Supplementary Information for:

Structure of a model TiO_2 photocatalytic interface

H. Hussain[1,2]†, G. Tocci[1], T. Woolcot[1], X. Torrelles[3], C. L. Pang[1], D. S. Humphrey[1], C. M. Yim[1], D. C. Grinter[1]§, G. Cabailh[4,5], O. Bikondoa[6], R. Lindsay[7], J. Zegenhagen[2]‡, A. Michaelides[1], G. Thornton[1]*

[1] London Centre for Nanotechnology and Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ, UK.

[2] ESRF, 6 rue Jules Horowitz, F-38000 Grenoble cedex, France.

[3] Institut de Ciència de Materials de Barcelona (CSIC), Campus UAB, 08193 Bellaterra, Spain.

[4] Sorbonne Universités, UPMC Univ Paris 06, CNRS, 75005 Paris, France.

[5] CNRS, UMR 7588, Institut des NanoSciences de Paris, 75005 Paris, France.

[6] Department of Physics, University of Warwick, Gibbet Hill Road, Coventry C4 7AL, UK.

[7] Corrosion and Protection Centre, School of Materials, The University of Manchester, Sackville Street, Manchester, M13 9PL, UK.

* To whom correspondence should be addressed. Email: g.thornton@ucl.ac.uk

Current Addresses:

† Corrosion and Protection Centre, School of Materials, The University of Manchester, Sackville Street, Manchester, M13 9PL, UK.

§ Chemistry Department, Building 555, Brookhaven National Laboratory, Upton, NY 11973, USA.

‡ Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0DE, UK.

*To whom correspondence should be addressed. Email g.thornton@ucl.ac.uk

This pdf file contains:

Figures S1-S11

Tables S1, S2

Movie S1

References

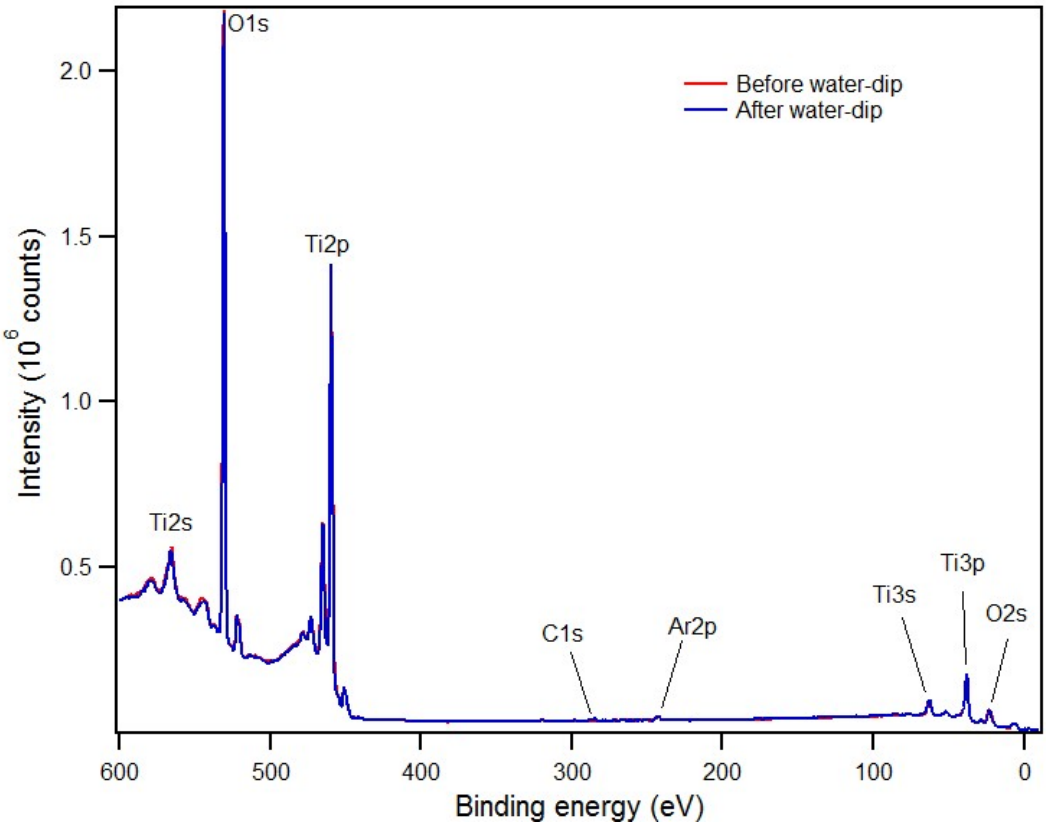

Fig. S1 | XPS spectra from TiO_2(110)/ H_2O_{dip}. Al Kα (hν = 1486.6 eV) photoelectron spectra recorded at normal emission from as-prepared TiO_2(110) and from the sample following immersion in liquid water. Analysis of the H_2O_{dip} spectrum using the methodology in Ref. 1 indicates a C coverage of 0.1 ML.

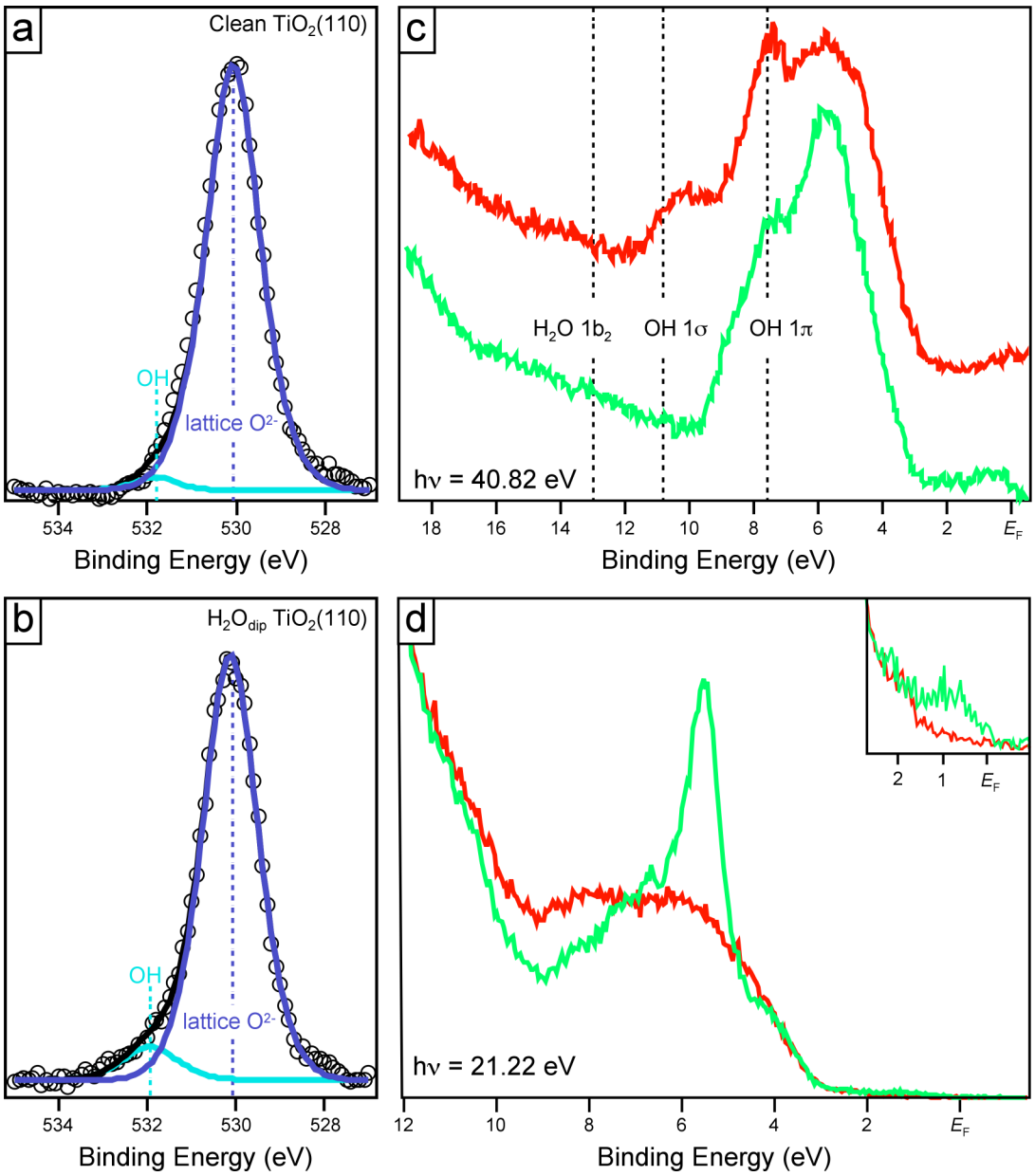

Fig. S2 | Photoemission spectra associated with the H_2O_{dip} sample. a, Al Kα (hν = 1486.6 eV) photoelectron spectra taken at normal emission from the as-prepared TiO_2(110) and **b**, the H_2O_{dip} sample after immersion in liquid water. The peaks were fitted using Gaussian-Lorentzian line shapes after removal of a Shirley background. Peaks are present at ~530 eV and 532 eV which arise from lattice oxygen and OH, respectively[2]. Molecular water, if it were present would appear at ~534 eV (Ref. 2). We note that X-ray induced beam damage is not expected on the basis of earlier work

which reported a photoemission study of TiO_2(110)-H_2O (Ref. 3). **c,** He II ($h\nu$ = 40.82 eV) photoemission spectra taken from the as-prepared surface before (green) and after (red) immersion in liquid water to form the H_2O_{dip} surface. The spectra are offset for clarity and the spectrum from the H_2O_{dip} sample is corrected for band bending. The positions of the OH 3σ and 1π peaks, as well as the absent H_2O $1b_2$ peak position, are marked with dashed lines[4]. **d,** He I ($h\nu$ = 21.22 eV) photoemission spectra taken from the as-prepared surface before (green) and after (red) immersion in liquid water to form the H_2O_{dip} surface. The H_2O_{dip} spectrum is corrected for band bending. The inset shows an expanded view of the band gap region and indicates that after immersion in water, the BGS is quenched.

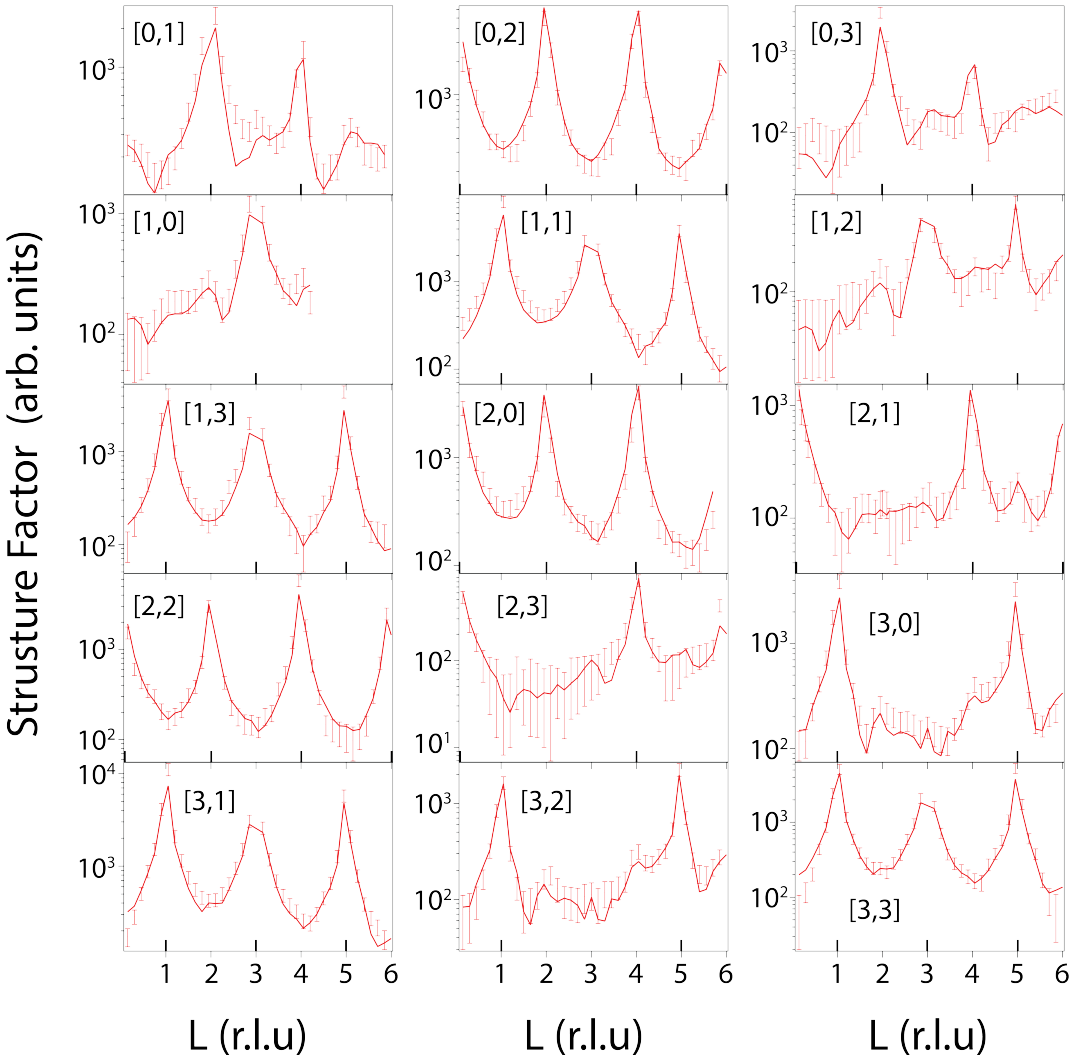

Fig. S3 | Representative CTRs measured for the H_2O_{dip} experiment. Error bars are the experimental data and the solid lines are the corresponding best fits to the data. Notches on the *x* axes correspond to Bragg peaks.

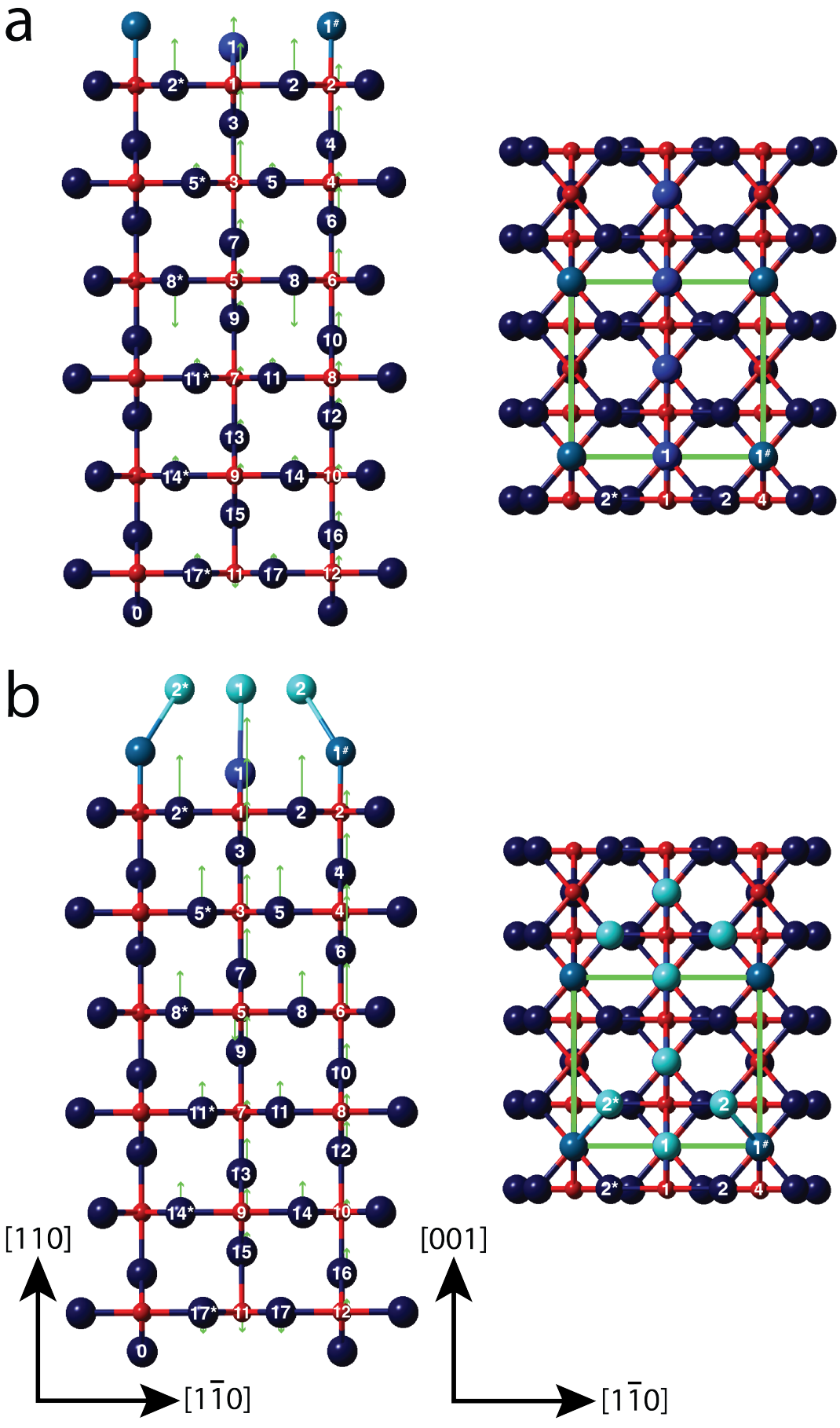
a
b
[110]
[1$\bar{1}$0]
[001]
[1$\bar{1}$0]

Fig. S4 | Best-fit ball and stick models determined from the SXRD data viewed along [001] and [110]. Large blue spheres are oxygen atoms, small red spheres are titanium atoms. O nearer the surface are shaded lighter, H_2O atoms the lightest. Green arrows represent the direction and magnitude of atomic displacements away from the bulk structure. Hydrogen atoms are purposely left out due to their low X-ray scattering factor. The numerical labeling of atoms is employed in Supplementary Table S1 and S2 for identification purposes. Symmetry-paired atoms are denoted as 2*, 5*, 8*, 11*, 14* and 17*. **a,** The OH_t model for the H_2O_{dip} sample and **b,** the hydrated model for the H_2O_{drop} sample. Green line indicates the (2x1) unit cell. Atom $O1^{\#}$ represents the $\underline{O}H_t$ molecule.

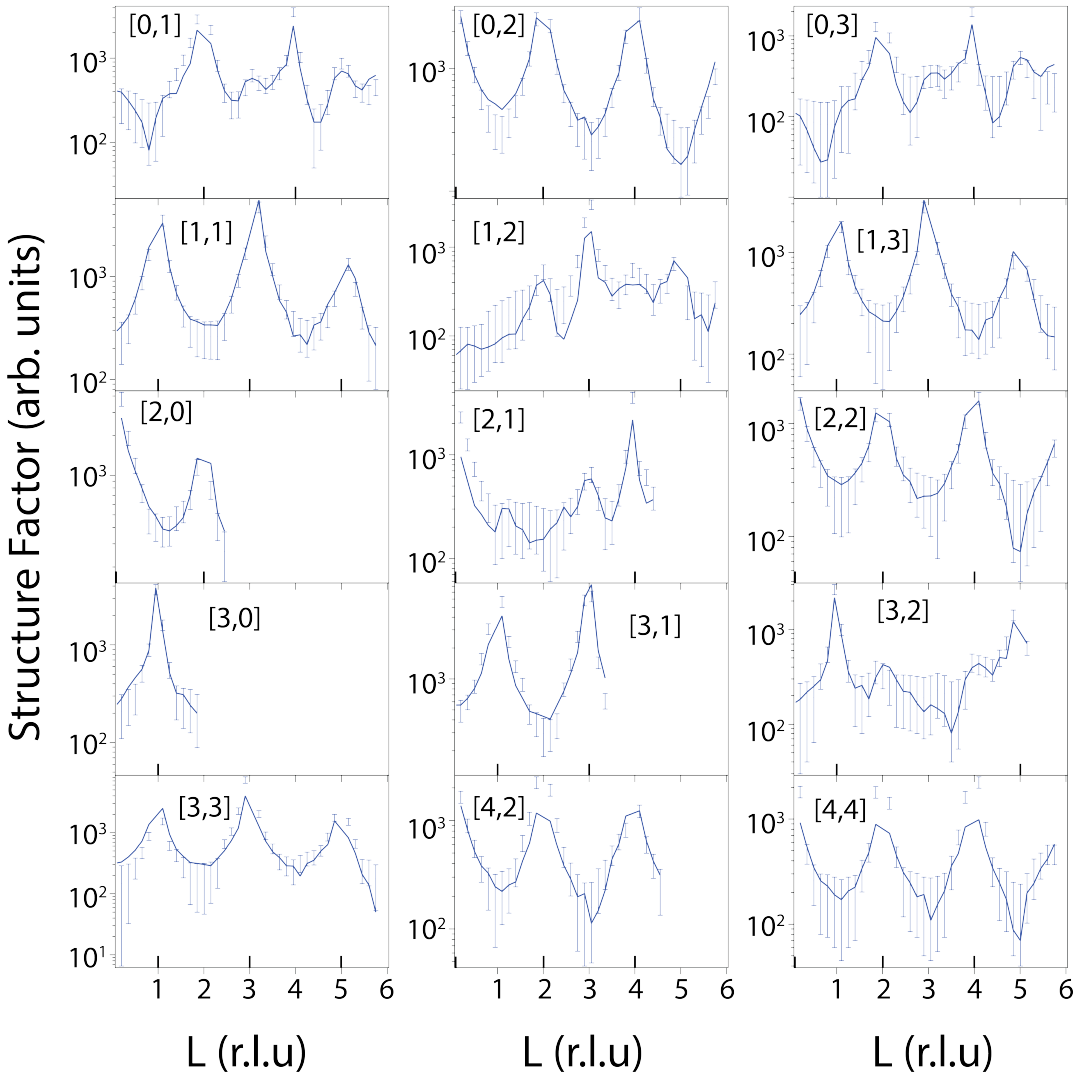

Fig. S5 | Representative CTRs measured for the H_2O_{drop} experiment. Blue error bars are the experimental data and solid blue lines are the corresponding best fits to the data. Notches on the *x* axes correspond to Bragg peaks.

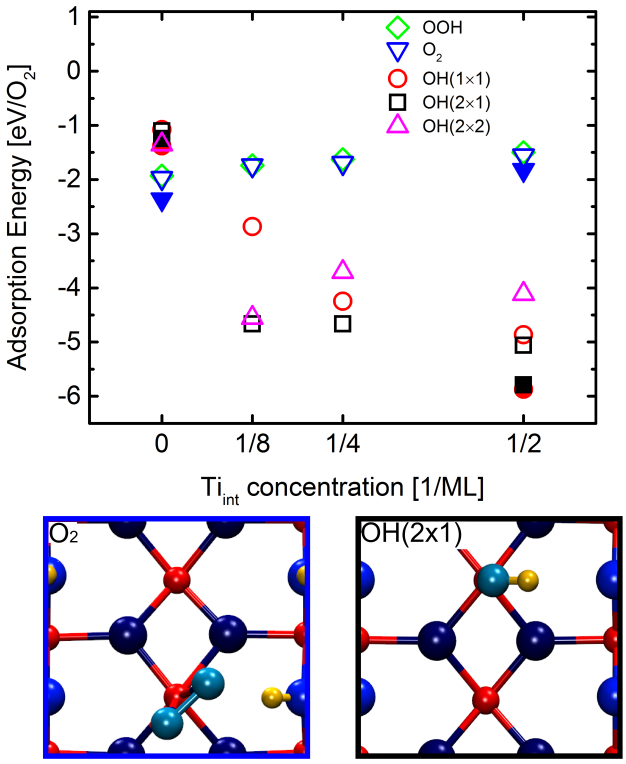

Fig. S6 Stability of overlayer as a function of Ti_{int} concentration. Adsorption energy of O_2 on a hydroxylated TiO_2(110) surface at different Ti_{int} concentrations. Without interstitials the adsorption of O_2 or of a peroxy group (OOH) is more favorable than the dissociation to OH_t. At Ti_{int} concentrations of 1/8 ML or larger the OH_t overlayer is more stable. Specifically, between 1/8 and 1/4 ML of Ti_{int} the OH_t (2 × 1) overlayer is the most stable structure. At a concentration of 1/2 ML the OH_t(1 × 1) becomes instead the most stable structure. This concentration, however, is likely too large to be observed experimentally. The data at 1/2 ML is shown to compare to HSE[5] results (filled symbols). Empty symbols are results obtained using PBE+U[6,7], with a value of U s3= 4.2 eV. Snapshots at the bottom indicate the two adsorption structures for the OH_t (2 × 1) overlayer and the O_2 overlayer with the frames in the same colours used for the symbols in the graph.

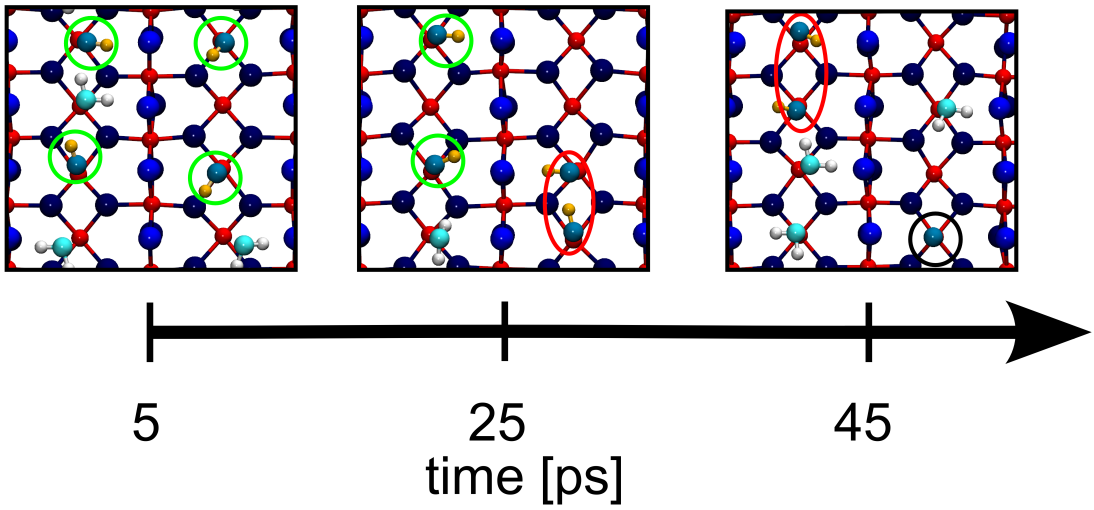

Fig. S7 | Instability of OH_t (2 × 1) overlayer without interstitials. Time evolution of a contact layer of hydroxide OH^- on defect-free TiO_2(110) under aqueous conditions obtained from AIMD. The snapshots show that the (2 × 1) symmetry of the OH_t overlayer is disrupted over the time of the simulation due to a sequence of proton transfer reactions involving the OH species and water. The (2 × 1) symmetry, apparent at the beginning of the AIMD trajectory (5 ps), is already broken after 25 ps, as an OH dimer is formed. Before 45 ps a proton hops from one of the two OH_t on to the other to form water, leaving an O-adatom adsorbed on a Ti_{5c}. Another OH_t dimer structure also forms, disrupting completely the initial symmetry. The green circles indicate single OH_t species, while red circles are drawn around adjacent OH_t species and black ones around the O-adatom. Water molecules above the contact layer are not shown.

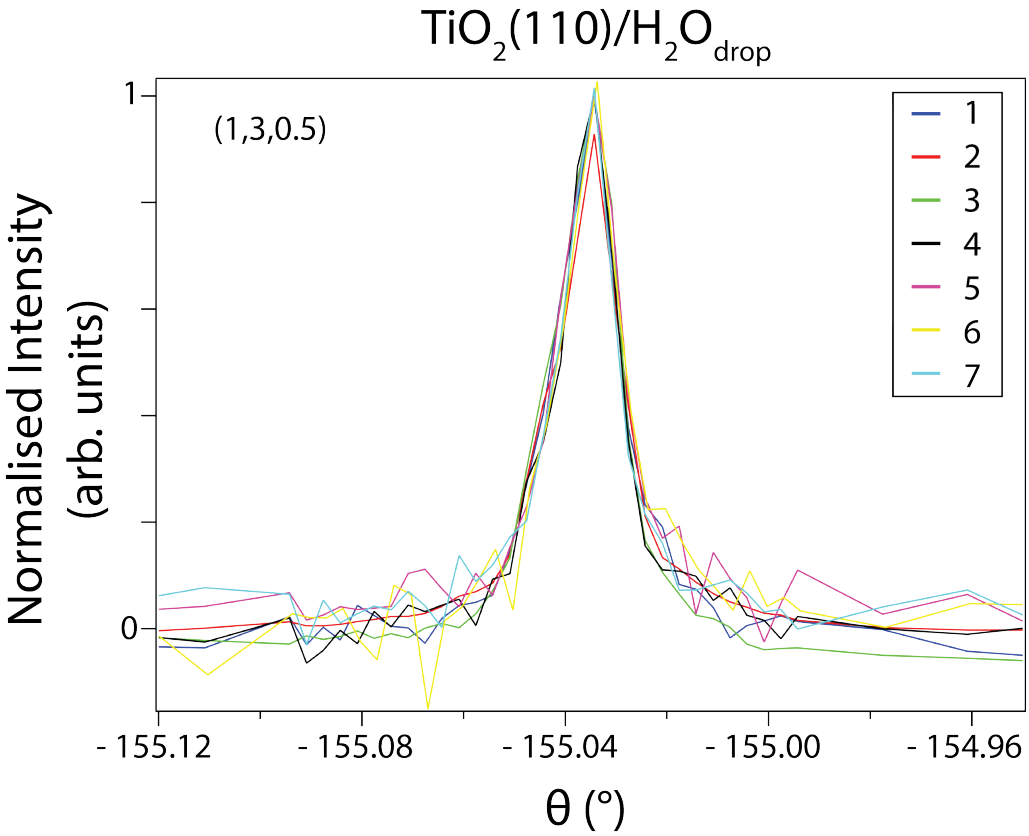

Fig. S8 | Monitoring the stability of the TiO_2(110)-H_2O_{drop} surface structure. Reference (1,3,0.5) reflections from TiO_2(110)-H_2O_{drop} recorded as θ scans at an average 5 hour intervals in the sequence 1-7, starting from time zero. The complete CTR dataset for this surface was recorded in 25 hours.

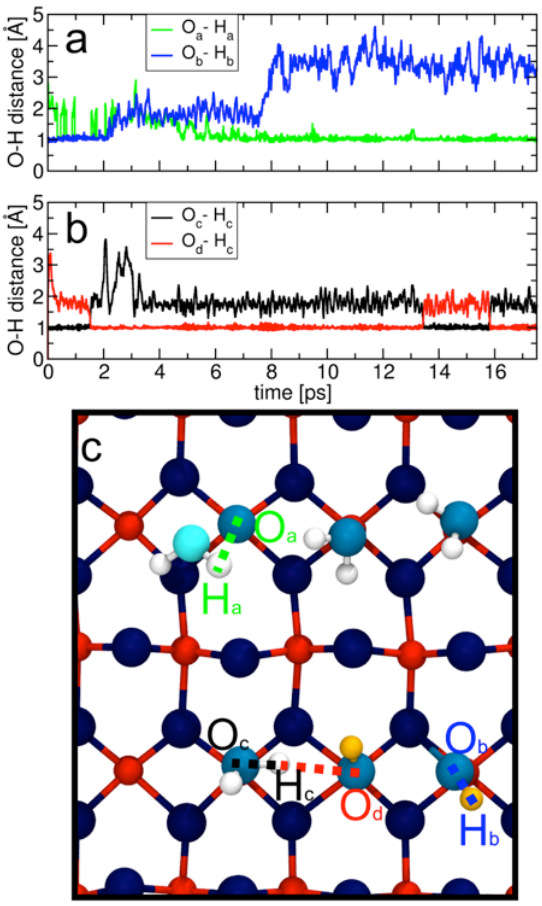

Fig. S9 | Facile proton transfer reactions in the $2OH_t$+O_{ad} overlayer. Time evolution of the distances between several O atoms and H atoms that are involved in different proton transfer reactions, as obtained from a 17.5 ps-long AIMD simulation of a TiO_2(110) surface under aqueous conditions and with 1/4 ML Ti_{int}. Time evolution of the distances between O atoms and H atoms, in which the protons diffuse to/from the liquid (a), or hop between two neighbouring O atoms (b). The starting configuration of the contact layer consists of 1/8 ML O_{ad} and two adjacent OH_t at a coverage of 1/4ML shown in top view (c). In the figures (a) and (b), the protons are bonded to the corresponding O atom when the O-H distances are around 1.0 Å. The dotted lines and the atom labels in c are colour-coded according to the graphs of figures (a) and (b).

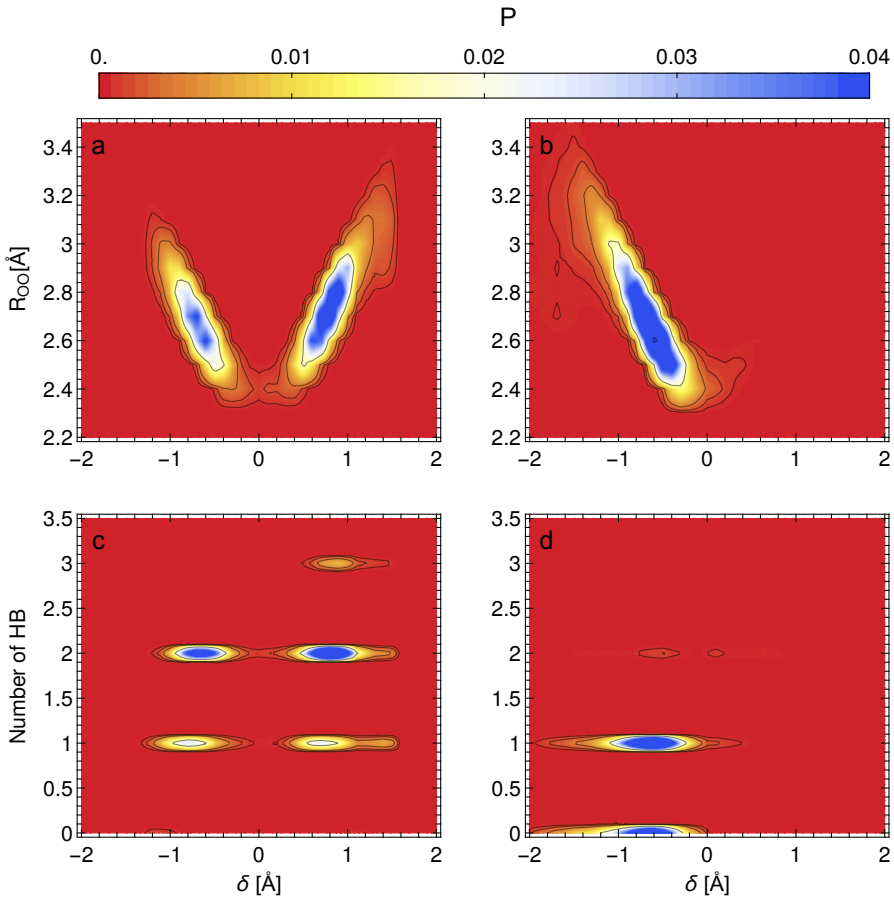

Fig. S10 | Facile proton transfer dynamics in the $2OH_t+O_{ad}$ overlayer compared to the OH_t (2 x 1) overlayer. Contour plots of the probability distribution for protons hopping between two oxygen atoms, as a function of the O-O distance $\boldsymbol{R_{OO}}$ and of the proton displacement $\boldsymbol{\delta}$ with respect to the two neighbouring oxygen atoms for (a) the $2OH_t+O_{ad}$ overlayer and (b) the OH_t (2 x 1) overlayer. δ is defined here as $\boldsymbol{R_{O_aH} - R_{O_bH}}$, where O_a is the oxygen atom that in the initial configuration of the AIMD simulation belongs to an OH_t or an O_{ad} species and O_b is the oxygen of a specie that is nearest to O_a. (c) and (d): Probability distribution as a function of δ and of the number of hydrogen bonds associated with the oxygen O_a and computed according to the geometric criterion of Ref. 8 for the $2OH_t+O_{ad}$ and the OH_t (2 x 1) overlayer, respectively. It can be seen that proton transfer is more facile at the $2OH_t+O_{ad}$ overlayer (see Fig. S9(b)) compared to the OH_t (2 × 1) overlayer. The hopping (or

not) of the protons in the two configurations is correlated to the distribution of H-bonds that the OH_t and the O_{ad} species engage in with the surrounding molecules. The analysis has been carried out on a total of 4 AIMD trajectories that have been started from different initial conditions. The two trajectories for the $2OH_t+O_{ad}$ overlayer, each of which is about 20 ps-long, while the ones for the OH_t (2 x 1) overlayer are 50 ps-long and 20 ps-long.

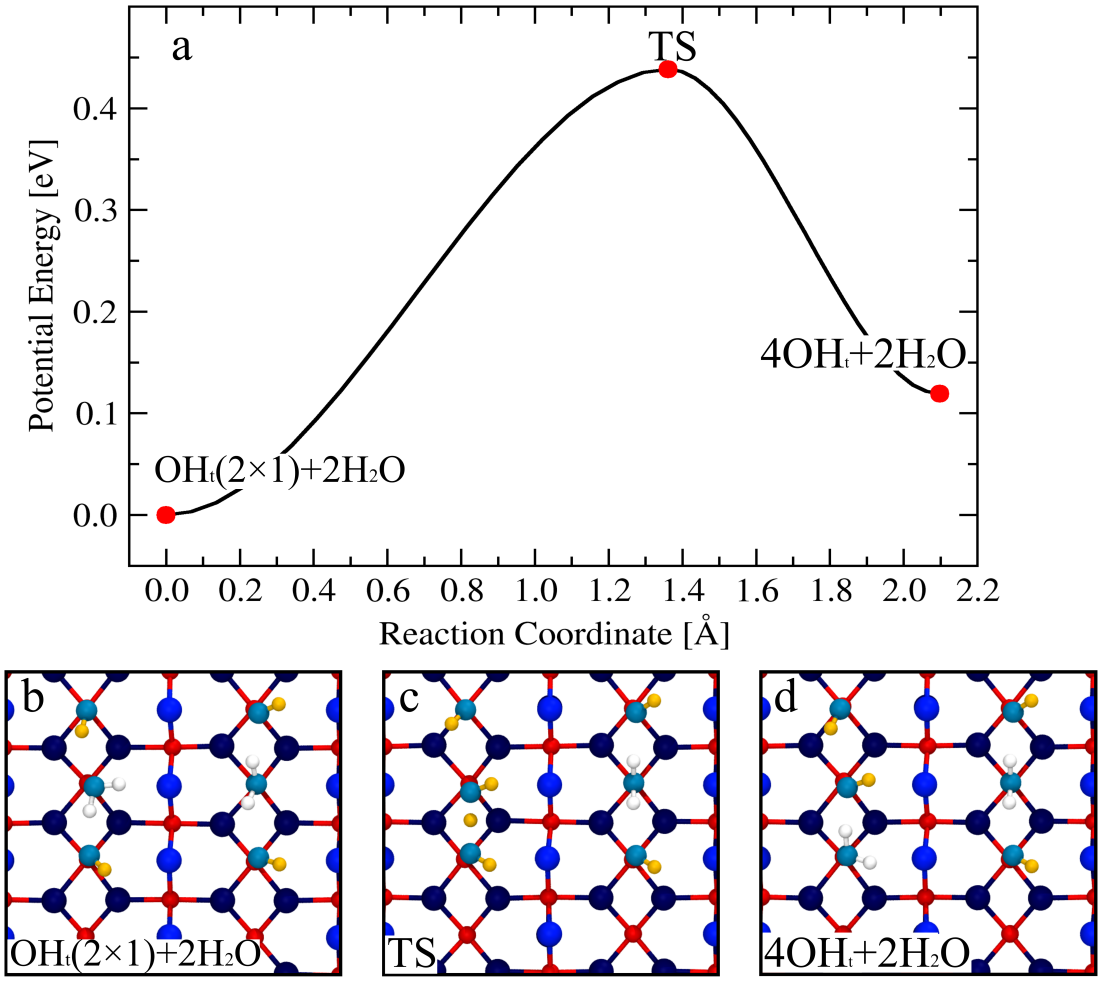

Fig. S11 | Energy path for the hopping of a proton from an H_2O to an OH_t at the OH_t (2 x 1) + $2H_2O$ overlayer. (a) Potential energy diagram computed with CP2K with the PBE0-TC-LR functional[9,10,11]. The transition state has been computed using the climbing image nudged elastic band method.[12] (b)-(d): Snapshots of the OH_t (2 x

1)+2H_2O overlayer (i.e. energy zero reference state), of the TS, and of the disordered 4OH_t+2H_2O overlayer (i.e the final state), respectively. It can be seen that the OH_t (2 x 1) + 2H_2O overlayer is about 0.10 eV more stable than the 4OH_t + 2H_2O overlayer and that there is a barrier of about 0.43 eV for this transition.

Supplementary Table S1 SXRD-derived substrate atomic displacements (Å) away from the bulk-terminated structure for the H_2O_{dip} and H_2O_{drop} samples. Also listed are the displacements for the as-prepared UHV $TiO_2(110)$ surface prior to the H_2O_{drop} experiment ($UHV_{as\text{-}prepared}$), values for previous SXRD measurements of $TiO_2(110)$ in UHV[13], as well as the bulk truncated coordinates for $TiO_2(110)(1\times1)$. It should be noted that the displacements given for the H_2O_{dip} and H_2O_{drop} samples are for the case where OH is adsorbed to surface Ti atoms. Unoccupied surface Ti atoms displace in quantitative agreement with the $UHV_{as\text{-}prepared}$ sample (see Methods). Supplementary Fig. S4 provides a key to the identity of the atoms. A negative value indicates that the atom moves towards the bulk for a displacement perpendicular to the surface plane, that is in the [110] direction, and in the $[1\bar{1}0]$ direction for a lateral displacement.

Atom	(1×1) Bulk Terminated Coordinates (Å)	Displacements (Å)			
		Ref. 13	$UHV_{as\text{-}prepared}$	$H_2O_{(l)\text{-}dip}$	$H_2O_{(l)\text{-}drop}$
O(1)	18.77	0.10 ± 0.04	0.10 ± 0.04	0.03 ± 0.03	0.08 ± 0.04
O(2) [110]	17.50	0.17 ± 0.03	0.13 ± 0.03	0.06 ± 0.03	0.08 ± 0.03
O(2) $[1\bar{1}0]$	5.23	0.01 ± 0.05	0.02 ± 0.04	0.01 ± 0.05	0.01 ± 0.05
Ti(1)	17.50	0.25 ± 0.01	0.17 ± 0.01	0.07 ± 0.01	0.09 ± 0.01
Ti(2)	17.50	-0.11 ± 0.01	-0.06 ± 0.01	0.03 ± 0.01	0.03 ± 0.01
O(3)	16.24	0.07 ± 0.04	0.07 ± 0.04	0.04 ± 0.04	0.07 ± 0.03
O(4)	15.52	0.00 ± 0.03	0.02 ± 0.03	0.05 ± 0.03	0.05 ± 0.05
O(5) [110]	14.25	0.04 ± 0.03	0.03 ± 0.03	0.01 ± 0.03	0.06 ± 0.03
O(5) $[1\bar{1}0]$	4.37	0.05 ± 0.05	0.02 ± 0.03	0.03 ± 0.03	0.05 ± 0.05
Ti(3)	14.25	-0.08 ± 0.01	-0.02 ± 0.01	0.07 ± 0.01	0.06 ± 0.01
Ti(4)	14.25	0.19 ± 0.01	0.12 ± 0.01	0.01 ± 0.01	0.04 ± 0.01
O(6)	12.99	0.01 ± 0.04	0.04 ± 0.04	0.04 ± 0.03	0.08 ± 0.05

O(7)	12.27	0.00 ± 0.04	0.01 ± 0.04	0.02 ± 0.03	0.06 ± 0.05
O(8) [110]	11.01	0.01 ± 0.03	0.01 ± 0.05	-0.06 ± 0.03	0.05 ± 0.03
O(8) [$1\bar{1}0$]	5.23	-0.03 ± 0.05	-0.02 ± 0.05	-0.01 ± 0.05	-0.03 ± 0.02
Ti(5)	11.01	0.08 ± 0.01	0.05 ± 0.01	0.01 ± 0.01	-0.04 ± 0.01
Ti(6)	11.01	-0.04 ± 0.01	-0.02 ± 0.01	0.05 ± 0.01	0.08 ± 0.01
O(9)	9.74	0.02 ± 0.04	0.03 ± 0.03	0.01 ± 0.03	0.04 ± 0.04
O(10)	9.02	-0.02 ± 0.04	-0.01 ± 0.03	0.03 ± 0.03	0.03 ± 0.03
O(11) [110]	7.76	0.01 ± 0.03	0.01 ± 0.02	0.01 ± 0.03	0.03 ± 0.03
O(11) [$1\bar{1}0$]	4.37	0.01 ± 0.04	0.01 ± 0.03	0.01 ± 0.03	0.02 ± 0.04
Ti(7)	7.76	-0.02 ± 0.01	-0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
Ti(8)	7.76	0.07 ± 0.01	0.04 ± 0.01	0.02 ± 0.01	0.02 ± 0.01
O(12)	6.50	0.02 ± 0.02	0.02 ± 0.03	0.01 ± 0.02	0.03 ± 0.04
O(13)	5.78	0.00 ± 0.02	0.01 ± 0.03	0.01 ± 0.02	0.04 ± 0.04
O(14) [110]	4.51	0.03 ± 0.03	0.03 ± 0.03	0.01 ± 0.04	0.03 ± 0.03
O(14) [$1\bar{1}0$]	5.23	-0.02 ± 0.03	-0.01 ±0.02	-0.01 ± 0.03	-0.02 ± 0.04
Ti(9)	4.51	0.02 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.03 ± 0.01
Ti(10)	4.51	-0.01 ± 0.01	-0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
O(15)	3.25	0.00 ± 0.02	0.01 ± 0.03	0.00 ± 0.02	0.01 ± 0.02
O(16)	2.53	-0.02 ± 0.02	-0.02 ± 0.03	0.02 ± 0.03	0.02 ± 0.02
O(17) [110]	1.26	0.01 ± 0.02	0.02 ± 0.02	0.01 ± 0.03	-0.01 ± 0.03
O(17) [$1\bar{1}0$]	4.37	0.02 ± 0.02	0.01 ± 0.02	0.01 ± 0.02	0.02 ± 0.02
Ti(11)	1.26	-0.01 ± 0.01	-0.01 ± 0.01	-0.01 ± 0.01	-0.02 ± 0.01
Ti(12)	1.26	0.03 ± 0.01	0.01 ± 0.01	0.00 ± 0.01	0.01 ± 0.01

Supplementary Table S2 SXRD-derived optimised locations of atoms (Å) relative to the position of O(0) at (0,0,0) for the H_2O_{dip} and H_2O_{drop} samples (see Supplementary Fig. S4 for a key to the identity of the atoms). Also listed are the atomic positions for the as-prepared UHV TiO_2(110) surface prior to the H_2O_{drop} experiment ($UHV_{as\text{-}prepared}$), values for previous SXRD measurements of TiO_2(110) in UHV[13], as well as the bulk truncated coordinates for TiO_2(110)(1×1). The O atoms in OH and H_2O are underlined in the table to highlight the fact that the positional parameters given are only for these atoms in the molecules.

Atom	(1×1) Bulk Terminated Coordinates (Å)	Optimised Positions (Å)			
		Ref. 13	$UHV_{as\text{-}prepared}$	$H_2O_{(l)\text{-}dip}$	$H_2O_{(l)\text{-}drop}$
$H_2\underline{O}$(2) [110]	-	-	-	-	21.35
$H_2\underline{O}$(2) [1$\bar{1}$0]	-	-	-	-	5.32
$H_2\underline{O}$(1)	-	-	-	-	21.34
$\underline{O}H(1^{\#})$	-	-	-	19.52	19.54
O(1)	18.77	18.87	18.87	18.80	18.85
O(2) [110]	17.50	17.67	17.63	17.56	17.58
O(2) [1$\bar{1}$0]	5.23	5.24	5.25	5.24	5.24
Ti(1)	17.50	17.75	17.67	17.57	17.59
Ti(2)	17.50	17.39	17.44	17.53	17.53
O(3)	16.24	16.31	16.31	16.28	16.31
O(4)	15.52	15.52	15.54	15.57	15.57
O(5) [110]	14.25	14.29	14.28	14.26	14.31
O(5) [1$\bar{1}$0]	4.37	4.42	4.39	4.40	4.42
Ti(3)	14.25	14.17	14.23	14.32	14.31
Ti(4)	14.25	14.44	14.37	14.26	14.29
O(6)	12.99	13.00	13.03	13.03	13.07
O(7)	12.27	12.27	12.28	12.29	12.33

O(8) [110]	11.01	11.02	11.02	10.95	11.06
O(8) [1$\bar{1}$0]	5.23	5.20	5.21	5.22	5.20
Ti(5)	11.01	11.09	11.06	11.02	10.97
Ti(6)	11.01	10.97	10.99	11.06	11.09
O(9)	9.74	9.76	9.77	9.75	9.78
O(10)	9.02	9.00	9.01	9.05	9.05
O(11) [110]	7.76	7.77	7.77	7.77	7.79
O(11) [1$\bar{1}$0]	4.37	4.38	4.38	4.38	4.39
Ti(7)	7.76	7.74	7.75	7.77	7.77
Ti(8)	7.76	7.83	7.80	7.78	7.78
O(12)	6.50	6.52	6.52	6.51	6.53
O(13)	5.78	5.78	5.79	5.79	5.82
O(14) [110]	4.51	4.54	4.54	4.52	4.54
O(14) [1$\bar{1}$0]	5.23	5.21	5.22	5.22	5.21
Ti(9)	4.51	4.53	4.52	4.52	4.54
Ti(10)	4.51	4.50	4.50	4.52	4.52
O(15)	3.25	3.25	3.26	3.25	3.26
O(16)	2.53	2.51	2.51	2.55	2.55
O(17) [110]	1.26	1.27	1.28	1.27	1.25
O(17) [1$\bar{1}$0]	4.37	4.39	4.38	4.38	4.39
Ti(11)	1.26	1.25	1.25	1.25	1.24
Ti(12)	1.26	1.29	1.27	1.26	1.27

Movie S1 | *Ab initio* molecular dynamics simulation of rutile TiO_2(110) in aqueous conditions. *Ab initio* molecular dynamics trajectory of liquid water on TiO_2(110) showing that the OH_t groups, with H atoms depicted in yellow, are stable during the full length of the 50 ps-long AIMD trajectory. It can also be seen that the water molecule in black diffuses between the contact layer and the layer above. The system is composed of 4-trilayers of rutile TiO_2(110), with a concentration of 1/4 ML of Ti-interstitials lying between the second and third trilayer. The green vertical lines indicate the unit cell used in the simulation, which corresponds to a (4×2) TiO_2(110) unit cell. The water contact layer consists of a mixture of OHt arranged in a (2×1) symmetry and intact water molecules that diffuse in and out of the layer during the time of the simulation. The atoms are colour-coded according to the figures in the manuscript.

References

1. D. Briggs, M.P. Seah, Practical Surface Analysis, Auger and X-ray Photoelectron Spectroscopy, 2nd Ed, Wiley (1990).

2. L. E. Walle, A. Borg, P. Uvdal, A. Sandell, Experimental evidence for mixed dissociative and molecular adsorption of water on a rutile TiO_2(110) surface without oxygen vacancies. *Phys. Rev. B*. **80,** 235436 (2009)

3. Allegretti, F., O'Brien, S., Polcik, M., Sayago, D. I. & Woodruff, D. P. *Phys. Rev. Lett.* 95, 226104 (2005).

4. Kurtz, R. L., Stockbauer, R., Madey, T. E., Román, E. & De Segovia, J. Synchrotron radiation studies of H_2O adsorption on TiO_2(110). *Surf. Sci.* **218,** 178–200 (1989).

5. Heyd, J.; Scuseria, G. E.; Ernzerhof, M., Hybrid functionals based on a screened Coulomb potential. *J. Chem. Phys.* **118**, 8207 (2003).

6. Perdew, J. P., Burke, K., Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77,** 3865 (1996).

7. Morgan, B. J., Watson, G. W. A DFT+U description of oxygen vacancies at the TiO_2 rutile(110) surface. *Surf. Sci*. **601,** 5034 (2007).

8. Luzar, A, Chandler, D. Hydrogen-bond kinetics in Liquid Water. *Nature*, **379**, 55 (1996).

9. Guidon, M., Hutter, J. and VandeVondele, J. Auxiliary density matrix methods for hartree−fock exchange calculations. *J. Chem. Theor. Comput.* **6**(8), 2348-2364 (2010).

10. Guidon, M. Hutter, J. and VandeVondele, J. Robust Periodic Hartree−Fock Exchange for Large-Scale Simulations Using Gaussian Basis Sets. *J. Chem. Theor. Comput.* **5**(11) 3010-3021 (2009).

11. Spreafico, C., and VandeVondele, J. Excess Electrons and Interstitial Li Atoms in TiO_2 Anatase: Properties of the (101) Interface. *J. Phys. Chem. C* **119**(27) 15009-15018 (2015).

12. Henkelman, G., Uberuaga, B. P., Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.* **113**(22) 9901-9904 (2000).

13. Cabailh, G. *et al.* Geometric structure of TiO_2(110)(1×1): Achieving experimental consensus. *Phys. Rev. B* **75,** 241403 (2007).