

Characterization of Materials for Photoelectrochemical Hydrogen Production (PEC)

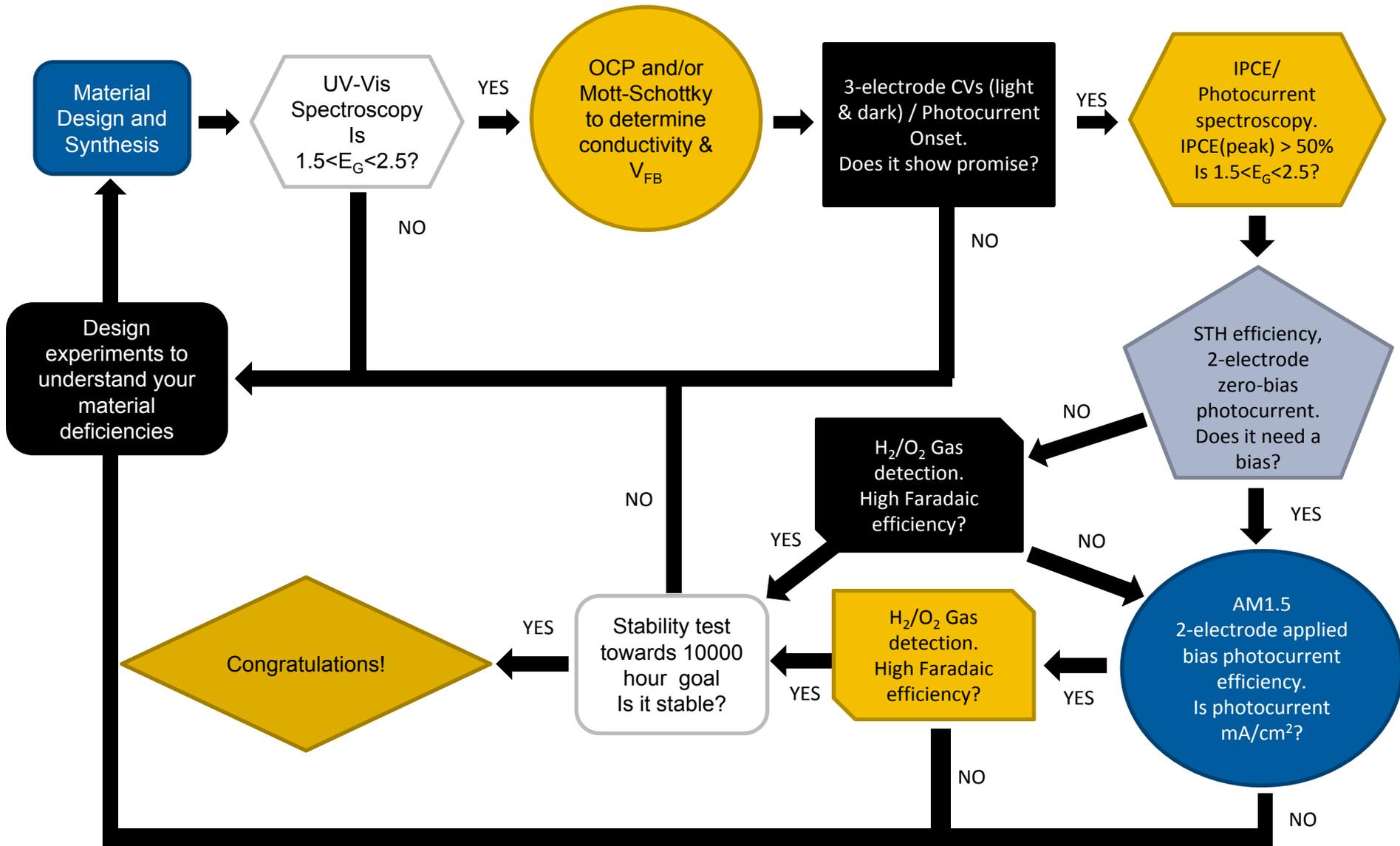
Clemens Heske

Department of Chemistry,
University of Nevada Las Vegas

May 20, 2009

Project ID #
pd_24_heske

PEC Working Group: Characterization Flow Chart



Standard PEC Characterization Working Group



**2009 Annual Merit
Review**

Huyen Dinh

May 20, 2009

International Collaboration

Zhebo Chen (SU), US
Todd Deutsch (NREL), US
Huyen Dinh (NREL), US
Kazunari Domen (U of Tokyo), Japan
Arnold Forman (UCSB), US
Nicolas Gaillard (HNEI), US
Roxanne Garland (DOE), US
Thomas Jaramillo (SU), US
Alan Kleiman (UCSB), US
Grant Mathieson (Ansto), Australia
Mahendra Sunkara (U of L), US
Kazuhiro Takanabe (U of Tokyo), Japan



Project Objective

Goals:

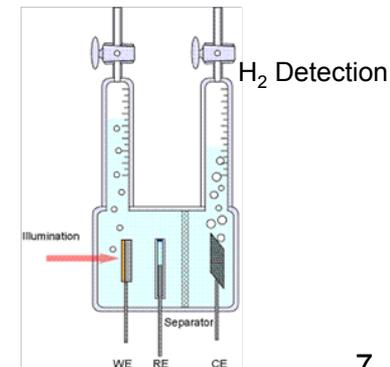
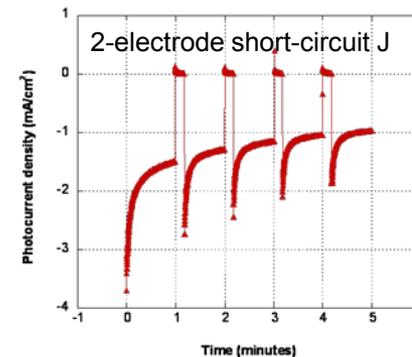
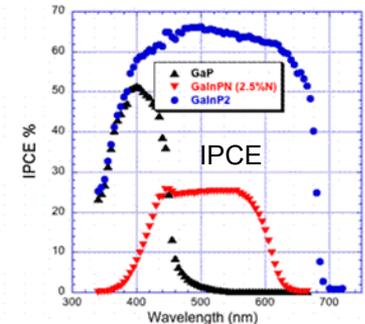
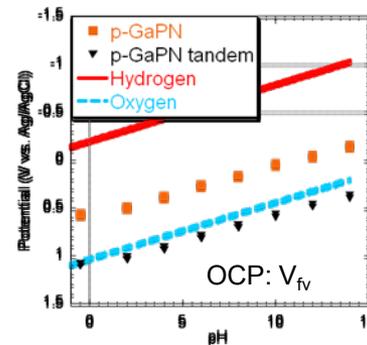
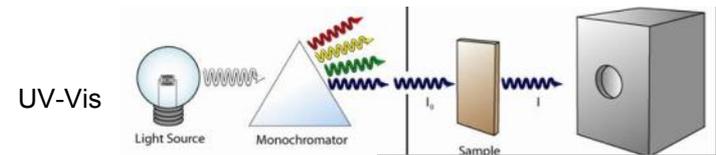
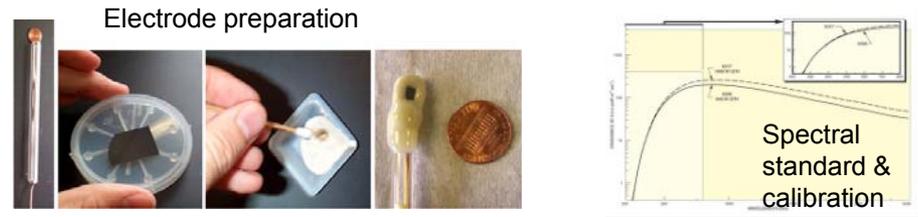
- Develop standardized testing and reporting protocols for PEC material/interfaces evaluation
- Publish the standardized PEC characterization techniques in a peer-reviewed journal to reach a maximum number of people

Purpose & Scope:

- Properly define the efficiencies (STH) that should be used for wide-scale reporting vs. efficiencies (IPCE) that are useful for scientific, diagnostic purposes only
- Describe proper PEC procedures for characterizing planar photoelectrode materials
- Focus on single band gap absorber material only
- Describe the techniques, the knowledge gained, the experimental set-up and procedure, the data analysis, and the potential pitfalls/limitations

Approach (Outline of a Paper)

- A. Introduction – purpose & scope
- B. Efficiency Definitions
- C. Experimental Set-up
 - 1. Electrode preparation
 - 2. Surface area determination
 - 3. 3- and 2-electrode cell set up & connections
 - 4. Catalyst surface treatments
 - 5. Spectral standard & calibration
- D. PEC characterization flow chart
- E. PEC techniques
 - 1. UV-Vis (Band gap)
 - 2. Illuminated Open Circuit Potential (OCP)
 - 3. Mott-Schottky (Vfb)
 - 4. Dark, Light, & Chopped I-V
 - 5. Photocurrent Onset
 - 6. Incident Photon Conversion Efficiency (IPCE)
 - 7. Photocurrent spectroscopy
 - 8. 2-electrode short current density and J-V (STH efficiency)
 - 9. Hydrogen Detection (STH efficiency)
 - 10. photocurrent density vs. time stability
- F. Glossary of terminology
- G. References

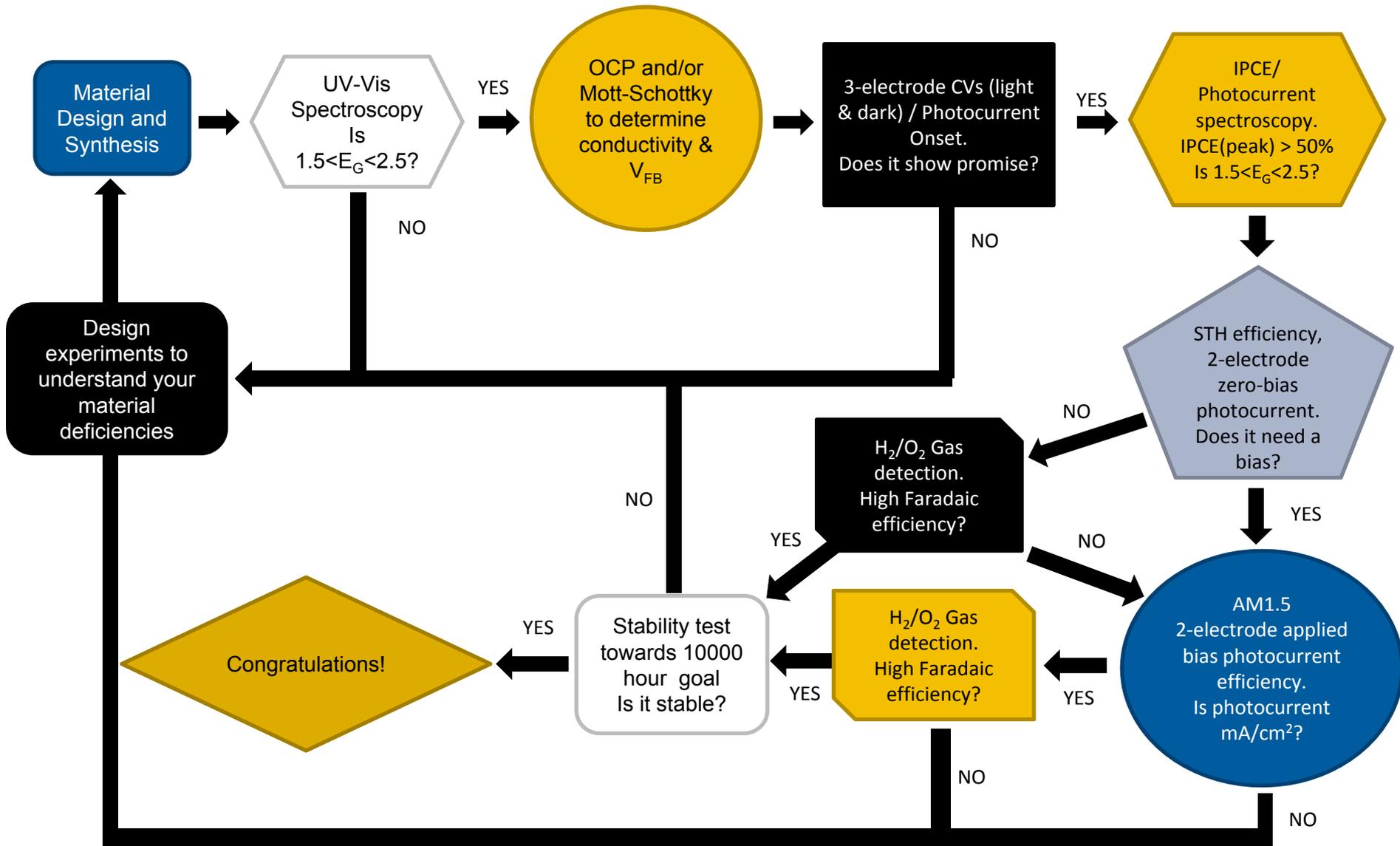


Working Group (WG) Approach & Accomplishments

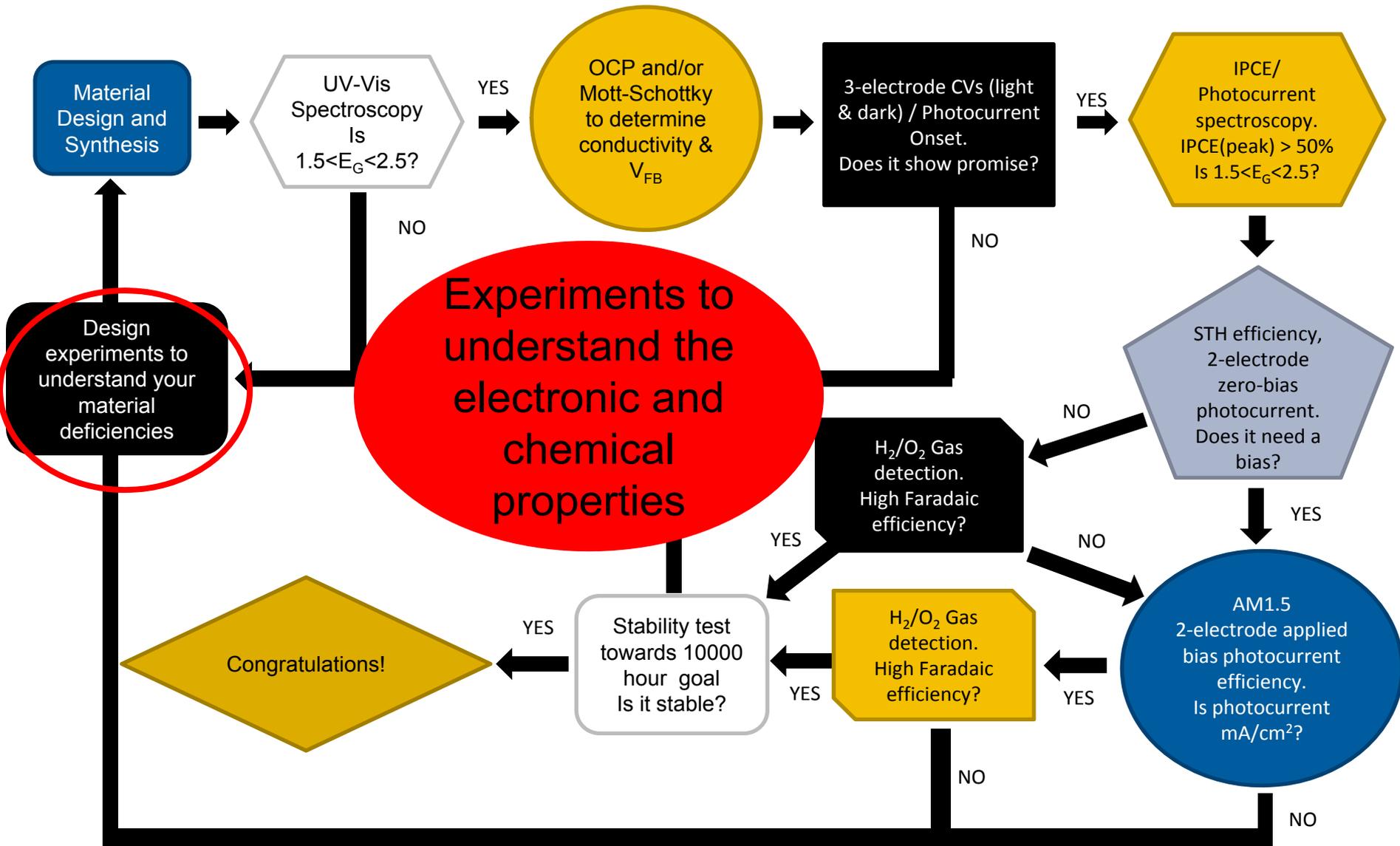
Date	Task	% Complete
05/2008	Formed Working Group & set purpose & scope	100%
07/2008	Completed first drafts of documents	100%
12/2008	Completed first review of documents via weekly telecoms/webcasts	100%
04/2009	Complete second review of documents	70%
05/2009	Complete external review of documents	10%
05/2009	Complete paper for submission to a peered review journal	80%

- Each member volunteered to write a number of documents
- WG reviews drafts weekly via webcast and telecom

PEC Working Group: Characterization Flow Chart



PEC Working Group: Characterization Flow Chart



Optimization of Interfaces and Surfaces for Photoelectrochemical Hydrogen Production (PEC)

Clemens Heske

Department of Chemistry,
University of Nevada Las Vegas

May 20, 2009

Project ID #
pd_24

Overview

Timeline

- Project start date: 5/6/08
- Project end date: 5/5/09
(no-cost extension requested)
- Percent complete: (50%)

Budget

- Total project funding
 - DOE share: \$200k
 - Contractor share: \$50k
- Funding received in FY08: \$200k
- Funding for FY09: unknown

Barriers

- Barriers addressed
 - H. System Efficiency
 - Lifetime
 - Indirectly: G. Capital Cost

Partners

- Interactions/collaborations: DOE EERE PEC WG (HNEI, NREL, MVSsystems, UCSB, Stanford), Berkeley Lab, HZB Berlin, U Würzburg
- Project lead: C. Heske

Activity Overview: Electronic and Chemical Properties of PEC candidate materials (Relevance)

To enhance understanding of PEC materials and interfaces and promote break-through discoveries:

- Utilize cutting-edge soft x-ray and electron spectroscopy characterization
- Develop and utilize novel characterization approaches (e.g., *in-situ*)
- **Address materials performance, materials lifetime, and capital costs through intense collaboration within the PEC WG**

Research Activity (*Approach*)

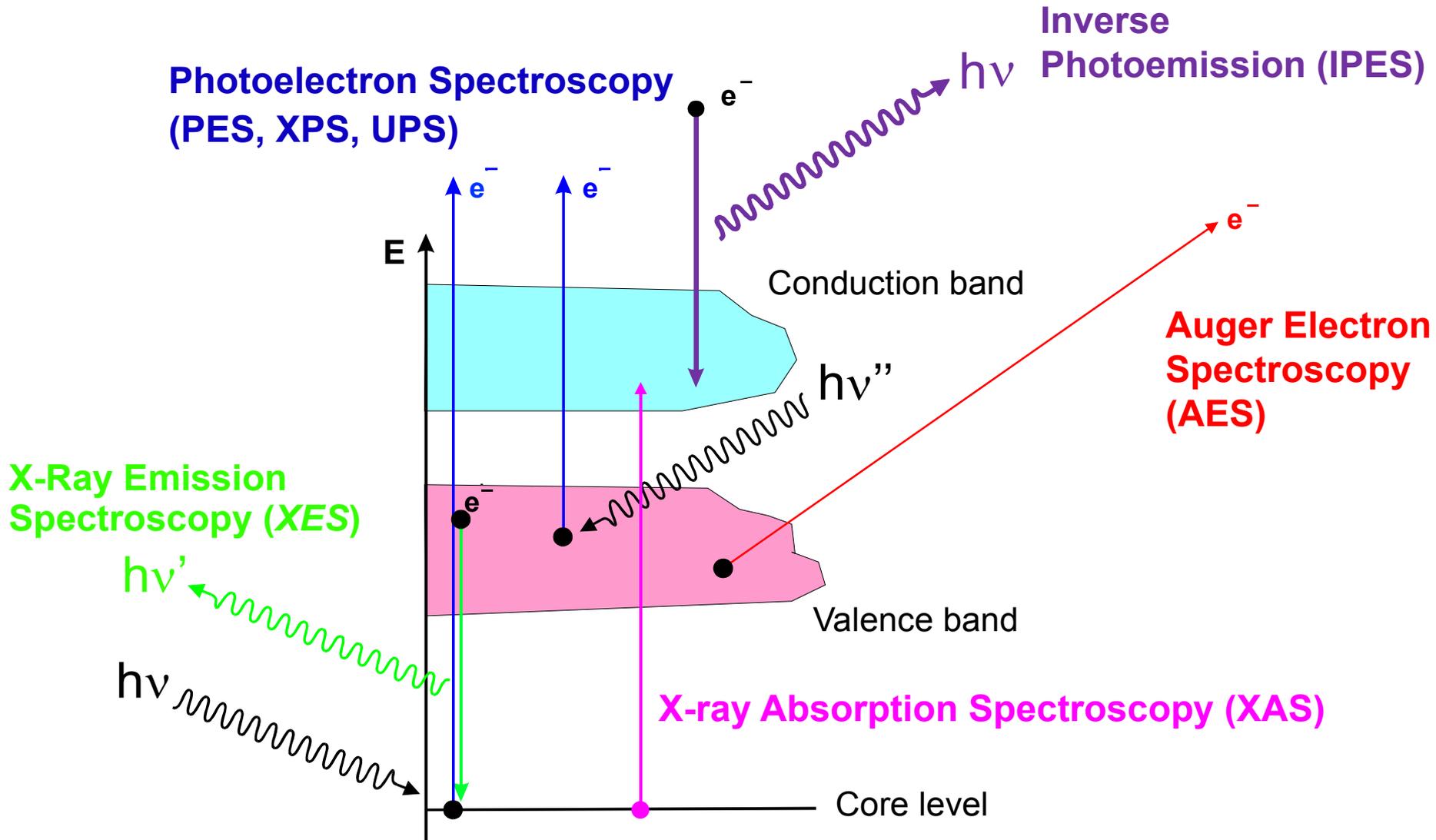
- **Overarching goal: compile experimental information about the electronic and chemical properties of the candidate materials produced within the PEC WG**
 - Determine *status-quo* (includes: find unexpected findings)
 - Propose modifications (composition, process, ...) to partners
 - Monitor impact of implemented modifications
- **Use a world-wide unique “tool chest” of experimental techniques**
- **Address all technical barriers related to electronic and chemical properties of the various candidate materials, in particular:**
 - Bulk and surface band gaps
 - Energy-level alignment
 - Chemical stability
 - Impact of alloying/doping

Collaborations

(Relevance, Approach, & Collaborations)

- **Collaborations are at the heart of our activities:**
 - Supply of samples
 - **Most important: supply of open questions, issues, challenges**
 - Interactive interpretation of results
 - Joint discussion of potential modifications
 - Involvement in implementing modifications
- **Great collaboration partners in the PEC WG:**
 - U Hawaii (E. Miller et al.): WO_3 , W(X)O(Y)_3 , Cu(In,Ga)(S,Se)_2
 - NREL (M. Al-Jassim et al., J. Turner et al.): Zn(O,N) , III-V-SC
 - UC Santa Barbara (E. McFarland et al.): Fe_2O_3 et al.
 - MVSsystems (A. Madan et al.): SiC
 - Stanford U (T. Jaramillo et al.): WS_2 , MoS_2
 - Open for more!

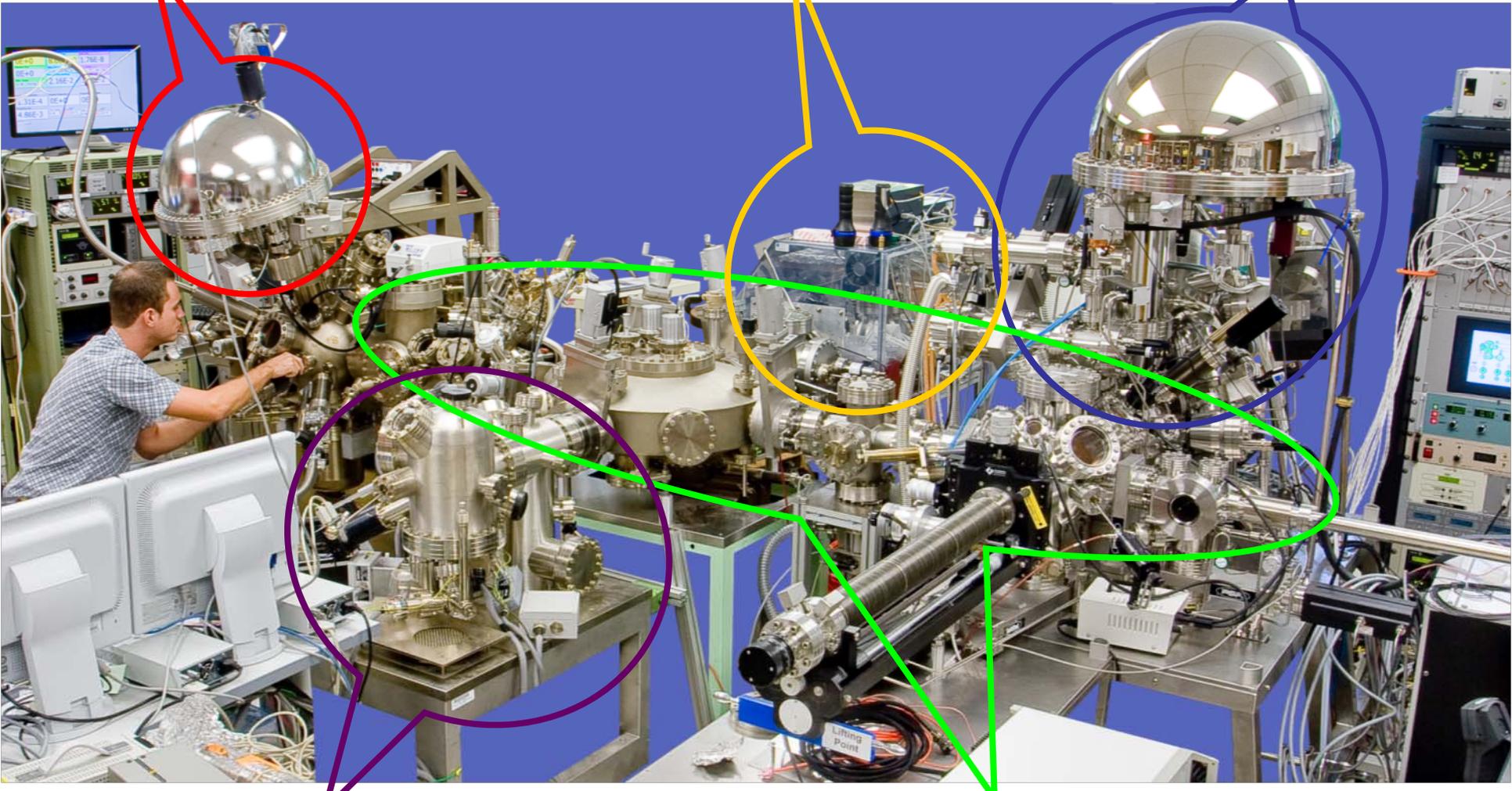
UV/Soft X-ray Spectroscopies (Approach)



High dynamic range
XPS, UPS, Auger, IPES

Glovebox

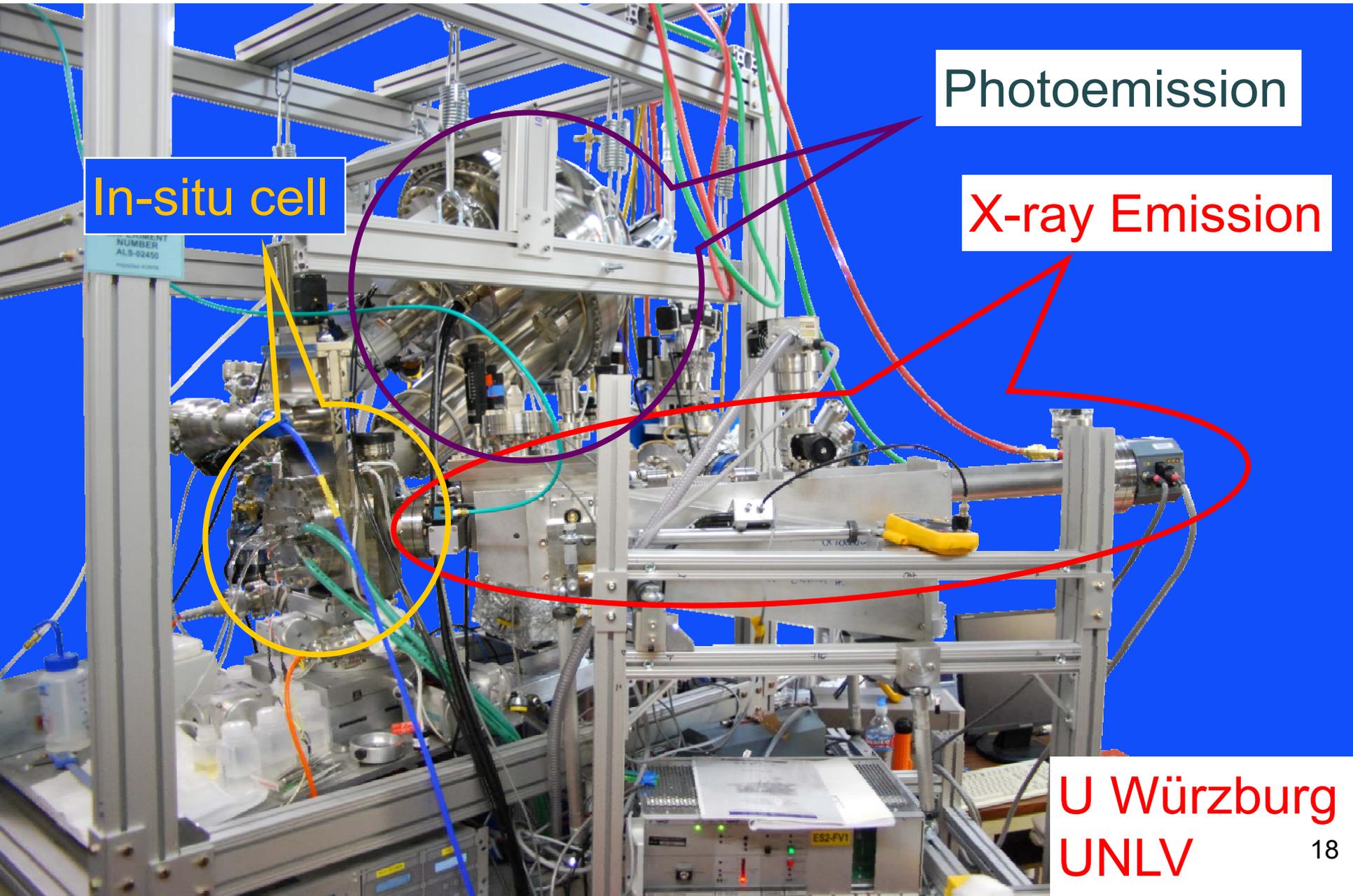
High resolution
XPS, UPS, Auger



Scanning Probe
Microscope

Sample preparation
and distribution

SALSA: Solid And Liquid Spectroscopic Analysis



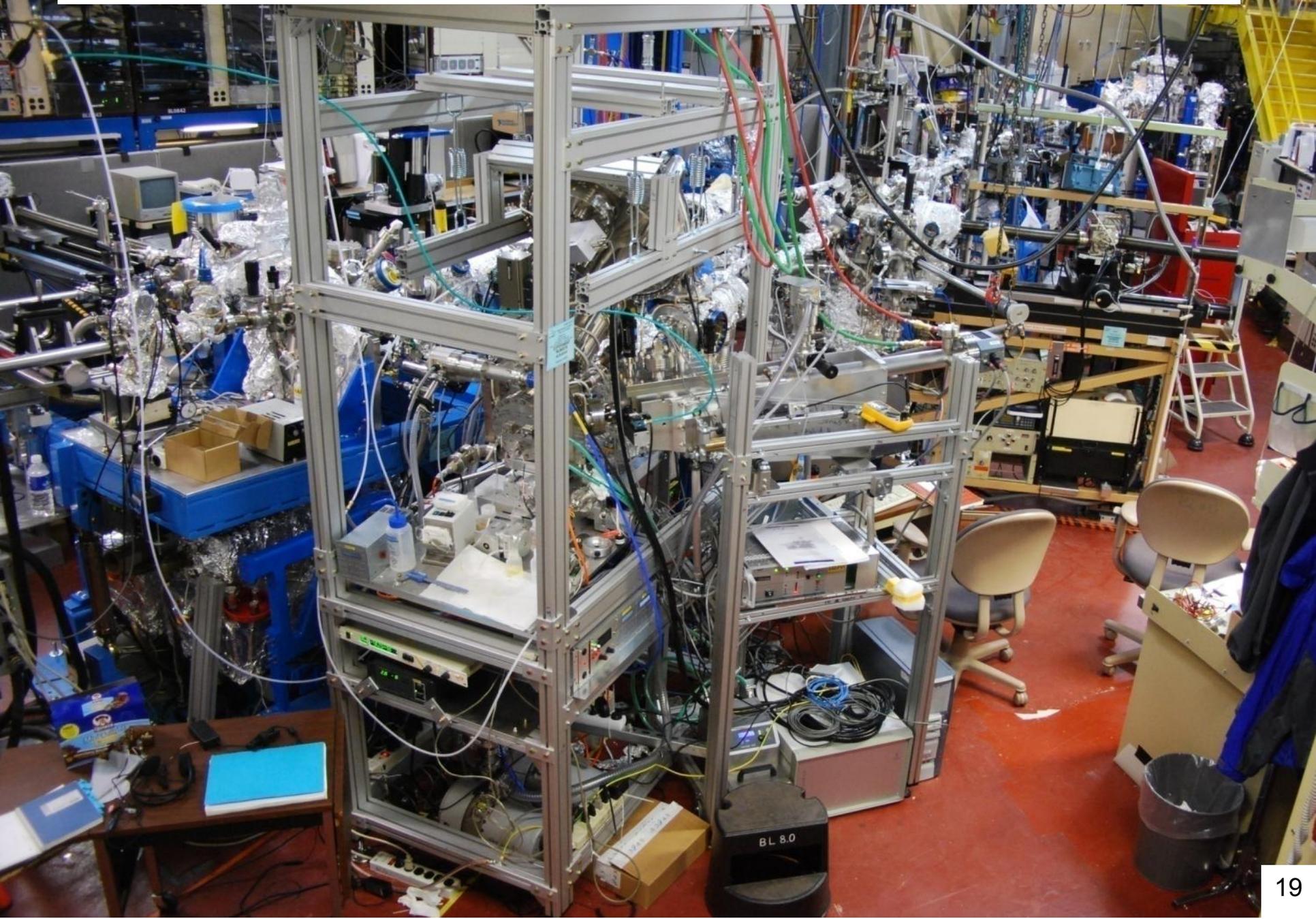
In-situ cell

Photoemission

X-ray Emission

U Würzburg
UNLV

Beamline 8.0 – Advanced Light Source – Lawrence Berkeley National Lab

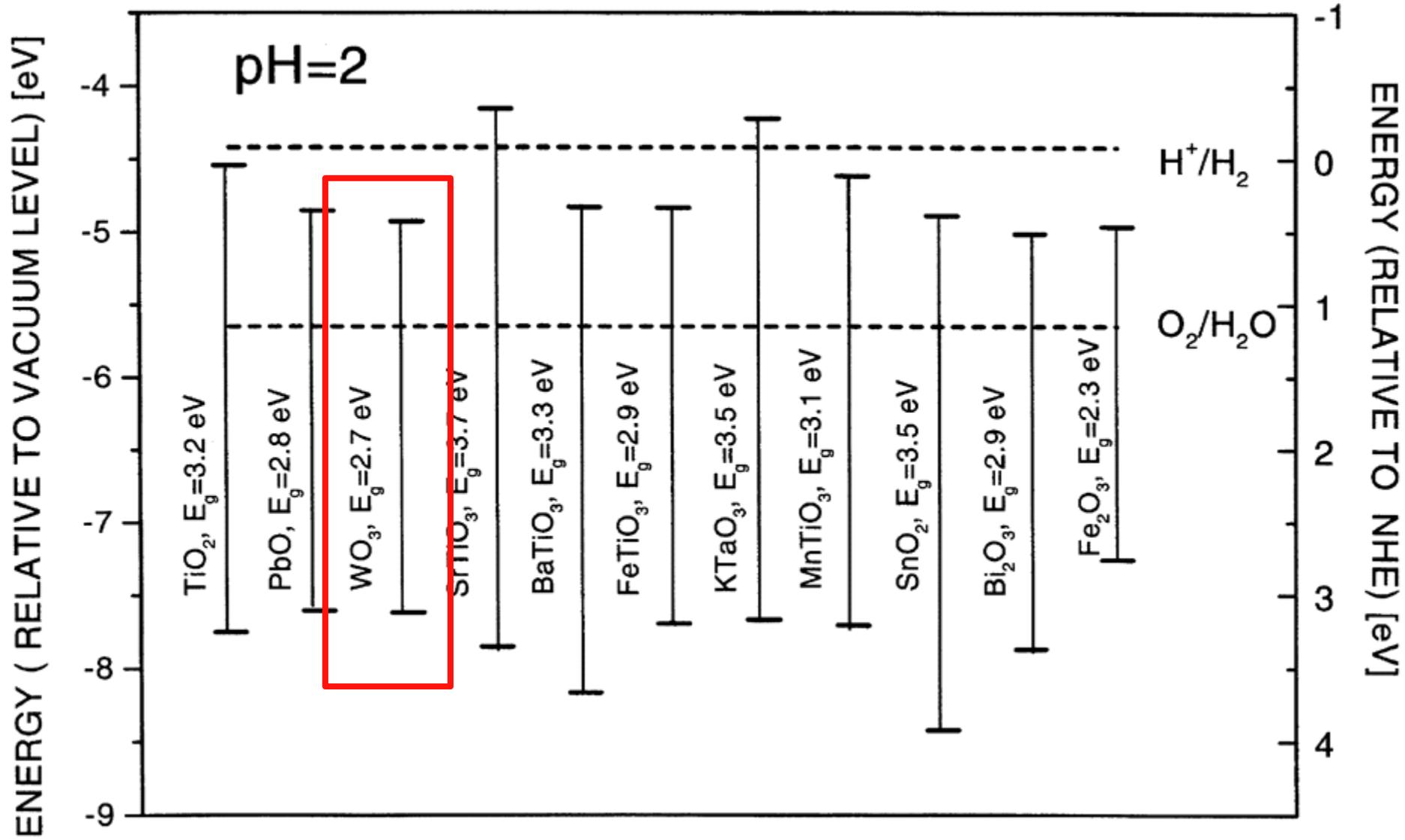


Requirements for PEC Materials

(Relevance)

- Chemical stability
- Optimized bulk band gap for photon absorption
- Optimized band edge positions at the relevant surfaces
- ... (e.g., cost!)

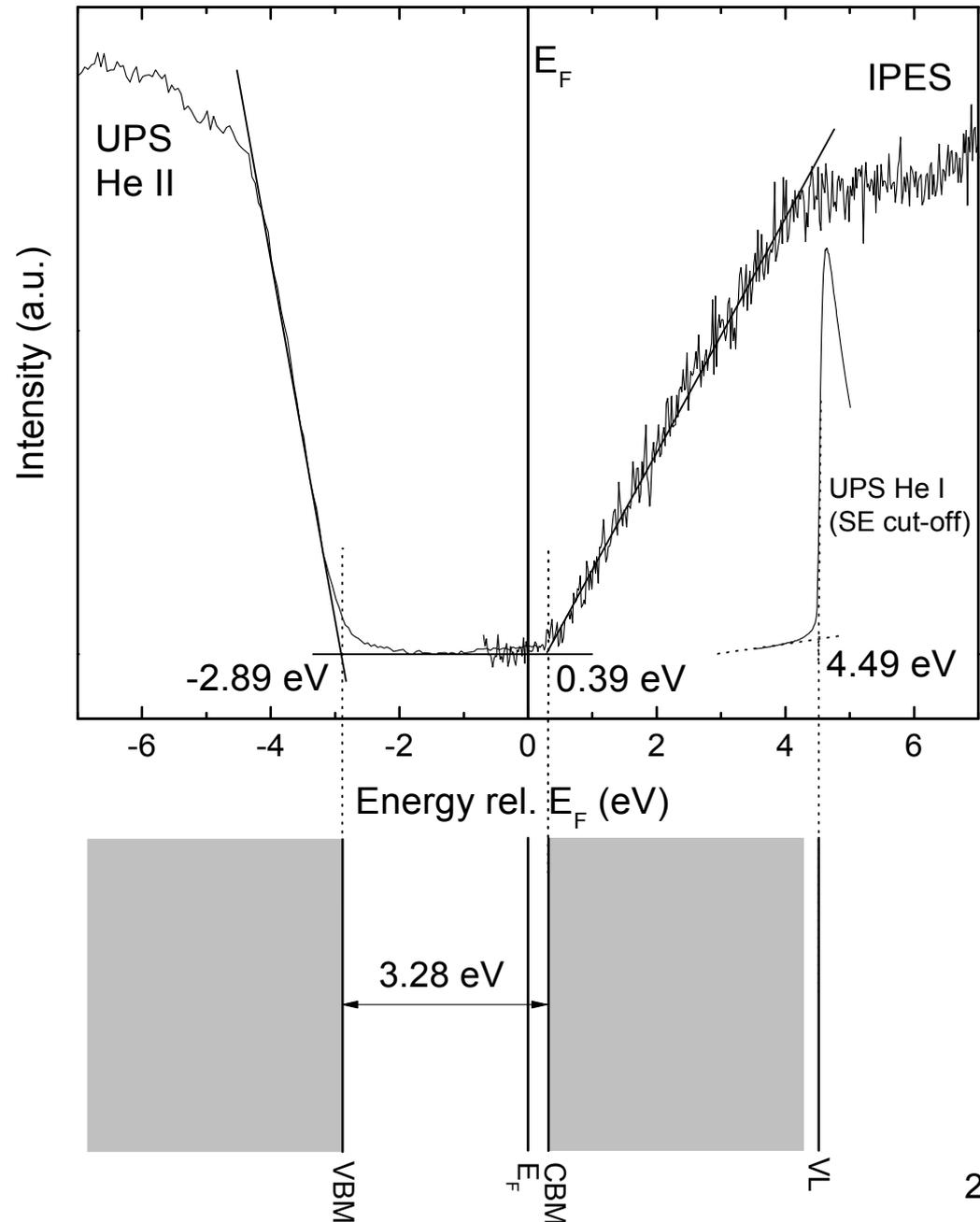
Band gap energy of different oxide materials and relative energies with respect to vacuum level and normal hydrogen electrode level in electrolyte of pH = 2



T. Bak et al., Int. J. of Hydrogen Energy **27**, 991 (2002).
 Original source: Chandra S. Photoelectrochemical solar cells. New York: Gordon and Breach, 1985. p. 98.

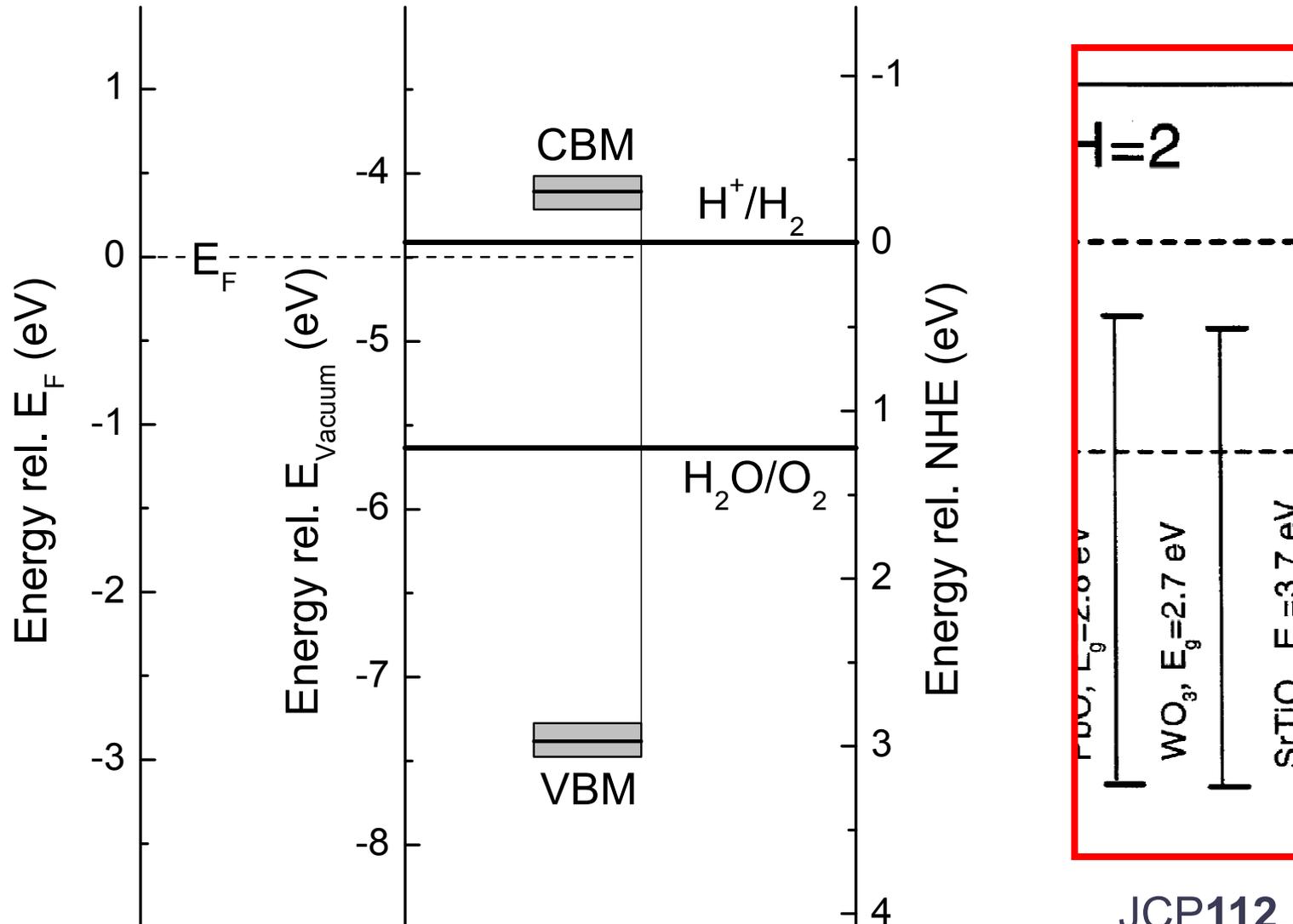
Electronic Surface Structure of WO_3 (Accomplishments)

- Combination of UPS and IPES:
 - Valence band maximum
 - Conduction band minimum
 - Work function/vacuum level
- Complete electronic surface structure!
- Experimentally!



First all-experimental depiction of the WO_3 surface electronic structure!

(Accomplishments, PD highlight 2008 Review)

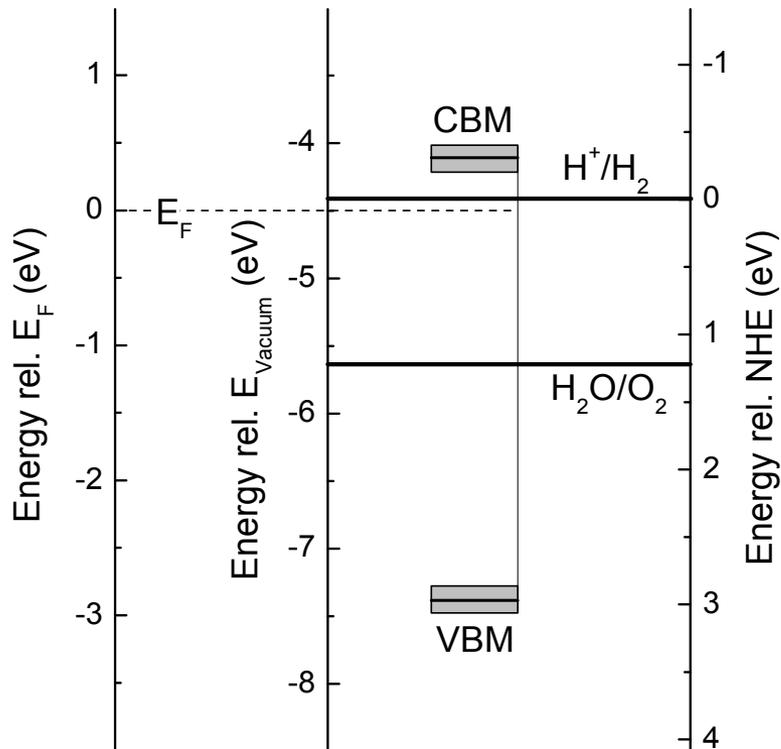


Comparison: WO_3 and $WO_3:MoO_3$

(Accomplishments)

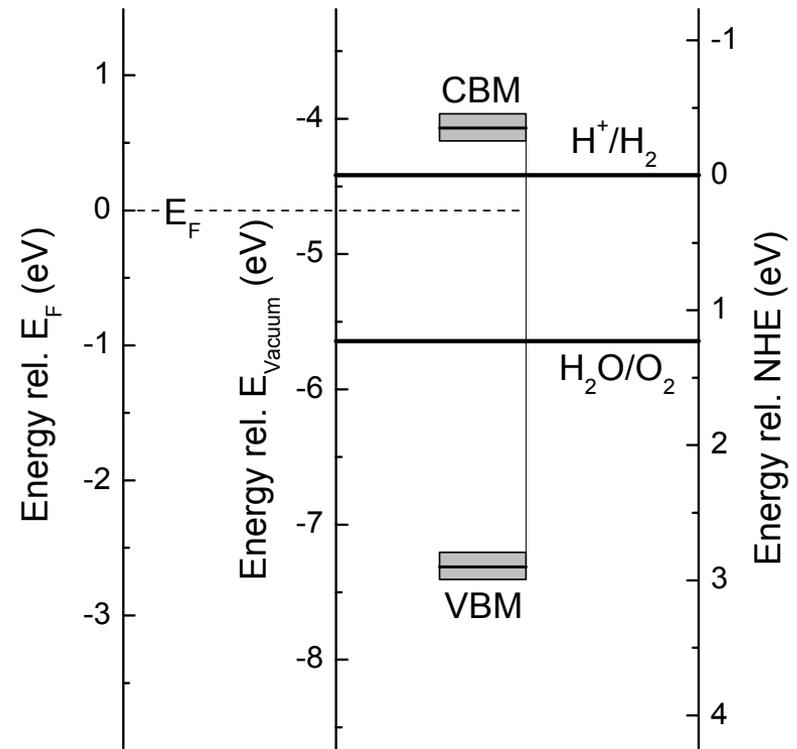
WO_3

J. Phys. Chem. C 112, 3078 (2008)



$WO_3:MoO_3$

(sample #341 B)



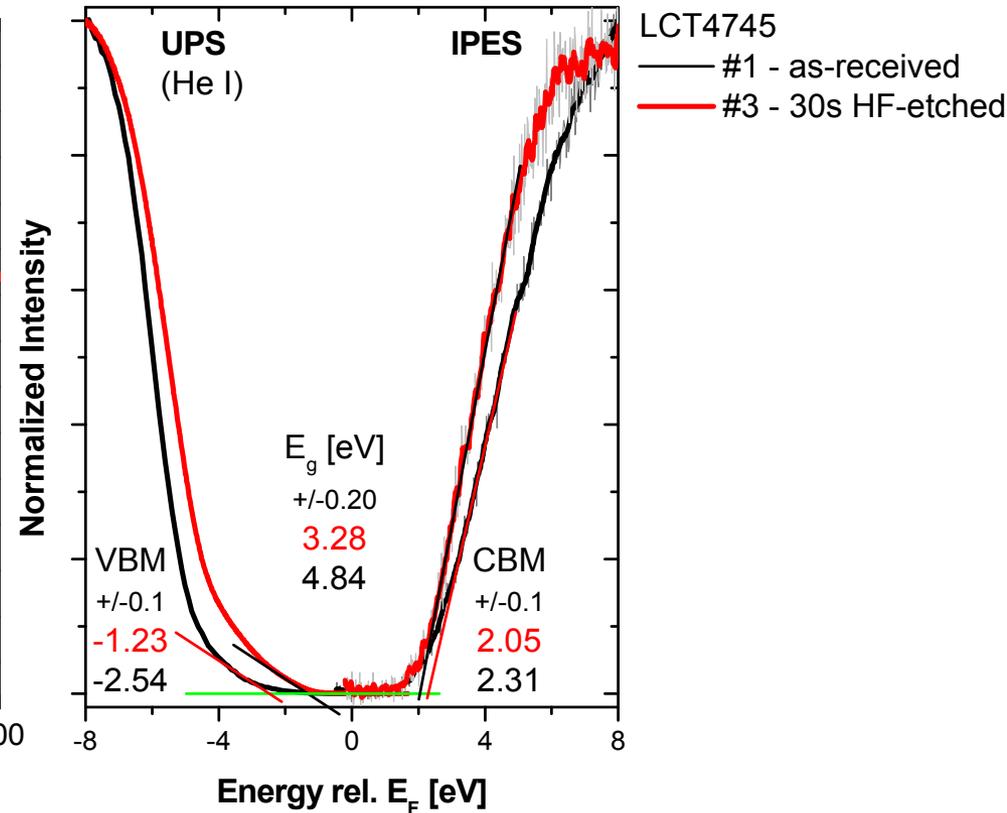
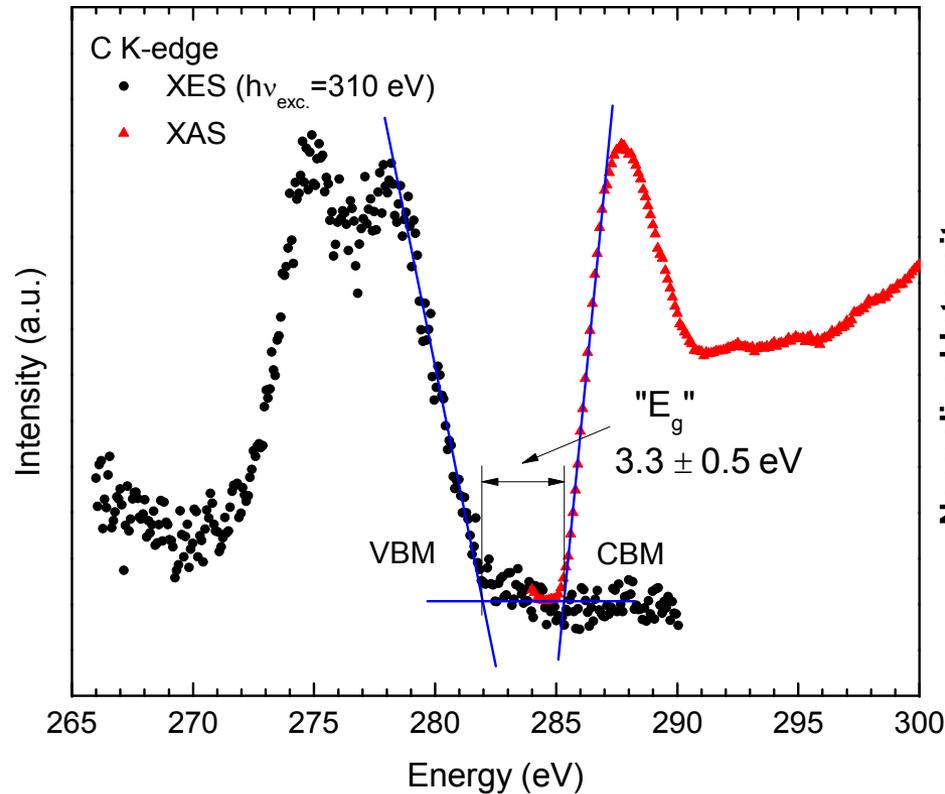
- Work function is (4.49 +/- 0.05) eV
- VBM = (-2.89 +/- 0.10) eV
- CBM = (0.39 +/- 0.10) eV
- Surface band gap = (3.28 +/- 0.15) eV

- Work function is (4.67 +/- 0.05) eV
- VBM = (-2.64 +/- 0.10) eV
- CBM = (0.60 +/- 0.10) eV
- Surface band gap = (3.24 +/- 0.15) eV

a-SiC band gaps: bulk band gap vs. surface band gap

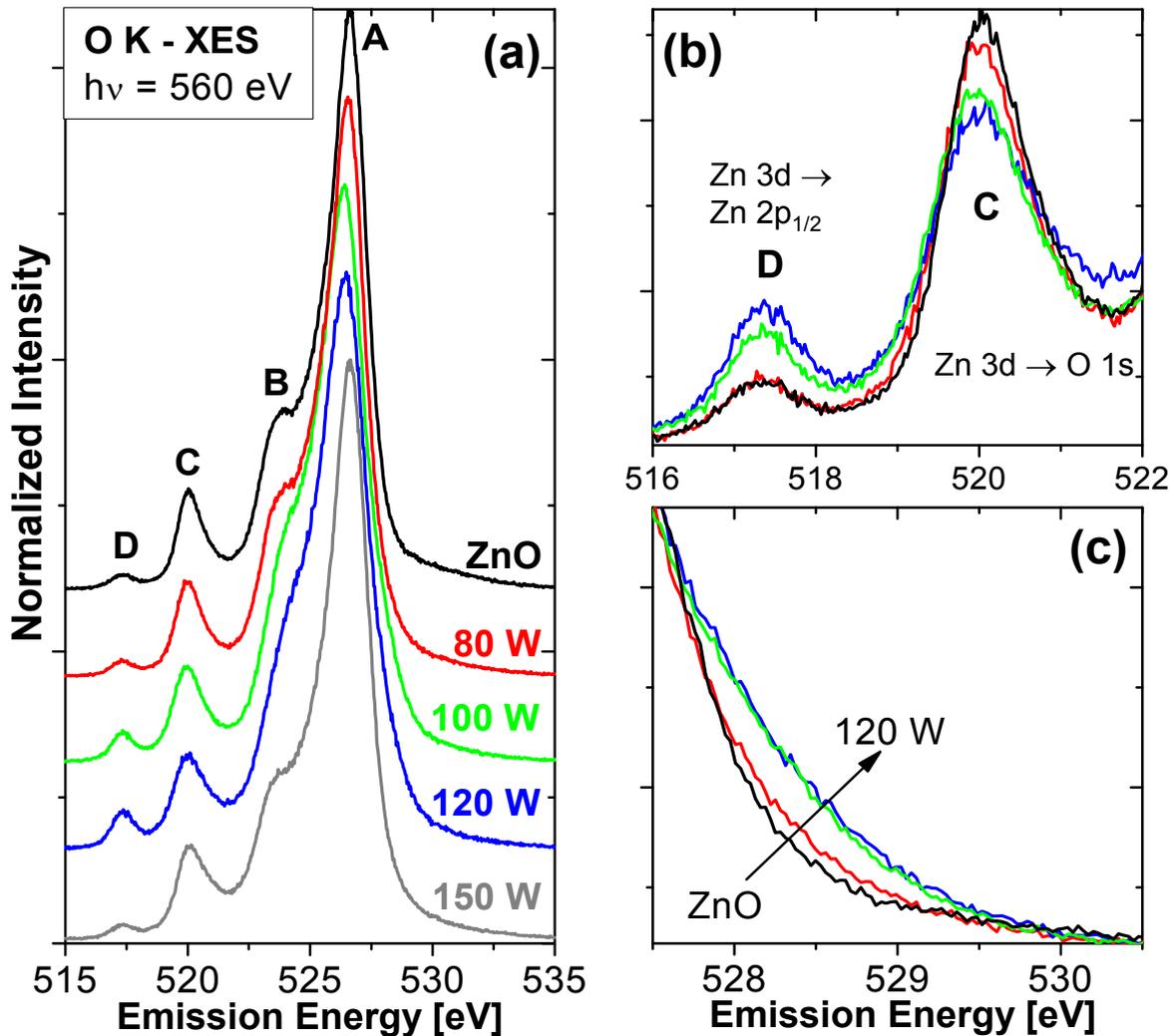
(Accomplishments)

a-SiC MVsystems #5701



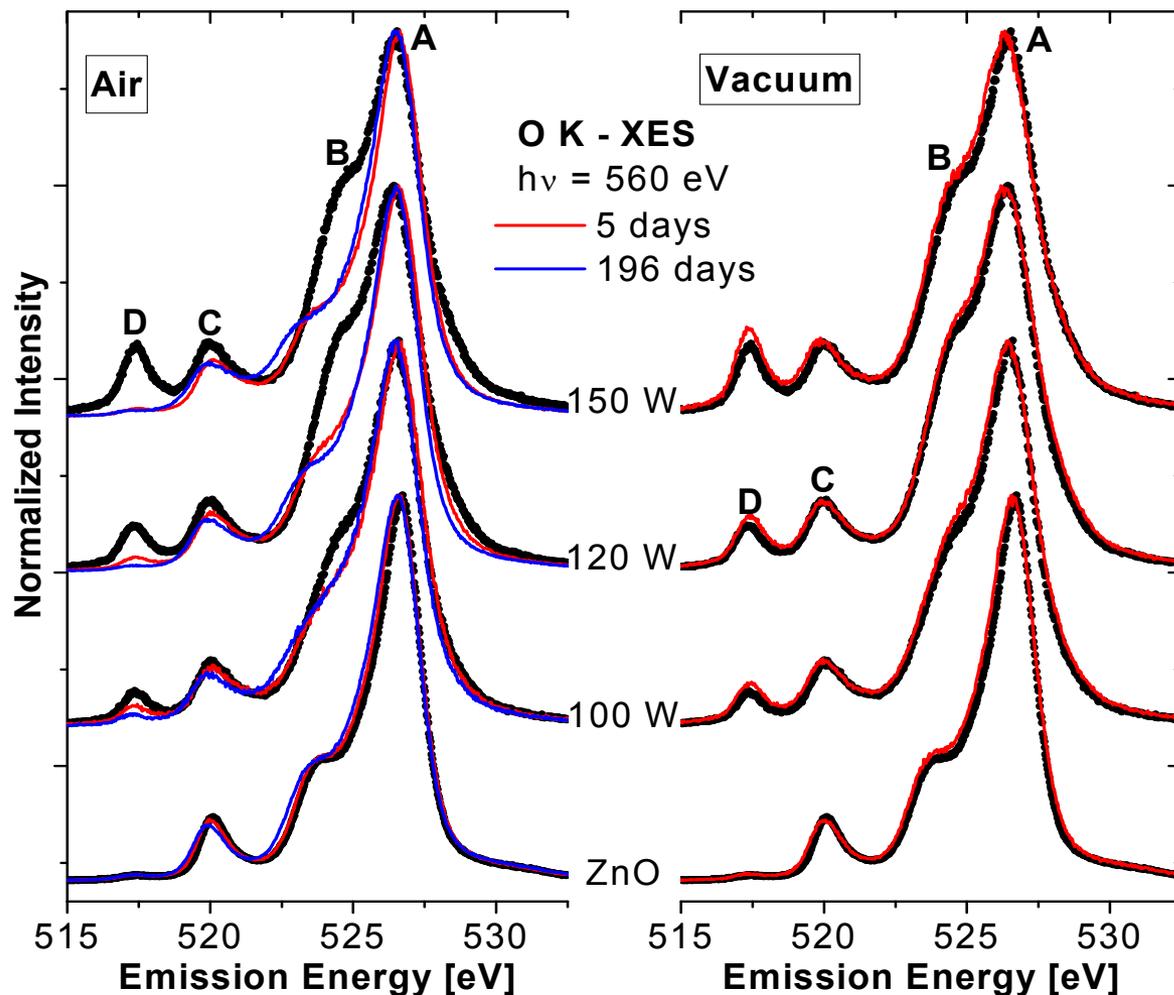
- XES/XAS (left) gives lower bound for the near-surface bulk band gap
- UPS/IPES (right) gives electronic band gap at the surface
- a-SiC band gaps are reported between 1.8 eV and 3.6 eV (Ref: T. Ma et al., J. Appl. Phys. **88**, 6408 (2000))
- Influence of oxygen and nitrogen: band gap widening

ZnO:N – Chemical Composition and Stability (Accomplishments)



- Formation of ZnO:N with increasing N content as a function of RF sputter power
- Variation of Zn₃N₂/ZnO ratio can be directly measured by XES
- 0 W – 120 W “well behaved”, 150 W not
- Valence band edge shifts due to N incorporation

ZnO:N – Chemical Composition and Stability (Accomplishments)



- ZnO:N is unstable under storage in air (reverting back to ZnO), but stable under storage in vacuum
- Effect is most pronounced for high N content

Research Plan & Basis for Continuation of Research

(Proposed Future Work)

- Broaden the collaborations with our existing partners (HNEI, NREL, MVSsystems, UCSB, Stanford) and bring new partners “on board”
- Determine electronic and chemical properties of various PEC candidate materials (see list on collaboration slide) and answer as many questions as possible
- Find unexpected things
- Continuously improve our currently available experimental approaches
- (Develop experimental in-situ capabilities)

The Group at UNLV

*now at Experimentelle Physik II,
University of Würzburg, Germany



Sharath
Sudarshanam

Yufeng
Zhang

Clemens Heske

Timo Hofmann

Marcus Bär**

Lothar
Weinhardt*

Roberto Félix**

Sujitra
Pookpanratana

Alessio
Luinetti

Ich Tran

Kyle George

Moni Blum(*)

Other key people: J.D. Denlinger, W. Yang, Advanced Light Source, Berkeley Lab
**now at Helmholtz-Zentrum Berlin, Germany

Summary *(Relevance)*

- Unprecedented insight into the electronic and chemical structure of PEC candidate materials from the DOE WG
- Portfolio of experimental techniques ranging from “standard” to “pushing the edge forward”
- Requires close collaboration with synthesis groups, theory groups, and other characterization groups
- Results will be as good as the questions we ask!
- Addresses materials performance, lifetime, and cost directly or indirectly through collaboration partners