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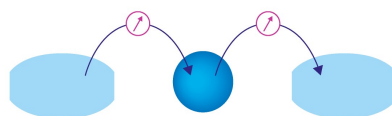
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ABSTRACT

Titanium dioxide in the anatase configuration plays an increasingly important role in photo(electro)catalytic applications due to its superior electronic properties when compared to rutile. In aqueous environments, the surface chemistry and energetic band positions upon contact with water determine charge-transfer processes over solid–solid or solid–electrolyte interfaces. Here, we study the interaction of anatase (001) and (101) surfaces with water and the resulting energetic alignment by means of hybrid density functional theory. While the alignment of band positions favors charge-transfer processes between the two facets for the pristine surfaces, we find the magnitude of this underlying driving force to crucially depend on the water coverage and the degree of dissociation. It can be largely alleviated for intermediate water coverages. Surface states and their passivation by dissociatively adsorbed water play an important role here. Our results suggest that anatase band positions can be controlled over a range of almost 1 eV via its surface chemistry.

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I. INTRODUCTION

Titania (TiO₂) is one of the most prominent materials in (electro)catalysis, notably in the function as a photocatalyst or protection layer for solar water splitting.^{1,2} Here, the application case crucially depends on the energetic alignment of the bands with respect to the electrolyte or the underlying photoabsorber. Furthermore, titanium dioxide is the model system par excellence for a wide-gap metal-oxide to study the electronic properties of a semiconductor in contact with water, both experimentally^{3–5} and theoretically,^{4,6–16} hereby also playing an important role in method development and validation.

Anatase is, though metastable, considered the more interesting polymorph of TiO₂ for photocatalysis as it exhibits superior electronic properties, manifested in longer charge-carrier lifetimes when compared to rutile.¹⁷ In a density functional theory (DFT)-based molecular dynamics study, evidence was found for

a trapping mechanism of excess electrons on the anatase (101) surface, whereas the (001) surface acts as a hole acceptor.¹² Experimentally, photoelectron spectroscopy at differently treated (101) and (001) surfaces of single crystals evidenced a band offset favoring electron migration to the (101) facets, whose magnitude depends on prior sample treatment.^{18,19} Such a driving force could help in improving the catalytic activity of TiO₂ nanoparticles or improve the charge-transport over hetero-interfaces for TiO₂-based protection layers. A key question, to be addressed in this study, is to what extent the contact with water modifies this surface electronic structure behavior.

In this work, we have considered the (101) and (001) surfaces of anatase, as illustrated in Fig. 1. The (101) surface is characterized by a ridge-like structure with every second titanium atom being coordinatively saturated and buried in the trenches of the surface steps. The other half entails a five-fold coordination, exposing one free coordination site that can function as an anchoring point for

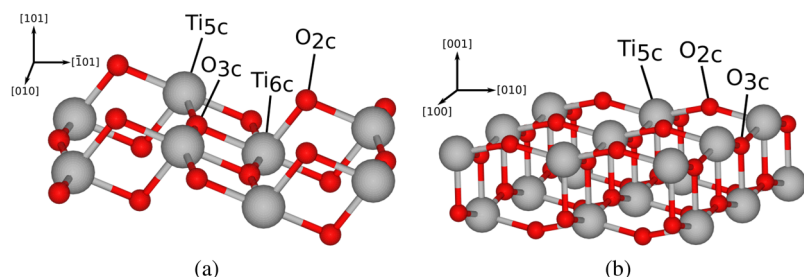


FIG. 1. Ball-and-stick models of the atomic upper layers for the considered anatase surfaces: (a) (101) and (b) (001).

adsorbate molecules. In contrast, all titanium and half of the oxygen atoms constituting the (001) surface are coordinatively unsaturated, with the uppermost oxygen atoms bearing large bond angles of around 150° . The high degree of unsaturation and the strained bonding situation lead to the well-known increased reactivity of this surface. It can undergo reconstruction under ultra-high vacuum conditions,²⁰ yet also the unreconstructed surface has been observed.¹⁹ As adsorption of water prevents reconstruction in an aqueous environment,^{21,22} the slab models employed in this work correspond to the unreconstructed surface.

Experimental and theoretical work on the initial water layer in contact with anatase surfaces found a mixture of dissociative and molecular adsorption, with temperatures beyond 120 K initiating dissociation on (101) surfaces.⁵ Furthermore, intermediate water coverages are believed to lower the dissociation barrier.²³ Slow adsorption at low temperatures can, however, result in the formation of an ordered, full coverage of molecular water.⁵ A detailed insight into the interplay between surface chemistry and surface electronic states is required to understand the interfacial energetic alignment between the solid and the electrolyte, as well as different facets of anatase (nano)crystals.

Here, we present electronic structure calculations of titanium dioxide surfaces in the anatase structure, investigating the energetic band alignment with and without (fractional) water coverage. We find that facet-driven charge-carrier separation is favored in a static picture by a band offset. However, band positions can be modified significantly through the adsorption of water. The magnitude of the surface chemistry-induced shifts of the band levels depends on the coverage and degree of dissociation and can be in the order of up to 1 eV.

II. METHODS

We performed DFT electronic ground state calculations with the CP2K code,²⁴ employing the Gaussian-and-plane-wave scheme with Goedecker–Teter–Hutter (GTH) pseudopotentials. The Gaussian basis sets were of double- ζ quality,²⁵ and an energetic cutoff of 600 Ry was used. Initial optimizations of our slabs were carried out within the generalized gradient approach (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional.^{26,27} The resulting structures were then subjected to further relaxation with the Heyd–Scuseria–Ernzerhof hybrid functional (HSE06), using the auxiliary density matrix method as implemented in CP2K.^{28,29} In the subsequent hybrid functional optimizations, all atoms were allowed to relax further, while keeping the cell sizes fixed at the PBE-calculated

values. Total energies were evaluated at the Γ -point. For the (001) surface, the in-plane dimensions of our model systems comprised four unit cells in the x - and y -direction, extending 15.08 Å in each direction. The (101) surface was modeled by supercells composed of one unit cell in the x - and three in the y -direction, corresponding to the dimensions of 10.26 Å and 11.31 Å, respectively. The slabs were separated by 20 Å of vacuum along the z -direction. No constraints on atomic positions were applied, and the full slabs were allowed to relax. For the geometry optimizations, we first optimized the crystal structures in vacuum, with, in the case of the water-covered surfaces, a subsequent further relaxation after addition of 0.25 [in the case of the (001) surface], 0.5, or 1.0 monolayers (ML) of water. Water molecules were initially positioned on the surfaces in a way to facilitate coordination of the oxygen atoms to the under-coordinated titanium atoms and to allow for hydrogen bonding with the surface oxygen atoms.^{30,31} Based on full ML coverage, removal of certain water molecules resulting in high-symmetry overstructures provided starting points for optimizations with sub-ML coverages. Additionally, we varied the number of Ti-layers along the z -direction between 8 and 20 to investigate the bandgap convergence and to confirm the absence of any intrinsic dipole of the surfaces. For these considerations, we applied the PBE functional and, in the case of the (001) surface, a smaller 3×3 supercell. The presented surface structures, bandgap values, adsorption energies, heats of formation, and partial density of states (PDOS) were obtained using slabs with 20 Ti-layers in the z -direction and the HSE06 hybrid functional. These structures were chosen to be in a well-converged regime for band positions and energy gaps, as confirmed beforehand.

III. RESULTS AND DISCUSSION

The main structures resulting from our geometry optimizations for the different water coverages are shown in Figs. 2 and 3 and in the [supplementary material](#), Figs. 1 and 2. Irrespective of the coverage, we obtain only molecular adsorption on the (101) surface. This is consistent with previous reports,³¹ in which molecular adsorption was identified as energetically favorable over dissociative adsorption. In the resulting structures, the water molecules are coordinated to the surface titanium atoms, and hydrogen bonds to the surface oxygen atoms are formed.

For full ML coverage on the (001) surface, on the other hand, we observe partial dissociation, as shown in Fig. 3(a). The resulting structure is similar to a previously reported result,⁷ in which adsorption of 1 ML of water on the (001) surface led to the dissociation

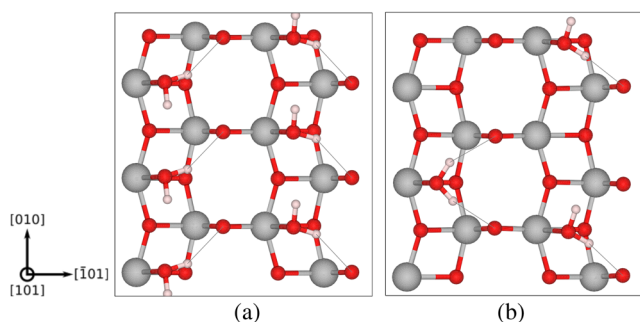


FIG. 2. Top view of water adsorbed on the (101) surface, with one (a) and half a monolayer (b) coverage. Hydrogen bonds are represented as thin gray lines.

of one quarter of the water molecules. The remaining molecularly adsorbed water forms complex networks of hydrogen bonds, also including surface oxygen atoms. This structure was obtained after application of the HSE06 hybrid functional, whereas the initial optimization with PBE resulted in an ordered, fully non-dissociated, adsorbed layer of water. For half ML coverage, we observe mixed molecular and dissociative adsorption [Fig. 3(b)], while quarter ML coverage led to fully dissociative adsorption [Fig. 3(c)]. In both of these cases, the resulting total number of surface hydroxyl groups is the same. Dissociative water adsorption presents an energetically favorable process, as it alleviates some of the strain caused by the large bond angles around the oxygen atoms present in the pristine surface. The final structures are further stabilized by hydrogen bonds between the surface hydroxyl groups, if present, also including the molecularly adsorbed water. Interestingly, the geometric motif around the pairs of surface hydroxyl groups shows a close similarity to the common 1×4 reconstruction of the pristine (001) surface, as previously reported.⁷

Mixed dissociative adsorption of water on the (001) surface allows for the formation of various geometrically distinct final structures, differing in the relative positioning of the resulting surface hydroxyl groups. While we have not realized an extensive search over these geometrically distinct structures, we have considered various representative examples for each water coverage. We found their

TABLE I. Heat of formation energies (per surface unit cell) and adsorption energies (per water molecule). Different degrees of dissociation are labeled as: fd: fully dissociated, pd: partially dissociated, and ud: undissociated.

Water coverage (ML)	E_{ads} (eV)	ΔH_f (eV)
(001) surface		
0.25 fd	−2.34	−0.35
0.25 pd	−1.92	−0.25
0.5 pd	−1.43	−0.25
1.0 pd	−0.94	0.00
(101) surface		
0.5	−0.77	−0.04
1.0	−0.73	0.00

differences in relative stability, water adsorption energy, and electronic structure to be negligible. Experimentally, we expect them, in principle, to be distinguishable by surface-sensitive methods, such as low-energy electron diffraction. However, for real surfaces at finite temperatures, different superstructures might coexist.

To assess the stability and likelihood of actual occurrence, we calculated the heat of formation energies, $\Delta H_f(\theta)$, and adsorption energies, E_{ads} , as a function of the coverage, θ . The resulting values per (1×1) surface unit cell are listed in Table I for different coverages and different degrees of dissociation. The heat of formation energy as a measure for relative stability is obtained from the total energies, E^{tot} , neglecting the pV term and vibrational energies,³² as follows:

$$\Delta H_f(\theta) = E^{tot}(\theta) - E^{tot}(0) - \theta[E^{tot}(1) - E^{tot}(0)]. \quad (1)$$

Adsorption energies per water molecule were calculated as

$$E_{ads} \cdot n_{H_2O} = E^{tot}(\theta) - [E^{tot}(0) + n_{H_2O} \cdot (E_{H_2O,g}^{tot})], \quad (2)$$

with the total energy of a single gas-phase water molecule, $E_{H_2O,g}^{tot}$, and the number of water molecules, n_{H_2O} . In general, our values of the adsorption energies show a similar trend to that reported in the

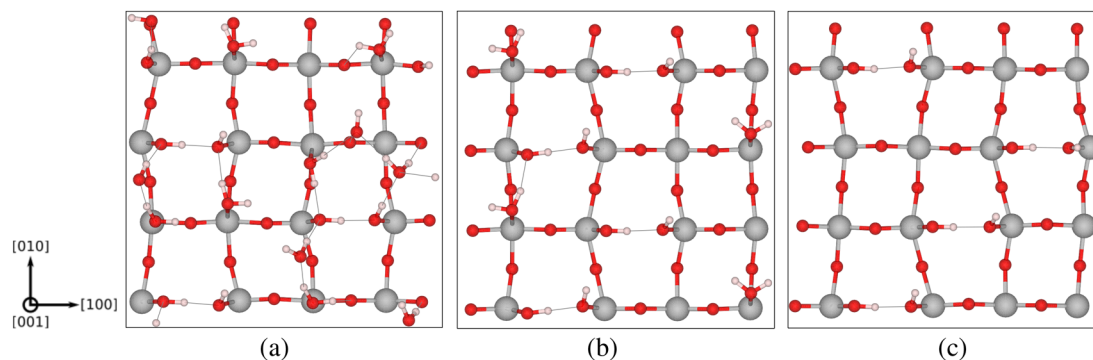


FIG. 3. Top view of mixed (a) 1ML, (b) 1/2, and (c) 1/4 ML water adsorption on the (001) surface from different water coverages: (a) 1 ML, (b) $\frac{1}{2}$ ML, and (c) $\frac{1}{4}$ ML.

literature.^{22,31} For the (001) surface, the most favorable structure at a quarter of a ML is a fully dissociated adsorption of water molecules, while for 0.5 ML, half of the water molecules stay intact, leading to a comparable heat of formation.

Density of states for the (001) surface with different water coverages are shown in Fig. 4. It should be noted that the seemingly large magnitude of the bandgaps is due to the fact that the lowest unoccupied states are too small to be visible in this representation. However, they lie in fact about 3.2–3.6 eV above the valence band maximum, as expected. Analysis of the density of states shows that the pristine (001) surface exhibits an occupied Ti-related surface state in the bandgap region close to the valence band maximum, which reduces the effective bandgap. It can be seen in Fig. 4(a) and is clearly visible in the local density of states of the very top Ti–O layer (supplementary material, Fig. 3). This occupied surface state leads to a charge redistribution between surface and bulk, hereby contributing to the shift of band positions (see below). However, dissociative adsorption of water causes the disappearance or a “passivation” of this state, as can be seen in Figs. 4(b) and 4(c). For the (101) surface, this state is absent, resulting in virtually unchanged Ti-related valence band features and a constant bandgap.

This is similar to the experimental photoelectron spectroscopy results of Kashiwaya *et al.*¹⁸ Their study on differently prepared

single crystals of anatase with x-ray and ultraviolet photoemission in vacuum found occupied surface states slightly above the bulk valence band maximum for the (001) surface that can be—apart from a shallow valence band surface state—largely suppressed by dedicated sputter-annealing routines followed by reoxidation. Their (001) surface without reoxidation still comprises a deep bandgap state very close to the middle of the bandgap. Though they consider this type of surface “stoichiometric,” our results show that the occupied surface state for the pristine (001) surface is very close to the highest occupied bulk states. Consequently, the signatures of their “oxidized” surface are closer to the pristine, unreconstructed surface. In the case of the (101) surface, the “stoichiometric” samples would indeed correspond to the pristine configuration, which means that the annealing procedure creates oxygen vacancies that have to be cured by dedicated oxidation.

The bandgaps of the different structures are presented in Fig. 5. These were obtained by taking the difference between the conduction band minimum (CBM) and the valence band maximum (VBM) for each system. As expected, the gaps for the (101) surface are with 3.64 eV largest and virtually unaffected by water in the vicinity of the surface. This value represents the well-known, slight overestimation of HSE06 in comparison to the experimental bandgap.³³ The picture for the (001) surface is, however, a completely different one. The pristine, unreconstructed surface shows a reduced gap of 3.24 eV,

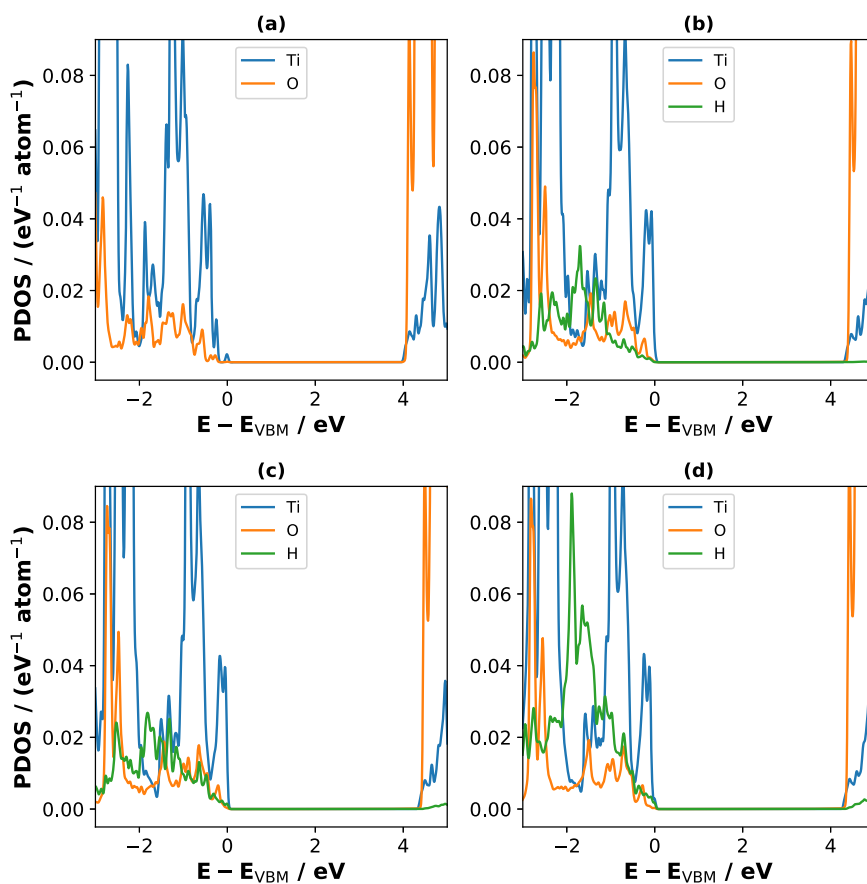


FIG. 4. Partial density of states (PDOS) for the lowest-energy (001) surfaces: (a) without water, (b) with a quarter ML of fully dissociated water, (c) with half a ML of partially dissociated, and (d) with a full ML of partially dissociated water. Energies are referred to the valence band maximum, E_{VBM} .

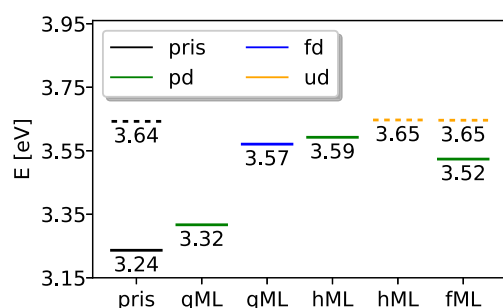


FIG. 5. Bandgaps for (001) and (101) surfaces of anatase, represented as solid and dashed lines, respectively. Different degrees of water dissociation are indicated by different coloring.

which can be attributed to the previously discussed surface state. The bandgap continuously increases with the number of dissociatively adsorbed water molecules. While partial dissociation of a quarter ML yields a value of 3.32 eV, about 80 meV above the gap of the pristine surface, fully dissociative adsorption causes a strong increase to 3.57 eV, over 330 meV above the pristine surface. In the case of partial dissociation of half a ML of water, the total concentration of the surface hydroxyl group is the same. Thus, the bandgap for this system is with 3.59 eV nearly identical. These values almost reach the bandgap magnitude of the (101) surface.

More relevant for charge-transfer processes between crystal facets or to electrolytes are, however, the relative and absolute energetic positions of valence and conduction bands. To obtain the absolute energetic positions of the VBM and CBM, we subtracted the Hartree potential in the vacuum region, projected onto the z axis, from the HOMO and LUMO energies of the DFT calculations. This referencing has initially no physical meaning in a 3D periodic calculation. However, as the vacuum level of the Hartree potential is dependent on the crystal-to-vacuum ratio, it converges to a specific value with the number of layers (not shown here). Thus, the dependency on the number of layers in the crystal—keeping the amount of vacuum fixed—cancels, and the obtained values quickly converge with the slab thickness.

Figure 6 shows the resulting band positions with respect to the Hartree potential in vacuum for each system. For the pristine surfaces, the CBM of the (101) surface lies 600 meV lower than for the (001) surface. With a value of 1 eV, this difference is even more pronounced for the VBM. In a nanocrystal, where both surfaces can be present on different facets, the band position difference of the two facets represents an intrinsic driving force for electron-hole separation after photoexcitation.¹² The hole should be more stable in the (001) system, whereas the electrons will be trapped in the lower energy levels of the (101) conduction band. However, we find that the electronic structures of the surfaces exposed by such a nanocrystal can be influenced considerably by the presence of water. While dissociative adsorption on the (001) surface mainly causes a decrease of the VBM level, molecular adsorption on both surfaces leads to an almost linear increase of both band positions. This is especially evident in the case of the (101) surface, where the band levels for the fully covered surface lie about 1.3 eV higher than for the pristine surface. The resulting position of the CBM at -3.75 eV, as compared

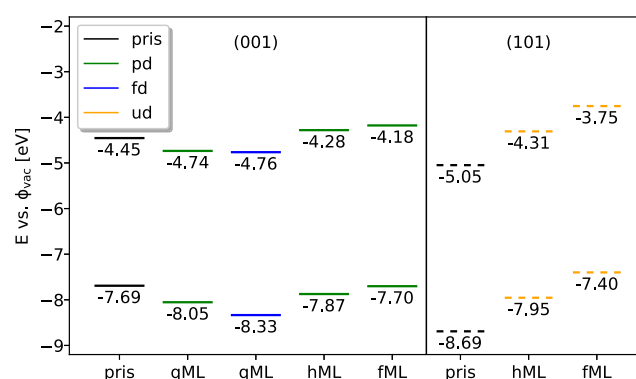


FIG. 6. Band positions for (001) and (101) surfaces of anatase. VBM and CBM levels are represented as solid and dashed lines, respectively.

to a value of -4.02 eV for the fully covered (001) surface, suggests a higher stability of electrons in the (001) surface. This stands in contrast to the previously mentioned trapping of electrons at the (101) facets. Similarly, coverage of half a ML of water causes the band positions of both surfaces to approach values of about -7.9 eV (VBM) and -4.3 eV (CBM), again reducing the driving force for electron-hole separation. Comparison of different coverages and degrees of dissociation for both surfaces, however, shows that the intrinsic band level differences between the two surfaces can also be further increased. For instance, full ML coverage on the (001) surface leads to an overall increase of band positions and therefore enhances the band level differences to the pristine (101) surface. This should in turn further improve the efficiency of electron-hole separation after photoexcitation.

Our findings are in good agreement with the results of Kashiwaya *et al.*,¹⁸ who found a difference in CBM levels of 150–450 meV. Their values for the Fermi level position and VBM are based on photoemission experiments, but as photoemission accesses only occupied states, they had to derive their CBM from an otherwise determined bulk bandgap. The Fermi level position in a DFT calculation of a semiconductor is, on the other hand, not very physical and placed on top of the highest occupied state here, so it cannot be compared to the experimental values. This shows that experimental band positions from photoelectron spectroscopy (PES) in vacuum with potentially only partial coverages are expected to deviate significantly from measurements of fully immersed surfaces or from ambient-pressure PES, where thin water layers are conserved. For molecular dynamics simulations, where timescales are often too short to account for surface chemical reactions, the large band position difference would, in combination with limited slab sizes, lead to large fluctuations in the band positions over time. This has indeed been observed by Guo *et al.*,¹⁴ where they could not identify a single final model for anatase TiO_2 from the MD simulations alone, albeit already for the (101) surface. Our results suggest that the situation for the (001) surface is even more challenging.

IV. CONCLUSION

Our investigations into the (101) and (001) surfaces of anatase in contact with water reveal a rich surface chemistry of anatase,

especially in the case of the (001) surface. For both surfaces, we identify considerable variations in the electronic structures and the resulting band levels that depend on the water coverage and the degree of dissociation. These variations can both improve and diminish the performance of anatase nanocrystals as photocatalysts, by modifying the relative band alignment as underlying driving force for electron–hole separation. Analysis of the density of states for the different structures allowed us to identify an occupied, Ti-related surface state for the (001) surface. Its passivation by dissociative adsorption of water plays a crucial role in the observed band level variations. Our results suggest that, especially for the (001) surface, a wide tuning of the band positions and hence charge-transfer properties for both solid–solid and solid–electrolyte interfaces should be possible by specifically conserving or passivating surface states. Preferential formation of {001} facets can be facilitated in the presence of fluorine ions.³⁴ The combination with subsequent, selective underpotential deposition³⁵ of different catalysts or not covalently bonded passivation layers, such as graphene (oxide), could then, in principle, allow for the control of relative band positions. Alternatively, physical methods, such as a combination of annealing and oxidation steps, can be used to fine-tune the density of surface states¹⁸ and, consequently, also band positions. We expect such modifications to allow for considerable improvements on the performance of anatase-based photocatalysts.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for different views of the relaxed structures as well as local density of states for the topmost layer of the bare (001) surface.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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