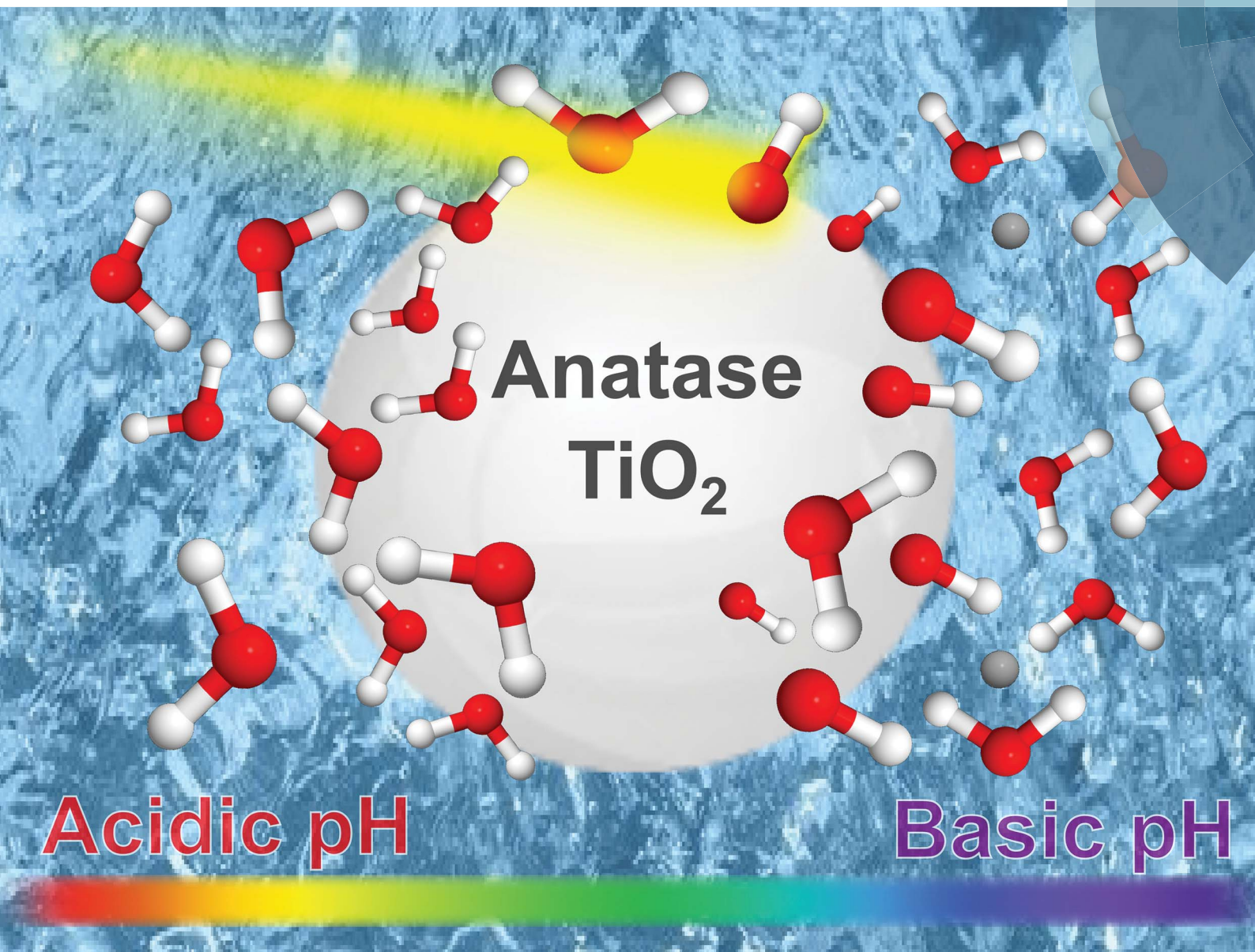


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# Electronic structure of aqueous-phase anatase titanium dioxide nanoparticles probed by liquid jet photoelectron spectroscopy†

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We report on the nature of water interactions with anatase TiO<sub>2</sub> surfaces. TiO<sub>2</sub> nanoparticles (NPs), 3, 6, 10, and 20 nm in diameter, dispersed in different aqueous solutions, were investigated by soft-X-ray photoemission spectroscopy from liquid microjets. One central aspect of this study is the characterization of the electronic structure and identification of the molecular species that exist at the NP–aqueous solution interface as a function of solution pH. Valence and core-level electron binding energies are determined by the respective non-resonant photoelectron spectra. In addition, we report resonant photoemission spectra at the Ti 2p and the O 1s edges, which considerably increases the detection sensitivity of the interfacial species. This also allows us to distinguish between titanium at the surface and inside the aqueous-phase NPs. Furthermore, from the Ti 2p resonant photoelectron spectra, we obtain the so-called partial electron yield X-ray absorption (PEY-XA) spectra, which help here to rule out an anatase-phase transformation or the occurrence of Ti<sup>3+</sup> sites due to oxygen defects. However, a more direct spectral feature that allows us to distinguish between molecularly and dissociatively adsorbed water is provided by the actual O 1s resonant photoelectron spectra. This is then exploited to show that water adsorbs molecularly at low pH, and dissociative adsorption at the TiO<sub>2</sub> NP (aq) surface is observed at basic pH. Based on our results, we propose a mechanism of the anatase TiO<sub>2</sub>–H<sub>2</sub>O interaction that explicitly accounts for the local solution chemical environment. Here, H<sub>2</sub>O and OH<sup>−</sup> adsorb at the Ti sites, and no oxygen defects exist.

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## Introduction

Titanium dioxide, TiO<sub>2</sub>, with its three phases in nature, anatase, rutile and brookite, is one of the most important transition metal oxides.<sup>1</sup> It offers wide-ranging properties for science and industry applications, and furthermore, it is a chemically stable, abundant and cheap material.<sup>2</sup> Exhibiting a large bandgap of 3.2 eV, TiO<sub>2</sub> absorbs light in the UV region,<sup>3,4</sup> which explains the extensive study of this material in photoelectric and photochemical research.<sup>5,6</sup> In 1972, Fujishima and Honda studied water photolysis on the TiO<sub>2</sub> electrode surface, which can be described by the reaction H<sub>2</sub>O + 2hν → 1/2O<sub>2</sub> + H<sub>2</sub>.<sup>7</sup> This photochemical reaction thus provides a clean and sustainable

way for hydrogen fuel production from solar energy. Many subsequent works have focused on water electrolysis to develop efficient photoelectrochemical cells (PECs) for solar hydrogen generation by immersing two electrodes (TiO<sub>2</sub> photoanode and a cathode).<sup>3,8–14</sup> The challenge in these studies is to minimize the unwanted back-reaction, *i.e.*, the recombination or non-separation of hydrogen and oxygen atoms, which reduces the PEC's efficiency. An ideally performing device, minimally suffering from electric current losses, would assure that the initial charge separation is very fast (on the femtosecond timescale) to slow down the back-reaction.<sup>15</sup> Despite active research, the conversion efficiency from solar to electric power with current PECs is still low, reaching up to 17%,<sup>15,16</sup> and prevents this path for solar hydrogen generation from being economically and commercially viable.<sup>17,18</sup>

As the TiO<sub>2</sub> electrode is immersed in an aqueous environment, it is essential to gain a detailed understanding of the electronic properties of the TiO<sub>2</sub>–water interface, and this has motivated many investigations of the water adsorption behavior on single crystals, in the rutile as well as anatase phase.<sup>3,19–25</sup> Likewise, the present study aims at determining the electronic structure of this interfacial layer. The novel approach here is to access the interface by soft X-ray photoelectron (PE) spectroscopy, which has not been accomplished previously for a TiO<sub>2</sub>

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surface fully contained in liquid water. The reason for this is that the detection of photoelectrons in a high-vapor pressure environment has only recently become possible with the introduction of the liquid microjet technique<sup>26–29</sup> and of ambient pressure photoelectron spectroscopy (AP-PES).<sup>21,30–33</sup> Liquid jets are ideally suited to study NPs dispersed in aqueous solutions,<sup>26–29</sup> while the latter technique typically refers to condensation of a few monolayers (MLs) of liquid water on a solid substrate at a suitable relative humidity.<sup>21,30–33</sup> Also, photoelectrons have been detected from liquid cells equipped with a few-nanometer thick graphene membrane to separate the liquid from a vacuum.<sup>34–36</sup>

The TiO<sub>2</sub> anatase phase has been found to exhibit higher photocatalytic activity<sup>37</sup> and higher efficiency in photoelectrochemistry applications,<sup>38,39</sup> and it is also more stable in the nanometer regime.<sup>40,41</sup> However, on the macroscopic size scale, rutile is the most stable phase,<sup>1,42</sup> and it has been studied more intensively, both theoretically<sup>3,19</sup> and experimentally.<sup>21,43,44</sup> Yet, the nature of water adsorption on TiO<sub>2</sub> surfaces remains unclear; depending on the specific study, water has been concluded to adsorb (1) dissociatively, (2) molecularly, or (3) mixed at the TiO<sub>2</sub> interface.<sup>3,19–23,45–49</sup> Furthermore, the adsorption mechanisms for these different cases were proposed to depend on whether or not the (vacuum) surface is defect-free. A defect surface site refers to a missing oxygen atom in the crystal structure (oxygen vacancy), and it is easily created by electron bombardment, ion sputtering, or thermal annealing.<sup>50</sup> In the aqueous phase, the situation is quite different; defects on the titania surface will be healed upon interaction with the water molecules.<sup>21,51</sup> Oxygen vacancies are accompanied by a change of the titanium charge state (Ti<sup>4+</sup> → Ti<sup>3+</sup>) and the occurrence of color centers,<sup>50</sup> which are the most active surface sites for water dissociation (mechanism (1)).<sup>50,52,53</sup> Defects on the TiO<sub>2</sub> surface are conveniently detected by the Ti<sup>3+</sup> signal,<sup>20,21</sup> a procedure also adapted here. For the interpretation of the results obtained in the present work, it is useful to briefly review the different adsorption mechanisms.

Dissociative adsorption (mechanism (1) of the TiO<sub>2</sub>–water interaction) depends entirely on the existence of surface defects; water molecules dissociate only at oxygen vacancy defects. The thus generated hydroxyl species fills the oxygen vacancies (denoted OH<sub>i</sub>), leaving the hydrogen to bond to a neighbor lattice oxygen atom (OH<sub>b</sub>) and forming what is termed paired hydroxyl groups.<sup>44</sup> Ketteler *et al.*<sup>21</sup> observed this paired OH for 0.25 ML coverage on rutile (110) using AP-PES. In addition, the authors detected an O 1s photoelectron signal from adsorbed molecular water at less than 1 ML coverage, with an approximately 0.5 eV lower binding energy (BE) as compared to bulk water. This PE peak could correspond to hydroxyl or to molecularly adsorbed water; pseudo-dissociated water has also been suggested.<sup>21</sup> In the latter process, the paired hydroxyl groups reform a water molecule by back-reaction. At higher coverage, water has been shown to adsorb molecularly, bonding to the OH groups that act as hydrogen-donors.<sup>21</sup> A similar conclusion has been drawn from PE spectroscopy measurements of TiO<sub>2</sub> nanoparticles (NPs) exposed to water vapor; experiments were conducted using an aerosol generator.<sup>54</sup> Mechanism (1) can

hence be represented as H<sub>2</sub>O + O<sub>b</sub> ↔ OH<sub>b</sub> + OH<sub>t</sub>.<sup>55,56</sup> The interconversion energy of the dissociated hydroxyl pair relative to the water molecule (back-reaction) has been estimated as  $\Delta E = 0.035 \pm 0.003$  eV, based on a combination of supersonic molecular-beam experiments, scanning tunneling microscopy, and *ab initio* molecular dynamics.<sup>55</sup> Given this very small energy difference between the two states, the re-formation of an adsorbed water molecule is slightly more likely over the paired hydroxyl configuration, but not dominating.<sup>56</sup> In this mechanism, OH<sub>t</sub> was assumed to form a covalent bond with the TiO<sub>2</sub> surface.<sup>21</sup> This interpretation is based on the detected energy of the O 1s and Ti 2p peak positions, both being different for the hydrated TiO<sub>2</sub> rutile crystal surface compared to the bulk crystal.<sup>43</sup>

In the second proposed mechanism (2) of the TiO<sub>2</sub>–water interaction, water is molecularly adsorbed on the surface at very specific geometries where the water oxygen atom binds to Ti<sup>4+</sup> sites and its hydrogens bind to two neighboring lattice oxygen atoms.<sup>57</sup> This raises the question whether water dissociates exclusively at oxygen vacancies or whether dissociation can also occur at Ti<sup>4+</sup> sites. Here, the third mechanism (3) of TiO<sub>2</sub>–water interaction comes into play, and it has been legitimated by experiments on defect-free surfaces of rutile<sup>46,58</sup> and anatase,<sup>20,22,45</sup> both showing a mixed adsorption behavior, with the OH signal being small relative to the signal from molecularly adsorbed water. Specifically, Walle *et al.*<sup>20</sup> reported that the first water layer is composed of  $0.47 \pm 0.05$  ML OH and  $0.77 \pm 0.55$  ML molecular water for the anatase TiO<sub>2</sub> (101) defect-free surface; the OH coverage stays nearly constant for higher water exposure. In a theoretical work, Zheng *et al.* studied the stability of the dissociated OH species on titanium sites using density function theory (DFT) on a rutile (110) surface edge.<sup>59</sup> The authors report that its lifetime is highly dependent on the location of the hydrogen species (the second product of the water dissociation) and that the recombination/reformation of the water molecule is possible.<sup>59</sup> This mechanism is the most related one to the present study, as detailed later in the Results section.

Here, we present PE measurements from anatase-phase TiO<sub>2</sub> NPs dispersed in liquid water, which we refer to as the “all-in-solution” surface-study approach. This is complicated, though, by the fact that NPs are not soluble in water due to the large surface potential. They tend to aggregate and sediment out near the point of zero charge (PZC), which is at pH ~6.4 for the anatase surface.<sup>60</sup> That is, when the surface is neutral, NPs reduce their surface energy by aggregating and thereby reducing their surface area. Such unwanted effects are avoided by adding stabilizers to the aqueous solutions, which inevitably leads to a change of pH. In this study, we use three different stabilizers, Cl<sup>–</sup> and NO<sub>3</sub><sup>–</sup>, resulting in a positive surface zeta potential of the TiO<sub>2</sub> NP (the potential between the TiO<sub>2</sub> surface and the surrounding aqueous solution), and NH<sub>4</sub><sup>+</sup>, yielding a negative surface zeta potential. Under these conditions, the NPs are stable in aqueous solution, and stable liquid microjets for the photoemission experiments can be obtained. Evidently, we are mostly interested in conditions where the stabilizer concentration is low enough such that a sufficiently large fraction of



free NP surface sites is available for water adsorption. This fraction can be estimated from the adsorbed ML density on TiO<sub>2</sub> (110) (5.2 nm<sup>-2</sup>).<sup>20,21</sup> Then, one of our major questions is whether water adsorbs molecularly or dissociatively on the anatase TiO<sub>2</sub> NP defect-free surface where no Ti<sup>3+</sup> sites are present. The other, equally important question is how the adsorption nature depends on pH, explored here for basic and acidic pH. This latter aspect has not been addressed experimentally before. We are aware of a single density functional theory (DFT) molecular dynamic work studying the acidity of the surface groups relevant in the water interaction with a rutile (110) surface.<sup>61</sup> It was predicted that the fraction of terminal water molecules (TiOH<sub>2</sub>) is small at neutral pH, and the surface pK<sub>a</sub> for this site has been estimated to be 9. In contrast, a pK<sub>a</sub> value of -1 was estimated for the surface hydroxide bridge groups (Ti<sub>2</sub>OH<sup>+</sup>). Most interesting for the present work is the TiOH<sub>2</sub> case. Deprotonation of TiOH<sub>2</sub> to TiOH<sup>-</sup>, which is coupled with the protonation of H<sub>2</sub>O in the liquid water, is paralleled by the reverse reaction where the solution proton is transferred to a TiOH<sup>-</sup> surface group<sup>61</sup> (TiOH<sup>-</sup> + H<sub>3</sub>O<sup>+</sup> → TiOH<sub>2</sub> + H<sub>2</sub>O). We can hence expect that in a basic solution environment, this reverse reaction is insignificant. Qualitatively, such a behavior is supported by our combined resonant and non-resonant PE spectroscopy, as well as partial-electron yield X-ray absorption (PEY-XA) measurements from TiO<sub>2</sub> NPs (aq) at different pH values.

## Experimental

Photoelectron measurements of TiO<sub>2</sub> NP solutions (*i.e.*, colloidal dispersions) were conducted using the SOL<sup>3</sup>PES setup at the U49/2-PGM-1 soft X-ray beamline, at the synchrotron radiation facility BESSY II, Berlin. The experimental details of SOL<sup>3</sup>PES have been described recently.<sup>62</sup> Briefly, synchrotron light, the liquid jet and the photoelectron detection are orthogonal to each other. The X-ray light at this beamline is linearly polarized in the floor plane, which is the plane spanned by jet propagation and light propagation. Focal size is approximately 60 × 20 μm<sup>2</sup>. Solutions were injected into the interaction vacuum chamber through a 25 μm glass capillary. Liquid flow rate was 0.7 ml min<sup>-1</sup> using a backing pressure of 10 bars. The liquid jet hits the X-ray beam at 0.5 mm distance from the capillary tip, and this interaction point is at 500 μm distance from the detector orifice. The pressure in this chamber was kept at approximately 3.0 × 10<sup>-4</sup> mbar by using a turbo molecular pump (1600 l s<sup>-1</sup>) and two liquid nitrogen cold traps. At 500 eV photon energy, using the 80 μm beamline exit slit, the energy resolution in our measurement is higher than 130 meV.

Four sets of anatase TiO<sub>2</sub> NP solutions were studied. The NP sizes used in this study were given by the samples that were commercially available. In addition to different NP sizes, the different vendors also use different stabilizers as well as different stabilizer concentrations. Then, together with the finding that anatase-phase TiO<sub>2</sub> NPs, of 2–200 nm diameter, have been demonstrated to exhibit no noticeable size effects on the electronic structure,<sup>63</sup> it is possible to solely vary the ratio of free-to-stabilizer covered surface sites as a single parameter.

**Dry NPs:** 20 nm diameter, 99.5% anatase TiO<sub>2</sub> NP sample purchased from Io-Li-Tec, Germany. This sample was used for the total electron yield measurements of the Ti L-edge XA and the O K-edge XA spectra for examining the similarity between the XA spectra of the anatase-phase TiO<sub>2</sub> NPs in a dry environment and the TiO<sub>2</sub> single crystal reported in the literature.

**TiO<sub>2</sub> NPs in HCl aqueous solution:** (acidic solutions without free surface sites) 10 nm, 99.9% pure anatase TiO<sub>2</sub> NPs coated with Cl<sup>-</sup>, purchased from Mknano, Canada, were used to prepare 20 wt% TiO<sub>2</sub> NPs in 0.5 M HCl aqueous solution (yielding pH 1.2) and in 1 M HCl aqueous solution (yielding pH 0.7). In both samples, the NPs are fully covered by Cl<sup>-</sup> ions with ratios of NP surface sites relative to stabilizer ions of [1 : 1]<sup>Cl<sup>-</sup></sup> and [1 : 2]<sup>Cl<sup>-</sup></sup>, respectively. In all these cases, water cannot interact with the actual TiO<sub>2</sub> NP. Our measurements from the HCl-stabilized NP solutions thus provide valuable reference O 1s non-resonant, resonant XPS and PEY-XAS spectra of the TiO<sub>2</sub> NPs, in the absence of interfacial oxygen species.

**TiO<sub>2</sub> NPs in HNO<sub>3</sub> aqueous solution:** (acidic solutions with free/no free surface sites) 20 wt%, 6 nm TiO<sub>2</sub> NPs in 0.5 M HNO<sub>3</sub> aqueous solution (yielding pH 1.2) and in 0.25 M HNO<sub>3</sub> aqueous solution (pH 0.9), purchased from PlasmaChem, Germany, which have ratios of TiO<sub>2</sub> surface sites relative to the stabilizer of [1 : 1]<sup>NO<sub>3</sub><sup>-</sup></sup> and [2 : 1]<sup>NO<sub>3</sub><sup>-</sup></sup>, respectively. Furthermore, in order to increase the [x : y]<sup>NO<sub>3</sub><sup>-</sup></sup> ratio, a 20 wt%, 3 nm TiO<sub>2</sub> NPs in 0.6 M HNO<sub>3</sub> aqueous solution (pH 0.7) yielding [4 : 1]<sup>NO<sub>3</sub><sup>-</sup></sup> was used; this ready-to-use solution was purchased from NYACOL, USA.

**TiO<sub>2</sub> NPs in NH<sub>4</sub>OH aqueous solution:** (basic solutions with free surface sites) 20 wt%, 20 nm TiO<sub>2</sub> NPs in 0.3 M NH<sub>4</sub>OH aqueous solution (pH 7.8; slightly above the neutral water pH) were obtained from NYACOL, USA. In addition, we added 0.5 M NH<sub>4</sub>OH to this NP (aq) solution to obtain 20 wt%, 20 nm TiO<sub>2</sub> NPs in 0.8 M NH<sub>4</sub>OH aqueous solution (pH 9.8). This leads to ratios of [2 : 1]<sup>NH<sub>4</sub><sup>+</sup></sup> and [1 : 1.5]<sup>NH<sub>4</sub><sup>+</sup></sup>, respectively. The latter sample was used to support our proposed TiO<sub>2</sub>-water interaction mechanism, as discussed in the Results section. It is interesting to mention that the estimated [2 : 1]<sup>NH<sub>4</sub><sup>+</sup></sup> ratio is in good agreement with measurements of the surface zeta potential. It is -16.9 mV for the [2 : 1]<sup>NH<sub>4</sub><sup>+</sup></sup> solution (measured with a "Zetasizer Nano ZS" spectrometer) and can be compared with a value of +30 mV<sup>64</sup> for a fully covered anatase TiO<sub>2</sub> NP surface in aqueous solution.

## Results and discussion

### Ti L-edge PEY-XA spectra

We start by exploring the X-ray absorption (XA) spectra of aqueous-phase TiO<sub>2</sub> NPs measured at the Ti<sup>4+</sup> 2p → valence 3d<sup>0</sup> resonance. We note that an electron-yield absorption spectrum essentially captures electrons that are emitted in an electronic relaxation process, which is mostly Auger decay. One typically assumes that the Auger-electron yield is proportional to the actual XA.<sup>65,66</sup> In the present work, we detect the partial electron yield corresponding to the refilling of a Ti 2p hole by a 3p electron and subsequent ejection of another 3p electron (Ti LMM Auger channel); this (resonant) Auger signal appears in the 360–420 eV kinetic energy range. More specifically, by



integrating the signal intensity over this energy range as a function of the excitation energy, we obtain the so-called partial electron yield XA (PEY-XA) spectrum. For the questions addressed here, the small difference that may occur between PEY and total electron yield (TEY) detection<sup>65</sup> is irrelevant; the important point here is that we can experimentally track the electronic structure changes that lead to the measured XA spectra. In Fig. 1, we show the Ti L-edge PEY-XA spectra of several NP solutions,  $[1:1]^{Cl^-}$ ,  $[1:1]^{NO_3^-}$ ,  $[4:1]^{NO_3^-}$  and  $[2:1]^{NH_4^+}$ . We present one sample from each set described in the Experimental section. For the  $NO_3^-$  sample set only, two samples provided from different companies are shown ( $[4:1]^{NO_3^-}$  and  $[1:1]^{NO_3^-}$ ). In addition, the dry NP (shown in the bottom of Fig. 1) XA spectrum was measured by detecting the drain current while sweeping the photon energies over the Ti L-edge. This is one way to obtain the total electron yields, and throughout the text, we will refer to the TEY-XA spectrum, serving as the reference.

The measured L-edge XA spectra, presented in Fig. 1, can be divided into two regions,  $L_2$  ( $2p_{1/2}$ ) and  $L_3$  ( $2p_{3/2}$ ) edges, due to the 2p spin orbital coupling splitting. Results are shown for the NP solutions  $[1:1]^{Cl^-}$ ,  $[1:1]^{NO_3^-}$ ,  $[4:1]^{NO_3^-}$ , and  $[2:1]^{NH_4^+}$ . Here, we largely focus on the  $L_3$  region. Our first observation is that the spectra of all solutions are nearly identical. The first prominent absorption band A results from the Ti  $2p_{3/2} \rightarrow 3d t_{2g}$  transition, and band B relates to the Ti  $2p_{3/2} \rightarrow 3d e_g$  transition. The energy difference between A and B, which quantifies the crystal field splitting,  $10 Dq$ , of the empty 3d orbital hybridized with the surrounding oxygen atoms, is indicated. Since  $10 Dq$  is sensitive to the Ti–O distance<sup>67</sup> its value is an indicator of changes in the Ti local environment. Arguably more important is the overall shape of the L-edge XA spectrum, the details of which are characteristic for a given  $TiO_2$  phase (anatase, rutile, or brookite). We see that the NP spectra in Fig. 1 match well the TEY-XA spectrum of the dry 20 nm NPs, which is also presented at the bottom of Fig. 1; and the latter spectrum perfectly reproduces the XA spectrum of anatase-phase  $TiO_2$  crystal.<sup>68–70</sup>

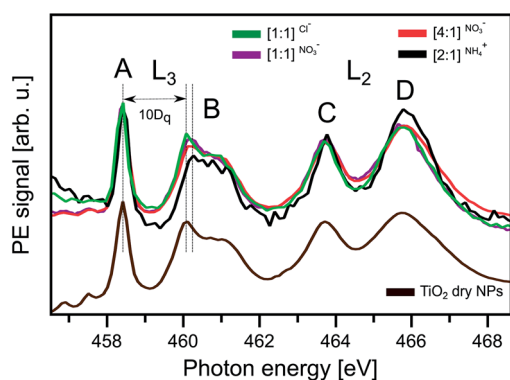


Fig. 1 (Top): Ti L-edge PEY-XA spectra of anatase  $TiO_2$  NPs dissolved in different aqueous solutions. Here,  $[x:y]^{ion}$  indicates the stabilizer ion that has been used, and inside the bracket, the ratio of available NP surface sites to surface sites covered by the stabilizer ion is shown. Labels A–D refer to the most prominent absorption bands. The splitting of the  $L_3$  edge feature,  $10 Dq$ , is indicated. (Bottom): Ti L-edge TEY-XA spectra of dry anatase  $TiO_2$  NPs.

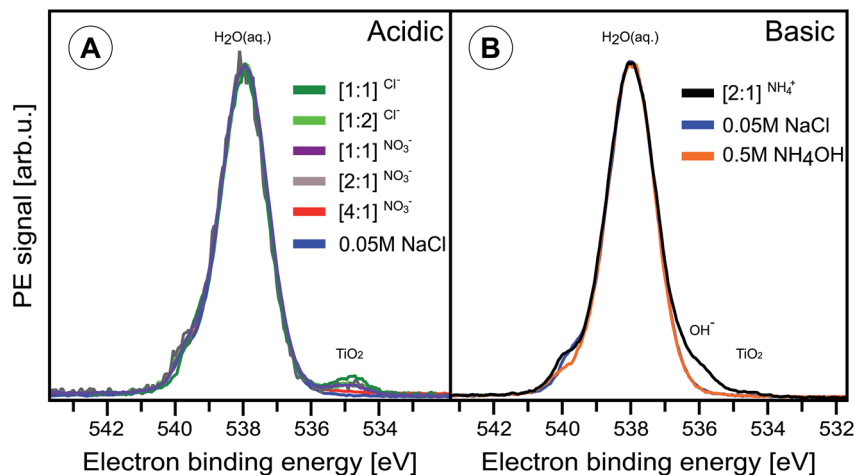
We particularly point out that the broadening of the  $e_g L_2$  edge (as well as the sub-splitting of the  $e_g L_3$  edge), which is very sensitive to the crystal phase, is the same in all spectra and reproduces the shape and width reported in the literature.<sup>68–70</sup> We can thus rule out any NP phase transition in the aqueous solutions, and also, oxygen defects are not detected, which would manifest in contributions from the  $Ti^{3+}$  signal.

To further confirm the non-existence of  $Ti^{3+}$ , we have also recorded the valence spectra at the various resonances A, B, C, and D identified in Fig. 1. The results are exemplarily shown for the  $[2:1]^{NH_4^+}$  solution in Fig SI-1 of the ESI,<sup>†</sup> where we also present an off-resonant spectrum measured slightly below the resonance, at 457 eV photon energy. None of the spectra display any signature of the 2p–3d3d (LVV)  $Ti^{3+}$  Auger decay, as judged from comparison with our previous study of atomic  $Ti^{3+}$  in  $TiCl_3$  aqueous solution.<sup>71</sup> Our conclusion is also supported by reported valence spectra of pure crystalline anatase  $TiO_2$  (containing no  $Ti^{3+}$ ) and  $Li^+$ -doped  $TiO_2$ , in which  $Ti^{3+}$  forms.<sup>72</sup> Hence, the spectra in Fig SI-1<sup>†</sup> prove that the Ti 3d orbital is empty, and the aqueous-phase NPs are indeed purely anatase-phase  $TiO_2$ . Adsorption mechanism (1), described in the introduction, is thus irrelevant for the  $TiO_2$  NP–aqueous solution interface. One further observation from Fig. 1 that is worth mentioning is that  $10 Dq$  appears to be slightly larger for the  $[2:1]^{NH_4^+}$  solution than for all other solutions. In Fig SI-2 of the ESI,<sup>†</sup> we have averaged the  $[4:1]^{NO_3^-}$ ,  $[1:1]^{Cl^-}$ , and  $[1:1]^{NO_3^-}$  solution spectra for better visualization of this pH-dependent effect. Arguably, this is an indication that  $NH_4^+$ , unlike the other stabilizing ions, has some specific effect on the interfacial structure. Indeed, a distinct adsorption behavior of  $H_2O$  occurs in the  $NH_4^+$ -stabilized NP solutions as we will show below.

### O 1s off-resonant photoemission spectra

Fig. 2 presents the (regular) oxygen 1s core-level photoelectron spectra measured at 1200 eV photon energy for all our NP solutions. Here, we have included the reference spectrum of the O 1s spectrum of the 0.05 M NaCl aqueous solution, representative of neat liquid water. We find that all PE spectra (Fig. 2A), again with the one exception of  $NH_4^+$  (Fig. 2B), are almost identical, exhibiting the main bulk water peak at 538.1 eV BE,<sup>73</sup> relative to the vacuum level, the water gas-phase (a shoulder) at 540.0 eV, and an additional small peak at 534.9 eV BE from the lattice oxygen of the  $TiO_2$  NPs, in agreement with the reported value for the  $TiO_2$  rutile crystal with a few layers of water prepared at a suitable relative humidity.<sup>21</sup> Similar to our previous study of aqueous-phase hematite NPs stabilized with  $NO_3^-$ ,<sup>26</sup> the PE signal from the  $NO_3^-$  cannot be observed (at 538.1 eV binding energy<sup>74</sup>) at such a low concentration because of overlap with the large signal intensity from bulk water.<sup>51,74</sup> The  $OH^-$  signal, on the other hand, gives rise to a peak at 536.0 eV BE (determined in the aforementioned ambient-pressure PE study on rutile  $TiO_2$  single crystal<sup>21</sup>), which is distinguishable from  $NO_3^-$  and water. But, there is no indication of adsorbed  $OH^-$  despite available free adsorption sites for interaction with water, for instance in the case of  $[4:1]^{NO_3^-}$  and  $[2:1]^{NO_3^-}$ . We thus conclude (and will later corroborate) that





**Fig. 2** Oxygen 1s photoelectron spectra of the different anatase  $\text{TiO}_2$  NP aqueous solutions, measured at 1200 eV photon energy. As in Fig. 1,  $[x : y]^{\text{ion}}$  indicates the stabilizer ion that has been used, and inside the bracket, the ratio of free NP surface sites to surface sites covered by the stabilizer ion is shown. NP size is given in the Experimental section. (A) Acidic NP solutions:  $[1 : 1]^{\text{Cl}^-}$  (pH 1.2),  $[1 : 2]^{\text{Cl}^-}$  (pH 0.7),  $[1 : 1]^{\text{NO}_3^-}$  (pH 1.2),  $[2 : 1]^{\text{NO}_3^-}$  (pH 0.9), and  $[4 : 1]^{\text{NO}_3^-}$  (pH 0.7). Also shown is the spectrum of 0.05 M NaCl. (B) Basic solution:  $[2 : 1]^{\text{NH}_4^+}$  (pH 7.8). Also shown are the O 1s spectra of the 0.05 M NaCl and 0.5 M  $\text{NH}_4\text{OH}$  aqueous solutions.

water does not dissociate on the  $\text{TiO}_2$  NP surface but rather adsorbs molecularly; yet, a small but negligible amount of dissociated water may exist at the NP surface. This is opposite to  $\alpha\text{-Fe}_2\text{O}_3$  NPs, where water dissociates when the NPs are stabilized by  $\text{NO}_3^-$ .<sup>26</sup> Note also that adsorbed water, similar to  $\text{NO}_3^-$ , has an O 1s BE strongly overlapping with bulk water (0.5 eV lower BE than bulk water<sup>21</sup>), which makes the detection of this contribution impossible in a liquid-jet experiment.

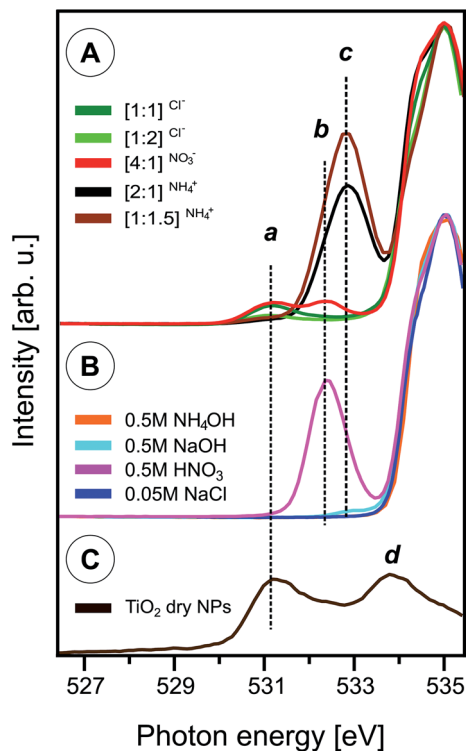
We now turn to the  $[2 : 1]^{\text{NH}_4^+}$  NP solution (Fig. 2B), where we observe a small intensity signal at 536.0 eV BE, which identifies the adsorbed  $\text{OH}^-$  species. This energy is in agreement with the previously reported value for adsorbed hydroxyl species on a  $\text{TiO}_2$  surface under near ambient pressure conditions.<sup>21,31,49</sup> Comparing with the reference O 1s PE spectra of the 0.5 M  $\text{NH}_4\text{OH}$  aqueous solution (pH 11.7) and 0.05 M NaCl aqueous solution, containing no NPs, the  $\text{OH}^-$  signal is seen to vanish. This implies that it is not produced by the  $\text{NH}_4^+$  interaction with bulk water. Notice that the higher-concentration solution, 0.5 M  $\text{NH}_4\text{OH}$  (compared to 0.3 M  $\text{NH}_4\text{OH}$ ), does not even show the slightest evidence of  $\text{OH}^-$  signal. Hence, the 536.0 eV BE signal must result from water interaction with the  $\text{TiO}_2$  free surface sites. Since the pH of the  $[2 : 1]^{\text{NH}_4^+}$  NP solution is 7.8, *i.e.*, the concentration of free  $\text{OH}^-$  in the solution is roughly  $10^{-7} \text{ mol L}^{-1}$ , the detected  $\text{OH}^-$  species must be immobilized within the  $\text{TiO}_2$  NP–solution interface rather than being free in the solution. One can also infer from Fig. 2 that dissociation of water on the  $\text{TiO}_2$  NP surface depends on solution pH, a hypothesis that we will verify with the help of oxygen K-edge PEY-XA spectra. In the present case of approximately 650 eV O 1s photoelectrons, the top-most layers of the NPs, including their adsorbed molecular layer, are probed. The relatively large  $\text{OH}^-$  signal intensity compared to the lattice oxide signal in Fig. 2B is attributed to the exponentially decreasing electron signal contribution as a function of distance from the (covered) NP surface–aqueous solution interface.

### O K-edge photoemission and PEY-XA spectra

Analogous to the Ti L-edge PEY-XA measurements, we also studied the valence photoemission signal (detected in the 510–525 eV kinetic energy range), sweeping the photon energy across the O 1s resonance. Fig. 3A presents the O 1s PEY-XA spectra of five selected NP solutions,  $[1 : 1]^{\text{Cl}^-}$ ,  $[1 : 2]^{\text{Cl}^-}$ ,  $[4 : 1]^{\text{NO}_3^-}$ ,  $[2 : 1]^{\text{NH}_4^+}$ , and  $[1 : 1.5]^{\text{NH}_4^+}$ . In Fig. 3B, we show the respective spectra of four relevant reference salt aqueous solutions, 0.5 M  $\text{HNO}_3$  (pH  $-0.2$ ), 0.5 M  $\text{NH}_4\text{OH}$  (pH 11.7), 0.5 M NaOH (pH 13.7), and 0.05 M NaCl (pH 7). Fig. 3C shows the TEY-XA spectrum of the dry  $\text{TiO}_2$  NPs, which was, however, recorded by measuring the resulting electric current through the sample.

In Fig. 3A and B, the large peak at 535 eV photon energy is due to the liquid water absorption pre-peak (O 1s  $\rightarrow$   $4a_1$  transition<sup>75</sup>), which is used here for energy calibration and intensity normalization. The shoulder at 534.5 eV photon energy is the respective  $\text{H}_2\text{O}$  gas-phase absorption. This contribution is seen to vary among different solutions, which is due to a combination of changing vapor pressure upon pH variation and perhaps a slight misalignment of the liquid jet when switching solutions. In addition to the water absorption bands, several smaller peaks, **a** (near 531.2 eV), **b** (532.3 eV), **c** (532.8), and **d** (533.8), can be seen in both Fig. 3A and B. More specifically, and starting with the TEY-XA spectrum of the dry NPs (Fig. 3C), the two main bands, **a** (531.2 eV) and **d** (533.8 eV), are the absorptions O 1s  $\rightarrow$  O 2p–Ti 3d ( $t_{2g}$  and  $e_g$ ); these metal orbitals are hybridized with lattice O 2p.<sup>63,76–79</sup> We next consider the solutions  $[1 : 1]^{\text{Cl}^-}$  and  $[1 : 2]^{\text{Cl}^-}$  for which no free adsorption sites on the NP surfaces are available. The respective spectra thus serve as a reference, representative of an O 1s XA spectrum in the absence of interfacial oxygen-containing species, and they are also useful to quantify the stabilizer ion and concentration effects on the detected signal intensities. Not surprisingly, these spectra exhibit just absorption **a**, corresponding to the  $\text{TiO}_2$  NP bulk,





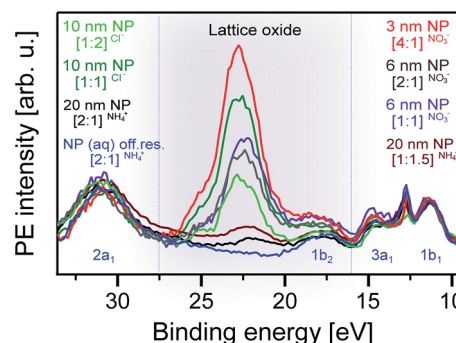
**Fig. 3** (A) O 1s PEY-XA spectra of different anatase TiO<sub>2</sub> NP aqueous solutions; see caption of Fig. 2 for the solution labels. Intensities are normalized at the water pre-peak band at 535.0 eV. (B) O 1s PEY-XA spectra of reference solutions, as labeled. (C) TEY-XA spectra of dry anatase TiO<sub>2</sub> NPs. Assignment of absorption bands: *a* and *d* (TiO<sub>2</sub> lattice oxide), *b* (NO<sub>3</sub><sup>-</sup>), and *c* (OH<sup>-</sup>).

and band *d* stays undetected, hidden under the water pre-edge peak. A small energy shift of band *a* with respect to the dry NPs is likely caused by the Cl<sup>-</sup> decoration. Turning now to the [4 : 1]<sup>NO<sub>3</sub><sup>-</sup></sup> NP solution – where we expect molecular water adsorption (as concluded from Fig. 2A) – an additional band *b* (at 532.3 eV photon energy) is observed. The same band occurs in the XA spectrum of the 0.5 M HNO<sub>3</sub> aqueous solution (Fig. 3B), and we can unequivocally assign band *b* to interfacial NO<sub>3</sub><sup>-</sup> species. For the [2 : 1]<sup>NH<sub>4</sub><sup>+</sup></sup> and [1 : 1.5]<sup>NH<sub>4</sub><sup>+</sup></sup> NP solutions, we find an intense band *c* (at 532.8 eV photon energy), *i.e.*, at a slightly larger absorption than *b*, and the intensity of band *a* is now very small. Comparing with the XA spectrum of the 0.5 M NaOH aqueous solution (pH ~13.7) in Fig. 3B, where we also find an absorption band (although small) at position *c*, shows that this band is due to free OH<sup>-</sup> (also in agreement with ref. 80 and 81). The comparison with NaOH solution was necessary here because the OH<sup>-</sup> signal from the 0.5 M NH<sub>4</sub>OH solution (our reference discussed along with Fig. 2) is below our detection limit. Note that NaOH is a stronger base than NH<sub>4</sub>OH. As a further remark, we point out that the intensities of interfacial OH<sup>-</sup> in the NP (aq) solutions are much larger than the signal of the free OH<sup>-</sup> in the reference solutions (particularly 0.5 M NaOH). This result would seem non-intuitive given the NP solution pH of 7.8. We attribute the large OH<sup>-</sup> signal to immobilized dissociated H<sub>2</sub>O at or near the TiO<sub>2</sub> surface; alternatively, this effect might be a consequence of the NP

position relative to the solution–vacuum interface to be detailed below. Complementary resonant X-ray scattering (RIXS) studies are underway to clarify the origin of this large signal from TiO<sub>2</sub> NPs in aqueous solution, at basic pH.

In order to explore the water–NP interaction mechanism, we performed O 1s RPE spectroscopy measurements at three selected excitation energies, the *t*<sub>2g</sub> lattice oxide (absorption *a*), the interfacial NO<sub>3</sub><sup>-</sup> (*b*) and OH<sup>-</sup> (*c*). Our initial focus is to identify the spectral contributions from the lattice oxide as this will guide us in singling out contributions from interfacial species. In Fig. 4, we present the RPE spectra of all our NP solutions measured at *a* (531.2 eV), and in addition, we show the off-resonance spectrum of the [2 : 1]<sup>NH<sub>4</sub><sup>+</sup></sup> NP solution. All spectra are displayed with a Shirley background subtracted. The off-resonance spectrum reproduces the water valence spectrum (in blue),<sup>82</sup> and the solute signal is below our detection limit. The most relevant feature in this comparison is the electron signal near 22.5 eV (grey-shaded), which results from Auger electron emission. It is specifically the spectator Auger decay, O<sup>2-</sup> 1s–1*t*<sub>2g</sub>–1*t*<sub>2g</sub>, occurring at 508.7 eV kinetic energy (equivalent to 22.5 eV BE), and has been assigned with the help of the TiO<sub>6</sub><sup>8-</sup> molecular orbital diagram from ref. 83. The other spectral features at approximately 18.0 and 24.5 eV BE are also due to spectator Auger decay but are not further considered here as their intensities are too small for a quantitative analysis of the interfacial species.

The next observation from Fig. 4 is the considerable intensity variation of the lattice oxide absorption band among the different solutions. At the applied 531.2 eV photon energy (resonance *a* in Fig. 3), the electron inelastic mean free path can be assumed to be less than 3 nm,<sup>84</sup> implying that the NPs are located within this range of the solution–vacuum interface. Arguably, there are several parameters that have direct influence on the exact position of a nanoparticle in the measured solutions, including particle size, stabilizer ion and concentration. The current experiment was not designed to systematically study such effects since the different solutions in this work



**Fig. 4** Valence resonant photoelectron (RPE) spectra of different anatase TiO<sub>2</sub> NP aqueous solutions measured at the O<sub>2</sub><sup>-</sup> resonance, *a* (531.2 eV photon energy; compare with Fig. 3). Also presented is the off resonance spectrum of the [2 : 1]<sup>NH<sub>4</sub><sup>+</sup></sup> NP solution, measured at 530.0 eV photon energy. Solutions are labeled as explained in the caption of Fig. 1. Here, we have added the NP diameters. The grey-shaded area highlights the contributions from the spectator Auger electrons originating from the TiO<sub>2</sub> lattice oxide.



usually differ by more than one parameter. However, the lattice signal contributions tend to be larger for the smaller NPs, which might be an indication of smaller NPs having a larger affinity for the solution interface. On the other hand, the comparison between the 10 nm  $[1 : 1]^{Cl^-}$  and the 6 nm  $[1 : 1]^{NO_3^-}$  NP solutions would suggest the opposite, indicating that the distance of the NPs from the solution surface depends on the complex interplay between size, charge, and adsorbate, and specifically on the respective nature of the so-called diffusive layer.<sup>85</sup> It should be stated here that electronic-structure size effects (see Experimental section) in the NP size range considered here can be expected to be negligible.

Having analyzed the oxygen signal from the NPs, based on the O 1s RPE spectra at the lattice oxide resonance, **a**, we now turn to exploring the contribution from oxygen-containing molecular species at the NP–water interface. We start with the acidic solution. Fig. 5 shows RPE spectra measured at the  $NO_3^-$  resonance, **b**, for the  $[1 : 1]^{NO_3^-}$ ,  $[2 : 1]^{NO_3^-}$ , and  $[4 : 1]^{NO_3^-}$  NP aqueous solutions. For comparison, we also include a spectrum of the 0.5 M  $HNO_3$  aqueous solution. All spectra are displayed with a Shirley background subtracted. As in Fig. 4, the signal near 30 eV ( $2a_1$ ) and 11 eV ( $1b_1$ ) is due to water,<sup>86</sup> and the latter was used for signal intensity normalization. The interesting features are the broad electron emissions in the 13–24 eV BE range due to  $NO_3^-$ . As in our previous work on hematite NPs,<sup>26</sup> the same four main photoemission bands are observed, at approximately 16.0, 18.0, 22.5, and 24.5 eV BE (all within the red-shaded area), assigned to various Auger-electron decays upon O 1s  $\rightarrow$  valence excitation at 532.2 eV photon energy.<sup>26</sup> The 24.5 eV peak strongly overlaps with the lattice oxide peak (black-shaded area); compare with Fig. 4. This peak can be most clearly observed for the  $[4 : 1]^{NO_3^-}$  NP solution, in which case, the  $NO_3^-$  contribution is the lowest; see the Experimental section. On the other hand, the  $NO_3^-$  signal increasingly dominates when going from  $[4 : 1]^{NO_3^-}$  to  $[1 : 1]^{NO_3^-}$  solutions. In fact, relative intensities (red-shaded area) almost quantitatively track our estimated NP surface sites-to-stabilizer ratios. Most

important for the present study are, however, the  $[2 : 1]^{NO_3^-}$  and  $[4 : 1]^{NO_3^-}$  solutions, which provide free surface sites for water to interact with the  $TiO_2$  surface. If this interaction were dissociative, Auger signal from adsorbed  $OH^-$  should appear in the 25–32 eV binding energy finger-print region (blue-shaded area) analogous to the hematite NP (aq) study;<sup>26</sup> this is because of the considerable spectral overlap between resonances **b** and **c** (of adsorbed  $NO_3^-$  and  $OH^-$ , respectively) seen in Fig. 3A. Obviously, no signal of adsorbed  $OH^-$  is observed here, corroborating our above finding (from the O1s non-resonant spectra, Fig. 2A, and O K-edge XAS, Fig. 3) that water adsorbs molecularly on the surface of  $TiO_2$  in an acidic environment. In the next paragraph, we discuss the interaction in basic solution.

Fig. 6 shows the respective O 1s RPE spectra of the basic  $[2 : 1]^{NH_4^+}$  and  $[1 : 1.5]^{NH_4^+}$  NP solutions. Measurements were performed right at the  $OH^-$  resonance (peak **c**, 532.8 eV photon energy), rather than at resonance **b**, which increases the spectral sensitivity to adsorbed  $OH^-$ . The figure also includes an off-resonance spectrum of the  $[2 : 1]^{NH_4^+}$  NP solution measured at 530 eV photon energy as well as a reference spectrum of the 0.5 M NaOH aqueous solution. All the spectra are Shirley-background subtracted. Again, the off-resonance spectrum (in dark blue) reproduces the water valence peaks.<sup>82</sup> The NaOH spectrum (light blue) exhibits the resonantly enhanced  $OH^-$  signal, dominated by Auger-electron emission, in the 15–25 eV BE range (corresponding to 505–514 eV kinetic energy range).<sup>80</sup> This signal contribution is found to be much larger in the spectra of the NP solutions, with an intensity being an order of magnitude larger than the signal from the water valence band. We note, though, that near the 25 eV BE position (grey-shaded area), the  $OH^-$  signal considerably overlaps with the electron emission from lattice oxide (see also Fig. 4 and 5). The remarkably large  $OH^-$  signal for the NP solutions, with pH 7.8 ( $[2 : 1]^{NH_4^+}$ ) and 9.7 ( $[1 : 1.5]^{NH_4^+}$ ), is a clear indication that this signal cannot be due to free  $OH^-$  in aqueous solution and rather arises from  $OH^-$  bound to the aqueous-phase NP surface.

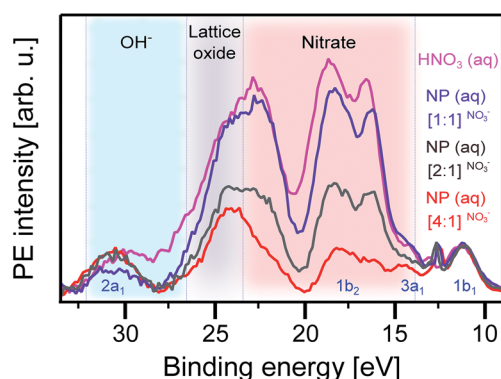


Fig. 5 Valence resonant photoelectron (RPE) spectra of different anatase  $TiO_2$  NP aqueous solutions measured at the  $NO_3^-$  resonance, **b** (523.2 eV photon energy; compare Fig. 3). Also presented is the spectrum of the 0.5 M  $HNO_3$  aqueous solution. Different shades indicate the regions of Auger-electron emission from different species:  $NO_3^-$  (red-shaded), lattice oxide (grey-shaded), and  $OH^-$  (blue-shaded).

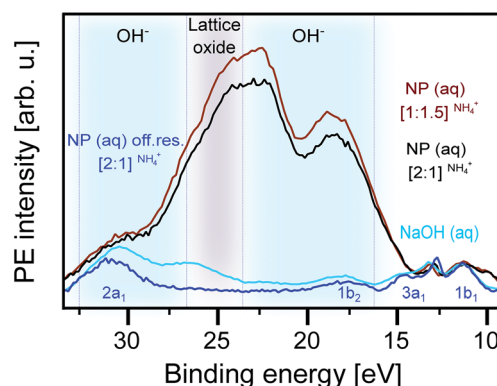


Fig. 6 Valence resonant photoelectron (RPE) spectra of different anatase  $TiO_2$  NP aqueous solutions measured at the  $OH^-$  resonance, **c** (532.8 eV photon energy; compare Fig. 3). Also presented is the spectrum of the 0.5 M NaOH aqueous solution, and in addition, the off-resonance spectrum measured at 530 eV photon energy of the  $[2 : 1]^{NH_4^+}$  NP solution is shown. Different shades indicate the regions of Auger-electron emission from different species: lattice oxide (grey-shaded) and  $OH^-$  (blue-shaded).



It is useful to recall our observation from Fig. 1 that in the case of the  $[2 : 1]^{NH_4^+}$  NP solution, 10 Dq is larger than for all other NP solutions. Together with our findings in Fig. 6, this corroborates that the split can be associated with the different specific interactions between a  $H_2O$  molecule and a Ti site at the anatase surface. Our final observation from Fig. 6 is the slight increase of the  $OH^-$  signal when increasing the  $NH_4^+$  concentration from 0.3 M ( $[2 : 1]^{NH_4^+}$ ) to 0.8 M ( $[1 : 1.5]^{NH_4^+}$ ), which is paralleled by an increase of the  $OH^-$  XA-band intensity, as was shown in Fig. 3A. This effect will be discussed next.

Our observations from Fig. 1–6 lead us to propose the following pH-dependent adsorption mechanisms for water on the anatase NP surface, as illustrated in Fig. 7. Here, we depict the interaction in the acidic environment in the top tier, and in basic solution in the bottom tier. Our starting point is the hypothetical (prepared) adsorption of a water molecule for both cases. This is followed by the dissociation of  $H_2O$  at the defect-free anatase surface, forming a hydroxyl/ $H^+$  pair similar to the processes discussed in ref. 20 and explained in the introduction. Above, we have inferred from the changes of 10 Dq that water dissociates at the Ti surface sites of the  $TiO_2$  NP. One crucial difference between the acidic and basic environment is then the probability of stabilizing the (paired) proton in the vicinity of  $OH^-$  at the surface. In fact, the aforementioned simulation of the dissociative/associative water adsorption on rutile  $TiO_2$  using DFT calculations<sup>59</sup> concludes that the stability of the hydroxylated configuration is largely dependent on the locations of the  $H^+$  species, and the recombination of water molecules from hydroxyls is observed under the fully hydroxylated condition. We argue that this is what our data show. Under acidic conditions, the free proton is locally rather confined due to hydronium molecules, and recombination to form water is likely. This is illustrated in the acidic-environment model (top tier of the second step) in Fig. 7. Possibly, also the surrounding hydronium in water may transfer a proton to a surface  $OH^-$  molecule (center tier of the second step). In any case, our experiments suggest that the lifetime of hydroxyl is very short, and this species can thus not be detected here. In contrast, such recombination is less likely in basic solution where  $H^+$  quickly diffuses away from the surface, and the  $OH^-$  lifetime is sufficiently large. This situation is illustrated at the right side of the bottom tier of Fig. 7. Our model mechanism would also account for the increase of  $OH^-$  signal suggested by the spectrum of the  $[1 : 1.5]^{NH_4^+}$  NP solution in Fig. 6. Here, due to the larger pH, the proton delocalization is even larger, which leads to the stabilization of more hydroxyl groups at the  $TiO_2$  surface.

## Conclusion

We have examined the solid–liquid interface of titania NPs in aqueous solutions of different pH. By measuring the Ti L-edge XA spectra, we confirmed that in all solutions studied here, the NPs exhibit an anatase  $TiO_2$  phase. Molecularly adsorbed  $H_2O$  molecules were found on the NP surface in the acidic solution. However, a dissociative water interaction, leading to  $OH^-$  species at the  $TiO_2$  surface, is observed for the near-neutral

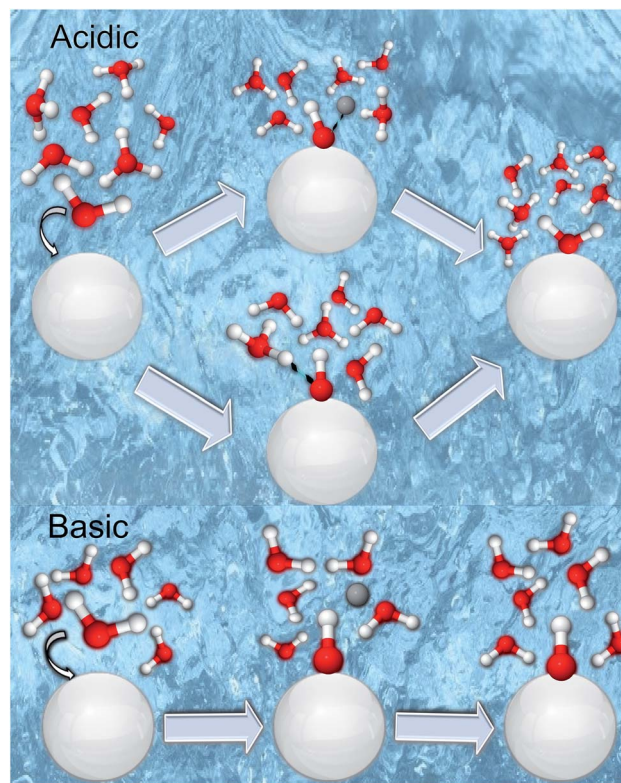


Fig. 7 Illustration of the proposed  $TiO_2$ –water interaction in acidic (top tier) and basic (bottom tier) aqueous solutions.  $TiO_2$  NPs are represented by the large white spheres. Water and hydronium oxygens are shown in red, bonded hydrogen atoms are shown in white, and a single free hydrogen (proton) in solution is shown in light-grey. The hydroxyl stability on the NP surface depends on its probability of forming a water molecule by capturing a free  $H^+$  or via proton transfer from a surrounding hydronium. This probability is largest in the acidic environment, either by recombination of the dissociated  $H^+$  and  $OH^-$  pairs (top panel in the acidic model second step) or by proton transfer from the surrounding hydronium (bottom tier in the acidic model second step). Such recombination and proton transfer processes do not occur in a basic or above neutral chemical environment; the basic–pH interaction model is illustrated in the bottom-most tier of the figure.

solutions. This behavior is inferred from the oxygen 1s core level non-resonant PE spectra, and corroborated by the O K edge XA as well as the resonant PE spectra. Specifically, the RPE spectra are a sensitive probe of the NP lattice oxide, and of the existence or absence of  $NO_3^-$  and  $OH^-$  interfacial species. The detailed spectral analysis of the 10 Dq value suggests that water interacts with the Ti sites of the NP surface. Our results lead us to propose that at acidic pH, the protonation of adsorbed  $OH^-$  at the Ti-site of the defect-free anatase NP surface is fast, leading to molecularly adsorbed water as the dominant species. This occurs either by recombination of the proton, which stays rather localized at the site where it was born, with surface  $OH^-$ , or by proton transfer from a hydronium to a surface  $OH^-$ . On the other hand, at basic pH, the proton can easily diffuse away from the surface, which makes the reformation of adsorbed  $H_2O$  unlikely. An interesting aspect of these findings is that the pH variation provides a means to control the molecular *versus*



dissociative water interaction with anatase surfaces. This finding is in agreement with previous theoretical studies on the stability of hydroxylated configurations<sup>59</sup> and on the proton transfer between a TiO<sub>2</sub> surface and hydronium in solution.<sup>61</sup>

We would also like to stress that the liquid-jet PE technique is truly complementary to ambient-pressure PE spectroscopy, with the latter ideally suited for investigation of crystalline surfaces covered by several water or aqueous solution monolayers at neutral pH. As shown here, investigation of the respective nanoparticles (TiO<sub>2</sub>) fully dispersed in an aqueous solution enables unique access to the study of the TiO<sub>2</sub>-water interface as a function of pH. Moreover, application of the multiple aspects of photoemission (beyond the mere measurement of photoelectron spectra) in ambient-pressure studies remains challenging. And yet, future investigations of catalytically-relevant NPs (aq), including also hybrid systems like core-shell nanoparticles,<sup>87</sup> or tailored nanoparticle properties in material research would benefit from measurements in the soft or even hard X-ray regime in order to better characterize the distribution of NPs at the aqueous solution-vacuum interface.

## Author contributions

H. A., R. S. and B. W. planned the experiments and selected the samples. All authors conducted the experiments during multiple beamtimes at BESSY II. H. A., R. S. and B. W. analyzed the data and wrote the article. All authors have given approval to the final version of the manuscript.

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## Conflicts of interest

The authors declare no conflict of interest.

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