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Probing electrons in TiO<sub>2</sub> polaronic trap states by IR-absorption: Evidence for the existence of hydrogenic statesSUBJECT AREAS:  
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Woell@kit.edu)Hikmet Sezen<sup>1</sup>, Maria Buchholz<sup>1</sup>, Alexei Nefedov<sup>1</sup>, Carsten Natzeck<sup>1</sup>, Stefan Heissler<sup>1</sup>, Cristiana Di Valentin<sup>2</sup> & Christof Wöll<sup>1</sup><sup>1</sup>Karlsruhe Institute of Technology (KIT), Institute of Functional Interfaces (IFG), 76021 Karlsruhe, Germany, <sup>2</sup>Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, via R. Cozzi 55, 20125 Milano, Italy.

An important step in oxide photochemistry, the loading of electrons into shallow trap states, was studied using infrared (IR) spectroscopy on both, rutile TiO<sub>2</sub> powders and single-crystal, r-TiO<sub>2</sub>(110) oriented samples. After UV-irradiation or n-doping by exposure to H-atoms broad IR absorption lines are observed for the powders at around 940 cm<sup>-1</sup>. For the single crystal substrates, the IR absorption bands arising from an excitation of the trapped electrons into higher-lying final states show additional features not observed in previous work. On the basis of our new, high-resolution data and theoretical studies on the polaron binding energy in rutile we propose that the trap states correspond to polarons and are thus intrinsic in nature. We assign the final states probed by the IR-experiments to hydrogenic states within the polaron potential. Implications of these observations for photochemistry on oxides will be briefly discussed.

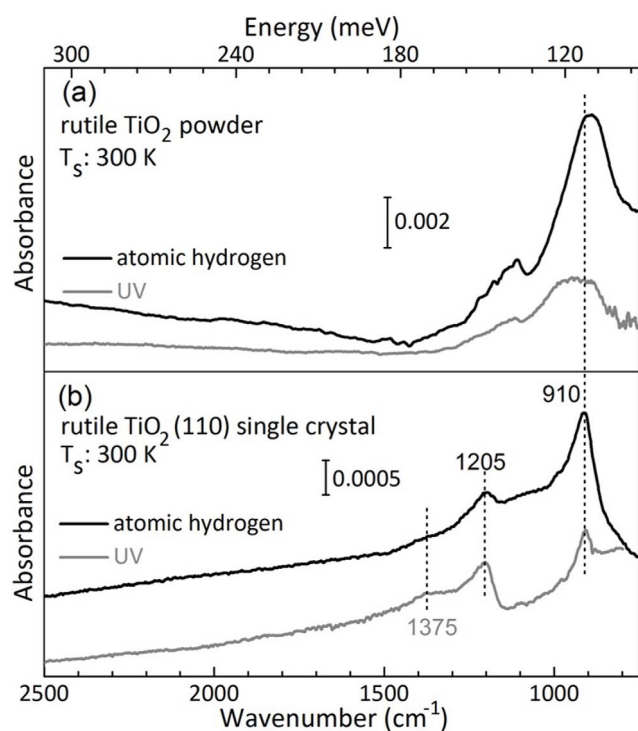
Titanium dioxide (TiO<sub>2</sub>, titania) is a wide-bandgap metal oxide with numerous applications based on its distinct chemical and physical properties<sup>1–5</sup>. In the area of solar energy harvesting via converting photon energies into electrical (Grätzel cell)<sup>6</sup> or chemical energy (photocatalysis)<sup>7,8</sup> the two different modifications of titania, rutile and anatase, are presently the materials receiving the most attention. Despite the importance of these processes for the future of energy productions, several of the key photophysical and photochemical have not yet been understood in sufficient detail. A prominent example is the nature of the electron trap states which are populated by photo-excited electrons<sup>9–15</sup>. To some extent the problem in more precisely characterizing the trapping and re-excitation from these states results from the fact that so far experimental data has been reported only for TiO<sub>2</sub> powder particles, but not for single crystals with well-defined structures and low defect densities. The availability of high-resolution data for such model systems with precisely known structure, however, is of crucial importance with regard to the validation of theoretical models. The latter is a key issue, since the description of excited states in wide-bandgap oxides represents a formidable challenge to available theories and, in case of titania, so far only few theoretical predictions have been reported for anatase<sup>16,17</sup> and rutile<sup>18,19</sup>.

In this work we focus on shallow trap states located below the conduction band minimum of rutile, r-TiO<sub>2</sub><sup>10–12,15,18–22</sup>. Since these states play a crucial role in photo- and charge-induced photocatalytic reactions, they have been studied in a number of previous works<sup>3,5</sup>. Reliable information on the precise binding energies of these states and a proper description of their nature, in particular that of the final states, however, has so far been missing.

## Results

In Fig. 1(a) we show IR-spectra recorded in transmission geometry for r-TiO<sub>2</sub> powder particles exposed to UV-light. In agreement with previous works<sup>7,9–14,21,22</sup> on such powders, we find that photoexcited electrons trapped in shallow states below the conduction band give rise to pronounced absorption features located at 900–940 cm<sup>-1</sup>. The corresponding results for the r-TiO<sub>2</sub>(110) single crystal surface are also shown in Fig. 1(b). Clearly, for the single crystal surface the main feature localized at 910 cm<sup>-1</sup> is much sharper and better defined. The higher quality of the single crystal data allows to identify two additional features at 1210 cm<sup>-1</sup> and 1375 cm<sup>-1</sup>.

Recent works by Yates, Panayotov and co-workers have demonstrated that electron trap states on titania surfaces can also be filled by exposing the powder particles to H atoms<sup>11,20,23</sup>. According to the mechanism proposed in this earlier work, first H-atoms are incorporated into the bulk of TiO<sub>2</sub><sup>20,24</sup>, a behavior which has



**Figure 1** | Recorded after the exposure of (a) powders and (b) a *r*-TiO<sub>2</sub>(110) single crystal to UV-light or atomic H. The difference spectra shown in Fig. 1 were obtained by subtracting a background spectrum for the pristine sample recorded directly before filling the trap states from the raw data. The background spectrum data (see supporting information, SI) also show a feature at 910 cm<sup>-1</sup>, consistent with a population of trap states by residual bulk dopants (see SI).

also been seen for *r*-TiO<sub>2</sub> bulk samples<sup>24</sup>. Since the binding energy of the electron to these interstitial H-atoms is rather low (values of 10 meV have been reported<sup>25</sup>), at room temperature they are ionized and the electron is transferred to the conduction band, from where they can populate the electron traps. The corresponding IR-data shown in Fig. 1 are, in fact, quite comparable to the earlier results of Yates and coworkers<sup>11,20,23,26</sup>. As in case of the UV-induced filling of the trap states, the IR-absorption features are quite broad. Systematic studies revealed that the width of the IR absorption features could be reduced substantially to values below those reported in previous works by reducing H-atom exposure times and flux densities. Still, for the powder TiO<sub>2</sub> sample, the full width at half maximum (FWHM) of the first transition at 900 cm<sup>-1</sup> amounts to 155 cm<sup>-1</sup>.

We now turn our attention to data recorded for bulk single crystal surfaces. Prior to 2007, because of technical problems resulting from the low reflectivity of semiconductors and insulators for IR-light, applications of the IRRAS method to titania single crystals has been reported in one case only<sup>27</sup>. Only recently optimized equipment has made it possible to record IRRAS-data for TiO<sub>2</sub> single crystal surfaces in a routine fashion<sup>8,28,29</sup>. As shown in Fig. 1(b), for the single crystal *r*-TiO<sub>2</sub>(110) surface the FWHM of the IR-bands observed after filling the trap states is reduced to only 45 cm<sup>-1</sup>. As in the case of the powder material, the IR-data recorded after populating the traps with the two different methods employed here, n-doping via exposure to H-atoms and photoexcitation, are found to be quite similar, see Fig. 1(b).

## Discussion

The trap state in *r*-TiO<sub>2</sub> giving rise to the pronounced features in the IR-absorption spectra has been discussed in many previous experimental and theoretical studies<sup>9–14,20–23,26,30</sup>. Several authors have

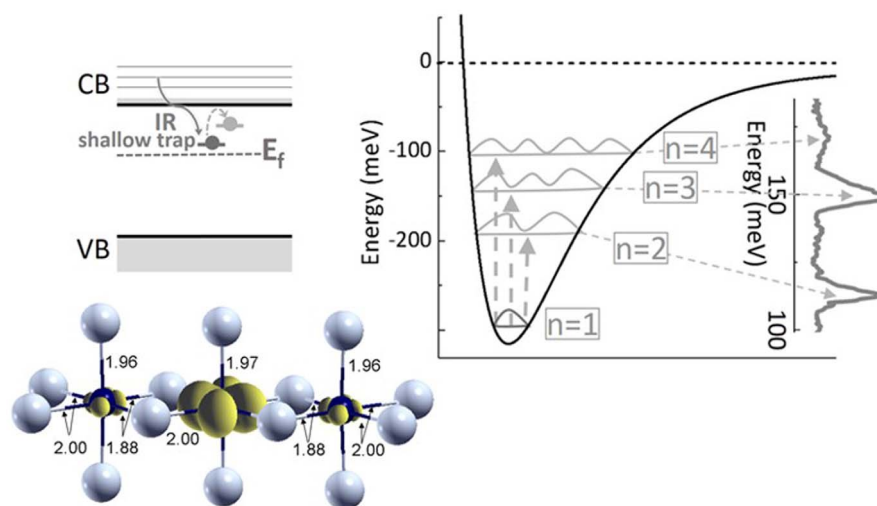
related this state to bulk defects, and it has been proposed that the absorption feature seen in the IR-experiments corresponds to an excitation of electrons from this trap state into empty levels at the bottom of the conduction band<sup>14,20</sup>. The single-crystal data reported here, however, show sharp lines. More importantly, the pronounced broadening towards higher energies as expected from an excitation into a continuum of empty states above the bottom of the conduction band<sup>20,23</sup> is clearly absent. Therefore, we challenge this previous assignment of the final states and propose instead that the sharp, fairly symmetric peak at 112 meV (910 cm<sup>-1</sup>) actually corresponds to an excitation of electrons from the ground state of an intrinsic trap (a polaron state, see below) into the first excited state within the polaron trap potential well, see Fig. 2. In principle, such hydrogenic states within a polaronic trap state have to be expected, but to our knowledge, have not yet been proposed for trap states in titania (see, however, the discussion in Ref. 19). In accordance with this hypothesis, we assign the features at 1205 cm<sup>-1</sup> and at 1375 cm<sup>-1</sup> to excitations in the second and third excited states within the hydrogenic potential (see Fig. 2).

The fact that the higher (hydrogenic) excited states cannot be identified easily in the TiO<sub>2</sub> powder data is explained by the rather pronounced inhomogeneous broadening (the first peak at 900 cm<sup>-1</sup> has a width of around 100 cm<sup>-1</sup>) seen for the 200 nm-sized particles which expose surfaces with many different orientations. Careful inspection of the data, however, reveals a broad, weak feature at 1100 cm<sup>-1</sup>–1200 cm<sup>-1</sup>, which we tentatively assign to the second excited state located at 1205 cm<sup>-1</sup> for the single crystal.

Our new assignment is consistent with theoretical findings. Using previously established computational procedures<sup>17</sup> the energy associated to the self-trapping of a conduction band electron at a bulk six-fold coordinated Ti ion (Ti<sup>3+</sup> center) in rutile is computed to be 380 meV (see Methods section for computational details). This value corresponds well to the case of bulk anatase for which a recent work<sup>17</sup> has revealed that the nature of the intrinsic trap state with a binding energy of 230 meV can be best described as a polaron. Basically, this polaron is a self-trapped state resulting from a complex interplay between a relaxation of the lattice ions and the trapped electron. This trap state does not require the presence of an actual atomic defect<sup>17</sup> and involves primarily the d<sub>xy</sub> state of one Ti lattice ion (0.7 fraction of electron) and the d<sub>xy</sub> states of two neighboring Ti ions in the xy plane (0.1 fraction of electron each) as represented in Fig. 2. The approximate radius of this intrinsic polaron in rutile is at least 4–5 Å, according to the spin density distribution (even though relaxation effects associated to the polaron are longer range, see below in Computational Details), with a binding energy of around 380 meV, defined as the energy difference between having the electron self-trapped or free into the conduction band. This value is consistent with a recent estimation of the vertical ionization energy (500–610 meV) in terms of the optical transition energy level (Ti<sup>3+</sup>/Ti<sup>4+</sup>) by means of the HSE06 hybrid functional<sup>18,19</sup> and with the results of optical studies<sup>9,11–14,20,22</sup>.

Clearly, direct excitations of electrons trapped in such a polaron state into the conduction band cannot explain the feature observed in our data for rutile because the energy of 112 meV is clearly too small, on the basis of the above-mentioned calculation energies of around 380 meV are expected. The possibility that what we see might be a surface trap can be safely excluded, since the results do not depend on surface preparation. In particular, exposure to molecular oxygen did not result in any detectable changes in the IR-data.

In conclusion, our data demonstrates that IR-spectroscopy is well suited to probe electrons loaded into shallow trap states in TiO<sub>2</sub> with either UV-irradiation or exposure to H atoms. While the broad IR absorption features recorded for powder samples are in a good agreement with previous work, the new results obtained from grazing incidence IR-spectroscopy for single crystal titania substrates reveal a number of previously unobserved sharp features. The absence of a



**Figure 2** | Schematic electronic structure, the hydrogenic potential, and the electron spin density. **Left panel, top:** Schematics showing the excitation of electrons within shallow trap states by absorption of IR photons. **Left panel, bottom:** Electron spin density at self-trapped polaron  $\text{Ti}^{3+}$  site in bulk rutile as obtained from DFT calculations (see text). Axial and equatorial Ti–O distances are given in Angstrom. Stoichiometric bulk values are 1.951 (axial) and 1.939 (equatorial). **Right panel:** Hydrogenic potential at polaron  $\text{Ti}^{3+}$ -site in bulk rutile showing the different excitations giving rise to absorption bands in the IR data. A polynomial baseline was subtracted from the raw IR data presented in Fig. 1(b) to enhance the visibility of additional hydrogenic states.

high-energy tail allows to effectively ruling out excitations from the trap state directly into the conduction band. Instead we propose transitions into excited “hydrogenic” states within the polaron trap potential. This hypothesis also accounts for the sharp features seen at higher excitation energies; they must correspond to transitions into higher excited states in the hydrogenic potential. An important implication of this study is that the trap states commonly seen after photoexcitation in titania are not defect related but are intrinsic to titania and correspond to polarons. Our findings urgently call for more work on the photophysics in oxides, in particular on the interaction between excited electrons and the oxide lattice. In addition, more information on the mechanisms governing diffusion of electrons trapped after the photoexcitation process through the lattice and to the surface is needed, since for the photoreactions the electrons must be transferred to adsorbed molecular species.

## Methods

**Experimental.** In the present study the trap states were populated using two different methods, UV irradiation and n-doping via exposure to atomic H atoms. The characterization of electrons loaded into these traps was carried out by IR-spectroscopy. For powders a transmission geometry was used, whereas for the well-defined rutile  $\text{TiO}_2(110)$  single crystal substrates a reflection geometry was employed. Experiments were carried out using an ultrahigh vacuum (UHV) chamber (base pressure better than  $5 \times 10^{-10}$  mbar) equipped with an infrared reflection absorption spectroscopy (IRRAS) setup (Bruker Vertex 80v), a hemispherical energy analyzer (VG-Scienta R4000) allowing to carry out x-ray photoelectron spectroscopy (XPS) as well as ultraviolet photoelectron spectroscopy (UPS) measurements, and (in case of the single crystals) a device for recording low energy electron diffraction (LEED) data.

Rutile  $\text{TiO}_2$  powder particles (average particle size 200 nm) were pressed on a metal grid with spacing of 103  $\mu\text{m}$  and a total optical transmission of 37%. To remove contaminations present on the surface of the powder particles, the supporting metal grid was heated to 700 K for 60 min under UHV conditions, as used in previous works<sup>11,20,23</sup>. For the single crystal experiments a r- $\text{TiO}_2(110)$  specimen (MATECK GmbH, Jülich, Germany) with a size of  $10 \times 10 \text{ mm}^2$  was cleaned using previously published preparation procedures<sup>1-21</sup> including  $\text{Ar}^+$  ion sputtering and annealing steps until the sample was a clean (as judged from XPS data), well-ordered (as judged from the presence of well-defined spots in the LEED-pattern) and largely defect-free (as judged from the comparison of UPS-data with those reported in<sup>22</sup>). Exposure to H atoms was carried out by operating a hot tungsten filament in line of sight of the titania samples in an atmosphere of  $1 \times 10^{-6}$ – $5 \times 10^{-7}$  mbar of  $\text{H}_2$ , as described previously<sup>23</sup>. UV-light from a N-8 L Herolab lamp (8 Watt, 365 nm) entered the UHV-chamber through a quartz window. Previous work has shown that under these conditions H-atom diffusion into the bulk is observed before a full monolayer coverage is reached<sup>24,33</sup>. All IRRAS-data shown here were background-corrected by subtracting the signal recorded for the clean substrate.

**Computational details.** The calculations were done for bulk rutile  $2 \times 2 \times 3$  and  $3 \times 3 \times 4$  supercell models (72 and 216 atoms, respectively) with the B3LYP functional, as implemented in the CRYSTAL09 code, and the all-electron basis sets O 8-411(d1), Ti 86-411(d41). The k-space sampling for the bulk geometry optimizations include eight k points ( $2 \times 2 \times 3$ ) or only  $\Gamma$  point ( $3 \times 3 \times 4$ ). The trapping energy, derived from total energy differences between the self-trapped and the free conduction band electron, increases from 300 to 380 meV with the cell size, indicating a long range relaxation effect associated to the polaron self-trapping. Optical and adiabatic transition energy levels were also computed for the 72-atoms model as 620 and 300 meV, respectively.

- Diebold, U. The surface science of titanium dioxide. *Surf. Sci. Rep.* **48**, 53–229 (2003).
- Henderson, M. A. A surface science perspective on photocatalysis. *Surf. Sci. Rep.* **66**, 185–297 (2011).
- Linsebigler, A. L., Lu, G. & Yates, J. T. Jr. Photocatalysis on  $\text{TiO}_2$  surfaces: Principles, mechanisms, and selected results. *Chem. Rev.* **95**, 735–758 (1995).
- Pang, C. L., Lindsay, R. & Thornton, G. Structure of clean and adsorbate-covered single-crystal rutile  $\text{TiO}_2$  surfaces. *Chem. Rev.* **113**, 3887–3948 (2013).
- Thompson, T. L. & Yates, J. T. Surface science studies of the photoactivation of  $\text{TiO}_2$ -new photochemical processes. *Chem. Rev.* **106**, 4428–4453 (2006).
- O’Regan, B. & Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal  $\text{TiO}_2$  films. *Nature* **353**, 737–740 (1991).
- Fujishima, A. & Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **238**, 37–38 (1972).
- Xu, M. *et al.* Photocatalytic activity of bulk  $\text{TiO}_2$  anatase and rutile single crystals using infrared absorption spectroscopy. *Phys. Rev. Lett.* **106**, 138302 (2011).
- Berger, T. & Anta, J. A. IR-Spectrophotoelectrochemical characterization of mesoporous semiconductor films. *Anal. Chem.* **84**, 3053–3057 (2012).
- Berger, T., Anta, J. A. & Morales-Flórez, V. C. Electrons in the band gap: spectroscopic characterization of anatase  $\text{TiO}_2$  nanocrystal electrodes under fermi level control. *J. Phys. Chem. C* **116**, 11444–11455 (2012).
- Panayotov, D. A., Burrows, S. P. & Morris, J. R. Infrared spectroscopic studies of conduction band and trapped electrons in UV-photoexcited, H-atom n-doped, and thermally reduced  $\text{TiO}_2$ . *J. Phys. Chem. C* **116**, 4535–4544 (2012).
- Savory, D. M., Warren, D. S. & McQuillan, A. J. Shallow electron trap, interfacial water, and outer-sphere adsorbed oxalate IR absorptions correlate during UV irradiation of photocatalytic  $\text{TiO}_2$  films in aqueous solution. *J. Phys. Chem. C* **115**, 902–907 (2011).
- Szczepankiewicz, S. H., Moss, J. A. & Hoffmann, M. R. Slow surface charge trapping kinetics on irradiated  $\text{TiO}_2$ . *J. Phys. Chem. B* **106**, 2922–2927 (2002).
- Yamakata, A., Ishibashi, T.-a. & Onishi, H. Time-resolved infrared absorption spectroscopy of photogenerated electrons in platinumized  $\text{TiO}_2$  particles. *Chem. Phys. Lett.* **333**, 271–277 (2001).
- Yamakata, A., Ishibashi, T.-a. & Onishi, H. Kinetics of the photocatalytic water-splitting reaction on  $\text{TiO}_2$  and Pt/ $\text{TiO}_2$  studied by time-resolved infrared absorption spectroscopy. *J. Mol. Catal. A: Chem.* **199**, 85–94 (2003).



16. Di Valentin, C., Pacchioni, G. & Selloni, A. Reduced and n-type doped TiO<sub>2</sub>: Nature of Ti<sup>3+</sup> species. *J. Phys. Chem. C* **113**, 20543–20552 (2009).
17. Di Valentin, C. & Selloni, A. Bulk and surface polarons in photoexcited anatase TiO<sub>2</sub>. *J. Phys. Chem. Lett.* **2**, 2223–2228 (2011).
18. Deák, P., Aradi, B. & Frauenheim, T. Quantitative theory of the oxygen vacancy and carrier self-trapping in bulk TiO<sub>2</sub>. *Phys. Rev. B* **86**, 195206 (2012).
19. Janotti, A., Franchini, C., Varley, J. B., Kresse, G. & Van de Walle, C. G. Dual behavior of excess electrons in rutile TiO<sub>2</sub>. *Phys. Status Solidi Rapid Res. Lett.* **7**, 199–203 (2013).
20. Panayotov, D. A. & Yates Jr, J. T. n-Type doping of TiO<sub>2</sub> with atomic hydrogen-observation of the production of conduction band electrons by infrared spectroscopy. *Chem. Phys. Lett.* **436**, 204–208 (2007).
21. Takahashi, H., Watanabe, R., Miyauchi, Y. & Mizutani, G. Discovery of deep and shallow trap states from step structures of rutile TiO<sub>2</sub> vicinal surfaces by second harmonic and sum frequency generation spectroscopy. *J. Chem. Phys.* **134**, 154704 (2011).
22. Takeshita, K. *et al.* Transient IR absorption study of charge carriers photogenerated in sulfur-doped TiO<sub>2</sub>. *J. Photochem. and Photobiol. A: Chem.* **177**, 269–275 (2006).
23. Panayotov, D. A. & Yates, J. T. Spectroscopic detection of hydrogen atom spillover from Au nanoparticles supported on TiO<sub>2</sub>: Use of conduction band electrons. *J. Phys. Chem. C* **111**, 2959–2964 (2007).
24. Yin, X.-L. *et al.* Diffusion versus desorption: Complex behavior of H atoms on an oxide surface. *ChemPhysChem* **9**, 253–256 (2008).
25. Herklotz, F., Lavrov, E. V. & Weber, J. Infrared absorption of the hydrogen donor in rutile TiO<sub>2</sub>. *Phys. Rev. B* **83**, 235202 (2011).
26. Panayotov, D. A., Burrows, S. P., Yates, J. T. Jr. & Morris, J. R. Mechanistic studies of hydrogen dissociation and spillover on Au/TiO<sub>2</sub>: IR spectroscopy of coadsorbed CO and H-donated electrons. *J. Phys. Chem. C* **115**, 22400–22408 (2011).
27. Hayden, B. E., King, A. & Newton, M. A. Fourier transform reflection-absorption IR spectroscopy study of formate adsorption on TiO<sub>2</sub>(110). *J. Phys. Chem. B* **103**, 203–208 (1999).
28. Kimmel, G. A. *et al.* Polarization- and azimuth-resolved infrared spectroscopy of water on TiO<sub>2</sub>(110): Anisotropy and the hydrogen-bonding network. *J. Phys. Chem. Lett.* **3**, 778–784 (2012).
29. Rohmann, C. *et al.* Direct monitoring of photo-induced reactions on well-defined metal oxide surfaces using vibrational spectroscopy. *Chem. Phys. Lett.* **460**, 10–12 (2008).
30. Deskins, N. A., Rousseau, R. & Dupuis, M. Localized electronic states from surface hydroxyls and polarons in TiO<sub>2</sub>(110). *J. Phys. Chem. C* **113**, 14583–14586 (2009).
31. Osterloh, N., Silber, D., Traeger, F. & Wöll, C. Water adsorption on r-TiO<sub>2</sub>(110): Presence of a well-defined (1 × 1)-structure as evidenced by He-atom scattering. *Phys. Status Solidi B* **250**, 1235–1241 (2013).
32. Sambì, M., Sangiovanni, G., Granozzi, G. & Parmigiani, F. Growth and the structure of epitaxial VO<sub>2</sub> at the TiO<sub>2</sub>(110) surface. *Physical Review B* **55**, 7850–7858 (1997).
33. Kunat, M., Gil Girol, S., Becker, T., Burghaus, U. & Wöll, C. Stability of the polar surfaces of ZnO: A reinvestigation using He-atom scattering. *Phys. Rev. B* **66**, 081402 (2002).

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## Author contributions

H.S., M.B., A.N., C.N. and S.H. carried out the measurements on the bulk and powder titania samples. C.D.V. carried out the calculations. Data analysis was carried out by H.S. and C.W. H.S., C.D.V. and C.W. contributed equally in writing the manuscript.

## Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

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