

Structure of a model TiO₂ photocatalytic interface

H. Hussain^{1,2†}, G. Tocci^{1†}, T. Woolcot¹, X. Torrelles³, C. L. Pang¹, D. S. Humphrey¹, C. M. Yim¹, D. C. Grinter^{1†}, G. Cabailh⁴, O. Bikondoa⁵, R. Lindsay⁶, J. Zegenhagen^{2†}, A. Michaelides¹ and G. Thornton^{1*}

The interaction of water with TiO₂ is crucial to many of its practical applications, including photocatalytic water splitting. Following the first demonstration of this phenomenon 40 years ago there have been numerous studies of the rutile single-crystal TiO₂(110) interface with water. This has provided an atomic-level understanding of the water-TiO₂ interaction. However, nearly all of the previous studies of water/TiO₂ interfaces involve water in the vapour phase. Here, we explore the interfacial structure between liquid water and a rutile TiO₂(110) surface pre-characterized at the atomic level. Scanning tunnelling microscopy and surface X-ray diffraction are used to determine the structure, which is comprised of an ordered array of hydroxyl molecules with molecular water in the second layer. Static and dynamic density functional theory calculations suggest that a possible mechanism for formation of the hydroxyl overlayer involves the mixed adsorption of O₂ and H₂O on a partially defected surface. The quantitative structural properties derived here provide a basis with which to explore the atomistic properties and hence mechanisms involved in TiO₂ photocatalysis.

The generally accepted mechanism of photocatalysis by TiO₂ involves photoexcitation of electrons from the valence band to the conduction band by light with energy greater than the 3 eV bandgap^{1,2}. Holes in the valence band and electrons in the conduction band created by this excitation travel to the surface where they initiate chemical reactions. For example, the electrons can reduce water to hydrogen. The potential for harvesting light in this way to produce a portable fuel in the form of H₂ has motivated the study of technical catalysts. It has also motivated the study of model systems in the form of single-crystal surfaces as a route to understanding the nature of the surface reactions **at the atomic and molecular scale**. Indeed, the interaction of water with TiO₂ in **ultrahigh vacuum (UHV)** has been extensively studied (see, for example, refs 1,3–10). This is especially true for the most commonly explored rutile TiO₂(110) surface (depicted in Fig. 1a), which is the lowest energy termination of rutile¹¹ and hence is the most appropriate model system for a technical catalyst.

The surface chemistry of water interacting with TiO₂(110) under UHV is complex and has been the subject of considerable debate, mostly focusing **on the level of water dissociation and the role of surface defects** (see, for example, refs 1,3–7,10,12). However, many aspects of the adsorption process have now been established. It is known, for example, that at room temperature water dissociates at bridging oxygen vacancies (O_b-vac) as well as ⟨111⟩-oriented steps, producing bridging OH (OH_b) groups^{1,3–7,10,12}. These groups can be converted into terminal OH groups bound to five-fold-coordinated Ti atoms by reaction with O₂ (ref. 13).

Although in the past the emphasis has been on studies of the gas-phase H₂O interface with TiO₂, it is clear that the liquid/solid interface is more relevant for practical applications. Surface X-ray

diffraction (SXRD) provides a potential means of elucidating the structure of this model photocatalytic interface at a quantitative level. This technique has been used extensively to determine metal/liquid interfacial structures under electrochemical control¹⁴, which allows the metal surface to be cleaned *in situ*. This procedure is less straightforward for a semiconducting oxide substrate such as TiO₂. There has been a ground-breaking SXRD measurement of a TiO₂(110)/water interface¹⁵, and one of the first near-ambient-pressure photoemission measurements investigated the chemical states at the interface between TiO₂(110) and an ultrathin film of water¹⁶. However, in both cases a non-standard surface preparation method was employed. As for related modelling of the interface, there have been several computational studies of the water interface formed by the perfect TiO₂(110) surface. The results of these calculations are controversial, being centred around the question of dissociation on the pristine surface^{17–22}.

Here we employ a novel approach to provide the first quantitative structure of a well-defined metal oxide/water interface, which also represents a model of the interface present in the rutile TiO₂ photocatalyst. More specifically, we perform both *ex situ* and *in situ* measurements of the liquid water/TiO₂ interface in an aerobic environment, formed by either temporarily immersing (dipping) a rutile TiO₂(110) surface into water or by depositing a water droplet, respectively. Here we simplify the model photocatalyst to its oxide component in the absence of bandgap light and metal co-catalyst. However, we note that ultraviolet light does not modify TiO₂(110)²³. Moreover, the most effective co-catalyst is well-dispersed Pt nanoparticles²⁴, which are not expected to affect the TiO₂(110)/water component. Understanding a simple model system such as the one considered here is an essential first step towards the characterization of more complex TiO₂ photocatalysts.

¹London Centre for Nanotechnology and Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK. ²ESRF, 6 rue Jules Horowitz, F-38000 Grenoble cedex, France. ³Institut de Ciència de Materials de Barcelona (CSIC), Campus UAB, 08193 Bellaterra, Spain. ⁴Sorbonne Universités, UPMC Univ Paris 06, CNRS-UMR 7588, Institut des NanoSciences de Paris, F-75005 Paris, France. ⁵Department of Physics, University of Warwick, Gibbet Hill Road, Coventry C4 7AL, UK. ⁶Corrosion and Protection Centre, School of Materials, The University of Manchester, Sackville Street, Manchester M13 9PL, UK. [†]Present addresses: Diamond Light Source Ltd, Diamond House, Harwell Science and Innovation Campus, Didcot OX11 0DE, UK (H.H.); Laboratory for Fundamental BioPhotonics and Laboratory of Computational Science and Modeling, Institutes of Bioengineering and Materials Science and Engineering, School of Engineering, and Lausanne Centre for Ultrafast Science, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland (G.T.); Chemistry Department, Building 555, Brookhaven National Laboratory, Upton, New York 11973, USA (D.C.G.); Diamond Light Source Ltd, Diamond House, Harwell Science and Innovation Campus, Didcot OX11 0DE, UK (J.Z.). *e-mail: g.thornton@ucl.ac.uk

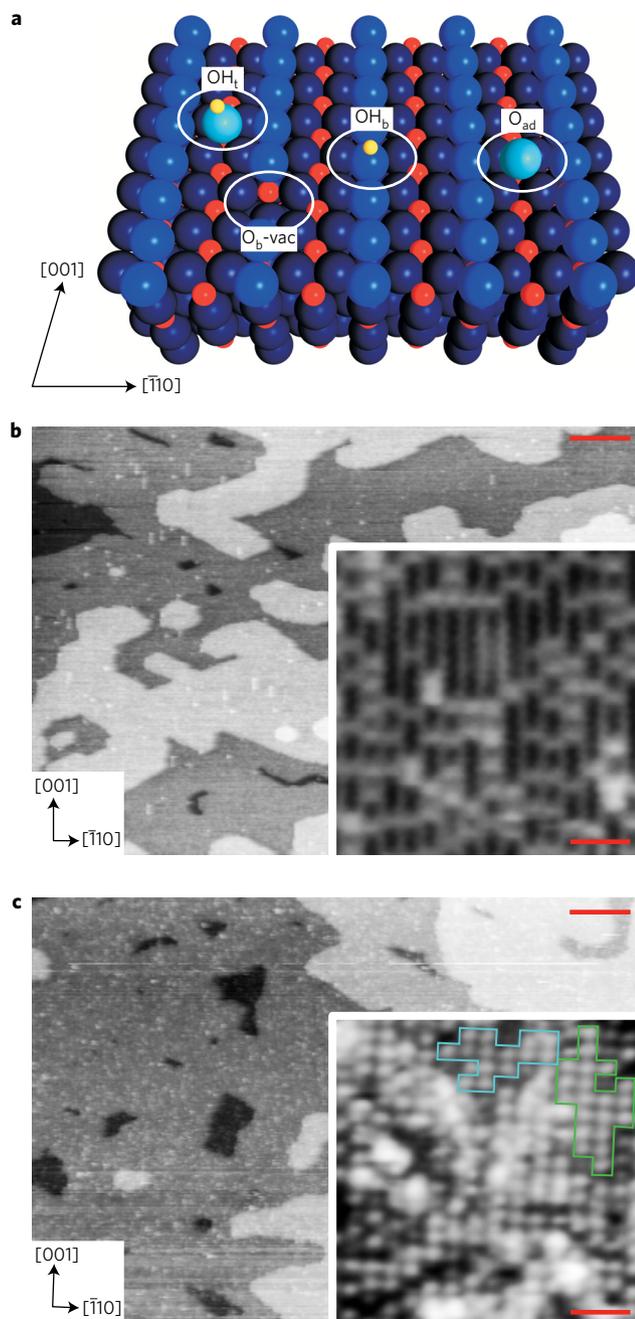


Figure 1 | The $\text{TiO}_2(110)$ surface. **a**, Ball model of $\text{TiO}_2(110)$ together with O_b -vac, OH_b , OH_t and O_{ad} . Ti is shown red and O blue: O_b is shown lighter, and adsorbed O lighter still. H is shown yellow. **b,c**, STM images (0.2 nA, $V_s = 1.2$ V) of the surface before and after immersion in liquid water, respectively. In the large-area images, the red scale bars are 100 Å and in the insets 20 Å. Before immersion, the $\text{TiO}_2(110)$ surface is characterized by bright rows that arise from Ti_{5c} atoms and bright spots that correspond to O_b -vac (0.11 ML) and OH_b (0.10 ML). After immersion in liquid water to form the H_2O_{dip} sample, the surface is characterized by bright spots arranged with a (2×1) periodicity. The blue and green shapes mark areas that are particularly well ordered. Note that these two areas are antiphase domains; the bright spots are offset by one TiO_2 surface unit cell in the [001] direction.

The surfaces were characterized before and after exposure to liquid water using UHV scanning tunnelling microscopy (STM) and SXRD. STM measurements in conjunction with photoelectron spectroscopy in the same instrument evidence the formation of

an ordered (2×1) hydroxyl overlayer formed after dipping. The SXRD results identify the bonding site as the five-fold-coordinated Ti atoms. This site is also occupied at the *in situ* liquid water/ $\text{TiO}_2(110)$ interface, with ordering of molecular water in the second layer. This result is surprising on the basis of what is known from UHV studies. It appears to arise from the availability of a small concentration of O_2 during the formation of the interface, which was not previously anticipated. This work demonstrates the importance of *in situ* structural characterization of model photocatalytic interfaces and provides the basis for the modelling of the photocatalytic interface under aqueous conditions.

In order for our liquid-phase experiments to be connected with the results from $\text{TiO}_2(110)$ UHV studies and to ensure accurate comparison with calculations^{19,20,25}, we employ UHV preparation and analysis methods that are known to produce and verify the presence of an atomically ordered substrate¹. A section of the vacuum chamber (base pressures $\sim 1 \times 10^{-10}$ mbar) is then vented to N_2 (BOC, 99.998% purity) before dipping the sample in water or depositing a droplet of water to form a meniscus. The N_2 gas used has a nominal O_2 content of 5 ppm by volume, which introduces an aerobic environment as found in a real photocatalytic system. At the near-atmospheric pressure used for venting, this equates to a partial O_2 pressure of $\sim 5 \times 10^{-3}$ mbar and an equivalent exposure of $\sim 10^5$ langmuir ($1\text{L} = 1.33 \times 10^{-6}$ mbar sec).

Figure 1b shows STM images of the as-prepared $\text{TiO}_2(110)$ surface¹⁰. In the high-resolution image of the inset, bright (Ti) rows are seen that run in the [001] direction. Bright spots are also present and these are a mixture of O_b -vacs and bridging hydroxyls (OH_b), the latter being formed by water dissociation at defect sites. After venting to N_2 and immersion in 10 ml water (18.2 MΩ cm, total organic content <2 ppm) for 5 min, the sample (H_2O_{dip} sample) was reintroduced to UHV. STM images of the H_2O_{dip} sample are shown in Fig. 1c. The basic morphology of the surface is the same as that in Fig. 1b. There is no evidence of any pitting or erosion of the step edges following immersion in water²⁶.

The high-resolution image shown in the inset of Fig. 1c evidences a (2×1) overlayer. Antiphase domains of this overlayer can form by an offset of one unit cell along the [001] direction. The domains are small, most being shorter than ten $\text{TiO}_2(110)$ unit cell lengths in [001] (~ 30 Å) and four units in $[1\bar{1}0]$ (~ 26 Å). Half-order low-energy electron diffraction beams were not observed, most likely due to either the small domain size and/or electron-stimulated desorption of the adsorbate. X-ray photoelectron spectroscopy (XPS) measurements indicate the level of C contamination to be around 0.1 monolayer (ML) (see Supplementary Fig. 1), where 1 ML is the density of primitive surface unit cells. Venting an as-prepared $\text{TiO}_2(110)$ sample to air or pure O_2 without immersion in water was found not to form a (2×1) overlayer. A previous study also noted the absence of an ordered overlayer after exposure to a nitrogen atmosphere²⁷. Hence, we conclude that the (2×1) overlayer is formed specifically by immersion in liquid water.

From the STM images, we find the coverage of the ordered overlayer to be 0.30 ± 0.05 ML. This coverage and the domain size did not vary when we used samples with different initial O_b -vac concentrations of 0.16 and 0.07 ML. This suggests that neither O_b -vacs nor OH_b (the coverage of which is proportional to the initial O_b -vac density) play a key role in the nucleation process. Hence, strain is a likely origin of the limited domain size²⁸.

To probe the chemical nature of the (2×1) overlayer, we employed XPS and ultraviolet photoelectron spectroscopy (UPS). A peak at ~ 532 eV binding energy in the O 1s spectrum that originates from OH becomes more intense after immersion. Supplementary Fig. 2a,b shows a pair of XPS spectra taken before and after immersion of $\text{TiO}_2(110)$ in water. Similarly, in UPS spectra taken after immersion in water, peaks appear at 8.0 and 10.2 eV below the Fermi level (E_F) that are characteristic of chemisorbed

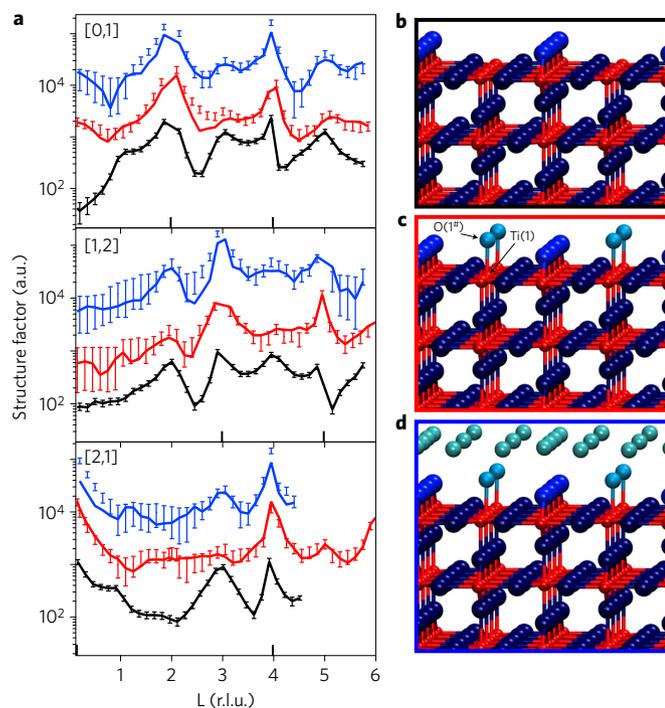


Figure 2 | Selected CTRs from the SXRD measurements alongside proposed models. **a**, The structure factors of the different $\text{TiO}_2(110)$ surfaces are plotted for the (0,1,1), (1,2,1) and (2,1,1) CTRs. Black, red and blue error bars represent the measured experimental data from the as-prepared surface, $\text{H}_2\text{O}_{\text{dip}}$ and $\text{H}_2\text{O}_{\text{drop}}$ samples, respectively, with solid lines being the calculated data. Profiles are offset for clarity. Notches on the x axes correspond to Bragg peaks. **b–d**, Ball-stick models for clean, $\text{H}_2\text{O}_{\text{dip}}$ and $\text{H}_2\text{O}_{\text{drop}}$ samples, respectively.

OH (ref. 2) (Supplementary Fig. 2c). UPS also detects a bandgap state (BGS) associated with O_b -vac and OH_b that lies ~ 0.8 eV below E_F (refs 29–31). This BGS is quenched after immersion in water, which can be explained by healing of the O_b -vacancies/ OH_b by exposure to O_2 during the N_2 venting procedure (Supplementary Fig. 2d). The O_2 exposure of $\sim 10^5$ L is at least an order of magnitude larger than that required to attenuate the BGS (~ 400 L)^{3,29}.

Figure 2a shows selected SXRD results in the form of crystal truncation rods (CTRs) recorded from the $\text{H}_2\text{O}_{\text{dip}}$ surface together with those from the as-prepared UHV surface. The latter results are consistent with those reported previously³². Best fits to the data are also shown in Fig. 2a, with a larger data set being presented in Supplementary Fig. 3. A model for the clean surface is shown in Fig. 2b and the best-fit model for the $\text{H}_2\text{O}_{\text{dip}}$ surface is shown in Fig. 2c. Supplementary Tables 1 and 2 show the atomic displacements, the key for each atom being obtained from Supplementary Fig. 4.

Due to its low X-ray scattering contribution, hydrogen is not included in the analysis and is not shown in the model. Instead, water molecules or hydroxyls are represented only by their oxygen atoms. The bond distance between $\text{O}(1^\#)$ and $\text{Ti}(2)$ (see Fig. 2c) is 1.95 ± 0.03 Å, which is in good agreement with the literature value for the $\text{Ti}-\text{OH}_t$ (terminal OH) bond of 1.85 ± 0.08 Å (ref. 33), whereas the $\text{Ti}-\text{H}_2\text{O}$ bond is much longer at 2.21 ± 0.02 Å (ref. 34). Hence, we assign $\text{O}(1^\#)$ to OH_t , which is also consistent with our photoelectron spectroscopy data. The SXRD data cannot rule out the presence of OH_b ; however, both the XPS and STM results from the $\text{H}_2\text{O}_{\text{dip}}$ surface suggest that only one form of OH species is present. In the case of XPS, the OH-related peak in the O 1s spectrum increases by a factor of 5 ± 1 after dipping. The STM image appears to contain only one type of adsorbate in the (2×1) overlayer.

As STM showed very little change to the morphology of the surface after immersion in liquid water, a near-perfect model was simulated; that is, the occupancies were fixed to 1 during the fit, except that of the OH_t molecule. This has an occupancy of 0.45 ± 0.1 , consistent with the STM results. If the occupancy of the OH_t molecule is fixed at unity, the goodness of fit (χ^2) worsens to 1.6 from a minimum value 1.4 at 0.45 ML. This occupancy of below 0.5 is what one would expect for the (2×1) overlayer with domain wall absences and therefore supports the model. There is no intensity in the position of half-order rods, which is consistent with the small domain sizes found in STM.

The dipping (*ex situ*) experiments allow us to gain chemical composition as well as direct (STM) and reciprocal space (SXRD) information about the interface initially formed at the liquid water interface. Taken together, these measurements paint a robust picture of the interface. Only *in situ* SXRD measurements are possible at the liquid water interface ($\text{H}_2\text{O}_{\text{drop}}$ sample). As we shall show below, a clear connection can be made between the structures obtained from the *in situ* and *ex situ* measurements.

Selected CTRs of the $\text{H}_2\text{O}_{\text{drop}}$ surface are shown together with those from the $\text{H}_2\text{O}_{\text{dip}}$ and as-prepared UHV surfaces in Fig. 2. A larger data set is shown in Supplementary Fig. 5. The best-fit model (hydrated model) is shown in Fig. 2d and has a χ^2 of 1.7. The model is essentially the same as that of the OH_t model (Fig. 2c), except for the presence of a hydration layer above the (2×1) OH_t contact layer. As with the $\text{H}_2\text{O}_{\text{dip}}$ sample, evidence for OH_t (and not H_2O molecules) at the Ti_{5c} sites comes from the bond distance between OH_t and $\text{Ti}(2)$ of 1.95 ± 0.03 Å (see Supplementary Fig. 4 and Supplementary Table 1). Our model differs from that derived from a previous SXRD measurement of a $\text{TiO}_2(110)$ /liquid water interface. In this case an experimental $\text{Ti}-\text{OH}_t$ bond distance of 2.12 ± 0.02 Å was found³⁵, which is closer to the $\text{Ti}-\text{H}_2\text{O}$ bond distance³⁴. Our model also differs from that obtained from the near-ambient-pressure photoemission study, which concluded that only bridging hydroxyls were present at the interface¹⁶. In both cases the discrepancy will arise from the difference in sample preparation and characterization. A (2×1) overlayer was recently observed in STM measurements of a $\text{TiO}_2(110)$ /liquid water interface, where the substrate was prepared in the same manner employed here. By comparison with DFT calculations, water dimers are thought to form the overlayer³⁵. However, on the basis of the work presented here, it seems more likely that the (2×1) overlayer arises from OH_t groups.

To understand the formation of OH_t from exposure of the $\text{TiO}_2(110)$ surface to liquid water, we note that UHV-prepared samples contain O_b -vac and that these react with water in the residual vacuum to form OH_b (refs 3–7,10,12). Approximately 10^5 L O_2 is also supplied here during the N_2 venting procedure. Thus, water, $\text{O}_2(\text{g})$, OH_b and O_b -vac are all potential reactants when we expose our $\text{TiO}_2(110)$ surfaces to liquid water and when combined, OH_t is a likely candidate product¹³. Subsurface defects, such as subsurface Ti interstitials (Ti_{int}), can also participate in the reaction process, by providing a source of excess electrons for the dissociation of $\text{O}_2(\text{g})$ ^{30,36}.

With the above considerations in mind, we performed an extensive series of density functional theory (DFT) calculations to understand the formation of the (2×1) OH_t overlayer. Both geometry optimizations for the interface under UHV-like conditions and *ab initio* molecular dynamics (AIMD) under aqueous conditions were performed. Taken together these suggest that this overlayer most likely forms through the mixed dissociation of O_2 and H_2O on a $\text{TiO}_2(110)$ surface containing point defects, in the form of OH_b , oxygen adatoms (O_{ad}) and Ti_{int} . Specifically, in Fig. 3 we show the potential energy diagram obtained for the vacuum interface for a possible mechanism through which the (2×1) OH_t overlayer can form. The mechanism that governs the stabilization of the overlayer

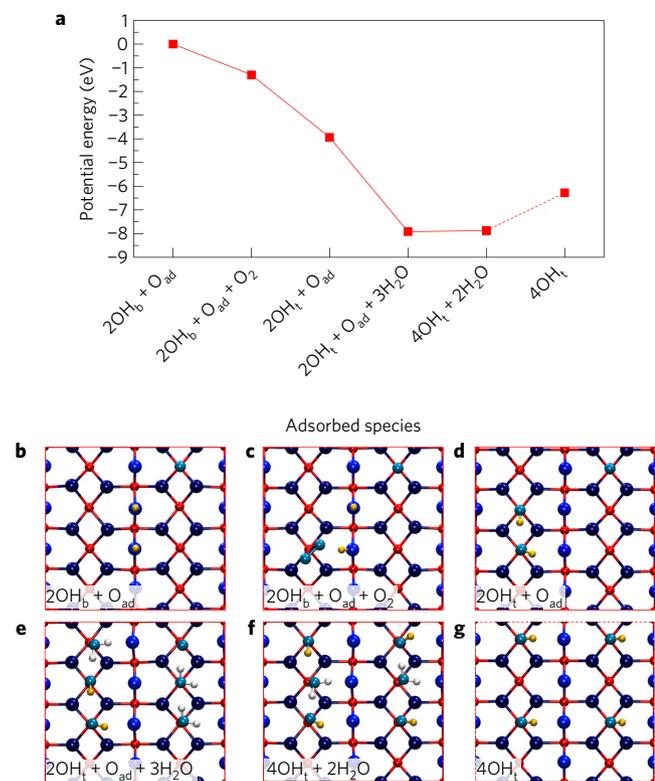


Figure 3 | Possible sequence of reaction steps leading to the formation of the OH_t (2 × 1) overlayer. **a**, Potential energy diagram for the formation of the OH_t overlayer resulting from the mixed adsorption of O₂ and H₂O on a defective TiO₂(110) surface model. The value of the potential energy ΔE at each state s is obtained as the difference between the total energy of that state E_s and that of the previous state E_{s-1} , that is, $\Delta E_s = E_s - E_{s-1} - E_s^{(\text{gas-ads})} + E_s^{(\text{gas-des})}$, and where $E_s^{(\text{gas-ads})}$ and $E_s^{(\text{gas-des})}$ are the total energy of any gas-phase species that has been adsorbed or desorbed upon going from state $s-1$ to state s , respectively. The index s goes from 1 to 5 and the state for $s=0$ corresponds to the reference zero state composed of a surface with 1/4 ML of subsurface Ti_{int}, 1/4 ML of OH_b, and 1/8 ML of O_{ad}, where the OH_b and the O_{ad} are formed from the pre-adsorption of H₂O at an Ob-vac and 1/2O₂ from the gas-phase. The values of the potential energy refer to a (4 × 2) unit cell. The dashed line connecting the 4OH_t + 2H₂O state with the 4OH_t state indicates the desorption of two water molecules to the gas phase. **b-g**, Structures of adsorbates on the defective TiO₂(110). The configurations are labelled according to the states shown in the potential energy diagram in **a**.

relies on a competition between charge transfer arising from the presence of defects (see Supplementary Fig. 6) and the surface distortion due to the adsorption of the OH_t (refs 37,38).

In the process shown in Fig. 3, the energy zero reference state (see Fig. 3a,b) is represented by a TiO₂(110) surface model with 1/4 ML of OH_b, 1/8 ML of O_{ad} and 1/4 ML of subsurface Ti_{int}. From this initial state, the formation of the (2 × 1) OH_t overlayer proceeds with the adsorption of O₂ from the gas phase on a Ti_{5c} site adjacent to a OH_b site (Fig. 3c). O₂ can then react with the OH_b to form a pair of OH_t (Fig. 3d). Following this step, water may adsorb on Ti_{5c} sites to form a mixed overlayer made of an OH_t pair, an O_{ad} and three H₂O (Fig. 3e). Through a sequence of proton transfer events involving the water and the OH_t pair, as well as water and the O_{ad}, a (2 × 1) OH_t overlayer can form. In this state (see Fig. 3f), two water molecules are co-adsorbed with four OH_t arranged in a (2 × 1) symmetry. The 4OH_t + 2H₂O and the 2OH_t + O_{ad} + 3H₂O states are almost degenerate (the 4OH_t + 2H₂O state is about 50 meV less stable). In the final step shown in Fig. 3, water is desorbed to the

gas phase, leaving only a (2 × 1) overlayer of OH_t (Fig. 3g). From Fig. 3 it is clear that the bare OH_t (2 × 1) overlayer is less stable than the state where water is present. This result is consistent with our STM measurements, where it has been observed that the OH_t species are arranged in (2 × 1) symmetry only after dipping the sample in water. Under aqueous conditions instead, the OH_t (2 × 1) overlayer may be stabilized by the presence of water molecules from the liquid phase. This is indeed what we find from analysis of our AIMD simulations of the interface under aqueous conditions, where we find that; the OH_t (2 × 1) overlayer remains stable over two separate AIMD simulations with a total length of 70 ps; and on average 0.18 ML of the Ti_{5c} sites adjacent to the terminal OH groups are occupied by water molecules.

The AIMD simulations also provide an understanding of the second-layer water structure in the case of the H₂O_{drop} surface. Figure 4 shows a comparison between the results from SXR and from AIMD on the structure of the top TiO₂ layers and of the first two overlayers. Figure 4a illustrates a typical structure extracted from an AIMD trajectory of a liquid water film on TiO₂(110) with 1/4 ML Ti_{int} and the (2 × 1) OH_t overlayer structure. The histograms in Fig. 4b show a comparison between the number of O and Ti atoms per unit cell obtained from SXR and from AIMD as a function of the height from the surface. It can be seen that the histogram of the number of O and Ti atoms computed from AIMD overall agrees well with that extracted from SXR. In terms of the location of the first adsorption layer, AIMD predicts a height of 2.07 Å, which is only moderately larger than the height of 1.95 ± 0.03 Å measured in SXR. The location of this first peak is actually rather similar to what one obtains from AIMD and classical force field simulations for both intact and dissociated water on TiO₂ (refs 15,19). Our AIMD simulations predict that there are on average 0.68 O atoms per unit cell in this layer and also that a fraction of water molecules (~1/8 molecules per unit cell) diffuse in and out of this layer during the course of the simulation (see Supplementary Movie 1). The second adsorption layer consists of water molecules that are H-bonded to OH_t, to the transient molecular water in the first adsorption layer, or to O_b atoms. Our AIMD simulations predict that this layer is at a height of 3.98 Å from the top surface layer, in reasonable agreement with the height extracted from SXR of 3.80 ± 0.04 Å. It is interesting to note that our AIMD simulations do not show any evidence of facile proton transfer within the (2 × 1) OH_t overlayer. We cannot exclude that proton hopping and/or proton diffusion events could occur on longer timescales than we have been able to simulate. Nevertheless, the rate for such processes at this interface would still be significantly lower than proton transfer events in liquid water or at other liquid water/oxide interfaces (see for example, refs 39,40). As shown in the Supplementary Information, individual proton transfer events invariably destabilize the overlayer by causing pairs of OH groups to be adsorbed at adjacent adsorption sites.

Our measurements were carried out at near-neutral pH, which is the optimum for photocatalysis by TiO₂/Pt (see ref. 24). Thermodynamic models suggest that at pH 7 there could be a coverage of hydroxyls on TiO₂ associated with a pH greater than the point of zero charge¹⁸. This has been measured to be around 5 for the (110) termination⁴¹. To examine this further, we carried out an additional AIMD simulation to examine the possibility that the OH_t overlayer was formed from the type of OH⁻ diffusion to the oxide/water interface predicted by an AIMD study of liquid water on anatase TiO₂(101)⁴². The results of this simulation are shown in Supplementary Fig. 7. An OH_t (2 × 1) overlayer made of OH⁻ ions is found to be unstable as evidenced by frequent proton transfer events, which disrupt the (2 × 1) symmetry and also result in the formation of O adatoms. This suggests that the OH_t (2 × 1) overlayer instead arises from a mixed O₂ and H₂O dissociation in the presence of point defects as described above.

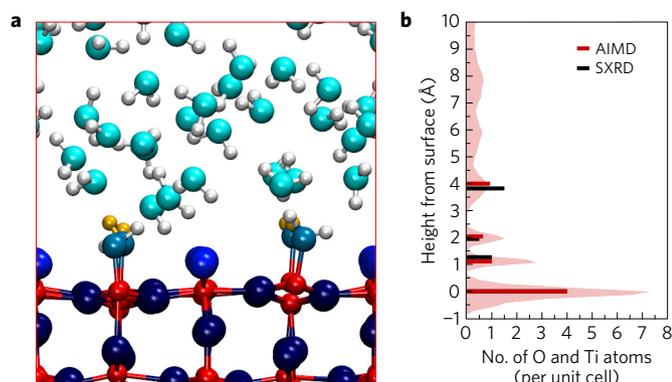


Figure 4 | Structure of the water/TiO₂ interface in aqueous conditions.

a, Snapshot of a liquid water film on TiO₂ obtained from AIMD simulation. **b**, Comparison between the number of Ti and O atoms per unit cell obtained from AIMD and from SXRD as a function of the height from the surface. The zero in the height corresponds to the top surface layer of the Ti_{5c} atoms. The shaded red curve in **b** is the number density of the O and Ti atoms per unit cell $n(z)$ as a function of the height z , obtained from the AIMD. Integration of $n(z)$ between the minima of each peak p (delimited by the heights z_p and z_{p+1}) gives the number of O and Ti atoms per unit cell for a given layer $N(\bar{z}_p)$, which is shown in **b** by the red bar charts for each interface layer: $N(\bar{z}_p) = \int_{z_p}^{z_{p+1}} n(z) dz$, and where $\bar{z}_p = \int_{z_p}^{z_{p+1}} zn(z) dz / \int_{z_p}^{z_{p+1}} n(z) dz$.

In summary, we have shown that a model for a photocatalytic interface between liquid water and rutile TiO₂(110) has terminal hydroxyls in the contact layer. This picture comes from a combination of data from real-space imaging, spectroscopic measurements and surface X-ray diffraction, with interpretation aided by DFT calculations. The ideal coverage of OH₁ is half a monolayer, corresponding to a (2 × 1) structure, but this is decreased to approximately 0.4 monolayers by absences at domain wall boundaries. This interface structure, created in the aqueous aerobic environment considered here, had not been anticipated and is different from what has been established for water on TiO₂(110) under UHV conditions. It is likely to have important implications for the chemistry of wet TiO₂ surfaces. For example, proton hopping and proton transfer is likely to be more facile at an aqueous interface with a high proportion of hydroxide groups (see, for example, ref. 40). Of greatest importance, perhaps, is that the energetics of each elementary step and possibly also the mechanism of the water oxidation process could be altered by the new interface structure identified here^{43,44}. Understanding of water oxidation processes in TiO₂ interfaces under operating aqueous conditions is key to improve the activity of photoelectrochemical cells. Because the presence of OH₁ is likely to open up new reaction pathways to water oxidation, it could be possible to enhance the degree of hydroxylation further through, for example, self-doping of the substrate and exposure to O₂. We hope that by providing accurate experimental structural data for a model photocatalytic interface, this work paves the way to the investigation of the elementary steps involved in water splitting under operating aqueous conditions, including a treatment of the excited-state electronic properties. Ultimately, this will lead to an atomistic-level understanding of the photocatalytic process of water splitting in more complex systems.

Methods

Methods and any associated references are available in the [online version of the paper](#).

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Author contributions

G.Thornton, J.Z. and A.M. designed the project. D.S.H., T.W., C.L.P., C.M.Y., D.C.G. and H.H. performed the STM measurements and T.W. analysed the data. T.W. and C.M.Y. performed the UPS experiments with T.W. analysing the data. H.H., G.C., O.B., X.T., R.L. and G.Thornton performed the SXR measurements and H.H. and X.T. analysed the data. G.Tocci and A.M. conceived, designed and analysed the *ab initio* calculations. G.Tocci performed the *ab initio* calculations. H.H., T.W., G.Tocci, C.L.P., A.M. and G.Thornton wrote the manuscript and the Supplementary Information with input from all authors. All authors participated in discussing the data.

Additional information

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Competing financial interests

The authors declare no competing financial interests.

Methods

The TiO₂(110) (Pi-Kem) samples were prepared following an established procedure¹⁰ involving cycles of Ar⁺ ion sputtering and annealing to ~1,000 K in UHV. Auger electron spectroscopy or X-ray photoelectron spectroscopy was used to confirm the surface cleanliness and low-energy electron diffraction or scanning tunnelling microscopy (STM) was used to ensure that the surfaces were well ordered and unreconstructed. For all three methods, any adventitious ultraviolet-induced modification was avoided by using a red light. Prior to dipping, ultrapure water was de-aerated by bubbling N₂ through the liquid for >1 h. This results in a pH of 6.9.

Scanning tunnelling microscopy. STM measurements were performed with an Omicron UHV variable-temperature STM. Tunnelling was into empty sample states with the sample bias ($V_s = 1.2\text{--}1.5\text{ V}$) and tunnelling current ($I_t = 0.2\text{--}0.5\text{ nA}$). The sample was dipped in ultrapure, deoxygenated H₂O for a range of volumes (2 ml–2 l) and times (15 s–10 min). Surface contamination was minimized by purging the load-lock with N₂. Immediately after the immersion, the sample was reintroduced into UHV where it was transferred to the analysis chamber for STM measurements.

Photoelectron spectroscopy. Normal emission measurements were performed at room temperature in an Omicron UHV low-temperature STM system, incorporating an Omicron HA125 hemispherical energy analyser. Ultraviolet photoelectron spectra used He II ($h\nu = 40.80\text{ eV}$) and He I ($h\nu = 21.20\text{ eV}$) excitation to monitor the valence band and bandgap regions. The Fermi energy (E_F) was determined from the tantalum sample holder that was in electrical contact with the sample. Samples were also monitored using the *in situ* STM to ensure the presence of a (2 × 1) overlayer.

Surface X-ray diffraction. All surface X-ray diffraction measurements were carried out on the ID32 beamline at the European Synchrotron Radiation Facility, employing UHV facilities located in the associated surface characterization laboratory for sample preparation. Once prepared, the sample was transferred under UHV to one of two bespoke, small portable UHV chambers that were mounted on a six-circle diffractometer with the sample surface in the horizontal plane. For the H₂O_{dip} measurements, data acquisition and analysis followed the procedures described in ref. 32 and references therein. For H₂O_{drop} measurements, a total of 1,450 non-equivalent reflections were measured, employing an ‘electrochemical cell’ apparatus⁴⁵. H₂O_{dip} measurements, following a similar procedure to STM measurements, were conducted on a sample that was dipped in ~20 ml of ultrapure, deoxygenated H₂O for approximately 15 s. A large data set of 20 crystal truncation rods was collected that, after corrections, comprised of 835 non-equivalent reflections. The following reflections were monitored at regular intervals to ensure that there was no sample degradation: (1,0,1) H₂O_{dip}; (1,0,0,2) UHV_{as-prepared}; (1,3,0,05) H₂O_{drop}. Data for the last reflection are shown in Supplementary Fig. 8. The best-fit model takes into account Ti sites that are both occupied/unoccupied with OH, with the latter simulating domain walls.

Theoretical. Adsorption of the various species on TiO₂(110) was modelled through spin-polarized DFT structure optimizations using periodic supercells ranging from (2 × 1) to (4 × 2). Adsorption on one side of a four tri-layer TiO₂(110) surface was considered with the bottom tri-layer fixed at its bulk position and at least 15 Å separating periodic images along the surface normal.

We considered a degree of hydroxylation of the surface ranging from 1/4 to 1 ML and a range of Ti_{int} located in the second subsurface layer in a range of concentrations between 0 and 1/2 ML (see Supplementary Fig. 5). The reference states for the adsorption of O₂ or H₂O (see Fig. 3 and Supplementary Fig. 5, for O₂ only) were taken to be their total energies in the gas phase. Interstitials were located

in the second subsurface layer, and the position of defects has shown only a little effect on the adsorption of O₂ on the surface³⁷. The VASP^{46,47} code was used for these calculations with a plane-wave cutoff of 400 eV and projector augmented wave potentials⁴⁸. Sampling of the Brillouin zone was achieved using a Γ -centred (4 × 2 × 1) per primitive surface cell k-point mesh. The PBE⁴⁹ exchange–correlation functional with a Hubbard-*U* correction of 4.2 eV was used. By comparing our results with the hybrid functional HSE06⁵⁰ (see Supplementary Information) we ensured that the chosen value of *U* did not significantly affect the results regarding the formation of the (2 × 1) OH₁ overlayer.

The other set of simulations performed as part of this study involved spin-polarized DFT-based molecular dynamics. These AIMD simulations were performed to investigate the structure of the liquid water/TiO₂ interface and the stability of the OH₁ (2 × 1) overlayer under aqueous conditions. The computational details are similar to those reported in our previous work (see refs 19,20) but are included here for clarity. In brief, we used the CP2K/QUICKSTEP⁵¹ code with the PBE exchange–correlation functional. CP2K/QUICKSTEP employs a mixed Gaussian and plane-wave basis set and norm-conserving pseudopotentials. We used a short-range double valence polarized Gaussian basis⁵² and a 480 Ry cutoff for the plane-wave expansion. The AIMD trajectory analysed in the main text is 50 ps in length, with a 1 fs time step and deuterium masses for the hydrogens in the canonical ensemble with a target temperature of 360 K. As with the static DFT calculations, TiO₂(110) was modelled using a (4 × 2) unit cell, comprised of four tri-layers and 15 Å of vacuum. The liquid water film in contact with the surface was about 2 nm thick, being comprised of 87 molecules. The (2 × 1) overlayer was modelled with neutral OH₁ adsorbed at Ti_{5c} sites with Ti_{int} positioned in the second subsurface layer at a concentration of 1/4 ML. We also performed an additional 50-ps-long AIMD simulation without interstitials to test their effect on the stability of the OH₁ overlayer. The results of these tests show that the OH₁ (2 × 1) overlayer is stable only in the presence of interstitials and with neutral OH species as opposed to OH⁻ (results are shown in Supplementary Figs 5 and 6). Finally, we performed a number of additional AIMD simulations (each of which is about 20 ps long) of TiO₂(110) under aqueous conditions as well as static DFT calculations under UHV-like conditions to compare the stability of the OH₁ (2 × 1) overlayer against that of other less ordered overlayers and to investigate the proclivity of proton transfer at the water/TiO₂(110) interface. Overall, we find that proton transfer and proton diffusion is much more facile at less ordered structures compared with the OH₁ (2 × 1) overlayer (see Supplementary Figs 9–11).

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