

Fuel from the Sun: Insight into Electrode Performance



For more than two billion years, nature, through photosynthesis, has used the energy in sunlight to convert water and carbon dioxide into fuel (sugars) for green plants. Scientists hope to mimic and condense this process to more efficiently harness energy from the sun. (Photo by Roy Kaltschmidt)

Water splitting—key to photosynthesis

In photosynthesis, plants use sunlight to split water into oxygen and hydrogen. The oxygen is released into the atmosphere, and the hydrogen is used to produce molecules—such as carbohydrates and sugars—that store energy in chemical bonds. Such compounds constitute the original feedstocks for subsequent forms of fuel consumed by society.

Photoelectrochemical (PEC) water splitting is a form of “artificial” photosynthesis that uses semiconductor material, rather than organic plant material, to facilitate water splitting. Electrodes made of semiconductor material are immersed in an electrolyte, with sunlight driving the

water-splitting process. The performance of such PEC devices is largely determined at the interface between the photoanode (the electrode at which light gets absorbed) and the electrolyte.

Probing the hematite/electrolyte interface

A widely studied photoanode material is hematite ($\alpha\text{-Fe}_2\text{O}_3$), a cheap, earth-abundant semiconductor with a favorable band gap and high chemical stability under the harsh conditions of many PEC reactions. However, it’s still not efficient enough to be widely used in these devices. To gain insight into why, the researchers studied thin (30-nm) films of hematite, a thickness optimized for maximum PEC performance. They studied both doped

Scientific Achievement

Soft x-ray studies of hematite electrodes—potentially key components in producing fuel from sunlight—revealed the material’s electronic band positions under realistic operating conditions.

Significance and Impact

By clarifying the mechanisms limiting hematite’s photoelectrochemical (PEC) performance, this work brings us a step closer to directly converting solar energy into easily storable chemical fuel.

and undoped hematite to learn from their different behaviors about the root causes for limited PEC performance.

APXPS experiments with “tender” x-rays

Past experiments at the ALS have shown that ambient-pressure x-ray photoelectron spectroscopy (APXPS) can be used to study the heterogeneous interfaces of aqueous solutions. It provides an interface-specific, noncontact probe based on measuring the kinetic energy of photoelectrons originating from the interface. It’s also an excellent tool for measuring changes in interfacial electrical potentials. This is because electrons, being charged particles, change their kinetic energy (i.e., “speed”) when the electrical

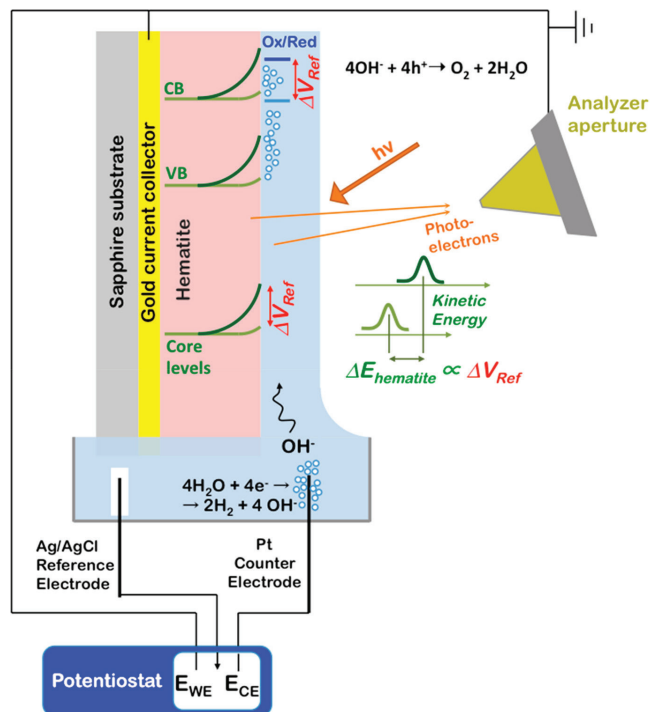
potential at the interface is changing. With these capabilities, the researchers were able to directly measure shifts in valence and conduction band positions at the hematite/electrolyte interface of an operating PEC cell as a function of solar illumination, applied potential, and doping.

For this work, the researchers took a liquid cell normally mounted on Beamline 11.0.2 and moved it to Beamline 6.0.1, a source of “tender” x-rays (about 3.5 keV). Photoelectrons generated by the tender x-rays have kinetic energies (about 2 keV and higher) capable of penetrating the thin electrolyte film in contact with the hematite.

Missing “in-gap” states

Surprisingly, the data showed that both doped and undoped hematite samples exhibited so-called “ideal semiconductor” behavior, appearing to be unaffected by an expected interfacial effect (“Fermi-edge pinning”) that would allow electronic states to populate the band gap, where they are normally forbidden. A commonly accepted scenario assumes that in-gap states act as trap centers for holes, increasing the probability for hole recombination with electrons, thus degrading performance.

The results contradict previous reports (based on less-direct methods) that in-gap states are responsible for the decreased PEC performance of hematite. Instead, the results imply that the poor PEC performance of hematite is due to other reasons, such as the small charge-carrier concentration for undoped hematite and tunneling-mediated recombination of electrons and holes in the case of doped hematite.



Measurement of band positions at the hematite/electrolyte (KOH) interface. The hematite thin film (30 nm) is deposited on a gold current collector and is the working electrode in the system. A thin electrolyte film (10–20 nm) was prepared by dipping the sample into a beaker containing a 0.1 M KOH solution and pulling it out slowly. Photoelectron spectra are recorded using an APXPS system. Changes in the oxidation/reduction (Ox/Red) levels of the electrolyte (blue horizontal lines inside of liquid film) lead to analogous shifts (ΔV_{Ref}) of the semiconductor band positions (green lines in the hematite film), affecting the measured kinetic energy of the electrons from the core levels (green peaks).

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Publication: A. Shavorskiy, X. Ye, O. Karslıoğlu, A.D. Poletayev, M. Hartl, I. Zegkinoglou, L. Trotochaud, S. Nemsak, C.M. Schneider, E. Crumlin, S. Axnanda, Z. Liu, P.N. Ross, W. Chueh, and H. Bluhm, “Direct mapping of band positions in doped and undoped hematite during photoelectrochemical reactions,” *J. Phys. Chem. Lett.* **8**, 5579 (2017), doi:10.1021/acs.jpcclett.7b02548.

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Funding: Global Climate and Energy Project at Stanford University, Stanford University, and U.S. Department of Energy, Office of Science, Basic Energy Sciences Program (DOE BES). Operation of the ALS is supported by DOE BES.

Published by the
**ADVANCED LIGHT SOURCE
COMMUNICATIONS GROUP**



U.S. DEPARTMENT OF
ENERGY
Office of Science

