

pH-dependent surface chemistry and catalytic reaction pathway from first-principles

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We present a theoretical formulation for studying the pH-dependent interfacial coverage of semiconductor-water interfaces through *ab initio* electronic-structure calculations, molecular dynamics simulations, and the thermodynamic integration method [1]. This general methodology allows one to calculate the acidity of the individual adsorption sites on the surface and, consequently, the pH at the point of zero charge, pH_{PZC} , and the preferential adsorption mode of water molecules, either molecular or dissociative, at the semiconductor-water interface. The proposed method is applied to study the $\text{BiVO}_4(010)$ -water interface and yields a pH_{PZC} in excellent agreement with the experimental characterization. Furthermore, from the calculated $\text{p}K_a$ values of the individual adsorption sites, we construct an *ab initio* concentration diagram of all the adsorbed species at the interface as a function of the pH of the aqueous solution. The diagram clearly illustrates the pH-dependent coverage of the surface and indicates that protons are found to be significantly adsorbed only in highly acidic conditions. The surface is found to be mostly covered by molecularly adsorbed water molecules in a wide interval of pH values ranging from 2 to 8. Hydroxyl ions are identified as the dominant adsorbed species at pH larger than 8.2. The achieved results are used in conjunction with the band alignment at the $\text{BiVO}_4(010)$ -water interface, in order to study the pH-dependent catalytic reaction pathway for water splitting [2]. In fact, we align the band edges of BiVO_4 at the interface with liquid water by combining electronic-structure calculations, molecular dynamics simulations, and a computational hydrogen electrode [3,4]. We demonstrate that the sizable band gap renormalization of this material [5] induced by spin-orbit coupling, thermal and nuclear quantum motion effects, has to be considered to achieve an accurate band alignment. In particular, we find that one-shot *GW* calculations and semi-empirically tuned hybrid functionals provide the closest agreement with the experiment. Then, we combine the band alignment calculated at the pH corresponding to the point of zero charge, the $\text{p}K_a$ of water molecules adsorbed on the BiVO_4 surface, and the redox levels associated with the first step of the water oxidation reaction, in order to discuss the pH-dependent mechanism of the heterogeneous water oxidation reaction. Our results indicate that the mechanism of water splitting in acidic conditions dominates the reaction over a large range of pH values. In contrast, the kinetically more favourable oxidation of hydroxyl ions is found to be strongly favoured only in highly alkaline conditions, for which, however, corrosion phenomena take place. We also remark that the use of advanced electronic-structure methods is critical, as results achieved at the semilocal level give an erroneous physical picture.

References:

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