# PD053

# PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

PI: Arun Madan

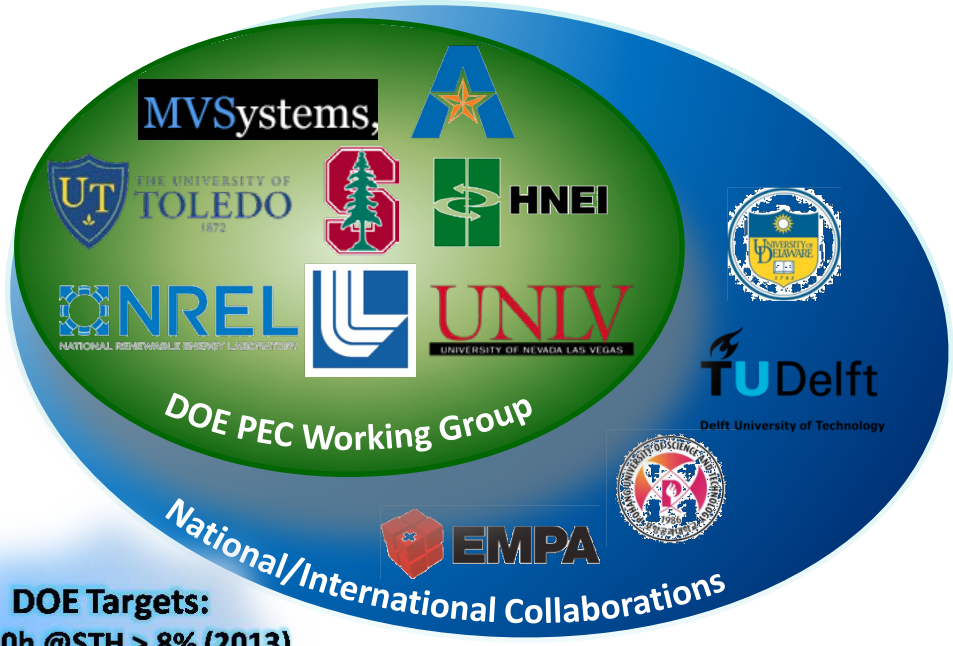
MVSystems, Inc.

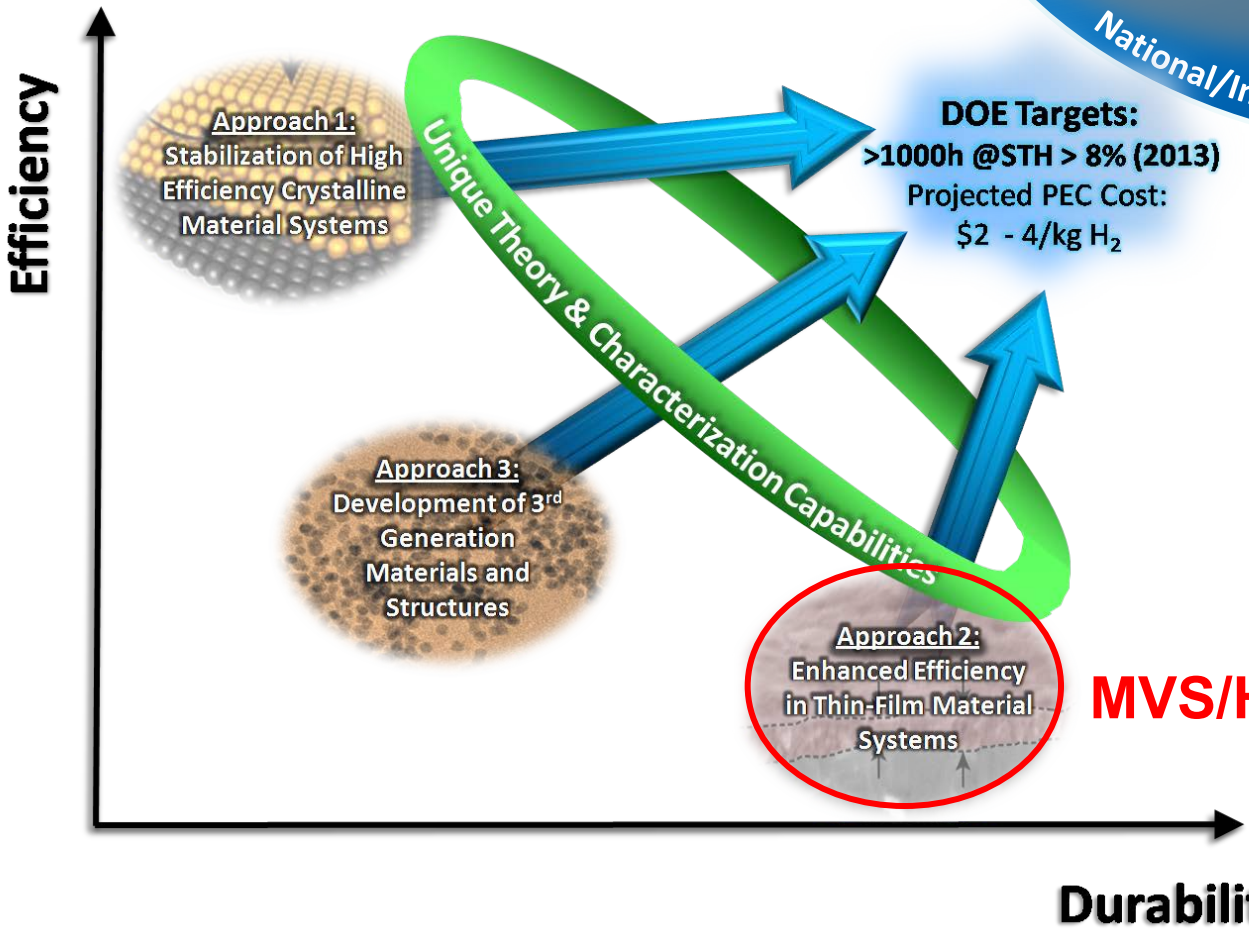
May 14-18, 2012

Project ID # DE-FC36-07GO17105, A00

# Approach

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




**MVS/HNEI program**

# 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

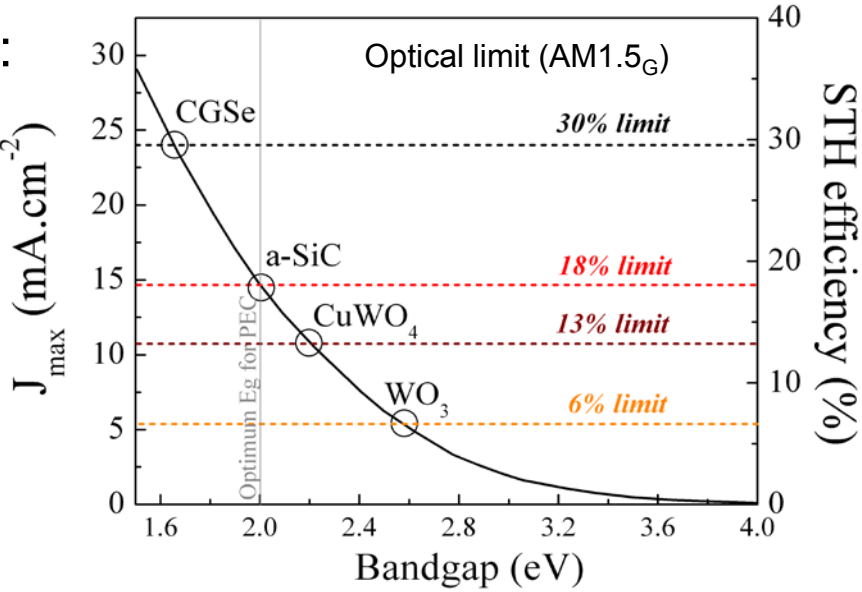
## Partners

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

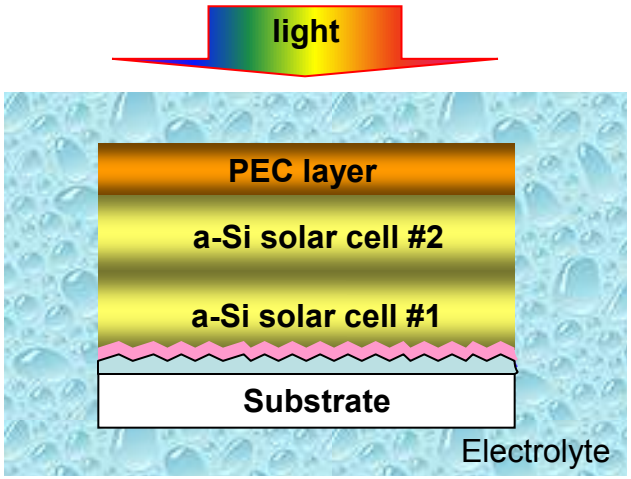
# Relevance - Objectives

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<br>- Achieved:<br>**- Barriers:** | Monolithic device<br>**No** | Hybrid PEC device concept demonstrated with mechanical stack<br>**Current deposition temperature requires innovative integration scheme** | Hybrid PEC device concept demonstrated with co-planar PV/PEC<br>**Current deposition temperature requires innovative integration scheme** |
| Z: Durability<br>- Achieved: (so far tested) | 310-hrs | 600-hrs | 420-hrs |
| Y: Efficiency<br>- Achieved:<br>**- Barriers:** | Less STH (3%) compared to the solid state version (>5%)<br>**Need to modify surface to lower overpotential** | 3.1% STH with pure $WO_3$ (2.6 eV).<br>**Need to discover metal oxides with appropriate band-gap** | 4.34% STH achieved with co-planar integration.<br>**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

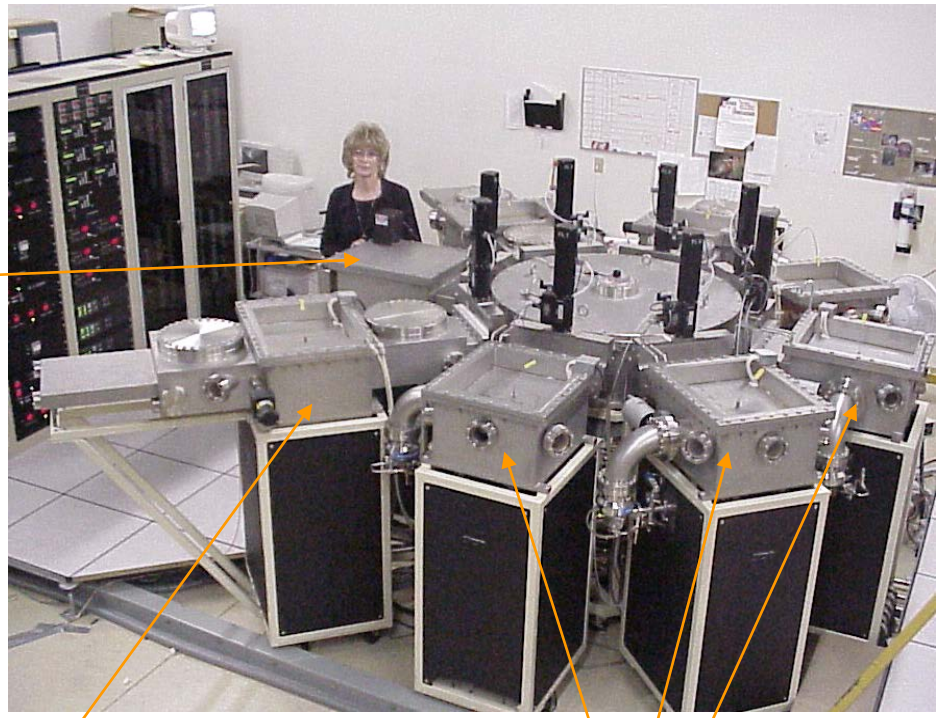
# I-III-$VI_2$ (Copper Chalcopyrite-based)

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.**



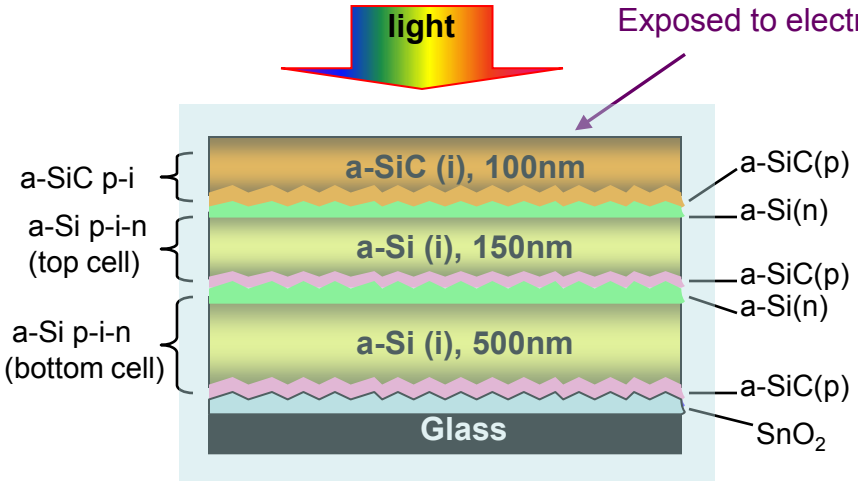

## Main deposition parameters:

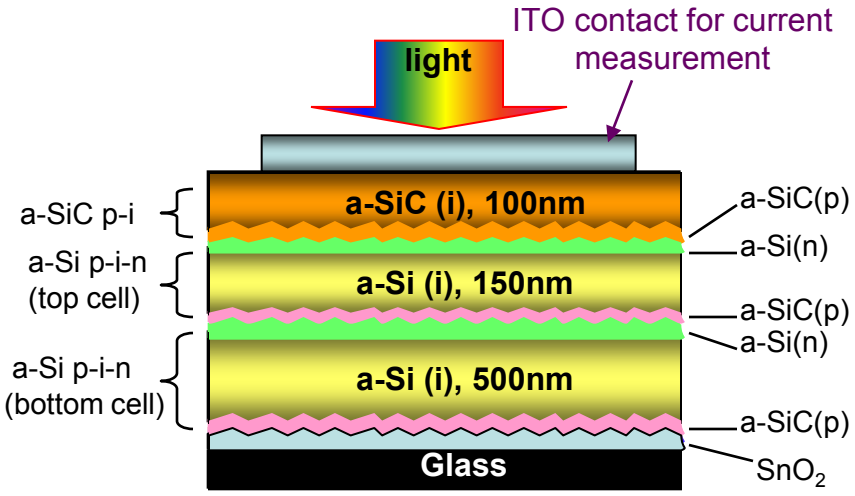
| | |
|---|---|
| **RF power:** | **10-20 W** |
| **Excitation frequency:** | **13.56 MHz** |
| **Pressure:** | **300-550 mTorr** |
| **$SiH_4$ flow rate:** | **20 sccm** |
| **$CH_4$ flow rate:** | **0-20 sccm** |
| **$H_2$ flow rate:** | **0-100 sccm** |
| **Substrate temperature:** | **200°C** |

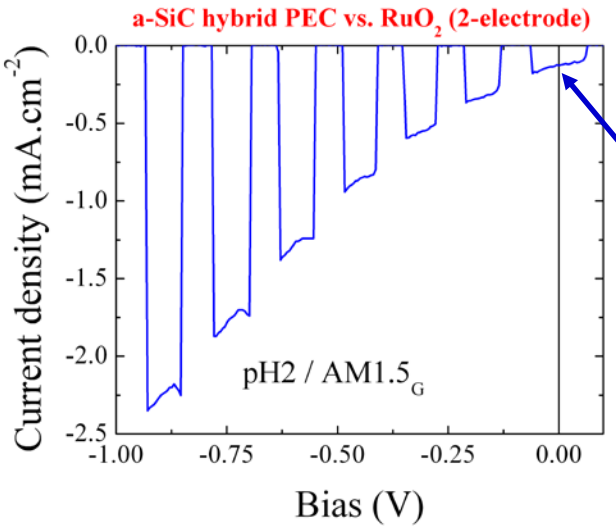
http://www.mvsystemsinc.com

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

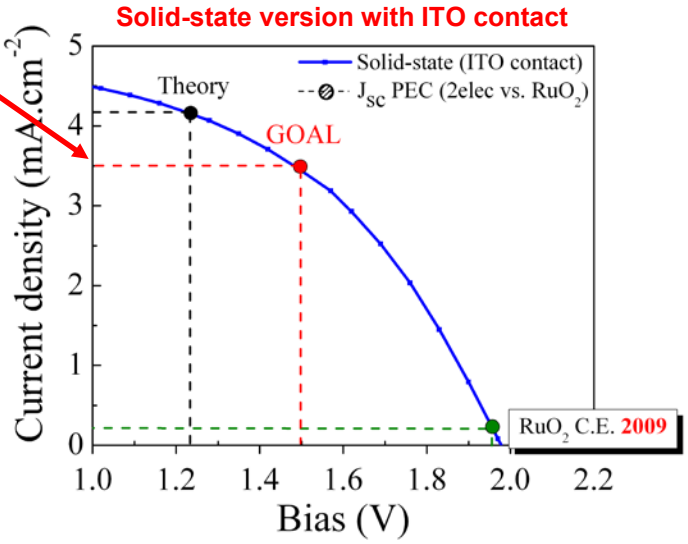



>3.5 mA/cm$^2$ as a solid-state device assuming 0.3V overpotential

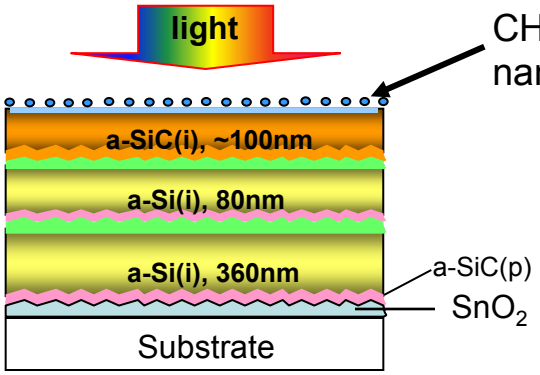
0.25 mA/cm$^2$ in electrolyte




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

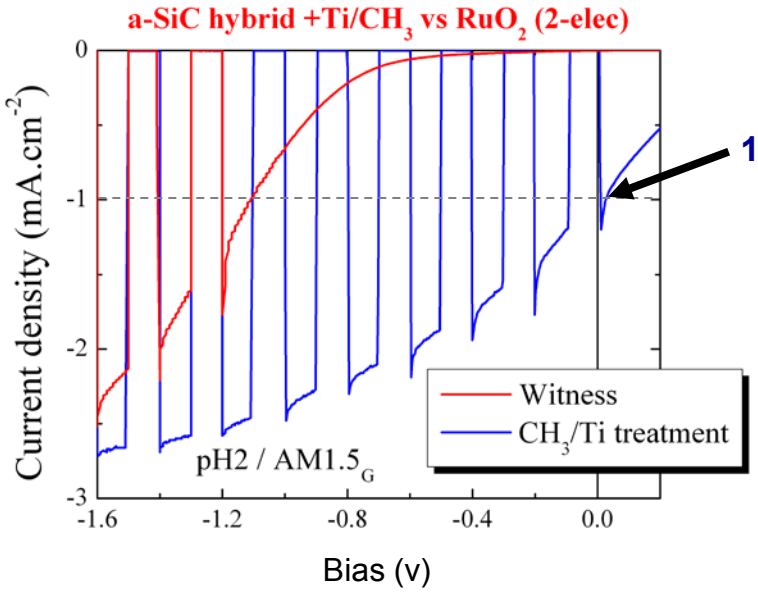
# Progress: Surface Modification – by methylation ($CH_3$-termination)

## Addressing efficiency with catalytic surface treatment



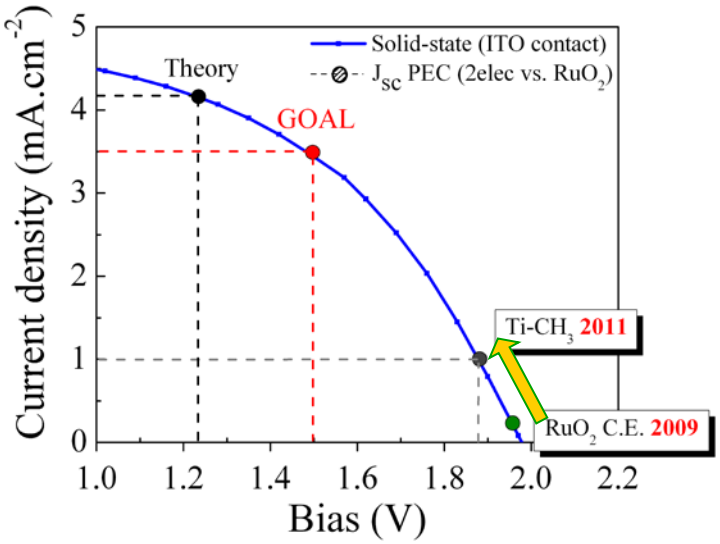

Surface treatment procedure:

- 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




**Jsc= 1 mA/cm²**
**1.2% STH efficiency**

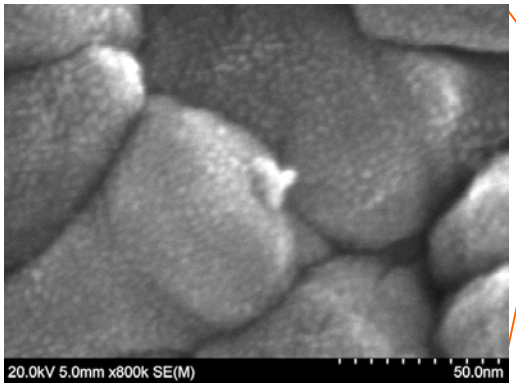
$J_{sc}$ increase after $CH_3$/Ti treatment



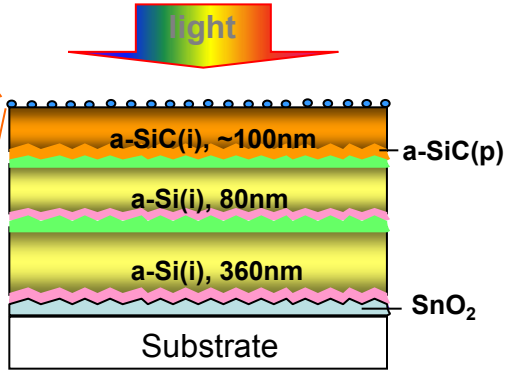

[ Data measured by NREL ]

# Progress: Surface Modification – Use of Ru Nanoparticles

## Addressing efficiency with catalytic surface treatment

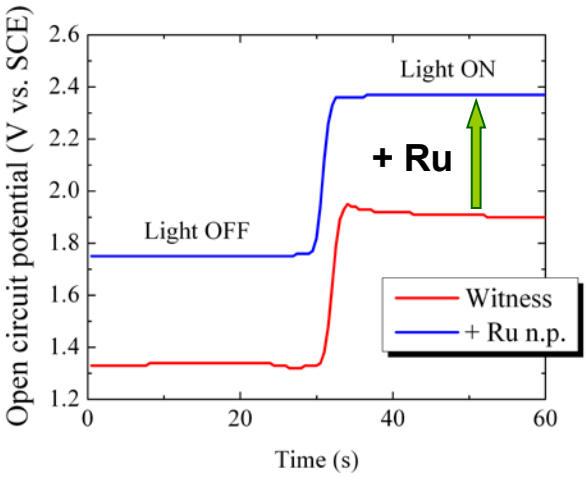



Ru nanoparticle coating (HNEI)

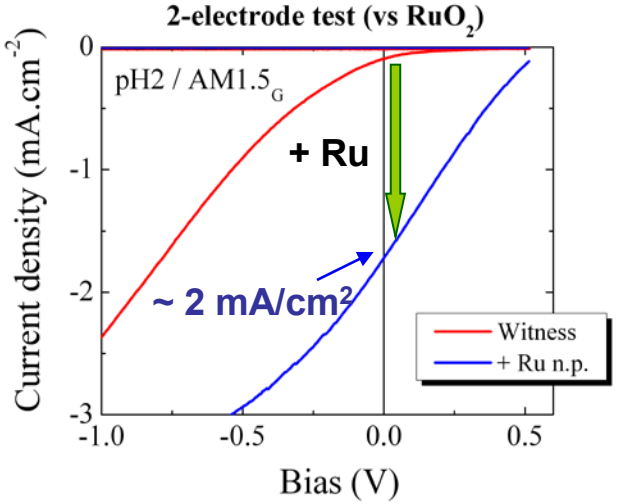



PV/a-SiC hybrid device

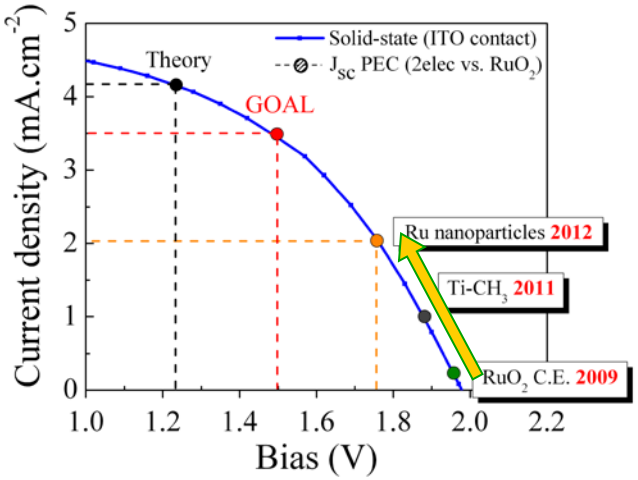
- **Ru alloys (i.e. Ru-Ni) with high HER catalytic activity demonstrated**
- **Ru nanoparticles with activity comparable with Pt recently reported(*)**




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




STH efficiency of ~2.5% is achieved

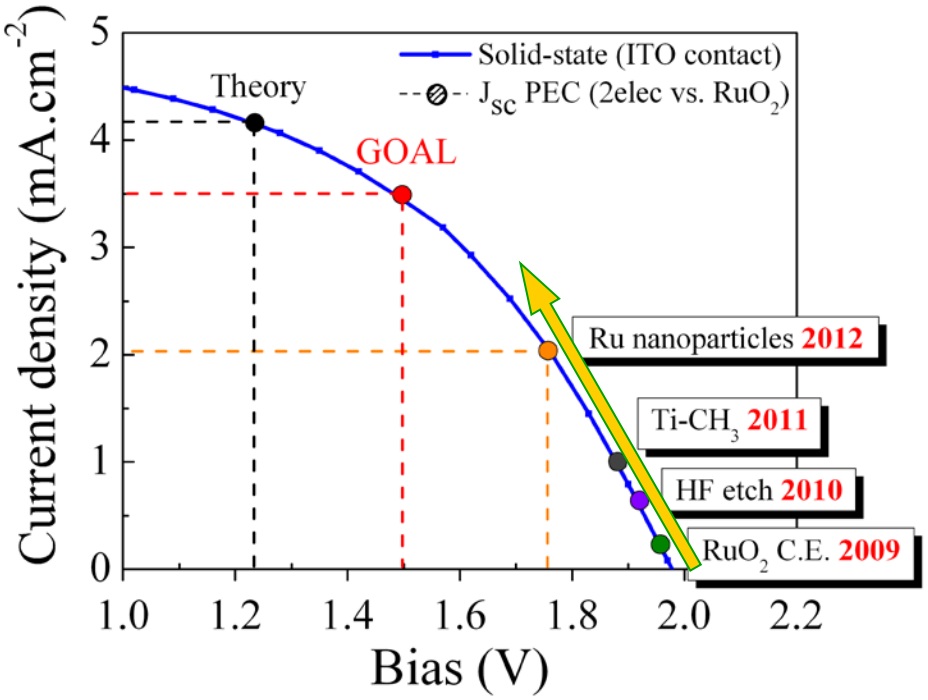



(*) Yamada, J. Am. Chem. Soc., 2011, 133 (40), pp 16136–16145

[ 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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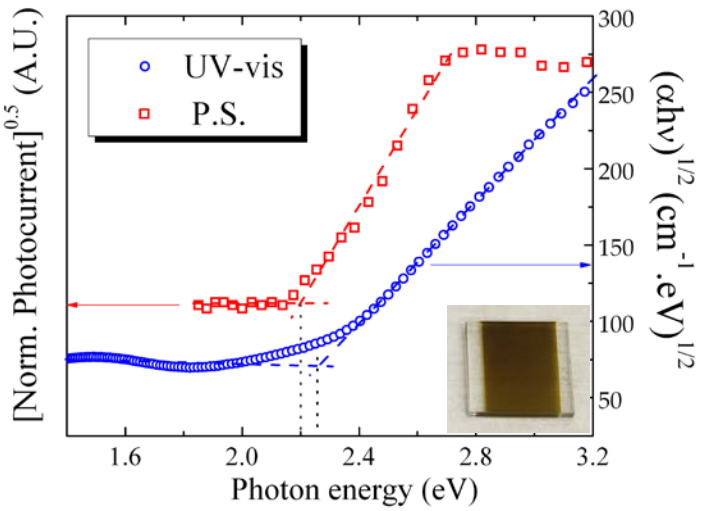
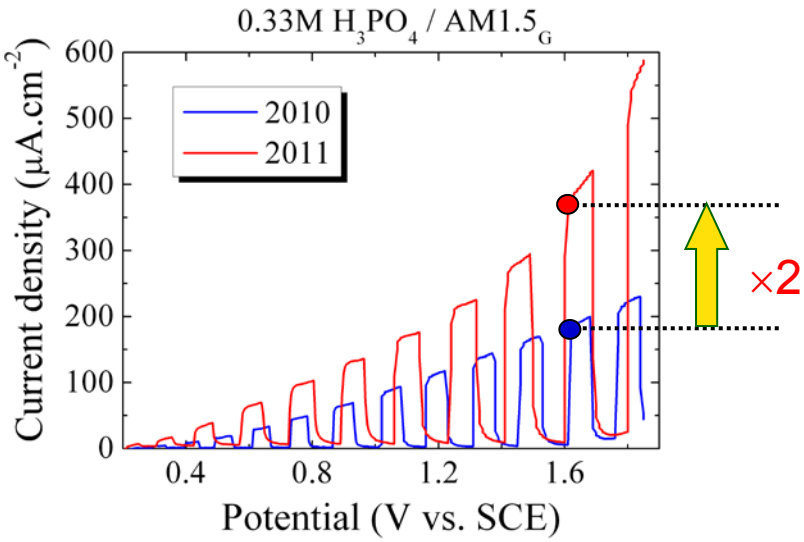
# **Progress:** New metal oxides with $E_G$ =2.0-2.2eV

Addressing efficiency

## $CuWO_4$ fabricated with co-sputtering process

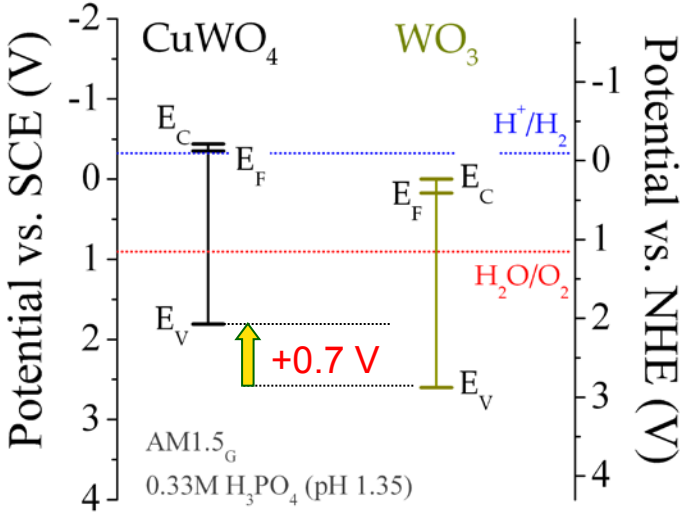



Band-gap ≈ 2.2 eV ($STH_{theor.}$=13%)

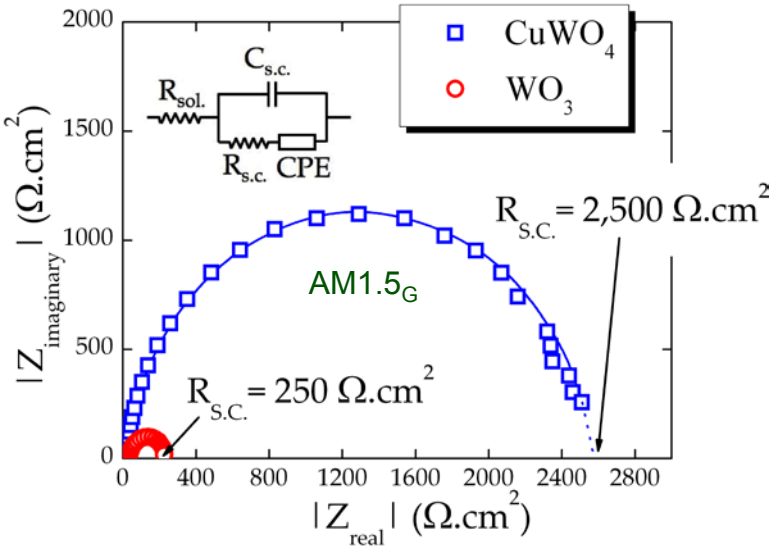



0.4 mA/cm² under $AM1.5_G$ illumination

*Band structure derived from MS and UV-VIS*




Ideal surface energetics



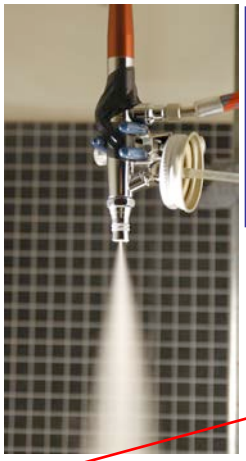

Transport properties must be addressed !

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

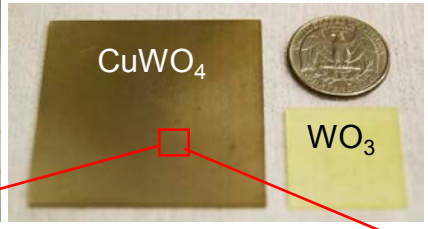
# **Progress:** New metal oxides with $E_G$ =2.0-2.2eV

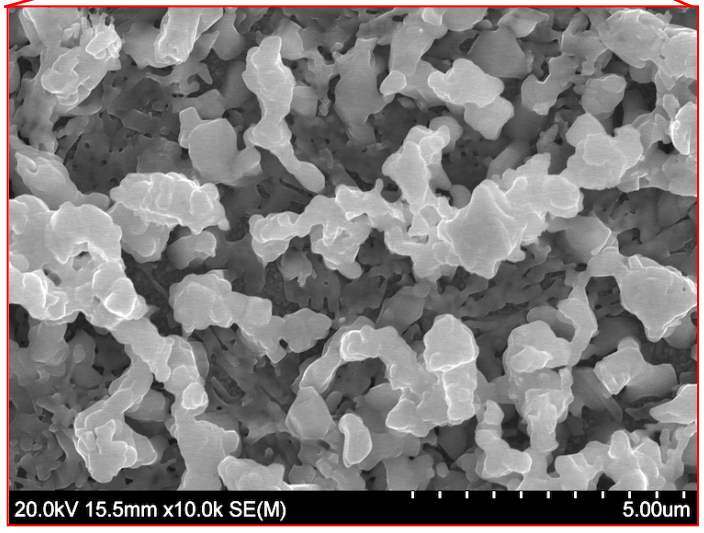
Addressing efficiency

## $CuWO_4$ fabricated by spray-pyrolysis



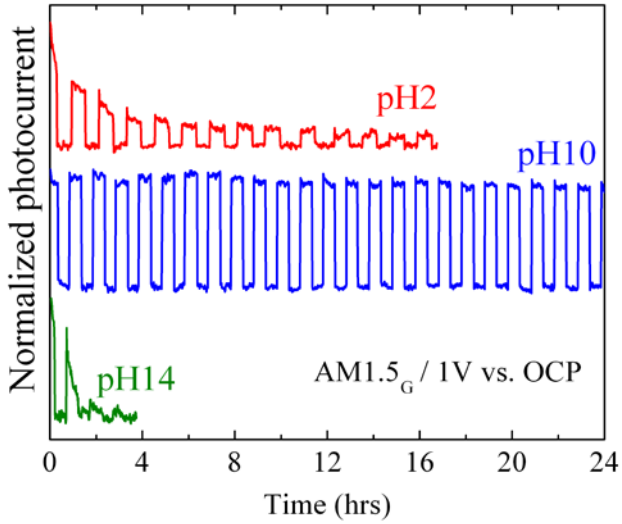
**Process:**
*Precursors*: Cu(ac)+AMT
*Temperature*: 275°C
*Uniformity*: ± 5% (1 inch²)
*Annealing*: 500°C



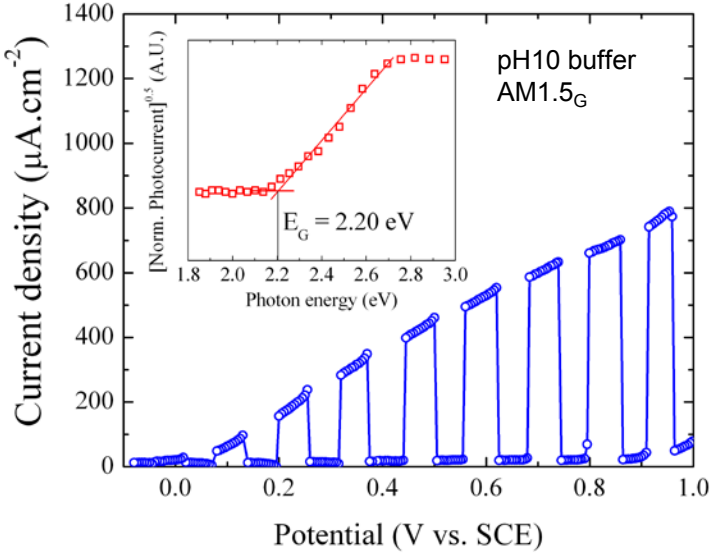




Porous $CuWO_4$ thin film ⇒ high surface area

$CuWO_4$ stability in various pH




Stability demonstrated for 24 hrs (so far tested)

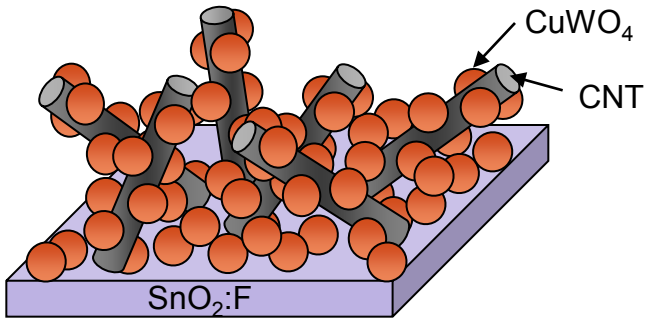



0.7 mA/cm² under $AM1.5_G$ illumination

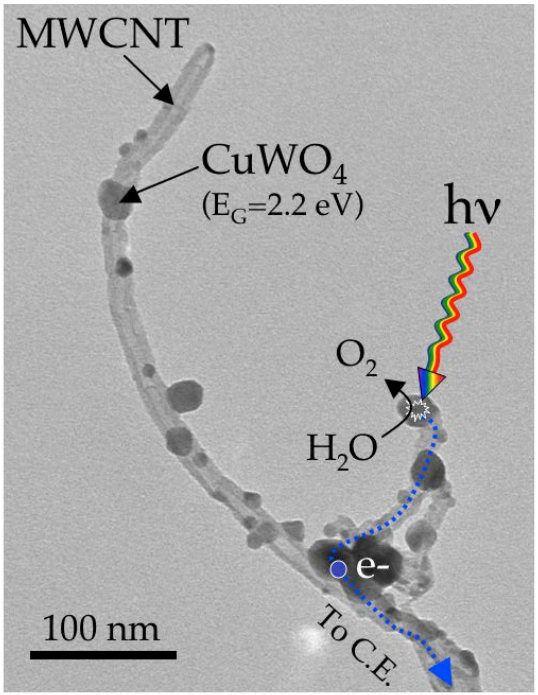
# **Progress:** New metal oxides with $E_G$ =2.0-2.2eV

Addressing efficiency

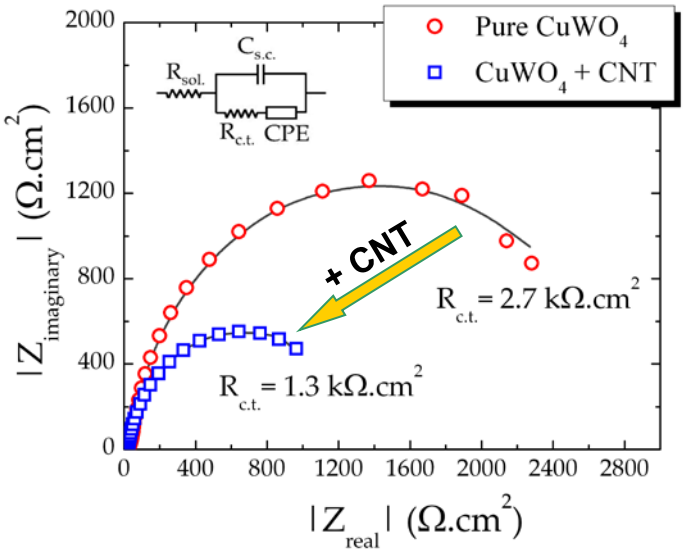
## Improving $CuWO_4$ transport properties with CNT

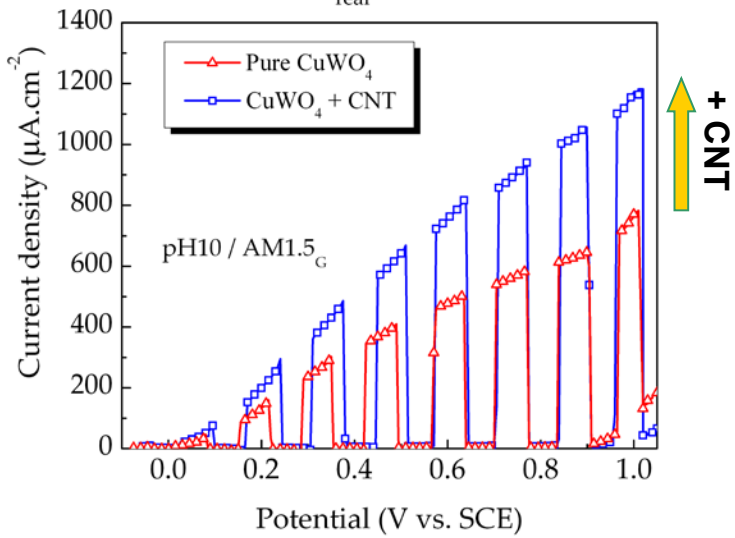



*Light absorber / charge collector*




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%)

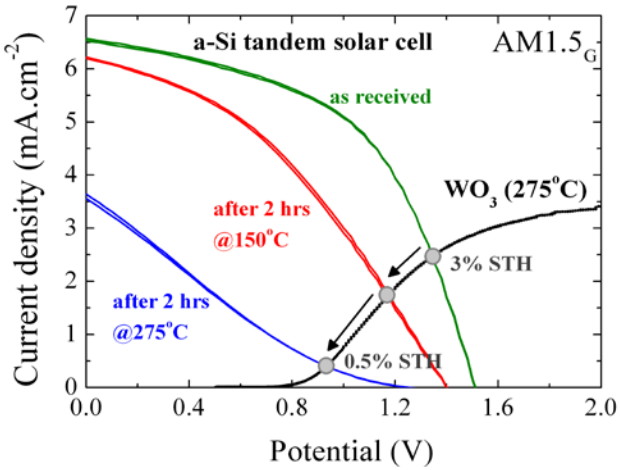
# **Progress:** new monolithic integration for hybrid PEC device

Addressing Design

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

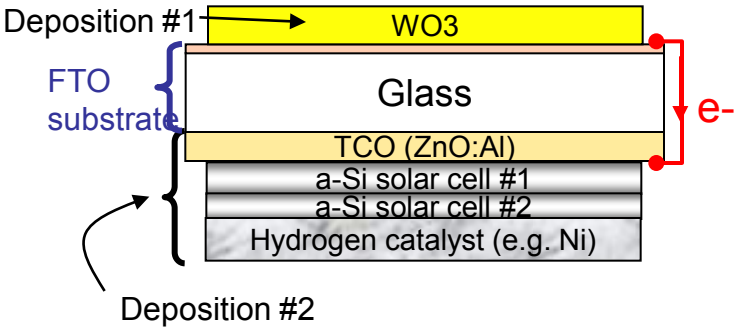
## Issue

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

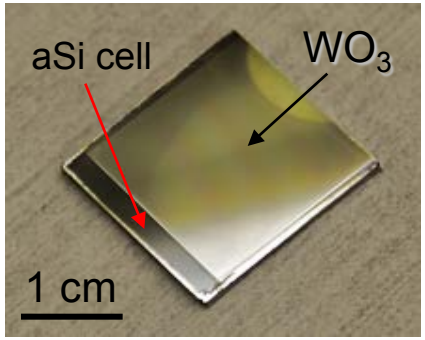


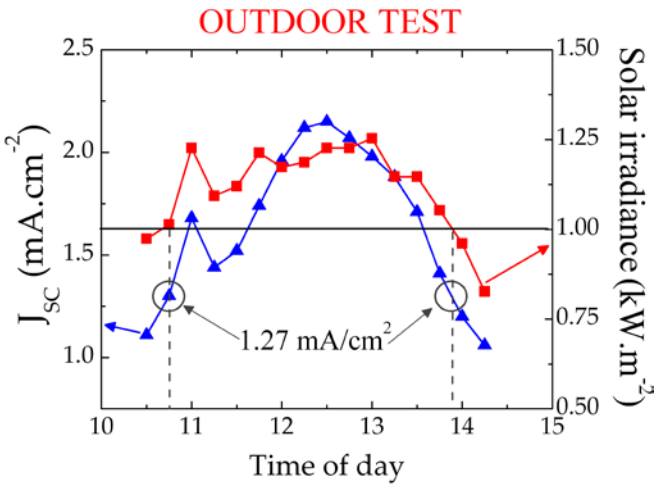

## Solution

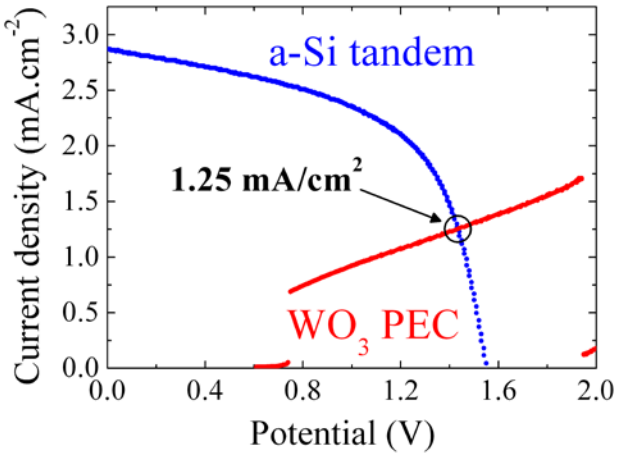
Bifacial integration




*$WO_3$-based PEC hybrid device*




→ **Bifacial monolithic integration demonstrated**

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

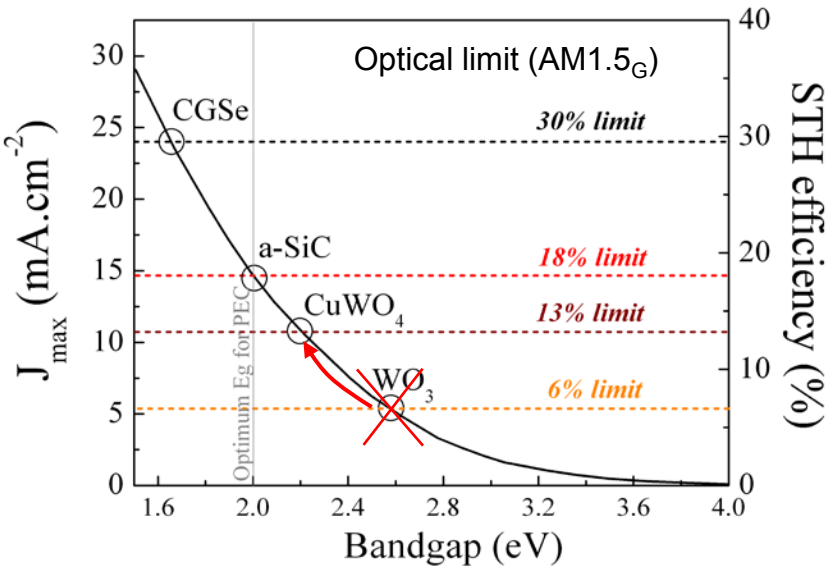
→ **New hybrid device being tested**

# 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.

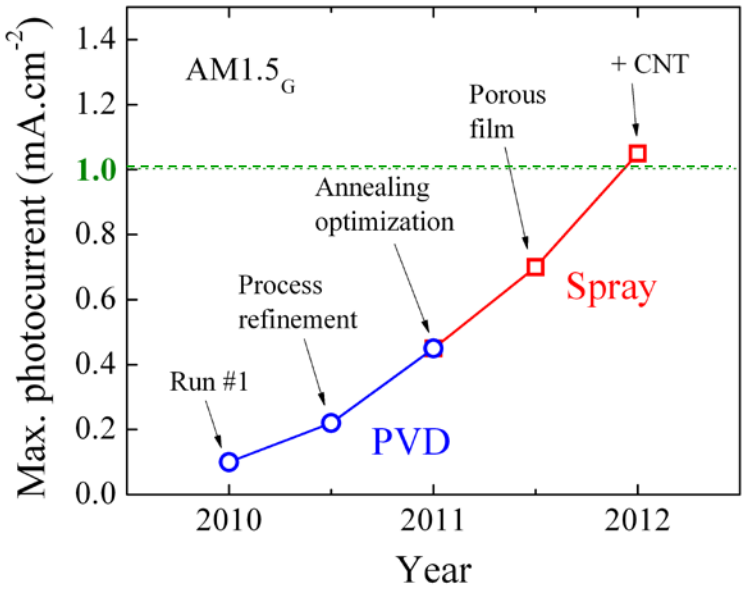
$CuWO_4$ transport properties have been identified as main limitation




## 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).

**Progress made by HNEI on $CuWO_4$**



Part I

# Amorphous Silicon Carbide (a-SiC)

Presenter: *Jian Hu*, MVSystems, Inc

Part II

# Metal Oxide Compounds

Presenter: *Nicolas Gaillard*, Hawaii Natural Energy Institute

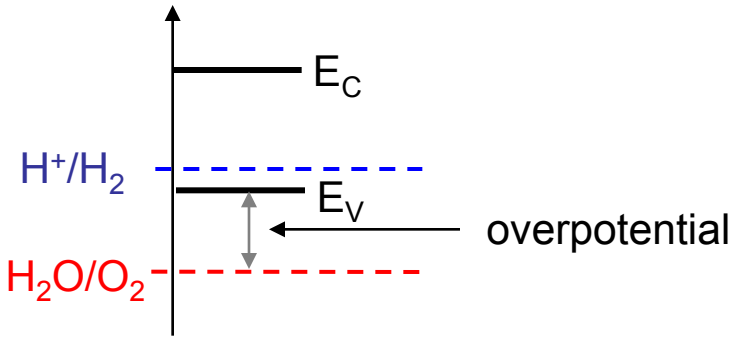
Part III

# I-III-$VI_2$ (Copper Chalcopyrite-based)

Presenter: *Nicolas Gaillard*, Hawaii Natural Energy Institute

# **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

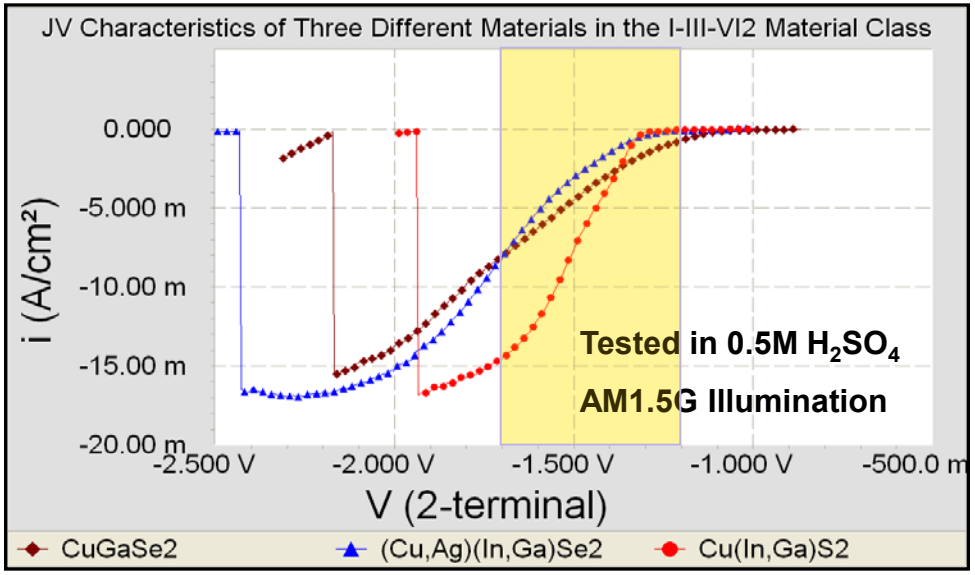
Bandgap:

$CuGaSe_2$ = 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**



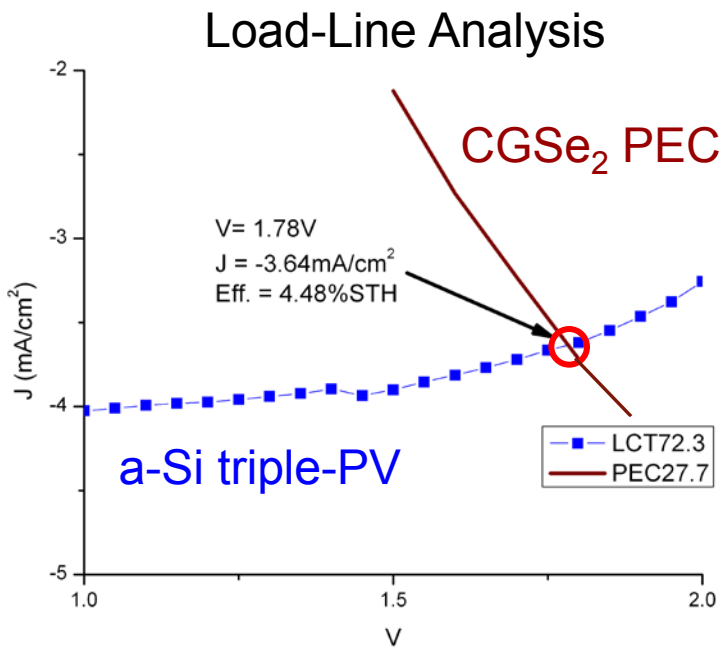

**Highlighted in yellow is the voltage region where completed devices typically operate.**

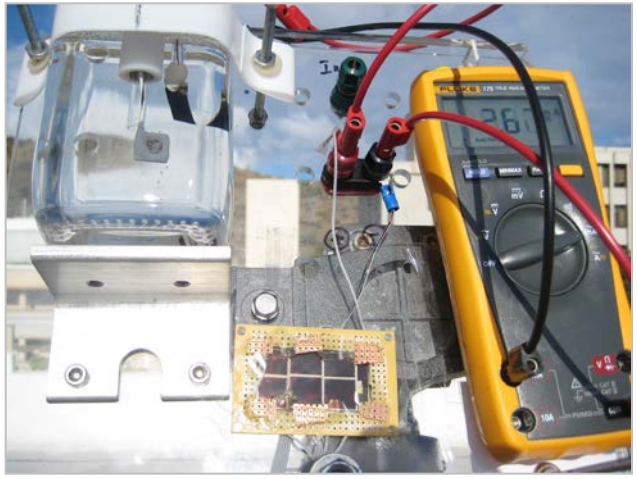
# **Progress:** STH efficiency with co-planar integration

**Addressing "Device design"**

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

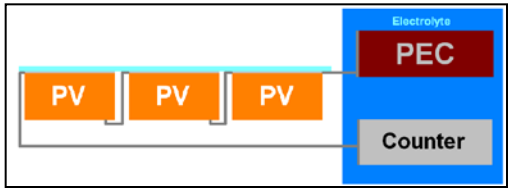
Solution: Large photocurrent produced by materials in this class allow co-planar PV-PEC integration



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

3 PV + PEC serial device



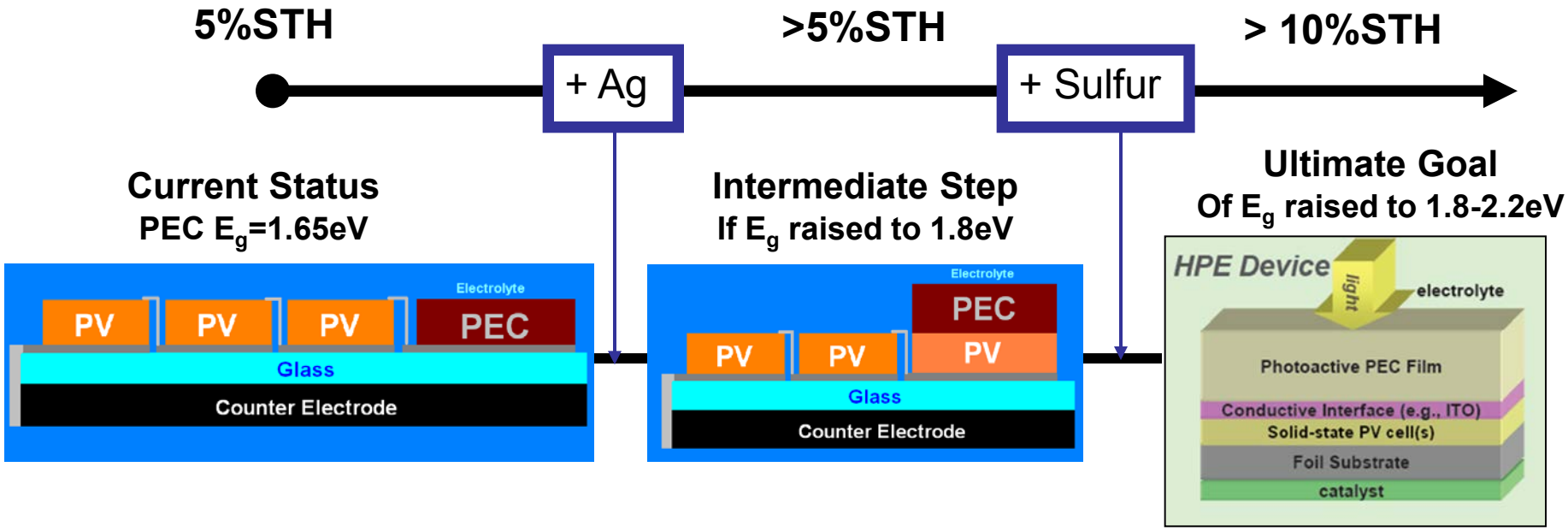

- 3 a-Si PV cells
- $CGSe_2$ PEC
- Outdoor Standalone (no external voltage):
  - $3.53mA/cm^2$ = 4.34%STH
- **Surpasses old record while using much cheaper materials**

# Future Work (I-III-$VI_2$ hybrid photoelectrode)

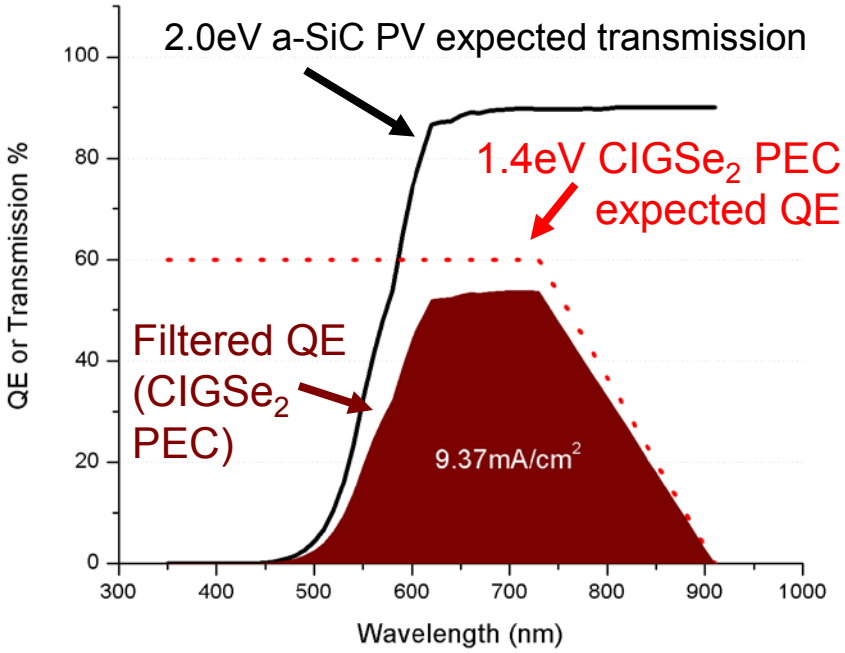
- **Coplanar Device utilizing 3 PV cells of suitable performance can surpass 5% STH.**
- **Lowering the valence band to increase $E_g$ and decrease overpotential is THE key to high performance chalcopyrite-based PEC hybrid devices.**

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)

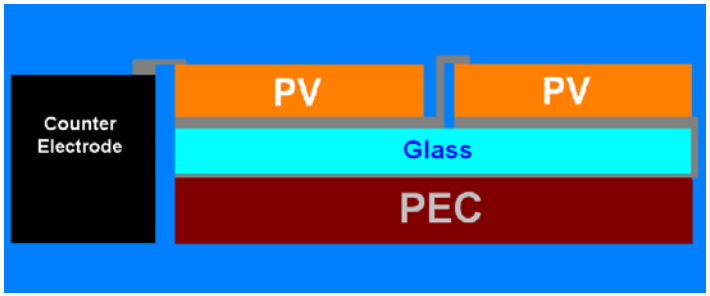


# Future Work (Novel Inverted Monolithic Stack)

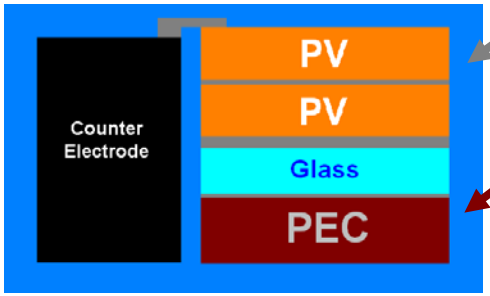



- Progress at MVSystems utilizing higher-bandgap a-SiC (~2.0eV) in PV applications
- Lowering I-III-$VI_2$ bandgap much easier than raising it
- Device development underway, possibility of 8-10%STH efficiency
- Highly dependent on voltage characteristics when fabrication proceeds

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




Step 2: Inverted Monolithic Integration




Higher Bandgap PV

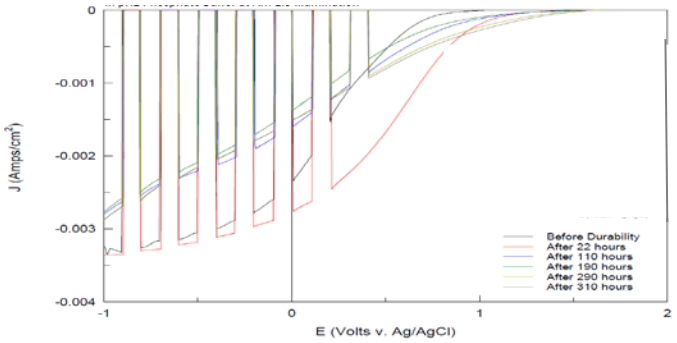
Slight Lower Bandgap PEC

# Durability test

**Addressing "Durability"**

## a-SiC photoelectrode:

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

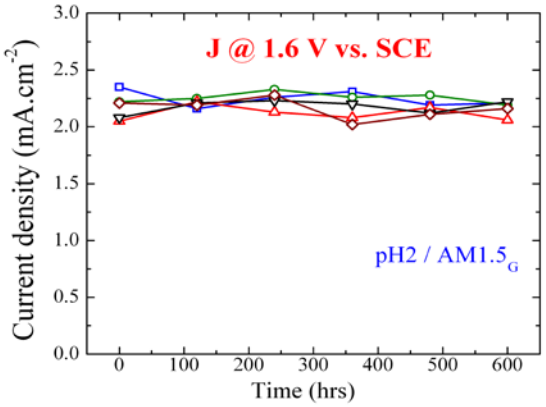



Hybrid PV/a-SiC device after 310-hrs

[ Data measured by NREL ]

## $WO_3$ photoelectrode:

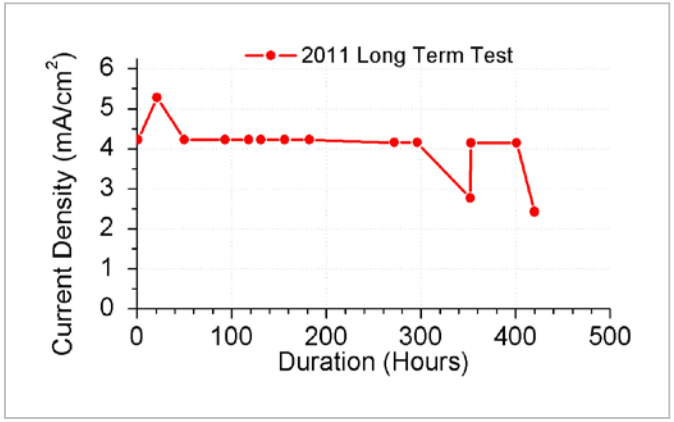
- Under AM1.5G @1.6V vs. SCE in pH2.
- High corrosion resistance of tungsten oxide in acidic solution for up to 600 hrs.




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 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:

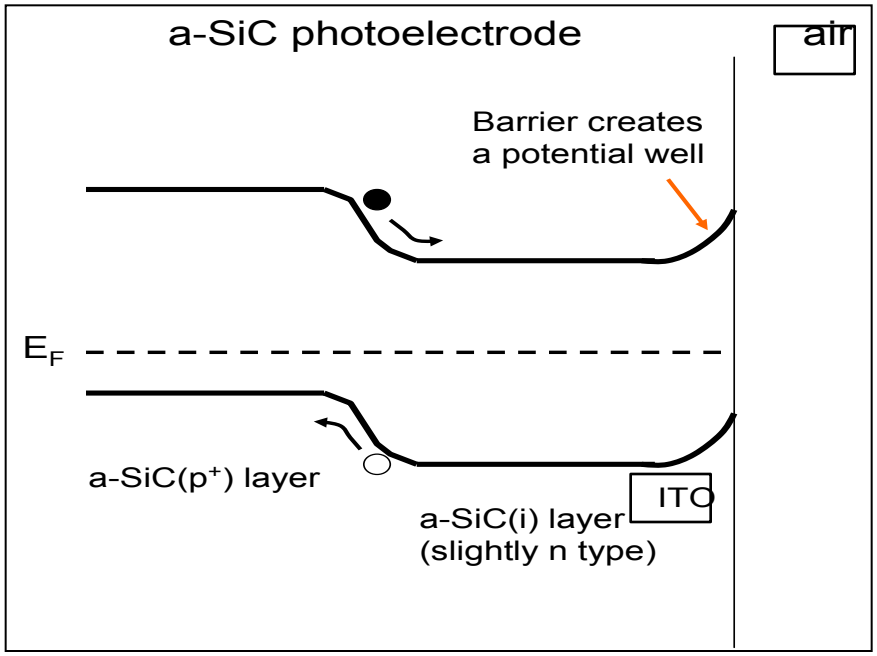
- Durability of CGSe PEC cell: 420 hrs
- Photocurrent density of PEC film: 20 mA/cm$^2$ (offers novel device integration)
- Photocurrent density of coplanar hybrid device: 3.53 mA/cm$^2$ (4.34% STH efficiency)

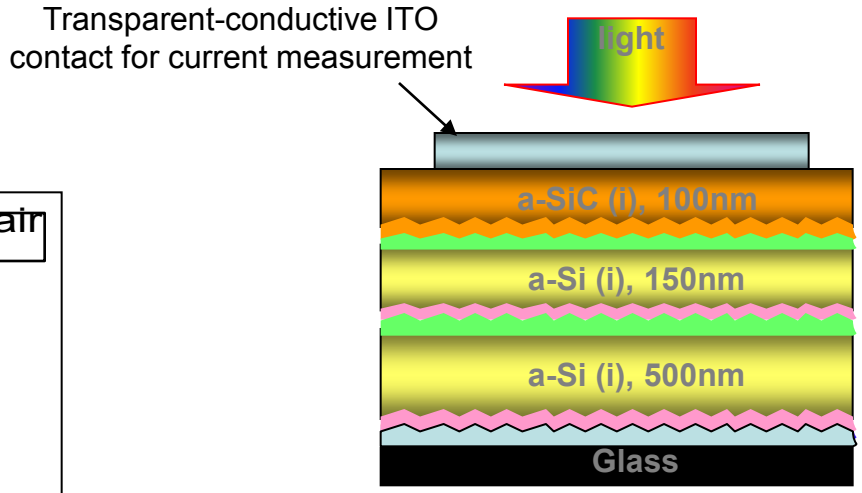
Future work: develop robust sulfurization process (↗ $E_G$) and create CIGSe with lower $E_G$

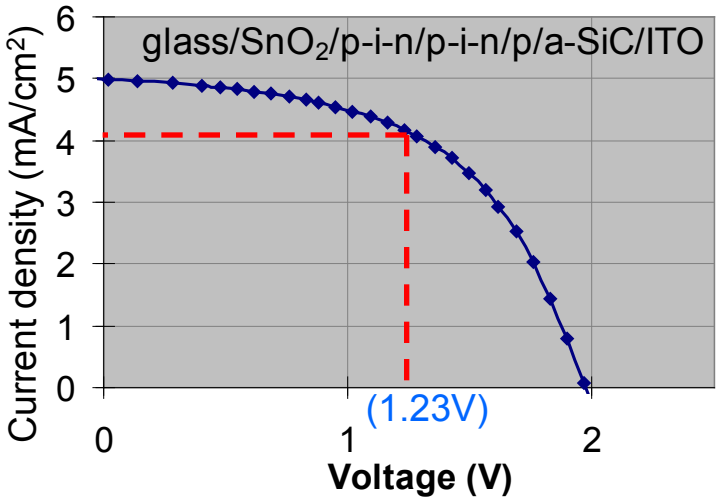
# Technical Back-Up Slides

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

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



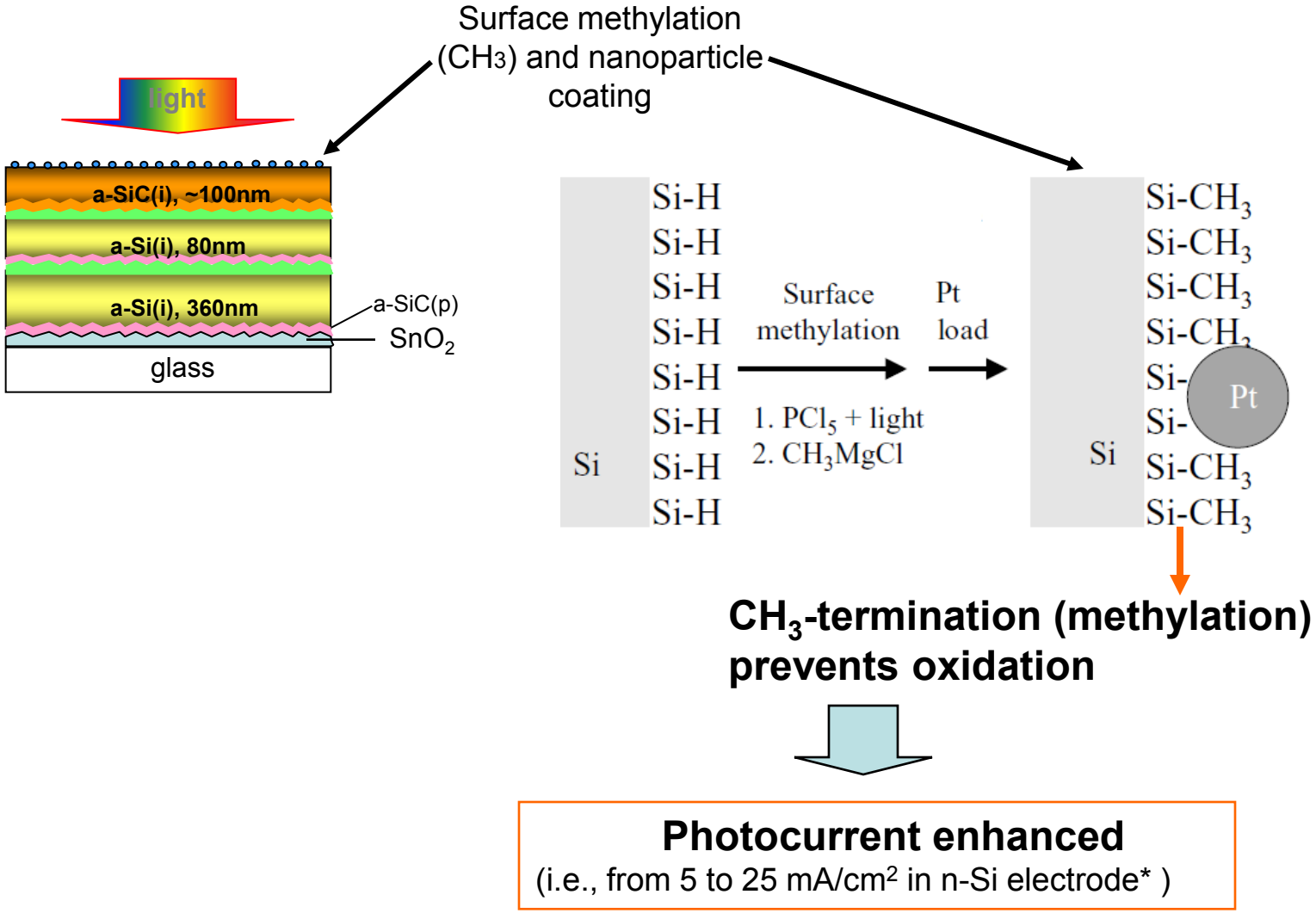




Hence current density is low ( ~4mA/cm$^2$) and FF is low

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

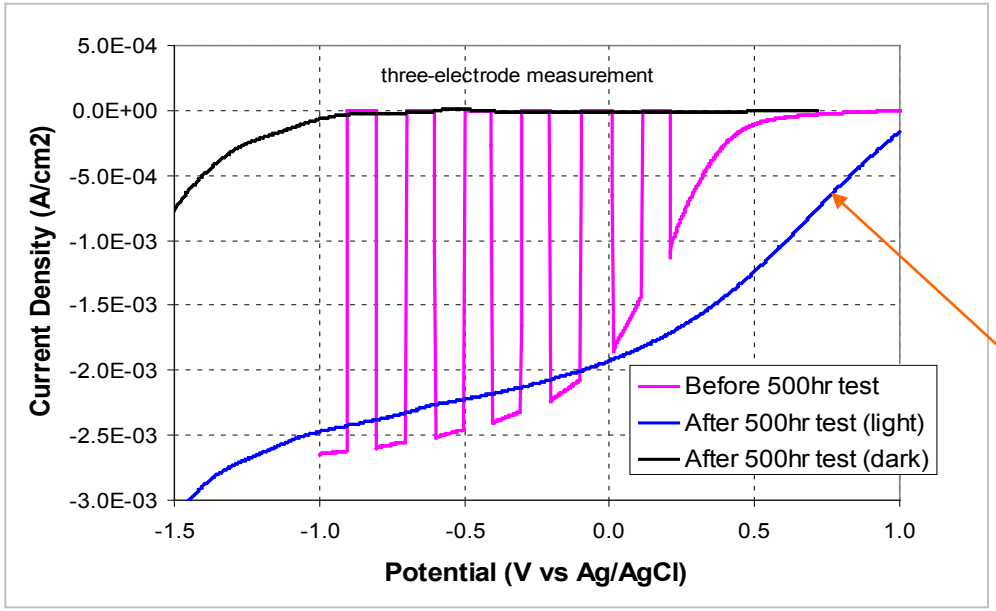



* Takabayashi, Nakamura, & Nakato, Journal of Photochemistry & Photobiology A, 166 (2004).

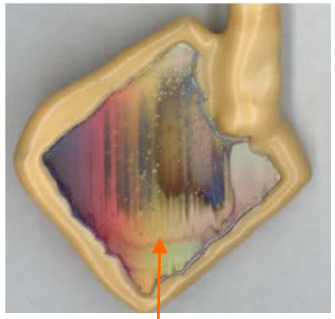
# 500-hr durability test on hybrid PV/a-SiC device

**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 ]

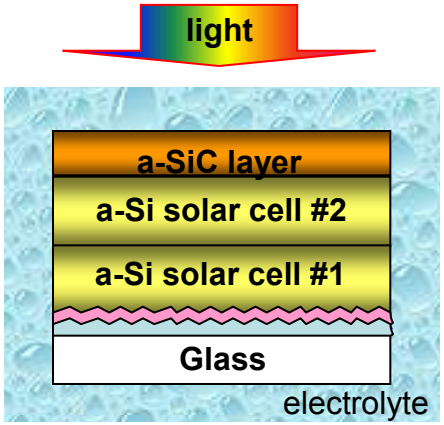
- Surface morphology changed
- Investigation underway (ie by EDS)

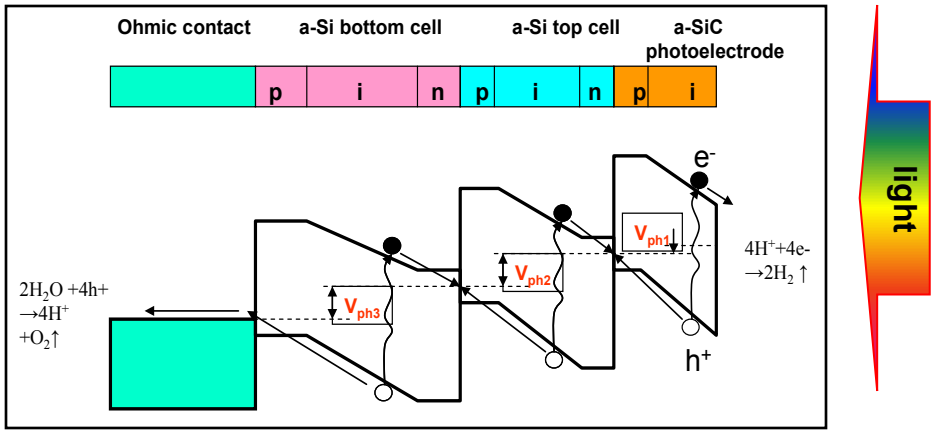
- Photocurrent remains largely unchanged with improved fill-factor
- Dark current increase @>-1V

# 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:

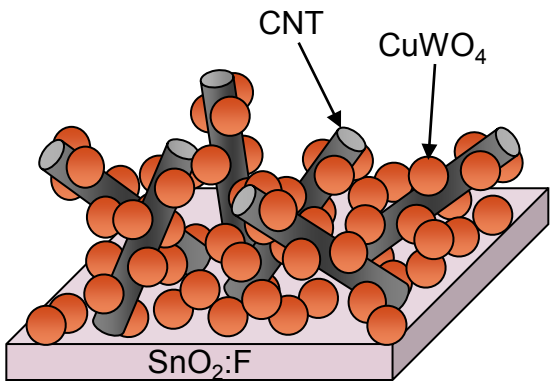
| Photo-electrode | Eg (eV) | Jsc (mA/cm²) Available | Voc (V) | PV cell configuration | Filtered Available | Voc (V) | STH (%) Possible |
|---|---|---|---|---|---|---|---|
| a-SiC:H (1) | 2 | 8.85 (100 nm) | 0.6 (p-i) | a-Si/a-Si (620nm/132nm) | 7.1 | 1.9 | 8.73 |
| a-SiC:H (2) | 2 | 8.85 (100 nm) | 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

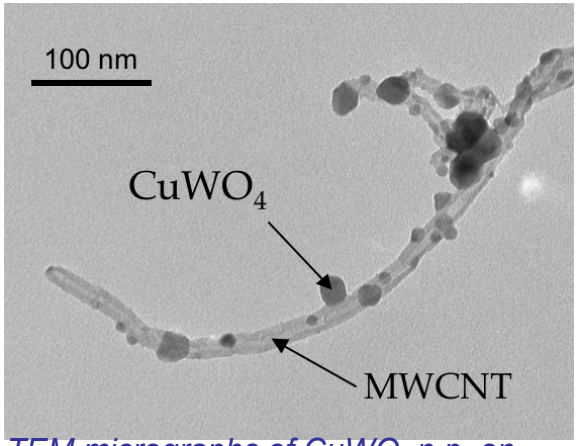
Addressing "Y"

## Improving $CuWO_4$ transport properties with CNT

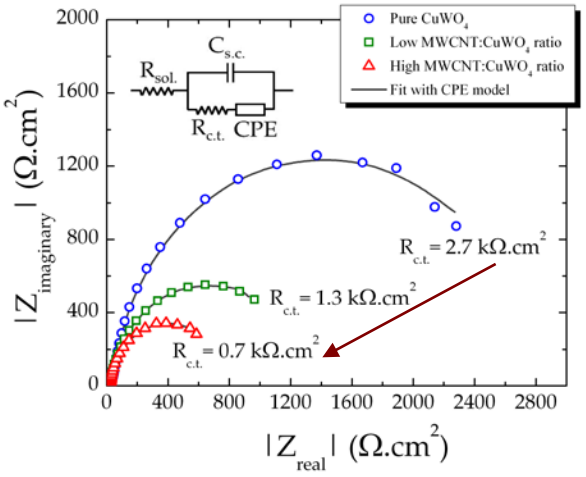



*Light absorber / charge collector*

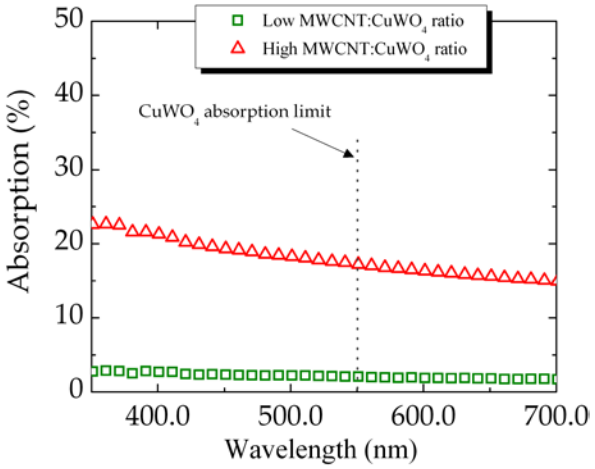
1. Various CNT:$CuWO_4$ w.t. %
2. Spray on $SnO_2$:F substrate
3. Annealing @ 500°C in air

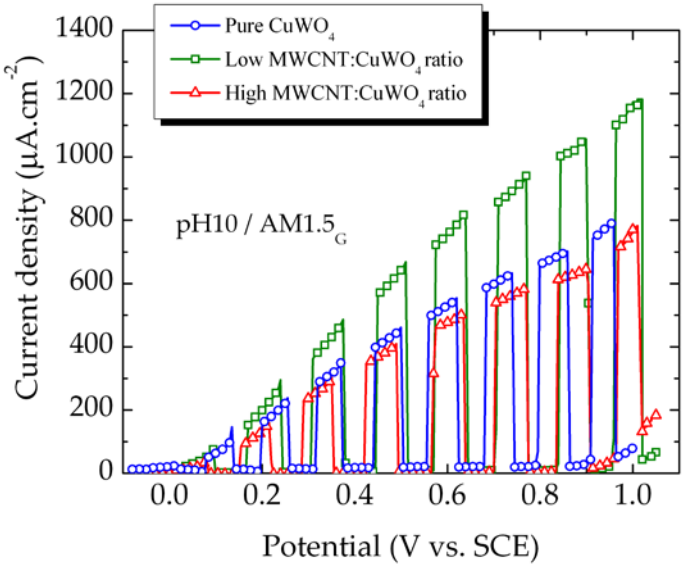



*TEM micrographs of $CuWO_4$ n.p. on CNT*




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"