

II.G.4 Characterization of Materials for Photoelectrochemical (PEC) Hydrogen Production

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- Monitor deliberately introduced modifications of PEC candidate materials in view of the electronic and chemical structure.

FY 2011 Accomplishments

- Investigation of the chemical and electronic surface properties of GaInP₂ thin films and their variation after PEC testing (with the National Renewable Energy Laboratory, NREL, and Lawrence Livermore National Laboratory, LLNL, in the joint NREL/LLNL/UNLV surface validation group).
- Development of the benchmark electronic surface structure of a Fe₂O₃ thin film (with University of California, Santa Barbara).
- First exploratory experiments for the (Mo,W)(S,Se)₂ materials class (with Stanford University).
- First steps towards developing in situ PEC capabilities in soft X-ray spectroscopy (XPS).

Fiscal Year (FY) 2011 Objectives

Enhance the understanding of 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (H) System Efficiency
- (K) Durability
- (G) Capital Cost

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 and modification of novel candidate materials.



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 us 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 (PES) with XPS [1] 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 surface-sensitive 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 within the DOE PEC Working Group, we have investigated a variety of PEC candidate materials. Results were immediately shared with the collaboration partners and discussed in detail through powerpoint presentations, at phone conferences, and working group meetings. In this report, we will focus on the chemical surface properties of GaInP₂ samples obtained from NREL (T. Deutsch and J. Turner) and the electronic structure of Fe₂O₃ samples obtained from University of California, Santa Barbara (A. Forman, A. Kleiman-Shwarscstein, and E. McFarland). Further results, also for other material classes, are shown in the annual review presentation.

For the GaInP₂ experiments, two lines of work were pursued. First, we analyzed a series of samples that were deliberately exposed to PEC-relevant conditions, as listed in Table 1.

TABLE 1. Experimental Details of the GaInP₂ Samples Tested at NREL

Sample	Treatment	Electrolyte
MJ247-4	30 sec etch in concentrated sulfuric acid	none
MJ247-3	-8 mA/cm ² , 22 hrs, AM1.5G	0.1M HNO ₃ + 0.5M NH ₄ NO ₃ with Zonyl FSN-100
MJ247-2	-8 mA/cm ² , 22 hrs, AM1.5G	1M KOH with Zonyl FSN-100
MJ247-1	-8 mA/cm ² , 22 hrs, AM1.5G (+8 mA/cm ² applied for ~1 sec prior to run)	0.5M H ₂ SO ₄ with Zonyl FSN-100
MJ200	as-grown	none

An XPS surface chemical characterization of the samples is presented in Figure 1. The survey spectra in Figure 1 are normalized to the same height and offset for presentation. In addition to the expected Ga, In, and P peaks, the spectra also show O 1s and C 1s peaks of varying intensities. Samples MJ247-1 and MJ247-3 also show F 1s peaks, with this peak being the dominant feature in Sample MJ247-3. This is likely due to the Zonyl FSN-100

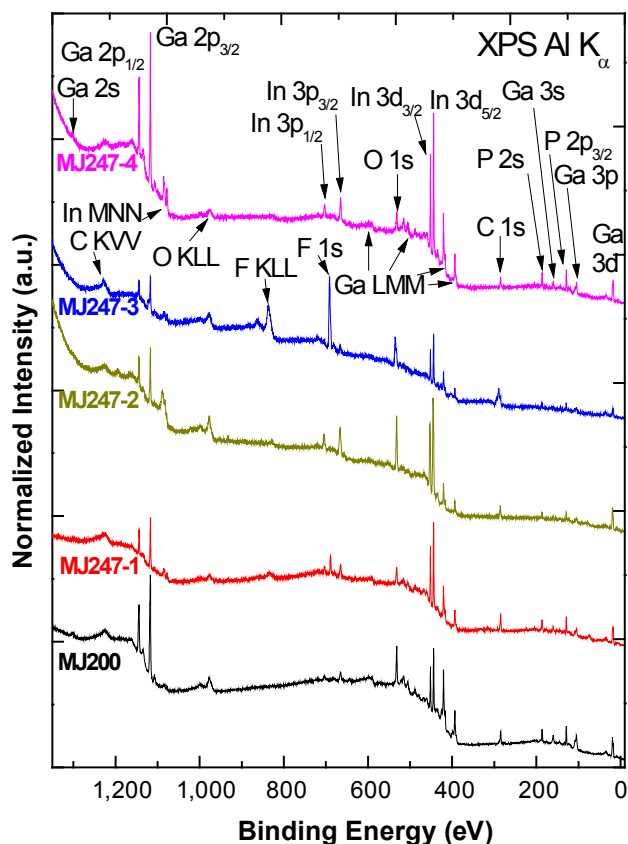


FIGURE 1. XPS survey spectra of selected GaInP₂ thin film samples after deliberate exposure to PEC-relevant environments, as listed in Table 1.

fluorosurfactant applied to the sample surfaces to facilitate movement of evolved H₂ from the electrode, but could also stem from the Teflon[®]-based environment of the sample surface during the tests.

As an example for the analysis of detail XPS spectra, we note that the Ga 2p region (not shown) clearly indicates the presence of multiple Ga species in the fluorine-rich sample MJ247-3 and, furthermore, exhibits variations in the lineshape of all samples, suggesting the presence of multiple chemical environments in those cases as well. For example, the MJ200 sample exhibits a shoulder at higher binding energy, most likely due to the native oxide- and carbon-containing surface contamination layer. Future experimental steps (currently being conducted in our lab at UNLV) thus focus on a removal of this surface contamination layer, such that “benchmark” spectra, e.g., of the Ga 2p core levels, but also of the valence and conduction band region of clean GaInP₂, can be obtained.

The second line of work on GaInP₂ focuses on a derivation of the electronic surface structure, as will be demonstrated below for the Fe₂O₃ system. In particular for the band gap determination, our experimental tool chest allows three different approaches, namely ultraviolet/visible light absorption (the “optical bulk band gap”), combining XES and XAS (the “electronic surface-near

band gap”), and combining UPS and IPES (the “electronic surface band gap”, see discussion of Fe_2O_3). In fact, a combination of all three approaches can be used to follow band gap gradients [2]. Here, we show first experiments to combine XES and XAS studies on the same samples. For this purpose, we have studied the $\text{P L}_{2,3}$ edge of (air-exposed) GaP and InP reference powders, as well as one (untreated) GaInP_2 thin film. Figure 2 shows the associated spectra, demonstrating that it will be possible to determine both valence-band maxima (VBM) and conduction band minima (CBM) with this method. Note that, due to the above-mentioned surface contamination, the derived band gaps are not yet representative of functioning PEC devices (in which electrolyte exposure is expected to “clean” the surfaces), and hence no band gaps are given here. In future

steps (currently being performed at UNLV), samples will be cleaned with an ion-stimulated desorption approach, which will allow us to determine depth-dependent band gaps of representative GaInP_2 surfaces. These can then be compared with theoretical results from our project partners at Lawrence Livermore National Laboratory (T. Ogitsu and B. Wood).

Having elucidated the impact of calcination (as shown in Figure 3) on the chemical surface properties of the University of California, Santa Barbara thin films in the previous FY, in particular uncovering significant Ti and Pt segregation processes, we focused on the analysis of the *electronic structure* of a Fe_2O_3 sample that demonstrated particularly high solar water splitting performance.

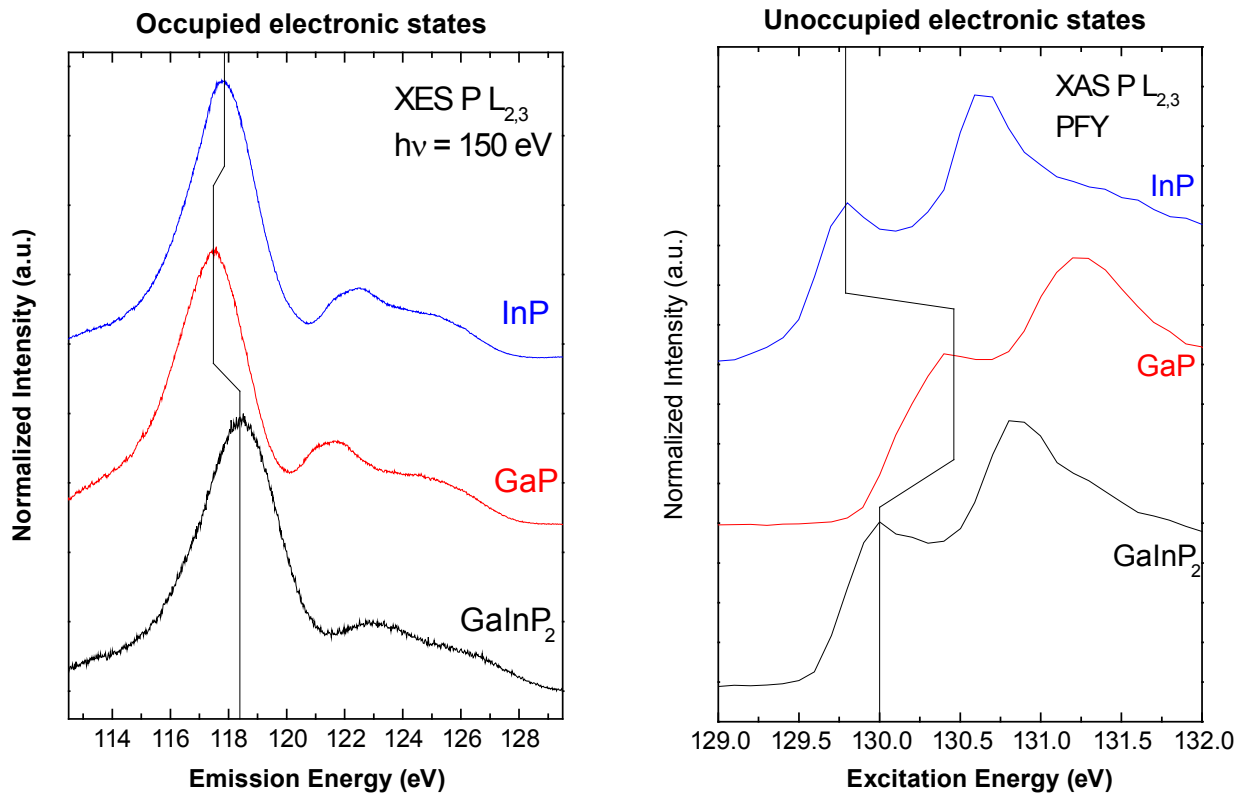


FIGURE 2. $\text{P L}_{2,3}$ XES (left) and XAS (right) of InP and GaP reference powders, as well as a GaInP_2 thin film (after air exposure, but without additional PEC testing). XES spectra probe the occupied states of the valence band, while XAS spectra give insights into the unoccupied conduction band states.

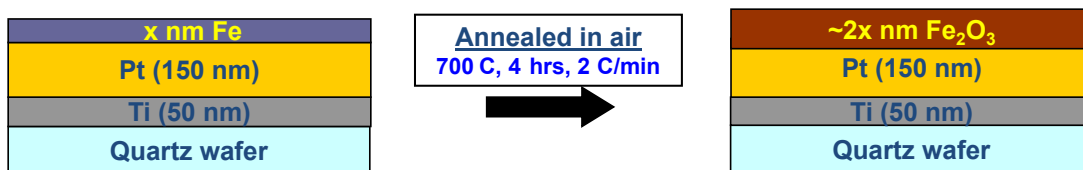


FIGURE 3. Schematic Calcination Process to Prepare Fe_2O_3 Thin Films at the University of California, Santa Barbara

The occupied and unoccupied electronic states were probed with UPS and IPES, respectively, as shown in Figure 4, left. The binding energies (abscissa) were adjusted relative to the Fermi Energy and plotted within the same graph. The leading edges of each spectrum were then extrapolated to the baseline. The positions of the intercepts with the baseline determine the positions of the VBM, in the UPS spectrum, (left) and CBM in the IPES spectrum, (right). The combination of both band edges allows a determination of the electronic surface band gap (2.0 ± 0.2 eV). Combining the band edge positions with the work function (4.23 ± 0.05 eV) of the sample, the band edge positions can be given with respect to the vacuum level. Furthermore, by applying an International Union of Pure and Applied Chemistry recommendation [3] and as done earlier for the case of WO_3 [4] and Mo:WO_3 [5], the vacuum level scale can be related to the normal hydrogen electrode (NHE) scale. By plotting the position of the VBM and CBM relative to the Fermi energy, vacuum level, and NHE on one plot, a comprehensive picture of the electronic picture can be painted, as shown in Figure 4 on the right.

Note that the plot in Figure 4 is derived from vacuum-based measurements and thus includes a potential surface band bending at the solid/vacuum interface. It does not,

however, include potential variations of this band bending upon formation of the liquid-solid interface in an electrolyte environment. As is well known, a Helmholtz layer is formed in this case, and experimental and theoretical approaches to assess the impact of this layer on the electronic structure will need to be performed in subsequent experiments. In the current state, the plot in Figure 4 shows that the Fe_2O_3 sample surface simultaneously satisfies two conditions necessary for solar water splitting: the CBM and VBM straddle the H^+/H_2 reduction and $\text{H}_2\text{O}/\text{O}_2$ oxidation potentials, and the surface band gap lies in the optimal range for PEC hydrogen production with a single-gap material. However, a bias will clearly be needed to drive significant currents during PEC water splitting using this surface, since the CBM lies only slightly above the H^+/H_2 reduction level.

Conclusions and Future Directions

Conclusions:

- Successfully maintained operations of our multi-chamber ultra-high vacuum spectroscopy system despite limited funding.

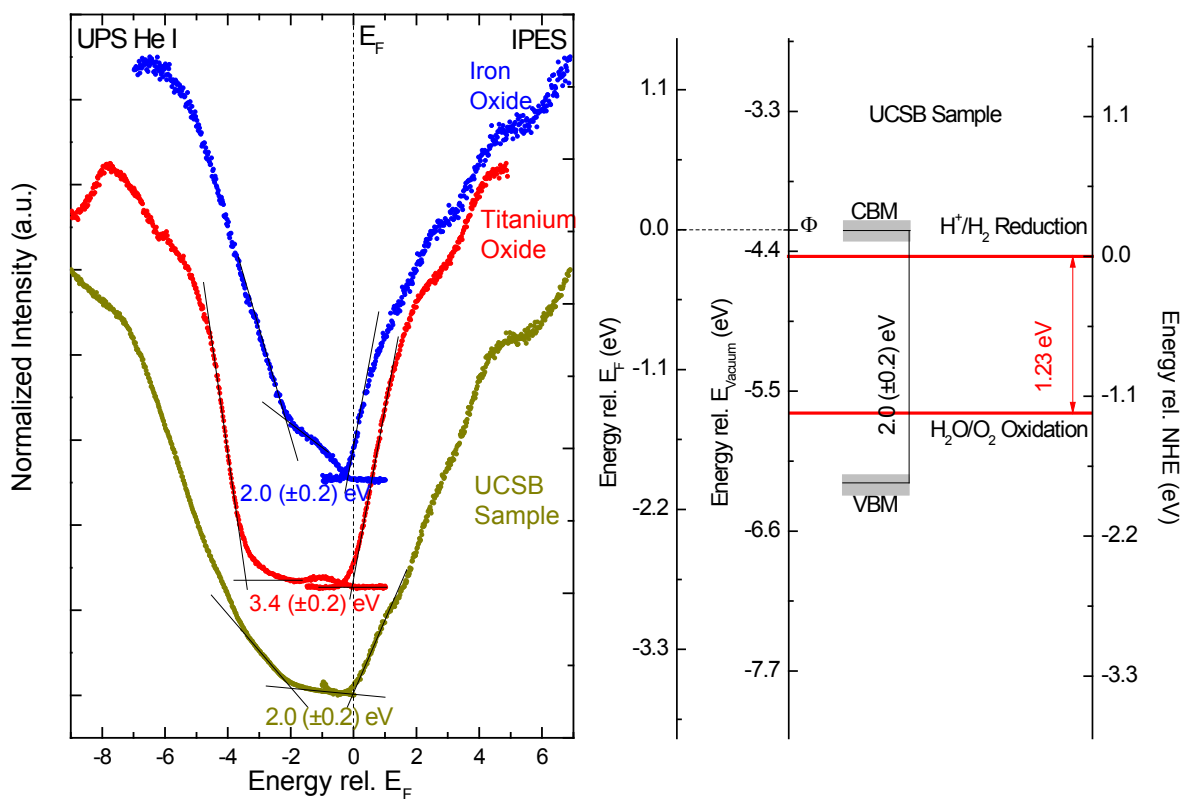


FIGURE 4. Left panel: UPS (left) and IPES (right) spectra of an Fe_2O_3 thin film grown at University of California, Santa Barbara (UCSB), and two *in-vacuo* grown reference systems (iron oxide and titanium oxide). Right panel: tentative electronic surface structure of the University of California, Santa Barbara Fe_2O_3 thin film.

- Continued experiments with select partners of the DOE PEC Working Group, primarily focusing on GaInP₂ and Fe₂O₃ thin films.
- Evaluated PEC candidate materials in view of their electronic and chemical properties, with primary focus on band gaps and level alignment.

Future Directions:

- Future directions will depend on availability of funding.
- If possible, we will continue the collaborations with our existing partners and bring new partners “on board”.
- We will continue to determine electronic and chemical properties of various PEC candidate materials manufactured by the collaboration partners within the DOE PEC Working Group.
- For GaInP₂, we will focus on establishing a benchmark electronic structure of optimally cleaned thin film surfaces, which will allow us to monitor deliberate modifications of the GaInP₂ material and to correlate our results with theoretical calculations and predictions.

FY 2011 Publications/Presentations

1. “Using soft x-rays and electrons to characterize (understand?) materials for solar energy conversion”, C. Heske, Heraeus-Seminar: “Energy Materials Research by Neutrons and Synchrotron Radiation”, Bad Honnef, Germany, May 10, 2011 (invited).
2. “An International Effort to Develop Photoelectrochemical (PEC) Hydrogen Production Research Standards and Methods”, H.N. Dinh* (NREL), Z. Chen, T.G. Deutsch, A. Kleiman-Shwarsstein, A.J. Forman, N. Gaillard, R. Garland, K. Takanabe, C. Heske, M. Sunkara, E.W. McFarland, K. Domen, E.L. Miller, J.A. Turner, and T.F. Jaramillo, MRS 2011 Spring Meeting, San Francisco, April 2011 (invited).
3. “So, when will there finally be a breakthrough for these solar thingies?”, C. Heske, High School Day, American Chemical Society National Meeting, Anaheim, CA, March 27, 2011 (invited).
4. “Soft x-ray spectroscopy of materials for photoelectrochemical devices”, C. Heske, M. Bär, and L. Weinhardt, Pacifichem 2010 conference, Waikiki, December 18, 2010 (contributed oral).
5. “Using soft x-rays to understand and optimize materials for energy conversion”, C. Heske, Department of Physics, Hanoi University of Technology, Hanoi, Vietnam, Nov. 1, 2010 (invited).
6. “Using soft x-rays to look into (buried) interfaces of energy conversion devices based on compound semiconductors”, C. Heske, 218th Electrochemical Society Meeting, Las Vegas, Oct. 12, 2010 (invited).
7. “Using soft x-rays to optimize materials for energy conversion devices”, C. Heske, Department of Physics, Renmin University, Beijing, China, Oct. 10, 2010 (invited).
8. “Using soft x-rays to study the electronic and chemical properties of thin film solar devices”, C. Heske, 15th International Conference on Solid Films and Surfaces (ICSFS-15), Beijing, China, Oct. 9, 2010 (invited).
9. “Using soft x-rays to understand and improve materials for energy conversion devices”, C. Heske, Department of Chemistry, University of California Santa Cruz, September 29, 2010 (invited).
10. “SALSA – a soft x-ray spectroscopy endstation for the investigation of solids, liquids, and gases”, M. Blum*, L. Weinhardt, O. Fuchs, M. Bär, Y. Zhang, M. Weigand, S. Krause, S. Pookpanratana, T. Hofmann, W. Yang, J.D. Denlinger, Z. Hussain, E. Umbach, and C. Heske, SRI2010 conference, Chicago, IL, September 2010 (contributed oral).
11. Invited, but symposium was canceled: “Soft x-ray spectroscopy of the electronic structure of water and materials for photoelectrochemical water splitting”, C. Heske, Symposium on “In Situ Microscopy and Spectroscopy of Large Surfaces and Interfaces”, XIX International Materials Research Congress 2010, Cancun, August 15–20, 2010 (invited).
12. “Soft x-ray and electron spectroscopies to study the electronic and chemical structure of surfaces and interfaces in photoelectrochemical devices”, C. Heske, Solar Hydrogen and Nanotechnology V, SPIE International Symposium on Optics & Photonics, San Diego, August 1–5, 2010 (invited).
13. “Photoelectrochemical (PEC) hydrogen production research standards and methods development”, H.N. Dinh* (NREL), Z. Chen, T.G. Deutsch, A. Kleiman-Shwarsstein, A.J. Forman, N.M. Gaillard, R. Garland, K. Takanabe, C. Heske, M.K. Sunkara, E.W. McFarland, K. Domen, E.L. Miller, J.A. Turner, and T.F. Jaramillo, “Solar Hydrogen and Nanotechnology V” Symposium, SPIE Optics and Photonics Conference, San Diego, CA, August 2010 (invited oral).
14. “Characterization of Fe₂O₃ thin films for photoelectrochemical hydrogen production”, K. George*, C. Heske, S. Krause, Y. Zhang, E.W. McFarland, A.J. Forman, A. Kleiman-Shwarsstein, M. Bär, L. Weinhardt, W. Yang, and J.D. Denlinger, “Solar Hydrogen and Nanotechnology V” Symposium, SPIE Optics and Photonics Conference, San Diego, CA, August 1–5, 2010 (contributed oral).
15. “Using soft x-rays to look at surfaces and interfaces of photoelectrochemical devices”, C. Heske, New Science with Resonant Elastic and Inelastic X-ray Scattering Satellite Meeting of the VUVX conference, University of Saskatchewan, Saskatoon, SK, Canada, July 8, 2010 (invited).
16. “Wie man mit Röntgenspektroskopie energierelevante Materialien und Systeme verstehen und verbessern kann”, C. Heske, Organisch-Chemisches Kolloquium im Sommersemester 2010, Karlsruhe Institute of Technology, July 2, 2010 (invited).
17. “Using soft x-rays to look at surfaces and interfaces for energy conversion and storage”, C. Heske, National Renewable Energy Lab (NREL), June 21, 2010 (invited).
18. “Using soft x-rays to look into interfaces of photoelectrochemical devices”, C. Heske, Symposium on

Synchrotron and Neutron Techniques for Energy Materials Research, Materials Research Society Spring Meeting, San Francisco, April 5–9, 2010 (invited).

References

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