# II.H.3 Characterization of Materials for Photoelectrochemical Hydrogen Production (PEC)

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Contract Numbers: DE-FG36-03GO13062 and DE-AC36-99GO10337

Project Start Date: October 1, 2004 Project End Date: May 5, 2010

# **Objectives**

Enhance the understanding of photoelectrochemical (PEC) materials and interfaces and promote break-through discoveries by:

- Utilizing and developing cutting-edge soft X-ray and electron spectroscopy characterization.
- Determining electronic and chemical structures of PEC candidate materials.
- Addressing materials performance, materials lifetime, and capital costs through close collaboration with partners from the PEC working group.

## **Technical Barriers**

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AD) Systems Design and Evaluation

## **Technical Targets**

• Collaborate closely with partners within the DOE PEC working group to determine the electronic and chemical structure of candidate materials for solar water splitting.

- Aid the collaboration partners in the development/ modification of novel candidate materials.
- Monitor deliberately introduced modifications of PEC candidate materials in view of the electronic and chemical structure.

## Accomplishments

- Experimental determination of complete electronic surface structure of WO<sub>3</sub> and the impact of Mo doping/alloying in order to understand improved performance by a WO<sub>3</sub>:Mo/WO<sub>3</sub> bilayer structure (with the University of Hawaii/Hawaii Natural Energy Institute, HNEI).
- Determination of the band gap of a-SiC and its change after oxygen/nitrogen exposure, hydrofluorhydric acid (HF) treatment, and/or annealing (with MVSystems).
- Investigation of the chemical composition and stability of ZnO, and particularly, the deliberate modification of the electronic structure through nitrogen incorporation (with the National Renewable Energy Laboratory, NREL).
- Comparison of PEC-tested and untested CuGaSe<sub>2</sub> samples (with the University of Hawaii/HNEI and NREL).
- Investigation of Fe<sub>2</sub>O<sub>3</sub> thin films (with University of California, Santa Barbara).

#### Introduction

This project is embedded into the Department of Energy's efforts to develop materials for PEC water splitting. If successful, PEC will provide an important route to convert the energy supplied by solar irradiation into a transportable fuel. In order to achieve this goal, suitable materials need to be developed that simultaneously fulfill several requirements, among them chemical stability and optimized electronic structure, both for absorption of the solar spectrum and for electrochemical water splitting at a solid/ electrolyte interface. This project experimentally derives the chemical and electronic structure information to (a) judge the suitability of a candidate material, (b) show pathways towards a deliberate optimization of a specific material, and (c) monitor whether deliberate modifications of the material indeed lead to the desired changes in electronic and chemical structure.

#### Approach

A unique "tool chest" of experimental techniques is utilized that allows to address all technical barriers related to electronic and chemical properties of various candidate materials. With these techniques it is possible to measure surface and bulk band gaps, the energy level alignment at interfaces, the chemical stability of the materials, and the impact of alloying and doping.

The tool chest includes photoelectron spectroscopy with X-ray and ultraviolet (UPS) excitation to determine the occupied electronic states (core levels and valence electrons) and inverse photoemission (IPES) to determine the unoccupied electronic states. These techniques, performed in the lab at UNLV, are surfacesensitive and allow a complete determination of the electronic and chemical surface structure. They are complemented by X-ray emission (XES) and X-ray absorption spectroscopy (XAS), performed at Beamline 8.0 of the Advanced Light Source, Lawrence Berkeley National Laboratory. XES and XAS also probe the occupied and unoccupied electronic states, but with a larger information depth. Furthermore, they also give insight into the chemical structure, again complementary to the electron-based techniques performed in the lab at UNLV.

#### Results

In collaboration with our partners, we have investigated numerous sample series on a variety of PEC candidate materials.

With the University of Hawaii/HNEI, we have determined the electronic level alignment of WO<sub>3</sub> thin film surfaces, as shown in Figure 1. Great care had to be taken to minimize radiation damage effects [1], and the data in Figure 1 represents such a "pristine" measurement series. From the shown UPS and IPES spectra, it is possible to derive a complete picture of the electronic structure at the sample surface, including the positions of valence band maximum and conduction band minimum, Fermi energy, and vacuum level/work function. Apart from establishing the benchmark picture of the electronic surface structure of WO<sub>3</sub>, one of the main goals was to elucidate the impact of Mo incorporation on the electronic surface properties. The results are shown in Figure 2, where the complete electronic surface structure of WO<sub>3</sub> (left) and WO<sub>3</sub>:Mo (right) is compared. Close inspection of the schematics reveals an upward shift of the vacuum level with respect to the Fermi energy, indicative of an increased work function for WO<sub>3</sub>:Mo. Consequently, the alignment of the band edges is shifted with respect to the redox potentials responsible for water splitting. Furthermore, the upward shift of the band edges suggests that a WO<sub>3</sub>:Mo/WO<sub>3</sub> bilayer structure, which has shown improved current collection with respect to both bulk materials (WO<sub>3</sub>:Mo and WO<sub>3</sub>) [2], might possess an



**FIGURE 1.** UPS and IPES spectra of a WO<sub>3</sub> surface, together with the secondary electron (SE) cut-off measured by UPS. The linear extrapolations of the edges give the positions of the valence band minimum (VBM), the conduction band minimum (CBM), and the vacuum level (VL), respectively, as schematically shown below the panel. Error bars are  $\pm 0.10$  eV for the VBM and CBM positions,  $\pm 0.14$  eV for the derived electronic surface band gap, and  $\pm 0.05$  eV for the VL (work function).

additional electrostatic field at the interface, enhancing the charge carrier separation upon solar irradiation.

With our partners in Hawaii and at NREL, we have investigated  $CuGaSe_2$  chalcopyrite thin film materials before and after PEC testing. For these studies, we have performed XES and XAS experiments to elucidate the chemical impact of PEC testing on these surfaces. Data analysis is currently in progress.

With our partners at MVSystems, we have conducted a variety of experiments to study the chemical surface structure and the associated electronic properties of a-SiC thin films. Figure 3 shows an example of this study. In the left panel, XES (black) and XAS (red) experiments are shown and analyzed to derive the electronic bulk band gap near the surface (note that the given value is a lower bound due to the potential presence of a core excitation in the XAS spectrum). The observed band gap of 3.3 eV is in good agreement with that found by our surfacesensitive techniques (after suitable surface cleaning). This is shown in the right panel of Figure 3, where UPS (left)



**FIGURE 2.** Positions of VBM and CBM of WO<sub>3</sub> and WO<sub>3</sub>:Mo relative to  $E_P E_{Vacuum'}$  and the normal hydrogen electrode (NHE). For comparison, the  $H_2O/O_2$  oxidation and the  $H^+/H_2$  reduction potentials are given. Grey bars for VBM and CBM indicate the error bars along the energy axis.



FIGURE 3. Valence and conduction band extrema of a-SiC, together with the derived band gap. Left: XAS (black) and XES (red) data to derive the band gap near surface (in the presence of a core hole). Right: UPS (left two curves) and IPES (right two curves) before (black) and after (red) HF treatment to derive the surface band gap.

and IPES (right) spectra are shown; spectra were taken before (black) and after (red) an HF etch treatment. Due to the high surface sensitivity of the UPS and IPES techniques, the surface band gap of the untreated sample is significantly enlarged (due to silicon oxide formation at the surface). In contrast, the HF etch treatment removes silicon oxide from the surface and consequently also reduces the band gap value found at the surface.

With our partners at University of California, Santa Barbara, we have begun to investigate  $Fe_2O_3$  thin films, in particular in view of the electronic band gap at the surface. Experiments are ongoing and will be described in the next report.



**FIGURE 4.** (a) 0 K XES spectra of a ZnO:N sample set with varying RF sputter power (i.e., varying N content). (b) Detailed presentation of features C and D (0-120 W), ascribed to Zn 3d states decaying into the 0 1s core hole and to Zn  $L_2$  emission (detected in 2<sup>nd</sup> order of the spectrometer and excited by higher orders of the beamline), respectively. (c) Detailed presentation of the valence band onset at high emission energies (0-120 W), indicating a shift of the valence band maximum.

With our partners at NREL, we have studied the suitability of ZnO and ZnO:N thin films for PEC applications [3]. As an example, Figure 4a shows O K XES spectra of a ZnO:N sample set with varying radio frequency sputter power (i.e., varying N content). The spectra contain a wealth of information about the chemical and electronic bulk structure near the surface. For example, the features C and D (Figure 4b) are ascribed to Zn 3d states decaying into the O 1s core hole and to Zn L<sub>2</sub> emission, respectively, and thus allow a quantitative analysis of the chemical environment of Zn, N, and O atoms. Furthermore, a detailed look at the valence band onset at high emission energies (Figure 4c), indicates a shift of the valence band maximum, while no significant shift in the XAS-derived conduction band minimum is found. This indicates that (a) the band gap is indeed reduced by the incorporation of N, and that (b) the main shift responsible for this reduction is found in the valence band (and not the conduction band). Further studies revealed that ZnO:N is stable when stored under vacuum conditions, but reverts back to ZnO when stored in air for longer periods of time.

### **Conclusions and Future Directions**

• Established excellent collaboration structures with a large number of partners within the DOE PEC working group.

- Evaluated a variety of PEC candidate materials in view of their electronic and chemical properties.
- Developed the spectroscopic "tool chest" to give comprehensive picture of the electronic and chemical structure.
- Continue the collaborations with our existing partners and bring new partners "on-board" (e.g., Stanford University, studying tungsten and/or molybdenum dichalcogenide nanoclusters).
- Continue to determine electronic and chemical properties of various PEC candidate materials manufactured by the collaboration partners within the DOE PEC working group.
- Continue to improve the currently available experimental approaches.

#### FY 2009 Publications/Presentations

**1.** "Electronic surface level positions of  $WO_3$  thin films for photoelectrochemical hydrogen production", L. Weinhardt, M. Blum, M. Bär, C. Heske, B. Cole, B. Marsen, and E.L. Miller, J. Phys. Chem. C **112**, 3078-3082 (2008).

**2.** "Impact of air-exposure on the chemical and electronic structure of  $ZnO:Zn_3N_2$  thin films", M. Bär, K.-S. Ahn, Y. Yan, L. Weinhardt, O. Fuchs, M. Blum, K. George, S. Pookpanratana, W. Yang, J.D. Denlinger, M. Al-Jassim, and C. Heske, Appl. Phys. Lett. **94**, 012110 (2009).

**3.** C. Heske, "Using XES and RIXS to investigate the chemical and electronic structure of materials for energy conversion", RIXS 08 Workshop, Uppsala, Sweden, June 13–14, 2008 (invited).

**4.** C. Heske, "How soft x-ray spectroscopy can help the 'Hydrogen Economy' (hopefully)", Seminar Experimentelle Physik II, University of Würzburg, Germany, July 8, 2008 (invited).

**5.** "Spectroscopic characterization of thin films used in energy conversion devices", M. Bär, 2008 American Chemical Society Western Regional Meeting, Las Vegas, Sept. 24–27, 2008 (Invited Oral).

**6.** C. Heske, "So, when will there finally be a breakthrough for these solar thingies?", Western Regional Meeting of the American Chemical Society, Education Program Keynote Address, Las Vegas, September 27, 2008 (invited).

**7.** C. Heske, "How soft x-ray spectroscopy can shed light on the electronic and chemical properties of interfaces," PIRE-ECCI (Partnership for International Research and Education) Seminar, Electron Chemistry and Catalysis at Interfaces, Department of Chemistry and Biochemistry, University of California, Santa Barbara, November 5, 2008 (invited).

8. "Impact of air-exposure on the chemical and electronic structure of ZnO:Zn<sub>3</sub>N<sub>2</sub> thin films", M. Bär, L. Weinhardt, S. Pookpanratana, K. George, Y. Zhang, C. Heske, K.-S. Ahn, S. Shet, Y. Yan, M. Al-Jassim, O. Fuchs, M. Blum, W. Yang, and J.D. Denlinger, 2009 Materials Research Society Spring Meeting, San Francisco, CA, April 13–17, 2009 (oral).

**9.** "Chemical and Electronic Structure of a-SiC Thin Films for Photoelectrochemical Water Splitting", Y. Zhang, K. George, M. Bär, C. Heske, J. Hu, F. Zhu, and A. Madan, 2009 Materials Research Society Spring Meeting, San Francisco, CA, April 13–17, 2009 (oral).

**10.** "Experiment-based electronic surface level positions of WO<sub>3</sub> thin films for photoelectrochemical hydrogen production", L. Weinhardt, M. Blum, M. Bär, C. Heske, B. Cole, B. Marsen, N. Gaillard, and E.L. Miller, 2009 Materials Research Society Spring Meeting, San Francisco, CA, April 13 −17, 2009 (oral).

## References

**1.** "Electronic surface level positions of  $WO_3$  thin films for photoelectrochemical hydrogen production", L. Weinhardt, M. Blum, M. Bär, C. Heske, B. Cole, B. Marsen, and E.L. Miller, J. Phys. Chem. C **112**, 3078-3082 (2008).

**2.** "Origin of improved current collection in WO<sub>3</sub>/WO<sub>3</sub>:Mo bilayer photoelectrodes", N. Gaillard, B. Cole, B. Marsen, J. Kaneshiro, E.L. Miller, L. Weinhardt, M. Bär, C. Heske, K.-S. Ahn, Y. Yan, and M.M. Al-Jassim, J. Mat. Research, in print.

**3.** "Impact of air-exposure on the chemical and electronic structure of  $ZnO:Zn_3N_2$  thin films", M. Bär, K.-S. Ahn, Y. Yan, L. Weinhardt, O. Fuchs, M. Blum, K. George, S. Pookpanratana, W. Yang, J.D. Denlinger, M. Al-Jassim, and C. Heske, Appl. Phys. Lett. **94**, 012110 (2009).