

## **UCL**





# Solvation and Charge Transfer Processes at Semiconductor/Liquid Water Interfaces

The generation of hydrogen and oxygen through water splitting is considered to be a key technology for energy storage. However, no efficient catalyst for this process has yet been found. Researchers at University College London have used the power of ARCHER2 to investigate the microscopic behaviour of water molecules at their interface with semiconductors to help in rationalising catalyst performance.



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**Figure 1:** Side view of the water layering at the hematite (001) slab, illustrating the different surface dynamics from fast H-bonding to slow residence lifetimes and their respective time scales. The corresponding atom density as a function of distance to the hematite slab is shown on the right side. Reproduced from P. Schienbein and J. Blumberger, Phys. Chem. Chem. Phys. 24, 15365 (2022).

#### Background

Understanding the microscopic processes at the interface between metal oxide semiconductors and water in its liquid phase is key to better understanding the process of generating hydrogen and oxygen via water splitting. This is considered to be a key technology for energy storage. However, despite the recognised importance of this issue, and the ongoing scientific efforts to address it, no catalyst has yet been found which can efficiently catalyse the water splitting reaction.

To date researchers have had a very poor mechanistic understanding of the microscopic processes at the semiconductor / liquid water interface because these are difficult to access experimentally and expensive to calculate computationally. The main goal of this research was therefore to understand the microscopic behaviour of water molecules at the interface using state-of-the-art ab initio molecular dynamics accelerated by machine learning.

#### Hematite/water interface

In the first part of the project, we investigated the hematite (001)/ water interface (Figure 1). Hematite ( $Fe_2O_3$ ) is one of the most abundant metal oxides on earth and is thus a very cheap material to use for photocatalysis. In our study, we used ARCHER2 to perform so-called "hybrid Density Functional Theory (DFT) calculations" to access the electronic structure. As such calculations are extremely computationally demanding, their application is limited. We therefore trained a machine learning model utilising active learning to replace these expensive calculations with a cheaper model, while keeping the accuracy of the underlying DFT calculations.

Using this machine learning model, we were able to perform extensive atomistic simulations of the hematite/water interface, where we identified the precise surface structure and the water layering at the interface. We furthermore quantified water dynamics and adsorption strengths at the interface, which were previously inaccessible. This research is currently continuing. Therein, we investigate the adsorption of an iron ion at the hematite interface. This will shed light on the biomineralization pathways of hematite and associated phenomena including interfacial electron transfer, polaron formation, dissolution kinetics, crystal growth and rust formation.

#### Bismuth vanadate/water interface

In the second part of the project, we went on to investigate the bismuth vanadate  $(BiVO_4)/liquid$  water interface illustrated in Figure 2.  $BiVO_4$  has shown remarkable efficiencies for photocatalytic water splitting in the lab. It is therefore interesting to understand how water behaves microscopically at the interface and how the surface chemistry differs compared to other interfaces, e.g. hematite.

Using ARCHER2, we computed the surface acidity in terms of the pK<sub>a</sub> value and the redox potential of the BiVO<sub>4</sub> crystal using thermodynamic integration. These values are crucial for the water splitting process at the interface, since they fully capture water dissociation. Thermodynamic integration is a technical procedure to calculate free energy differences between a reactant and a product state and is a highly expensive calculation; usually several million core-hours are required to calculate a single pKa value or redox potential.

To accelerate such calculations and to provide statistically accurate results, we again employed machine learning. On top, we developed a general simulation protocol to routinely and reliably calculate these properties for any kind of system. Remarkably, this novel simulation protocol also allows the straightforward computation of chains of reaction mechanisms (Figure 3) because we significantly reduce the training cost of the machine learning potential via active learning techniques. A publication presenting our novel simulation protocol is currently in preparation.

#### Conclusions

Our preliminary findings are that the neutral  $BiVO_4$  (010) interface features a pK<sub>a</sub> value of about 2, meaning that the water molecules do not dissociate at the interface if the water phase is pH neutral. Indeed, it is well known that the  $BiVO_4$  (010) facet is not covered by hydrogen atoms (see Figure 2), while the hematite interface is protonated (see Figure 1). Consequently, the surface adsorption behavior of water molecules at  $BiVO_4$  (010) is fundamentally different compared to hematite (001). Using the same technique, we show that the  $BiVO_4$  crystal is rather easily reduced by a potential of about 0.3V. After the reduction, a negative charge is present at the interface and consequently we find a larger pK<sub>a</sub> value of about 4. This implies that the reduced interface is protonated more easily compared to the neutral  $BiVO_4$  interface.

Our work on the BiVO<sub>4</sub>(010)/water interface showcased the application of an easy-to-use simulation protocol to reliably compute free energy differences and thus assess surface chemistry at such interfaces. We intend to publish all details about the protocol to ensure that it can be utilised by the scientific community. We aim to use the same protocol ourselves to further unveil surface chemistry of different oxides and different exposed surface cuts in the future. This might ultimately lead to a profound understanding of microscopic protonation states which would then help in the search for an efficient catalyst for water splitting, the latter being envisaged as a major source of "green" hydrogen.



**Figure 2:** Side view of the BiVO4/water interface (left), containing a protonated oxygen site (=OH) at the interface which is marked with a blue circle. View of liquid water (right) containing a hydronium ion (H<sub>3</sub>O<sup>+</sup>) marked by a blue circle. The pK<sub>3</sub> value captures the chemical equilibrium between the two species by quantifying their ratio at a given pH value of the liquid phase.

$$\equiv OH + H_2O \stackrel{pK_a}{\longleftrightarrow} \equiv O^- + H_3O^+ \quad \stackrel{U}{\longleftrightarrow} \equiv O + H_2O + \frac{1}{2}H_2$$
(1)  
$$\equiv O^+H + H_2O \stackrel{pK_a}{\longleftrightarrow} \equiv O + H_3O^+ \quad \stackrel{U}{\longleftrightarrow} \equiv O^+ + H_2O + \frac{1}{2}H_2$$
(2)

**Figure 3:** Chemical reactions at the interface, where  $\equiv \mathbf{O}$  denotes a surface oxygen site. The deprotonation reactions are quantified by the respective pK<sub>a</sub> value, while the redox reactions are quantified by their respective redox potential U. Note that the equations (1) and (2) differ by the net surface charge.



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#### **Reference:**

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