

Self-Assembled Water Monolayer on TiO₂ Anatase (101)

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ABSTRACT

The molecular structure and interactions of interfacial water, i.e. the first monolayers of water adsorbed on surfaces, are critical to determine the microscopic properties of solid-liquid interfaces. In particular, interfacial water on TiO_2 anatase (101) is of specific relevance to industrial, environmental and medical applications. However, owing to the complexity and challenges in sample preparation, direct observation has been limited to individual or short-range ordered water molecules adsorbed on anatase. In this article, we report the direct observation of an unprecedented long range ordered water monolayer on TiO_2 anatase (101). The adsorption structure and inter/intramolecular interactions of the water molecules have been investigated using scanning tunneling microscopy (STM) at 5 K in conjunction with density functional theory (DFT) calculations. The water monolayer commensurately adsorbs on the anatase (101) substrate; each oxygen atom of water forms a dative bond with one of its lone pair electrons to a surface Ti_{5c} atom. The remaining lone pair electron and the OH bonds are oriented in the surface plane resulting in hydrophobic properties. The here presented results are important to understand the complex wetting properties of the TiO_2 anatase surface.

INTRODUCTION

Titanium dioxide (TiO_2) is an inexpensive, nontoxic metal oxide with applications in a wide range of areas, such as photocatalysis, self-cleaning, and medical materials.¹⁻² Of the different mineral forms, anatase is the technologically most relevant one, since TiO_2 nanoparticles, which are mostly used thanks to their high surface to bulk ratio, coalesce into the anatase (101) termination.³ As most applications of TiO_2 involve an aqueous environment, fundamental understanding of the interfacial water layer is critical to rational design and improved devices.

The TiO_2 anatase (101) surface is composed of twofold coordinated oxygen (O_{2c}) and fivefold coordinated titanium (Ti_{5c}).⁴ When H_2O is adsorbed on the anatase surface molecularly,

the oxygen of the water molecule forms a dative bond to a surface Ti_{5c} atom.⁵⁻⁶ In dissociative adsorption, water initially adsorbs to a Ti_{5c} and subsequently donates one hydrogen atom to a neighboring surface O_{2c} to form a hydroxyl.⁷ For an isolated water molecule, the dissociation reaction is endothermic, which means that molecular adsorption is favored.⁷

However, the adsorption structure of water molecules at higher coverage is governed by several factors: hydrogen bonding between two neighboring water molecules, water molecule-surface O_{2c} hydrogen bonding, water molecule-surface Ti_{5c} dative bonding and steric hindrance between adsorbed molecules.⁸ Despite the apparent importance of the fundamental understanding of high-coverage water on TiO_2 anatase (101), previous works are limited.⁹⁻¹¹ Thus far, adsorption of water monolayers on the anatase (101) surface has been claimed to be both molecular⁹ and partially dissociated, which mainly depends on the sample preparation temperature.¹⁰ As water molecules can dissociate in the range of 120-400 K, the amount of surface hydroxyls changes depending on temperature.⁷

Here, we present a globally ordered self-assembled water monolayer on the TiO_2 anatase (101) surface, prepared by slow water exposure at 77 K over 24 hours. Based on our findings using STM in conjunction with DFT calculations, we propose this monolayer to only consist of molecular water. We discuss the properties and adsorption structure of the water monolayer also in relation to the wetting properties of the anatase (101) surface. Moreover, the adsorption structure of the partially dissociated water monolayer is also presented, as it is expected to form at higher temperature.

EXPERIMENTAL AND COMPUTATIONAL SECTION

The experiments were carried out in our homebuilt 5K STM using constant-current mode with a typical bias voltage of 1 V and a setpoint current of 0.05 to 1 nA. Electrochemically etched Pt-Ir tips bought from Agilent Technologies (N9801A) were used. The surface preparation of the

natural grown TiO_2 anatase crystal (SurfaceNet GmbH, Germany) can be found in the method section of our previous publications.¹²⁻¹³ The details about STM-inelastic tunneling spectroscopy (STM-IETS) are explained in ref ⁷.

Previous TPD experiments have shown that water on TiO_2 anatase (101) has three desorption peaks at 160, 190, and 250 K.⁹⁻¹⁰ To achieve water monolayer adsorption on the anatase (101) surface, the sample was cooled below the desorption temperatures ($T_s = 120$ K) and the preparation chamber was backfilled with water (7.5×10^{-10} mbar for 5 minutes). With this, we created short-range ordered water networks on the anatase surface (Supplementary Figure S1). However, lots of physisorbed water molecules and amorphous water clusters were adsorbed on the surface. Those water molecules are weakly bound to the surface and hence, influence tip stability and reduce the resolution of our STM images. To circumvent the formation of amorphous water clusters, we sought to further reduce the water flux. Owing to the technical limitations of our commercial needle valve, we pursued a different preparation procedure to obtain a single layer of water: First, we backfilled our cryogenic STM chamber (5 K) with water to trap water molecules on the chamber walls. Subsequently, the sample was introduced into the STM cryostat. The cryostat was slowly warmed up to liquid nitrogen temperature and stayed at 77 K over 24 hours. During this procedure, the trapped water molecules desorbed from the cryostat due to vibrations induced by boiling of the cooling liquids as well as thermal desorption and adsorbed on the sample. Afterwards, the system and sample were cooled down back to 5 K. Additional to monolayer adsorption discussed below, low amounts of small amorphous water clusters are still present (< 2 nm). However, these clusters are formed preferentially on step edges and do not interfere with the stability of our STM experiment.

Computational details. We study structural and electronic properties using density functional theory (DFT), as implemented in the Quantum Espresso package.¹⁴ We employ the GGA approximation of Perdew, Burke and Ernzerhof (PBE) to the exchange-correlation

functional.¹⁵ The core-valence interactions are taken into account by means of ultrasoft pseudopotentials.¹⁶ The wavefunctions and charge density are represented by means of plane-wave basis sets with energy cut-offs of 35 and 140 Ry, respectively. We use a 2x2 Monkhorst-Pack k -point grid to sample the first Brillouin zone of the surface unit cell. In order to correctly describe the energetics of the Ti 3d states, we included Hubbard-like corrections by means of the simplified rotational-invariant formulation of ref.¹⁷. All the calculations are performed using a Hubbard parameter U of 3.5 eV. This value is close to the Hubbard parameter derived from first-principles calculations using the linear-response theory.^{12, 18-19} The anatase TiO₂ (101) surface is modelled using a TiO₂ slab oriented along the [101] direction, containing four layers of TiO₂. The surface unit cell and atoms are relaxed until the largest force on the atoms is smaller than 0.04 eV/Å. The width of the vacuum region between periodic images along the direction perpendicular to the (101) surface is set to 10 Å. The optimized lattice parameters of the surface unit cell are 10.42 and 3.82 Å. Using this unit cell, 1x2 and 1x3 supercells are built to investigate the water monolayer, respectively.

To simulate the effect of the electric field induced by the STM tip on the H₂O molecules and hydroxyls (OH) forming the monolayer, we perform calculations in the presence of an applied electric field using a saw-like potential²⁰ and the modern theory of polarization.²¹⁻²² In all the cases the applied electric field is perpendicular to the (101) surface, and its magnitude was 1.6×10^{10} V/m for the monolayer. This value is reasonable since typical bias values (1-3 V) in STM experiments induce electric fields between 1.6×10^9 and 1.0×10^{10} V/m,²³⁻²⁴ and in our STM measurements we employ a bias voltage of 1 V. We calculate unoccupied-states STM images at constant current using the Tersoff-Hamann approximation,²⁵ by considering the unoccupied electronic states within 1.1 eV from the conduction band bottom of the TiO₂ substrate. In these calculations, the unoccupied electronic states are obtained by performing calculations in the presence of the electric field.

RESULTS AND DISCUSSION

High-resolution STM images (Figure 1) show a globally ordered self-assembled water monolayer adsorbed on TiO_2 anatase (101). The distances between oval-shaped protrusions are 3.8 and 5.5 Å along the [010] and the [11-1] crystallographic direction, respectively. These distances are equal to the distances of Ti-O pairs in the anatase (101) lattice. Hence, we conclude that one oval-shaped protrusion in the water monolayer sits atop one Ti-O pair. Although the monolayer also inhabits defects attributed to missing water molecules as indicated by white arrows in Figure 1b, it shows remarkable long-range order. It is interesting to note that water molecules adsorbed in the vicinity of the low-reactive [010] step edge¹² are mobile during the measurements causing blurred STM image as shown in Figure 1c.⁵ On the other hand, molecules adsorbed at the high-reactive [-111] step edges, which are decorated by oxygen vacancies,¹² are clearly imaged. Hence, we believe that the water molecules interact with the oxygen vacancies stabilizing their adsorption.

To identify the adsorption site the surface lattice in the surrounding of the molecule needs to be resolved. Using tip pulses or scanning at 3 V, we could desorb some water molecules from the monolayer creating clean substrate areas as shown in Figure 2 (overview in Supplementary Figure S3). Taking a closer look at the protrusions, we find three different species owing to their differences in size and shape; blue, black, and red circled protrusions in Figure 2a. The blue encircled protrusion is isolated and appears as a symmetric dumbbell shape protrusion. It has a height of 1.5 nm and a length of around 0.7 nm based on STM linescans (cf. Figures 2b and d). Thanks to the high resolution of the STM images, the surface lattice was overlaid to define the positions of the different protrusions. As shown in Figure 2c, the blue-circled protrusion was identified as a molecular water adsorbed on a surface Ti_{5c} atom in accordance to our previous publication.⁷

The black circle highlights a dimer, i.e. a pair of two connected dumbbell shaped protrusions, dimer, which are not incorporated into the self-assembled monolayer. The length of each protrusion is 0.5 nm along the [010] direction. The protrusions reveal a darker feature in the center and brighter features at the edges. A similar appearance can be seen for the intermediate structure (green circled in Figure 2a), which is connected to the monolayer on only one side. Hence, one part of the dumbbell shaped protrusion appears darker where it is connected to the monolayer and brighter at the other, unconnected side. Protrusions in the monolayer, which are fully incorporated with adjacent molecules, only show a single round shaped protrusions with a length of 0.3 nm (red circled in Figure 2a).

To gain insight into the adsorption structure of the water monolayer, we perform first-principles calculations. We consider two atomistic models: a molecular monolayer comprising of only water molecules, and a partially dissociated monolayer consisting of water molecules and hydroxyls with a composition of 50/50 ($\text{H}_2\text{O}/\text{OH}$) as described in ref. ⁵(Supplementary Figure S4). In all our atomistic models, the H_2O molecules and hydroxyls are placed on top of two adjacent undercoordinated Ti_{5c} atoms along the [010] direction of the TiO_2 (101) surface resulting in a 1x1 superstructure. For the partially dissociated monolayer, the water molecules and hydroxyls alternate along the [010] direction of the anatase surface. In both atomistic models, H-bonds are formed between adjacent water molecules (molecular monolayer) or between adjacent water molecules and hydroxyls (partially dissociated monolayer).

In our previous work of ref. ⁷, we found that the interaction between the electric field induced by the STM tip and the intrinsic electric dipole of a single H_2O molecule or hydroxyl on TiO_2 modifies their adsorption structure. Including these field effects, we achieved a better agreement between simulated and experimental STM images. Following these observations, we initially search for the atomistic models with the lowest total energy. Subsequently, we investigate

here whether the electric field induced by the STM tip yields structural changes on the adsorption structures of the molecular and of the partially dissociated water monolayer. The electric field induced by the STM tip is simulated by applying a constant electric field perpendicular to the (101) surface (Methods). The intrinsic electric dipoles of the water and hydroxyl constituting the monolayer tend to align with the applied electric field, giving rise to a structural change in the adsorption structure, as previously observed in a single H₂O molecule⁷ (see video S5 and S6).

The optimized adsorption configurations in the presence of the electric field are shown in Figures 3f and 3i, respectively. The same adsorption configurations are obtained using the modern theory of polarization²¹⁻²² to account for the applied electric field. From Figures 3f and 3i one can observe that, in the molecular monolayer, the interaction with the applied electric field breaks the H-bonding present in the unperturbed structure, while in the partially dissociated monolayer the H-bonding is preserved after applying an electric field. This result indicates that the H-bonds formed by the H₂O molecules and hydroxyls are stronger in the partially dissociated monolayer.

Next, we calculated the STM images of the monolayers in the presence of the electric field. Our results are depicted in Figures 3d,e and 3g,h for molecular and partially dissociated water monolayers, respectively. In both calculated STM images, we observe bright round protrusions arising primarily from H 1s states of either H₂O or hydroxyl. In the molecular monolayer, each bright protrusion corresponds to one water molecule adsorbed atop of one Ti-O pair. Hence, a 1x1 superstructure is formed with a distance between neighboring water molecules of 3.8 Å along the [010] direction. In the partially dissociated monolayer, the bright protrusions correspond alternately to water molecules and hydroxyls. It is important to note an important difference between the two calculated models. In the case of the molecular monolayer (Figure 3e) all hydrogen atoms are located in close proximity to the surface Ti_{5c} atoms, while in the case of the partially dissociated monolayer (Figure 3h and 3i) hydrogen atoms are also bound to

surface bridging O_{2c}. The dissociated H from the water molecule exhibits an additional density of states (DOS) at the position of the surface oxygen, which is shown in theoretical simulation in Figure 3h but was not observed in our experimental data. Hence, we conclude that the monolayer consists out of non-dissociated water molecules only. Furthermore, if the monolayer would be a mixture of molecular and dissociated water molecules, isolated hydroxyls should be present after the voltage pulses. We found all isolated protrusions to be water molecules.

To confirm this assignment, we functionalized our tip (Figure 4a) enabling the detection of substructures of the different protrusions.²⁶ Regardless of the formation of dimer or monolayer, all the water molecules in Figure 4a appear now as contracted dumbbell shaped protrusions composed of two oval shaped protrusions along the [010] direction. It is important to note that the appearance of water molecules fully incorporated into the monolayer, i.e. having two neighboring molecules, is the same. To interpret our results, we carried out first-principles calculations. The shape of the contracted dumbbells observed in experiment (Figure 4b) suggests that they may originate from O 2p states of the water molecules. By analyzing the density of states of the molecular monolayer calculated in the presence of the applied electric field, we find that within 0.6 eV from the CB bottom, the contribution of the water molecules to the density of states is primarily from O 2p states. The contribution arising from H 1s states is negligible in this energy window. In the case of a partially dissociated monolayer, the empty electronic states always contain non-negligible contributions from the O 2p and H 1s states of the water molecules and the hydroxyls, up to at least 1.5 eV from the CB bottom. Based on these observations, we simulate STM images of the H₂O monolayer with a functionalized tip, which couples with O 2p states by considering empty states within 0.6 eV from the CB bottom. As shown in Figure 4c, the calculated STM image reproduces nicely the dumbbell-shaped protrusions observed in the experiment. The dumbbells are oriented along the [010] crystallographic direction of the substrate, and centered

on top of adjacent surface Ti_{5c} atoms. Therefore, this result further supports the notion that the water monolayer observed in our experiment is comprised of molecular water only.

Additionally, we performed STM-IETS on different positions of the monolayer revealing always a distinct peak at 193 mV, which is associated to the $\delta(\text{H-O-H})$ bending mode (Supplementary Figure S2d).⁷ Again, this supports our assignment of the water monolayer to only consist of H_2O molecules.

Comparing the DOS of an isolated water molecule to the distance between adjacent Ti-O pairs, a repulsive interaction for water dimers is expected, i.e. the formation of water dimers costs additional energy. According to previous calculations, this energy cost ranges in the 100-400 mV regime but is strongly depending on the hybrid functional used.⁵ This is the reason why water dimers along the [010] direction have not been observed at sub-monolayer coverages on the TiO_2 anatase (101) surface.⁶⁻⁷ Here, we observe these contracted dimers by removing surrounding water molecules from the water monolayer using tip pulses. The contracted water molecules in the dimer cannot diffuse to form relaxed isolated molecules. This also allows us to discuss the formation process of the monolayer. Owing to the constant stream of water molecules over 24 h at 77 K, water molecules slowly adsorb to the surface until all the Ti_{5d} atoms are saturated. The calculated adsorption energy of an isolated water molecule is 318 meV, whereas the adsorption energy of a water molecule in the molecular monolayer is - 469 meV, which means the forming of molecular monolayer is an endothermic reaction (Table 1). At elevated temperatures where water dissociation occurs, the first monolayer might adapt the partially dissociated monolayer structure as it is energetically similar with the molecular water monolayer (ΔE of partially dissociated monolayer = - 487 meV, table 1).

CONCLUSIONS

The molecular water monolayer and its adsorption structure without applied electric field holds important implications. While the oxygen of the water molecule forms a dative bond to a surface Ti_{5c} atom, the remaining lone pair electron and the OH bonds of the water monolayer are oriented in the surface layer. In contrast to “water wets water”, where dangling OH bonds are oriented normal to the surface,²⁷ the structure presented here results in hydrophobic properties. This also explains why we do not observe multilayer adsorption even though the long exposure time.²⁸⁻²⁹

Based on our theoretical calculation, the adsorbed water molecules align their dipole due to the electric field from the STM tip resulting in the breaking of weak hydrogen bonding between the water molecules. Consequently, an OH bond is oriented normal to the surface vacuum. We hypothesize that this alters the surface properties switching from hydrophobic to hydrophilic and could be a potential general strategy to influence water adsorption on TiO_2 anatase using electric fields.

In summary, we have created a self-assembled molecular water monolayer on TiO_2 anatase (101) by controlling temperature and water flux. The water monolayer exhibits long-range order. We presented a structural model for the here observed molecular water and a partially dissociated water monolayer, which we expect to exist at higher temperatures where dissociation occurs. Knowing the structure of the first layer of water molecules on the anatase surface is an important starting point for a general understanding of water structures in contact with the TiO_2 anatase (101) surface.

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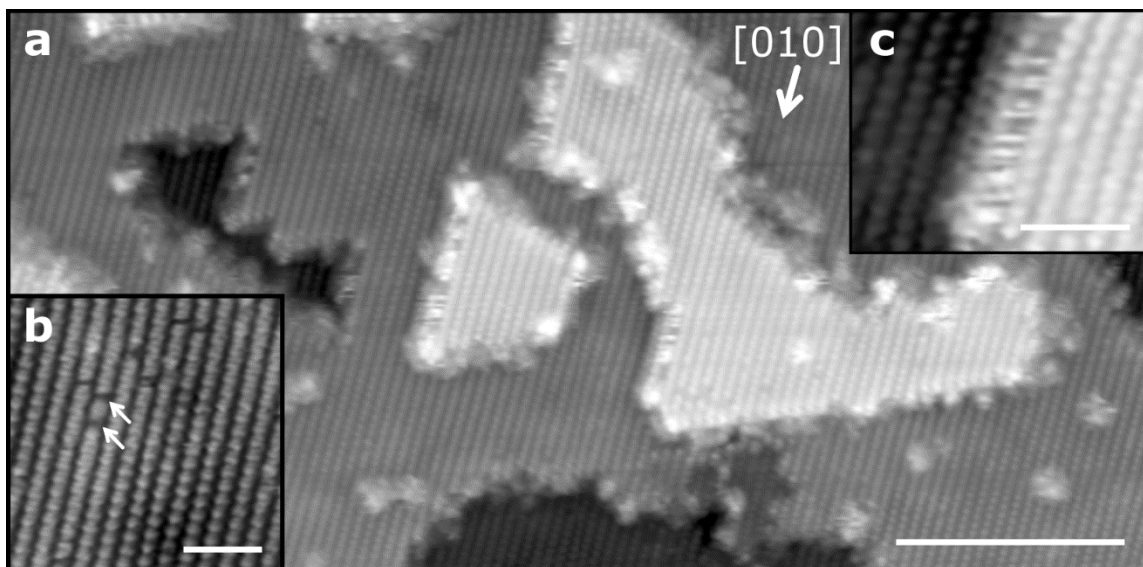


Figure 1. Formation of a water monolayer on TiO_2 anatase (101) using the STM chamber. (a) STM image after using desorption of water from our STM cryostat by heating up to liquid nitrogen temperature (77 K). (b) This leads to the formation of a nearly perfect monolayer of water on the anatase surface. The white arrows mark positions of missing water molecules. (c) Water molecules adsorbed on the low-reactive [010] step edge are unstable in the electric field of the scanning tip in contrast to water molecules adsorbed on oxygen vacant high-reactive [-111] step edges. (scalebars: (a) = 10 nm, (b),(c) = 2 nm).

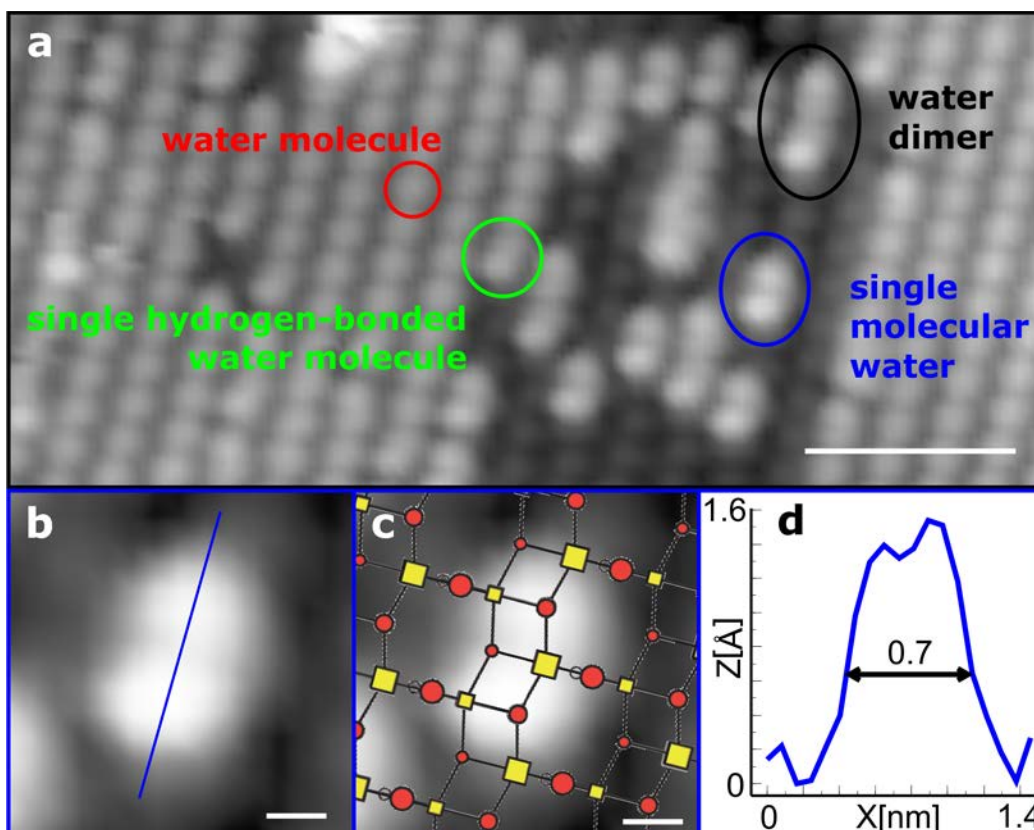


Figure 2. Different adsorptions of water molecules on TiO_2 anatase (101). (a) High-resolution STM image of the water monolayer with a small clean substrate patch. Water molecules can adsorb isolated (blue), with a single neighbor along the [010] direction (water dimer, black; water molecule in the monolayer, green) or with two neighbors (red). (b) STM images of the isolated dumbbell shaped protrusions, with overlaid TiO_2 anatase (101) lattice structure ((c), yellow = Ti, red = O), and corresponding linescan (d). The protrusion is symmetric with a size of 0.7 (blue circle) and binds with its center on top of a surface Ti_{5c} atom. We identify this protrusion to be an isolated H_2O molecule.⁷ (scalebars: (a) = 2 nm, (b),(c) = 2 Å).

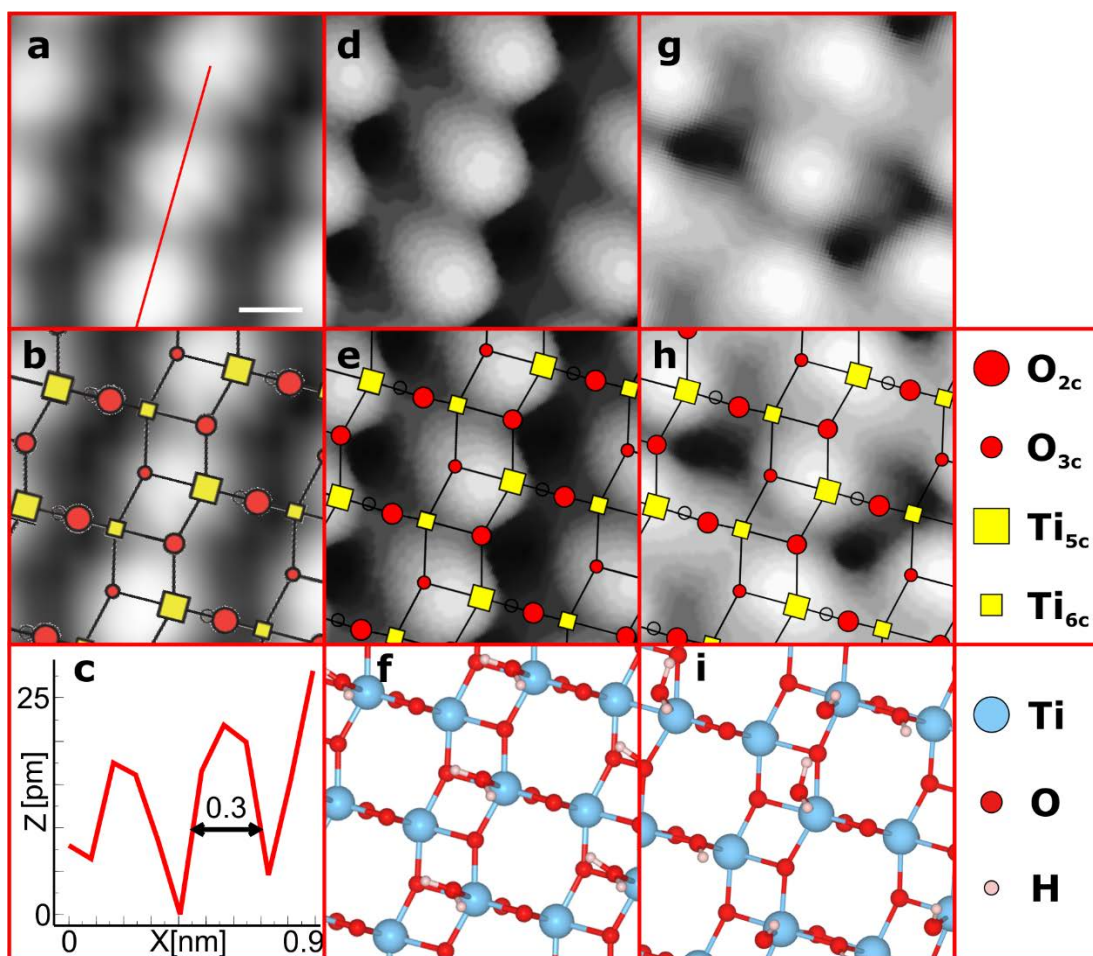


Figure 3. Proposed model of the water monolayer on TiO_2 anatase (101). (a) STM images of the water monolayer with overlaid TiO_2 anatase (101) lattice structure (b), and corresponding linescan ((c), length: 0.3 nm). (d),(g) Simulated STM images of the molecular and of the partially dissociated water monolayers, respectively. In (e) and (h), the calculated STM images are overlaid with a schematic representation of the surface lattice. (f) and (i), Ball-and-stick models of the adsorption structures adopted by the molecular water monolayer and by partially dissociated monolayer in the presence of an applied electric field, respectively. Taken together, we assign the water monolayer to only consist of H_2O molecules. (scalebars: (a) = 2 Å).

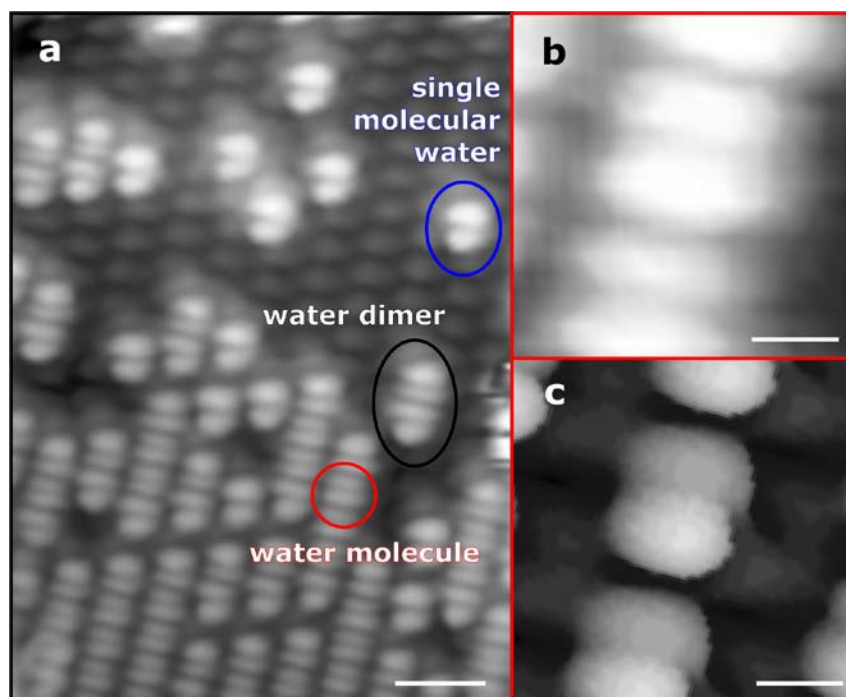


Figure 4. STM images of water molecules using a functionalized tip. (a) High-resolution STM image of the water monolayer adsorbed on TiO_2 anatase (101) using a functionalized tip. The functionalized tip resolves the substructure of the water molecules. (b) Water molecules fully incorporated into the monolayer, i.e. having two neighbors along the [010] direction exhibit two oval shape protrusions. (c) Calculated STM images of the molecular monolayer by simulating a functional tip using a bias voltage of 0.6 eV from the conduction band bottom. Since hydroxyls would show a non-negligible contribution of H1s states away from the [010] direction in the energy range of our STM image, this supports our assignment of the monolayer to consist of molecular H_2O . (scalebars: (a) = 1 nm, (b),(c) = 2 Å).

System	ΔE (meV)
Single H ₂ O	318
Single OH + H	475
Molecular Monolayer	-469
Partially Dissociated Monolayer	-487

Table 1. Total energies per molecule (ΔE) of the different water systems on anatase TiO₂ (101).

The energies are calculated using the following equation: $\Delta E = (1/n)(E_{\text{system}} - E_{\text{substrate}} - nE_{\text{H}_2\text{O}})$ where n is total number of molecules on the TiO₂ substrate, E(system) is the total energy of the TiO₂ slab with molecular and/or dissociated water in the ground state, E(substrate) stands for the total energy of the TiO₂ slab, and E(H₂O) corresponds to the total energy of one isolated water molecule.

TOC graphic

