Progress: Surface modification by metal nanoparticles

(reported in 2011’ & 2012’ AMR meeting)

High work function metals (Pt, Pd, Au) *decrease* photocurrent:



Low work function matals (Ti, Ru, W) *increase* photocurrent



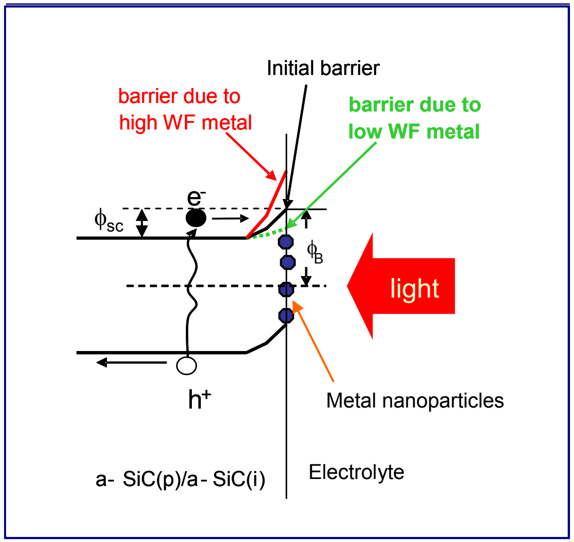
[Data measured by HNEI]

Potential shift ΔV for metals of different work functions

Metal	WF ϕ_m (eV)	ΔV* (V vs. SCE)	ϕ_{sc} ** (eV)
Pt/Au	5.4 (Pt)	-0.7~ -0.8	1.46 (Pt)
Pd/Au	5.6	-0.8~ -1.1	1.66
Ti	4.33	0.2 ~ 0.4	0.39
Ru	4.71	0.3 ~0.75	0.77
W	4.8	0.6	0.84

* Measured at current density of 2 mA/cm^2.

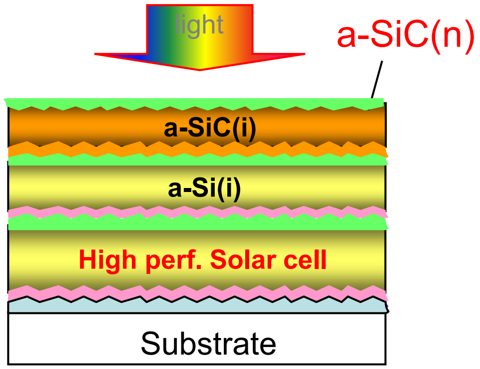
** $\phi_{sc}= \phi_m- \phi_s$. ($\phi$s from reported surface data)



Progress: Further improvement in surface energetics

Addressing “Efficiency”

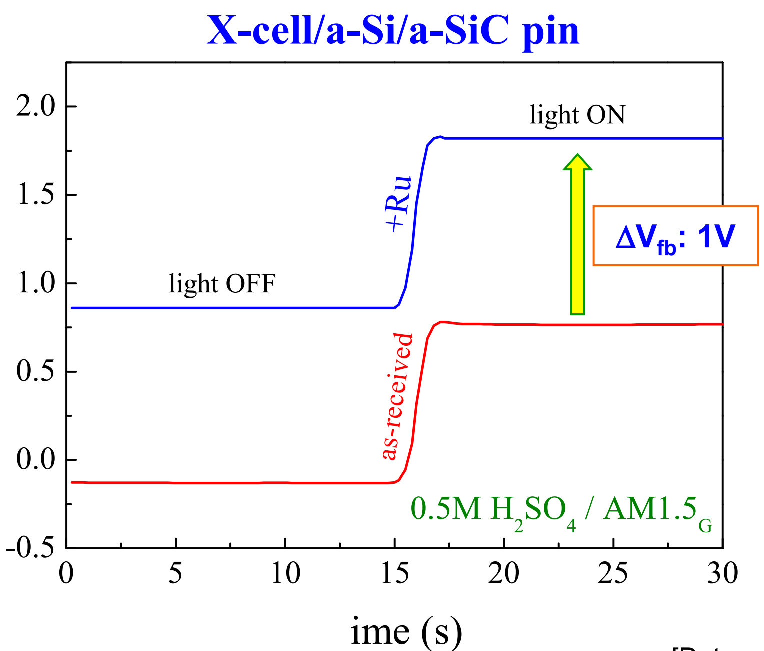
New configuration: (X-cell pin/ aSi-pin/a-SiC pin)

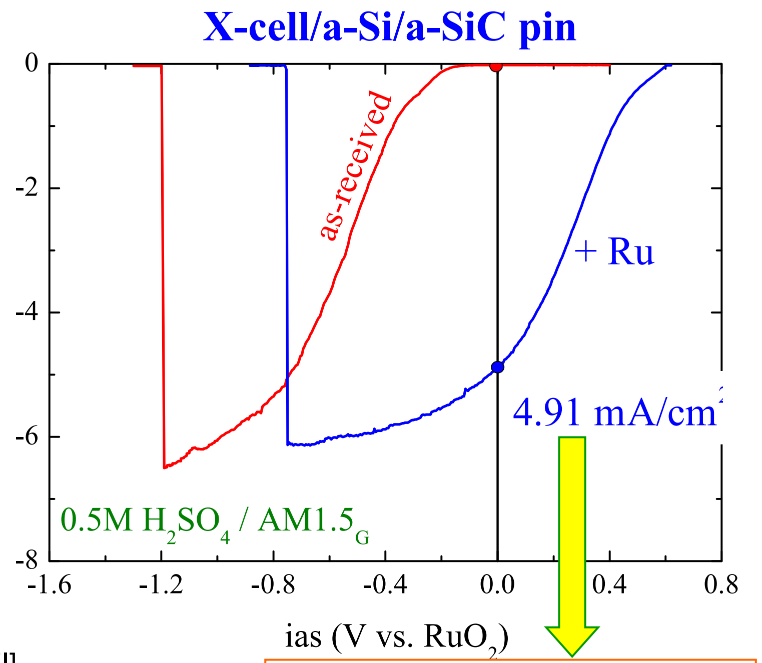


Comparison of PEC performances:

(a-Si pin-pin/a-SiC pi *vs* X-cell/aSi/a-SiC pin)

Configuration	V_{fb} shift (V)	J_{ph} @0V (mA/cm²)	STH efficiency (%)
a-Si PV/a-SiC p-i	0.45	2.0	2.46
X-cell/a-Si/a-SiC pin	1.0	4.9	6.10





[Data measured by HNEI]

STH efficiency = **6.10%**

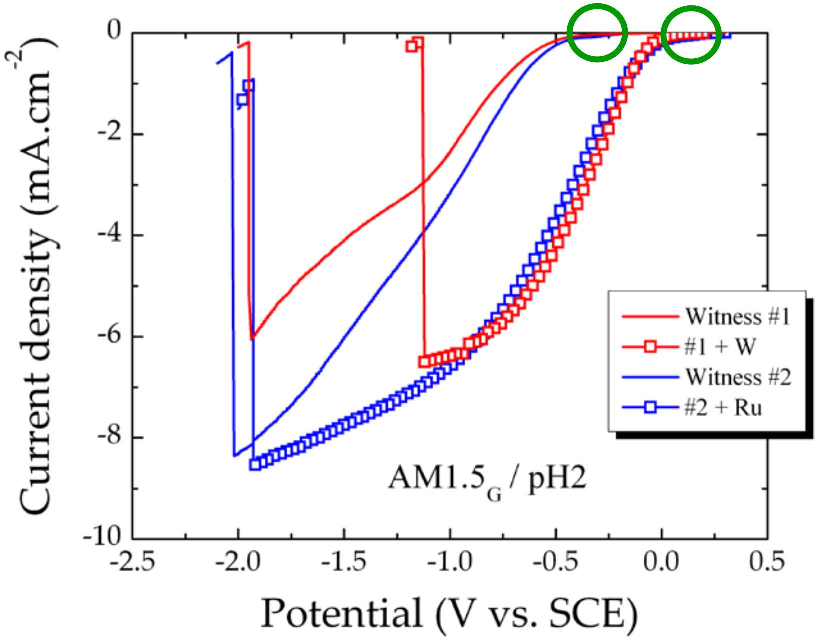
Progress: Surface modification using W nanoparticles

Addressing "Efficiency"

Motivation:

- low work function: ~4.8 eV
- *much cheaper* than Ru

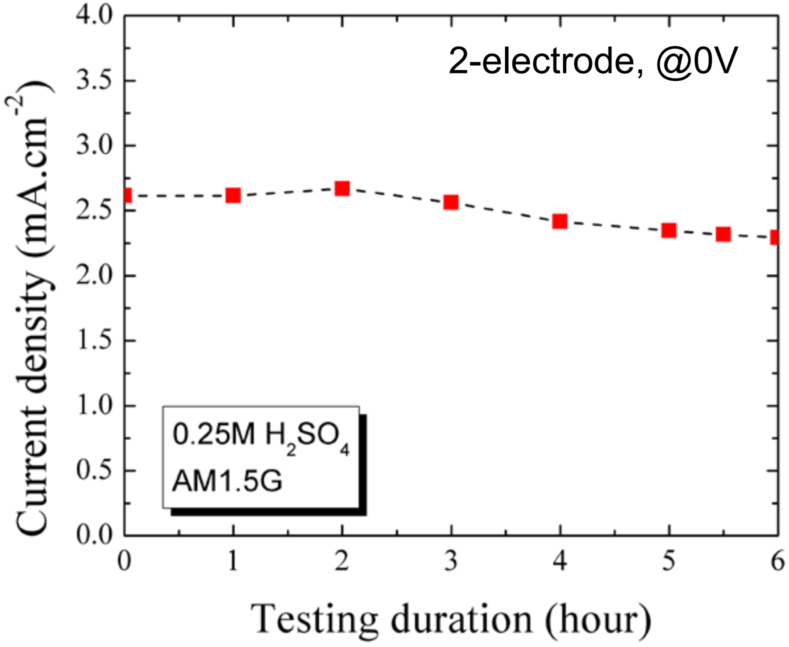
On a-SiC Photoelectrodes:



[Data measured by HNEI]

Ru and W lead to identical onset V anodic shift

On hybrid PV/a-SiC pi devices:



- Good surface energetics is likely due to a low WF (~4.8eV)
- Initial durability test is promising

Part I

Amorphous Silicon Carbide (a-SiC)

Part II

Metal Oxide Compounds

Part III

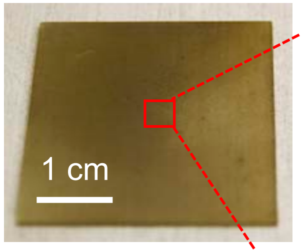
I-III-VI_2 (Copper Chalcopyrite-based)

Progress: New metal oxides with E_G =2.0-2.2eV

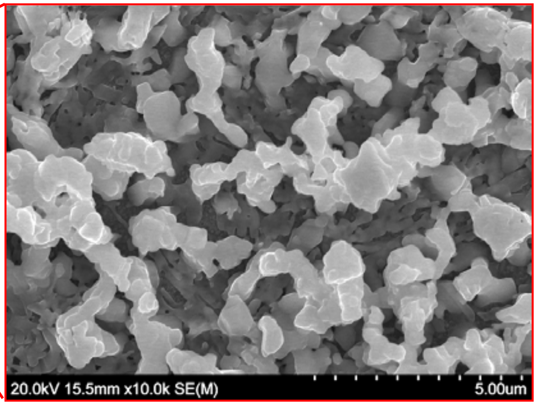
Addressing efficiency

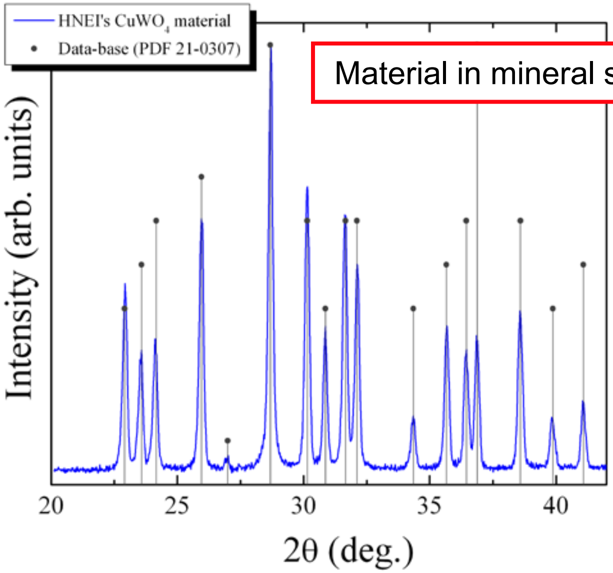
$CuWO_4$ fabricated by spray-pyrolysis

EMPA

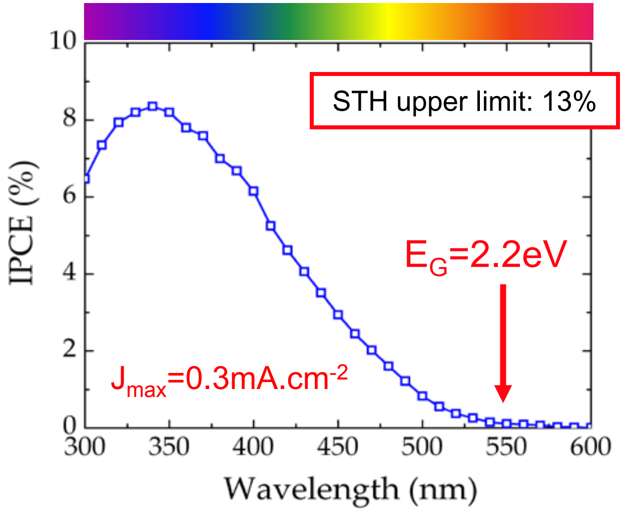


Sprayed @ 300°C
Annealed @ 500°C

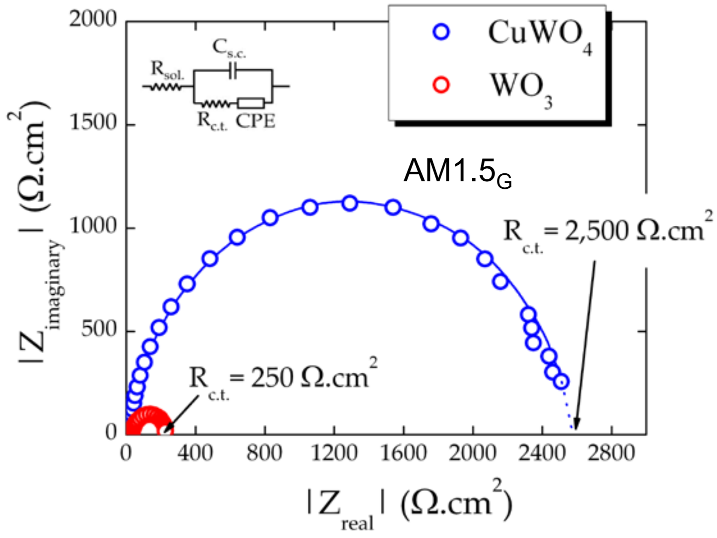




Material in mineral state



STH upper limit: 13%



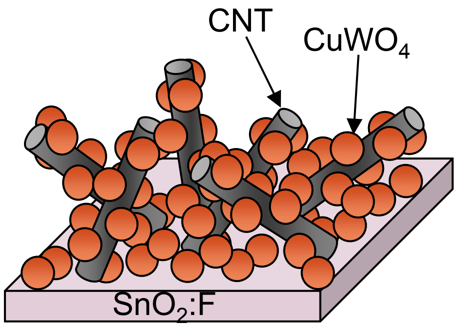
Transport properties must be addressed

Y. Chang, J. Phys. Chem. C 115, 25490 (2011)

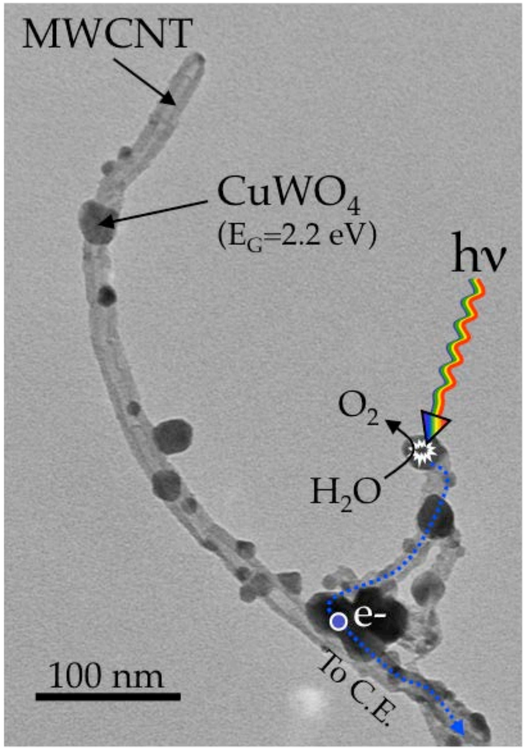
Progress: New metal oxides with E_G =2.0-2.2eV

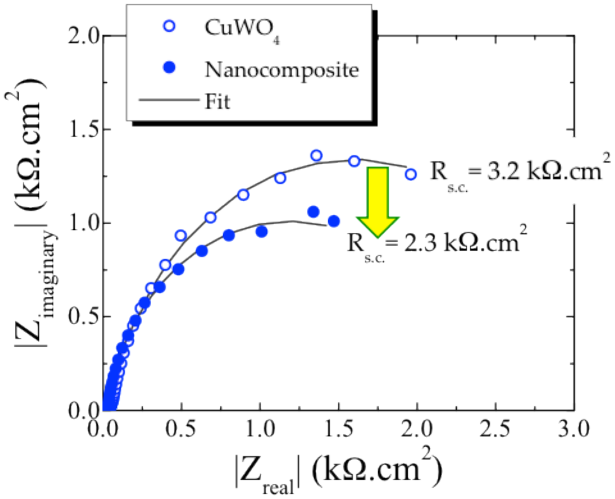
Addressing efficiency

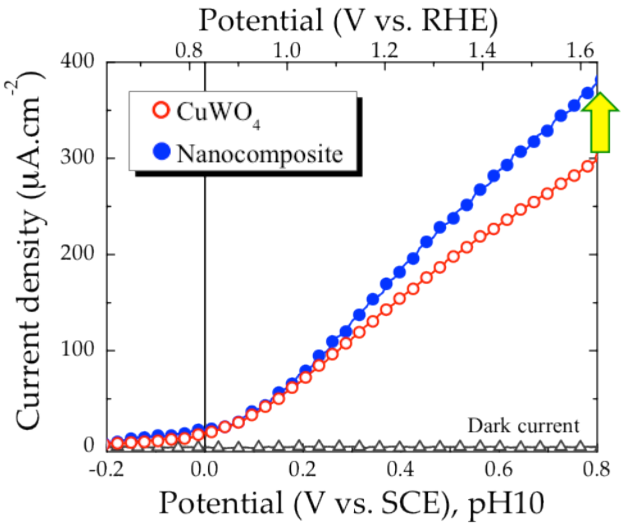
Improving $CuWO_4$ transport properties with CNT

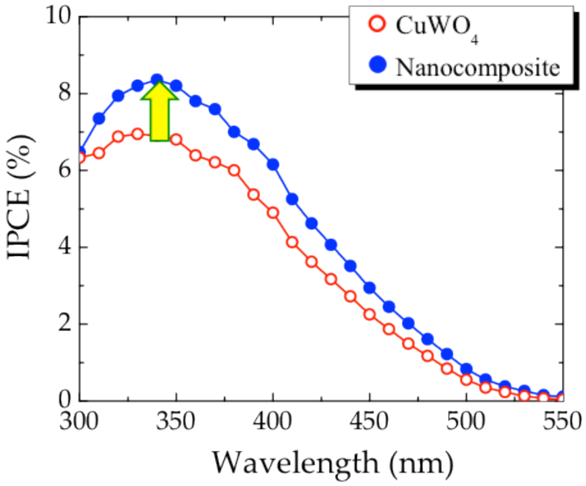


Light absorber / charge collector









→ **Bulk resistance drops by 30% ➔ current density increases by 30%**

→ **CNTs act as distributed current collector in $CuWO_4$**

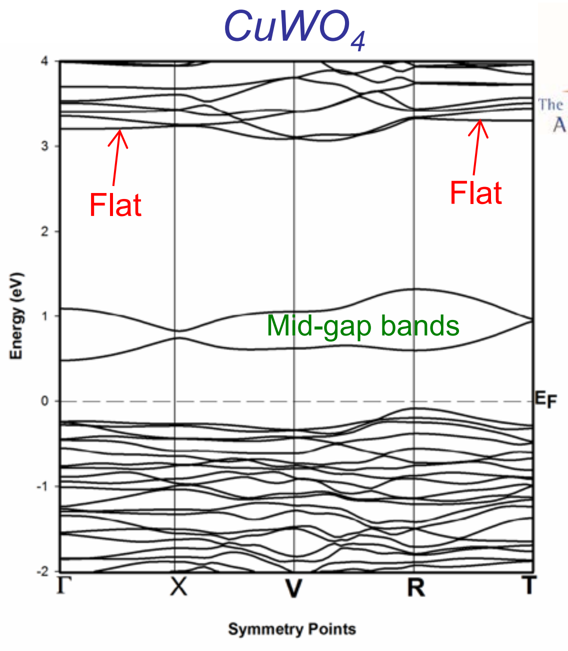
N. Gaillard, Int. J. Hydrogen Energ. 38, 3166 (2013)

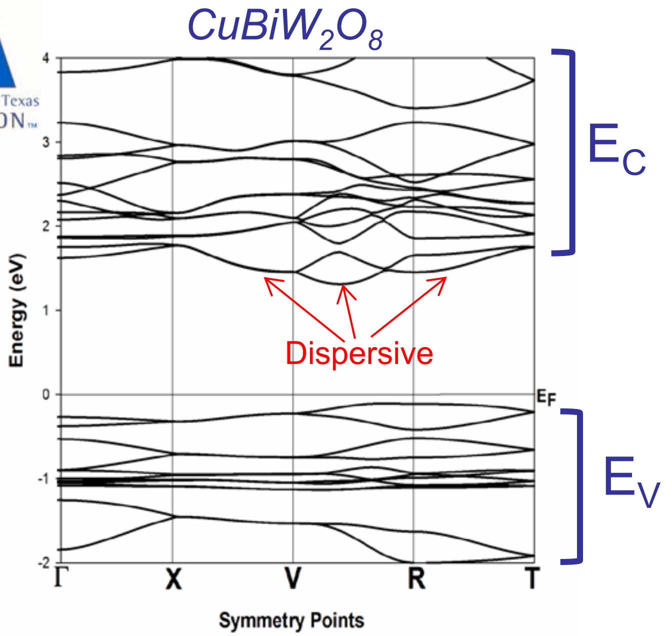
Progress: New metal oxides with E_G =2.0-2.2eV

Addressing efficiency

➯Extending tungstate material class to ABW_2O_8, A=Cu and B=Bi

Electronic structure calculated by Pr. Huda using Density Functional Theory





The University of Texas ARLINGTON™

When compared to $CuWO_4$, $CuBiW_2O_8$ has:

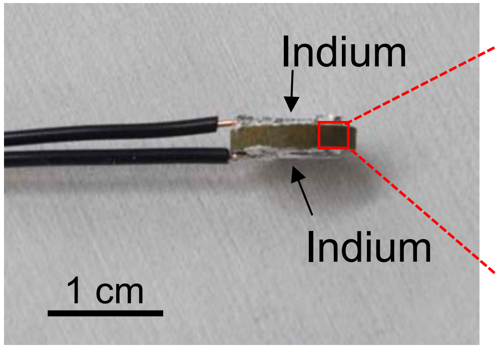
1. no mid-gap bands: reduce charge trapping
2. more dispersive conduction band: lower effective mass

➲ $CuBiW_2O_8$ should have a higher electrical conductivity than $CuWO_4$

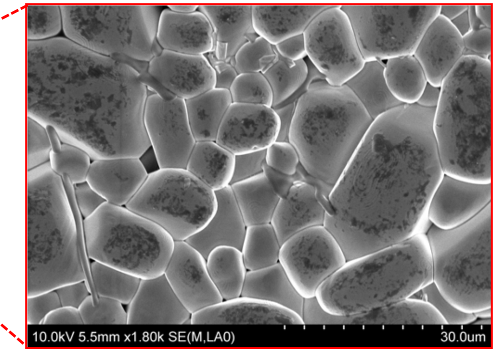
Progress: New metal oxides with E_G =2.0-2.2eV

Addressing efficiency

Density functional theory (DFT)-driven material down-selection

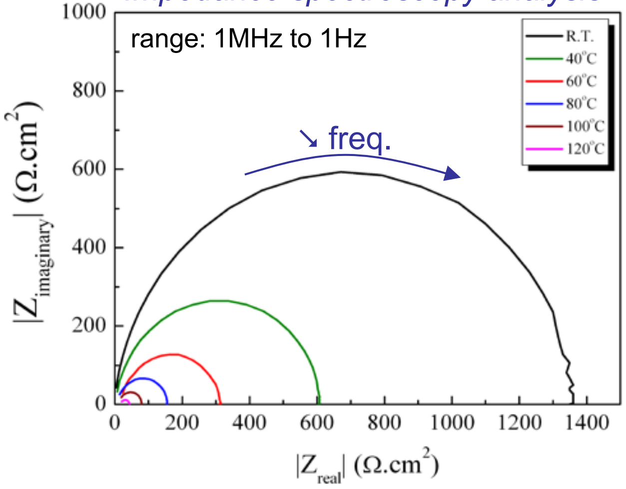


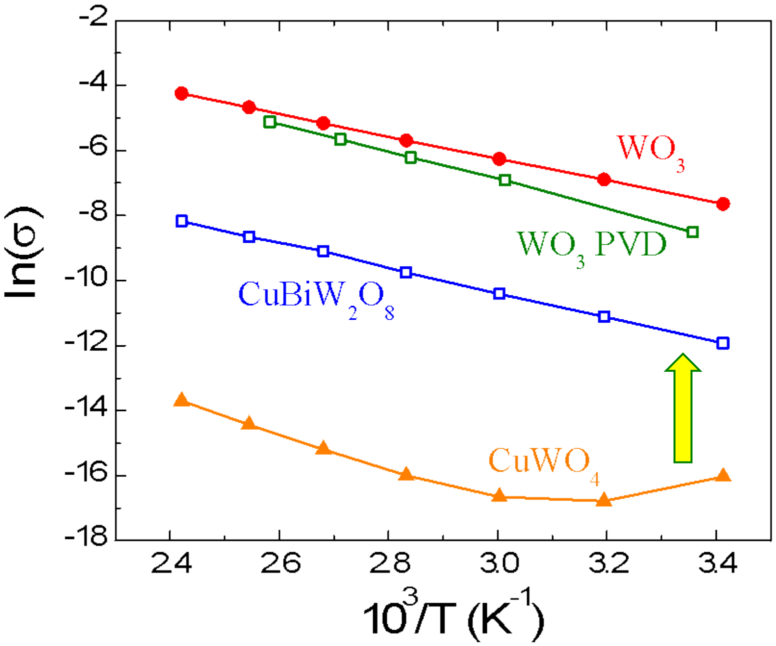
Electrode for conductivity test



Pellet density ≈ 95% bulk density

Impedance spectroscopy analysis





Material	Synthesis Method	T	σ at R.T. ($S.cm^{-1}$)	$E_{activation}$ (meV)
WO_3	PVD	275°C	2.1×10^{-4}	377
	SSR	1200°C	3.5×10^{-4}	293
$CuBiW_2O_8$	SSR	800°C	6.8×10^{-6}	326
$CuWO_4$	SSR	850°C	1.1×10^{-7}	440

Clear improvement with introduction of Bi in $CuWO_4$:

$\sigma(CuBiW_2O_8) = \sigma(CuWO_4) \times 100$

Part I

Amorphous Silicon Carbide (a-SiC)

Part II

Metal Oxide Compounds

Part III

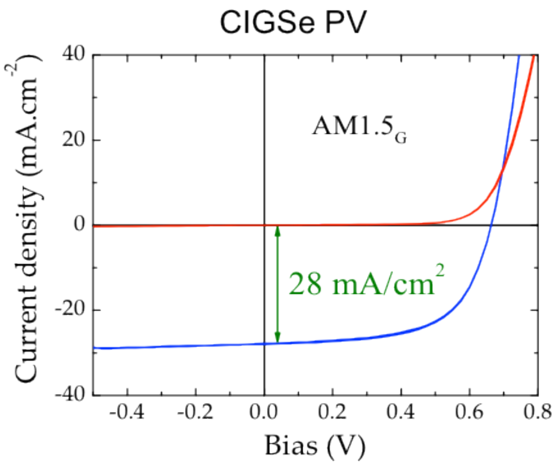
I-III-VI_2 (Copper Chalcopyrite-based)

Progress: synthesis of 2.0eV chalcopyrite

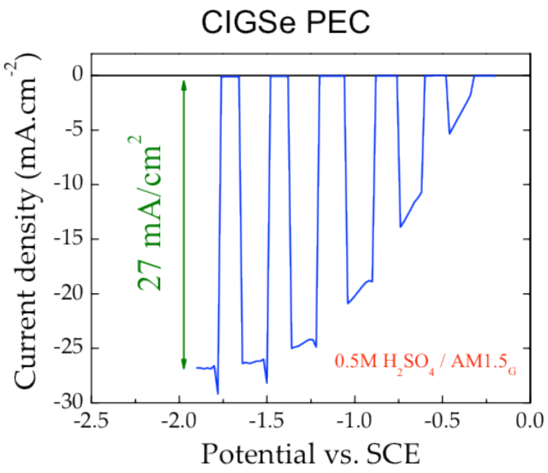
Addressing "Efficiency"

Benefits of chalcopyrite class:

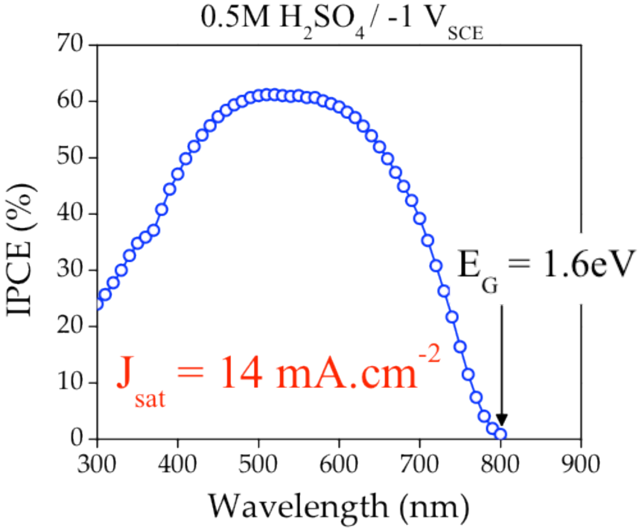
1. Technology ready
2. PV grade material
3. Alloying possible
4. Highly tolerant to defects
5. Bandgap tunable


CIGSe PV

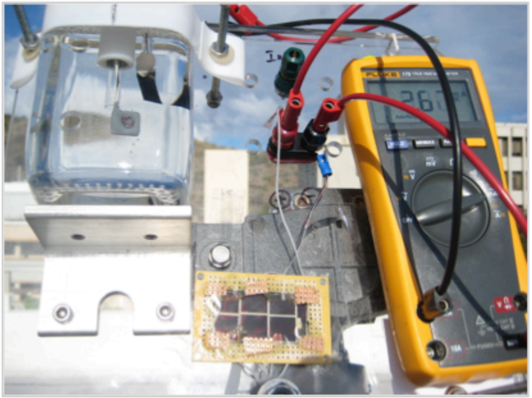
VS.


CIGSe PEC

$CuGaSe_2$ baseline material

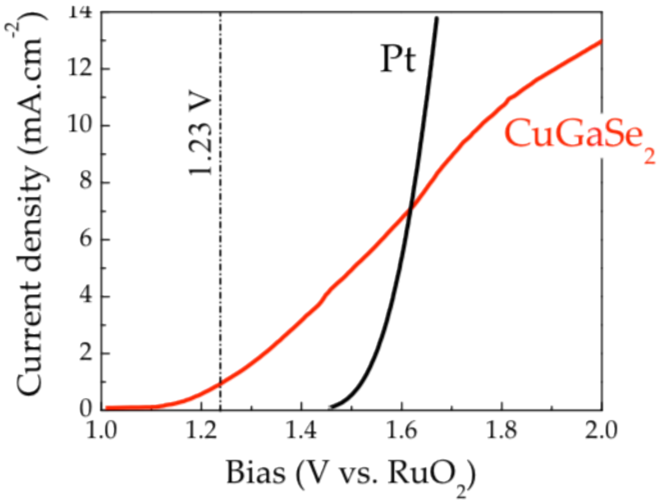

0.5M H_2SO_4 / -1 V_{SCE}

Demo: 3 aSi PV–CGSe PEC



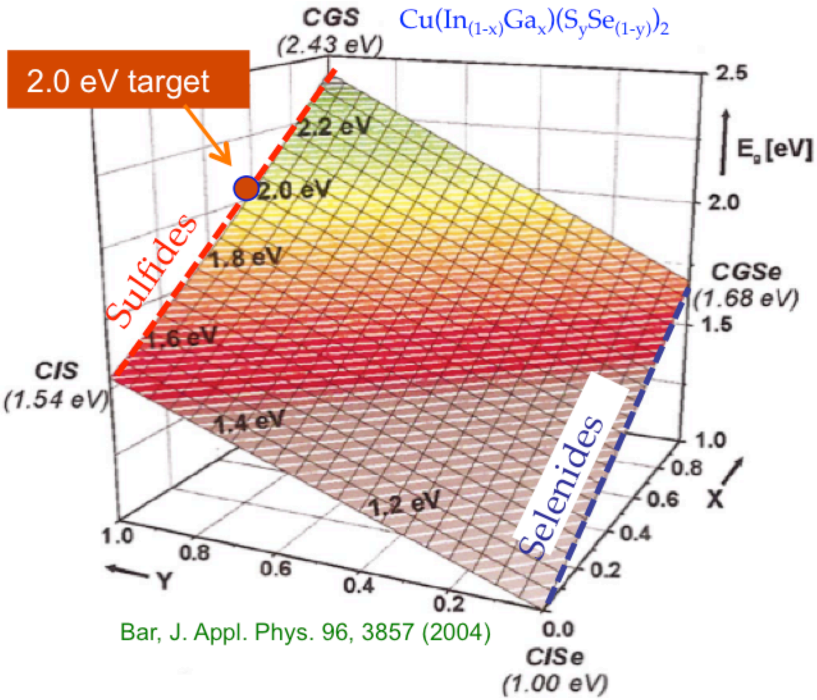
Jsc: 3.5 mA/cm^2 → STH: 4.34%

A "non-precious" electro-catalyst rather than a photocatalyst…



Progress: synthesis of 2.0eV chalcopyrite

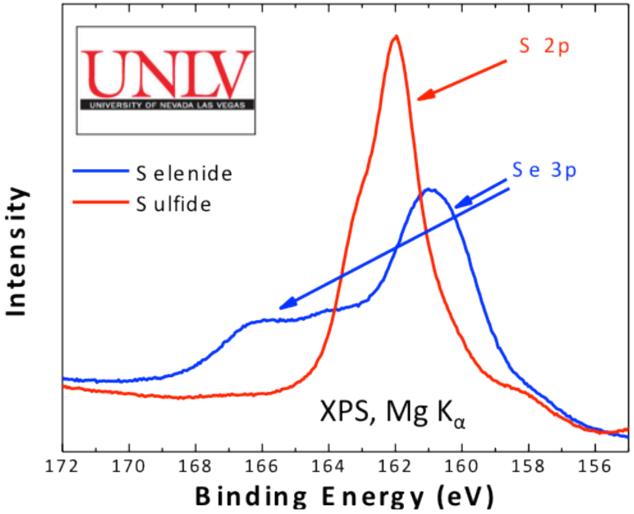
Addressing "Efficiency"

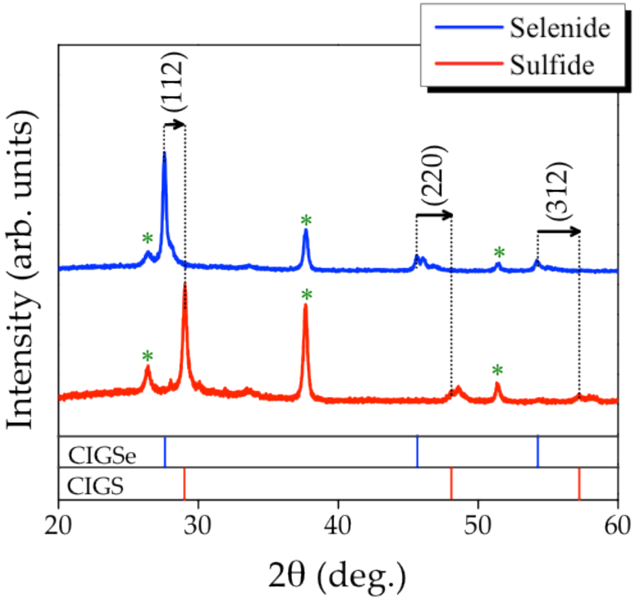


Bar, J. Appl. Phys. 96, 3857 (2004)

Method: sulfurization of CuIn$_x$Ga$_{(1-x)}$Se$_2$

- Sample & sulfur sealed under argon
- 450-550°C for 1 to 10 minutes

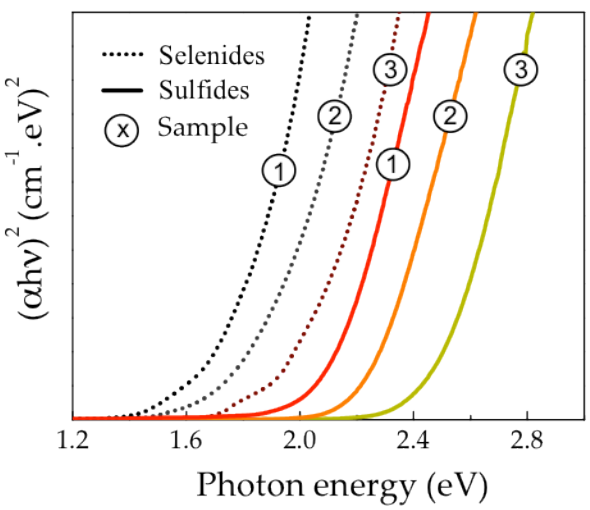




Substitution of Se with S at surface (XPS) and bulk (EDX: [Se]<2%)

Progress: synthesis of 2.0eV chalcopyrite

Addressing "Efficiency"



Optical band gaps

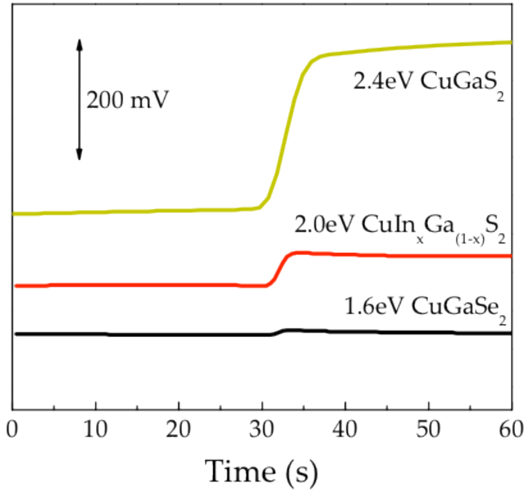
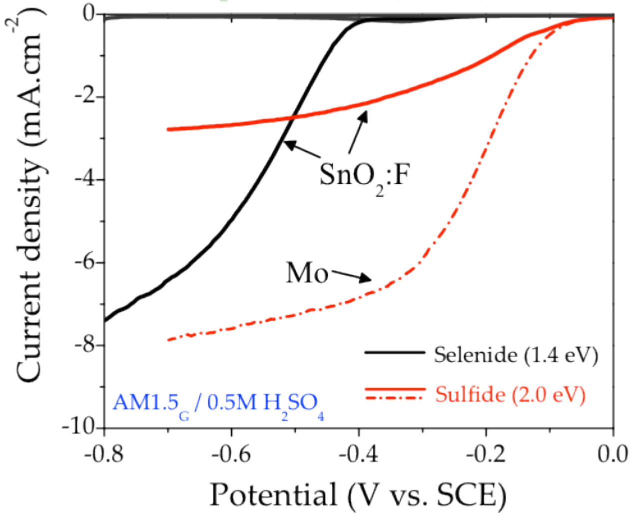
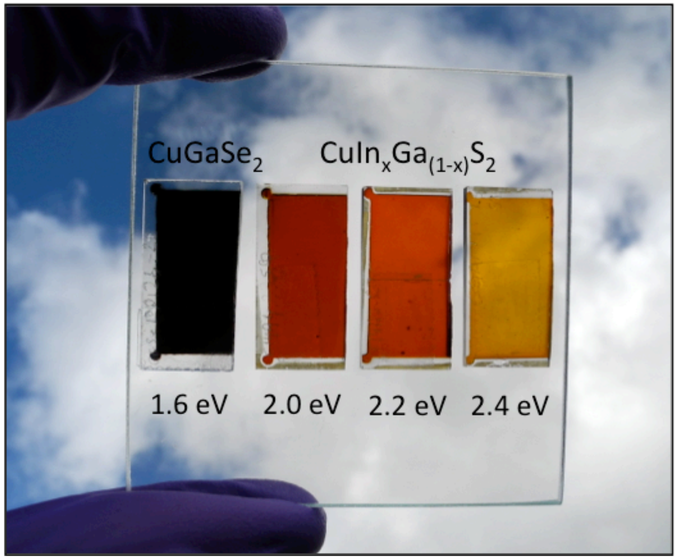


Photo-voltages



PEC characteristics

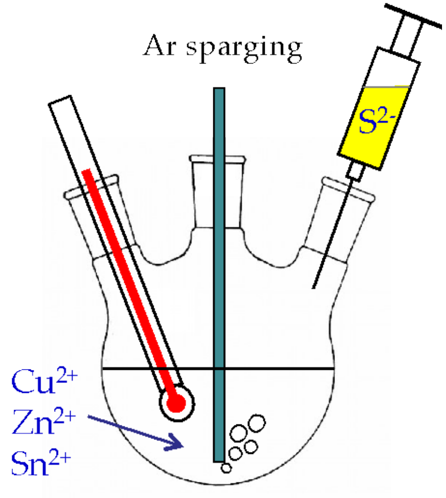


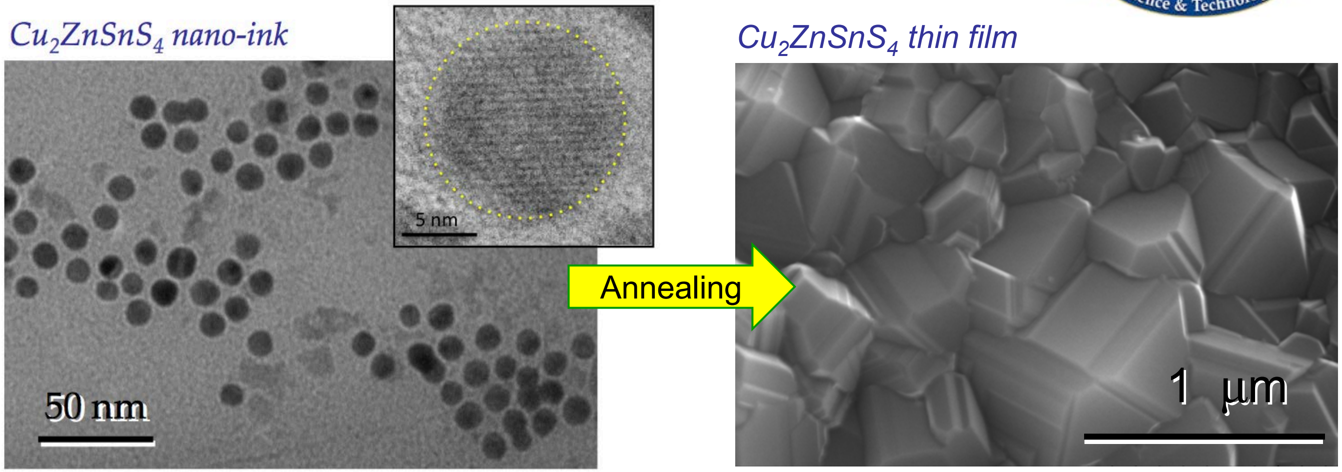
- Chalcopyrites with Eg ranging from 1.1eV (selenides) to 2.5eV (sulfides) successfully fabricated,
- **In/Ga ratio in sulfides adjusted to match 2.0eV Eg target,**
- PEC tests show significant charge carriers generation.

Future work: low-cost efficient chalcogenides

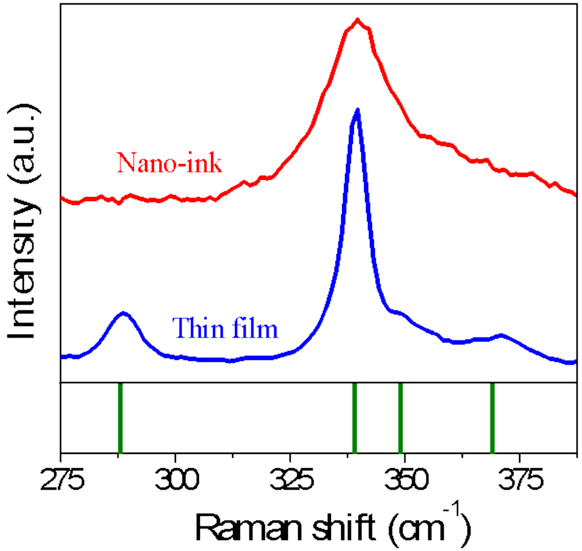
Addressing "material costs"

Chemical synthesis of Cu_2ZnSnS_4





Microstructure



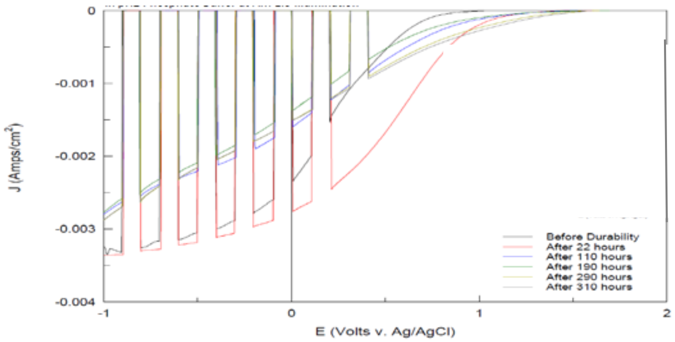
- Low-cost synthesis route for chalcogenide-based absorber developed,
- **Single phase Cu_2ZnSnS_4 achieved,**
- Method to be used to synthetized 2.0eV CIGS.

Durability test

Addressing “Durability”

a-SiC photoelectrode:

- Under AM1.5_G @1mA/cm^2, in pH2 buffer solution.
- No dark current increase for 310 hours

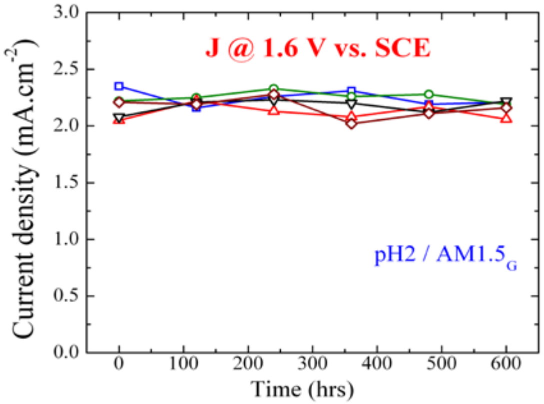


Hybrid PV/a-SiC device after 310-hrs

[Data measured by NREL]

WO_3 photoelectrode:

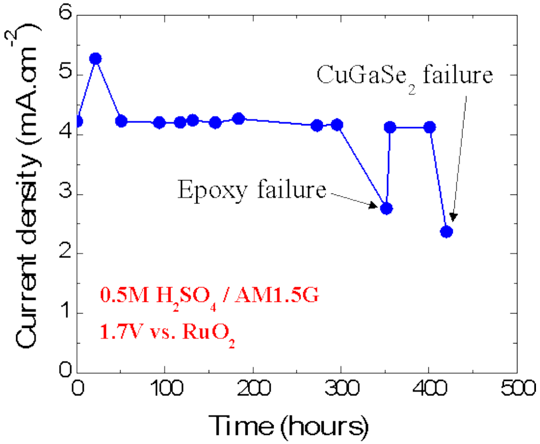
- Under AM1.5G @1.6V vs. SCE in pH2.
- High corrosion resistance of tungsten oxide in acidic solution for up to 600 hrs.



Five WO_3 samples after 600-hrs

CGSe photoelectrode:

- Under AM1.5_G @1.7V (4mA/cm^2), in 0.5M H_2SO_4 for 420 hours total
- Sealant and illumination issues may have led to degradation



$CGSe_2$ sample after 420-hrs

Collaborations

– *US Department of Energy PEC working group*: Leading task force on WO_3,I-III-VI_2 and a-SiC photoelectrodes

– *National Renewable Energy Laboratory*: collaboration to perform theoretical research and advanced morphological analysis of new materials.

– *University of Nevada at Las Vegas*: collaboration to analyze the surface energy band structure of new photoelectrode materials.

– *University of Texas in Arlington*: DFT calculation to establish new metal oxide.

– *University of California in Santa Barbara*: collaboration on surface treatment for catalytic purposes.

– *Stanford University*: collaboration on surface treatment for catalytic purposes.

– *Helmholtz Centre Berlin*: New alloy composition (sulfurization) fabrication, material/device theory

– *International Energy Agency/HIA/Annex 26*: collaboration with international institutes and universities including EMPA (Swiss) and University of Warsaw (Poland).

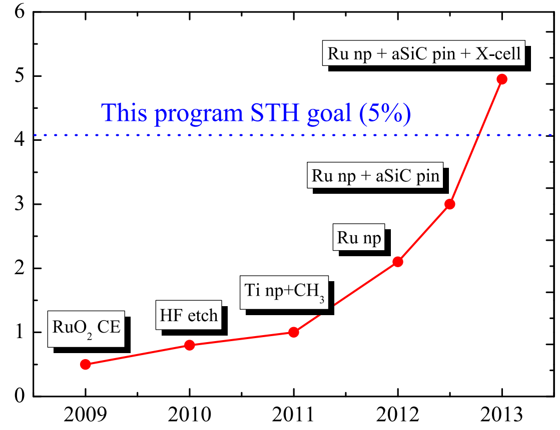
Project summary – Future work

a-SiC photoelectrodes:

- STH demonstrated: 6.1% — > 100% Achieved
- Durability achieved: 310 hours — 62% Achieved

Major achievement: decoupling energetics from kinetics

- Improve the PV cell and develop new surface treatments.
- Need to perform durability tests under working condition (i.e. @3mA/cm^2).

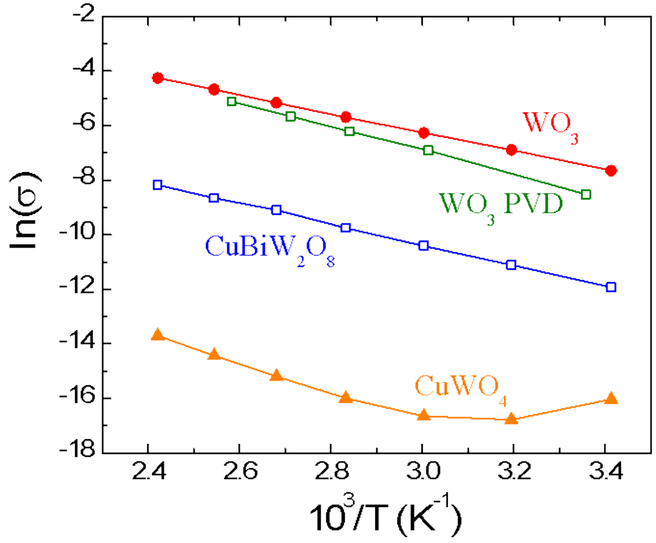


Metal oxides photoelectrodes:

- STH demonstrated: 3.1% — 62% Achieved
- Durability achieved: 600 hours — > 100% Achieved

Major achievement: DFT-driven metal oxide engineering

- Promising results with ternary metal tungstate
- New alloy identify via DFT: thin film synthesis on going



The University of Texas ARLINGTON

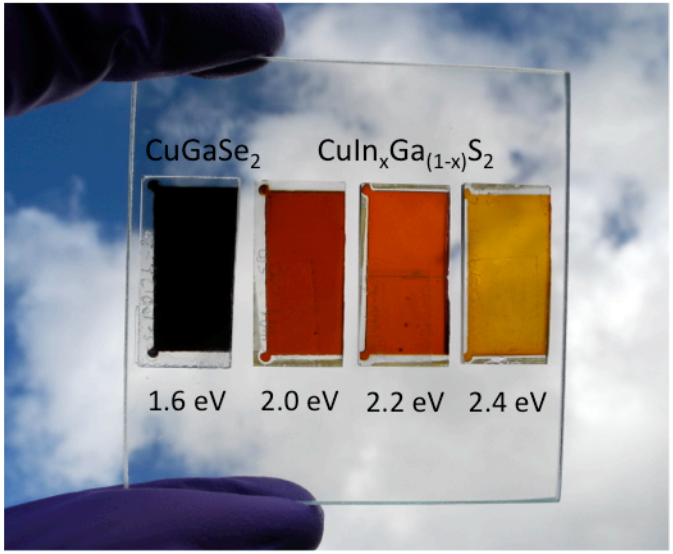
Project summary – Future work

Chalcopyrite photoelectrodes:

- STH demonstrated: 4.34% *87% Achieved*
- Durability achieved: 420 hours *84% Achieved*

Major achievement: synthesis of ‘Red’ (2.0eV) CIGS

- Develop low-cost (chemical) thin films synthesis
- Faradaic efficiency: 87%
- Durability: close collaboration with surface validation team



What we have learned from this study?

Lessons and recommendations

- Hybrid PV/PEC devices powered with low-cost a-Si solar cells work.
- Important work was done at solid-state level to improve devices efficiency.
- It is critical to decouple energetics from catalysis (Ru and W for PV/a-SiC cell are great example of this).
- Can not just go with “trial and error” approach (DFT was a great tool to improve oxides properties, as demonstrated with $CuWO_4$, $CuBiW_2O_8$).
- Improving durability will require input from PEC Working Group, especially the surface validation team (LLNL for theory, UNLV for advanced surface characterization…etc.)

Documents information

Main progress and results for this study (including all three thin film material classes will be described and documented in the final report at the end of this project.

Technical Back-up Slides

Progress : 500-hour durability tests

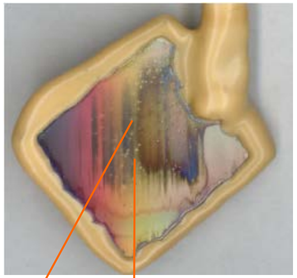
Addressing “z”

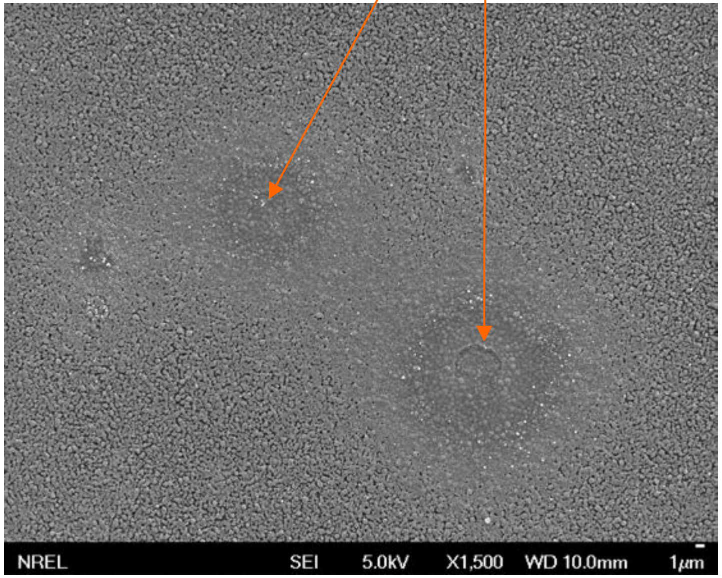
Test conditions:

- pH 2 Phosphate Buffer with 0.4M K2SO4& 2g/L Zonyl® FSN surfactant
- Under AM1.5G @1mA/cm^2
- Without surface treatment

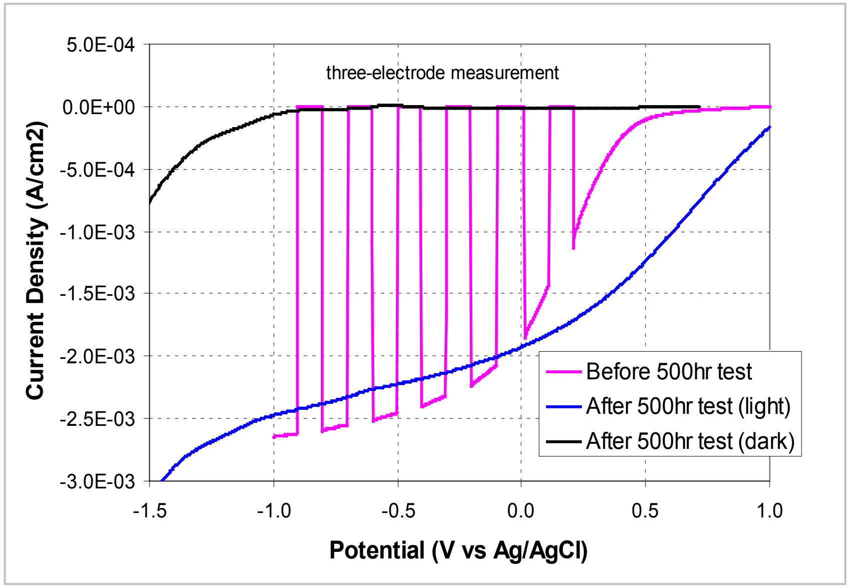
before testing

after 500 hours





J-V characteristics prior to and after 500hr test



- No major change in photocurrent
- But dark current increases

- a-SiC film is not corroded
- Localized defects may cause “shunts” in film

[Data measured by NREL]