

# Functional solid/liquid interfaces for photocatalytic applications

## Designing the electrolyte/rutile TiO<sub>2</sub>(110) interface for water splitting

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### In Short

- Multiscale modeling using first-principles and molecular dynamics simulations of photocatalytic solid-liquid interfaces.
- Action of surface defects and surface charge on electrolyte double-layer structure and water dissociation.
- Long term: Formation of polarons and their propagation in the solid and the interface; action of light on water splitting.
- Direct comparison to core level photoelectron spectroscopy (PES) at BESSY.

Water splitting is one of the most promising processes within heterogeneous photocatalysis [1–4] and the focus of this project. Transition-metal oxides and semiconductors are common materials used as photocatalysts due to their unique characteristics.

Rutile TiO<sub>2</sub>(110) has become the prototypical oxide surface in surface science and its interaction with water a model system for the water-oxide interface [5]. Conclusive experimental evidence exists for the case of water dissociation on the TiO<sub>2</sub>(110) surface in the presence of oxygen vacancies and steps, but whether a water molecule is adsorbed as an intact molecule or in its dissociated state is still a highly debated issue [5]. There is a clear need of understanding the interaction of liquid water with TiO<sub>2</sub>(110) as model surface beyond the interaction at the single-molecule level for the systematic development of materials suitable for water-splitting applications. Furthermore, recent *ab-initio* MD (AIMD) simulation studies [6] indicate that the action of adsorbed ions and the electrolyte double layer on the interface (redox) potential and capacitance is substantial. Concerning ionic adsorption, the action of surface defects is essentially not understood.

Our project goal is, employing electronic-structure theory and statistical physics in a multiscale approach, to study the effects of the molecular structure and surface defects on the TiO<sub>2</sub>(110)/water interface at the microscopic scale and its influence on mesoscale phenomena such as ion adsorption, formation of the electric double layer, and resulting

potentials and capacitances. On a long term, this will be extended to study polarons and electrolyte-dependent water splitting under active photocatalytic conditions ('light on' vs 'light off' conditions) in close cooperation with our experimental partners at Helmholtz-Zentrum-Berlin (HZB).

We focus on the water splitting processes involved at the interface of liquid water in contact with *a*) the pristine TiO<sub>2</sub>(110) surface and *b*) the TiO<sub>2</sub>(110) surface including different oxygen vacancy concentrations. As a starting point, these systems have been studied by means of reactive molecular dynamics simulations by our collaborators at the University of Freiburg [7]. Our goal is to use these studies as an input and extend them across scales by including monovalent ions in solution using classical, non-reactive molecular dynamics (MD) simulations, but retaining atomistic resolution by bridging local structures to *ab-initio* MD and theoretical spectroscopic simulations; thus yielding relevant information across scales on the influence of vacancies and ions in the formation of the electric double layer (EDL) (see Figure 1).

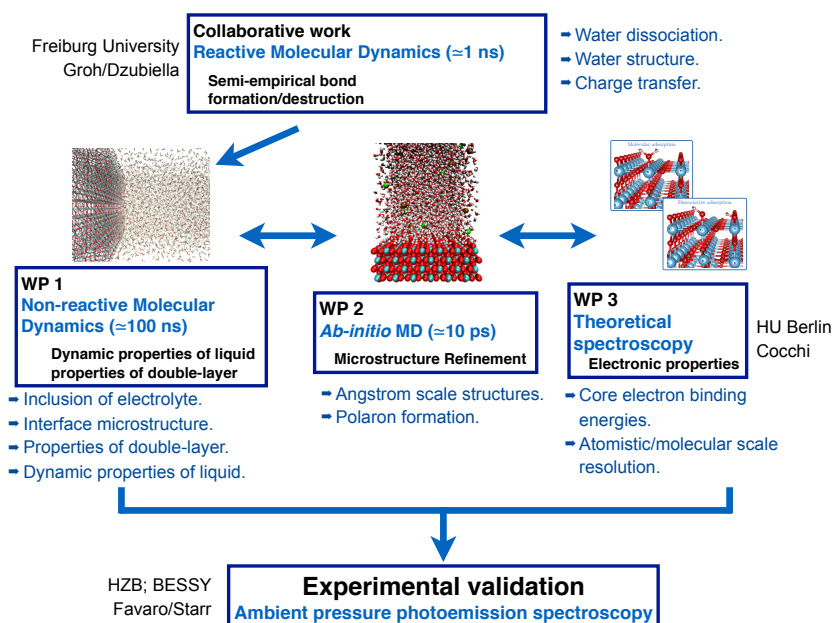
The complexity of solid-liquid interfaces calls for collaborative approaches in which theory and state-of-the-art computational simulations work hand in hand with modern experimental techniques. Ambient pressure photoelectron spectroscopy using soft and hard x-rays (AP-PES) is a recent novel experimental technique that can be used to study the solid-liquid interface in a fashion closely resembling the operation conditions of a functioning water-splitting device [8]. Our experimental partners at the Helmholtz-Zentrum Berlin (HZB) have implemented this experimental technique [8] for the study of solid-liquid interfaces in solar fuel cell applications.

By integrating our expertise in state-of-the-art atomistic simulations with experimental information and validation, our main goal is to achieve a realistic molecular-level description of the water/TiO<sub>2</sub> interface. Our long-term objective is not only to address fundamental molecular processes at this interface, but also to contribute in the development of a theoretical multiscale modeling strategy to study solid-liquid interfaces, hand-in-hand with our experimental partners.

### WWW

[https://www.helmholtz-berlin.de/forschung/oe/ee/simulation/index\\_en.html](https://www.helmholtz-berlin.de/forschung/oe/ee/simulation/index_en.html)

### More Information



**Figure 1:** Illustration of the multiscale modeling strategy. Different parts of the project are merged into three work packages (WPs). In WP 1 large-scale MD simulations ( $\approx 100$  ns) of the aqueous electrolyte, featuring specific site-adsorption and the double-layer, will be performed with input structures taken from reactive MD (REAXFF) from our collaboration partners, overcoming a limitation of non-reactive MD simulations, the inclusion of bond formation and bond breaking. The results can be integrated to electrostatic potentials and capacitances on hand, and on the other hand provide input structures for first-principles calculations in WP 2. In WP 2, DFT-based ab-initio MD simulations will be used for a refinement of local structures coming from structures taken from WP 1 ( $\approx 10$  ps). These refined structures are the input for WP 3, which consists in direct spectroscopic simulations, using DFT, of snapshots that are statistically representative of the processes modeled by the synergy among our joint work, WP 1, and WP 2. The results from WP 3 and their comparison to AP-PES experiments are essential to draw conclusions with atomistic/molecular resolution about the electrolyte-water/ $\text{TiO}_2$  interface.

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### Project Partners

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