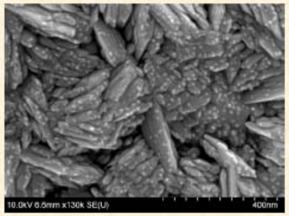
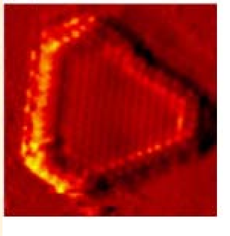



PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION:
DOE PEC Working Group Overview

Eric L. Miller

Hawaii Natural Energy Institute

University of Hawaii at Manoa

10 June 2010

D.O.E Hydrogen Program Review

Arlington, VA

 # PD032

This presentation does not contain any proprietary or confidential information

OVERVIEW

The US DOE WORKING GROUP ON PHOTOELECTROCHEMICAL (PEC) HYDROGEN PRODUCTION

Roxanne Garland: Group Chair
U.S. Department of Energy

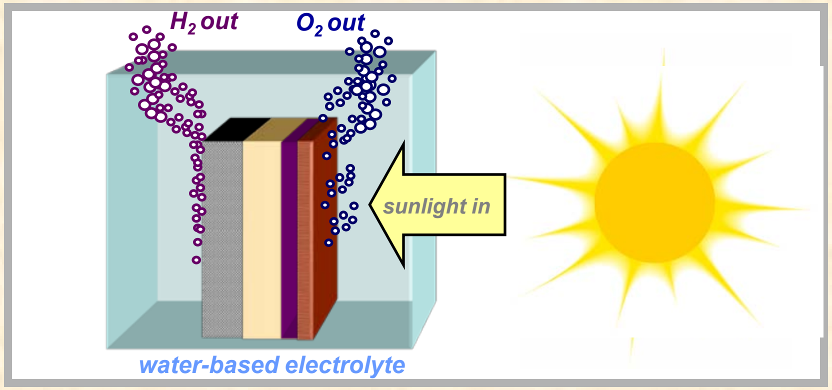
Eric Lars Miller: Group Co-Chair
University of Hawaii at Manoa

OVERVIEW

PEC WORKING GROUP

The US DOE Photoelectrochemical (PEC) Working Group brings together Academic, Industry and National Laboratory leaders in the research and development of practical PEC semiconductor systems to produce hydrogen via solar water-splitting

photoelectrode-based PEC solar-H_2 production:



MULTIPLE PEC PROJECTS ARE FUNDED BY DOE: BUDGETS AND TIME-LINES VARY

WORKING GROUP ADDRESSES ALL PEC BARRIERS, INCLUDING:

Y: Materials Efficiency, Z: Materials Durability,

AB: Bulk Materials Synthesis, AC: Device Configuration Designs

OVERVIEW

GROUP PARTNERS

Partner	oral	poster
Stanford University	PD033	
National Renewable Energy Laboratory	PD035	PD052
Lawrence Livermore National Laboratory	PD058	
University of California, Santa Barbara		PD034
University of Nevada Las Vegas		PD051
MVSystems Incorporated		PD053
University of Hawaii at Manoa		PD054, PD055
Midwest Optoelectronics		PD056
University of Arkansas, Little Rock		PD057
Physical Optics Corporation		PD061
Synkera Technologies		PD062
University of Nevada Reno		PD076

RELEVANCE

WORKING GROUP GOALS

The DOE PEC Working Group's primary objective is to develop practical solar hydrogen-production technology, using innovative semiconductor materials & devices R&D to foster the needed scientific breakthroughs for meeting DOE Hydrogen Program goals

DOE PEC "Multi-Year Program Plan" Targets

Table 3.1.10. Technical Targets: Photoelectrochemical Hydrogen Production[a]

Characteristics	Units	2003 Status	2006 Status	2013 Target	2018 Target[b]
Usable semiconductor bandgap[c]	eV	2.8	2.8	2.3	2.0
Chemical conversion process efficiency (EC)[d]	%	4	4	10	12
Plant solar-to-hydrogen efficiency (STH)[e]	%	not available	not available	8	10
Plant durability[f]	hr	not available	not available	1000	5000

RELEVANCE THE PEC PROMISE

IMPORTANT LABORATORY BENCHMARK

- ***NREL High-performance (>12%) GaInP/GaAs tandem PEC cell demonstrates technological feasibility of PEC H_2 production***
- ***Durability has been limited, and cost prohibitive with the III-V materials***

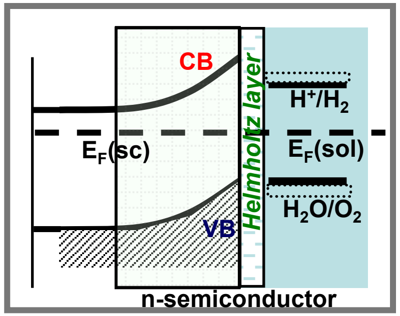
- ***PRACTICLE PEC*** **hydrogen production requires materials systems with high-efficiency , long-life & low cost.**
- **The development of new semiconductor materials meeting *ALL* criteria is the key objective of the PEC working group efforts**

RELEVANCE

THE PEC CHALLENGE

NO **Material System satisfies** ***ALL*** **requirements to practically split H_2O:**
Many have potential... ***Thus the PROMISE & CHALLENGE of PEC***

- **ABSORBER MATERIAL**
  - *Sunlight conversion depends on bulk optical bandgap*
  - *Nature of optical transitions ('direct' vs. 'indirect') is important*
  - *Good bulk transport properties key to harnessing photo-carriers*
- **INTERFACE DESIGN**
  - *Band-edge alignment important to reaction energetics*
  - *Surface bandgap plays an important role at interface*
  - *Interface kinetics critical in harnessing photo-carriers*



- **INTEGRATED DEVICE DEVELOPMENT**
  - *Multi-junction configurations important for maximum solar utilization*
  - *Auxiliary components and proper integration key to efficiency*
- **HYDROGEN PRODUCTION SYSTEM DEVELOPMENT**
  - *Balance of plant considerations could limit practicality*
- **COST OF LARGE-SCALE FABRICATION**

PEC WORKING GROUP APPROACH

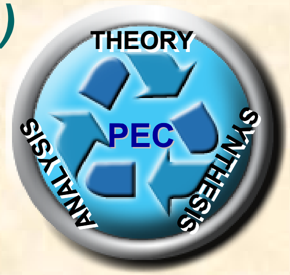
Collaborative efforts integrating state-of-the-art theoretical, synthesis and analytical techniques to identify and develop the most promising materials classes to meet the PEC challenges in efficiency, stability and cost.

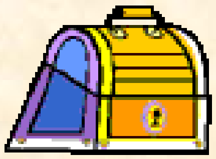
PEC R&D "Tool Chest"

- **THEORY: Materials & Interface Modeling**
  - *Theoretical Calculations of Semiconductor Band Structures*
- **SYNTHESIS: Materials Discovery / Development**
  - *Physical and Chemical Vapor Deposition*
  - *Combinatorial & Manufacture-Scale Synthesis Techniques*
- **ANALYSIS: Materials & Device Characterization**
  - *Physical/Solid-State Electronic/Optoelectronic Properties*
  - *Solid-Solid & Solid-Liquid Interface Characteristics*
  - *Photoelectrochemical Behavior Analysis*
  - *Techno-Economics Systems Analysis*

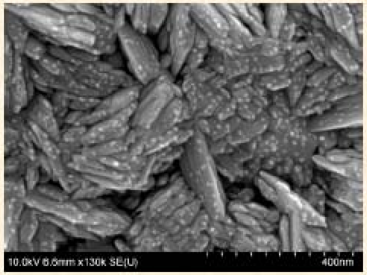
PEC WORKING GROUP APPROACH

- **The PEC tool-chest used to develop promising materials systems for meeting DOE targets using the following strategies:**
  - *Further development of the "standard" PEC semiconductor thin-films and nano-structures for higher efficiencies (e.g., iron-oxide and tungsten trioxide)*
  - *Development of efficient PV semiconductor thin-films and nano-structures for effective use in PEC (e.g., copper chalcopyrites and amorphous silicon compounds)*
  - *Development of new processes and technologies to reduce the cost and enhance the stability of high-performance (e.g., III-V nitrides)*
  - *Discovery and development of "new" materials classes based on advanced theories, and on the accumulated knowledge-base from PEC research efforts (e.g., MoS_2 nanoparticles)*





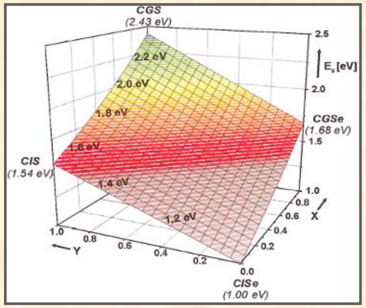
PEC WORKING GROUP PROGRESS



- **Tungsten-Oxide-Based Materials**
  - ***Nicolas Gaillard (UH-HNEI)***

  a stable & inexpensive material used in PEC applications, but band-gap and interface need to be optimized

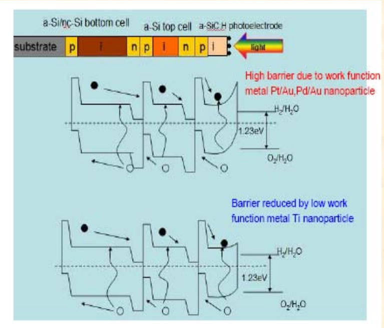
PD054



- **Copper-Chalcopyrite-Based Materials**
  - ***Jess Kaneshiro (UH-HNEI)***

  efficient photon absorbers with alloy-tunable bandgap, but interface needs to be improved and stabilized

PD055

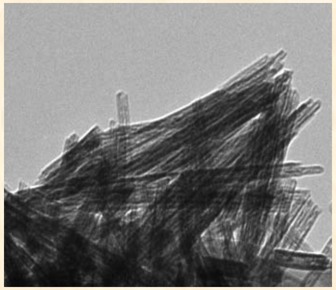


- **Amorphous-Silicon-Based Materials**
  - ***Arun Madan (MVS)***

  inexpensive & well-understood thin-films of variable bandgap, but interface needs to be improved and stabilized

PD053

PEC WORKING GROUP PROGRESS



- **Iron-Oxide-Based Materials**
  - *Eric McFarland (UCSB)*

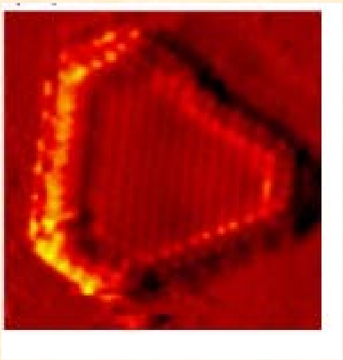
PD034

inexpensive material of near-ideal bandgap, but extremely poor optoelectronic properties have limited its application

- **Crystalline III-V-Based Materials**
  - *Todd Deutsch (NREL)*

PD035

high quality semiconductor class with tunable bandgap, but interface stability and cost remain the primary barriers

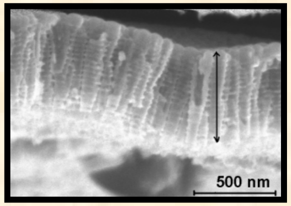


PD033

- **MoS_2 / WS_2-Based Materials**
  - *Tom Jaramillo (Stanford)*

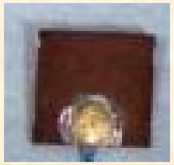
good hydrogen catalysts, but quantum-confinement is needed to raise bandgap for PEC, and stable configurations are needed

PEC WORKING GROUP PROGRESS



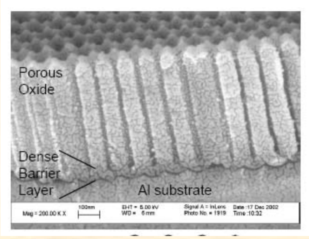
- **PEC Interfaces**
  - *Malay Mazumder (UALR)*

PD057

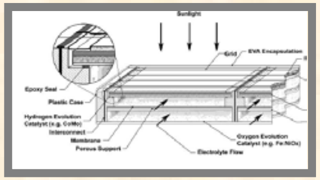
- **CdS & ZnTe Materials**
  - *Juan Hodelin (Physical Optics)*

PD061



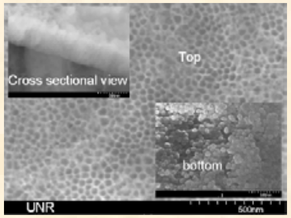
- **Nanotemplates for PEC**
  - *Rikard Wind (Synkera)*

PD062



- **Integrated PV/Electrolysis**
  - *William Ingler (MWOE)*

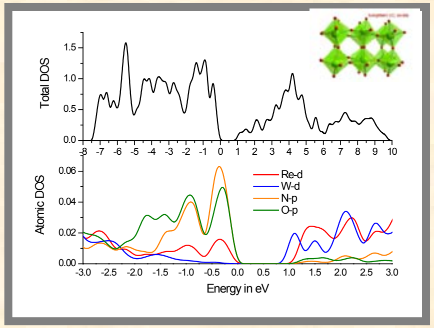
PD056

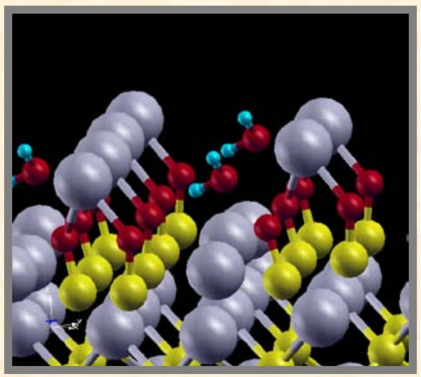


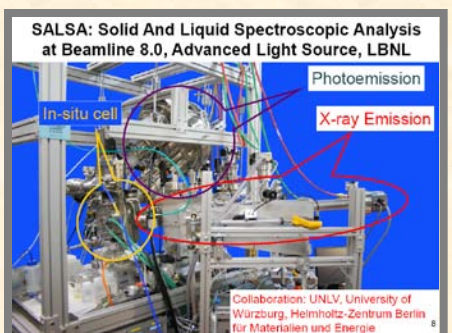
- **TaON Nanotubes**
  - *Mano Misra (UNR)*

PD076

PEC WORKING GROUP PROGRESS







- ***Advances in PEC Materials Theory***
  - *–Yanfa Yan (NREL)* **PD052**
  - *–Tadashi Ogitsu (LLNL)* **PD058**

sophisticated theoretical models of band states and bandgap, including effects of surface, interfaces and grain-boundaries, are vital to breakthroughs in PEC materials

- ***PEC Characterizations Advances*** **PD051**
  - *–Clemens Heske (UNLV)*

state-of-the-art techniques in materials & surface characterizations, in-situ and ex-situ, are providing keys to understanding the complex PEC interface

PEC PROGRESS HIGHLIGHTS

- **Significant Progress in Establishing PEC Testing Standards**
  - *First revision drafts of 16 protocol documents completed*
  - *Summary paper published in Journal of Materials Science*
  - *Website set up to facilitate international review/revision process*
- **Advances in Characterization "Tool Chest"**
  - *UV/Soft X-ray/electron spectroscopic tools for evaluating optoelectronic and chemical properties of PEC materials' surfaces, near-surfaces and bulk fully operational*
  - *SALSA "Solid And Liquid Spectroscopic Analysis" characterization facility installed at LBNL for the in-situ evaluation of PEC semiconductor/electrolyte interfaces*
- **Advances in PEC Materials Theory "Tool Chest"**
  - *First principle models of the PEC interface constructed based on III-V semiconductors exploring effects of O, H and OH termination*
  - *Important correlations between surface morphology and H_2O interactions found*
  - *Theoretical band structures of new PEC materials classes investigated*
- **Progress Toward DOE PEC Materials & Device Targets**
  - *Successful demonstration of bandgap tailoring in photoactive MoS_2 nanoparticles*
  - *Identification of crystalline semiconductor device configurations based on current III-V materials with >15% STH conversion efficiency*
  - *Identification of thin-film device configurations based on current chalcopyrite and silicon compound materials with >5% STH conversion efficiency*

PEC STANDARDIZED TESTING

KEY PROGRESS IN ESTABLISHING STANDARDS:

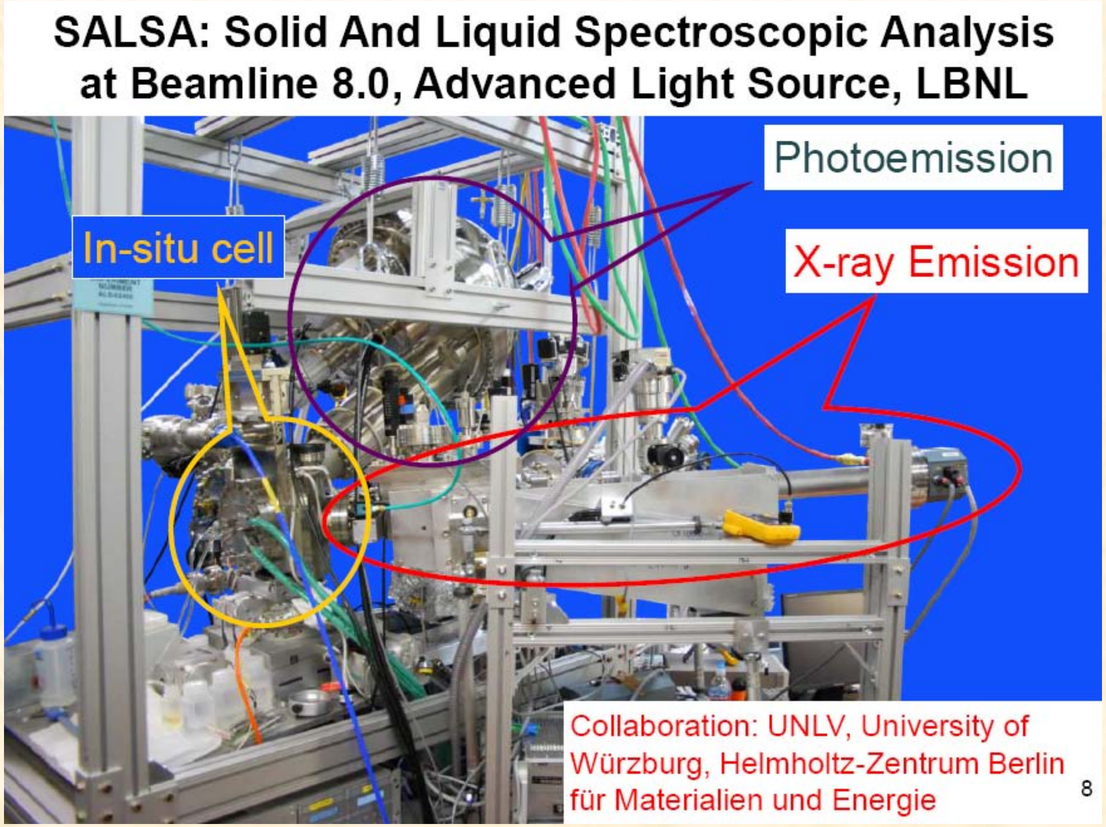
H. Dinh (NREL) Task Leader

- **Completed writing & reviewing of 16 standard PEC protocols**
  - *A successful telecom/webcasting collaboration among a diverse group of universities and National Labs, including NREL, DOE, Stanford University, University of Hawaii, University of Santa Barbara, University of Louisville, University of Tokyo and Australian Nuclear Science and Technology Organization*
- **Published Review Paper in Journal of Material Science**
  - *Introduce PEC efficiency definitions and include excerpts of the PEC test protocols*
- **Deployed PEC Standards Review Website (active since 10/2009)**
  - *www2.eere.energy.gov/hydrogenandfuelcells/pec_standards_review.html#standards*
  - *Received 14 international requests to-date (include Australia, Denmark, Japan, Malaysia, UK, and US) to comment on the documents*
  - *Received 14 feedbacks on the various documents. All documents ranked well (5-10 out of 10)*

PEC CHARACTERIZATION TOOLS

ADDING NEW IN-SITU PEC INTERFACE TOOLS:

C. Heske (UNLV) Task Leader

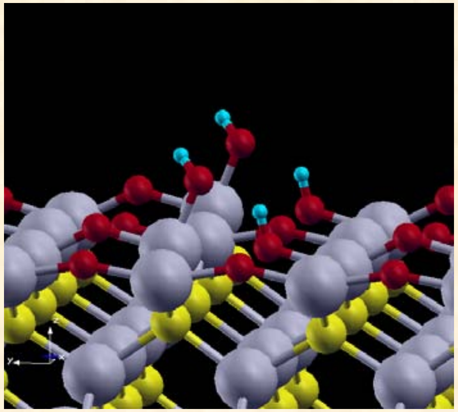


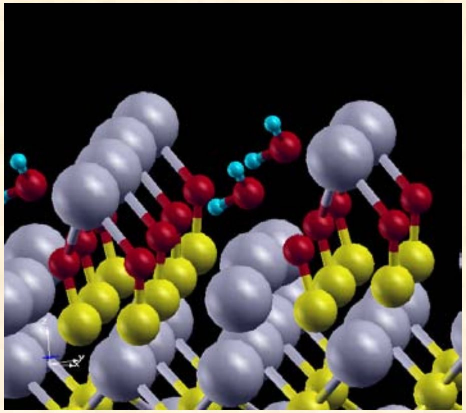
first deployment of in-situ tools to evaluate solid/liquid PEC interfaces in operational settings

PEC THEORETICAL TOOLS

ADVANCED MODELS OF THE PEC INTERFACE:

T. Ogitsu, B. Wood (LLNL) Task Leaders

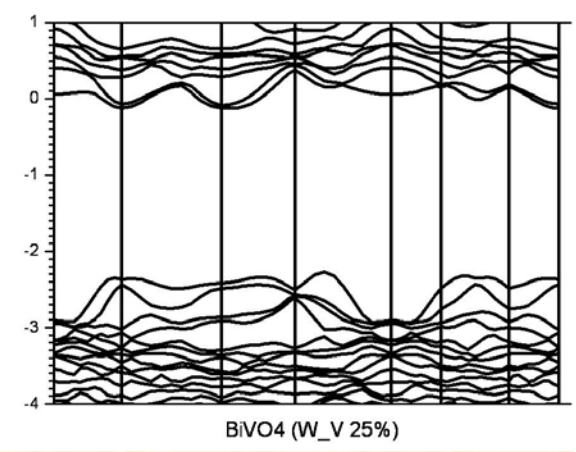


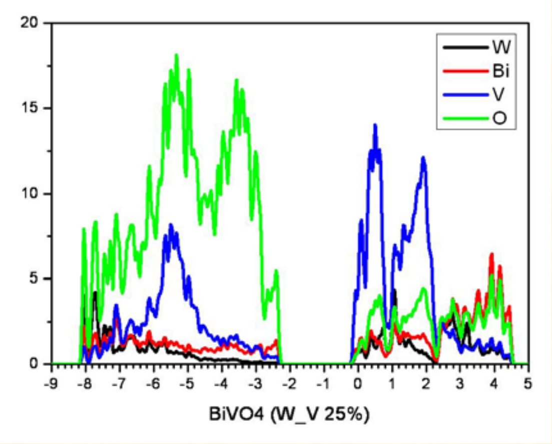


semiconductor / electrolyte PEC junctions based on III-V model systems

BAND STRUCTURES OF 'NEW' PEC MATERIALS:

Y. Yan (NREL) Task Leader



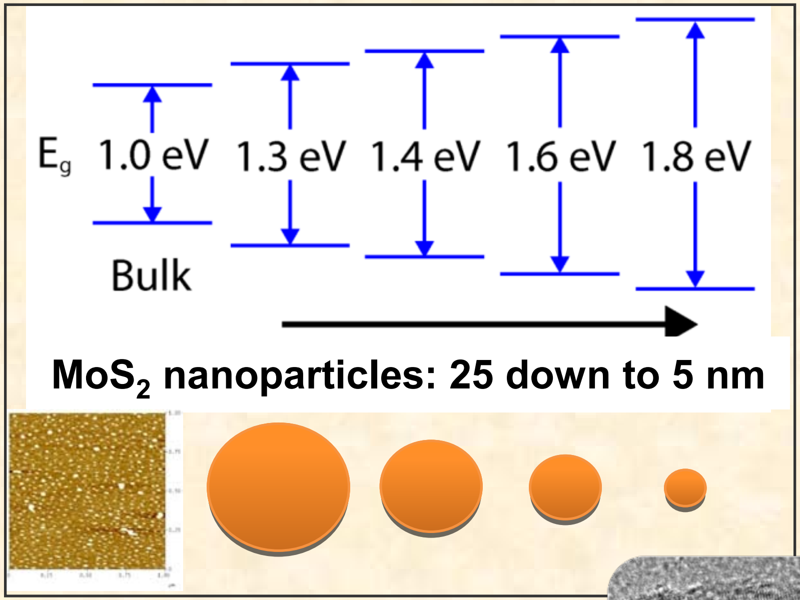


doping of BiVO4,W on V site – band structure and DOS

PEC MATERIALS ADVANCES

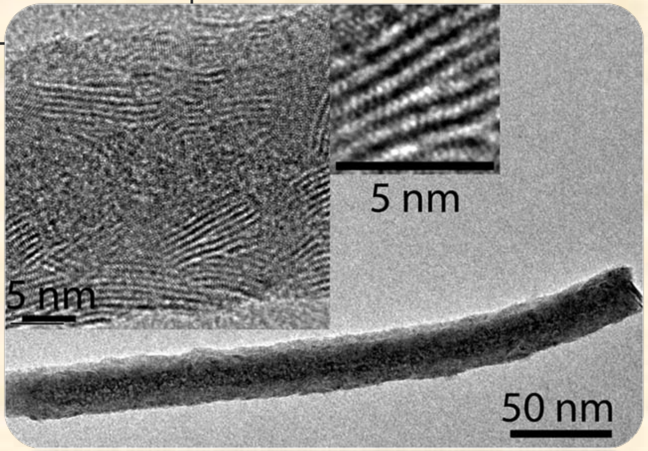
MoS_2 NANOPARTICLE PHOTOCATALYSTS

T. Jaramillo (Stanford) Task Leader



MoS_2 nanoparticles

first demonstration of bandgap engineering in nanoparticle photocatalysts; initial exploration of photocatalyst nanorods (in collaboration with U. Louisville)

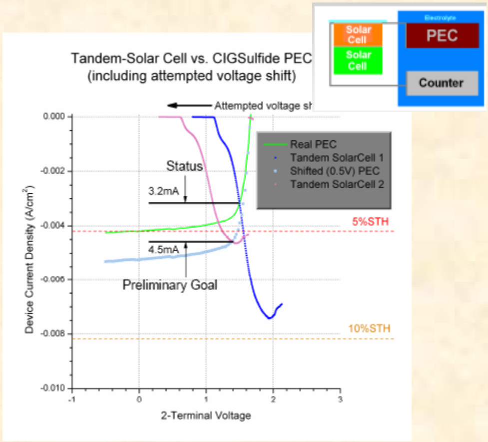


MoS_2 nanowires

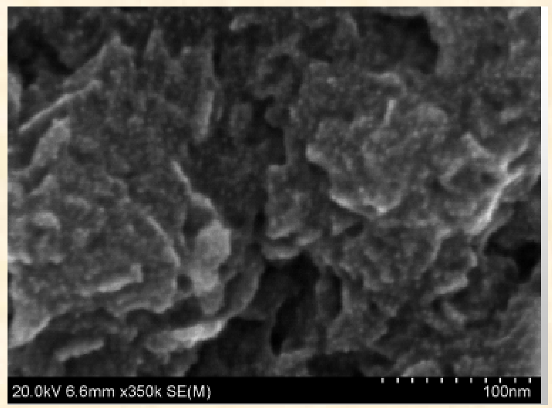
PEC DEVICE ADVANCES

MULTIJUNCTION ROUTES USING CGS_e ABSORBERS

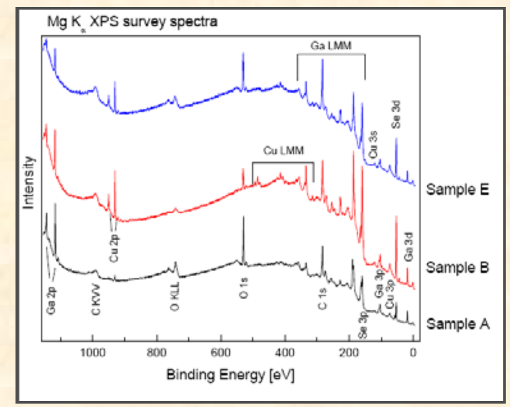
J. Kaneshiro (UH), A. Madan (MVSystems)



CGS based PEC multijunctions



catalytically enhanced CGS



CGS surface changes under PEC

- **Identified complex MJ device >5% STH using current CGS_e materials**
- **PEC interfacial barrier identified as limit to >10%STH tandem**
- **New theory and characterization tools to be used to address the interface barrier problem for meeting DOE performance targets**

COLLABORATION IS KEY

- The DOE PEC Working Group encourages collaboration among its members, and with the broader research community (e.g., through the international IEA-HIA Annex-26 activities)
- Dozens of collaborative Working Group publications this past year, including journal articles, book chapters and reviewed conferences papers
- Collaboration enables effective pooling of Working Group resources in theory, synthesis, characterization and analysis
- Growing collaboration based on common research synergies in materials and interface science is the key to success. Improved organizational tools are being developed to facilitate this success

WORKING GROUP FUTURE PLANS

- **Continued Development of the PEC Tool Chest:**
  - –Improved theoretical models
  - –Innovative synthesis improvements
  - –Advanced ex-situ and in-situ materials characterizations
  - –Continued Techno-Economics analyses
  - –Continued refinement of standard testing & screening protocols
- **Continued Development of PEC Focus Class Materials:**
  - –Ongoing implementation of “White Paper” approach
  - –Research progress benefiting from Tool Chest advances
- **Deployment of Screening Protocols to Focus R&D:**
  - –Up-selection of promising new materials classes
  - –Down-selection of materials with unyielding barriers

PEC WORKING GROUP SUMMARY

The PROMISE: PEC is Promising for Solar-to-Hydrogen Conversion

- *Efficient STH conversion possible at low temperature operations*
- *Successful laboratory demos: >12% STH in high-cost, low durability systems, 3-4% in low-cost, high durability systems*

The CHALLENGE: Breakthroughs are Needed for Practical PEC

- *Material systems meeting ALL required criteria are starting to appear*

US DOE PEC Working Group is Facing the Challenge, Collaboratively

- *Building a Tool Chest of the most advanced scientific techniques*
- *Applying Tool Chest in the R&D of the most promising materials classes*
- *Building an ever-growing international network of bright young scientists to break the barriers!*

Acknowledgements

- **The U.S. Department of Energy**
- **The International Energy Agency, and**
- **ALL the Talented, Enthusiastic and Hard-Working PEC Working Group Members**

Mahalo Nui Loa