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Unraveling the atomic structure and dissociation of interfacial water on anatase TiO₂ (101) under ambient conditions with solid-state NMR spectroscopy†

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Anatase TiO₂ is a widely used component in photo- and electro-catalysts for water splitting, and the (101) facet of anatase TiO₂ is the most commonly exposed surface. A detailed understanding of the behavior of H₂O on this surface could provide fundamental insights into the catalytic mechanism. This, however, is challenging due to the complexity of the interfacial environments, the high mobility of interfacial H₂O, and the interference from outer-layer H₂O. Herein, we investigate the H₂O/TiO₂ interface using advanced solid-state NMR techniques. The atomic-level structures of surface O sites, OH groups, and adsorbed H₂O have been revealed and the detailed interactions among them are identified on the (101) facet of anatase TiO₂. By following the quantitative evolution of surface O and OH sites along with H₂O loading, it is found that more than 40% of the adsorbed water spontaneously dissociated under ambient conditions on the TiO₂ surface at a loading of 0.3 mmol H₂O/g, due to the delicate interplay between water–surface and water–water interactions. Our study highlights the importance of understanding the atomic-level structures of H₂O on the surface of TiO₂ in catalytic reactions. Such knowledge can promote the design of more efficient catalytic systems for renewable energy production involving activation of water molecules.

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Introduction

The behavior of water on the surface of metal oxide or metal is a subject of immense importance in a variety of fields such as heterogeneous catalysis, energy science, and materials science.^{1–8} This is because water plays a critical role in various chemical processes that occur on the surface of these materials.^{9–19} A detailed understanding of the structure and behavior of interfacial H₂O on these surfaces can help

researchers to develop more efficient and effective catalytic systems and materials for energy storage and conversion.

One material that has been extensively studied in this regard is titanium dioxide (TiO₂). TiO₂ is widely used in various fields, including photocatalysis, solar cells, and sensors.^{1–3,20–22} The surface of TiO₂ is highly hydrophilic, and therefore water molecules readily adsorb onto the surface. However, details of the interaction of water with the surface, the reactivity of the TiO₂ surface, the rupture of the water O–H bond and consequently the formation of the water–oxide interface structure are essential for the understanding of the interfacial water behavior on the TiO₂ surface.

A number of studies have been conducted to investigate the behavior of water on the TiO₂ surface. By using scanning tunneling microscopy (STM), it was reported that water molecules form a highly ordered structure on the TiO₂ surface, and depending on the conditions, one/two/three-dimensional water structures (monomer, dimer, trimer, tetramer, chains, and networks) could be formed on the surface.^{23–27} In other reports, it was suggested that a water molecule could react with the oxygen vacancy/defect or rupture over the low coordination surface Ti sites of TiO₂, and forms two hydroxyls.^{11,28–31} Very recently, by an elegant environmental TEM method, Wang *et al.* reported that the four-coordinated Ti on a (1 × 4) reconstructed

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TiO₂ (001) surface is highly active for water activation.³² However, water adsorption and dissociation on non-defect TiO₂ has been disputed for decades.^{33–36} For the interfacial H₂O on the (101) facet of anatase TiO₂, a number of theoretical calculations^{37–40} and some experimental studies, including temperature-programmed desorption (TPD)⁴¹ and STM,²³ have concluded an intact molecular adsorption of H₂O on the TiO₂ surface. In contrast, a partial dissociation of H₂O has been inferred through the observation of hydroxyls formed on the TiO₂ surface by using spectroscopic techniques, such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), sum frequency generation (SFG) and so on.^{42–49} However, it is challenging to distinguish the OH groups formed by H₂O dissociation on the non-defect TiO₂ surface from either the OH groups generated by H₂O reaction with defect sites or the original OH groups present on TiO₂. Therefore, while progress has been made, the atomic-level structures of interfacial H₂O and especially its detailed interaction with the TiO₂ surface are still to be resolved. Significantly, several challenges need to be addressed⁵⁰ to get the atomic-level structures of the interplay, including how to reveal the interaction of surface oxygen and titanium atoms with interfacial H₂O, how the water splitting and hydroxyl formation occur, and the quantitative evolution of these surface oxygen species at the water/TiO₂ interface during the hydration process. All these problems are difficult to solve under working reaction conditions due to the interference from outer-layer H₂O, the high mobility of interfacial H₂O, and the complexity of interfacial environments.^{15,51,52}

¹⁷O NMR has long been a powerful and attractive approach for characterizing the atomic-level structure of various oxygen-containing materials due to the wide ¹⁷O chemical shift range.^{53–63} For nano-oxides, the relatively low gyromagnetic ratio, low ¹⁷O abundance (0.037%), quadrupolar nature, and especially low proportion of surface oxygen atoms lead to a great challenge to investigate the detailed structure of surface oxygen atoms. The sensitivity and resolution were still limited despite ¹⁷O isotopic enrichment. Recently, Peng and Grey *et al.* selectively enriched surface oxygen atoms on metal oxides (including CeO₂, TiO₂, and ZnO) with H₂¹⁷O, and distinguished surface O/OH sites from bulk oxygen by using one-dimensional (1D) ¹⁷O MAS NMR spectra combined with DFT calculations.^{64–66} We identified surface OH groups and (sub-)surface O sites on γ -Al₂O₃ by using the 2D proton-detected ¹H–¹⁷O heteronuclear correlation technique to improve the sensitivity and resolution of ¹⁷O NMR spectra,⁶⁷ which would make it possible to study interactions between interfacial H₂O and oxide surfaces. To date, the detailed structures of the surface O/OH sites and their interactions with interfacial H₂O are still ambiguous, let alone quantitative evolution of the structure of these surface O/OH sites in the presence of interfacial H₂O, which should be the key to understand the H₂O–oxide interaction.

In this study, we choose anatase TiO₂ nanoparticles as the oxide model owing to their wide practical application in photo- and photoelectro-catalysis, on which the most frequently exposed surface is the (101) facet with the lowest energy, and investigated the ability of anatase (101) facet-dominated TiO₂ nanoparticles to adsorb and activate water on their surface. By

using the 2D ¹⁷O MQMAS and ¹H{¹⁷O} J-HMQC NMR methods and other techniques, we examined the atomic-level structures of interfacial water and surface O/OH sites of TiO₂ at different water loading levels, as well as the through-bond interactions between them. Our findings show that due to the delicate interplay between water–surface and water–water interactions, the O–H bond of the adsorbed water is broken through the joint effort of coordination-unsaturated Ti_{5C} and the adjacent surface O_{2C} sites, resulting in a terminal OH group (Ti_{5C}–OH) and a proton accommodated on the surface O_{2C} site to form a bridging hydroxyl (O_{2C}H). By following the quantitative evolution of surface O and OH sites along with H₂O loading, it is demonstrated that at a loading of 0.3 mmol H₂O g^{–1}, over 40% of the adsorbed water was dissociated spontaneously on the TiO₂ surface. The understanding over the structure and behavior of interfacial H₂O is helpful for developing more efficient and effective catalytic systems for energy storage and conversion.

Results and discussion

Interaction of surface oxygen sites with H₂O on the (101) facet of TiO₂

Anatase TiO₂ (Fig. S1–S4 in ESI[†]) with predominantly (101) facets (95% percent) has been synthesized.^{68,69} No oxygen vacancies were detected at liquid nitrogen temperature by the ESR spectra (Fig. S5[†]) before and after dehydration of the TiO₂ sample at 160 °C. The morphology of the (101) facet of anatase is well-documented.²³ It features a saw-tooth-like shape, and its top layer is composed of two coordination-unsaturated species in close proximity: the five-coordinated Ti (Ti_{5C}) and two-coordinated surface O (O_{2C}) atoms, as illustrated in Fig. 1a.

To investigate the surface sites on the (101) facet of TiO₂ that interact with H₂O, one-dimensional (1D) and two-dimensional (2D) ¹⁷O MAS NMR experiments were performed on ¹⁷O-enriched TiO₂ (with the surface layer of TiO₂ enriched with ¹⁷O, see methods for details) with different H₂¹⁷O loadings. As shown in Fig. 1b, the resonances at 600–800 ppm in the ¹⁷O MAS NMR spectrum of bare TiO₂ were observed, the chemical shift of which is well above the three-coordinated oxygen in the bulk (around 400–600 ppm, Fig. S6[†]).⁶⁵ The signal shows a broad second-order quadrupolar interaction lineshape (11.7 T), with its line width sharply decreasing with the increase of magnetic field (18.7 T, Fig. 1c). We assign the resonance to a surface O_{2C} site without interaction with H₂O on bare TiO₂, marked as O_I. Upon loading 0.03 mmol H₂¹⁷O over 100 mg TiO₂ (0.3 mmol g^{–1}), the shape of the signal at 600–800 ppm changes significantly, with a tip appearing at 700 ppm (Fig. 1b). At the same time, two new resonances centered at 0 and 150 ppm emerge. To gain insight into the structure of the surface oxygen sites interacting with H₂O, we used the 2D ¹⁷O 3Q MAS NMR technique to remove the quadrupolar broadening and enhance the spectral resolution. For TiO₂ loaded with 0.3 mmol g^{–1} H₂¹⁷O, clearly, the 2D 3Q MAS spectrum resolved the overlapped resonances in the ¹⁷O MAS NMR spectrum (Fig. S7[†]), revealing two new two-coordinated O_{2C} sites (O_{II} and O_{III}). However, the large quadrupolar interaction of the O_I site made it hardly



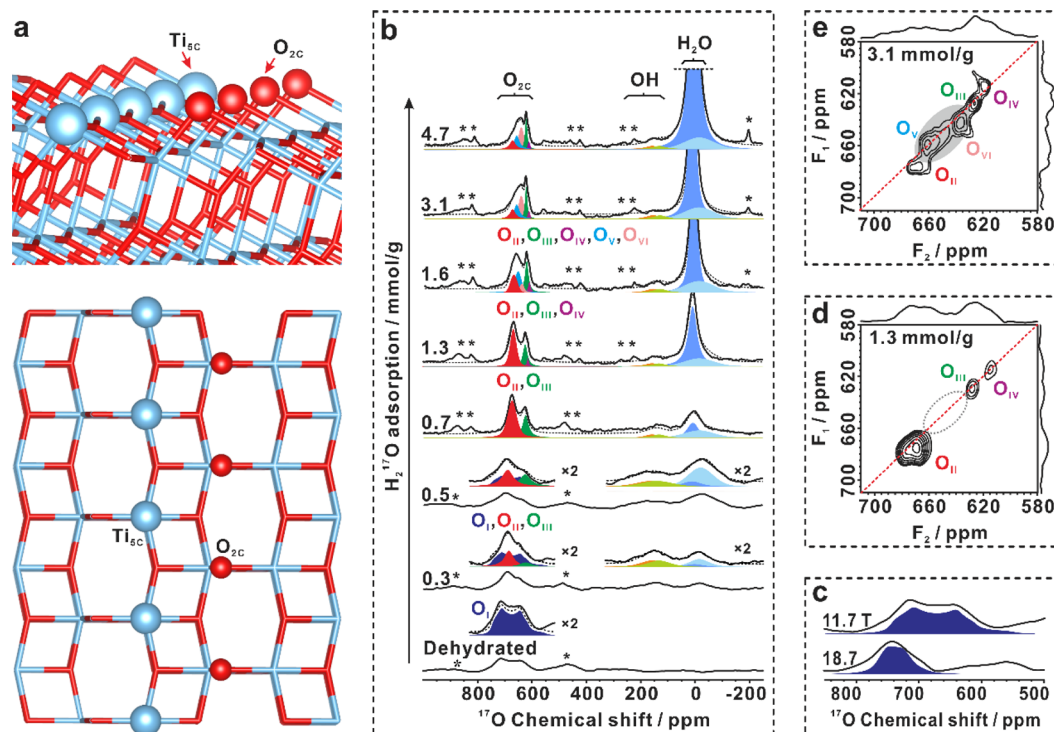


Fig. 1 Surface O_{2C} sites interacting with H_2O . (a) Ball-and-stick model of the anatase TiO_2 (101) surface with five-coordinated Ti (Ti_{5C}) and two-coordinated surface O (O_{2C}) atoms. Titanium and oxygen atoms are plotted in blue (Ti) and red (O). (b) 1D ^{17}O MAS NMR spectra of dehydrated ^{17}O -enriched TiO_2 samples with $H_2^{17}O$ loading from 0 to 4.7 mmol g^{-1} , acquired at a magnetic field of 11.7 T. Note that six O_{2C} sites (O_I – O_{VI}), two types of OH groups, and two types of adsorbed H_2O correspond to different ^{17}O peaks marked by different colors. (c) 1D ^{17}O MAS NMR spectra of ^{17}O -enriched bare TiO_2 , acquired at magnetic fields of 18.7 and 11.7 T. (d–e) 2D ^{17}O 3Q MAS NMR spectra of dehydrated ^{17}O -enriched TiO_2 samples with 1.3 (d) and 3.1 mmol g^{-1} (e) $H_2^{17}O$ loading, acquired at a magnetic field of 11.7 T. Asterisks denote spinning sidebands.

observable in the 2D 3Q MAS spectrum. When the $H_2^{17}O$ loading increased to 1.3 mmol g^{-1} and then to 3.1 mmol g^{-1} , up to five signals were identified, representing five types of O_{2C} sites (O_{II} , O_{III} , O_{IV} , O_V , and O_{VI}) (Fig. 1d and e). The appearance of new O_{2C} sites at the expense of O_I sites demonstrates that a fraction of two-coordinated surface oxygen sites can interact with water molecules, leading to changes in their coordination environments.

The NMR parameters of these O_{2C} sites (O_I – O_{VI}) obtained from 1D and 2D ^{17}O 3Q MAS NMR spectra (Table S1†) were used to deconvolute the 1D ^{17}O MAS NMR signals acquired at 11.7 T and 18.7 T (Fig. 1b and S8†). The different oxygen species (O_I – O_{VI}) obtained upon water loading indicate different interplays between the O_{2C} sites and water. Notably, the ^{17}O MAS NMR spectrum of bare TiO_2 does not exhibit any signals of adsorbed H_2O or surface OH groups (usually at -200 to 200 ppm) (Fig. 1b). At a water loading of 0.3 mmol g^{-1} , besides the change in O_{2C} sites, the adsorbed H_2O at -50 – 10 ppm and two new overlapped species of surface hydroxyls at around 150 ppm emerge (Fig. 1b), which can be well resolved by the following 2D $^1H\{^{17}O\}$ J-HMQC NMR experiments. The appearance of hydroxyls suggests that water splitting occurs, which is also confirmed by 2H MAS NMR (see the following). These results demonstrate that: (1) water can interact with the surface O_{2C} site, resulting in a change in its chemical environment, although the type and strength of the interaction cannot be

determined at the present time; and (2), ^{17}O MAS NMR experiments confirm the formation of hydroxyls arising from the dissociation of water on the TiO_2 surface.

Detailed interaction of surface oxygen/hydroxyl sites with interfacial H_2O

To better understand the structure of the interfacial scenario during water adsorption, a series of 2D $^1H\{^{17}O\}$ J-HMQC NMR experiments were conducted. These experiments allowed for the identification of 1H – ^{17}O correlation/connectivity through chemical bonds and strong hydrogen bonds. There are three types of 1H NMR signals at 1.7, 5.4, and 7.0 ppm, which can be assigned to the proton of terminal hydroxyl, adsorbed H_2O , and bridging hydroxyl, respectively.^{13,14} At $H_2^{17}O$ loadings of 0.5, 1.3 and 3.1 mmol g^{-1} , the result showed that O_{2C} sites were strongly correlated with adsorbed H_2O (5.4 ppm, Fig. S9†), indicating that the surface coordination-unsaturated O_{2C} sites were responsible for the interaction with water. Interestingly, no correlation was observed between the O_{2C} sites and terminal/bridging hydroxyls, indicating that the hydrogen in surface hydroxyls is not connected to the adjacent O_{2C} site *via* hydrogen-bonds.

The spatial relationship between the adsorbed water and the two surface hydroxyls was also investigated. Fig. 2a and b display the 1H – ^{17}O correlations between adsorbed H_2O and



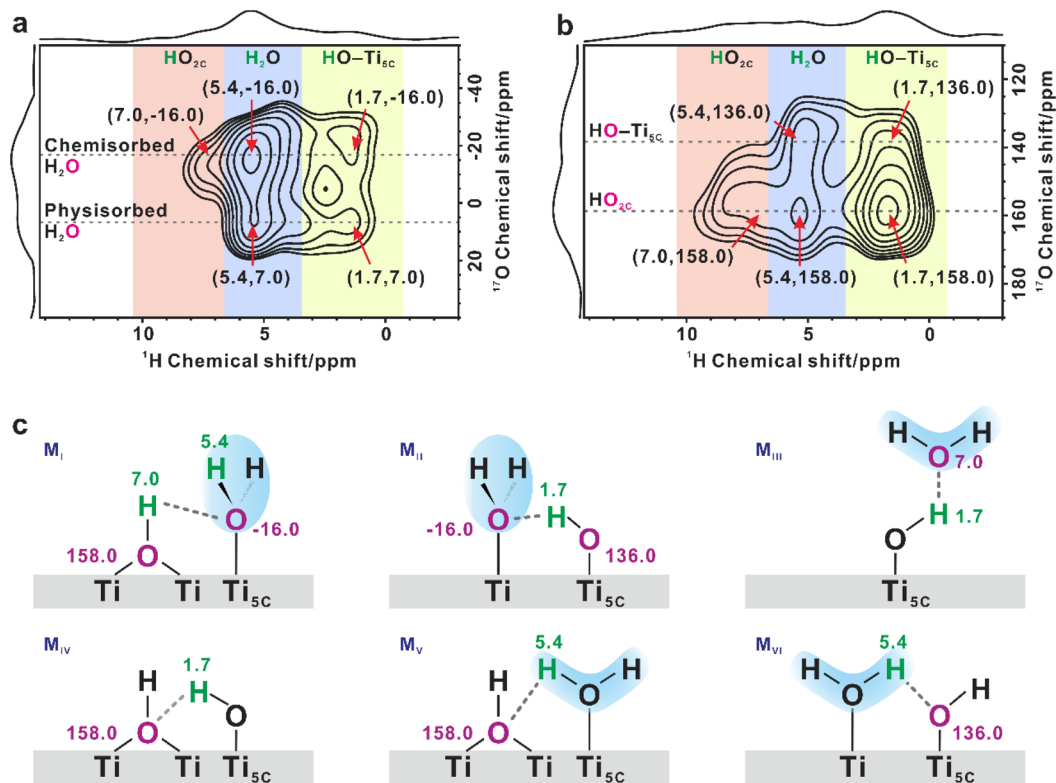


Fig. 2 Detailed structure of interfacial H_2O and OH groups on TiO_2 . (a and b) 2D ^1H (^{17}O) J-HMQC NMR spectra of the dehydrated ^{17}O -enriched TiO_2 sample with $0.5 \text{ mmol g}^{-1} \text{H}_2^{17}\text{O}$ loading in different ^{17}O chemical shift ranges. (c) The schematic illustration of the different structures (M_{I} – M_{VI}) of surface hydroxyls and adsorbed H_2O molecules over the surface of TiO_2 , with the ^1H and ^{17}O chemical shift values marked. Water molecule is shadowed in blue.

surface OH groups on TiO_2 with a $0.5 \text{ mmol g}^{-1} \text{H}_2^{17}\text{O}$ loading in different ^{17}O chemical shift ranges. As shown in Fig. 2a, two cross peaks were visible at (5.4, -16) ppm and (5.4, 7.0) ppm in the correlation experiment, indicating the presence of two types of adsorbed H_2O on the TiO_2 surface. These were ascribed to chemisorbed and physisorbed H_2O , respectively, which was validated by variable-temperature ^2H static NMR experiments (Fig. S10†). In the 1D ^{17}O MAS NMR spectra (Fig. 1b), when the H_2O loading increases from 0.3 to 4.7 mmol g^{-1} , the ^{17}O signal of adsorbed H_2O gradually narrows and shifts from -16.0 to 7.0 ppm, suggesting that the H_2O molecule is preferentially adsorbed on the unsaturated $\text{Ti}_{5\text{C}}$ site to form chemisorbed H_2O ($\text{Ti}_{5\text{C}}\text{-OH}_2$, ^{17}O signal at -16 ppm), while excess H_2O molecules adsorb on the outer layer of chemisorbed H_2O and hydroxyls through hydrogen bonds to form physisorbed H_2O (^{17}O signal at 7.0 ppm).

Interestingly, the ^1H signal (7.0 ppm) of bridging hydroxyl ($\text{HO}_{2\text{C}}$) only correlates with the ^{17}O signal of chemisorbed H_2O (-16.0 ppm); with the most possible structure illustrated in Fig. 2c M_{I} , while the ^1H signal (1.7 ppm) of the terminal hydroxyl ($\text{Ti}_{5\text{C}}\text{-OH}$) correlates with the ^{17}O signals of both chemisorbed (Fig. 2c M_{II}) and physisorbed H_2O (7.0 ppm, Fig. 2c M_{III}). At the same time, as shown in Fig. 2b, there are two types of oxygen of hydroxyls present at 136 and 158 ppm, respectively. The ^1H (7.0 ppm) signal of $\text{HO}_{2\text{C}}$ is only correlated with the ^{17}O signal at 158 ppm. As such, we assigned the cross

peak at (7.0, 158) ppm to the ^1H - ^{17}O correlation from $\text{HO}_{2\text{C}}$, and ascribed the cross peak at (1.7, 136) ppm to the $\text{Ti}_{5\text{C}}\text{-OH}$ correlation. The cross peak at (1.7, 158) ppm represents the correlation between them (Fig. 2c M_{IV}). It is worth noting that the ^1H signal of adsorbed H_2O (5.4 ppm) correlates with the ^{17}O signals of both bridging OH (158 ppm, Fig. 2c M_{V}) and terminal OH groups (136 ppm, Fig. 2c M_{VI}), leading to two cross peaks at (5.4, 158) and (5.4, 136) ppm. As the H_2O loading increases to 1.3 mmol g^{-1} , the cross peaks become more prominent, but the interplay remains the same (Fig. S11†).

These results indicate that water splitting is easy to happen under ambient conditions over the practical TiO_2 sample under conditions close to the working catalytic conditions, and more importantly, the interplay mode between the physisorbed or chemisorbed H_2O and the different types of hydroxyls is very complicated (Fig. 2c M_{I} to M_{VI}), but it could be well resolved by NMR methods. However, questions remain to answer are, how the O-H bond of water ruptured over the TiO_2 surface and whether the vacancy gets involved.

Quantitative evolution of surface oxygen/hydroxyl sites at the water/ TiO_2 interface during the hydration process

To answer the questions, quantitative information about different sites and species during water adsorption was estimated from 1D ^{17}O MAS NMR spectra (Fig. 3a). As shown in Fig. 3a, the only surface $\text{O}_{2\text{C}}$ site present on the bare TiO_2



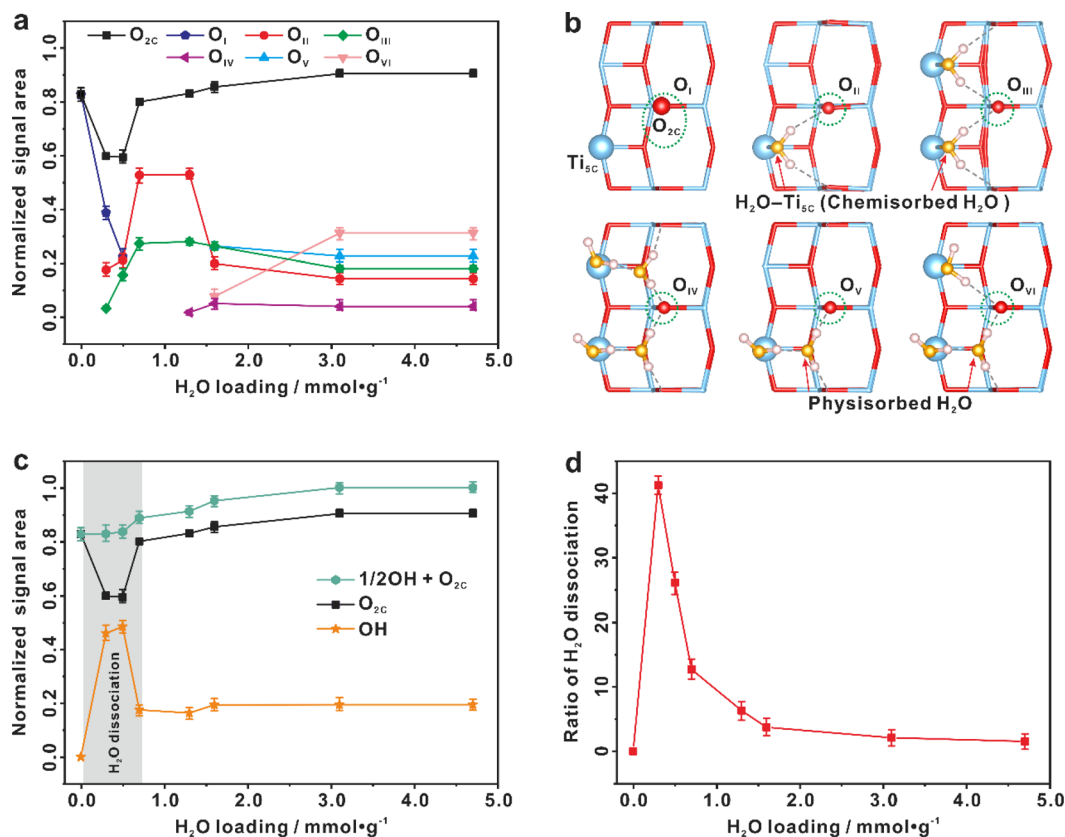


Fig. 3 Spontaneous dissociation of interfacial H₂O on the (101) facet of TiO₂ (100 mg) at room temperature. (a) Quantitative evolution of various surface two-coordinated oxygen sites (O_{2c}, including O_I–O_{VI}) with the increase of H₂O loading. (b) The possible configurations of six O_{2c} sites (O_I, O_{II}, O_{III}, O_{IV}, O_V, and O_{VI}) on the (101) facet of TiO₂ optimized from theoretical calculations. (c) Quantitative evolution of surface O_{2c} sites and hydroxyls with the increase of H₂O loading. (d) The proportion of H₂O dissociation with the increase of H₂O loading. Quantification of the O_{2c}/OH sites is conducted by fitting the main peaks and their spinning sidebands in the 1D ¹⁷O MAS NMR spectra (Fig. 1b). Error bars in a, c, and d represent s.d. for each data point (three independent experiments), and points are the average values.

sample is O_I. When the H₂O loading is 0.3–0.5 mmol g⁻¹, two new O_{2c} sites (O_{II}, O_{III}) appear at the expense of the O_I site. When the H₂O loading grows up to 0.7 mmol g⁻¹, the O_{II} and O_{III} sites reach maximum, while the O_I site disappears completely. As shown in Fig. 1b, the chemisorbed H₂O (Ti_{5c}–OH₂) is predominant in the H₂O loading range of 0–0.7 mmol g⁻¹. Therefore, the O_{II} and O_{III} structures should originate from the O_I site interacting with chemisorbed H₂O. With further increasing the H₂O loading to 1.3 and then to 1.6 mmol g⁻¹, the adsorbed H₂O exists mainly in the form of physisorbed H₂O (those without direct bonding with Ti sites), and meanwhile new O_{2c} sites (O_{IV}, O_V, O_{VI}) appear (Fig. 3a). In addition, the amount of O_{II} and O_{III} sites remains almost unchanged, implying that the physisorbed H₂O molecules are mainly adsorbed on the outer-layer of chemisorbed H₂O and OH groups rather than the surface O_{2c} site. When the H₂O loading is increased to 3.1 mmol g⁻¹, the O_{VI} site increases remarkably at the expense of O_{II}, O_{III}, and O_V sites, indicating the further evolution of surface O_{2c} sites interacting with the additional physisorbed H₂O. The relative content of the O_I–O_{VI} sites eventually remains unchanged even when the H₂O loading is further increased to 4.7 mmol g⁻¹. With the above information,

we constructed six O_{2c} sites with possible H₂O adsorption patterns (Fig. 3b), which are derived from a series of calculated structures with different H₂O adsorption configurations on (2 × 2) surface slabs (Fig. S12–S24[†]). Obviously, the calculated ¹⁷O NMR chemical shifts of these O_{2c} sites just correspond to experimental observation (Fig. S25[†]).

The sum of O_{2c} (O_{2c} = O_I + O_{II} + O_{III} + O_{IV} + O_V + O_{VI}) sites shows quantitative information about the surface O_{2c} sites (Fig. 3a and c). It is relatively constant except at the water loading of 0.3–0.5 mmol g⁻¹, where the total content of surface O_{2c} sites is decreased by ca. 20% (see the grey region highlighted in Fig. 3c). Very interestingly, this is just the time for the appearance of OH groups whose content is increased by ca. 40% (Fig. 3c). This, together with the above results (Fig. 2), shows that the chemisorbed H₂O molecule on the Ti_{5c} site (H₂O–Ti_{5c}) is apt to dissociate into a terminal OH group (Ti_{5c}–OH) and a proton (H⁺), and the latter protonates an adjacent surface O_{2c} site to form a bridging OH group (HO_{2c}), which “consumes” an adjacent O_{2c} site (see below Fig. 4). The proportion of water dissociation relative to total water loaded was also calculated, as depicted in Fig. 3d. Intriguingly, the highest proportion of H₂O dissociation, at 41.2%, was found at a water loading of 0.3 mmol





Fig. 4 Schematic diagram of H₂O dissociation and regeneration on the TiO₂ surface.

g⁻¹. With increasing the H₂O loading from 0.5 to 4.7 mmol g⁻¹, the content of surface O_{2C} sites gradually recovered and that of the hydroxyls decreased (Fig. 3c). The results point to the reaction of HO_{2C} groups with nearby Ti_{5C}-OH groups, leading to the regeneration of H₂O-Ti_{5C} and the recovery of surface O_{2C} sites. The schematic diagram of H₂O dissociation and regeneration on the TiO₂ surface is illustrated in Fig. 4.

The dissociation process of interfacial H₂O could be also confirmed by 1D ²H MAS NMR experiments on the TiO₂ samples (Fig. 5 and S26†). The dehydrated ²H-enriched TiO₂ was prepared by exchanging TiO₂ with 4.7 mmol g⁻¹ of ²H₂O at room temperature for 2 h, and then the ²H-enriched sample was dehydrated at 160 °C and then loaded with different amounts (0.3–4.7 mmol g⁻¹) of ²H₂O at room temperature. Since the proton of the bridging OH group is readily exchanged with ²H of D₂O, only the ²H signal of the deuterated bridging OH group (DO_{2C}) is observable at 7.4 ppm in the 1D spectrum of dehydrated TiO₂ (Fig. 5a). When 0.3 mmol g⁻¹ D₂O is adsorbed on the deuterated TiO₂, in addition to the increase of the deuterated bridging OH group, a new signal at 1.6 ppm due to the deuterated terminal OH group (Ti_{5C}-OD) appears, which originates from the dissociation of D₂O (Fig. 5a). The broad signal at 4.4 ppm corresponds to adsorbed D₂O. With the increase of D₂O loading, there is a similar evolution trend for the DO_{2C} and Ti_{5C}-OD groups, especially their signal increment is roughly equal (Fig. 5b), consistent with the theoretical content ratio (1 : 1) of the two types of deuterated hydroxyls originating from the D₂O dissociation. As shown in Fig. 5b, the content of DO_{2C} and Ti_{5C}-OD groups on the TiO₂ surface reaches maximum at a 0.5 mmol g⁻¹ H₂O loading, in line with the result of 1D ¹⁷O MAS NMR analysis (Fig. 3c).

Theoretical insight into the adsorption and dissociation of interfacial H₂O

Based on our NMR results, a series of structures with different H₂O adsorption configurations on (2 × 2) surface slabs are optimized (Fig. S12–S24†) by density functional theory (DFT) calculations. From the adsorption energy points of view, it can be found that when the same amount of H₂O is adsorbed onto the TiO₂ (101) (2 × 2) surface slabs, the more the chemisorbed H₂O (Ti_{5C}-OH₂), the greater the adsorption energy of H₂O will be released (Table S2†), indicating that H₂O is preferentially chemisorbed on the Ti_{5C} site, forming Ti_{5C}-OH₂, and then excess H₂O is physisorbed on the Ti_{5C}-OH₂ site through the hydrogen bond, consistent with our NMR experimental results. Thus, with the increase of H₂O loading, the constructed 1H₂O/1Ti_{5C}, 2H₂O/2Ti_{5C}, 3H₂O/3Ti_{5C}, 4H₂O/4Ti_{5C}, 5H₂O/4Ti_{5C}, 6H₂O/4Ti_{5C}, and 8H₂O/4Ti_{5C} configurations are energy optimal and appear gradually on the TiO₂ (101) surface with the surface O_{2C} sites consisting of the O_I-O_{VI} sites (Fig. 6a).

Our DFT calculations revealed that water dissociation is a coverage-dependent process. Increasing the H₂O loading on the Ti_{5C} site of (2 × 2) surface slabs from 1H₂O/1Ti_{5C} to 4H₂O/4Ti_{5C}, the H-O-H bond angle of chemisorbed H₂O is gradually twisted (Fig. 6b), leading to a decline of the dissociation energy of chemisorbed H₂O (Fig. 6c). At the optimal water coverage of 4H₂O per TiO₂ (101) (2 × 2) surface slab (4H₂O/4Ti_{5C}), water splitting is enhanced, with the dissociation energy dropping to as low as -0.03 eV. This suggests that H₂O dissociation is both exothermic and spontaneous, aligning with our experimental findings. Obviously, the more chemisorbed H₂O on the localized (101) facet of TiO₂, the more favorable to the dissociation of H₂O to form OH. With the further increase of the H₂O loading on the Ti_{5C} site of (2 × 2) surface slabs (5H₂O/4Ti_{5C}, 6H₂O/4Ti_{5C}, and 8H₂O/4Ti_{5C}), the presence of physisorbed H₂O causes a recovery in the average bond angle of H₂O (Fig. 6b) and an increase in dissociation energy (Fig. 6c), implying that physisorbed H₂O impedes the dissociation of chemisorbed H₂O.

To further address the importance of the interplay between OH and H₂O, we also computed the optimized configurations of

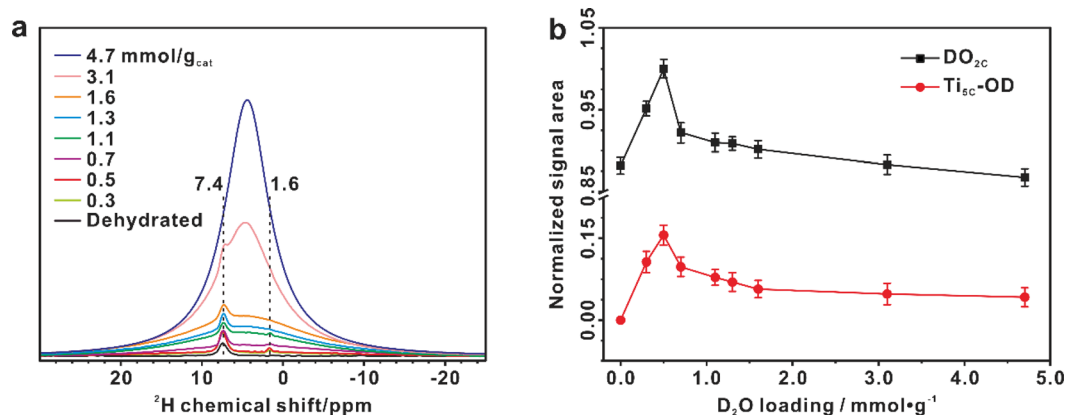


Fig. 5 Dissociation of interfacial H₂O validated by 1D ²H MAS NMR spectra. (a) ²H MAS NMR spectra of dehydrated ²H-enriched TiO₂ samples with ²H₂O loading from 0 to 4.7 mmol g⁻¹. (b) Quantitative evolution of the deuterated bridging OH (DO_{2C}, at 7.4 ppm) and terminal OH (Ti_{5C}-OD, at 1.6 ppm) groups with the increase of H₂O loading, derived from the simulation of the 1D ²H MAS NMR spectra (Fig. S26†).



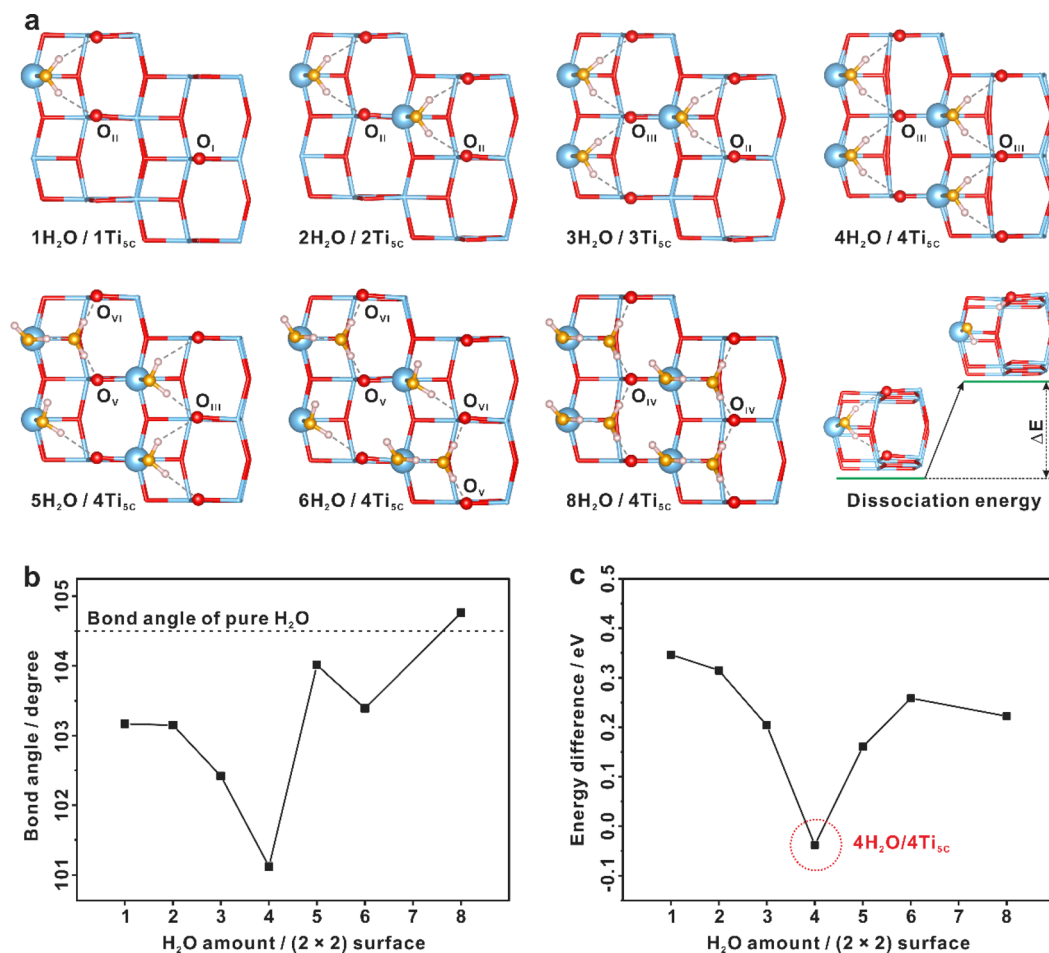


Fig. 6 Dissociation of interfacial H₂O on the TiO₂ surface revealed by DFT calculations. (a) Calculated structures of the TiO₂ (101) (2 × 2) surface slabs with different H₂O adsorption configurations. Titanium and oxygen atoms of TiO₂ are plotted in blue (Ti) and red (O), oxygen atoms originating from the adsorbed H₂O are plotted in yellow (H₂O), and hydrogen atoms are plotted in the pink (H). (b) The average bond angle of interfacial H₂O on the (2 × 2) surface slabs with different H₂O adsorption configurations, calculated from Table S3.† (c) Dissociation energy of interfacial H₂O in the optimized structures of different H₂O adsorption configurations on (2 × 2) TiO₂ (101) surface slabs.

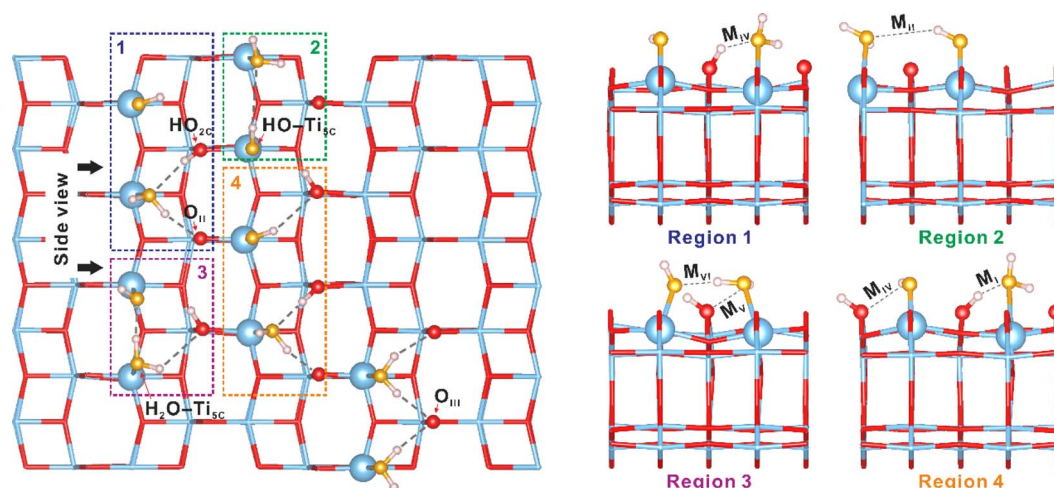


Fig. 7 The role of the OH–H₂O interactions in the dissociation of interfacial H₂O revealed by DFT calculations. The interaction modes of the hydroxyls with chemisorbed H₂O on the (101) facet of TiO₂ at a 40% coverage of water by using a large (5 × 5 × 1) supercell slab with 300 atoms (100 Ti atoms and 200 O atoms), which highlights the optimized atomic structures (M_I–M_{IV}) of hydroxyls and adsorbed H₂O molecules on the surface of TiO₂ shown in Fig. 2c. Regions 1–4 show side views of those structures (M_I–M_{IV}) in the 1–4 regions. Titanium and oxygen atoms of TiO₂ are plotted in blue (Ti) and red (O), oxygen atoms originating from the adsorbed H₂O are plotted in yellow (H₂O), and hydrogen atoms are plotted in pink (H).



the H₂O dissociation state on the (101) facet of TiO₂ at 40% coverage by using a large (5 × 5 × 1) supercell slab with 300 atoms (100 Ti atoms and 200 O atoms), as presented in Fig. 7 and S27.† It's evident that the OH groups originating from water dissociation have strong interactions with the neighboring chemisorbed H₂O in the M_I–M_{VI} conformations, corroborating with our 2D ¹H{¹⁷O} J-HMQC NMR findings (Fig. 2). This robust interaction stabilizes H₂O dissociation, serving as the driving force for the event. Therefore, at water loadings ranging from 0.3 to 0.5 mmol g⁻¹ (approximately 28–46% coverage), massive H₂O dissociation takes place. At elevated water loadings, physisorbed H₂O molecules appear, potentially disrupting the interaction between bridging OH groups (Ti–HO_{2C}–Ti) and chemisorbed H₂O. This promotes the reaction of bridging OH groups with nearby terminal OH groups, leading to the reformation of molecular H₂O (Fig. S28†). All these findings underscore the crucial role of the interplay between OH–H₂O and H₂O–H₂O interactions in determining the behavior of interfacial H₂O on the TiO₂ surface.

Conclusions

In summary, the atomic-level structures and quantitative evolution of surface O/OH sites along with H₂O loading are identified on the TiO₂ (101) surface by solid-state NMR spectroscopy coupled with theoretical calculations. Two types of H₂O (chemisorbed H₂O, *i.e.* Ti_{5C}–OH₂ and physisorbed H₂O) are present on the H₂O/TiO₂ interface, and detailed interactions between the interfacial H₂O and surface O_{2C}/OH sites are ascertained. We need to mention that the results of the quantitative ¹⁷O NMR and ²H NMR tests have confirmed that, under ambient conditions, a maximum of 41.2% of the total adsorbed H₂O on TiO₂ spontaneously dissociates at a water loading of 0.3 mmol g⁻¹. This means that approximately 0.124 mmol g⁻¹ of water dissociates over TiO₂ under these conditions. Our NMR findings and DFT calculations, together with ESR results, confirm that the responsible factor for the observed water rupture at room temperature over the TiO₂ (101) surface is not defects such as oxygen vacancies and impurities, but the joint effect of the coordination-unsaturated Ti_{5C} site and adjacent O_{2C} site, as well as the delicate interplay between water–surface and water–water interactions.

Data availability

The data that support the findings of this study are available within the article and the ESI.†

Author contributions

F. D., N. F., and D. M. conceived the project. N. F. designed the studies. L. Y. synthesized the TiO₂ photocatalysts. N. F., L. Y., J. X., M. W. performed NMR experiments. M. W., Y. J., D. M., L. Y., N. F. and F. D. analyzed all the experimental data. M. H. performed theoretical calculations. N. F., D. M. and F. D. wrote the manuscript. All authors interpreted the data and contributed to the preparation of the manuscript.

Conflicts of interest

The authors declare no competing interests.

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Notes and references

- 1 A. Fujishima and K. Honda, Electrochemical Photolysis of Water at a Semiconductor Electrode, *Nature*, 1972, **238**, 37–38.
- 2 S. U. M. Khan, M. Al-Shahry and W. B. Ingler, Efficient Photochemical Water Splitting by a Chemically Modified n-TiO₂, *Science*, 2002, **297**, 2243–2245.
- 3 A. Kudo and Y. Miseki, Heterogeneous photocatalyst materials for water splitting, *Chem. Soc. Rev.*, 2009, **38**, 253–278.
- 4 Z. Zou, J. Ye, K. Sayama and H. Arakawa, Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst, *Nature*, 2001, **414**, 625–627.
- 5 R. D. Cortright, R. R. Davda and J. A. Dumesic, Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water, *Nature*, 2002, **418**, 964–967.
- 6 Q. Fu, H. Saltsburg and M. Flytzani-Stephanopoulos, Active Nonmetallic Au and Pt Species on Ceria-Based Water-Gas Shift Catalysts, *Science*, 2003, **301**, 935–938.
- 7 T. Takata, J. Jiang, Y. Sakata, M. Nakabayashi, N. Shibata, V. Nandal, K. Seki, T. Hisatomi and K. Domen, Photocatalytic water splitting with a quantum efficiency of almost unity, *Nature*, 2020, **581**, 411–414.
- 8 Z. Liu, E. Huang, I. Orozco, W. Liao, R. M. Palomino, N. Rui, T. Duchon, S. Nemšák, D. C. Grinter, M. Mahapatra, P. Liu, J. A. Rodriguez and S. D. Senanayake, Water-promoted interfacial pathways in methane oxidation to methanol on a CeO₂-Cu₂O catalyst, *Science*, 2020, **368**, 513–517.
- 9 J. Saavedra, H. A. Doan, C. J. Pursell, L. C. Grabow and B. D. Chandler, The critical role of water at the gold-titania interface in catalytic CO oxidation, *Science*, 2014, **345**, 1599–1602.
- 10 L. R. Merte, G. Peng, R. Bechstein, F. Rieboldt, C. A. Farberow, L. C. Grabow, W. Kudernatsch, S. Wendt, E. Lægsgaard, M. Mavrikakis and F. Besenbacher, Water-Mediated Proton Hopping on an Iron Oxide Surface, *Science*, 2012, **336**, 889–893.
- 11 H. Hussain, G. Tocci, T. Woolcot, X. Torrelles, C. L. Pang, D. S. Humphrey, C. M. Yim, D. C. Grinter, G. Cabailh,



- O. Bikondoa, R. Lindsay, J. Zegenhagen, A. Michaelides and G. Thornton, Structure of a model TiO₂ photocatalytic interface, *Nat. Mater.*, 2017, **16**, 461–466.
- 12 O. Björneholm, M. H. Hansen, A. Hodgson, L.-M. Liu, D. T. Limmer, A. Michaelides, P. Pedevilla, J. Rossmeisl, H. Shen, G. Tocci, E. Tyrode, M.-M. Walz, J. Werner and H. Bluhm, Water at Interfaces, *Chem. Rev.*, 2016, **116**, 7698–7726.
- 13 F. Liu, N. Feng, Q. Wang, J. Xu, G. Qi, C. Wang and F. Deng, Transfer Channel of Photoinduced Holes on a TiO₂ Surface As Revealed by Solid-State Nuclear Magnetic Resonance and Electron Spin Resonance Spectroscopy, *J. Am. Chem. Soc.*, 2017, **139**, 10020–10028.
- 14 L. Yang, N. Feng, Q. Wang, Y. Chu, J. Xu and F. Deng, Surface Water Loading on Titanium Dioxide Modulates Photocatalytic Water Splitting, *Cell Rep. Phys. Sci.*, 2020, **1**, 100013.
- 15 Y.-H. Wang, S. Zheng, W.-M. Yang, R.-Y. Zhou, Q.-F. He, P. Radjenovic, J.-C. Dong, S. Li, J. Zheng, Z.-L. Yang, G. Attard, F. Pan, Z.-Q. Tian and J.-F. Li, In situ Raman spectroscopy reveals the structure and dissociation of interfacial water, *Nature*, 2021, **600**, 81–85.
- 16 S. Nihonyanagi, S. Yamaguchi and T. Tahara, Ultrafast Dynamics at Water Interfaces Studied by Vibrational Sum Frequency Generation Spectroscopy, *Chem. Rev.*, 2017, **117**, 10665–10693.
- 17 I. V. Stiopkin, C. Weeraman, P. A. Pieniazek, F. Y. Shalhout, J. L. Skinner and A. V. Benderskii, Hydrogen bonding at the water surface revealed by isotopic dilution spectroscopy, *Nature*, 2011, **474**, 192–195.
- 18 Y. Wang and C. Wöll, IR spectroscopic investigations of chemical and photochemical reactions on metal oxides: bridging the materials gap, *Chem. Soc. Rev.*, 2017, **46**, 1875–1932.
- 19 J. G. Davis, K. P. Gierszal, P. Wang and D. Ben-Amotz, Water structural transformation at molecular hydrophobic interfaces, *Nature*, 2012, **491**, 582–585.
- 20 M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori and N. S. Lewis, Solar Water Splitting Cells, *Chem. Rev.*, 2010, **110**, 6446–6473.
- 21 M. Grätzel, Photoelectrochemical cells, *Nature*, 2001, **414**, 338–344.
- 22 A. L. Linsebigler, G. Lu and J. T. Yates Jr, Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results, *Chem. Rev.*, 1995, **95**, 735–758.
- 23 Y. He, A. Tilocca, O. Dulub, A. Selloni and U. Diebold, Local ordering and electronic signatures of submonolayer water on anatase TiO₂ (101), *Nat. Mater.*, 2009, **8**, 585–589.
- 24 J. Matthiesen, J. O. Hansen, S. Wendt, E. Lira, R. Schaub, E. Laegsgaard, F. Besenbacher and B. Hammer, Formation and Diffusion of Water Dimers on Rutile TiO₂ (110), *Phys. Rev. Lett.*, 2009, **102**, 226101.
- 25 J. Carrasco, A. Michaelides, M. Forster, S. Haq, R. Raval and A. Hodgson, A one-dimensional ice structure built from pentagons, *Nat. Mater.*, 2009, **8**, 427–431.
- 26 K. Onda, B. Li, J. Zhao, K. D. Jordan, J. Yang and H. Petek, Wet Electrons at the H₂O/TiO₂ (110) Surface, *Science*, 2005, **308**, 1154–1158.
- 27 R. Mu, Z.-j. Zhao, Z. Dohnálek and J. Gong, Structural motifs of water on metal oxide surfaces, *Chem. Soc. Rev.*, 2017, **46**, 1785–1806.
- 28 Y. Du, N. A. Deskins, Z. Zhang, Z. Dohnálek, M. Dupuis and I. Lyubinetsky, Two Pathways for Water Interaction with Oxygen Adatoms on TiO₂ (110), *Phys. Rev. Lett.*, 2009, **102**, 096102.
- 29 H. H. Kristoffersen, J. Ø. Hansen, U. Martinez, Y. Y. Wei, J. Matthiesen, R. Streber, R. Bechstein, E. Lægsgaard, F. Besenbacher, B. Hammer and S. Wendt, Role of Steps in the Dissociative Adsorption of Water on Rutile TiO₂ (110), *Phys. Rev. Lett.*, 2013, **110**, 146101.
- 30 C. Kamal, N. Stenberg, L. E. Walle, D. Ragazzon, A. Borg, P. Uvdal, N. V. Skorodumova, M. Odelius and A. Sandell, Core-Level Binding Energy Reveals Hydrogen Bonding Configurations of Water Adsorbed on TiO₂ (110) Surface, *Phys. Rev. Lett.*, 2021, **126**, 016102.
- 31 S. Selcuk and A. Selloni, Facet-dependent trapping and dynamics of excess electrons at anatase TiO₂ surfaces and aqueous interfaces, *Nat. Mater.*, 2016, **15**, 1107–1112.
- 32 W. Yuan, B. Zhu, X.-Y. Li, T. W. Hansen, Y. Ou, K. Fang, H. Yang, Z. Zhang, J. B. Wagner, Y. Gao and Y. Wang, Visualizing H₂O molecules reacting at TiO₂ active sites with transmission electron microscopy, *Science*, 2020, **367**, 428–430.
- 33 M. A. Henderson, The interaction of water with solid surfaces: fundamental aspects revisited, *Surf. Sci. Rep.*, 2002, **46**, 1–308.
- 34 U. Diebold, The surface science of titanium dioxide, *Surf. Sci. Rep.*, 2003, **48**, 53–229.
- 35 C. L. Pang, R. Lindsay and G. Thornton, Structure of Clean and Adsorbate-Covered Single-Crystal Rutile TiO₂ Surfaces, *Chem. Rev.*, 2013, **113**, 3887–3948.
- 36 Z. Dohnálek, I. Lyubinetsky and R. Rousseau, Thermally-driven processes on rutile TiO₂ (110)-(1 × 1): a direct view at the atomic scale, *Prog. Surf. Sci.*, 2010, **85**, 161–205.
- 37 A. Vittadini, A. Selloni, F. P. Rotzinger and M. Grätzel, Structure and Energetics of Water Adsorbed at TiO₂ Anatase (101) and (001) Surfaces, *Phys. Rev. Lett.*, 1998, **81**, 2954–2957.
- 38 A. Tilocca and A. Selloni, Vertical and Lateral Order in Adsorbed Water Layers on Anatase TiO₂ (101), *Langmuir*, 2004, **20**, 8379–8384.
- 39 M. Sumita, C. Hu and Y. Tateyama, Interface Water on TiO₂ Anatase (101) and (001) Surfaces: First-Principles Study with TiO₂ Slabs Dipped in Bulk Water, *J. Phys. Chem. C*, 2010, **114**, 18529–18537.
- 40 D. Selli, G. Fazio, G. Seifert and C. Di Valentin, Water Multilayers on TiO₂ (101) Anatase Surface: Assessment of a DFTB-Based Method, *J. Chem. Theory Comput.*, 2017, **13**, 3862–3873.
- 41 G. S. Herman, Z. Dohnálek, N. Ruzycki and U. Diebold, Experimental Investigation of the Interaction of Water and Methanol with Anatase-TiO₂ (101), *J. Phys. Chem. B*, 2003, **107**, 2788–2795.
- 42 L. E. Walle, A. Borg, E. M. J. Johansson, S. Plogmaker, H. Rensmo, P. Uvdal and A. Sandell, Mixed Dissociative



- and Molecular Water Adsorption on Anatase TiO₂ (101), *J. Phys. Chem. C*, 2011, **115**, 9545–9550.
- 43 C. E. Patrick and F. Giustino, Structure of a Water Monolayer on the Anatase TiO₂ (101) Surface, *Phys. Rev. A*, 2014, **2**, 014001.
- 44 M. J. Jackman, A. G. Thomas and C. Muryn, Photoelectron Spectroscopy Study of Stoichiometric and Reduced Anatase TiO₂ (101) Surfaces: The Effect of Subsurface Defects on Water Adsorption at Near-Ambient Pressures, *J. Phys. Chem. C*, 2015, **119**, 13682–13690.
- 45 C. Dette, M. A. Pérez-Osorio, S. Mangel, F. Giustino, S. J. Jung and K. Kern, Single-Molecule Vibrational Spectroscopy of H₂O on Anatase TiO₂ (101), *J. Phys. Chem. C*, 2017, **121**, 1182–1187.
- 46 I. M. Nadeem, J. P. W. Treacy, S. Selcuk, X. Torrelles, H. Hussain, A. Wilson, D. C. Grinter, G. Cabailh, O. Bikondoa, C. Nicklin, A. Selloni, J. Zegenhagen, R. Lindsay and G. Thornton, Water Dissociates at the Aqueous Interface with Reduced Anatase TiO₂ (101), *J. Phys. Chem. Lett.*, 2018, **9**, 3131–3136.
- 47 C. Dette, M. A. Pérez-Osorio, S. Mangel, F. Giustino, S. J. Jung and K. Kern, Atomic Structure of Water Monolayer on Anatase TiO₂ (101) Surface, *J. Phys. Chem. C*, 2018, **122**, 11954–11960.
- 48 M. F. Calegari Andrade, H.-Y. Ko, L. Zhang, R. Cara and A. Selloni, Free energy of proton transfer at the water–TiO₂ interface from *ab initio* deep potential molecular dynamics, *Chem. Sci.*, 2020, **11**, 2335–2341.
- 49 F. Fasulo, G. M. Piccini, A. B. Muñoz-García, M. Pavone and M. Parrinello, Dynamics of Water Dissociative Adsorption on TiO₂ Anatase (101) at Monolayer Coverage and Below, *J. Phys. Chem. C*, 2022, **126**, 15752–15758.
- 50 U. Diebold, Perspective: A controversial benchmark system for water-oxide interfaces: H₂O/TiO₂ (110), *J. Chem. Phys.*, 2017, **147**, 040901.
- 51 Q. Guo, Z. Ma, C. Zhou, Z. Ren and X. Yang, Single Molecule Photocatalysis on TiO₂ Surfaces, *Chem. Rev.*, 2019, **119**, 11020–11041.
- 52 J. Chen, M. A. Hope, Z. Lin, M. Wang, T. Liu, D. M. Halat, Y. Wen, T. Chen, X. Ke, P. C. M. M. Magusin, W. Ding, X. Xia, X.-P. Wu, X.-Q. Gong, C. P. Grey and L. Peng, Interactions of Oxide Surfaces with Water Revealed with Solid-State NMR Spectroscopy, *J. Am. Chem. Soc.*, 2020, **142**, 11173–11182.
- 53 S. Schramm and E. Oldfield, High-resolution oxygen-17 NMR of solids, *J. Am. Chem. Soc.*, 1984, **106**, 2502–2506.
- 54 S. Yang, K. D. Park and E. Oldfield, Oxygen-17 labeling of oxides and zeolites, *J. Am. Chem. Soc.*, 1989, **111**, 7278–7279.
- 55 T. J. Bastow and S. N. Stuart, ¹⁷O NMR in simple oxides, *Chem. Phys.*, 1990, **143**, 459–467.
- 56 A. V. Chadwick, I. J. F. Poplett, D. T. S. Maitland and M. E. Smith, Oxygen speciation in nanophase MgO from solid-state ¹⁷O NMR, *Chem. Mater.*, 1998, **10**, 864–870.
- 57 N. Kim and C. P. Grey, Probing Oxygen Motion in Disordered Anionic Conductors with ¹⁷O and ⁵¹V MAS NMR Spectroscopy, *Science*, 2002, **297**, 1317–1320.
- 58 S. E. Ashbrook and M. E. Smith, Solid state ¹⁷O NMR—an introduction to the background principles and applications to inorganic materials, *Chem. Soc. Rev.*, 2006, **35**, 718–735.
- 59 N. Merle, J. Trebosc, A. Baudouin, I. D. Rosal, L. Maron, K. Szeto, M. Genelot, A. Mortreux, M. Taoufik, L. Delevoye and R. M. Gauvin, ¹⁷O NMR gives unprecedented insights into the structure of supported catalysts and their interaction with the silica carrier, *J. Am. Chem. Soc.*, 2012, **134**, 9263–9275.
- 60 G. P. M. Bignami, D. M. Dawson, V. R. Seymour, P. S. Wheatley, R. E. Morris and S. E. Ashbrook, Synthesis, isotopic enrichment, and solid-state NMR characterization of zeolites derived from the assembly, disassembly, organization, reassembly process, *J. Am. Chem. Soc.*, 2017, **139**, 5140–5148.
- 61 E. N. Basseby, P. J. Reeves, I. D. Seymour and C. P. Grey, ¹⁷O NMR Spectroscopy in Lithium-Ion Battery Cathode Materials: Challenges and Interpretation, *J. Am. Chem. Soc.*, 2022, **144**, 18714–18729.
- 62 F. Tielens, C. Gervais, G. Deroy, M. Jaber, L. Stievano, C. C. Diogo and J.-F. Lambert, Characterization of Phosphate Species on Hydrated Anatase TiO₂ Surfaces, *Langmuir*, 2016, **32**, 997–1008.
- 63 J. Chen, X.-P. Wu, M. A. Hope, Z. Lin, L. Zhu, Y. Wen, Y. Zhang, T. Qin, J. Wang, T. Liu, X. Xia, D. Wu, X.-Q. Gong, W. Tang, W. Ding, X. Liu, L. Chen, C. P. Grey and L. Peng, Surface differences of oxide nanocrystals determined by geometry and exogenously coordinated water molecules, *Chem. Sci.*, 2022, **13**, 11083.
- 64 M. Wang, X.-P. Wu, S. Zheng, L. Zhao, L. Li, L. Shen, Y. Gao, N. Xue, X. Guo, W. Huang, Z. Gan, F. Blanc, Z. Yu, X. Ke, W. Ding, X.-Q. Gong, C. P. Grey and L. Peng, Identification of Different Oxygen Species in Oxide Nanostructures with ¹⁷O Solid-State NMR Spectroscopy, *Sci. Adv.*, 2015, **1**, e1400133.
- 65 Y. Li, X.-P. Wu, N. Jiang, M. Lin, L. Shen, H. Sun, Y. Wang, M. Wang, X. Ke, Z. Yu, F. Gao, L. Dong, X. Guo, W. Hou, W. Ding, X.-Q. Gong, C. P. Grey and L. Peng, Distinguishing Faceted Oxide Nanocrystals with ¹⁷O Solid-State NMR Spectroscopy, *Nat. Commun.*, 2017, **8**, 581.
- 66 B. Song, Y. Li, X.-P. Wu, F. Wang, M. Lin, Y. Sun, A.-P. Jia, X. Ning, L. Jin, X. Ke, Z. Yu, G. Yang, W. Hou, W. Ding, X.-Q. Gong and L. Peng, Unveiling the Surface Structure of ZnO Nanorods and H₂ Activation Mechanisms with ¹⁷O NMR Spectroscopy, *J. Am. Chem. Soc.*, 2022, **144**, 23340–23351.
- 67 Q. Wang, W. Li, I. Hung, F. Mentink-Vigier, X. Wang, G. Qi, X. Wang, Z. Gan, J. Xu and F. Deng, Mapping the oxygen structure of γ-Al₂O₃ by high-field solid-state NMR spectroscopy, *Nat. Commun.*, 2020, **11**, 3620.
- 68 L. Liu, X. Gu, Z. Ji, W. Zou, C. Tang, F. Gao and L. Dong, Anion-Assisted Synthesis of TiO₂ Nanocrystals with Tunable Crystal Forms and Crystal Facets and Their Photocatalytic Redox Activities in Organic Reactions, *J. Phys. Chem. C*, 2013, **117**, 18578–18587.
- 69 A. Jia, Y. Zhang, T. Song, Z. Zhang, C. Tang, Y. Hu, W. Zheng, M. Luo, J. Lu and W. Huang, Crystal-plane effects of anatase TiO₂ on the selective hydrogenation of crotonaldehyde over Ir/TiO₂ catalysts, *J. Catal.*, 2021, **395**, 10–22.

