II.G.12 Characterization and Optimization of Photoelectrode Surfaces for Solar-to-Chemical Fuel Conversion

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Objectives

- Understand the underlying mechanism of surface corrosion of semiconductor-based photoelectrochemical (PEC) cells.
- Understand the dynamics of water dissociation and hydrogen evolution at the water-photoelectrode interface.
- Understand the electronic properties of the water-electrode interface.
- Identify the relationship between corrosion and catalysis.

Technical Barriers

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

(Y) Materials Efficiency (Photoelectrochemical Hydrogen Production)
(Z) Materials Durability (Photoelectrochemical Hydrogen Production)

Technical Targets

This project is conducting fundamental theoretical studies of mechanisms of corrosion and catalysis in III-V semiconductor-based photoelectrode materials for PEC hydrogen production. Insights gained from these studies will be applied toward the optimization and design of semiconductor materials that meet the following DOE 2013 PEC hydrogen production targets:

- Usable semiconductor bandgap: 2.3 eV
- Chemical conversion process efficiency: 10%
- Plant solar-to-hydrogen efficiency: 8%
- Plant durability: 1,000 hrs.

Accomplishments

- Discovered that spontaneous dissociative adsorption of water could be observed in simulations of oxide-decorated InP(001) surfaces.
- Discovered that oxide reactivity can be categorized generally according to oxygen bond topology.
- Isolated possible mechanism for water dissociation on oxide surfaces with In–O–In bond topology.
- Determined that hydroxide bridges are more stable than oxides, and demonstrated that conversion between hydroxide topologies is facilitated by hydrogen-bond network in water.
- Isolated two possible mechanisms for corrosion nucleation in InP(001), both of which will be tested further for compatibility with experimental measurements.

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Introduction

Development of efficient processes for the carbon-free production of hydrogen is key to sustainable realization of a future hydrogen economy. One particularly promising approach is to use sunlight to catalyze direct evolution of hydrogen from water in a PEC cell. Semiconductor-based PEC devices are particularly attractive, thanks to a relatively simple device design and a wealth of data available for engineering efficient photon harvesting [1]. Results have demonstrated that one can achieve solar-to-fuel conversion efficiency in excess of the 2013 DOE targets (>12% using a tandem GaAs/$GaInP_2$ cell); however, this has come at the expense of short device lifetime due to fast degradation of the electrode [2]. Further progress has been hindered by a poor understanding of the fundamental hydrogen evolution processes operating at the electrode-water interface. Our research addresses this need from a theoretical perspective, leveraging realistic ab-initio simulations to determine the key mechanisms governing corrosion and catalysis at the water-semiconductor interface.

Approach

Further progress in semiconductor-based PEC photoelectrodes requires in-depth understanding of the complex relationship between surface stability and catalytic activity. This in turn relies on knowledge of the fundamental nature of the electrode-water interface, and of the chemical pathways explored during surface-active hydrogen evolution. As such, we have been carrying out finite-temperature ab-initio molecular dynamics simulations and energetics calculations based on density functional theory to understand the chemical, structural, and electronic properties of water/electrode interfaces under equilibrium conditions, as well as to understand the competing chemical reaction pathways visited during photocatalysis. Our approach uses InP(001), which has known water-splitting activity, as a model semiconductor electrode. Currently, our chief interest is in investigating the role of oxygen at the semiconductor surface, in response to experimental observations of high oxygen contaminant concentration in the samples evaluated by our collaborators in J. Turner's group at the National Renewable Energy Laboroatory [3] and suggestions that this oxide may play a key role in motivating both the surface photocorrosion and the catalytic water splitting reaction [4,5]. Accordingly, we are evaluating the stability and reactivity of the InP(001) surfaces in the presence of oxide and hydroxide species, correlating results to oxide topology and surface morphology. In each instance, the role of the surrounding water is also assessed.

Results

To evaluate the role of oxygen contaminants in the reactivity and stability of the InP(001) surfaces, we extracted low-energy oxide configurations by adsorbing atomic oxygen on high-symmetry sites of an initially unreconstructed In-rich surface slab. The atoms were then allowed to relax to their local-minimum configuration. Atop, hollow, and both bridge sites were tested at single-monolayer coverage limit, giving rise to several relaxed oxide structures. All tested configurations show that incorporation of oxygen is strongly thermodynamically favored with respect to the clean surface in the presence of gaseous O_2 (by an average of 2.5 eV per oxygen atom), in agreement with experimental observations of high surface oxygen contamination. Several of the tested configurations resulted in the oxygen in the subsurface layer rather than the surface layer. These generally feature oxygen simultaneously bonded to one indium and one phosphorous. Surface oxygens, on the other hand, generally bridge two indium atoms. Oxygen is more stable in the subsurface than on the surface (by 0.5 eV per oxygen, on average), reflecting the strength of the In–O–P complex with respect to In–O–In.

To test whether oxide formation affects reactivity for water dissociation, single water molecules were adsorbed near the oxygen sites on each of the morphologies. In each case, oxygen bond topology proves an excellent predictor of gas-phase dissociative adsorption of water: oxygen sites in In–O–P bonds bind water weakly and do not encourage dissociation, whereas sites in In–O–In bonds promote spontaneous dissociative adsorption. For morphologies containing both types of oxide bonds, reactivity depends on the specific adsorption site. To illustrate this point, the results of water adsorption on three representative oxide surfaces are shown in Figure 1.

Figure 1 indicates that the result of water reaction with certain bridge oxide structures is local surface hydroxylation. Accordingly, we also examined hydroxylated InP(001) surfaces, generated by placing OH in high-symmetry sites. Only three unique relaxed configurations were found for OH coverage, although we are currently mining additional morphologies for further study. Hydroxide formation is thermodynamically favored with respect to oxide formation (by an average of 1.3 eV per oxygen). This reflects the thermodynamic driving force for the dissociation of water on the reactive oxide surfaces, which results in surface hydroxylation. Interestingly, the bridge configuration, which was the least stable oxide configuration we tested, proved the most stable hydroxide configuration.

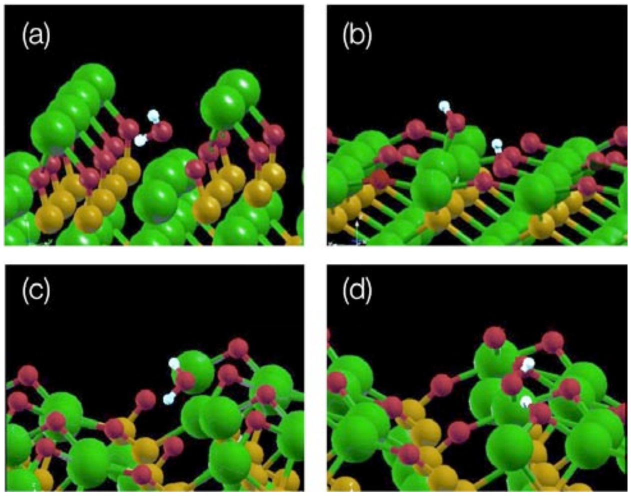

FIGURE 1. Result of gas-phase water molecule adsorption on representative oxide-contaminated In-rich InP(001) surfaces. For oxides consisting exclusively of In-O-P oxygen bond topologies (a), the water molecule does not dissociate. For oxides consisting exclusively of In-O-In oxygen bond topologies (b), the water molecule dissociates, resulting in local surface hydroxylation. For oxides containing both In-O-P and In-O-In oxygen bond topologies (c and d), dissociation of the water molecule does not occur if adsorption is near the In-O-P site (c), whereas dissociation does occur if adsorption is near the In-O-In site (d). Color scheme: hydrogen = small white spheres; oxygen = small dark red spheres; phosphorous = medium gold spheres; indium = large green spheres.

We have also been running ab initio molecular dynamics calculations of the full semiconductor-water interface to examine the influence of dynamics on the reactivity and stability of the surface. In order to isolate the two oxide bond topologies and examine them individually, we have been running two oxide surface simulations, one using a low-energy configuration with 100% In–O–P bond topology and the other using a higher-energy bridge-site configuration with 100% In–O–In bond topology. For the hydroxide surface, we have been running only one simulation (bridge-site hydroxide), recognizing the fact that the shallow free energy surface should mean realization of the other morphologies in the course of the dynamics.

As expected, the In–O–In surface oxide demonstrated much higher reactivity than the In–O–P subsurface oxide. The mechanism of dissociative water adsorption on the reactive In–O–In oxide is depicted in Figure 2. The reaction begins with the adsorption of a water molecule on a surface indium site to form a bond between the water oxygen (O1) and the indium. The water molecule is initially oriented such that one of the O1–H bonds lies generally parallel to the surface, with the other pointing upwards into the solution. The parallel-lying O1–H bond is thereby free to engage in hydrogen bonding with one of the surface oxygens (O2). The subsequent cleavage occurs via proton transfer across the O1–H· · ·O2 complex, such that the covalent and hydrogen bonds are exchanged. The result is the hydroxylation of two neighboring indium atoms, the first of which (the one to which the water O1 was originally bound) forms an atop-site hydroxide, and the second of which forms either an atop- or bridge-site hydroxide. In vacuum calculations, the atop and bridge sites were nearly isoenergetic. Therefore, the choice between the two is determined by the local structure visited during the dynamics and appears to be strongly dependent on number and strength of the hydrogen bonds formed with neighboring water molecules.

For many water cleavage events, the reaction culminates in two surface hydroxyl groups. However, there are also instances in which one oxygen atom further binds to a second-layer phosphorous and is pulled into the subsurface. This phenomenon can be seen in Figure 2e and f. Since subsurface oxygen that bridges In and P is not generally reactive, the choice the system makes could have significant consequences on further surface catalytic activity. In summary, there is a competition between three possibilities for the product hydroxide groups: first, formation of a bridge-site hydroxide configuration; second, formation of an atop-site hydroxide which strongly hydrogen-bonds with the solution; and third, a subsurface hydroxide that bridges In and P. Qualitatively, the choice between these three seems to be related to the nature of the surrounding hydrogen-bond network. To be pulled into the subsurface, the product oxygen must not be engaged in significant hydrogen bonding. On the other hand, to be converted into the atop hydroxyl configuration, a product oxygen must be engaged in very strong hydrogen bonding.

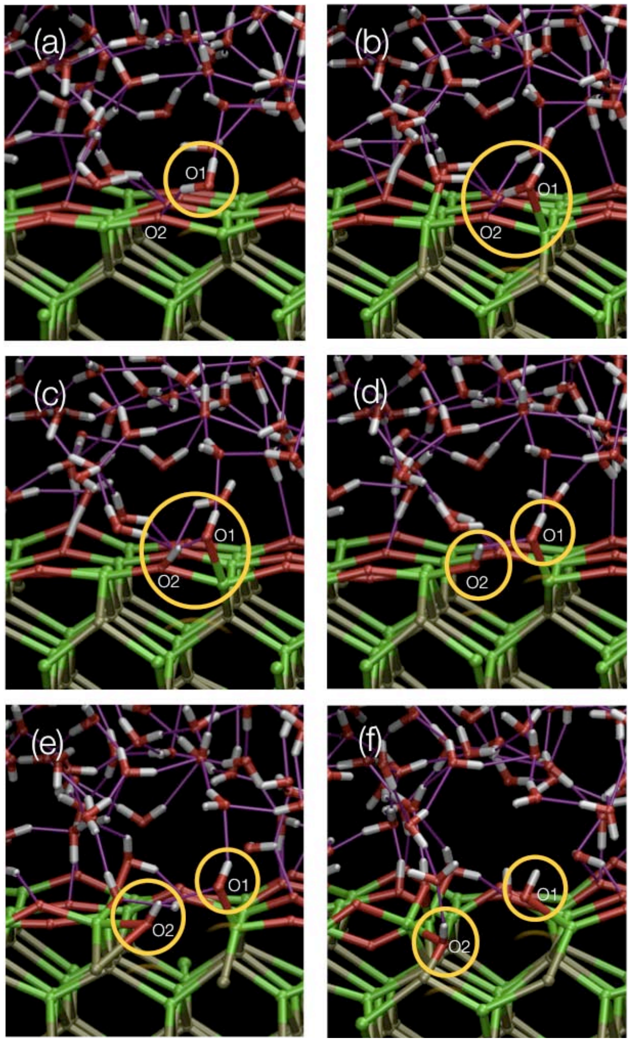

FIGURE 2. Mechanism of water dissociation on a bridge-site oxide of In-rich InP(001). O1 and O2 refer to the oxygen atoms originally associated with the water molecule and the oxide surface, respectively. (a) and (b) O1 binds to indium, and a hydrogen bond is formed with O2. (c) The water molecule transfers a hydrogen across the O1–H· · ·O2 complex. (d) The In–O2 bond breaks. (e) and (f) Optionally, O2 is pulled below the surface to form a bond with P. Color scheme: white = hydrogen; dark red = oxygen; light green = In; medium gold = phosphorous. The thin purple lines represent hydrogen bonds.

Although we start the simulation with all hydroxide groups in the bridge-site configuration, we quickly see conversion of several of these to the atop-site configuration, consistent with the zero-temperature predictions of facile exchange between the two. This exchange is bidirectional, indicating a dynamic equilibrium between the two configurations. As with the oxide simulations, whether a conversion takes place seems to largely depend on the structure of the hydrogen-bond network surrounding the hydroxide group. If the group is involved in strong hydrogen bonding, the atop-site configuration is preferred, whereas the converse is true for the bridge-site configuration.

Occasional dissociative adsorption of water is observed in the hydroxide simulations, although it is generally associated with temporary breaking of an O–H surface bond to form bridge-site In–O–In. Water cleavage then proceeds via an identical mechanism to that observed in the reactive In–O–In oxide (Figure 2). Since these local-oxide configurations are relatively rare, the rate of water dissociation is significantly slower than for the reactive oxide (almost an order of magnitude). In addition, hydrogen atoms can sometimes transfer from a water molecule in solution across a hydrogen bond to OH groups on the surface. This turns surface OH into an indium-adsorbed H_2O, which may then be released back into the solution to free up an indium for further reactions. This also leaves one OH in the solution for further surface reactions, such as the surface hydroxide-to-oxide conversion via further water dissociation. The suitability of this reaction depends on temporary stabilization via local fluctuations in the hydrogen-bond network.

Conclusions and Future Directions

- We investigated oxides and hydroxides of InP(001) and found that surface reactivity can be correlated with local oxygen bond topology.
- Our ab initio molecular dynamics simulations of the oxide- and hydroxide-decorated surfaces show possible mechanisms for corrosion and catalysis.
- Dynamics appear to be very important in understanding surface behavior, particularly in reference to the water structure at the interface. Further analysis of the water structure to identify the nature of these correlations is currently underway.
- These mechanisms will be tested further by running additional simulations, and the results will be compared with X-ray absorption spectroscopy spectra currently being obtained by our collaborator, Prof. Clemens Heske.
- We have yet to assess the effect of surface and solution treatments on stability and reactivity. These include modification of the water pH and inclusion of nitrogen additives.

FY 2010 Publications/Presentations

1. "*Ab-initio* modeling of semiconductor-water interfaces for direct solar-to-chemical fuel conversion," 2010 International Conference on Materials for Energy, Karlsruhe, Germany.

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