PD054

PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

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MVSystems, Inc.

June 7th, 2010

DE-FC36-07GO17105

Overview

Timeline

- Project start date: 9/1/2007
- Project end date: 12/31/2010
- Percent complete: ~75%

Budget

- Total project funding*
  - DOE share: **$1,508,827**
  - Contractor share: **$415,128**

** funds cover work reported in posters PD053, PD054, and PD055*

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.

Overview

poster #PD053
Progress in the Study of ***Amorphous Silicon Carbide*** as a Photoelectrode in Photoelectrochemical Cells

poster #PD054
Progress in the Study of ***Tungsten Oxide Compounds*** as Photoelectrodes in Photoelectrochemical Cells

poster #PD055
Progress in the Study of ***Copper Chalcopyrites*** as Photoelectrodes in Photoelectrochemical Cells

Poster PD054

Progress in the Study of ***Tungsten Oxide Compounds*** as Photoelectrodes in Photoelectrochemical Cells

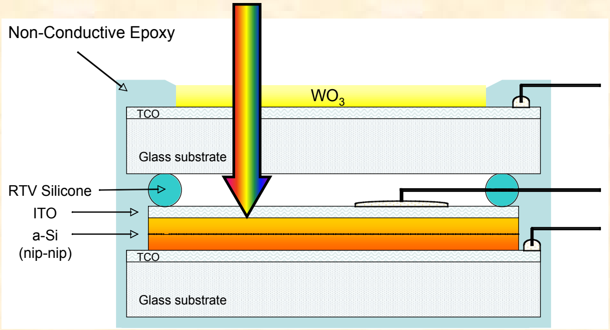
Nicolas Gaillard
Hawai'i Natural Energy Institute
University of Hawai'i

June 7th, 2010

Relevance - Objectives

Advantages of tungsten oxide:

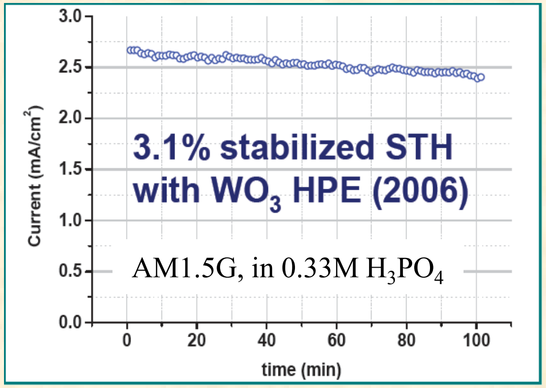
1) Good performance demonstrated in several applications
2) Film can be deposited using low-cost processes
3) WO_3 satisfies main criteria for water splitting



Solar cell - PEC mechanical stack

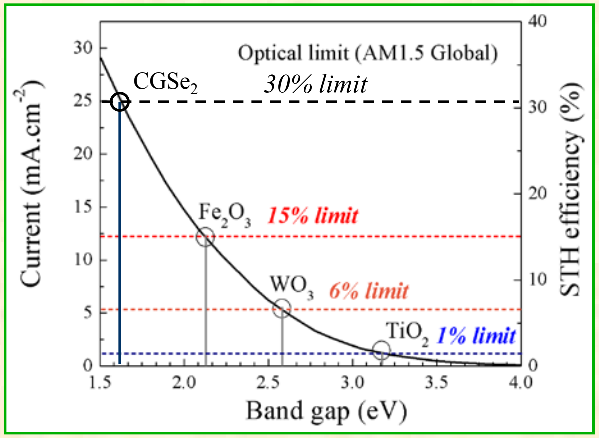
WO_3 PEC champion device:

→3.1% STH efficiency demonstrated in a mechanical stack configuration (using MVSystems' solar cell).



…but this material suffers from :

1) its bandgap value (2.6 eV) that limits light absorption
2) the position of the valence band (E_V) vs. oxygen half-reaction potential: external bias needed.



Relevance-milestones

Program targets		WO$_3$ progress status
Year 1: 10/2007----9/2008		
✓ Material Photocurrent ≥ 3 mA/cm^2	100% @ 12/2007	2.8 to 3 mA/cm^2 demonstrated with pure WO$_3$-based PEC electrode
✓ Durability 100 hrs	100% @ 1/2008	100 hr durability achieved in 0.33M H_3PO_4 solution
✓ Device STH efficiency ≥ 3.7%	85% @ 12/2007	3.1% achieved with mechanical stack using underlying PV cell
Year 2: 10/2008----09/2009		
✓ Material Photocurrent ≥ 4 mA/cm^2	90% @ 3/2008	3.6 mA/cm^2 demonstrated with WO$_3$-based bilayer PEC electrode
✓ Durability 200 hrs	50% @ 1/2008	100 hr durability achieved in 0.33M H_3PO_4 solution (so far tested)
✓ Device STH efficiency ≥ 5%	62% 88%	3.1% STH (62% of goal) demonstrated, 4.4% STH (88% of goal) expected with available components for multi-junction device (see slide #18)
Extended year: 10/2009----12/2010		
✓ Material Photocurrent ≥ 4 mA/cm^2	90% @ 3/2008	New synthesis techniques are under investigation to reduce band gap
✓ Device STH efficiency ≥ 5%	62% 88%	Building test protocols to measure optoelectronic properties of PEC material candidates using solid state integration

Relevance-barriers

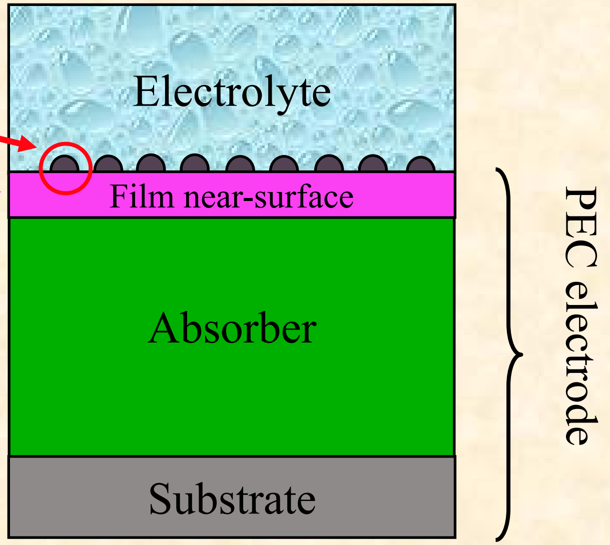
Barrier	Challenges	Strengths
Y. Materials Efficiency	**- Reducing WO_3 band gap to achieve STH of ~5%.** - The position of the conduction band minimum for pure WO_3 in standard acidic media is low, requiring additional biasing.	- Has "direct-like" bandgap and good carrier transport properties resulting in a high PEC photocurrent collection efficiency. **- Alloying of the material can theoretically lead to a reduction of bandgap** by raising the valence band while potentially increasing the conduction band at the same time, thereby reducing bias requirements.
Z. Materials Durability	The photostability over extended time periods for new tungsten-alloy compositions requires validation.	**Stability of pure tungsten oxide in acidic media is well documented and verified in various combinations of time and operating conditions.**
A.C. Device Configuration Designs	**Optimized tandem/multijunction device** configurations need to be developed to match the photocurrent and photovoltage characteristics of newly-developed tungsten-based compounds.	Thin films in general are compatible with the concept of multijunction devices, such as the hybrid photoelectrode. Sputtering, for example, of PEC top layer is compatible with an underlying solar cell.

Approach

<u>Interface</u>: **nano-particles and nano-rods**
Deposition to enhance charge transfer at the interface.
(under investigation since 2009)

<u>Near-surface</u>: band-edge position tuning **with bilayer** to reduce external bias
(under investigation since 2008)

<u>Absorber (bulk)</u>: bandgap decrease **with ion incorporation** to enhance light absorption
(under investigation since 2006)



Every component of the PEC system (not only electrode bulk) is tuned to increase H_2 production

(*) Theory predicts a maximum photocurrent of 5 $mA.cm^{-2}$

Approach-Collaborations

THEORY

Effect of ions incorporation on material E_G and band-edges position.

NREL Lawrence Livermore National Laboratory

CHARACTERIZATIONS

Photocurrent, Flat-band potential, OER/HOR, efficiency, morphology, advanced spectroscopy

UNLV University of Nevada, Las Vegas NREL

SYNTHESIS

Bulk materials, bilayers, catalyst nano-particles

UCSB

MVSystems, Inc.

UNIVERSITY OF LOUISVILLE

Progress: Work Performed since 2009 AMR

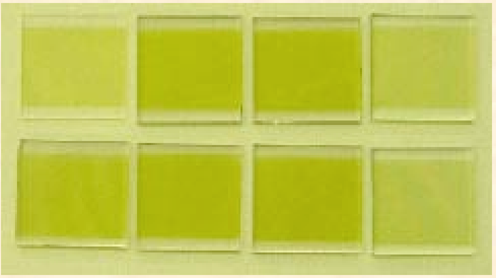
- Continuing WO_3 bulk modification using ion incorporation:
  - *Synthesis of new alloys using house-made sputtering targets (UH)*

- WO_3-based hybrid device integration evaluation:
  - *Fabrication of WO_3 samples using industrial deposition tool (MVS)*

- Study of new nano-materials for catalytic treatment
  - *Fabrication of RuO_2 nano-rods (UH)*
  - *Synthesis of PdAu nano-particles (UH)*

Progress: deposition and performance of WO_3

Perkin-Elmer 2400 three-gun Sputtering system



Pure WO_3 films

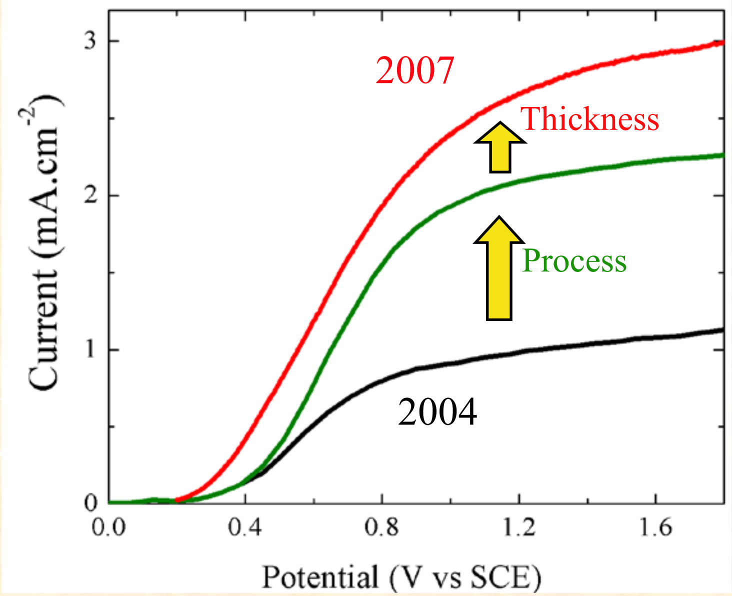
WO_3 E_G (2.6 eV) solves barrier AC

Reactive sputtering deposition:

- RF mode (13.56 MHz)
- material target: pure W
- gas: argon (7 mT) + oxygen (2.2 mT)
- deposition temperature: 270°C

Low temperature process solves barrier AB

PEC performances (AM1.5_G / 0.33M H_3PO_4)

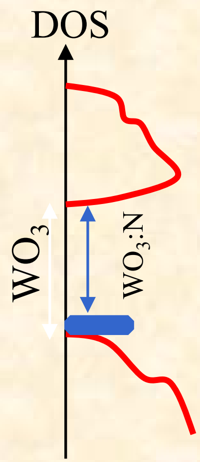


Continuous improvement since 2004

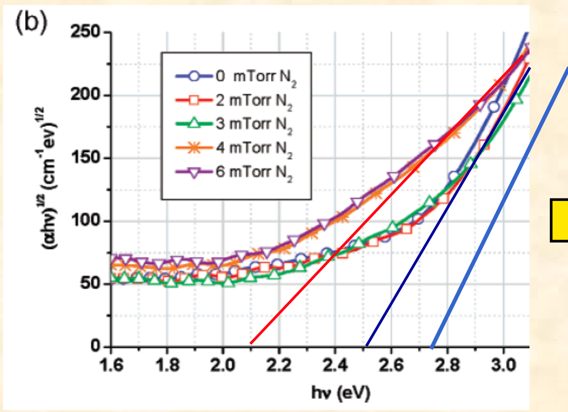
Progress: WO_3-based alloy synthesis

Presented at AMR09

⇒ WO_3 band gap can be reduced using foreign element incorporation, such as nitrogen:

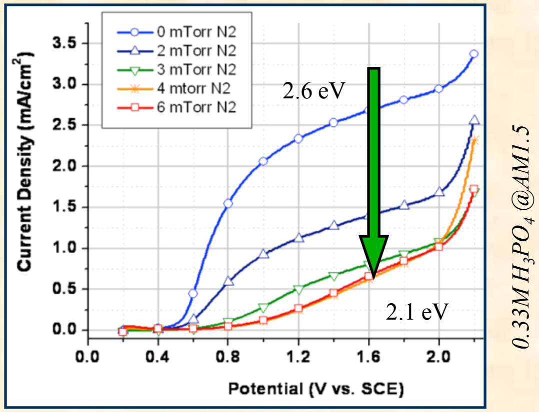


Successful E_G reduction



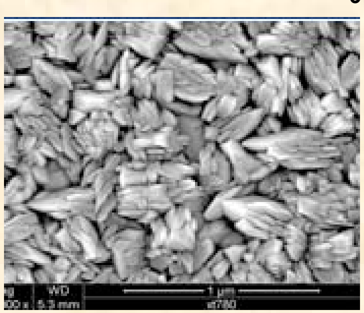
…but

Poor PEC performances

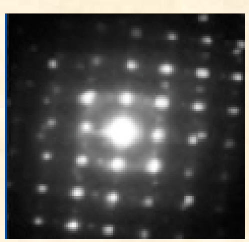


B. Cole et al., J. Phys. Chem. C, 2008, 112, 5213-5220.

Pure WO_3

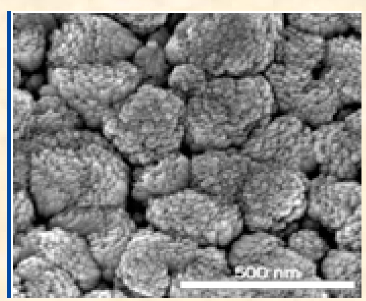


SEM

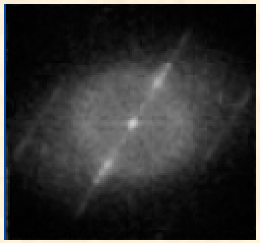


HRTEM

WO_3:N



SEM



HRTEM

Defect formation → e- and h+ recombination → poor electrical conductivity

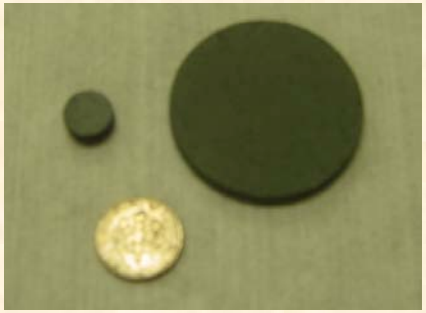
Progress: WO_3-based alloy synthesis

NEW ! Nitrogen incorporation into WO_3 using N-based material as host, such as BN or WN_2

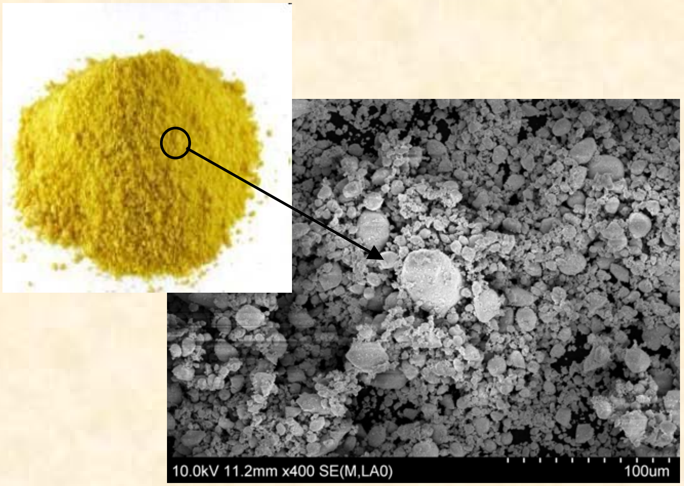
Method: House-made WO_3-based sputtering target using powder sintering process

Nanopowder compaction

High temperature sintering

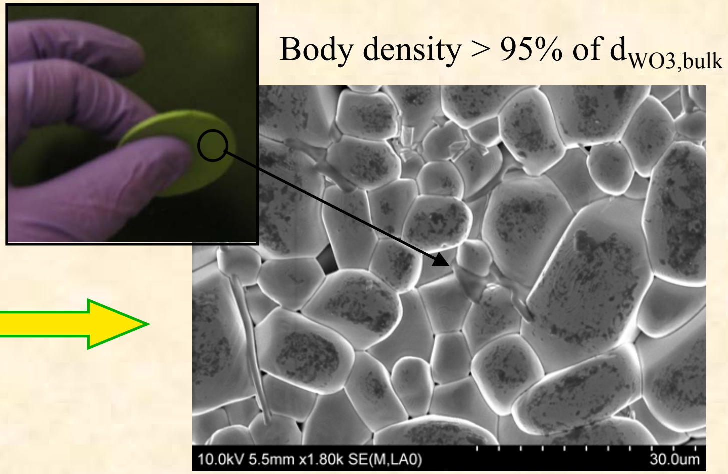


WO_3 control sample (left) and 2” target (right)



SEM micrograph of WO_3 nano-powder

Body density > 95% of $d_{WO3,bulk}$



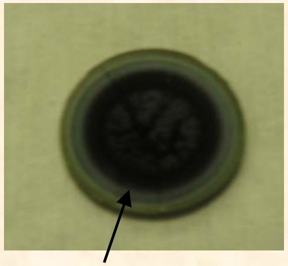
SEM micrograph of WO_3 sintered body

Progress: WO_3-based alloy synthesis

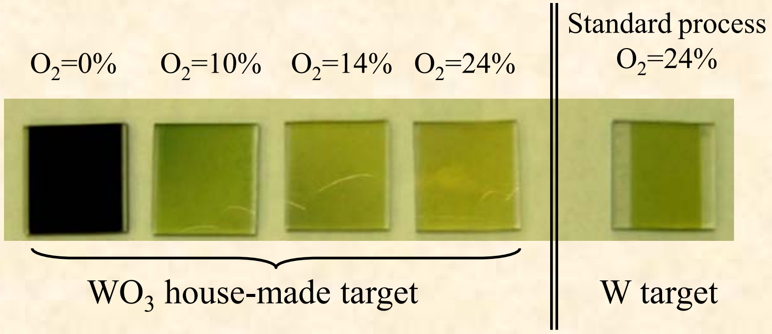
NEW !

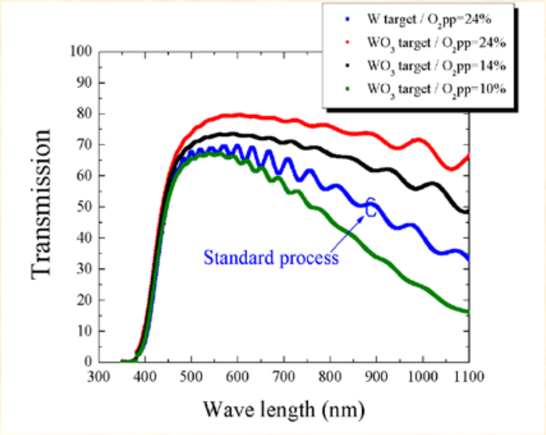
1) Evaluation of WO_3 films synthesized with HNEI's sintered WO_3 target

Sputtering target after 10 depositions

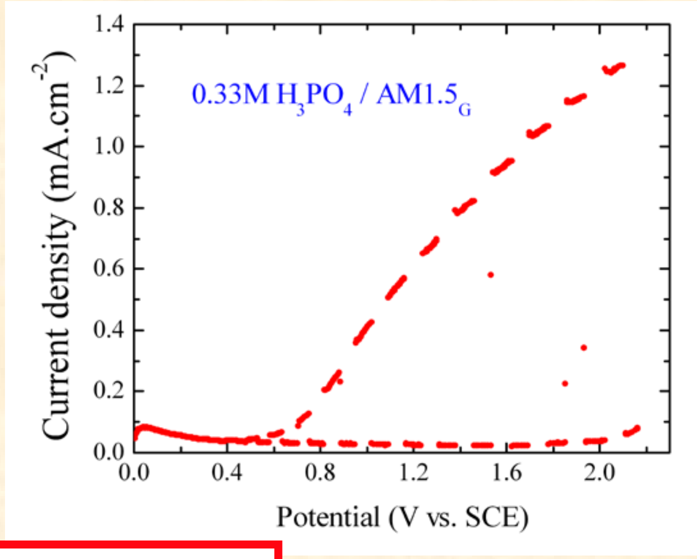


Center is dark blue (WO_{3-x}) due to Ar+ bombardment





Effect of O_2 partial pressure on WO_3 transmission



Promising first results with home-made WO_3 target

Improvements can be done on:

1. Onset potential (need to lower surface states)
2. Saturation I_{photo} (need to improve film crystallinity)

Addressing barrier Y

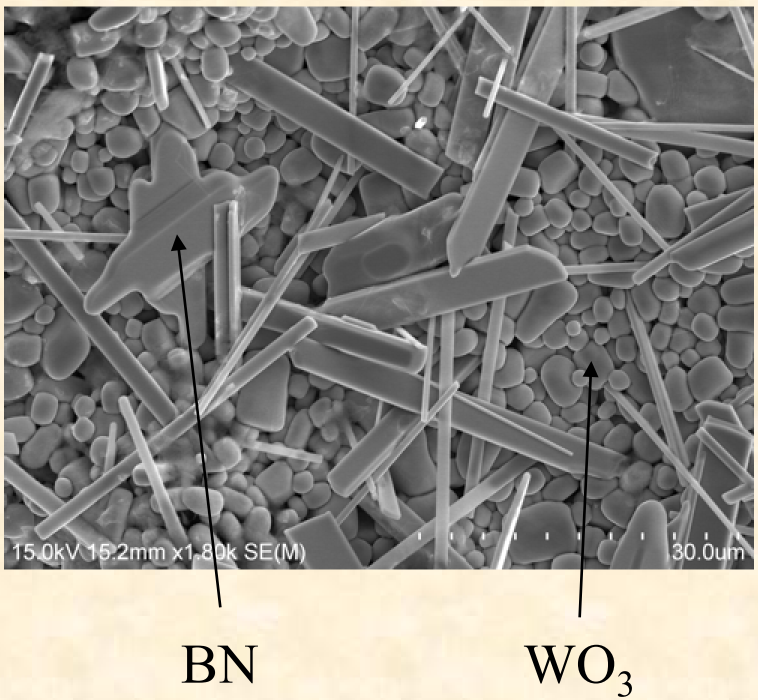
Progress: WO_3-based alloy synthesis

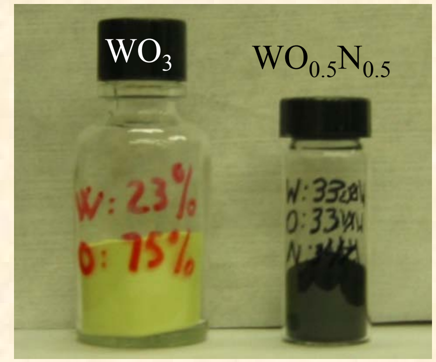
NEW !

2) Sintering of WO_3 and N-based nanopowders to form a sputtering target

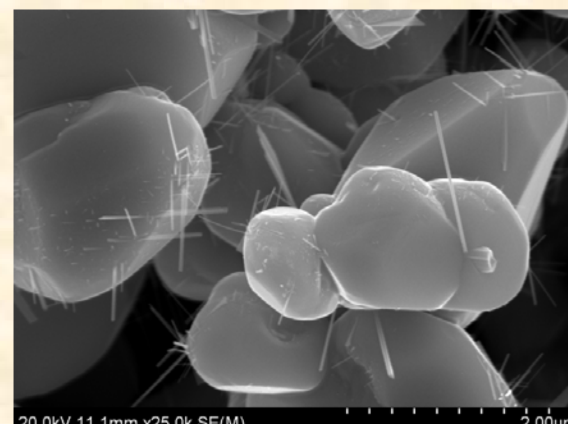
WO_3/BN   94%w.t. / 6%w.t.

SEM picture of sintered target (surface)





WO_3 nanopowder nitridation (done at Louisville Univ.)



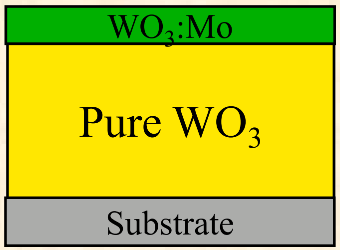
SEM picture of $WO_{0.5}N_{0.5}$ sintered body

Addressing barrier Y

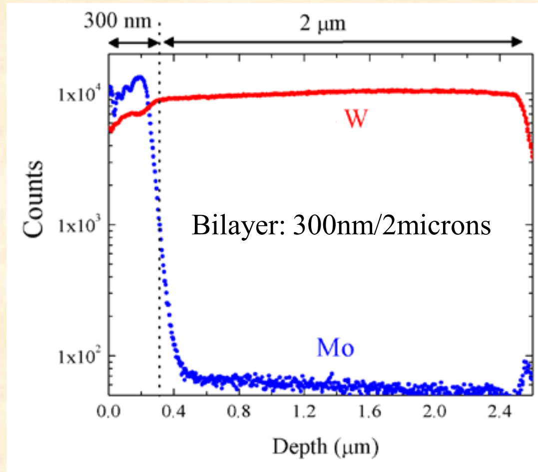
Progress: WO_3-based bilayer PEC electrode

Presented at AMR09

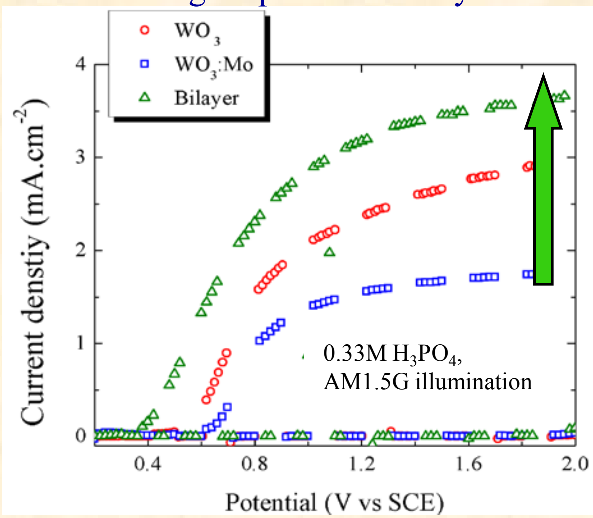
Surface energetics modification using bilayer concept



SIMS analysis of the bilayer (NREL)

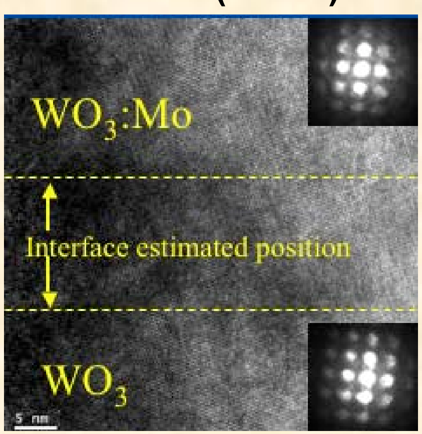


Higher perf. with bilayer



N. Gaillard et al., J. Mat. Res., ***25,*** *45 (2010).*

HRTEM (NREL)



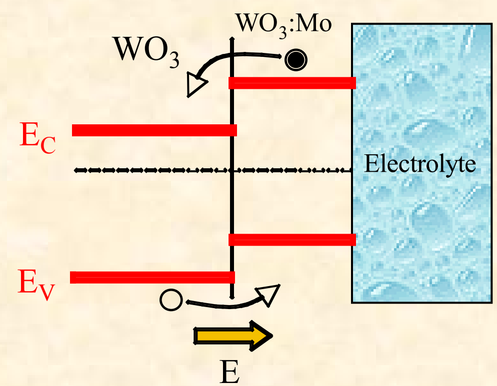
Coherent growth of WO_3:Mo = reduction of defects

UPS and IPES analysis (UNLV)

	E_C-E_F	E_F-E_V
WO_3	0.39 eV	2.89 eV
WO_3:Mo	0.60 eV	2.64 eV

Resolution : +/-0.1 eV

0.25 eV downward shift of E_F with Mo

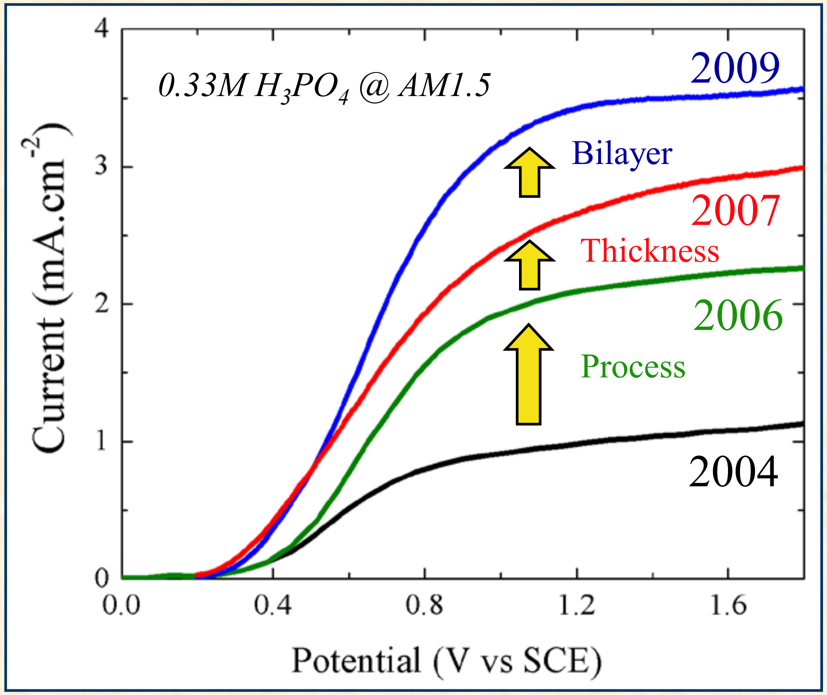


M. Bär et al., Applied Physics Letters, ***96****, 032107 (2010).*

Addressing barrier Y

Progress: WO_3-based bilayer PEC electrode

Presented at AMR09



Continuing WO_3-based PEC electrodes performances improvement with bilayer

Addressing barrier Y

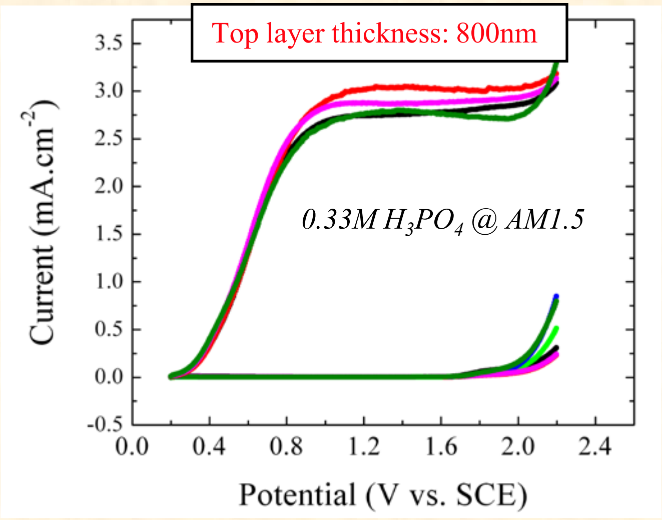
NEW !

- WO_3:Mo formation using single sputtering target

⇒ improve process control and homogeneity

Optimization of top layer thickness

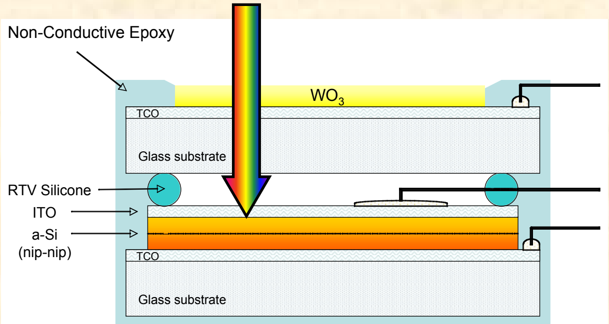
⇒ enhance built-in potential strength



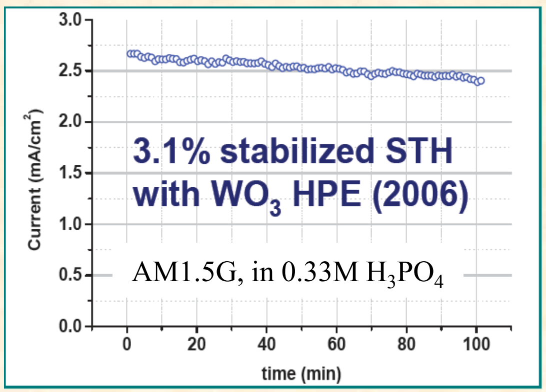
- Low sample-to-sample variation
- 800 nm top layer: too thick

Progress: WO_3-based hybrid device integration

Presented at AMR09

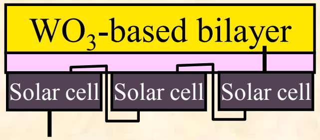


Solar cell - PEC mechanical stack



3% STH demonstrated using mechanical stack configuration with pure WO_3 material

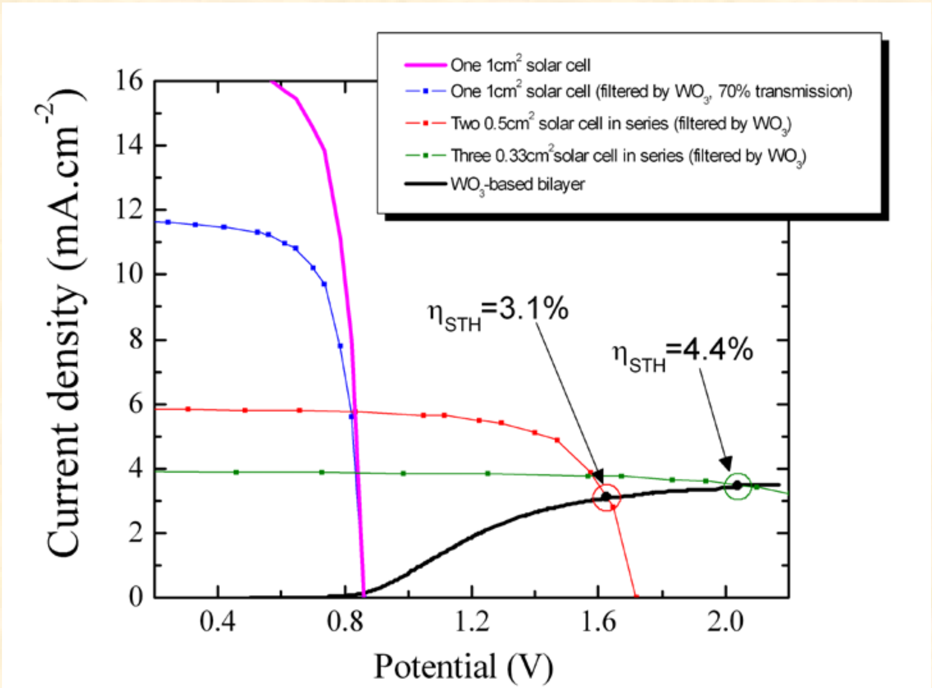
NEW ! Device integration toward 5% STH efficiency



4.4% STH efficiency can be achieved using three single-junction solar cells + WO_3

The number of solar cells will be reduced if one can lower photocurrent onset potential and or achieve a better fill factor

→ Need to improve surface catalysis



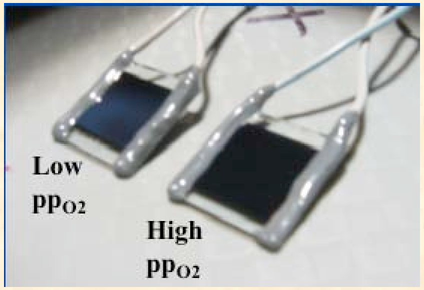
Addressing barrier AC

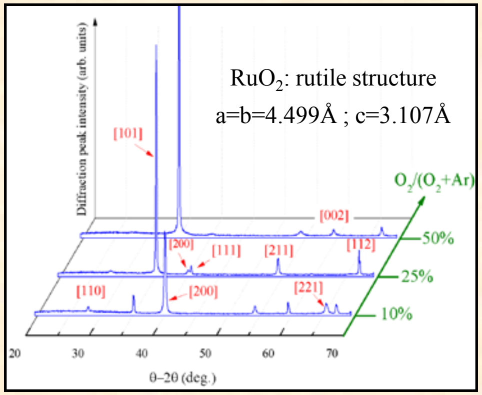
Progress: Surface catalytic improvement

Presented at AMR09

Evaluation of RuO_2 for O_2 gas evolution

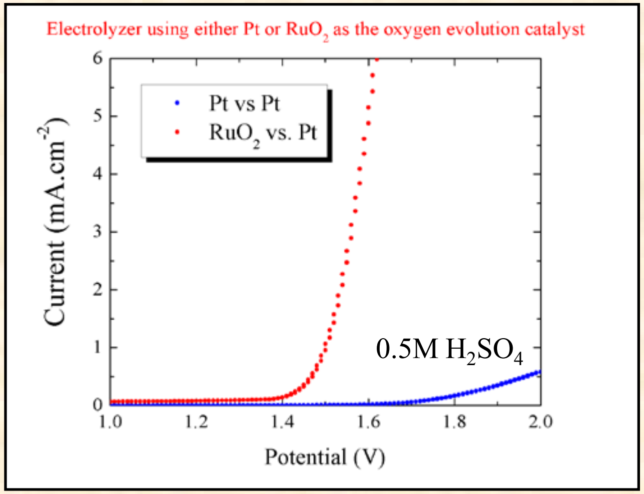
First test: **as counter electrode (thin film)**



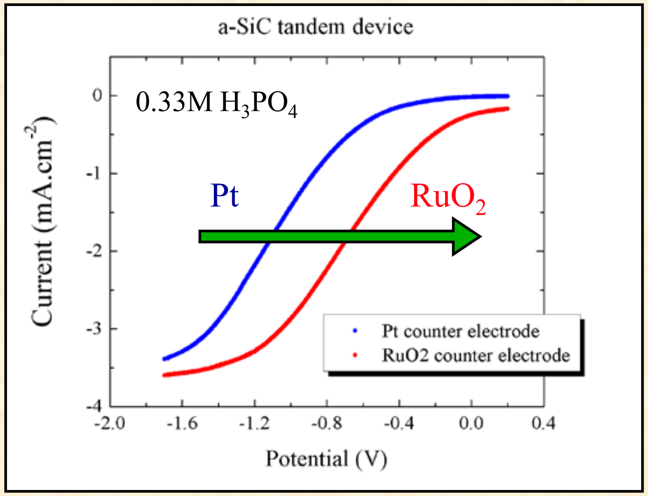


Control of catalytic properties with process parameters

→ *Electrical characterization: electrolyzer*



→ *Electrical characterization: PEC device*

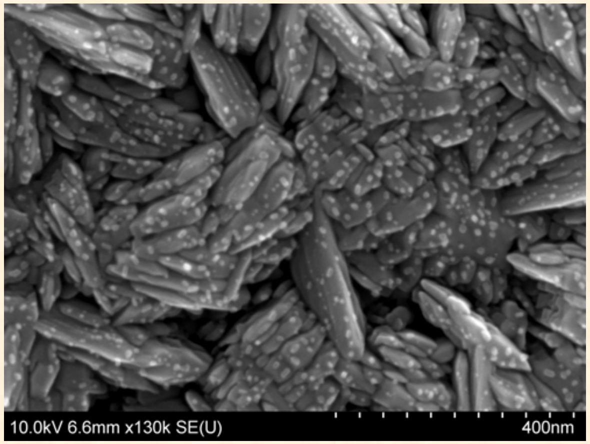


HNEI's RuO_2 thin film shows high catalytic activity for O_2 production than Pt

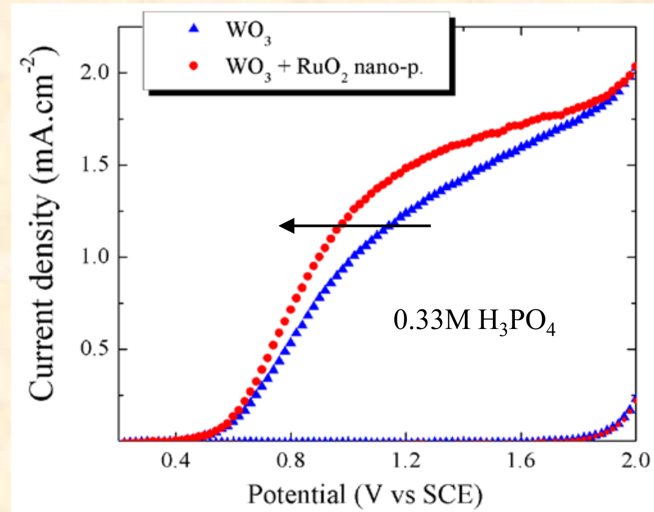
Addressing barrier AC

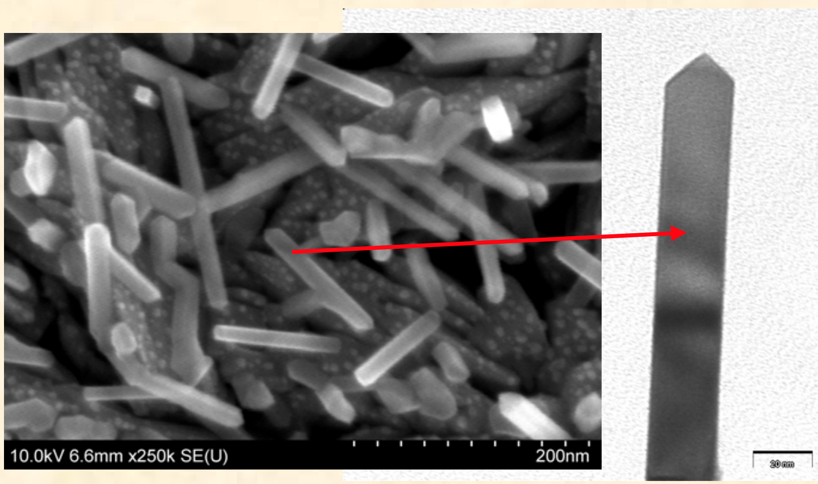
Progress: Surface catalytic improvement

NEW ! Deposition of RuO_2 nano-particles and nano-rods on WO_3 thin films



SEM picture of RuO_2 nano-particles on WO_3





SEM picture of RuO_2 nano-rods on WO_3 *TEM picture*

- Catalytic effect of nano-particles on WO_3 thin film demonstrated

- Fabrication of monocrystalline nano-rods to increase the contact area between WO_3 and electrolyte (test ongoing)

Addressing barrier Y

Collaborations

– US Department of Energy PEC working group: Leading task force on WO_3 and active participation to the Working Group on PEC measurement standardization.

– National Renewable Energy Laboratory: collaboration to perform theoretical research and advanced morphological analysis of new WO_3-based 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.

– MVSystems Incorporated: development of solar cell to demonstrate hydrogen production in a standalone configuration.

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

Research Plan

1) New approaches for ion incorporation into WO_3 bulk to modify band gap

- Continuing nitrogen incorporation using commercial sputtering targets (WN_2)
- Pursuing house-made sputtering target manufacturing:
  - WO_3 deposition process optimization
  - Reactive sputtering using WO_3/WO_xN_{1-x} mixed targets
- Evaluating other element incorporation (Se, S) and alloys ($W_{1-x}Si_xS_{2-y}O_y$) (#)

2) Development of new surface modification techniques

- Optimization of RuO_2 nano-particles and nano-rods to enhance catalytic activity
- Investigation of new catalytic materials

(#) as proposed by NREL theoretical group

Research Plan (cont'd)

3) Thorough analyses of WO_3-based alloys bulk defects and interface properties

- Thin film characterization: XRD, Hall measurements and Raman
- **Device: building test protocols to measure optoelectronic properties of PEC material candidates using solid state integration (as introduced by MVS, PD053 – see Project Summary below)**

4) Tungsten oxide-based hybrid device integration

- Continuing WO_3 thin film synthesis research with MVSystems
- Evaluate newly developed WO_3-based PEC electrode using mechanical stack

Tungsten Oxide Summary

- **Relevance**
  - 3.1% STH efficiency demonstrated in a standalone configuration with underlying solar cell.
  - WO_3-based materials corrosion resistant in acidic solutions demonstrated worldwide.
- **Approach**
  - Synthesis: improvements can be performed on each component of the PEC electrode: absorber (light absorption), surface (band-edge position), interface (catalyst) and electrolyte (MeOH).
  - Characterization: large tool chest of specific techniques available from DOE working group.
- **Progress**
  - Increased photocurrent using bilayer # Band gap reduction demonstrated using nitrogen # Evaluation of new alloys using house-made sputtering target # Development of integrated WO_3-based hybrid device using industrial deposition tools # Successful synthesis of catalytically active RuO_2 nano-particles and nano-rods
- **Collaborations**
  - Intensive collaborations with DOE working groups ("WO_3 task force" + "Measurement standardization WG") and international teams to effectively address key issues.
- **Research Plan**
  - Continuing investigation of WO_3-based alloys with new ions (absorber) # Optimization of Mo-based WO_3 bilayer (band-edge position) # Continuing efforts on catalyst research (interface and electrolyte) # Thorough analysis of WO_3 optoelectronic properties using solid-state integration # Fabrication of fully integrated WO_3-based hybrid device.

Project Summary

- Relevancy

The MVSystems/UH project is accelerating the development of **three important PEC thin-film materials classes** (a-SiC, WO_3 and CGSe) with high potential for reaching DOE goals of practical PEC water-splitting.

- Approach

Use test protocols to measure optoelectronic properties of PEC material candidates using solid state integration to isolate the semicond./electrolyte interface (as introduced by MVS, PD053):

#1: Opto-electronic properties (Eg, dark and light conductivity, Fermi level position, extended state/hopping conduction) to match a set of predetermined criteria.
#2: Basic solid state Schottky barrier device for extraction of current
#3: Use semiconductor/electrolyte techniques at HNEI to match a set of predetermined criteria.

- Collaboration

In order to promote the needed scientific breakthroughs in PEC R&D, collaborations have been developed within the US DOE PEC Working Group and with the IEA-HIA PEC Annex-26.

Project Summary

➢Progress

Items	Thin-film materials	2008			2009-2010		
		Target	Achieved	Status	Target	Achieved	Status
Material photocurrent	a-SiC	≥ 3 mA/cm^2	7-8 mA/cm^2	**100%**	≥ 4 mA/cm^2	7-8 mA/cm^2	**100%**
	WO_3		2.9 mA/cm^2	90%		3.6 mA/cm^2	90%
	CGSe		20 mA/cm^2	**100%**		20mA/cm^2	**100%**
Material/Device durability	a-SiC	≥ 100 hours	150 hours	**100%**	≥ 200 hours	200 hours	**100%**
	WO_3		100 hours	**100%**		100 hours*	50%
	CGSe		10 hours*	10%		10 hours*	5%
Device STH efficiency	a-Si/a-SiC	≥ 3.7%	1%	25%	≥ 5%	1.6% *(6% projected from solid-state device perf.)*	32%
	WO_3		3.1%	85%		3.1% *(4.4% projected using 4-junction configuration)*	62%
	CGSe		0%	0%		0% *(5% projected using 4-junction configuration)*	0%

* So far tested

➢ Future work

(1) Further improve the properties of thin-film materials.
(2) Develop new surface modification techniques.
(3) Establish band diagrams for the thin-film photoelectrode/electrolyte system.
(4) New techniques will be used to evaluate PEC films interface @ UNLV and use new information to focus fabrication and device matching efforts effectively.
(5) Improve the PV performance of the thin-film solar cell used in the hybrid PEC device.
(6) Test of solid state device made of the PEC material of interest to evaluate its intrinsic optoelectronic performances.

A Go/No Go decision will be made by the end of 2010.