A first-principles computational comparison of the aqueous anatase TiO$_2$ (001) interface and the disordered, fluorinated TiO$_2$ interface

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Chemical doping and other surface modifications have been used to engineer the bulk properties of materials, but their influence on the surface structure and consequently the surface chemistry are often unknown. Previous work has been successful in fluorinating anatase TiO$_2$ with charge balance achieved via the introduction of Ti vacancies rather than the reduction of Ti. Our work here investigates the interface between this fluorinated titanate with cationic vacancies and a monolayer of water via density functional theory based molecular dynamics. We compute the projected density of states for only those atoms at the interface and for those states that fall within 1eV of the Fermi energy for various steps throughout the simulation, and we determine that the variation in this representation of the density of states serves as a reasonable tool to anticipate where surfaces are most likely to be reactive. In particular, we conclude that water dissociation at the surface is the main mechanism that influences the anatase (001) surface whereas the change in the density of states at the surface of the fluorinated structure is influenced primarily through the adsorption of water molecules at the surface.

TOC GRAPHICS

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Investigating clean energy systems is becoming increasingly important in order to address future energy and environmental demands. Hydrogen generation from liquid water and sunlight at catalytic interfaces is a promising approach to generate large volumes of carbon-free chemical fuels that can be used in photo-electrochemical cells (PECs).\textsuperscript{1–3} This process of water splitting was first demonstrated by Fujishima and Honda in their work with aqueous rutile titanium dioxide (TiO$_2$) interface.\textsuperscript{4} Despite successfully splitting water, the quantum efficiency remains low, and photoreactivity on other surfaces of other polymorphs (e.g. anataste and brookite) suggest that remaining challenges associated with the rutile structure may be better understood or eliminated by investigating these other TiO$_2$ surfaces to split water.\textsuperscript{5}

One such challenge is the optical bandgap of the material. Electron-hole pairs generated following photoabsorption migrate to the material’s surface and are the species that ultimately drive the photocatalytic reactions. The size of a material’s bandgap therefore limits the amount of the solar spectrum that can be absorbed by the material, and consequently the number of electron-hole pairs that can be generated. Thus, one approach to improving the photocatalytic efficiency of a material is to reduce the optical bandgap, often via chemical doping. This approach has been used widely in semiconductor physics to influence carrier concentrations and energetics, and in particular, this approach is useful to influence the material’s bandgap.\textsuperscript{6,7}

Physical processes in photocatalysis occur at the surface, and thus while the bulk properties play a key role in the initial step of photoabsorption, examining only the bulk properties of the material will fall short of capturing the essential physics at the interface that drives the catalysis. Moreover, the electronic structure is sensitive to the surface structure and termination. The position and character of the band edges, for example, are sensitive to the surface structure, composition and termination.\textsuperscript{8} This complex relationship of surface structure and composition
makes it less obvious which substitutions and subsequent reconstructions of the surface may lead to an increased photocatalytic activity. This relationship between surface structure and the dynamics of liquid water has been studied for the pristine rutile TiO$_2$(001) surface by Michaelides et al. who concluded that the distinct layers of water with differing dynamics can be generated as a result of interactions with the varying features of the surface (e.g. bridging oxygen atoms, five-fold coordinated Ti sites, etc.).

Amongst the many polymorphs of TiO$_2$, rutile and anatase have been the most extensively studied for use in photocatalytic water splitting. In the case of anatase, the (101) has been shown to be the majority surface in anatase nanoparticles. In this work, however, we investigate the anatase TiO$_2$ (001) surface. Unlike rutile TiO$_2$ (110) surface and anatase (101), less is known about how water behaves at the anatase (001) surface. While the surface energy of this surface is larger than that of the (101), we investigate this (001) because of its reported greater photocatalytic activity. Additionally, this surface has been known to become more exposed following fluorination. Fluorination of anatase has commonly been a means to stabilize the surface during synthesis, but these approaches often stabilize the (001) via surface interactions rather than becoming incorporated into the anatase lattice which is less understood. Previously, work investigating the influence of fluorine doping in titanium suggested that the presence of fluorine atoms led to the reduction of Ti$^{4+}$ to Ti$^{3+}$. Contrary to this study, another material that incorporates fluorine into the lattice was recently synthesized where cationic vacancies are incorporated in the lattice to balance the additional charge of the fluorine dopant atoms. This alternative mechanism for the incorporation of fluorine atoms into the lattice likely has a significant impact on the surface of the fluorinated titanate and therefore the chemistry that may occur at the surface. In order to explore the implications of cationic vacancies at the surface,
we begin our investigation from another theoretical work performed by Corradini et al.\textsuperscript{20} who proposed a possible atomistic structure for the bulk fluorinated titanate which was corroborated via synchrotron data on the experimental material. The material synthesized in the previous work showed roughly 25\% vacancies. From their result, it was clear that the fluorination led to a greater amount of structural disorder in the material. In part, this distortion to the lattice was due to the introduction of titanium vacancies required to maintain charge balance: every four oxygens that are substituted by fluorine must also be accompanied by a titanium(IV) vacancy. While the general structure of the anatase is identifiable, the large number of vacancies generate a noticeable amount of disorder in the system. Moreover, the slight mismatch in the Ti-O and Ti-F bond lengths (~1.8Å and ~2.0Å respectively) lead to an additional contribution to the distortion of the overall structure. These structural differences between the pure and fluorinate anatase exist throughout their simulation cell, and thus the surface of the fluorinated titanate also show a greater variation in both the structural arrangement of atoms as well as the chemical composition.

Ultimately, the proposed structure for this work is one for the bulk material, however, and it remains unclear what the interfacial structure and the surface termination might be (i.e. the role of new elements and defects). It is the aim of this work, therefore, to provide greater insight into the nature of the fluorinated anatase surface and how the variation in the surface in both terms of chemistry and structure can influence the reactivity and chemical nature of the surface. For comparison, we will use the anatase (001) as a reference interface. We will systematically explore these two surfaces by considering the electronic structure of the interface of each material with vacuum and then later with a monolayer of water molecules.
Electronic structure of the vacuum interface.

The slabs of each material were constructed and centered along the z-axis of the simulation cell in order produce two different surfaces in which to investigate. To construct the simulation cell for the pure anatase, the coordinates and lattice parameters for anatase TiO$_2$ were taken from experiment, and a 3 x 3 x 2 supercell was constructed. The supercell was then cleaved on both the top and bottom (z-direction) of the cell such that the (001) surface as exposed and leaving the rows of 2-fold coordinated oxygens intact and coordinating the layer of Ti atoms adjacent to them. It is known from previous studies of the (001) surface that it is these oxygens that play the dominant role in the surface reaction with water.\textsuperscript{21} The slab was then centered in the z-direction of the simulation cell with approximately 12.5 Å of vacuum above and below the slab for a final simulation cell size of 11.3535 Å x 11.3535Å x 32.500Å. The simulation cell for the fluorinated TiO$_2$ was constructed by starting with the structure proposed by Corradini et al. This proposed structure was derived from a 4 x 4 x 2 supercell and represents the likely structure of the fluorinated anatase in bulk. Despite the different elemental composition and the presence of vacancies in the material, the proposed relaxed structure generally resembles anatase. It is, therefore, still possible to identify and to cleave the surface at the (001) surface. Again, the slab was centered in the simulation cell and a vacuum of ~10Å was added above and below for a final simulation cell size of 15.078Å x 15.078Å x 30.00Å. It should be noted that because of the disorder in the material, the plane through which the material is cleaved changes the exposed surface and consequently influences the relative numbers of interfacial oxygens and fluorine atoms as well as the number cationic vacancies. The atoms shown in Figure 1 represent only the top-most layers.
During the simulations, the layers of both oxygen and titanium atoms in the center of the slab were frozen to keep the slab from drifting during the simulation as well as to approximate the more rigid mechanical properties of the bulk material away from the surface. In the case of the pure anatase, it is clear that the surfaces (Figure 1a and 1c) resemble one another due to the periodicity of the material. On the other hand, the advantage of constructing the cell in this way when we compare the two fluorinate surfaces (Figure 1b and 1d) is clearer. The final decision of where to cleave the bulk structure was decided in an effort to generate the greatest variety in local environments at the fluorinated surfaces. One feature that is clear from these surfaces is the presence of cationic vacancies at the surface. This creates areas of the surface that are under-coordinated. The variation in the local chemical environment (i.e. Ti atoms surrounded by oxygen or fluorine) is also apparent when comparing the upper and lower slab surfaces. This variation provides us more insight into the nature of the fluorinated surface and thus how this variation influences its chemical reactivity.
**Figure 1.** The interfacial atoms for the two (001) surfaces of simulated pure anatase (a,c) and the fluorinated anatase (b,d) slabs. Titanium atoms are shown in pink, oxygen atoms in red and fluorine atoms in teal.

In this work, we are particularly interested in the interfacial electronic structure and its response when exposed to solvent molecules. While there are many computational tools to characterize a material’s surface at the vacuum, there is less consensus on the best way to characterize a material’s surface when exposed to solvent molecules at the interface.

We, therefore, propose an approach which investigates the electronic structure of the surface by constructing a two-dimensional map of the density of states that corresponds only to those contributions from surface atoms. Not only does this approach give us some spatial resolution (e.g. atoms within a cutoff depth normal to the interface), but we also have the ability to identify contributions from specific elements. Moreover, given our interest in the reactivity of the
surface, we also seek a tool that allows us to visualize only certain electronic states within a particular energy range, namely those states that fall at the band edges.

Atomic orbital projection\textsuperscript{22} is a well-known approach used to decompose electronic wavefunctions to understand the contributions from the hydrogenic wavefunctions corresponding to each of the atoms in the system. Assuming that the projection is able to account for a majority of the electron density (i.e. limiting electronic spilling), the projection of Kohn-Sham (KS) wave functions onto atomic orbitals can help to achieve our first goal of being able to partition and select for contributions from individual atoms. To achieve the energy selectivity, we project only those KS-wavefunctions that have corresponding eigenvalues that fall within an energy range of our choosing, here within 1 eV of the Fermi energy. This approach can be formalized with the expression below,

\[
I(i, \varepsilon_l, \varepsilon_u) = \sum_{l}^{\varepsilon_k<\varepsilon_u} \sum_{\varepsilon_k>\varepsilon_l} |\Phi_i\rangle \langle \Phi_i | \varphi_k = \sum_{l}^{\varepsilon_k<\varepsilon_u} \sum_{\varepsilon_k>\varepsilon_l} c_{ik} |\Phi_i\rangle
\]

Where \( \varphi^k \) are the Kohn-Sham wave functions with corresponding eigenvalues, \( \varepsilon_k \), that fall within the energy range set by the lower (\( \varepsilon_l \)) and upper (\( \varepsilon_u \)) energy bounds. \( \Phi_i \) represents the subset of atomic orbitals that correspond to those atoms \( i \) that fall within the region of space that is of interest. The result of this expression, \( I \), is a measure of the contribution from an individual atom to the total density of states. We visualize the result as \( I^2 \) which due to the orthonormality of the atomic orbital basis becomes the sum of \( |c_{ik}|^2 = c_{ik}^* c_{ik} \).

As is true in our case, we are interested in a two-dimensional region of atoms (or a three-dimensional region with a shallow depth) of the simulation cell, and so we visualize this value of
$I$ as a two-dimensional plot by mapping the atom index $i$ to its corresponding coordinates $(x_i, y_i)$.

**Interfacial Density of States: TiO$_2$-Vacuum Interface**

To characterize each surface interfaces with the vacuum, we perform a density functional theory (DFT) calculation (see Computational Methods) to determine the ground state electronic structure. The two-dimensional plot of the density of states can be seen in Figure 2 for which we show only one of the two layers for each slab for and electronic states that fall 1eV below the computed Fermi energy of the system. In Figure 2a, we compute the greatest contribution of the density of states for the clean surface. We observe that the greatest contribution comes from the titanium atoms at the surface. Whereas previous studies that have investigated the density of states for anatase suggest a large O$_p$ character for the band edge,$^{20}$ these calculations were performed for the bulk structure in which all titanium atoms were six-fold coordinated. In the case of the anatase (001) interface, the titanium atoms are under-coordinated with only five nearest oxygen atoms, and thus the additional electrons associated with the titanium are the highest energy, and therefore the most reactive. In Figure 2b, we see a similar case for the fluorinated anatase. The greatest contribution to the density of states again comes from under-coordinated titanium. We additionally observe a large contribution to the surface density of states from fluorine atoms, as well. Visualizing the highest occupied molecular orbitals (HOMO) for each system, we observe a similar result (isosurface plots in Supporting Information). In the case of anatase, the five highest-energy Kohn-Sham single-particle wavefunctions are all localized at the surface of the system with strong d-orbital character, although not localized specifically on any one titanium atom. The case of the fluorinated anatase is less clear, however. Only one of the
highest energy Kohn-Sham wavefunctions is localized at the surface. The other electronic states area localized inside the structures, stabilized by adjacent titanium (cationic) vacancies.

**Figure 2.** The density of states (HOMO-1eV to HOMO) for the pure anatase (a) and the fluorinated anatase (b) interfaces. Both surfaces are in contact with vacuum.

**Water Monolayer Structure at TiO₂ Surfaces**

Of course, in applications of photocatalysis such as water splitting, the interface is not exposed to vacuum, but instead solvated, likely by water. Water molecules adjacent to the surface are influenced by the electronic structure at the surface of the metal oxide, and similarly, the solvent molecules at the surface also influence the electronic structure at the surface. In the case of both rutile and anatase titanium dioxide, depending on the exposed facet, molecular dissociation and physis-absorption have been observed when the surface is exposed to water.\textsuperscript{21,23} Thus, in order to capture the possible changes to surface reactivity following the addition of a monolayer of H₂O, we investigate using density functional theory molecular dynamics (DFT-MD) simulations.
It is known that solvent molecules at different distances away from metal oxide interfaces can have significantly different dynamics, and in particular, the first layer can be involved in very strong interactions or dissociative reactions.\textsuperscript{24} We limit our investigation to the monolayer as a means to understand how the surface is likely initially stabilized. The results of this initial simulation would likely serve as a reasonable starting point for longer simulations with bulk water.

We initialize the simulation cell by adding a single monolayer of water adjacent to each surface of the slab. The number of water molecules in each monolayer is equal to the number of titanium atoms at the surface. In the case of the fluorinated anatase with titanium vacancies at the surface, a water was nonetheless placed over the site where the titanium atom would be expected. Each layer was placed 2.5 Å away from the TiO\textsubscript{2} surface, and each molecule was randomly oriented in space.

In the case of the monolayer of water on anatase (001), we immediately notice a large fluctuation in the density of states at the surface. At 45 fs (Figure 3), we see a large increase in the density of states associated with one of the two-fold coordinate oxygen atoms at the surface but with the greatest increases associated with the Ti atoms along the line defined by $x = 4\text{Å}$ in the two-dimensional cross section (notably Ti atoms at $y = 0\text{Å}$ and $4\text{Å}$). This fluctuation is accompanied with the movement of water molecules in the direction of the surface, followed by a proton transfer from the water molecule to the bridging oxygen. The structure at 45 fs is associated with coordination of a water molecule to the Ti atom labelled as $A$ in Figure 3. This dissociative event is illustrated in the Supporting Information and is consistent with previously observed dissociative mechanism observed in previous works.\textsuperscript{21} We continued to run the
TiO$_2$/H$_2$O monolayer simulation for roughly 1 ps at which point we determined that no further reactions were taking place. On the right-hand side of Figure 3, we observe that the density of states has evened out significantly and no longer shows the strong contribution from the titanium atoms. At the end of the simulation, we observed that on average 50% of the under-coordinated titanium atoms had accepted a new OH$^-$ group at the surface as a result of the dissociation of water. Since one of the bridging oxygens atoms accepts a proton from one water, only one water molecule is needed to dissociate at the service to generate two hydroxyl groups coordinated to surface titanium atoms. After 500 fs, we also observe that those titanium atoms that haven’t accepted a hydronium atom are instead coordinated by a water molecule.
Figure 3. The density of states of the anatase (001) surface after exposure to a monolayer of water at 45 fs (left) and 500 fs (right) into the DFT molecular dynamics simulations.

In the case of the fluorinated anatase, we first visualize the density of states at the beginning of the simulation by parsing out individual contributions from each element. Along the left-hand side of Figure 4, we can see that there is the same large contribution to the density of states from the titanium atoms, although there is now an oxygen atom and several fluorine atoms that also contribute to the density of states. Throughout the simulation, we observe three distinct categories of waters. First, there are water molecules that interact so weakly with the surface that they move away from the surface and into the vacuum. This accounts for 37.5% of the water molecules. A majority of the waters (75%) however remain close to the surface but do not
dissociate. Throughout the simulation, we observe just two molecular dissociation events. In both of these cases, unlike the pristine TiO$_2$, the dissociative event does not involve the bridging oxygens. Instead, the oxygen atoms adjacent to the cationic vacancy (O$^-$) accept a proton from the water molecule, and in each case this dissociation results in one of the two titanium atoms changing from five-fold coordinated to six-fold coordinated. We can see from Figure 4 that the density of states associated with the titanium atoms subsequently reduces after 750 fs into the simulation. Given that there are where only two water molecules that reacted with the surface, we conclude from these results that it is not strictly dissociative events that reduce and more evenly distribute the density of states at the surface, but rather it is likely driven by a variety of interactions between molecules, including physabsorption, at the surface.

Further examining Figure 4, it additionally becomes clear that one distinct difference between the anatase and the fluorinated anatase systems is the flexibility of the surface (i.e. the displacement of surface atoms throughout the simulation). The positions of the atoms at the surface move significantly both laterally and normal to the surface. This unique flexibility is directly related to the under-coordination introduced at the surface as a result of the presence of cationic vacancies. Ultimately, due to the flexibility and rearrangement of the surface, it is therefore difficult to make a strong argument that it is exclusively the coordination of water molecules that modulates the density of the states, as the flexible surface structure would also influence the surface density of state.

Following the initial reactions and adsorption of molecules at the fluorinated surface, the density of states still has localized regions of higher energy electronic states. In particular, we see that some fluorine atoms retain high-energy electrons suggesting that they may be likely sites at the surface for oxidation to occur.
Figure 4. The density of states (HOMO-1ev to HOMO) for the fluorinated anatase. Contributions are limited to titanium (top), oxygen (middle) and fluorine (bottom) atoms. The density of states at the surface are visualized at time 0 fs (left) and time 375 fs (right).

In conclusion, we first suggest that computing the density of states at material surfaces is a reasonable first step in determining the likely reactivity of the surface. We visualized the surface states by projecting a narrow range of KS-wavefunctions below the Fermi energy onto an atomic orbital basis set in order to localize the contributions spatially while only taking into account the electrons most likely to participate in the surface chemistry. We determined that the stabilization of the anatase is a result of water dissociation at the surface, the stabilization of the fluorinated anatase is due to a single-layer of tightly-bound water molecules at the surface. In both cases, the water molecules played a key role in stabilizing the under-coordinated titanium atoms at the surface. We observe that cationic vacancies at the surface in the fluorinated system participate
directly in the relatively rare instances of water dissociation. Additionally, these cationic vacancies lead to under-coordinated atoms at the surface which introduces greater flexibility at the surface. Future work naturally extends from this work to explore how additional layers of water (i.e. solid-liquid interfaces with bulk water) may be influenced by the new surface termination, and additionally to investigate the extent of the interaction of surface waters and their likelihood for exchange with waters in the bulk. Moreover, this new understanding of the anatase and fluorinated anatase structures serve as a starting place for further studies investigating electron and hole localization.

**Computational Methods**

The DFT-MD simulations were performed using the CP2K code\(^{25}\) via the Quickstep algorithm.\(^{26}\) For both systems, we perform the density functional theory calculation using via $\Gamma$-point sampling. The simulations were performed at the generalized-gradient approximation level using the PBE exchange-correlation functional.\(^{27}\) For the basis set, we used DZVP-MOLOPT-SR-GTH to construct the Kohn-Sham wavefunctions with a plane wave cutoff of 400 Rydberg. Goedecker-Teter-Hutter pseudopotentials\(^{28}\) were used to describe core electrons, where Ti atoms were represented explicitly using $3s^23p^63d^24s^2$ electronic orbitals, and O atoms were represented using $2s^22p^4$ electronic orbitals. We performed our simulations at a temperature of 330K with a Nosé-Hoover thermostat\(^{29,30}\) with a time constant of 25 fs. The integration timestep was 0.5 fs.

To compute the density of states, atomic positions were taken for the relevant time steps in the DFTMD trajectories. The density of states calculations and atomic orbital projections were performed with the Quantum Espresso package.\(^{31}\) DFT+U\(^{32,33}\) was used with $U = 3.3eV$, a value used in previous work on anatase.\(^{15}\)
ASSOCIATED CONTENT

**Supporting Information.** A listing of the contents of each file supplied as Supporting Information should be included. For instructions on what should be included in the Supporting Information as well as how to prepare this material for publications, refer to the journal’s Instructions for Authors.

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