

Structural and chemical properties of III-V
semiconductor-water interfaces for photoelectrochemical
hydrogen production

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Group III phosphides currently offer the highest solar-to-hydrogen conversion efficiency among known electrode materials in photoelectrochemical (PEC) cells [1]. However, photocathodes based on these materials tend to exhibit rapid photocorrosion in aqueous environments, limiting their practical use. *Ab initio* modeling can provide unique insight into the interfacial chemistry at the semiconductor-water interface, which ultimately drives both photocorrosion and hydrogen evolution, yet remains poorly understood.

To this end, we use advanced *ab initio* molecular dynamics simulations to study the interface of model GaP(001) and InP(001) surfaces with water. Our surface models account for the presence of oxygen and hydroxyl surface adsorbates, which are omnipresent in experimental analyses but are usually neglected in idealized models [2]. We find that the inclusion of realistic surface adsorbates fundamentally changes the nature of the aqueous interface, leading to spontaneous water dissociation and strong interfacial hydrogen bonding that are largely absent on pristine surfaces [3].

Surprisingly, GaP and InP demonstrate qualitatively different interfacial dynamics, despite identical crystal structures and very similar electronic properties. For instance, dynamical and structural features in the hydrogen-bond networks of the two materials permit InP to exhibit fast surface proton conductivity when GaP does not. Similarly, surface-adsorbed water and hydroxyl can exchange with the solvent environment on InP, but not on GaP.

We will discuss potential implications of the comparative interfacial dynamics of InP and GaP, including the relationship to the mechanisms that underlie hydrogen evolution, electrochemical surface stability, and native corrosion resistance. Our results point to the importance of key dynamical processes in determining the electrochemical properties of the semiconductor-water interface.

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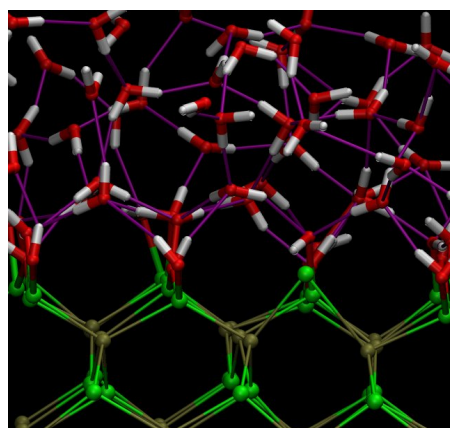


Figure 1. Equilibrium structure of the InP(001)-water interface, taken from a snapshot of an *ab initio* molecular dynamics simulation. Surface oxygen and hydroxyl cause formation of an interfacial hydrogen-bond network.

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