

## Supplementary Information for:

### Defect induced water bilayer growth on anatase TiO<sub>2</sub>(101)

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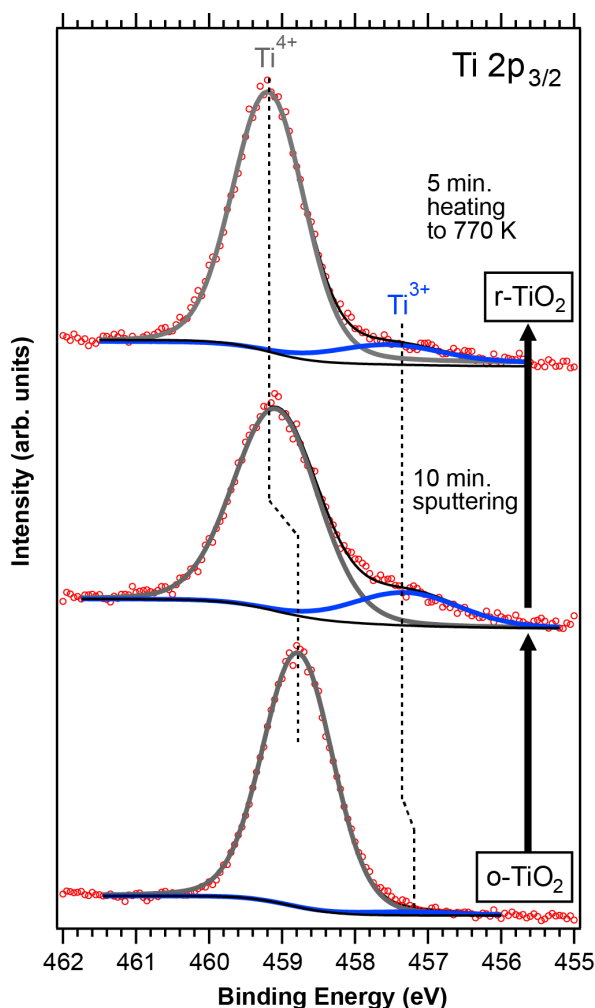
Number of figures: 3

### 1. The r- $\text{TiO}_2$ surface

The anatase  $\text{TiO}_2(101)$  single crystal (SurfaceNet) was prepared by several cycles of Ar ion sputtering at 1-2 keV and annealing to 870 K. The cleaning cycles were repeated until no contaminants (most notably C, K, Si) were observed in surface sensitive photoemission spectra. The oxidized surface (denoted o- $\text{TiO}_2$ ) was prepared by annealing in  $\text{O}_2$  ( $1.0 \times 10^{-6}$  mbar) in order to minimize the amount of oxygen vacancies. The reduced surface (denoted r- $\text{TiO}_2$ ) was prepared by sputtering the o- $\text{TiO}_2$  surface at 1 keV for 10 minutes followed by a brief annealing to 770 K. Figure S1 shows the evolution of the Ti  $2p_{3/2}$  state during this sequence. The Ti  $2p_{3/2}$  spectrum for r- $\text{TiO}_2$  displays a main peak at 459.2 eV BE associated with  $\text{Ti}^{4+}$  and a shoulder at 457.6 eV associated with  $\text{Ti}^{3+}$ . The relative intensities are 83% and 17% directly after sputtering, which changed to 92% and 8% after the brief annealing.

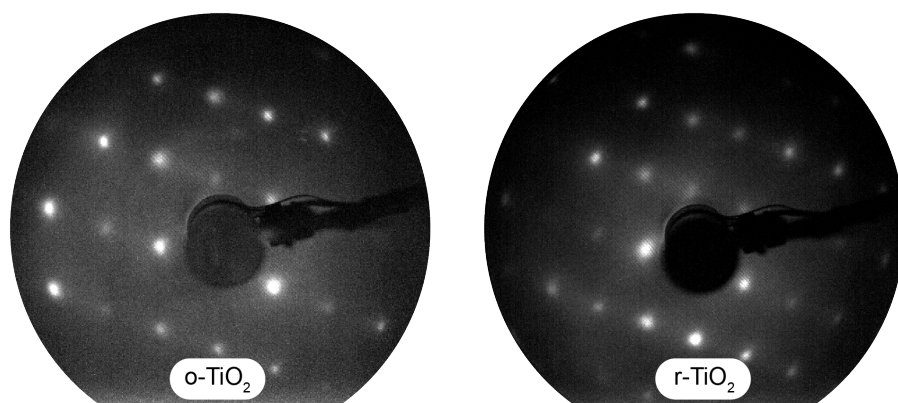
Figure S2 shows low-energy electron diffraction (LEED) patterns for the o- $\text{TiO}_2$  and r- $\text{TiO}_2$  surfaces. The LEED image of the o- $\text{TiO}_2$  surface is that of the pristine, as-prepared surface.

The image of the r- $\text{TiO}_2$  surface was taken after water exposure and subsequent heating since, unfortunately, we failed to image the clean, as-prepared surface in this case. However, given the quality of the pattern and the limited additional heating we infer that the r- $\text{TiO}_2$  surface must have had a high degree of order also before water exposure.



**Figure S1:**

*Ti  $2p_{3/2}$  spectra of the two different anatase (101) surfaces prepared. **Bottom:** oxidized o- $\text{TiO}_2$  surface. **Middle:** after 10 min of Ar ion sputtering. Clearly a  $\text{Ti}^{3+}$  component appeared. **Top:** annealing to 770 K for 5 min heals the surface layer, but a  $\text{Ti}^{3+}$ -related component remains. This forms the starting situation for the experiments on reduced r- $\text{TiO}_2$*



**Figure S2:**  
*LEED patterns of the  
 pristine, oxidized  
 oxide surface (left)  
 and the reduced  
 surface (right) after  
 water exposure and  
 subsequent heating.*

## 2. The O 1s spectra

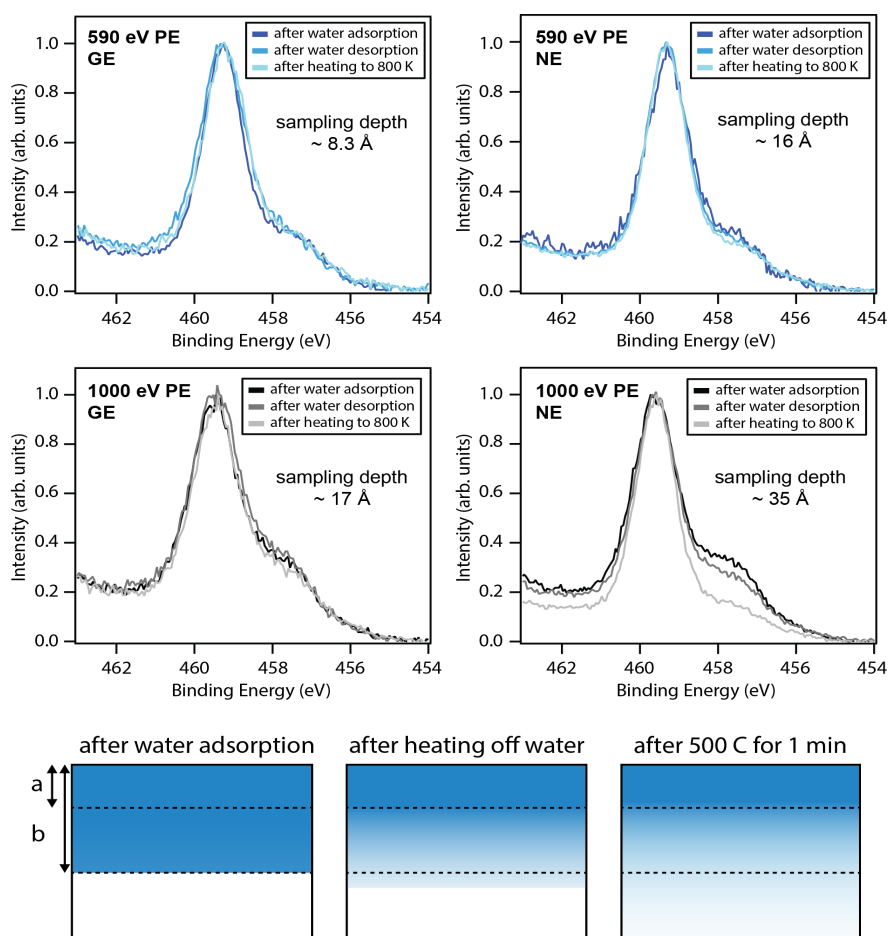
The O 1s spectra were first calibrated in binding energy (BE) vs. the Fermi level of a Pt foil mounted together with the sample. Next, the intensity was calibrated by normalizing to the low binding energy side of the spectrum. Before the curve fit, a model background was subtracted. The model background was matched to the low and high BE sides of the spectrum measured after water deposition and subtracted to give the difference spectrum. The final curve fit was done on the difference spectrum, using a Lorentzian width of 0.15 eV in all components. The procedure and its associated errors have been described and illustrated in detail in our recent study of water adsorption on the oxidized anatase  $\text{TiO}_2(101)$  surface (o- $\text{TiO}_2$ ).<sup>1</sup>

In case of the r- $\text{TiO}_2$  surface the OD component should in principle contain two contributions from bridging and terminal OD groups, respectively. The chemical shift between those two species is, however, likely too small, considering the large FWHM of the signals, to cause an observable change in the spectral shape. Hence, we treat the signals as one OD component in the further analysis.

## 3. Sampling depth in photoelectron spectroscopy

Changing the surface sensitivity by means of variation of the emission angle and/or photon energy provides further insight into the behavior of the  $\text{Ti}^{3+}$  species. In Figure S3 we compiled Ti 2p spectra of the r- $\text{TiO}_2$  surface recorded at 590 eV and 1000 eV photon energy with normal and grazing emission ( $30^\circ$  take-off angle). Each set contains spectra measured after water adsorption, after water desorption and after heating the samples to 800 K. The sampling depth provided in each diagram is defined as three times the inelastic mean free path (IMFP) of the respective photoelectrons. The IMFP was calculated following the approach by Tanuma, Powell and Penn.<sup>3</sup> The highest surface sensitivity at grazing emission and 590 eV photon energy corresponds to about once unit cell height in sampling depth. Normal emission at 590 eV and grazing emission at 1000 eV correspond essentially to the same sampling depth. Also in those

two cases we do not observe and loss of the Ti<sup>3+</sup> related signal even when annealing to 800 K. Only when increasing the sampling depth to more than 17 Å, as in the case of 1000 eV in normal emission, we can observe a clear decrease in the Ti<sup>3+</sup> signal. From this we conclude, as mentioned in the main text, that deeper layers first become depleted of Ti<sup>3+</sup>. This is illustrated in the sketch of the three situation in the bottom of figure S3. The density of the blue color corresponds to the density of Ti<sup>3+</sup> entities. The distances marked “a” and “b” correspond to the sampling depth of 590 eV NE/1000 eV GE and 1000 eV NE, respectively.



**Figure S3** Ti 2p spectra of the r-TiO<sub>2</sub> surface measured after water adsorption, after water desorption and after annealing to 800 K at 590 eV and 1000 eV photon energy and at emission angles of 0° and 60° with respect to the surface normal. The sketch in the bottom illustrates the depletion of Ti<sup>3+</sup> entities starting at deeper layers within the sample while the surface near region is virtually unaffected by the sample treatments applied.

#### 4. Exposure to the synchrotron light

An issue that has to be considered when measuring at a synchrotron is the possibility for beam induced effects. However, at the beamline used for these experiments, D1011 at the former MAX II ring, these effects can often be neglected by virtue of the moderate flux and large spot. This has been investigated and discussed by us in detail in connection with measurements on D<sub>2</sub>O on rutile TiO<sub>2</sub>(110).<sup>2</sup> One obvious test to do is to move the sample and measure at a different spot. However, this was not possible in this case since the anatase (101) sample was too small. Instead, we employed a method also employed in our recent study in ref. 1: a spectrum measured very quickly (two scans) after rapid dosing D<sub>2</sub>O at 100 K followed directly by heating was compared to a spectrum measured after a growth series at 100 K followed by heating, all this while measuring. The difference between the two spectra was negligible, from which follows that there were no significant beam effects in the measurements.

#### References

1. Schaefer, A.; Lanzilotto, V.; Cappel, U. B.; Uvdal, P.; Borg, A.; Sandell, A. First layer water phases on anatase TiO<sub>2</sub>(101). *Surf. Sci.* **2018**, *674*, 25–31.
2. Walle, L. E.; Ragazzon, D.; Borg, A.; Uvdal, P.; Sandell, A. Photoemission studies of water dissociation on rutile TiO<sub>2</sub>(110): Aspects on experimental procedures and the influence of steps. *Appl. Surf. Sci.* **2014**, *303*, 245–249.
3. Tanuma S.; Powell C.J.; Penn D.R. Calculations of electron inelastic mean free paths, *Surf. Interface Anal.*, **2005**, *37*, 1-14.