

**Supplemental Material for**  
**“Water dissociation and hydroxyl ordering on anatase**  
 **$\text{TiO}_2(001)-(1\times 4)$ ”**

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## THEORETICAL DETAILS

Density Functional Theory (DFT) calculations were carried out with the GPAW code[3] and the Atomic Simulation Environment.[4] We used the PBE exchange-correlation functional [5] the projector-augmented wave method of Blöchl,[6] and a real-space grid for the expansion of the wave functions. The geometries for the different models used were optimized until the forces on each relaxed atom were lower than  $0.05 \text{ eV}/\text{\AA}$  and the electronic structure at each geometry optimization step was self-consistently converged with energy, density, and eigenvalue thresholds of  $5\text{E-}5$ ,  $1\text{E-}4$ , and  $5\text{E-}8 \text{ eV}$ , respectively. A spacing of  $0.18 \text{ \AA}$  was used for the real space grid expanding the wave functions. We used the DFT+U approach[7] in order to partially correct the inherent self-interaction error of the PBE functional and to improve the description of Ti3d electrons in anatase. Following previous work,[8] we used a U value of  $4 \text{ eV}$ .

The structural models describing the (A)- $\text{TiO}_2(001)$ -( $1\times 4$ ) surface were formed by 9 atomic layers (3 of Ti and 6 of O) plus the ad-molecule ridge. The bottom 3 atomic layers (an O-Ti-O trilayer) were kept fixed during geometry optimization, while the rest of atoms were allowed to relax. Six different supercell models were used for describing varying adsorbate coverage  $\Theta$ . Namely, ( $n\times 1$ ) repetitions of the ( $1\times 4$ ) supercell representing the ADM reconstruction were used to describe ridge coverage values of  $\Theta = 1/n$ . Here, the water

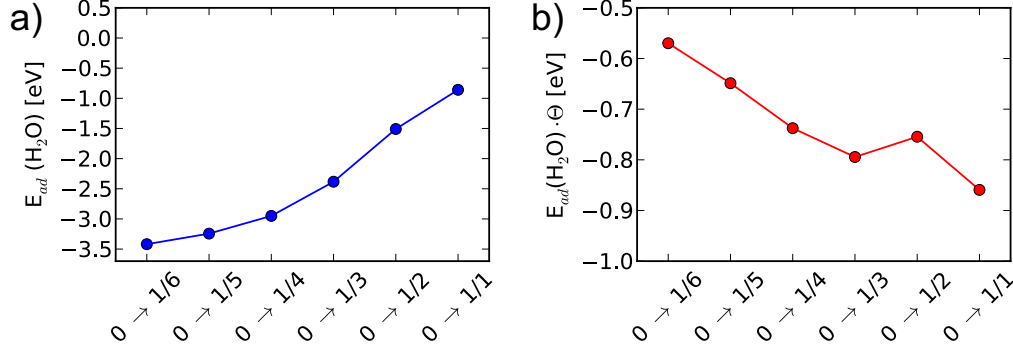


FIG. S1. (a) Adsorption energies (per  $\text{H}_2\text{O}$  molecule) calculated for coverage increases from  $\Theta=0$  to  $\Theta=1/n$ . (b) Adsorption energies from a) normalized by the coverage, which provides average adsorption energy of water molecules for each coverage.

coverage  $\Theta$  is defined with respect to the number of topmost ridge sites only and does not account for terrace sites, which were kept unoccupied, as observed experimentally. The reciprocal space of the resulting ( $n \times 4$ ) supercells for  $n = 1, 2, 3, 4, 5$ , and  $6$ , was sampled with k-point grids of ( $k \times 1 \times 1$ ) with  $k = 4, 2, 2, 1, 1$ , and  $1$ , respectively. The appropriateness of comparing adsorption energies using different combinations of supercells and k-point grids was examined by calculating the same adsorption energy using supercells of different size. Adsorption energies for  $\Theta = 1/2$  and  $1/3$  calculated with the ( $2 \times 4$ ) and ( $3 \times 4$ ) supercells, respectively, differ by less than 10 meV from those calculated by placing two water molecules on the ( $4 \times 4$ ) and ( $6 \times 4$ ) supercells, respectively.

## EXPERIMENTAL DETAILS

The STM experiments were carried out in a UHV chamber with a base pressures in the  $10^{-11}$  mbar range using a home-built Aarhus STM with a chemically etched tungsten tip. Natural anatase crystals (SurfaceNet GmbH) were mounted using Ta thin wires on a Ta sample plate. A small piece of Au foil was spot-welded to the sample plate and used for Fermi edge measurements. The sample temperature was measured using a K-type thermocouple spot-welded to the back side of the sample plate. The XPS experiments were carried out at the Matline end-station of ASTRID2 synchrotron facility in Aarhus, Denmark. The anatase (001) terminated single crystals were prepared by up to 20 cycles of  $\text{Ar}^+$  sputtering at RT

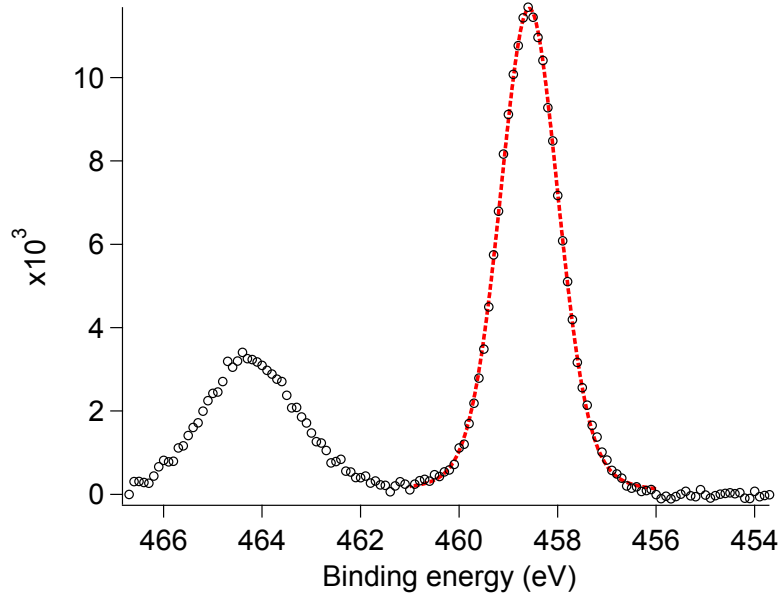


FIG. S2. Ti 2p peak measured on a bare  $1\times 4$  reconstructed surface using 542 eV photon energy (black circles). The fit of the Ti 2p<sub>3/2</sub> component by a Gaussian-Lorentzian shape is centered around 458.6 eV and is highly symmetric.

(1.5 kV, 5-10 min) followed by annealing at 950-1000 K for 20 min in UHV. Amount of C as well as common impurities such as Nb, Fe and V were below the detection limit of core-level XPS.

Water exposures were accomplished in the absence of X-ray irradiation using deionized water cleaned by up to 10 freezing-thawing cycles. O 1s and VB spectra were recorded using 610 eV and 47.5 eV photon energy, respectively. The O 1s peak recorded on the clean A-TiO<sub>2</sub>(001)-(1 $\times$ 4) surface is highly symmetric and the best fit is achieved using a single Voigt profile with Gaussian to Lorentzian ratio of 0.3. Similarly to Ref. 1, we put the following constraints in the fitting procedure of the O 1s peak structure: the OH was fixed at  $+1.4\pm 0.1$  eV with respects to the O 1s lattice component, which was found at 530.7 eV for the clean surface, whereas the H<sub>2</sub>O component was fixed at  $+3.4\pm 0.1$  eV with respect to the O 1s lattice oxygen component. The inelastic mean free path (IMFP) for the electrons emitted from the O 1s orbital (kinetic energy 79.3 eV) was estimated as  $\sim 5.5$  Å using TPP-2M predictive formula[2].

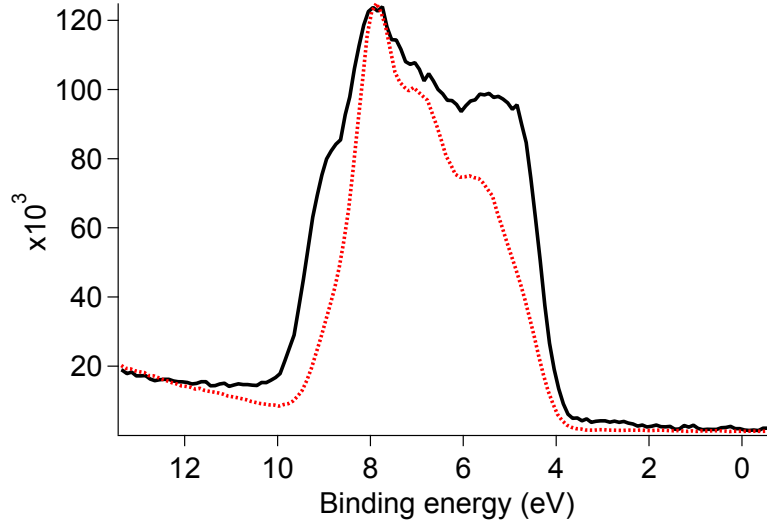


FIG. S3. Valence band spectra measured on a bare  $1\times 4$  reconstructed surface using 170 eV (solid black curve) and 47.5 eV (dashed red curve, repeated from the main text) photon energy. The curve recorded at 170 eV was normalized to match the intensity of the curve recorded at 47.5 eV.

## COVERAGE-DEPENDENT ADSORPTION ENERGY OF WATER

The change with respect to the bare surface in Gibbs surface free energy  $\Delta\gamma$  of each state with coverage  $\Theta_i$  was estimated as a function of the chemical potential of  $\text{H}_2\text{O}$  ( $\Delta\mu_{\text{H}_2\text{O}}$ ) as:  $\Delta\gamma(\Delta\mu_{\text{H}_2\text{O}}) = (E_{\text{ads},\text{DFT},\Theta_i}(\text{H}_2\text{O}) + \Delta\mu_{\text{H}_2\text{O}})/A$ , where  $E_{\text{ads},\text{DFT},\Theta_i}$  is the adsorption energy per water molecule when increasing coverage from zero to  $\Theta_i$  and  $A$  is the area of the supercell used.  $\Delta E_{\text{ads}}$  was calculated by the expression  $\Delta E_{\text{ads}}(\Theta_i \rightarrow \Theta_j) = \frac{\Theta_j}{\Theta_j - \Theta_i} E_{\text{ads}}(\Theta_j) - \frac{\Theta_i}{\Theta_j - \Theta_i} E_{\text{ads}}(\Theta_i)$ . Thus,  $\Delta E_{\text{ads}}$  is the gained energy (per added  $\text{H}_2\text{O}$  molecule) when the  $\text{H}_2\text{O}$  coverage increases from  $\Theta_i$  to  $\Theta_j$ .

## IS THERE ANY DAMAGE OF THE SAMPLE DUE TO X-RAYS?

It is known that intense and high-energy X-rays can cause sample degradation and/or induce water dissociation. In order to address this issue we have carried out a control experiment in which the sample was exposed to 2 L of water at 120 K and then annealed for 5 min at 230 K without being illuminated by the X-rays (i.e. omitting XPS measurements of adsorbed water at 120 K). In that case, only the products of water dissociation (i.e. hydroxyls) could be exposed to the beam irradiation and not the water molecules themselves,

since molecular water leaves the surface at temperatures below 200 K. We also detected OH groups in this control experiment, just as in the presented data set (main text Fig. 2). This confirms that water dissociation on the A-TiO<sub>2</sub>(001) surface is a thermally induced effect. We also checked the stability of the measured XPS peaks over time. The intensities of the O 1s component as well as the 3a<sub>1</sub>, 3σ, and 1b<sub>2</sub> components did not change upon prolonged illumination with X-rays during one hour, suggesting that the X-rays did not induce any significant change to the sample.

### **OXIDATION STATE OF FRESHLY PREPARED, BARE TiO<sub>2</sub>(001) SURFACES**

We found that the freshly prepared bare TiO<sub>2</sub>(001) surface is fully oxidized. This can be concluded from the VB spectrum shown in the main text (Fig. 2b). The same conclusion is derived from the analysis of the Ti 2p spectrum, shown in Fig. S2: Both Ti 2p components are highly symmetric and the spectrum does not show any shoulders that could be assigned to Ti in 3+ state. Accordingly, all surface Ti atoms are in 4+ oxidation state. Nevertheless, the subsurface region may contain a small amount of defects (oxygen vacancies and / or Ti interstitials) that originate from our preparation via cycles of sputtering and vacuum-annealing. The VB spectrum measured with 170 eV photon energy shown in Fig. S3 provides a hint, because in this case few states in the gap can be recognized, in contrast to the VB spectrum measured at 47.5 eV photon energy.

### **RELATION BETWEEN OUR WATER ADSORPTION STUDIES AND CATALYSIS/ PHOTO-CATALYSIS**

Numerous studies in catalysis and photo-catalysis reported that the A-TiO<sub>2</sub>(001) face is highly reactive [9–12]. In 2008, Yang et al. reported a recipe how uniform A-TiO<sub>2</sub> nanocrystals with a high percentage of reactive of (001) facets can be prepared, using hydrofluoric acid as a morphology controlling agent [10]. In the following years, numerous studies have been published, showing that the TiO<sub>2</sub>(001) surface is indeed very reactive [9, 11]. As an example, we refer to S. Liu et al. [11], wherein existing strategies for the synthesis of A-TiO<sub>2</sub> micro- and nanosheets with exposed high-energy (001) facets have been reviewed. Numerous studies indicate that the presence of high-energy facets in TiO<sub>2</sub> improves its adsorption,

electronic, and photocatalytic properties significantly [11]. Thus, designing A-TiO<sub>2</sub> micro- and nano-sheets with exposed high-energy (001) facets can make TiO<sub>2</sub>-based materials more attractive for various environmental and energy-related applications. In a recent example, Pei et al. reported that defective A-TiO<sub>2</sub> single crystals exposed by high-energy (001) facets are also promising for enhancing the oxygen reduction reaction (ORR) [12], which is believed to be the bottleneck in photo-electrochemical water splitting.

Several aspects have been elucidated to understand as to why A-TiO<sub>2</sub> nanocrystals with a high percentage of reactive of (001) facets show enhanced catalytic activity [9, 11]. A promising approach is to consider how water interacts with the various facets of A-TiO<sub>2</sub> nanocrystals [11], because water is always presents in the applications. In this regard, it is of great relevance whether water molecules dissociate or not, and what kind of hydroxyl groups are formed on the surface. For example, the so-called terminal hydroxyl groups are often considered as a crucial parameter for anchoring of molecules (and H<sub>2</sub>O) and as hole trapping sites [13].

Comparing our water adsorption studies and catalysis/photo-catalysis studies, it is essential to keep in mind that there is a pressure gap. Whereas we here study the 1×4 - reconstructed A-TiO<sub>2</sub>(001) surface at UHV, the pressure in Refs. 10–12 (and references therein) was several orders of magnitude higher. Accordingly, considering the p-T phase diagram, it is appropriate to compare our water adsorption data recorded at 120 K with Refs. 10–12 rather than our observations at RT. Thus, the high ability of the reconstructed A-TiO<sub>2</sub>(001) surface to dissociate water as found here, particularly for low water coverages, is a possible explanation for the enhanced activity of this face in catalysis/photo-catalysis studies.

When comparing our water adsorption studies and catalysis/photo-catalysis studies, another important aspect is the sample preparation. A striking feature is that frequently high catalytic activity of A-TiO<sub>2</sub> single crystals exposed by high-energy (001) facets is reported when a reduction step was included within the sample preparation. For example, Pei et al. prepared their A-TiO<sub>2</sub> ORR particle catalysts using an alcohothermal treatment at 200 °C for 24 h and denoted their blue A-TiO<sub>2</sub> single crystals as Ti<sup>3+</sup> self-doped TiO<sub>2-x</sub> [12]. Even though we here applied completely different sample preparations, a striking common feature is the blue color of the samples. Accordingly, it is possible that similar surface structure resulted in the different approaches. However, whereas we favour a model where all surface

Ti atoms are in 4+ oxidation state (see above), Pei et al. and others assumed that the A-TiO<sub>2</sub>(001) surface would be characterized by the presence of oxygen vacancies. Further studies may shed light onto this interesting issue, which remains to be resolved in the future.

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