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Connecting Interface Structure to Energy Level Alignment at Aqueous Semiconductor Interfaces

MARK HYBERTSEN, Center for Functional Nanomaterials, Brookhaven National Laboratory

Understanding structure-function relationships at aqueous semiconductor interfaces presents fundamental challenges, including the discovery of the key interface structure motifs themselves. Important examples include the alignment of electrochemical redox levels with the semiconductor band edges and the identification of catalytic active sites. We have developed a multistep approach, initially demonstrated for GaN, ZnO and their alloys, motivated by measured high efficiency for photocatalytic water oxidation. The interface structure is simulated using ab initio molecular dynamics (AIMD).[1] The calculated, average interface dipole is combined with the GW approach from many-body perturbation theory to calculate the energy level alignment between the semiconductor band edges and the centroid of the occupied 1b1 energy level of water and thus, the electrochemical levels.[2] Cluster models are used to study reaction pathways.[3] The emergent interface motif is the full (GaN) or partial (ZnO) dissociated interface water layer.

Here I will focus on the aqueous interfaces to the stable TiO_2 anatase (101) and rutile (110) facets. The AIMD calculations reveal interface water dissociation and reassociation processes through distinct pathways: one direct at the interface and the other via a spectator water molecule from the hydration layer. Comparisons between the two interfaces shows that the energy landscape for these pathways depends on the local hydrogen bonding patterns and the interplay with the interface template. Combined results from different initial conditions and AIMD temperatures demonstrate a partially dissociated interface water layer in both cases. Specifically for rutile, structure and the GW-based analysis of the interface energy level alignment agree with experiment. Finally, hole localization at different interface structure motifs will be discussed.

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[3]M. Z. Ertem, et al., *ACS Catal.* 5, 2317 (2015)