Characterization and Optimization of Photoelectrode Surfaces for Solar-to-chemical Fuel Conversion

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Lawrence Livermore National Laboratory
June 10, 2010

Project ID# PD058

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Overview

**Timeline**
- Start: March 2010
- End: February 2011
- Percent complete: 20%

**Barriers**
- Photoelectrochemical Materials Efficiency
- Photoelectrochemical Materials Durability

**Budget**
Total project funding
- DOE $100K
- Contractor $140K
  (5% of PI, 100% of postdoc)

Funding for FY09: N/A
Funding for FY10:
- 240K FY10

**Partners**
- NREL (J. Turner)
- UNLV (C. Heske)
Relevance

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

- Relevance to H₂ program
  - Inform experimental efforts to increase durability of photocatalyst
  - Inform experimental efforts to increase catalytic efficiency
Technical Approach

- Perform large-scale interfacial simulations of III-V semiconductor surfaces in contact with water
  - Use quantum molecular dynamics (Density Functional Theory, DFT) for accurate interfacial modeling
  - Electronic structure data permits materials characterization and experimental interpretation
- Examine different surface treatments, geometries, and solution chemistries
- Correlate surface degradation with atomistic surface structure, chemistry, and dynamics
- Relate interfacial water dissociation with tested surface morphology
## Milestones and Deliverables

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Technical Accomplishment – Structure and stability

Dynamical surface structure leads to dynamical electronic structure
Technical Accomplishment – Structure and stability

- Oxide is key to understanding corrosion, could also have relevance for reactivity (Heller, *Science* 223, 1141 [1984])
- Tested stability of various oxides:

<table>
<thead>
<tr>
<th>Site</th>
<th>InP (eV)</th>
<th>InP+N (eV)</th>
<th>GaP (eV)</th>
<th>GaP+N (eV)</th>
<th>(In/Ga-O-In/Ga)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bridge x (1)</td>
<td>0</td>
<td>0.04</td>
<td>0.32</td>
<td>1.24</td>
<td>0</td>
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<tr>
<td>Bridge x (2)</td>
<td>0.41</td>
<td>0.29</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Bridge y</td>
<td>1.05</td>
<td>0.47</td>
<td>0.67</td>
<td>0.63</td>
<td>1</td>
</tr>
<tr>
<td>Atop (1)</td>
<td>0.51</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.75</td>
</tr>
<tr>
<td>Atop (2)</td>
<td>0.46</td>
<td>0.67</td>
<td>0.06</td>
<td>0.86</td>
<td>0.75</td>
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<tr>
<td>Atop (3)</td>
<td>0.56</td>
<td>0.38</td>
<td>0.28</td>
<td>0.75</td>
<td>0.5</td>
</tr>
<tr>
<td>Hollow (1)</td>
<td>0.31</td>
<td>0.54</td>
<td>0.59</td>
<td>1.41</td>
<td>0</td>
</tr>
<tr>
<td>Hollow (2)</td>
<td>0.46</td>
<td>0.61</td>
<td>0.78</td>
<td>1.56</td>
<td>0</td>
</tr>
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Subsurface oxides

Surface oxides

Both surface and subsurface oxides should be considered
Technical Accomplishment – Structure and reactivity

- Photoexcitation is difficult to simulate, but we can look for precursors to photolysis
- “Inner-sphere” electron transfer: look for dissociative adsorption of water as precursor

Dynamics show evidence of dissociative adsorption
Technical Accomplishment – Surface oxides of InP(001)

Oxide reactivity can be categorized according to O bond topology

In-O-In bridges are reactive

100% In-O-P

100% In-O-In

50% In-O-In

50% In-O-P
Technical Accomplishment – Surface oxides of InP(001)

Locations of water cleavage for O-terminated InP(001)

Preferred reaction sites correlate with surface structure
Technical Accomplishment – Surface oxides of InP(001)

1) Formation of In-OH$_2$ bond
2) Transfer of H to neighboring O in In-O-In bridge
3) In-O-In bond cleavage
4) Optional formation of In-OH-P bond

Mechanism of dissociative adsorption of water on In-O-In bridge
Technical Accomplishment – Surface hydroxides of InP(001)

Barrier to break O-In bond: ~0.1 eV (vacuum)

Barrier is lowered by hydrogen bonding with surrounding water

Hydroxide bridge is most stable, but conversion to atop is facile
Dynamic equilibrium between atop and bridge hydroxide configurations
Technical Accomplishment – Surface hydroxides of InP(001)

Metastable H-bond bridges facilitate water dissociation and hydrogen transport
Technical Accomplishment – Surface hydroxides of InP(001)

Can use maximally localized Wannier functions to examine bonding

MLWF spread (related to bond strength)

Frequency (arb. units)

Spread of MLWF (Å)

Code developed by J.L. Fattebert under DOE SciDAC grant DE-FC02-06ER46262
Technical Accomplishment – Structure of interfacial H$_2$O

Time autocorrelation of H$_2$O orientation

Structure of water near OH-terminated surface

Water orientation is less dynamic near interface with reactive surface
Technical Accomplishment – Structure of interfacial H$_2$O

Water near interface has preferred orientation and different dipole strength.
Technical Accomplishment – Structure of interfacial H$_2$O

Radial distribution of atoms surrounding interfacial H$_2$O (for InP + oxide)

Surrounding water molecules are closer upon dissociation
Technical Accomplishment – Structure of interfacial H$_2$O

Surrounding water molecules more structured upon dissociation

Angular distribution of atoms surrounding interfacial H$_2$O (for InP + oxide)

Dissociating H$_2$O

Ordinary interfacial H$_2$O

Interfacial water structure is correlated with surface activity
Technical Accomplishment – Surface instability

Broken hydroxide bridge provides possible motivation for In dissolution

OH-terminated
Technical Accomplishment – Surface instability

Why don’t we see dissolution of In for the bare surface?

Exposed surface indium stabilizes through In-In dimerization, but dimerization is inhibited in InP+O by presence of oxide bridge.
Collaborations: Theory-experiment feedback cycle for accelerating development of efficient & robust electrode

NREL experiments: (DOE lab)
- J. Turner & T. Deutsche
- DOE H₂ program
- Synthesize electrode materials
- Assemble device
- Analyze H₂ production performance and corrosion resistance

NREL theory: (DOE lab)
- K. Kim & W. Ih Choi
- DOE H₂ program
- Ab initio surface simulations (mostly static)
- Gas phase reaction energetics

LLNL theory: (DOE lab)
- B. Wood & T. Ogitsu
- DOE H₂ program
- Large scale ab-initio MD of water-electrode interface

UNLV experiments: (University)
- C. Heske & G. Kyle
- DOE H₂ program
- Hi-fidelity (in-situ) characterization of water-electrode interface using X-ray spectroscopy

LBNL theory: (DOE lab)
- D. Prendergast
- Not in H₂ program
- X-ray spectrum simulations

Sample

Basic information on electrodes

Detailed microscopic informations

Choice of surface

X-ray interpretation
### Proposed future work

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Complete the rest of simulations and analysis. In particular, focus on the collaborations with the experimental groups (UNLV & NREL) to investigate on the photo induced hydrogen evolution reaction and the corrosion.
Summary

- We have performed the quantum MDs of water-electrode interfaces
  - At ambient condition, surface structure of InP dynamically changes, which affects on the dynamics of water
  - A few stable surface oxide morphologies were identified, which correlate with chemical activities
  - Upon a $\text{H}_2\text{O}$ dissociation, surrounding $\text{H}_2\text{O}$s evolve cooperatively

- The electronic excitation spectrum of a realistic water-electrode model can be calculated
  - X-ray spectroscopic information (e.g. XAS) can be directly compared between theory and experiments
  - Precise information on the nature of hydrogen evolution and the electrode corrosion will be obtained
  - Such an information will be used in finding a good electrode material or in an appropriate surface treatment