PD053

PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

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MVSystems, Inc.

May 14-18, 2012

Project ID # DE-FC36-07GO17105, A00

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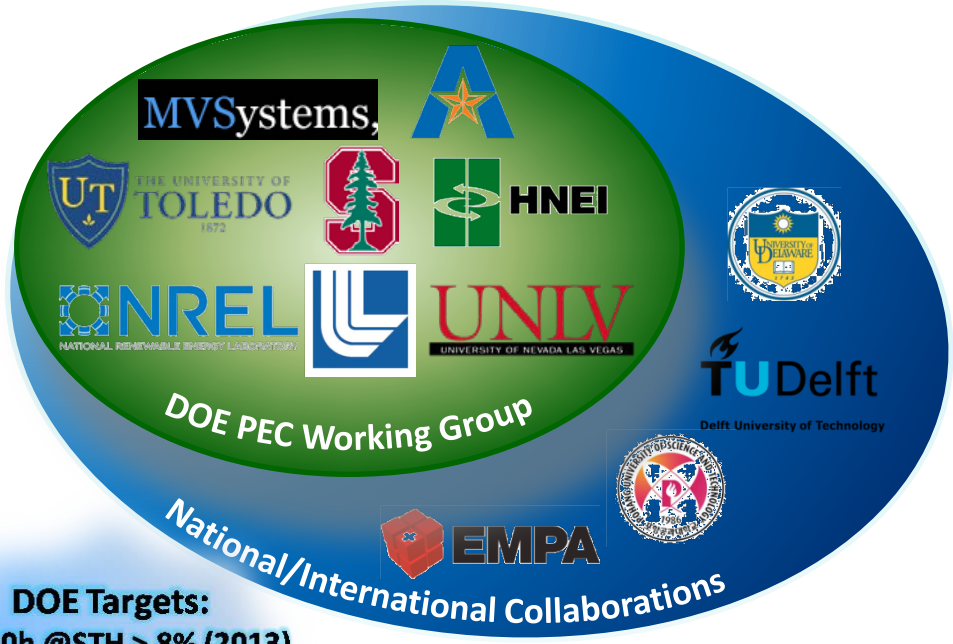
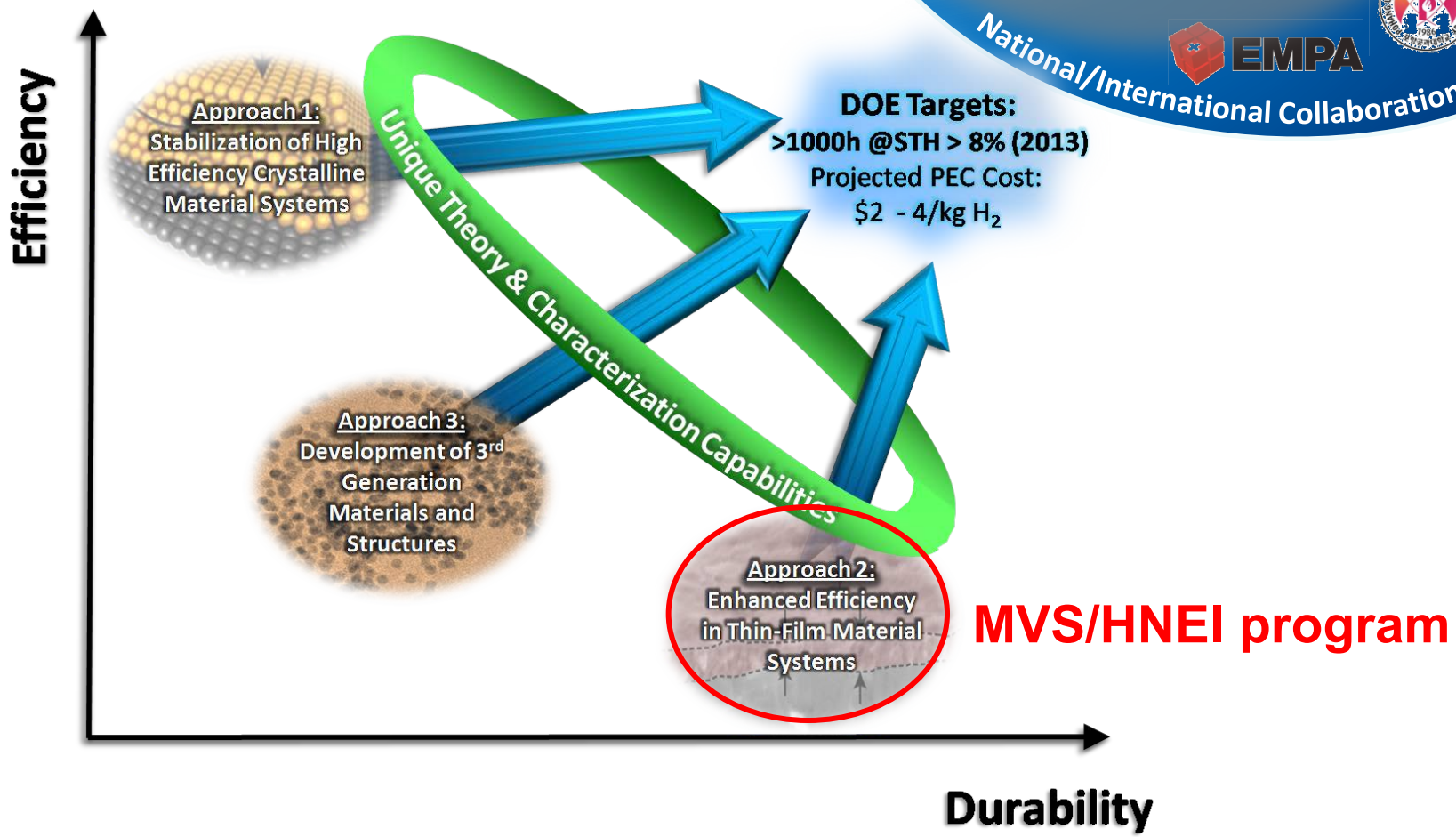
Approach

The US DOE PEC Working Group approach towards efficient and durable solar H_2 production





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

Budget

- Total project funding
  - DOE share: $ 2,970,172
  - Cost share: $ 820,000
- Funding received FY11: $686k
- Planned funding FY12: $556k

Barriers

- Challenges for photoelectrochemical hydrogen production technologies:

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

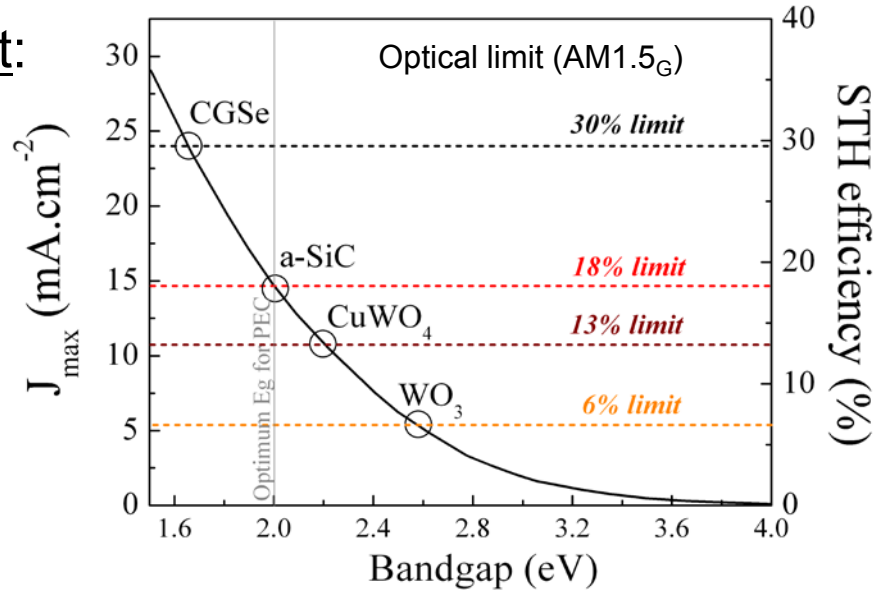
Partners

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

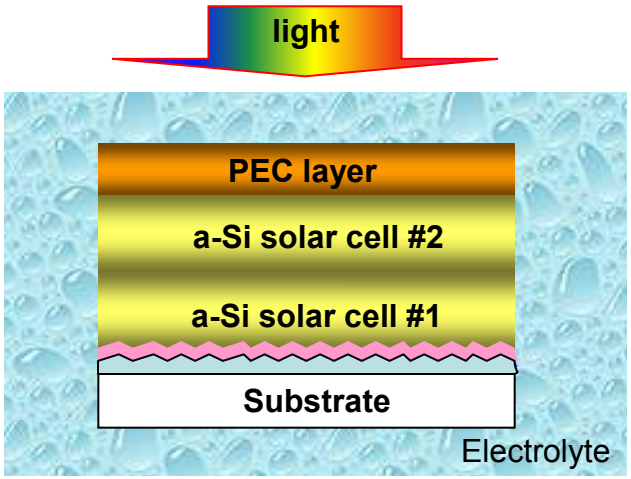
Relevance - Objectives

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:

- Solar-to-hydrogen efficiency: 5%
- Durability: 500-hrs (by the end of Phase II)

Relevance -Milestones

	Material Photocurrent	Material/Device Durability*	Device Efficiency (STH)
Goal ->	$4mA/cm^2$	500hrs	5%
Amorphous Silicon Carbide (a-SiC)	8mA/cm2	310hrs @ $1mA/cm^2$	2.5%STH
	>100% Achieved	*62% Achieved*	*50% Achieved*
Tungsten Oxide (WO_3)	$3.6mA/cm^2$	600hrs @ $1.5mA/cm^2$	3.1%STH
	90% Achieved	*>>100% Achieved*	*62% Achieved*
I-III-VI_2 (Copper Chalcopyrite-based)	$20mA/cm^2$	420hrs @ $4mA/cm^2$	4.34%STH
	>>100% Achieved	*84% Achieved*	*87% Achieved*

*** Test conditions in slide #24.**

Relevance – Barriers

	a-SiC	Metal oxides	I-III-VI_2 (Copper Chalcopyrite-based)
AB: Synthesis	Entire PEC device fabricated with low-cost PECVD in an 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**	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	600-hrs	420-hrs
Y: Efficiency - Achieved: **- Barriers:**	Less STH (3%) compared to the solid state version (>5%) **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

Synergetic work on 3 different material classes

1) All 3 hybrid PEC devices will use the same a-Si tandem solar cell "engine"

--> each improvement on the solar cell design benefits to the entire program

2) Both photo-anodes and photo-cathodes are evaluated under one program

--> Discovery on new surface catalysts can be implemented to new counter electrodes

3) All 3 material classes performances are evaluated in the same laboratory

--> all tests are performed under identical experimental conditions facilitating comparison

3 major tasks to achieve STH efficiency > 5%

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)

Presenter: *Jian Hu*, MVSystems, Inc

Part II

Metal Oxide Compounds

Presenter: *Nicolas Gaillard*, Hawaii Natural Energy Institute

Part III

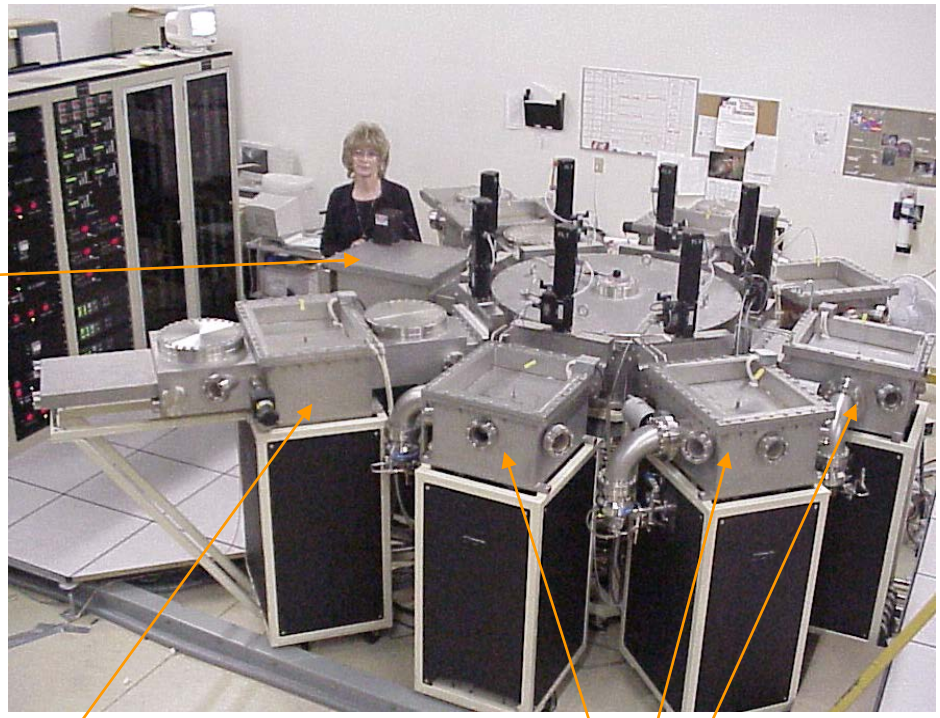
I-III-VI_2 (Copper Chalcopyrite-based)

Presenter: *Nicolas Gaillard*, Hawaii Natural Energy Institute

a-SiC: Cluster Tool PECVD/Sputtering System

Addressing "AB"

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.



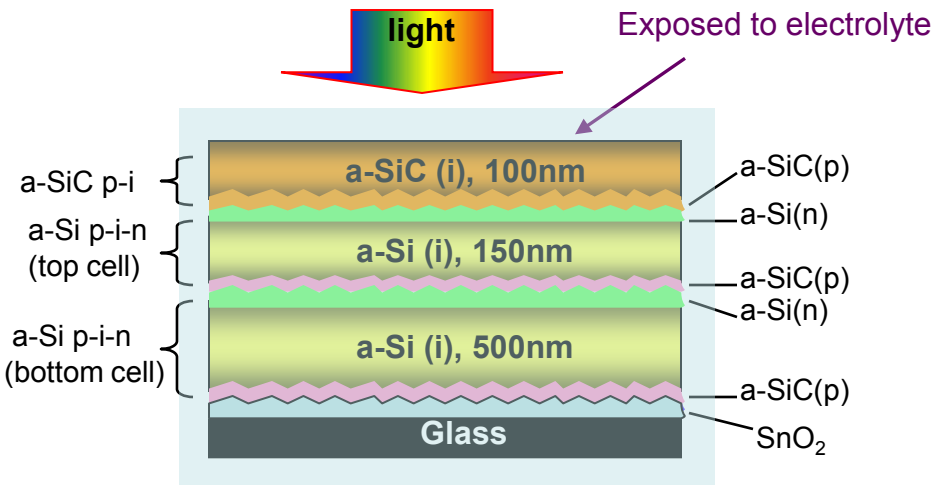
Main deposition parameters:

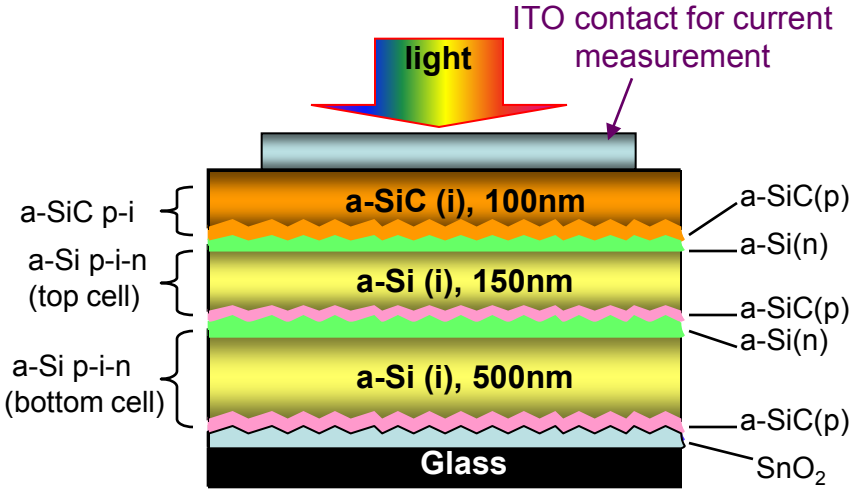
RF power:	**10-20 W**
Excitation frequency:	**13.56 MHz**
Pressure:	**300-550 mTorr**
SiH_4 flow rate:	**20 sccm**
CH_4 flow rate:	**0-20 sccm**
H_2 flow rate:	**0-100 sccm**
Substrate temperature:	**200°C**

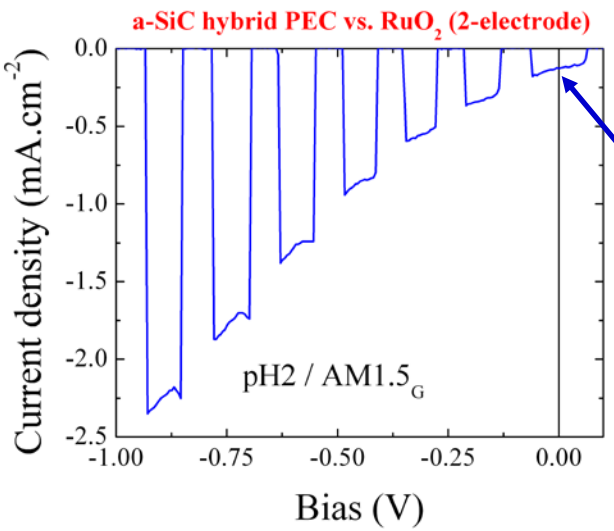
http://www.mvsystemsinc.com

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

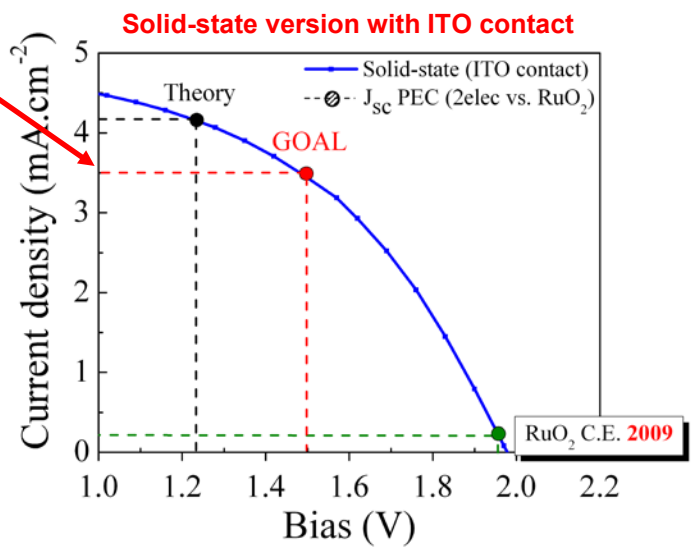






>3.5 mA/cm^2 as a solid-state device assuming 0.3V overpotential

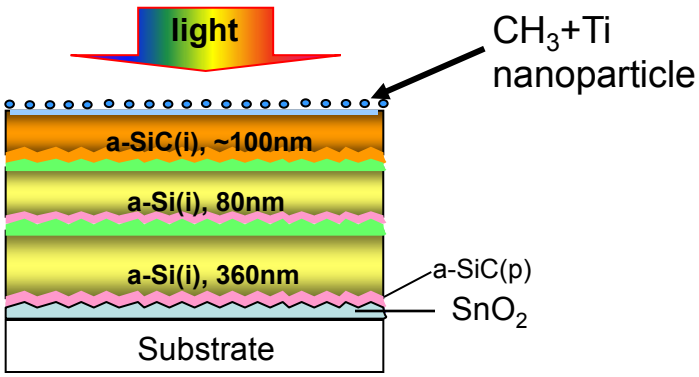
0.25 mA/cm^2 in electrolyte



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

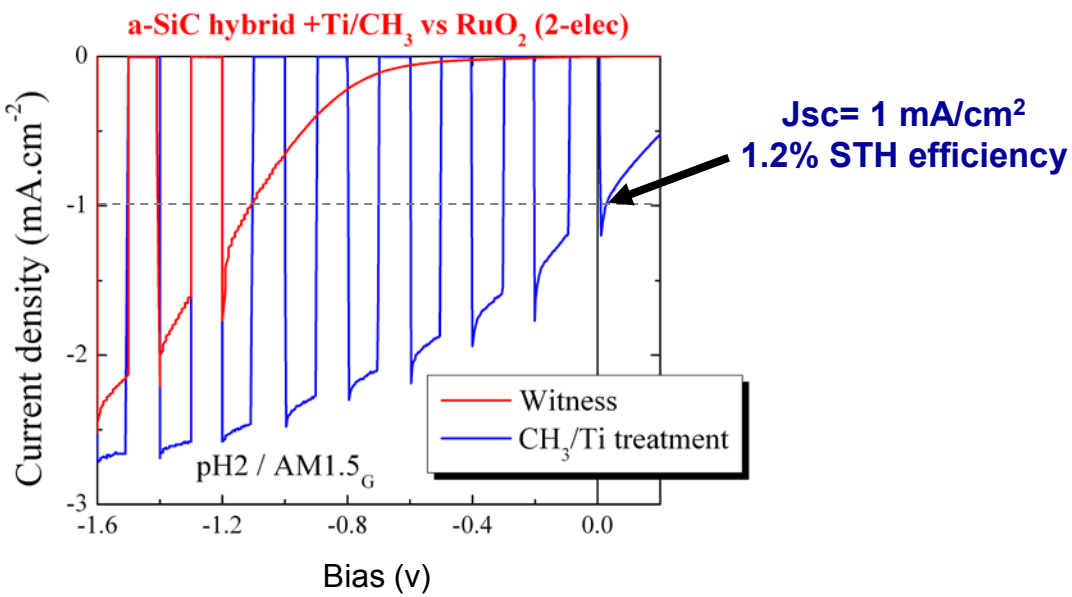
Progress: Surface Modification – by methylation (CH_3-termination)

Addressing efficiency with catalytic surface treatment



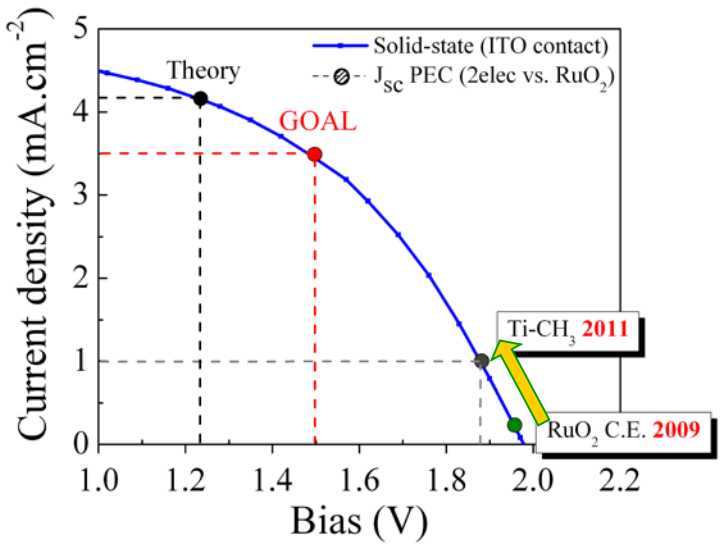
Surface treatment procedure:

- Step 1: Eliminate SiOx from a-SiC surface (via HF etch)
- Step 2: H-termination by immersing the sample into NH_4F
- Step 3: Treated with CH_3-containing species
- Step 4: Coated with Ti nano-particles



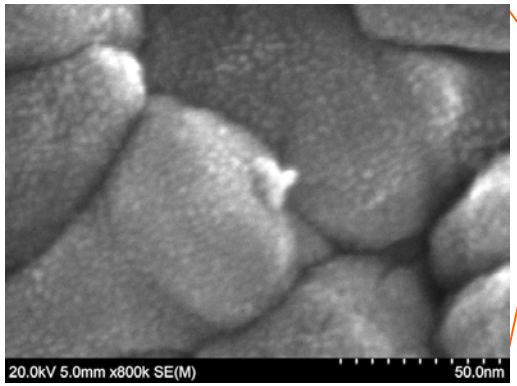
[Data measured by NREL]

J_{sc} increase after CH_3/Ti treatment

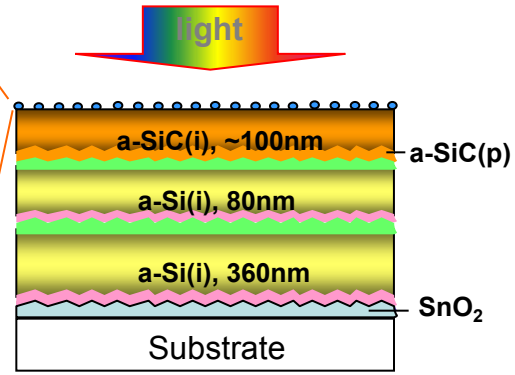


Progress: Surface Modification – Use of Ru Nanoparticles

Addressing efficiency with catalytic surface treatment

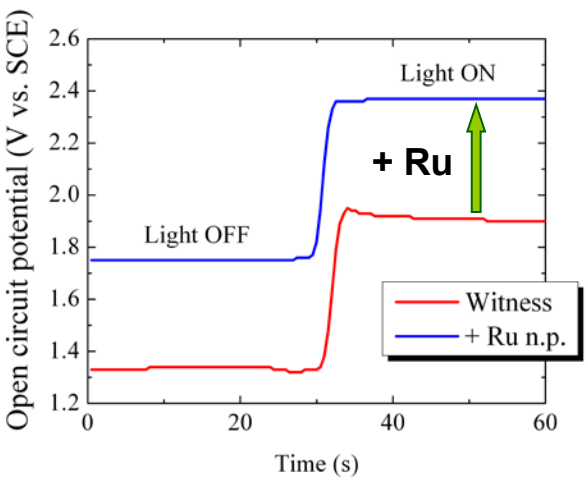


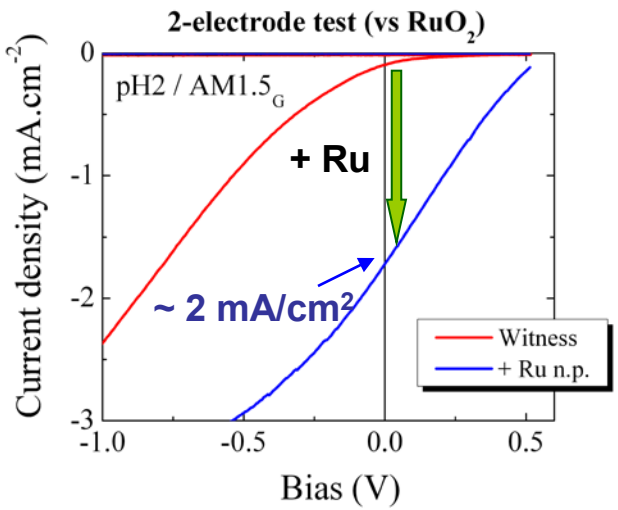
Ru nanoparticle coating (HNEI)

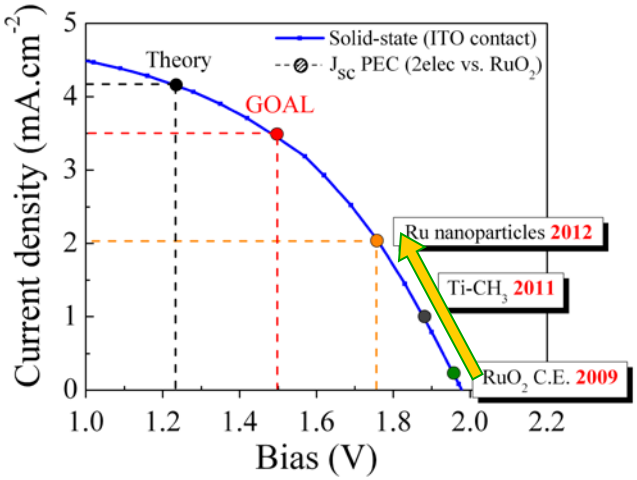


PV/a-SiC hybrid device

- **Ru alloys (i.e. Ru-Ni) with high HER catalytic activity demonstrated**
- **Ru nanoparticles with activity comparable with Pt recently reported(*)**







V_{FB} increased by 0.5V with Ru n.p.

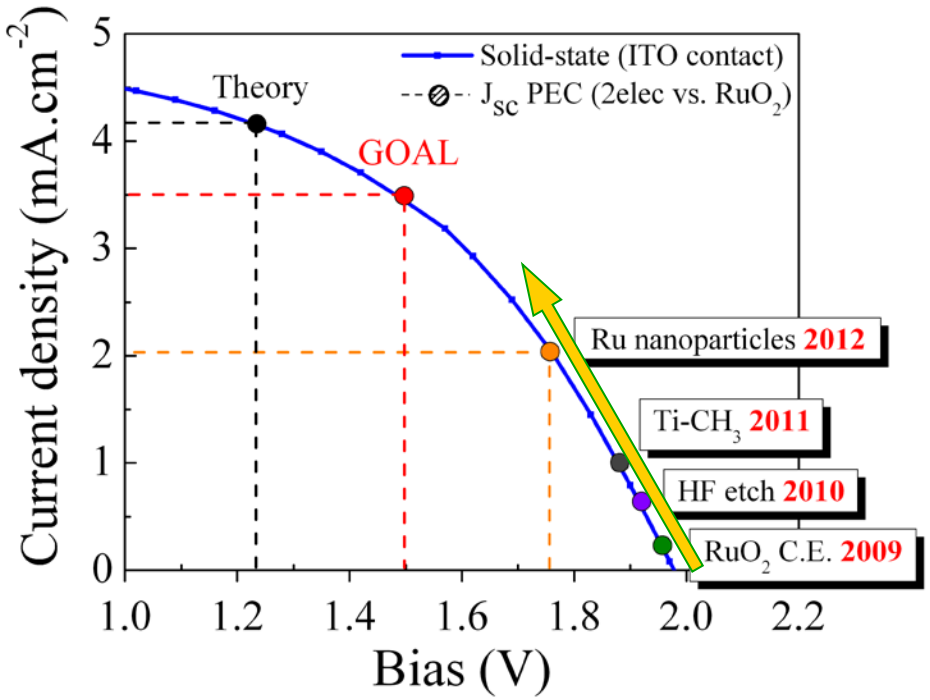
STH efficiency of ~2.5% is achieved

(*) Yamada, J. Am. Chem. Soc., 2011, 133 (40), pp 16136–16145

[Data measured by HNEI]

Future Work (a-SiC PEC electrode)

⇒ Catalytic activity of a-SiC PEC hybrid devices greatly improved with Ti-CH_3 or Ru surface treatments



- Improvement of photocurrent in the hybrid PEC cell.

  a. Refine surface treatment processes and further reduce over-potential:
  expected J_{ph} >3 mA/cm^2 and STH efficiency > 3%.

  b. Improve performance of a-Si tandem solar cell and PV/a-SiC photoelectrode triple junction device:
  expected FF>0.7 and J_{ph} > 4 mA/cm^2 @1.5V.

- Durability tests.

  - Perform more durability test up to ≥500 hours.

Part I

Amorphous Silicon Carbide (a-SiC)

Presenter: *Jian Hu*, MVSystems, Inc

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Part III

I-III-VI_2 (Copper Chalcopyrite-based)

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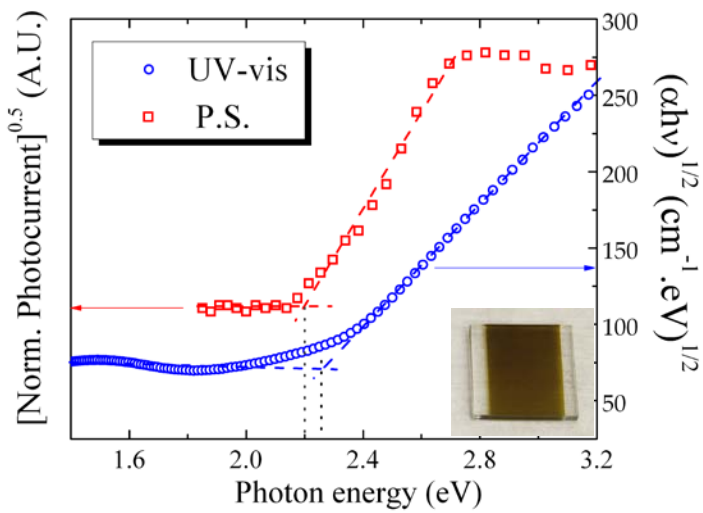
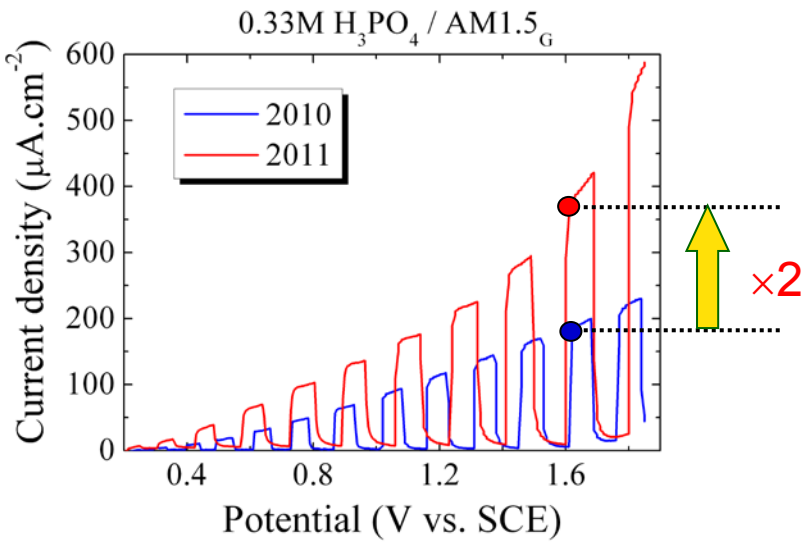
Progress: New metal oxides with E_G =2.0-2.2eV

Addressing efficiency

$CuWO_4$ fabricated with co-sputtering process

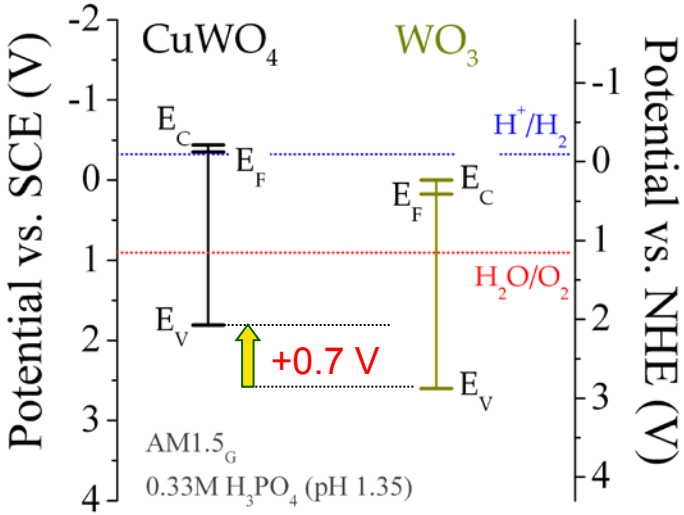


Band-gap ≈ 2.2 eV ($STH_{theor.}$=13%)

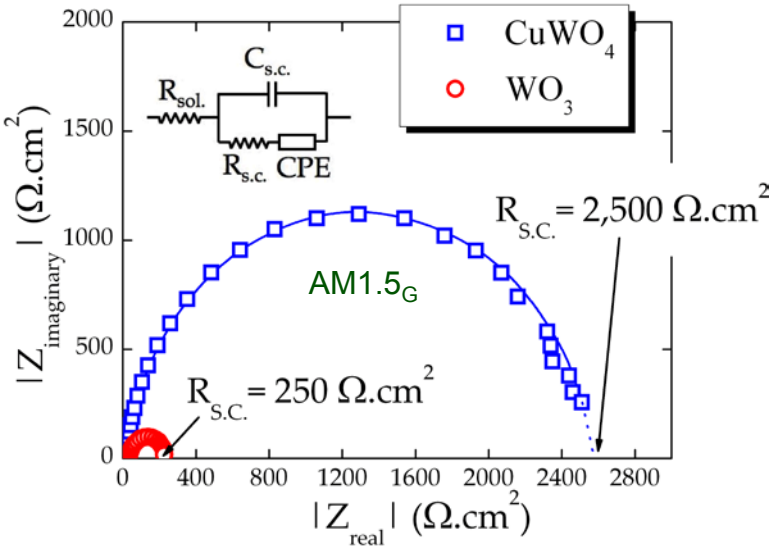


0.4 mA/cm² under $AM1.5_G$ illumination

Band structure derived from MS and UV-VIS



Ideal surface energetics



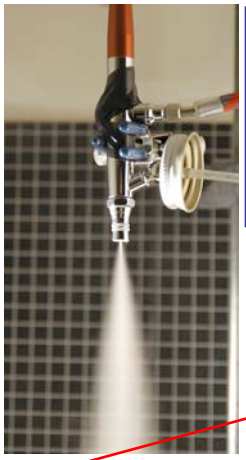
Transport properties must be addressed !

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

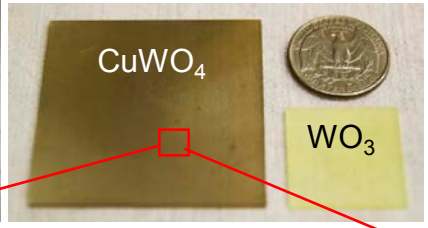
Progress: New metal oxides with E_G =2.0-2.2eV

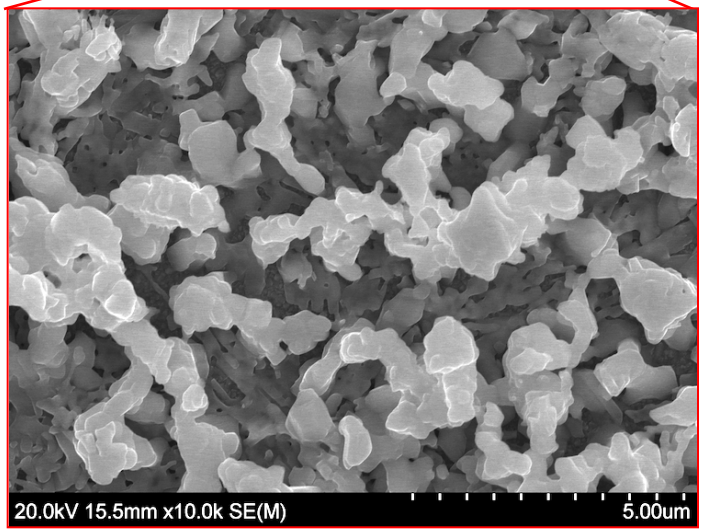
Addressing efficiency

$CuWO_4$ fabricated by spray-pyrolysis



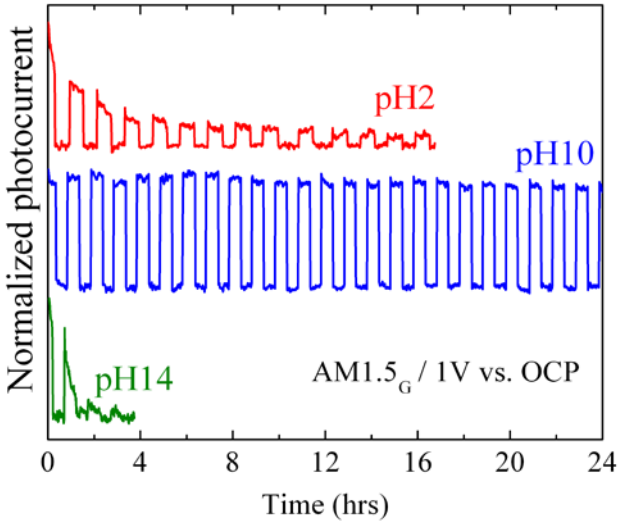
Process:
Precursors: Cu(ac)+AMT
Temperature: 275°C
Uniformity: ± 5% (1 inch^2)
Annealing: 500°C



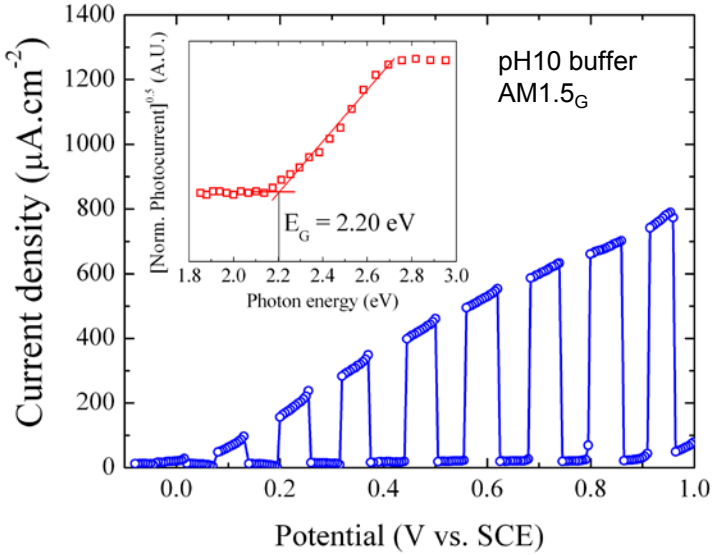


Porous $CuWO_4$ thin film ⇒ high surface area

$CuWO_4$ stability in various pH



Stability demonstrated for 24 hrs (so far tested)

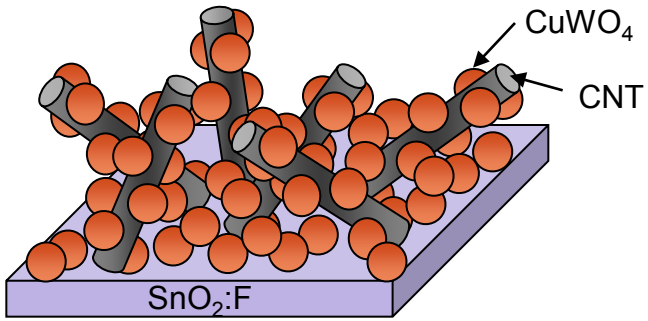


0.7 mA/cm^2 under $AM1.5_G$ illumination

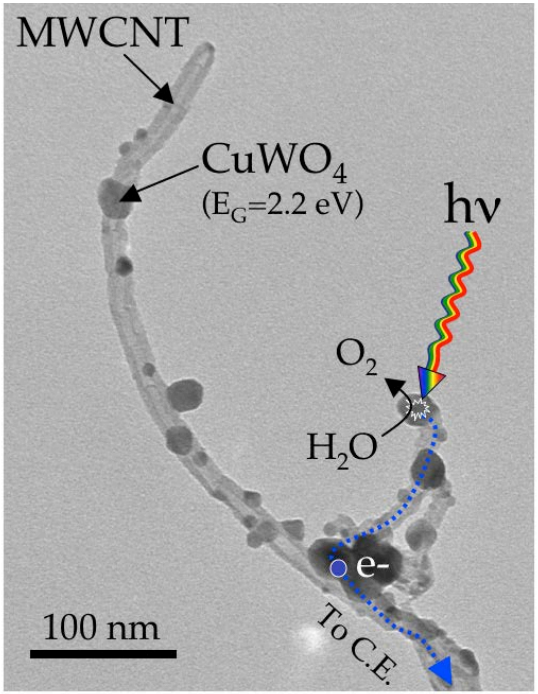
Progress: New metal oxides with E_G =2.0-2.2eV

Addressing efficiency

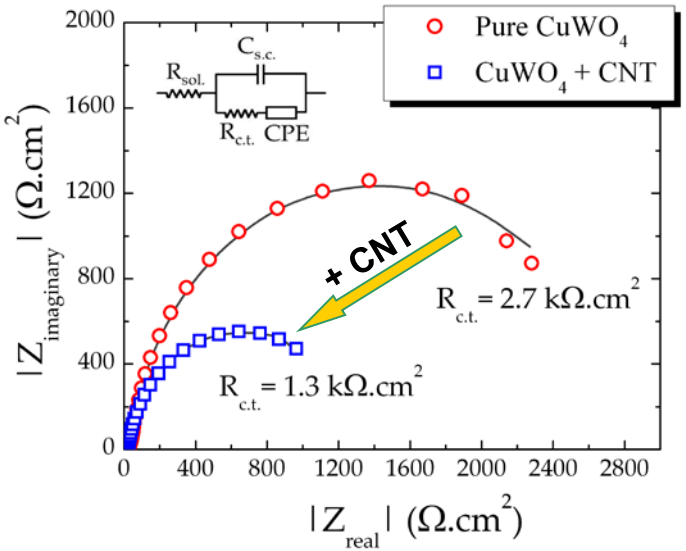
Improving $CuWO_4$ transport properties with CNT

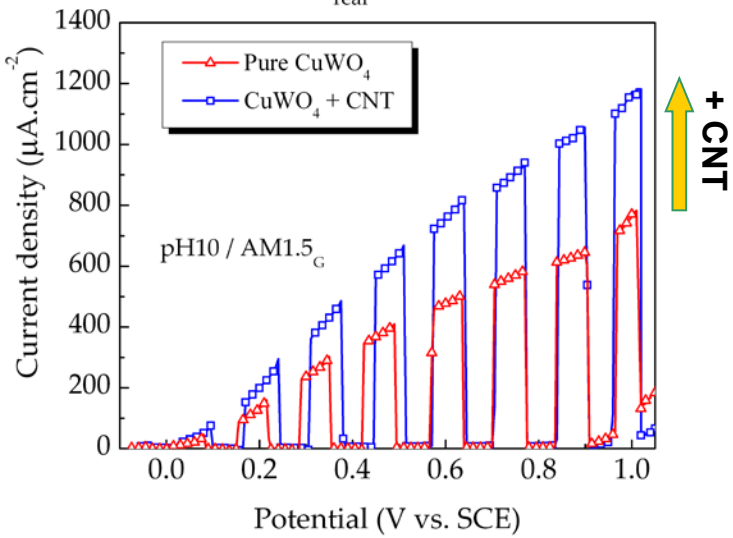


Light absorber / charge collector



TEM micrographs of $CuWO_4$ n.p. on CNT





→ **1 mA/cm² achieved with $CuWO_4$ / CNT nanocomposites**

→ **Compatible with hybrid concept (CNT absorb only 2.5%)**

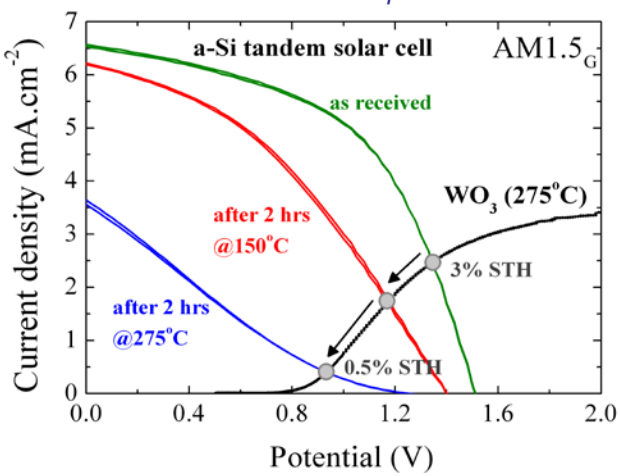
Progress: new monolithic integration for hybrid PEC device

Addressing Design

Main barrier: a-Si solar cells performances degraded after long exposure to heat

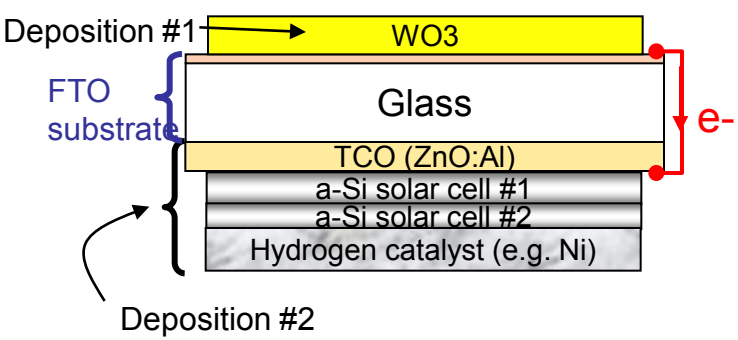
Issue

Effect of heat exposure on (WO_3 filtered) a-Si tandem solar cell performances

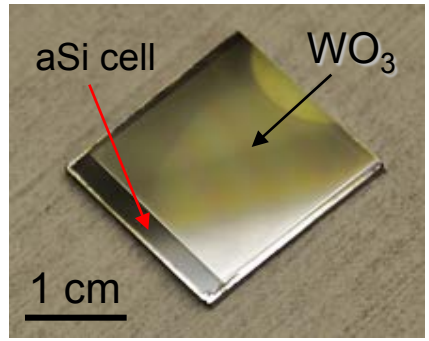


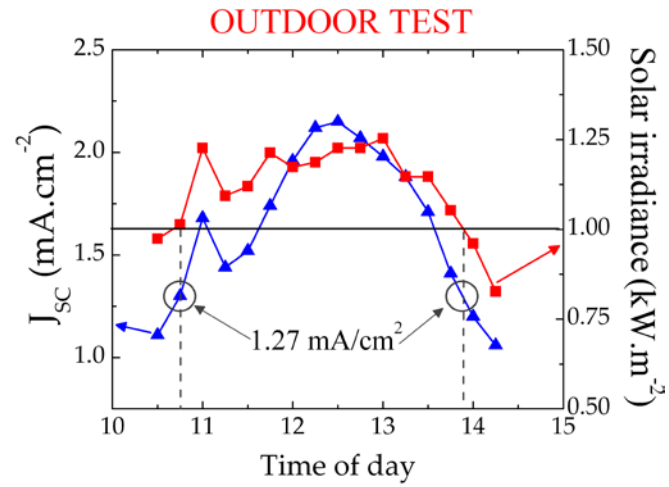
Solution

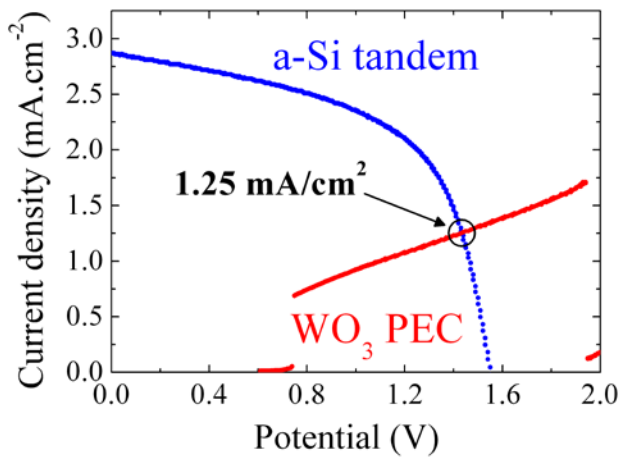
Bifacial integration



WO_3-based PEC hybrid device







→ **Bifacial monolithic integration demonstrated**

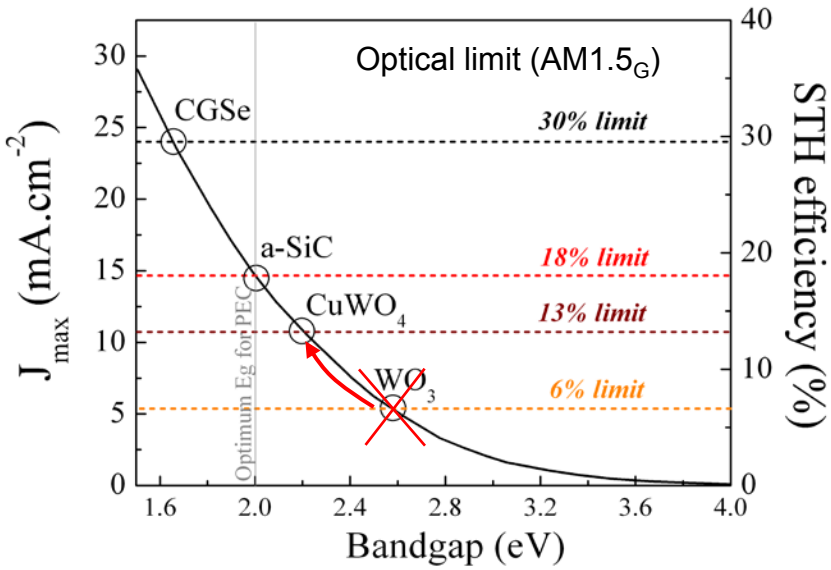
→ **WO_3 samples clearly underperformed in this test**

→ **New hybrid device being tested**

Future Work (Metal Oxides PEC electrode)

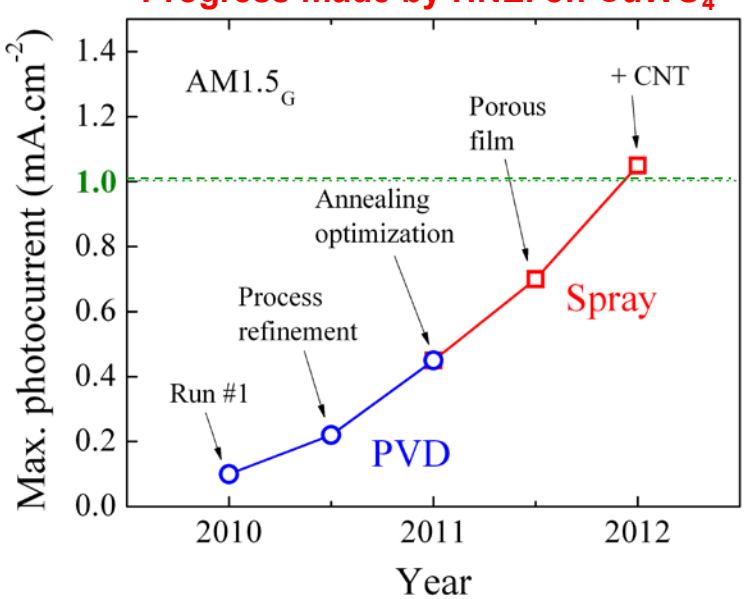
⇒ Theoretical STH limit with WO_3 is approx. 6%. All attempts to reduce E_G have been unsuccessful

⇒ With a band gap of 2.2 eV, $CuWO_4$ is a serious candidate for low cost PEC hydrogen production, with potentially 13% STH efficiency.



$CuWO_4$ transport properties have been identified as main limitation

Progress made by HNEI on $CuWO_4$



Plans to achieve higher efficiency:

1. Other *solar absorber/charge collector* architectures will be studied (Stanford).
2. Improvements could be also achieved with elemental doping (NREL).

Part I

Amorphous Silicon Carbide (a-SiC)

Presenter: *Jian Hu*, MVSystems, Inc

Part II

Metal Oxide Compounds

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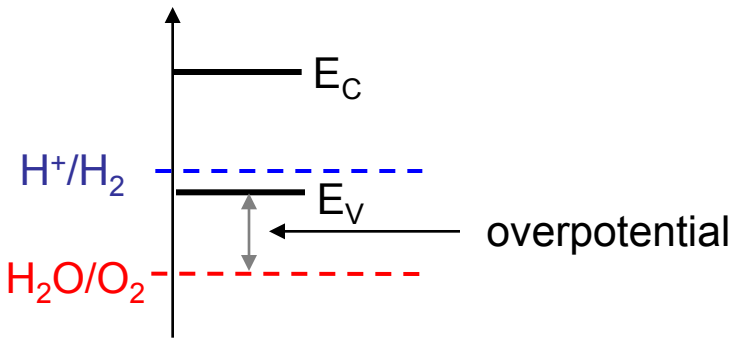
Part III

I-III-VI_2 (Copper Chalcopyrite-based)

Presenter: *Nicolas Gaillard*, Hawaii Natural Energy Institute

Progress: bulk modifications of CGSe baseline

Addressing "Efficiency"



Barriers:

1. Bandgap (1.65 eV) currently too small
2. Overpotential too high

Addressing both barriers by lowering valence band-edge with substitution of Ag and/or Sulfur

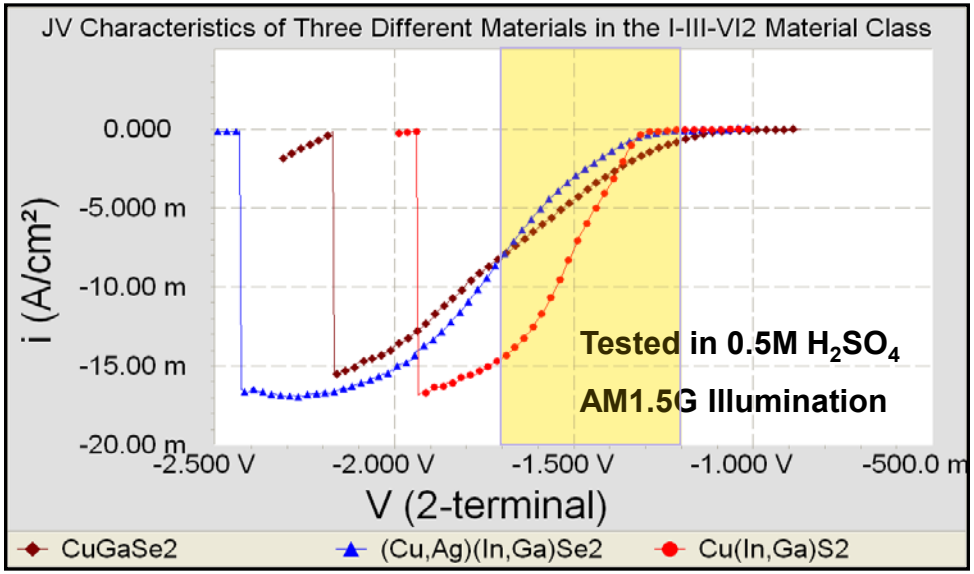
Bandgap:

$CuGaSe_2$ = 1.65eV (baseline)

$AgGaSe_2$ up to 1.85eV

$CuGaS_2$ up to 2.43eV

$(Cu_zAg_{(1-z)})(In_xGa_{(1-x)})(S_ySe_{(1-y)})_2$ alloys are bandgap-tuneable



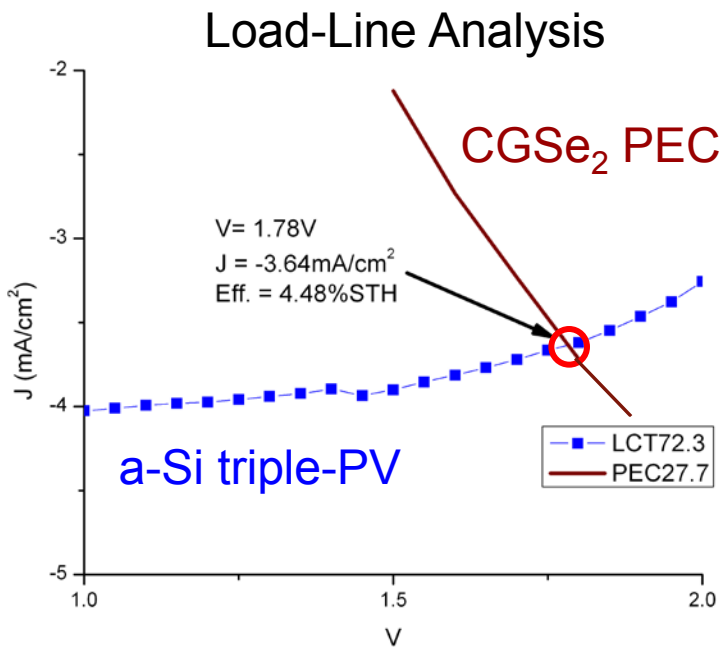
Highlighted in yellow is the voltage region where completed devices typically operate.

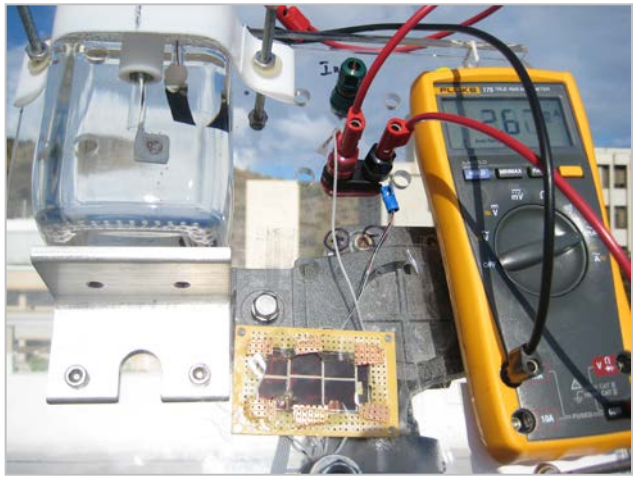
Progress: STH efficiency with co-planar integration

Addressing "Device design"

Barrier: Low band gap (1.65eV) materials currently produced require innovative device design

Solution: Large photocurrent produced by materials in this class allow co-planar PV-PEC integration

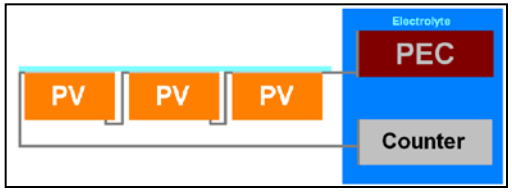




4.34% STH achieved! (AM1.5 1-sun)

- 3 a-Si PV cells
- $CGSe_2$ PEC
- Outdoor Standalone (no external voltage):
  - $3.53 mA/cm^2$ = 4.34%STH
- **Surpasses old record while using much cheaper materials**

3 PV + PEC serial device

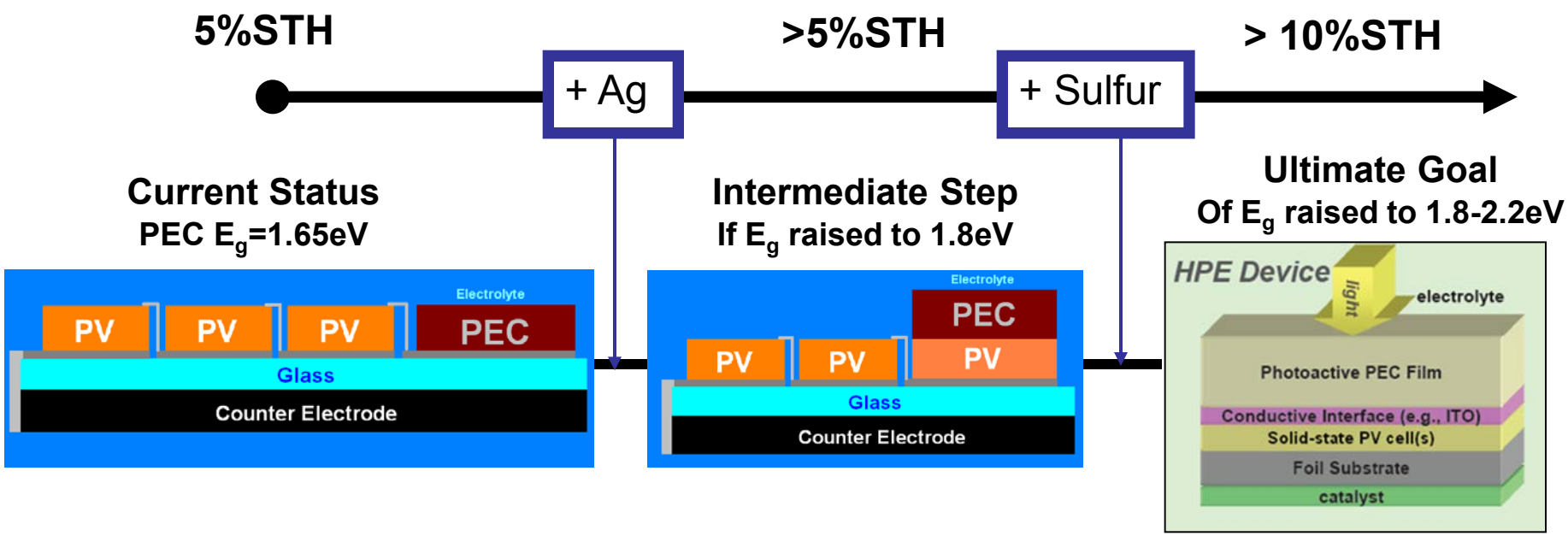


Future Work (I-III-VI_2 hybrid photoelectrode)

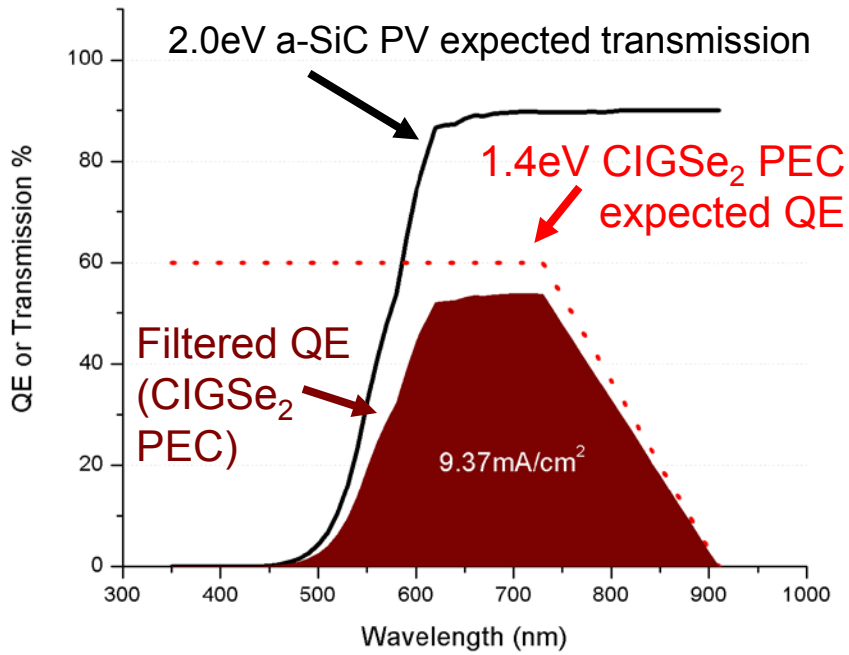
- **Coplanar Device utilizing 3 PV cells of suitable performance can surpass 5% STH.**
- **Lowering the valence band to increase E_g and decrease overpotential is THE key to high performance chalcopyrite-based PEC hybrid devices.**

Lower overpotential ⇒ fewer PV cells required ⇒ diminishes photocurrent division

Higher band gap: buried PV cell approach possible (synergy with ongoing research in PV industry towards tandem CIGSe-based PV cells)

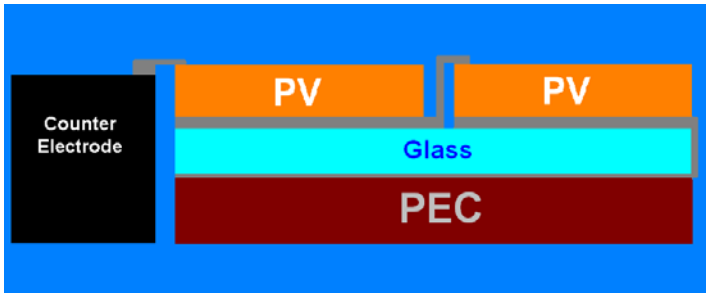


Future Work (Novel Inverted Monolithic Stack)

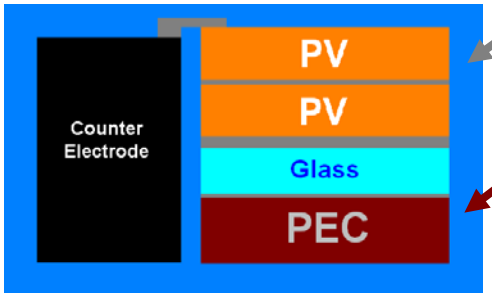


- Progress at MVSystems utilizing higher-bandgap a-SiC (~2.0eV) in PV applications
- Lowering I-III-VI_2 bandgap much easier than raising it
- Device development underway, possibility of 8-10%STH efficiency
- Highly dependent on voltage characteristics when fabrication proceeds

Step 1: Coplanar PV cells (~2.0eV) with ~1.4eV $CIGSe_2$ PEC



Step 2: Inverted Monolithic Integration



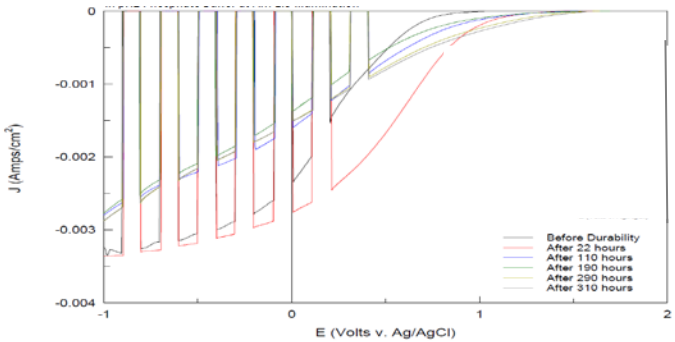
Higher Bandgap PV

Slight Lower Bandgap PEC

Durability test

a-SiC photoelectrode:

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

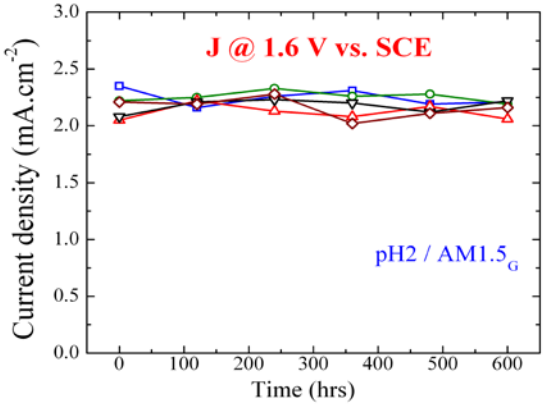


Hybrid PV/a-SiC device after 310-hrs

[Data measured by NREL]

WO_3 photoelectrode:

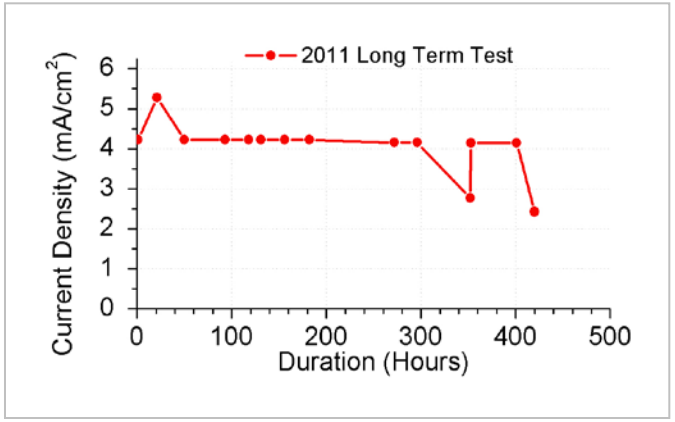
- Under AM1.5G @1.6V vs. SCE in pH2.
- High corrosion resistance of tungsten oxide in acidic solution for up to 600 hrs.



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 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

a-SiC photoelectrode:

- Durability of hybrid PV/a-SiC cell: 310 hours
- Photocurrent density (in solid state version): >4 mA/cm^2 (possible STH efficiency >5%)
- Photocurrent density in pH2 electrolyte: 2.0 mA/cm^2 (or STH efficiency of ~2.5%)

Future work: enhance surface catalysis and improve a-Si tandem solar cell (FF, Jsc)

Metal oxides photoelectrode:

- Durability of WO_3 sputtered material: 600 hrs.
- $CuWO_4$ (2.2 eV) is a promising PEC material, $J_{photo} \times 10$ over the past year.
- Bifacial monolithic integration demonstrated. Compatible with CGSe systems.

Future work: improve $CuWO_4$ transport properties (new architectures and/or doping)

I-III-VI$_2$ photoelectrode:

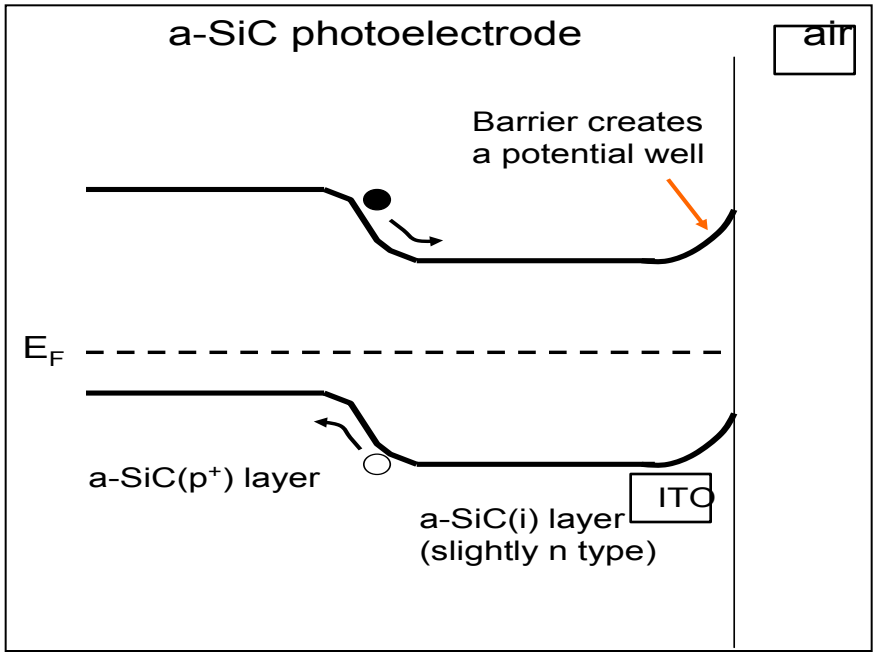
- Durability of CGSe PEC cell: 420 hrs
- Photocurrent density of PEC film: 20 mA/cm^2 (offers novel device integration)
- Photocurrent density of coplanar hybrid device: 3.53 mA/cm^2 (4.34% STH efficiency)

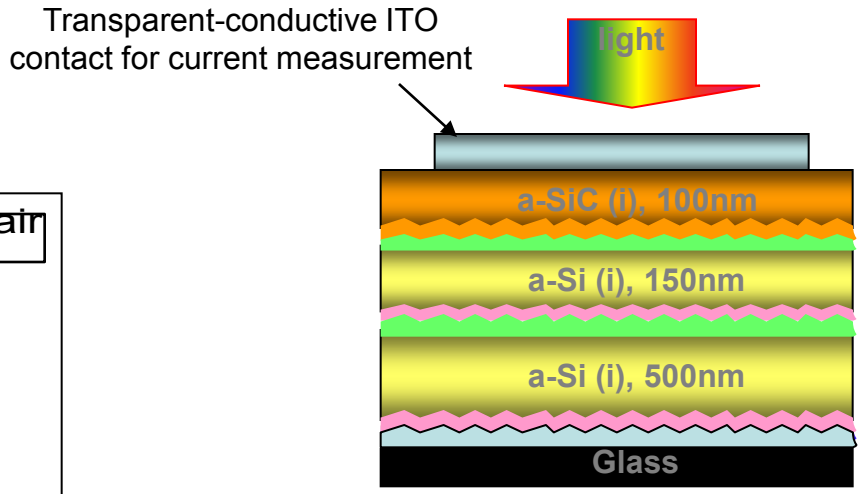
Future work: develop robust sulfurization process (↗ E_G) and create CIGSe with lower E_G

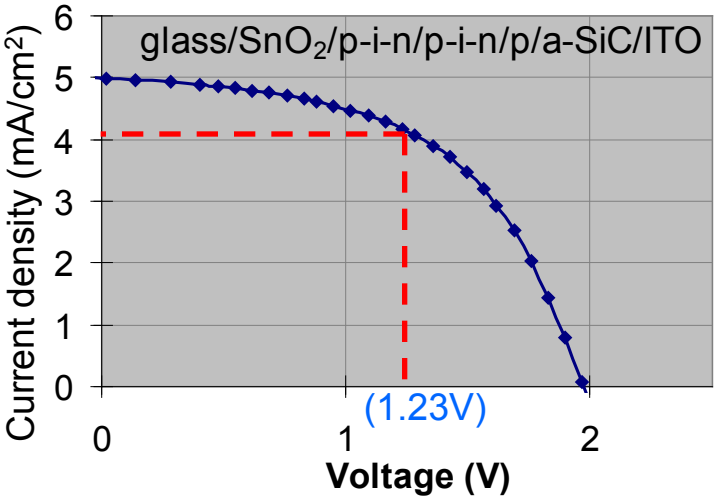
Technical Back-Up Slides

a-SiC: Barrier at a-SiC/ITO interface

Solid state device has a barrier at the a-SiC /ITO interface







Hence current density is low (~4mA/cm^2) and FF is low

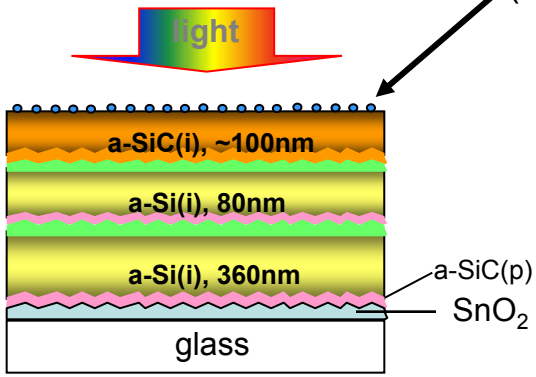
Despite this we can still get 4mA/cm^2

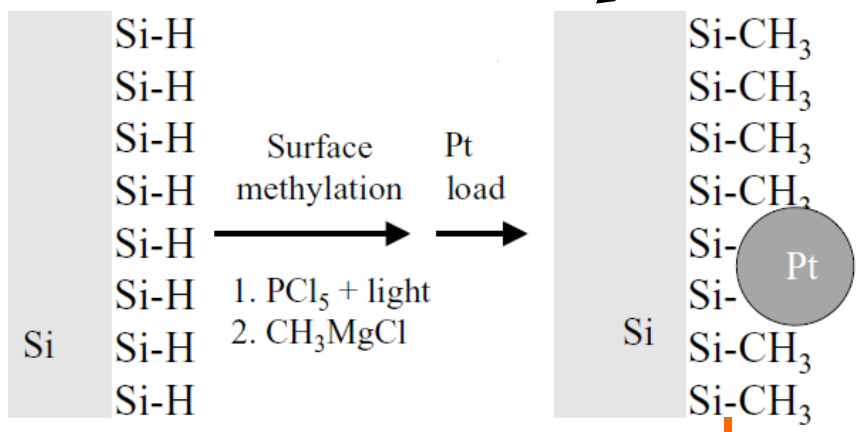
Which could translate to STH >5%

Removal of barrier will improve the solid state device substantially

a-SiC: Surface methylation and nanoparticles

Surface methylation (CH_3) and nanoparticle coating





CH_3-termination (methylation) prevents oxidation

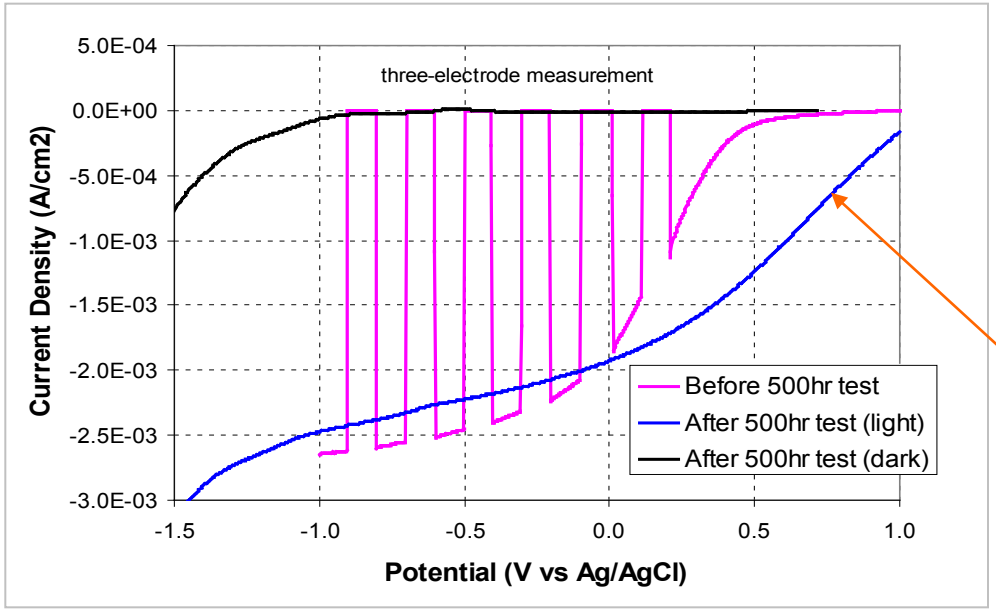
Photocurrent enhanced
(i.e., from 5 to 25 mA/cm^2 in n-Si electrode*)

* Takabayashi, Nakamura, & Nakato, Journal of Photochemistry & Photobiology A, 166 (2004).

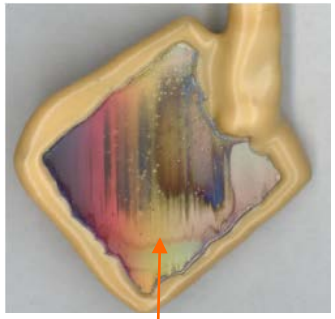
500-hr durability test on hybrid PV/a-SiC device

Addressing "Z"

- Under AM1.5G @1mA/cm^2, in pH2 buffer solution.



Hybrid PV/a-SiC device after 500-hrs (initial results)



[Data measured by NREL]

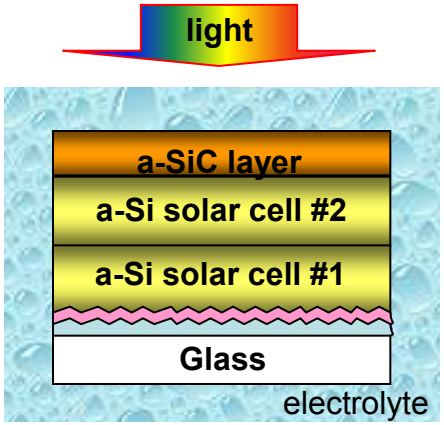
- Surface morphology changed
- Investigation underway (ie by EDS)

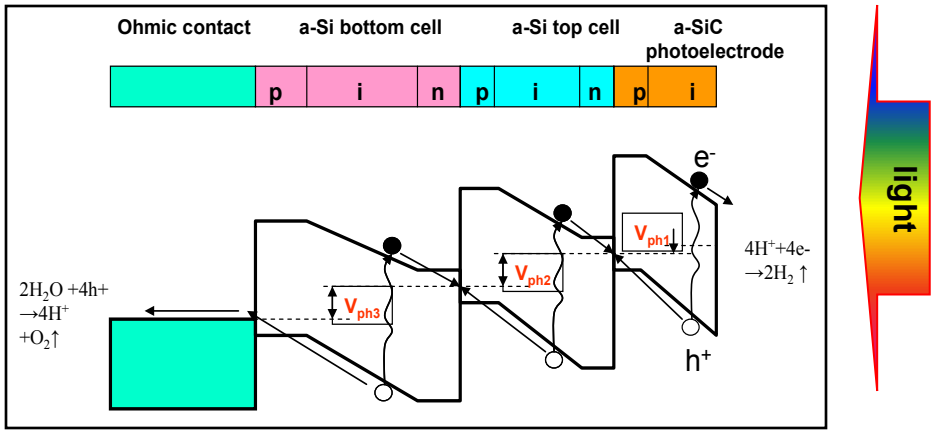
- Photocurrent remains largely unchanged with improved fill-factor
- Dark current increase @>-1V

a-SiC: Hybrid PV/a-SiC PEC Device - Simulation Results

Addressing "Y"

- Energy band diagram for hybrid PV/a-SiC PEC device





- Calculated photocurrent and STH efficiency for 3 different configurations:

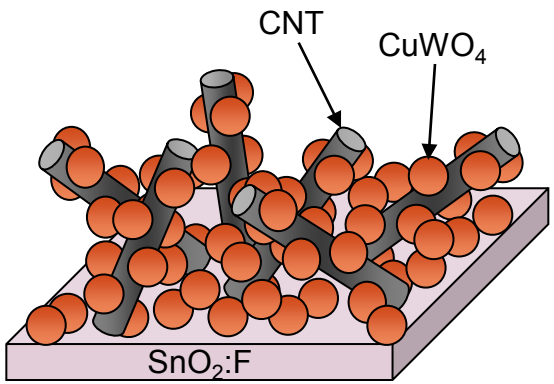
Photo-electrode	Eg (eV)	Jsc (mA/cm²) Available	Voc (V)	PV cell configuration	Filtered Available	Voc (V)	STH (%) Possible
a-SiC:H (1)	2	8.85 (100 nm)	0.6 (p-i)	a-Si/a-Si (620nm/132nm)	7.1	1.9	8.73
a-SiC:H (2)	2	8.85 (100 nm)	0.6 (p-i)	nc-Si/a-Si (1.5μm/244nm)	8.85	1.5	10.89
a-SiC:H (3)	2	12 (250 nm)	>1 (p-i-n)	nc-Si (1.5μm)	12.0	0.6	14.7

STH eff. >10%

Progress: reduction of WO_3-based material bandgap

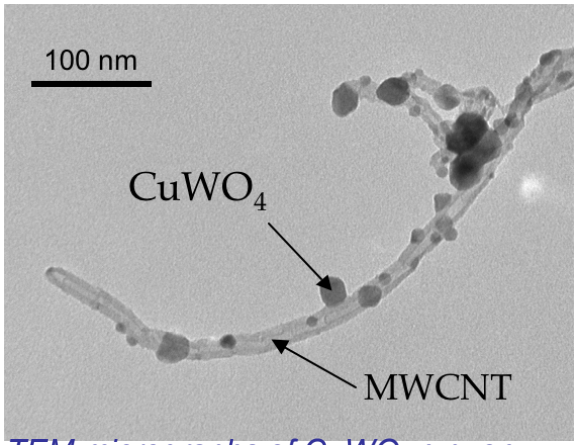
Addressing "Y"

Improving $CuWO_4$ transport properties with CNT

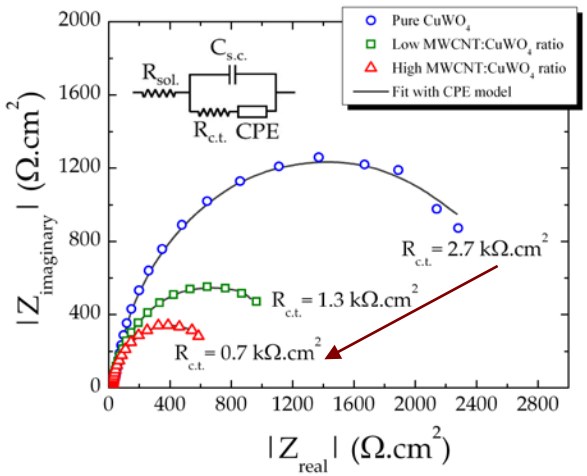


Light absorber / charge collector

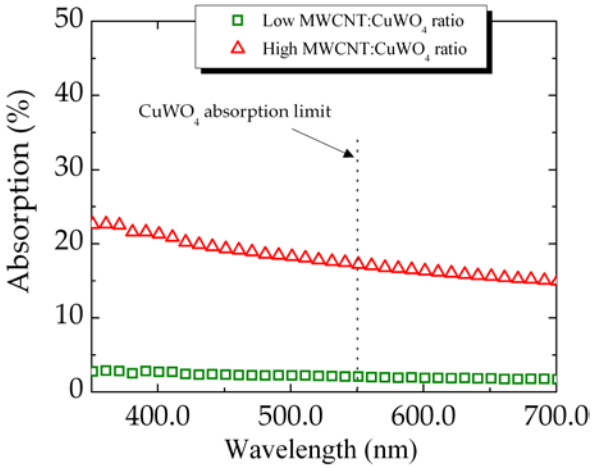
1. Various CNT:$CuWO_4$ w.t. %
2. Spray on SnO_2:F substrate
3. Annealing @ 500°C in air

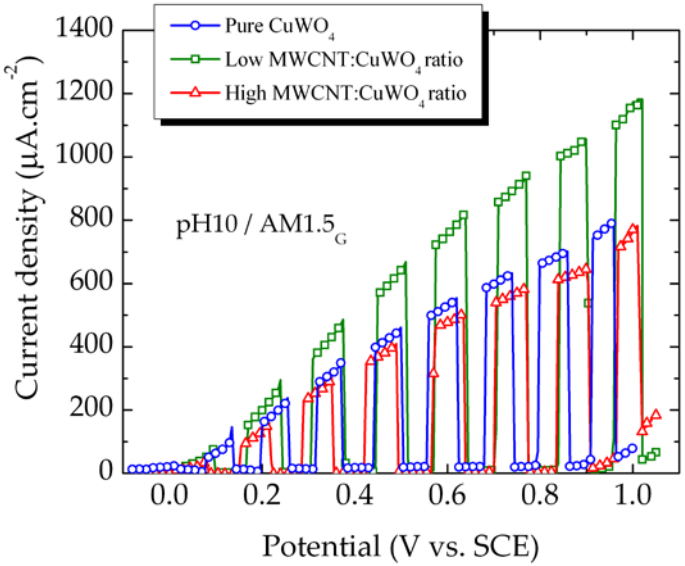


TEM micrographs of $CuWO_4$ n.p. on CNT



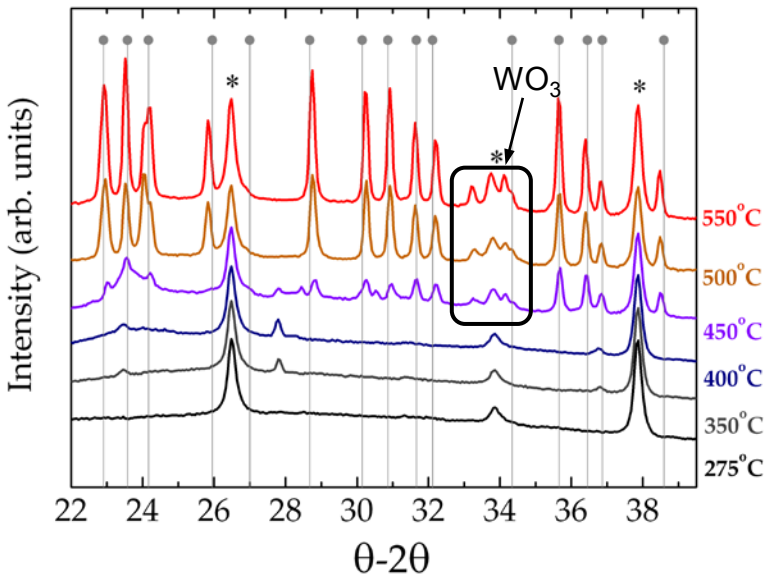
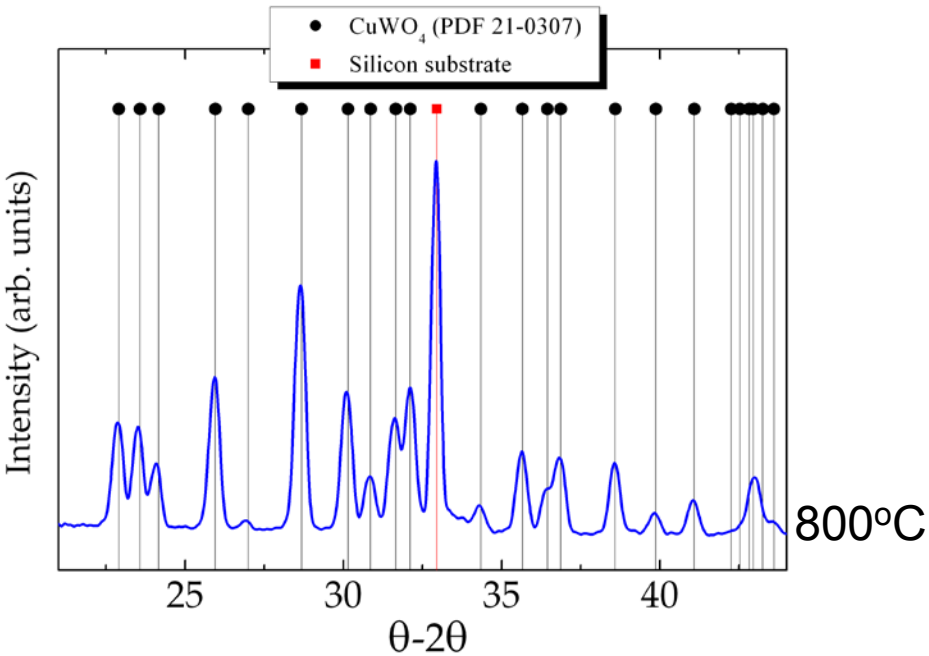
Absorption from CNT in $CuWO_4$





→ **1 mA/cm² achieved with $CuWO_4$CNT nanocomposites**

→ **Compatible with hybrid concept (only 2.5% transmission loss)**

Progress: reduction of WO_3-based material bandgap

Addressing "Y"