Comparing quasiparticle H$_2$O level alignment on anatase and rutile TiO$_2$

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ABSTRACT: Knowledge of the molecular frontier levels’ alignment in the ground state can be used to predict the photocatalytic activity of an interface. The position of the adsorbate’s highest occupied molecular orbital (HOMO) levels relative to the substrate’s valence band maximum (VBM) in the interface describes the favorability of photogenerated hole transfer from the VBM to the adsorbed molecule. This is a key quantity for assessing and comparing H$_2$O photooxidation activities on two prototypical photocatalytic TiO$_2$ surfaces: anatase (A)-TiO$_2$(101) and rutile (R)-TiO$_2$(110). Using the projected density of states (DOS) from state-of-the-art quasiparticle (QP) $G_0W_0$ calculations, we assess the relative photocatalytic activity of intact and dissociated H$_2$O on coordinately unsaturated (Ti$_{vac}$) sites of idealized stoichiometric A-TiO$_2$(101)/R-TiO$_2$(110) and bridging O vacancies (O$_{vac}$) of defective A-TiO$_2$(101)/R-TiO$_2$(110) surfaces ($x=\frac{1}{4},\frac{3}{4}$) for various coverages. Such a many-body treatment is necessary to correctly describe the anisotropic screening of electron-electron interactions at a photocatalytic interface, and hence obtain accurate interfacial level alignments. The more favorable ground state HOMO level alignment for A-TiO$_2$(101) may explain why the anatase polymorph shows higher photocatalytic activities than the rutile polymorph. Our results indicate that (1) hole trapping is more favored on A-TiO$_2$(101) than R-TiO$_2$(110) and (2) HO@Ti$_{vac}$ is more photocatalytically active than intact H$_2$O@Ti$_{vac}$.

KEYWORDS: water splitting, $G_0W_0$ calculations, photocatalysis, photooxidation, hole trapping, titania

1. INTRODUCTION

TiO$_2$ is widely used in photocatalysis, photoelectrocatalysis, and photovoltaics. In particular, the H$_2$O–TiO$_2$ interface has been intensively studied both experimentally and theoretically. This is due to both the ubiquitous nature of the aqueous environment, and the technological importance of water splitting. Because large single-crystal samples of the anatase polymorph are less stable than the rutile polymorph, most surface science studies have focused on the rutile (110) surface of TiO$_2$. However, in the nanoparticle form the anatase polymorph is more stable, and moreover it has a higher photocatalytic activity.

A proper assessment of an interface’s photocatalytic activity requires an accurate description of its frontier levels’ alignment. This is because interfacial electron transfer is controlled by the alignment of the highest occupied and lowest unoccupied molecular orbitals (HOMO/LUMO) relative to the valence band maximum (VBM) and conduction band minimum (CBM). In particular, H$_2$O photooxidation, i.e., the oxygen evolution reaction (OER), is initiated by the transfer of the photogenerated hole from the substrate’s VBM to the HOMO.

Based on the HOMO’s position relative to the VBM prior to irradiation, i.e., vertical alignment, one may establish trends in photocatalytic activity among a group of systems. Even in cases where the HOMO initially lies below the VBM after light absorption and nuclear relaxation, these levels may reorder, with the hole localized on the molecule. Essentially, the closer to the VBM and more localized on the molecule the HOMO is initially, the greater the molecule’s propensity for trapping the hole. For these reasons, the alignment of the H$_2$O occupied levelsprior to irradiation is most relevant for understanding the OER.

Recently, we applied many-body quasiparticle (QP) $GW$ techniques to determine the H$_2$O occupied levels’ alignment on rutile (R)-TiO$_2$(110). We found that an accurate description of the interfacial anisotropic screening via QP $GW$ is essential to ac-
accurately describe the interfacial level alignment. \(^{21,25,27}\) Specifically, the occupied QP density of states (DOS) projected onto the molecule is an effective means for interpreting difference spectra, i.e., the difference between spectra with a chemisorbed molecular overlayer and a clean TiO\(_2\) surface, from ultraviolet photoemission spectroscopy (UPS). \(^{28}\) Such theoretical approaches are necessary to disentangle highly hybridized adsorbate levels from those of the substrate, such as those of the H\(_2\)O–TiO\(_2\) interface. \(^{21}\)

Here, we investigate the H\(_2\)O occupied levels’ alignment on the anatase (A)-TiO\(_2\)(101) surface, as it is the most common surface in nanostructured TiO\(_2\). In the absence of UPS measurements for H\(_2\)O on A-TiO\(_2\)(101), we compare the results to the \(G_0W_0\) PDOS of H\(_2\)O on R-TiO\(_2\)(110), \(^{29}\) which is consistent with UPS difference spectra. \(^{31,33}\)

In particular, we perform \(G_0W_0\) and partially self-consistent \(^{25}\) (sc)QPGW \(^{25,26}\) calculations based on Kohn-Sham (KS) levels from density functional theory (DFT) using a local density approximation (LDA), \(^{36}\) generalized gradient approximation (PBE), \(^{37}\) or a range-separated hybrid (HSE) \(^{38,39}\) exchange correlation (xc)-functionals. From these calculations we obtain the total and projected QP DOS for a variety of coverages \(1/2\) to \(1/1\) monolayer (ML) of intact and dissociated H\(_2\)O adsorbed on coordinately unsaturated Ti sites (H\(_2\)O@Ti\(_\text{unsat}\)) of stoichiometric A-TiO\(_2\)(101) and bridging O vacancies (H\(_2\)O@O\(_\text{br}\)) of defective A-TiO\(_2\)(110) and A-TiO\(_2\)(111) surfaces with \(1/2\)ML and \(1/2\)ML O\(_\text{br}\) sites. The Ti\(_\text{unsat}\) and O\(_\text{br}\) sites of A-TiO\(_2\)(101) and R-TiO\(_2\)(110) are shown schematically in Figure 1.

**Figure 1.** Schematics of clean stoichiometric (a) A-TiO\(_2\)(101) and (b) R-TiO\(_2\)(110) surfaces. Ti and O atoms are depicted in silver and red, respectively. Coordinately unsaturated Ti sites (Ti\(_\text{unsat}\)) and bridging O atoms (O\(_\text{br}\)) are labelled.

On the one hand, by considering the absolute level alignment, i.e., relative to the vacuum level \(E_{\text{vac}}\), one obtains the interface’s ionization potential \(IP = -\epsilon_{\text{VBM}} + E_{\text{vac}}\). This is the quantity that can be compared with red-ox potentials. \(^{40,41}\) Moreover, the absolute level alignment allows a direct comparison between alignments across different substrates, \(^{35}\) such as A-TiO\(_2\)(101) and R-TiO\(_2\)(110). Finally, from the absolute level alignment, one can determine whether changes in the H\(_2\)O level alignment across different substrates are attributable to shifts of the substrate or molecular levels.

On the other hand, by considering the level alignment relative to the VBM of the substrate \(\epsilon_{\text{VBM}}\), one may directly compare the favorability of photogenerated hole transfer from the substrate’s VBM to the molecule’s HOMO. In combination with the \(IP\) this allows a robust comparison of photocatalytic activity across substrates. Moreover, by referencing the spectra to the VBM, one may directly compare the shape and dispersion of the valence band edge at the VBM. Finally, the VBM is the most reliable KS energy reference, from a theoretical perspective. \(^{42}\)

For these reasons, we shall make use of both VBM and \(E_{\text{vac}}\) energy references as appropriate. In particular, we provide the absolute level alignment when comparing to HSE DFT and \(G_0W_0\) PDOS. This is because the VBM and CBM from HSE DFT for clean \(^{40,41}\) and 1ML H\(_2\)O@Ti\(_\text{unsat}\) on R-TiO\(_2\)(110) are consistent with measurements for clean quasi-stoichiometric \(^{35,39,42}\) and liquid H\(_2\)O covered R-TiO\(_2\)(110), \(^{41}\) respectively.

We begin by providing a detailed description of the techniques, parameters, and terminology employed throughout in Section 2. In Section 3.1 we compare our results to calculated and measured electronic band gaps \(E_g\), optical band gaps \(h\omega_{\text{opt}}\), and macroscopic dielectric constants \(\varepsilon_{\infty}\) of bulk A-TiO\(_2\) and R-TiO\(_2\) available in the literature. To further test the robustness of our approach, and the parameters employed, we compare the dielectric function obtained by solving the Bethe-Salpeter equation (BSE) based on \(G_0W_0\) eigenvalues with that obtained from reflection spectra measurements for bulk A-TiO\(_2\). We also compare the \(IP\) for clean idealized stoichiometric A-TiO\(_2\)(101) and R-TiO\(_2\)(110). In Section 3.2 we provide a detailed comparison of the H\(_2\)O PDOS for intact and ½ dissociated H\(_2\)O@Ti\(_\text{unsat}\) on A-TiO\(_2\)(101) and R-TiO\(_2\)(110) relative to \(E_{\text{vac}}\) and \(\epsilon_{\text{VBM}}\) with PBE DFT, HSE DFT, PBE scQPGW1, PBE \(G_0W_0\) and HSE \(G_0W_0\). In Section 3.3 we provide a similar detailed comparison for dissociatively adsorbed H\(_2\)O@O\(_\text{br}\) on A-TiO\(_2\)(101) and R-TiO\(_2\)(110) relative to \(E_{\text{vac}}\). Finally, in Section 3.4 we extend the comparison of A-TiO\(_2\)(101) and R-TiO\(_2\)(110) to their adsorption energies and level alignments relative to \(\epsilon_{\text{VBM}}\) with H\(_2\)O coverage (½ to 1ML), H\(_2\)O dissociation (intact to fully dissociated), and surface composition (O\(_\text{br}\) coverage). This is followed by concluding remarks.

### 2. METHODOLOGY

#### 2.1. Theoretical Methods.

DFT based on standard xc-functionals, e.g., LDA and PBE, tends to significantly underestimate the electronic band gaps of semiconductor metal oxides, such as TiO\(_2\). \(^{43}\) This is in part due to their underestimation of the screening of the electron-electron interaction.

DFT based on hybrid xc-functionals, e.g., HSE, partially remedies this by replacing a fraction of the exchange term with Hartree-Fock exact-exchange. The fraction of Hartree-Fock exact-exchange included, \(\alpha\), acts as an effective constant screening of the Hartree-Fock electron-electron interaction term, i.e., an inverse dielectric constant for the system \(\alpha \sim \varepsilon_{\infty}^{-1}\). \(^{44}\) In particular, we use the HSE06 variant, with a range separation parameter of \(\mu = 0.2\ \text{Å}^{-1}\), of the HSE hybrid xc-functional, which includes 25\% exact-exchange (\(\alpha = 0.25\)). \(^{45}\) For systems where the screening is rather homogeneous, and \(\varepsilon_{\infty} \sim 4\), this leads to a better description of the electronic band gap e.g., of bulk TiO\(_2\). \(^{46}\)

However, since HSE applies the same screening to all the levels regardless of their nature, it fails to describe the anisotropic screening felt by molecular levels at an interface. As a result, localized occupied molecular levels are underbound by HSE. \(^{41,42}\)

This can lead to significant errors in HSE’s description of molecular/semiconductor interfacial level alignment. \(^{51,52}\) Instead, QP techniques, e.g., \(G_0W_0\) and scQPGW1, where the spacial dependence of the screening is explicitly included, provide a better description of the interfacial level alignment. \(^{35,39,42}\)

In the \(G_0W_0\) approach, the contribution to the KS eigenvalues from the xc-potential \(V_{\text{xc}}\) is replaced by the self energy \(\Sigma = iGW\), where \(G\) is the Green’s function and \(W\) is the spatial depen-
dent screening obtained from the KS wavefunctions. The dielectric function is obtained from linear response time-dependent (TD) DFT within the random phase approximation (RPA), including local field effects. From G0W0 one obtains first-order QP corrections to the KS eigenvalues, but retains the KS wavefunctions. Generally, these QP corrections to the occupied levels are linearly dependent on the fraction of the KS wavefunction’s density in the molecular layer. This means the screening of these levels W is quite anisotropic. For this reason, QP GW methods are necessary to accurately describe the interfacial level alignment.

Moreover, to include dependencies on the QP wavefunctions, and possibly obtain an improved absolute level alignment for the interface, one can also employ self-consistent QP techniques, such as scQPGW. Here, we have employed a single-shot scQPGW approach, where 100% of the DFT xc-potential is replaced by the QP self energy in a single self-consistent scQPGW cycle. We employ this procedure to make practical scQPGW calculations for large interfaces, such as H2O−A-TiO2(101). In so doing, one obtains eigenvalues comparable to those from G0W0, along with the QP wavefunctions. This differs from the scQPGW approach as previously applied to the H2O−O−Tio2(110) interface, where 25%, 25%, and 50%, of the QP self energies were “mixed” with the DFT xc-potential over three scQPGW cycles, respectively.

2.2. Computational Details. Our G0W0 calculations have been performed using vasp within the projector augmented wave (PAW) scheme. The G0W0 calculations are based on KS wavefunctions and eigenenergies obtained from DFT using either LDA, PBE, or HSE xc-functionals.

The geometries have been fully relaxed using LDA, PBE, or HSE with all forces ≤ 0.02 eV/Å. The HSE calculations have been performed for the relaxed geometries obtained with PBE. We have employed a plane-wave energy cutoff of 445 eV, an electronic temperature of 0 K, and a PAW pseudopotential for Ti which includes the 3s, 3p, and 3d semi-core levels. All calculations have been performed spin unpolarized.

For the clean stoichiometric A-TiO2(101) surface we have used a five-layer slab, an orthorhombic 1 × 1 unit cell of 10.23 × 3.78 × 40 Å3, a Γ-centered 4 × 8 × 1 k-point mesh, and approximately 9½ unoccupied bands per atom. For the clean defective A-TiO2−½(101) surface we have used a monoclinic 1 × 2 unit cell of 10.23 × 7.56 × 40 Å3 and a Γ-centered 4 × 4 × 1 k-point mesh. For the clean defective A-TiO2−½(101) surface we have used a 1 × 4 unit cell of 10.23 × 15.13 × 40 Å3 and a Γ-centered 4 × 2 × 1 k-point mesh. For the H2O covered surfaces, we have employed a five-layer slab with adsorbates on both sides, an orthorhombic 1 × 1 unit cell of 10.23 × 3.78 × 47 Å3, a Γ centered 4 × 8 × 1 k-point mesh, and approximately 9½ unoccupied bands per atom, i.e., including all levels up to 30 eV above the VBM, an energy cutoff of 80 eV for the number of G-vectors, and a sampling of 80 frequency points for the RPA dielectric function. The G0W0 parameters are consistent with those previously used for describing bulk R-TiO2, R-TiO2(110) clean surface and interfaces. Although our G0W0 calculations do not include electron-phonon and lattice polarization contributions, these parameters have been shown to provide accurate descriptions of bulk optical absorption spectra, and both clean surface and interfacial level alignment.

It has previously been shown that the experimental optical spectra for bulk A-TiO2 may be obtained via BSE based on G0W0 eigenvalues. In our BSE calculations, we include the electrostatic electron-hole interaction using the effective nonlocal frequency independent exchange correlation $f_{xc}(r, r, \omega = 0)$ kernel suggested in ref. 55. For bulk A-TiO2, we have used a tetragonal conventional 12 atom supercell with experimental lattice parameters $a = b = 3.78$ Å and $c = 9.5$ Å, and a dense Γ-centered 10 × 10 × 4 k-point mesh. For bulk R-TiO2, we have used a tetragonal 6 atom primitive cell with experimental lattice parameters $a = b = 4.5941$ Å and $c = 2.958$ Å, a Γ-centered 6 × 6 × 10 k-point mesh with PBE and HSE and a dense Γ-centered 8 × 8 × 12 k-point mesh with LDA. For both A-TiO2 and R-TiO2, we have included $n_{mocc} = 12$ unoccupied bands per atom. For the BSE calculations of bulk A-TiO2, we have used 480 sampling points for the RPA dielectric function, and included all the transitions between the 16 highest energy occupied bands and the 12 lowest energy unoccupied bands.

2.3. Terminology. To compare the relative stabilities of the H2O covered anatase and rutile polymorphs, we have performed single-point RPBE57 based DFT calculations using the PBE relaxed structure for the H2O adsorption energies $E_{ads}$ on stoichiometric A-TiO2(101) and defective A-TiO2−½(101) surfaces. The RPBE xc-functional was especially developed for the prediction of adsorption properties on metal surfaces.57 Furthermore, RPBE has been shown to provide accurate formation energies for metal dioxides58 and perovskites.

The H2O adsorption energy on the Ti$_{vac}$ site of a stoichiometric A-TiO2(101) surface is given by

$$E_{ads} = \frac{E[nH_2O + A-TiO_2(101)] - E[A-TiO_2(101)] - E[H_2O]}{n},$$

where $n$ is the number of adsorbed H2O functional units in the supercell, and $E[nH_2O + A-TiO_2(101)]$, $E[A-TiO_2(101)]$, and $E[H_2O]$ are the total energies of the covered and clean stoichiometric surfaces and gas phase water molecule, respectively. Similarly, the H2O adsorption energy on the O$_{vac}$ site of a defective A-TiO2−½(101) surface is given by

$$E_{ads} = \frac{E[nH_2O + A-TiO_2-½(101)] - E[A-TiO_2-½(101)] - E[H_2O]}{n},$$

where $E[nH_2O + A-TiO_2-½(101)]$ and $E[A-TiO_2-½(101)]$ are the total energies of the covered and clean defective surfaces, respectively.

To provide a quantitative comparison between the DOS for the H2O−A-TiO2 and H2O−R-TiO2 interfaces, we employ the interfaces’ IPs. These are obtained from the difference in energy between the vacuum level $E_{vac}$ and the VBM $E_{VBM}$, $IP = -E_{VBM} + E_{vac}$, where $E_{vac}$ is the maximum surface averaged electrostatic potential in the vacuum region between slabs.

Similarly, to provide a quantitative comparison between the PDOS for the H2O−A-TiO2 and H2O−R-TiO2 interfaces, we employ both the highest H2O PDOS peak $E_{peak}$ and the average energy of the highest energy electron, or HOMO, of the PDOS, $\bar{E}_{HOMO}$. To obtain $E_{peak}$ from the PDOS, we fit three Gaussians to the first few peaks below the VBM. In this way we may disentangle the highest energy peak when it forms a shoulder within the upper edge of the PDOS.

However, to assess trends in the comparative photocatalytic activity of the H2O−A-TiO2 and H2O−R-TiO2 interfaces, one should consider not only a peak’s energy, but also differences in its’ intensity, i.e., localization on H2O. Both quantities are incorporated within the single descriptor $\rho E_{PDOS}$. We define $\rho E_{PDOS}$ as the first moment of the PDOS, $\rho E_{PDOS}(e)$ over the interval encompassing the highest energy electron. More precisely,

$$\rho E_{PDOS} = \frac{\int_{E_1}^{E_2} E_{PDOS}(e) de}{\int_{E_1}^{E_2} de},$$

where $E_{VBM}$ is the VBM energy, $\Delta \sim 1$ eV ensures the tail of the VBM is included within the integral, and $E_1$ is the lower bound of
the energy range encompassing the highest energy electron of the PDOS, i.e.,
\[\int_{E_1}^{E_{VM} + \Delta} \rho^{PDOS}(\epsilon) d\epsilon \equiv 1.\]

3. RESULTS AND DISCUSSION

3.1. Bulk and (101) Surface of Anatase TiO\(_2\). To test the reliability of the parameters we have employed to calculate the \(G_0W_0\) levels of A-TiO\(_2\), we first consider the optical response of bulk anatase. Previous DFT band structure calculations\[14\] found A-TiO\(_2\) has an indirect electronic band gap between the VBM along the \(\Sigma\) path at 0.88\(\Gamma\) \(\rightarrow\) M\[46\], i.e., \(\Sigma\), and the CBM at \(\Gamma\). Our PBE \(G_0W_0\) calculation yields an indirect electronic band gap for A-TiO\(_2\) of 3.86 eV, from a VBM at 0.88\(\Gamma\) \(\rightarrow\) M. This is comparable with the \(G_0W_0\) indirect band gaps reported in the literature, as shown in Table 1.

| Method  | xc-functional       | A-TiO\(_2\) | R-TiO\(_2\) |
|---------|---------------------|-------------|-------------|
|         | \(\Gamma \rightarrow \Gamma\) | \(\Sigma \rightarrow \Gamma\) | \(\Gamma \rightarrow \Gamma\) | \(\Gamma \rightarrow \Gamma\) |
| DFT     | HSE                 | 3.72        | 3.63        | 3.40        | 3.40        |
|         | LDA                 | 3.93        | 3.86        | 3.33        | 3.26        |
|         | PBE                 | 4.14\(b\)  | 3.56\(b\)  | 3.38\(b\)  | 3.34\(b\)  |
|         | PBE+\(\Delta\)       | 4.29\(c\)  | 3.83\(c\)  | 3.46\(c\)  | 3.46\(c\)  |
|         | PES/IPES (\(\alpha_{KM} \cdot h\omega\))^2 | 3.57\(d\)  | 3.30\(d\)  | 3.23\(d\)  | 3.23\(d\)  |
| BSE     | LDA                 | 3.73        | 3.15        |             |             |
|         | PBE                 | 3.57\(d\)  | 3.28\(a\)  |             |             |
|         | Transmission        | 3.42\(f\)  |             |             |             |
|         | Absorption          |             | 3.03\(b\)  |             |             |
|         | Reflectance         | 3.21\(f\)  | 3.00\(j\)  |             |             |

In these calculations the \(\alpha_{KM}\) values were determined using a method described in ref. \[35\]. For pure-phase nanoparticles from ref. \[36\].

Table 1. Direct and Indirect Band Gaps \(E_g\) and Optical Gaps \(\hbar\omega_E\) in eV of A-TiO\(_2\) and R-TiO\(_2\).

Based on these \(G_0W_0\) levels, we obtain from the Bethe-Salpeter equation the imaginary and real parts of the dielectric function of bulk A-TiO\(_2\) for polarization perpendicular (ordinary) and parallel (extraordinary) to the tetragonal axis \(c\) shown in Figure 2. These are comparable to the dielectric functions obtained from reflection spectra polarized perpendicular to the \(a\) or \(c\)-axis at room temperature by Kramers-Kronig transformations\[46\]. Note that 86% of the experimental reflectivity spectra polarized perpendicular to the \(a\)-axis is parallel to the \(c\)-axis\[46\]. Furthermore, our dielectric functions agree well with those obtained from BSE calculations within the Tamm-Dancoff approximation\[46\]. In particular, we obtain excellent agreement both in position and intensity for the first bright exciton at \(\sim 4\) eV, which is perpendicular to the \(c\)-axis. The lowest energy BSE \(G_0W_0\) transition is at 3.73 eV, about 0.12 eV below the PBE \(G_0\) indirect electronic gap of A-TiO\(_2\), as shown in Table 2. This is significantly higher than the estimated optical band gap of 3.42 eV reported in ref. \[35\].

However, we tend to underestimate the real part of the dielectric function, shown in Figure 2(b,d). For example, as reported in Table 3 the dielectric constant \(\varepsilon_{\infty} = \varepsilon(\omega = 0)\) is underestimated by about 2 in our BSE calculations. This might be remedied by including a greater number of transitions within the BSE calculation.

Figure 2. (a,c) Imaginary and (b,d) real parts of the dielectric function of bulk A-TiO\(_2\) for polarization perpendicular (a,b) and parallel (c,d) to the A-TiO\(_2\) tetragonal \(c\)-axis, \(\varepsilon(\omega)\) versus energy (\(\hbar\omega_E\)), in eV. The BSE spectra from this work (red) and from ref. \[46\] (green) are based on \(G_0W_0\) eigenvalues. The experimental spectra (blue) are obtained from reflection spectra polarized perpendicular to the (a,b) \(c\)-axis or (c,d) \(a\)-axis by Kramers-Kronig transformation from ref. \[69\].

Table 2. Macroscopic Dielectric Constants \(\varepsilon_{\infty}\) Perpendicular (\(\perp\)) and Parallel (\(\parallel\)) to the Tetragonal \(c\)-Axis of A-TiO\(_2\) and R-TiO\(_2\).

| Method | xc-functional | A-TiO\(_2\) | R-TiO\(_2\) |
|--------|---------------|-------------|-------------|
|        | \(\perp\)     | \(\parallel\) | \(\perp\) | \(\parallel\) |
| LDA    | 7.18          | 6.81        | 7.83\(a\)  | 9.38\(a\)  |
| RPA    | 7.06          | 6.59        | 7.61        | 9.09        |
| HSE    | 4.91          | 4.83        | 5.21        | 6.09        |
| BSE    | 4.91\(c\)    | 4.76\(d\)  | 5.15\(c\)  | 6.22\(c\)  |
|        | 5.12\(d\)    | 4.98\(d\)  | 5.71\(d\)  | 7.33\(d\)  |

In any case, such computationally demanding calculations are beyond the scope of the present work. Overall, the agreement obtained for the BSE dielectric function based on \(G_0W_0\) eigenenergies demonstrates the robustness of the parameters we will use to calculate the \(G_0W_0\) PDOS for H\(_2\)O.

Figure 3 depicts schematically the clean and stoichiometric A-TiO\(_2\)(101) surface. For the clean surface, there are two \(T\) coordinate unsaturated sites (Ti\(_{\text{vac}}\)) and two bridging O atoms (O\(_{\text{br}}\)) in each unit cell.

PBE \(G_0W_0\) places the \(IP\) for A-TiO\(_2\)(101) at 7.15 eV, which is 0.14 eV below that of R-TiO\(_2\)(110)\[25\]. This ordering is consistent with, albeit significantly smaller than, that measured with XPS for the A-TiO\(_2\)–RuO\(_2\)–R-TiO\(_2\) interface of 0.7 \(\pm\) 0.1 eV\[25\]. This ordering also agrees with the 0.47 eV difference in \(IP\) calculated using a hybrid quantum-mechanical/molecular mechanical embedding technique\[25\]. In these calculations the \(IP\) was obtained from the total energy difference upon removal of an electron from the neutral A-TiO\(_2\) and R-TiO\(_2\) embedded cluster models. Our rela-
tive ordering is also consistent with that obtained from KS eigenvalues using the B3LYP xc-functional of 8.2 eV for A-TiO$_2$(101) and R-TiO$_2$(110), respectively. This qualitative agreement provides further support for the reliability of our $G_0W_0$ approach.

3.2. H$_2$O Intact and $\frac{1}{2}$ Dissociated on Coordinate Unsaturated Ti Sites. For coverages up to 1ML, H$_2$O adsorbs molecularly on the A-TiO$_2$(101) surface, with O bonding to Ti$_{\text{cus}}$ and one H forming an interfacial hydrogen bond with O$_{\text{br}}$ as shown in Figure 3(a). On R-TiO$_2$(110), the distance between the nearest neighboring Ti$_{\text{cus}}$ sites is shorter, allowing additional intermolecular hydrogen bonds to form along the [001] direction as shown in Figure 3(a).

The QP level alignment relative to the vacuum level $E_{\text{vac}}$ for 1ML of H$_2$O adsorbed intact on A-TiO$_2$(101) and R-TiO$_2$(110) are shown in Figure 3(b-f). These are compared to the 1b$_2$, 3a$_1$, and 1b$_1$ levels' absolute alignment for gas phase H$_2$O. Specifically, we analyze the dependence of the H$_2$O PDOS on the methodology: PBE DFT, HSE DFT, PBE scQPGW1, PBE $G_0W_0$, and HSE $G_0W_0$.

As was previously found for the H$_2$O–R–TiO$_2$(110) interface, the IP for H$_2$O–A–TiO$_2$(101) is ordered according to the method's description of the screening, $\varepsilon_{\text{scr}}$. As shown in Table 3, the IP is ordered as $G_0W_0$ = 7.6 eV for H$_2$O–A–TiO$_2$(101) and $G_0W_0$ = 7.2 eV for H$_2$O–R–TiO$_2$(110). However, this ordering of the IPs is completely different from that found for gas phase H$_2$O.

Note that the CBM and VBM relative to $E_{\text{vac}}$ from PBE scQPGW1 and PBE $G_0W_0$ are essentially the same for H$_2$O–A–TiO$_2$(101), but are significantly lower for H$_2$O–R–TiO$_2$(110). This is because the dielectric constant employed in both single-shot PBE scQPGW1 and PBE $G_0W_0$ are obtained from PBE DFT, whereas when the QP self energies are “mixed” with the DFT xc-potential in each cycle, as for H$_2$O–R–TiO$_2$(110), the scQPGW1 dielectric constant is significantly reduced relative to PBE DFT. This demonstrates that without mixing of the self energy, for the QP PDOS the PBE scQPGW1 procedure provides no advantage over PBE $G_0W_0$, as predicted in ref. 21.

Table 3. Ionization Potentials IP in eV of 1ML H$_2$O@Ti$_{\text{cus}}$ on A-TiO$_2$(101) and R-TiO$_2$(110).

| method xc-functional | H$_2$O@Ti$_{\text{cus}}$ (101) | R-TiO$_2$(110) |
|----------------------|--------------------------------|----------------|
| PBE                  | 6.4                           | 6.2$^a$        |
| HSE                  | 7.2                           | 7.3$^a$        |
| scQPGW1              | 6.3                           | 6.6$^a$        |
| PBE $G_0W_0$         | 6.3                           | 6.0$^a$        |
| HSE $G_0W_0$         | 6.9                           | 6.5$^a$        |

$^a$Ref 21

Generally, the highest H$_2$O PDOS peaks, $\varepsilon_{\text{peak}}$, follow the same ordering as the IPs. This suggests that $\varepsilon_{\text{peak}}$ is pinned to the VBM of the H$_2$O–A–TiO$_2$(101) interface. This is also the case for 1ML intact H$_2$O@Ti$_{\text{cus}}$ on R-TiO$_2$(110). However, this ordering of the IPs is completely different from that found for gas phase H$_2$O. In this case, the IP is the energy needed to remove one electron from the H$_2$O 1b$_1$ level. Here, the IPs increase with decreasing screening within the methodology until $\varepsilon_{\text{scr}} \sim 1$.

However, for 1ML intact H$_2$O@Ti$_{\text{cus}}$, the relative alignment of the A–TiO$_2$(101) and R–TiO$_2$(110) VBM's differs qualitatively with methodology. The IPs obtained from PBE DFT and PBE $G_0W_0$ are higher ($\sim 0.2$ and $0.3$ eV) for A–TiO$_2$(101) than for R–TiO$_2$(110). However, the IP from HSE DFT is lower ($\sim 0.1$ eV) for A–TiO$_2$(101) than R–TiO$_2$(110), while the opposite is true for HSE $G_0W_0$ ($\sim 0.4$ eV). Thus, independently of the xc-functional employed, $G_0W_0$ yields higher IPs for 1ML intact H$_2$O@Ti$_{\text{cus}}$ on A–TiO$_2$(101) than on R–TiO$_2$(110). This is contrary to our findings for the clean A–TiO$_2$(101) and R–TiO$_2$(110) surface, and sug-
gests that H2O adsorption inverts the relative positions of the A-TiO2(101) and R-TiO2(110) VBMs.

Although we find the position of the lower edge of the valence band is only weakly affected by adsorbing H2O on either A-TiO2(101) or R-TiO2(110), the VBM is shifted up by about 1 eV in both cases. This is consistent with the experimentally observed change in work function for the liquid water–R-TiO2(110) interface.[21,26,41–45,83]

The reordering of the HSE DFT and G0W0 IPs for 1ML intact H2O on A-TiO2(101) and R-TiO2(110) may be attributed to the greater difference between the constant screening built into HSE DFT[52] and the screening of rutile compared to anatase. Essentially, the fraction of the Hartree-Fock exact-exchange which is incorporated within HSE, $\alpha = 0.25$, acts as an effective inverse dielectric constant within the system, $\alpha \approx \frac{1}{\varepsilon_{\infty}}$. As a result, for materials with $\varepsilon_{\infty} \approx 4$, HSE DFT and G0W0 should provide similar descriptions of the screening.[52] From Table 2, we see that the RPA, BSE, and measured $\varepsilon_{\infty}$ agree qualitatively and are consistently lower and closer to the HSE DFT effective dielectric constant of $\varepsilon_{\infty} \approx 4$ for A-TiO2 compared to R-TiO2. For this reason, as shown in Figure 3, the difference between HSE DFT and G0W0 IPs is larger for R-TiO2 than A-TiO2, resulting in their relative reordering at the G0W0 level. This demonstrates the important role played by the screening in describing the relative alignment of anatase and rutile polymorphs.

Overall the H2O PDOS for 1ML intact H2O@TiO2 is similar for the A-TiO2(101) and R-TiO2(110) surfaces. In particular, the most strongly bound 1b2 peaks and the upper edges of the H2O PDOS spectra have similar energies for the two polymorphs over all five levels of theory (cf. Figure 3b-f).

On A-TiO2(101), the 1ML intact H2O QP PDOS generally consists of three distinct peaks, which have clear contributions from molecular 1b2, 3a1 and 1b1 levels (cf. Figure 3b and Figure 3a). This is in contrast to R-TiO2(110), where the H2O QP PDOS consists of many more peaks, with a greater hybridization at 1ML compared to ½ML coverage on the R-TiO2(110) substrate.[21] This may be attributed to stronger intermolecular interactions on R-TiO2(110) due to its shorter Ti−Ti nearest neighbor separations ($d[\text{Ti}_{\text{cis}}−\text{Ti}_{\text{cis}}] \approx 2.96$ Å) versus A-TiO2(101) ($d[\text{Ti}_{\text{cis}}−\text{Ti}_{\text{cis}}] \approx 3.78$ Å). This leads to intermolecular bonding and antibonding levels, which may further hybridize with the substrate.[31] For example, as shown in Figure 3, the bottom edge of the 3a1 peak for A-TiO2(101) is higher than that of R-TiO2(110). This is because on R-TiO2(110) the 3a1 levels of neighbouring molecules hybridize to form intermolecular bonding and antibonding combinations.[31] These give rise to separate peaks below and above the bottom edge of the R-TiO2(110) valence band. As a result, the QP H2O PDOS for 1ML intact H2O@TiO2 on R-TiO2(110) has the 3a1 intermolecular bonding level below the bottom of the valence band, while for A-TiO2(101), the 3a1 level is completely within the substrate’s valence band.

Figure 3g shows the structures of ½ dissociated H2O@TiO2 on A-TiO2(101) and R-TiO2(110). In both cases, one proton from H2O@TiO2 is transferred to the adjacent Obr. This results in two distinct OH groups: HO@TiO2 and Obr-H. This process is accompanied by a $-0.4e$ charge transfer from HO@TiO2 to Obr-H, as depicted schematically in Figure 3g.

Although the resulting PBE G0W0 QP DOS shown in Figure 3e...
and (b) are generally similar, there are important differences which are related to the H₂O@TiO₂ dissociation. For the dissociated H₂O molecule, the 1b₂ peak is replaced by separate HO@TiO₂ and O₂H peaks at about −12.5 and −13 eV below \( E_{\text{vac}} \) (see Figure 3(b)), with O–H σ character on both A-TiO₂(101) and R-TiO₂(110) (see Figure 4(b)). These peaks are at such similar energies on both A-TiO₂(110) and R-TiO₂(110) because they are well separated from the bottom edge of the TiO₂ valence band.

As mentioned above, the three distinct peaks in the H₂O PDOS on both A-TiO₂(101) and R-TiO₂(110) are associated with the 1b₂, 3a₁, and 1b₁ gas phase H₂O levels. This is clearly seen by comparing the molecular components of the orbitals depicted for 1ML intact and ½ dissociated H₂O@TiO₂ on both A-TiO₂(101) and R-TiO₂(110) in Figure 4. There is significantly greater hybridization between the molecular levels on R-TiO₂(110) compared to A-TiO₂(101). Specifically, on R-TiO₂(110) there are obvious bonding and antibonding combinations of the 1b₂ levels and 3a₁ levels between neighbouring H₂O molecules. Such intermolecular hybridization does not occur for A-TiO₂(101), as the molecules are too far apart.

More importantly, \( \epsilon^{\text{PDOS}}_{\text{peak}} \) is shifted to higher energy upon dissociation, with a greater shift for A-TiO₂(101) versus R-TiO₂(110). To explain these differences, and their potential impact on the interfaces’ photocatalytic activity, one should compare the level alignment relative to the VBM. In so doing, one can directly compare the relative propensity for photogenerated hole transfer from the substrate’s VBM to the molecular HOMO for A-TiO₂(101) and R-TiO₂(110).

In Figure 4 we provide the level alignment relative to the VBM for (a) intact and (b) ½ dissociated H₂O on A-TiO₂(101) and R-TiO₂(110). The level alignment shown in Figure 4 suggests that (1) hole trapping is more favored on A-TiO₂(101) than R-TiO₂(110) and (2) HO@TiO₂ is more photocatalytically active than intact H₂O@TiO₂. This is based on the following observations: (1) \( \epsilon^{\text{PDOS}}_{\text{peak}} \) is about 0.5 eV higher in energy for A-TiO₂(101) than R-TiO₂(110); (2) \( \epsilon^{\text{PDOS}}_{\text{peak}} \) is about 0.1 eV closer to the VBM for HO@TiO₂ than for intact H₂O@TiO₂; (3) the PDOS for HO@TiO₂ at \( \epsilon^{\text{PDOS}}_{\text{peak}} \) is an order of magnitude greater than for intact H₂O@TiO₂; and (4) the HOMO is more localized on the molecule for HO@TiO₂ than for intact H₂O@TiO₂.

These conclusions are reinforced by analyzing the HOMOs at \( \Gamma \) shown in Figure 4. Here, one clearly sees that the HOMOs have greater weight on the molecule for HO@TiO₂ than intact H₂O@TiO₂. Although there is only a small (0.1 eV) energy difference between the HOMO for ½ dissociated and intact H₂O@TiO₂, the latter level is not photocatalytically relevant for hole trapping on the molecule. This is because it is a lone-pair orbital that datively bonds to TiO₂. For this reason, if an electron were extracted from this level, one would instead expect the hole to remain on the surface, and H₂O to desorb from TiO₂. This agrees with previous studies of the liquid H₂O–A-TiO₂(101) interface, which found that localizing the hole on intact H₂O is inherently unstable, and leads to deprotonation. Instead, the hole localizes on 3-fold coordinated surface O (O_{3fold}) atoms.

In contrast to the intact H₂O@TiO₂(HOMOs), the HOMOs for HO@TiO₂ on A-TiO₂(101) and R-TiO₂(110) are the photocatalytically active levels for hole-trapping. Indeed, they have the same character as the hole trapping levels reported in the literature for A-TiO₂(101) and R-TiO₂(110). In particular, they have both O_{3fold} 2p and OH 2p character. While in the case of HO@TiO₂ this orbital is doubly occupied, in the trapped hole structures of refs. 17 and 22 the OH groups are bent towards the surface, with the hole shared between O_{3fold} 2p and OH 2p orbitals. This clearly demonstrates that a HOMO initially below the VBM can, upon light absorption and subsequent nuclear relaxation, evolve into a hole trapping level of the interface. This justifies our use of ground state level alignment for comparing photocatalytic activity among H₂O–TiO₂ interfaces.

Although hole trapping has been documented for both A-
3. H₂O Dissociated on Bridging O Vacancies. For R-TiO₂(110), the most stable O vacancies are at surface Oₜhr sites, i.e., Oₜhr⁻¹. These sites mediate H₂O dissociation on R-TiO₂(110) [21-23]. For A-TiO₂(101), the most stable O vacancies are subsurface. However, after H₂O adsorption, these subsurface vacancies migrate to the surface and are filled by H₂O, i.e., H₂O@Oₜhr⁻¹, which subsequently dissociates to form 2H₂O₁=₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~

Similarly, E_peak for dissociatively adsorbed H₂O@Oₜhr⁻¹ on A-TiO₂(110) is about 0.4 eV below that on R-TiO₂(110). Since E_peak is thus closer to the standard hydrogen electrode (SHE) for H₂O@Oₜhr⁻¹ on R-TiO₂(110) than A-TiO₂(110), one would expect the former structure to require a smaller overpotential and be more active than the latter within an electrochemical cell [25]. However, for photocatalysis, the alignment of E_peak relative to E_BM is the more relevant quantity. As we shall see in the next section, the relative electrochemical and photocatalytic activities of these two structures are reversed.

3.4. Coverage and Dissociation Dependence of H₂O Spectra for Stoichiometric and Defective Surfaces. To systematically investigate the similarities and differences between A-TiO₂(101) and R-TiO₂(110) surfaces, we consider a variety of coverages of intact and dissociated H₂O on stoichiometric A-TiO₂(101) [Figure 6(a)] and defective A-TiO₂(101) [Figure 6(b,c)]. As done previously for the rutile surface [21], these configurations are consistent with previous results for H₂O on A-TiO₂(110). The adsorption energies shown in Table 6 and Figure 7(a,b) for

| Table 4. Occupied Ti³⁺ 3d Level Energies Eₚₑᵃˢ for ½ML Dissociated H₂O@Oₜhr⁻¹ on A-TiO₂(110) and R-TiO₂(110). |
|-----------------|-----------------|-----------------|
| coverage        | surface         | IP(eV)          |
| clean A-TiO₂(101) | A-TiO₂(101)     | 7.15            |
| R-TiO₂(110)     | R-TiO₂(110)     | 7.29            |
| 1ML H₂O@Oₜhr⁻¹  | A-TiO₂(110)     | 6.25            |
| R-TiO₂(110)     | R-TiO₂(110)     | 6.03            |
| 1ML H₂O@Oₜhr⁻¹  | R-TiO₂(110)     | 6.19            |
| R-TiO₂(110)     | R-TiO₂(110)     | 5.37            |

*aRef. 25 bRef. 26

Similarly, E_peak for dissociatively adsorbed H₂O@Oₜhr⁻¹ on A-TiO₂(110) is about 0.4 eV below that on R-TiO₂(110). Since E_peak is thus closer to the standard hydrogen electrode (SHE) for H₂O@Oₜhr⁻¹ on R-TiO₂(110) than A-TiO₂(110), one would expect the former structure to require a smaller overpotential and be more active than the latter within an electrochemical cell. However, for photocatalysis, the alignment of E_peak relative to E_BM is the more relevant quantity. As we shall see in the next section, the relative electrochemical and photocatalytic activities of these two structures are reversed.

3.4. Coverage and Dissociation Dependence of H₂O Spectra for Stoichiometric and Defective Surfaces. To systematically investigate the similarities and differences between A-TiO₂(101) and R-TiO₂(110) surfaces, we consider a variety of coverages of intact and dissociated H₂O on stoichiometric A-TiO₂(101) [Figure 6(a)] and defective A-TiO₂(101) [Figure 6(b,c)], as done previously for the rutile surface. These configurations are consistent with previous results for H₂O on A-TiO₂(110). The adsorption energies shown in Table 6 and Figure 7(a,b) for

| Table 5. Ionization Potentials IP(eV) from PBE G₀W₀ for A-TiO₂(101) and R-TiO₂(110) |
|-----------------|-----------------|-----------------|
| coverage        | surface         | IP(eV)          |
| clean A-TiO₂(101) | A-TiO₂(101)     | 7.15            |
| R-TiO₂(110)     | R-TiO₂(110)     | 7.29            |
| 1ML H₂O@Oₜhr⁻¹  | A-TiO₂(110)     | 6.25            |
| R-TiO₂(110)     | R-TiO₂(110)     | 6.03            |
| 1ML H₂O@Oₜhr⁻¹  | R-TiO₂(110)     | 6.19            |
| R-TiO₂(110)     | R-TiO₂(110)     | 5.37            |

*aRef. 25 bRef. 26
H$_2$O on A-TiO$_2$, A-TiO$_{2-1/4}$, and A-TiO$_{2-1/6}$ (101) are generally similar to those on R-TiO$_2$, R-TiO$_{2-1/4}$, and R-TiO$_{2-1/6}$ (110) respectively. On both A-TiO$_2$ (101) and R-TiO$_2$ (110), intact H$_2$O adsorption is more stable than dissociative adsorption from 1/2 and 1 1/2 ML coverages. The adsorption energies for H$_2$O@Ti$_{cur}$ on A-TiO$_2$ (101) follow the same trend as on R-TiO$_2$ (110), but are somewhat stronger on A-TiO$_2$ (101), with the greatest differences seen for dissociatively adsorbed H$_2$O. Since the photocatalytically active species HO$_{br}$@Ti$_{cur}$ is more stable on A-TiO$_2$ (101) than R-TiO$_2$ (110), this also suggests that A-TiO$_2$ (101) should be more photocatalytically active than R-TiO$_2$ (110). This is because one expects there to be more HO$_{br}$@Ti$_{cur}$ on A-TiO$_2$ (101) than R-TiO$_2$ (110).

On the defective surfaces, intact H$_2$O adsorption is also more stable than dissociative adsorption on A-TiO$_{2-1/4}$ (101)/R-TiO$_{2-1/4}$ (110) and A-TiO$_{2-1/6}$ (101)/R-TiO$_{2-1/6}$ (110). Dissociative H$_2$O@O$_{br}$ adsorption is generally stronger on A-TiO$_{2-1/4}$ (101)/A-TiO$_{2-1/6}$ (101) than R-TiO$_{2-1/4}$ (110)/R-TiO$_{2-1/6}$ (110) surfaces, except for 1/2 ML 1/4D H$_2$O@O$_{br}$.

However, the adsorption energies shown in Figure 7(b) are strongly dependent on the stability of the defective A-TiO$_{2-1/4}$ (101)/R-TiO$_{2-1/4}$ (110) and A-TiO$_{2-1/6}$ (101)/R-TiO$_{2-1/6}$ (110) structures with surface O$_{br}$ . Since surface O$_{br}$ are less stable than subsurface O vacancies for A-TiO$_2$ (101), the adsorption energies on A-TiO$_{2-1/4}$ (101) provided in Figure 7(b) are somewhat overestimated.

Figure 7(c,d) shows the PBE G$_0$W$_0$ H$_2$O PDOS relative to $\varepsilon_{VBM}$ as a function of coverage and dissociation for the structures shown in Figure 6. Overall the PDOS on A-TiO$_2$ (101) and R-TiO$_2$ (110) are in surprisingly close agreement, both in shape and energy. For 1/2 ML of H$_2$O, peaks related to the H$_2$O 1b$_2$, 3a$_1$, and 1b$_1$ levels (cf. Figure 5(b)) are clearly evident. When the coverage is increased to more than 1 ML, there are larger differences between the H$_2$O PDOS on A-TiO$_2$ (101) and R-TiO$_2$ (110). This may be attributed to the different intermolecular and interfacial interactions induced by the different hydrogen bonding networks. For 1 1/2 ML H$_2$O on A-TiO$_2$ (101), the peak associated with the H$_2$O 1b$_2$ level, which is located at ~8 eV, is more delocalized than rutile. This is because there are more interfacial interactions between H$_2$O and A-TiO$_2$ (101). For 1 1/2 ML H$_2$O on O$_{br}$ (1/4D), the water 1b$_2$ level splits into two peaks, as H$_2$O and HO$_{br}$ form two lines of hydrogen bonding networks. We also find the bottom of the valence band for H$_2$O on A-TiO$_2$, A-TiO$_{2-1/4}$, and A-TiO$_{2-1/6}$ (101) is higher than that of R-TiO$_2$, R-TiO$_{2-1/4}$, and R-TiO$_{2-1/6}$ (110). This is attributable to the higher VBM of the clean A-TiO$_2$ (101) surface, as depicted by the gray regions in Figure 7.

Table 6. Adsorption Energies $E_{ads}$, Highest PDOS Peaks $\varepsilon_{PDOS}$ and Average PDOS HOMO Energies $\varepsilon_{PDOS}^{HOMO}$ in eV of H$_2$O on Ti$_{cur}$ of Stoichiometric A-TiO$_2$(101) and R-TiO$_2$(110) and O$_{br}$ of Defective A-TiO$_{2-1/4}$(101) and R-TiO$_{2-1/4}$(110) with $x$ = 1/4 or 1/2.

| Coverage | A-TiO$_{2-1/4}$(101) | R-TiO$_{2-1/4}$(110) |
|----------|---------------------|---------------------|
| ML       | $E_{ads}$ | $\varepsilon_{PDOS}$ | $\varepsilon_{PDOS}^{HOMO}$ | $E_{ads}$ | $\varepsilon_{PDOS}$ | $\varepsilon_{PDOS}^{HOMO}$ |
| 1/4      | 1/4D     | 0.27                | 0.17                | 1/4D     | 0.27                | 0.17                |
| 1/2      | 1/4D     | 0.24                | 0.12                | 1/4D     | 0.24                | 0.12                |
| 1/4      | 1/4D     | 0.21                | 0.11                | 1/4D     | 0.21                | 0.11                |
| 1/2      | 1/4D     | 0.20                | 0.10                | 1/4D     | 0.20                | 0.10                |

*Ref. 21.
and R-TiO$_2$-1/4 (110), respectively, as shown in Table 6 and Figure 8. Further, these differences in $\epsilon^{PDOS}_{PDOS}$ are larger for dissociated H$_2$O. Since it is the HOMO of HO@Ti$_{vac}$ which can trap a photogenerated hole, as discussed in section 3.2, the larger differences in $\epsilon^{PDOS}_{PDOS}$ shown in Figures 7(e) and 8 for dissociated H$_2$O suggest A-TiO$_2$ (101) should generally be more photocatalytically active than R-TiO$_2$ (110) from low coverage (2/3 ML H$_2$O) to multi-layered H$_2$O (1/2 ML H$_2$O).

For 2/3 ML of dissociatively adsorbed H$_2$O@O$_{br}$, $\epsilon^{PDOS}_{PDOS}$ relative to the VBM for R-TiO$_2$-1/4(110) is below that for A-TiO$_2$-1/4(101). This suggests HO$_{br}@O_{br}$ should be more photocatalytically active on A-TiO$_2$-1/4(101) compared to R-TiO$_2$-1/4(110). However, as shown in the previous section, the reverse is true for their relative electrochemical activity, i.e., HO$_{br}@O_{br}$ on R-TiO$_2$-1/4(110) is expected to be more electrochemically active than A-TiO$_2$-1/4(101). This demonstrates the importance of considering both the absolute level alignment relative to $E_{VBM}$, and the level alignment relative to $E_{VBM}$.

4. CONCLUSIONS

In heterogeneous catalysis, photocatalytic activity is controlled by the level alignment of the adsorbate and substrate levels. For this reason it is essential to obtain a quantitative description of the interfacial level alignment to determine and predict catalytic activity. This can only be obtained from many-body QP GW calculations, which are necessary to correctly describe the anisotropic screening of electron-electron interactions at the catalyst’s interface.

Previously, we have shown that HSE $G_0W_0$ reliably describes the interfacial level alignment relative to the VBM for highly hybridized and localized molecular levels of H$_2$O (26) and CH$_3$OH (27) on R-TiO$_2$ (110). Here, we have shown that HSE $G_0W_0$ also provides a quantitative description of the occupied Ti$^{3+}$ 3d level’s alignment relative to the Fermi level on both reduced anatase and rutile polymorphs. These are the levels from which electrons are typically excited in 2PP experiments (26). Since HSE DFT fails in both cases, these results clearly demonstrate the important role played by anisotropic screening of the electron-electron interaction in describing the alignment of these molecular and defect levels.

In this study we have performed an in-depth comparison of the QP GW level alignment for H$_2$O–A-TiO$_2$ (101) and H$_2$O–R-TiO$_2$ (110) interfaces for a range of chemically significant structure. We have considered the limits of low and high H$_2$O coverage, intact to fully dissociated H$_2$O, and stoichiometric to O defective surfaces. Using the HOMO–VBM level alignment for H$_2$O adsorbed on A-TiO$_2$ (101) and R-TiO$_2$ (110) shows that the reverse is true for their relative electrochemical activity, i.e., HO$_{br}@O_{br}$ on R-TiO$_2$-1/4(110) is expected to be more electrochemically active than A-TiO$_2$-1/4(101). This demonstrates the importance of considering both the absolute level alignment relative to $E_{VBM}$, and the level alignment relative to $E_{VBM}$.

Figure 7. Structure and coverage dependence of (a,b) $G_0W_0$ PDOS for H$_2$O adsorbed intact (I) or dissociated (D) on (a,c) coordinately unsaturated Ti sites (Ti$_{uns}$) of stoichiometric A-TiO$_2$ (101) (blue, Figure 7(a)) and R-TiO$_2$ (110) (green) and (b,d) bridging O vacancies (O$_{vac}$) of defective A-TiO$_2$ (101) (blue) and R-TiO$_2$ (110) (green), with $x = 1/3$ (thin lines, Figure 7(b)) or $x = 1/4$ (thick lines, Figure 7(c)). (a,b) RPBE $E_{ads}$ on A-TiO$_2$ (101) (110) and R-TiO$_2$ (110) (110) surfaces ($x = 0$, 1/3, 1/4) for (white) low (1/4 and 2/3 ML), (turquoise) medium (1/4 and 1 ML), and (blue) high (1/3 and 1/2 ML) coverage. (c,d) Energies relative to the VBM ($\epsilon_{VBM}$). The clean surface DOS of (c) A-TiO$_2$ (101)/R-TiO$_2$ (110) (dark/light gray regions) are shown for comparison.

Figure 8. Average energy of $G_0W_0$ PDOS HOMO $\epsilon^{PDOS}_{PDOS}$ in eV of H$_2$O@Ti$_{uns}$ on stoichiometric A-TiO$_2$ (101) versus R-TiO$_2$ (110) and of H$_2$O@O$_{vac}$ on defective A-TiO$_2$ (101) versus R-TiO$_2$ (110) for $x = 1/3$ or 1/4. H$_2$O total coverage in ML and fraction intact (I) or dissociated (D) are provided. A linear fit (red dashed line) with a standard deviation of ±0.1 eV (gray regions) is compared to the identity line (black solid line).
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