Nucleation and Growth of 1D Water Clusters on Rutile TiO$_2$ (011)-2×1

Yunbin He,$^{1,2}$ Wei-Kun Li,$^3$ Xue-Qing Gong,$^1$ Olga Dulub,$^1$ Annabella Selloni,$^8$ and Ulrike Diebold*$^{6,7}$

Department of Physics, Tulane University, New Orleans, Louisiana 70118, Laboratories for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China, and Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Received: April 2, 2009

We present a combined experimental and theoretical study of the adsorption of water on the rutile TiO$_2$(011)-2×1 surface, whose “brookite (001)-like” reconstruction has been recently elucidated. By using scanning tunneling microscopy and density functional theory calculations, we provide evidence that water adsorbs weakly on the stoichiometric surface, while hydroxyls resulting from water dissociation at surface O vacancies act as nucleation centers for the growth of H-bonded water clusters that are confined in one dimension.

Water at solid surfaces is of fundamental and practical interest.$^{1-3}$ Oxide surfaces are particularly relevant, since most metals are oxidized in the ambient. While a consensus emerges for the adsorption of the first water layer on noble metals,$^4$ adsorption on oxides is more complex, as surface oxygen provides sites for H-bonding, which can significantly influence water adsorption.$^5$ One of the few oxides on which water adsorption is well understood is TiO$_2$(110), where STM$^{6-8}$ spectroscopic, and diffraction$^9,10$ measurements in conjunction with DFT calculations$^1$ have provided a detailed and increasingly complete picture. On TiO$_2$(110), the adsorption of the first water layer is dominated by the interaction between 5-fold coordinated surface cations (Ti$_{5c}$) and the water oxygen. The water molecule adsorbs intact on perfect surfaces and dissociates at O vacancies. TiO$_2$ is a technologically important material, warranting efforts toward obtaining a complete understanding of its surface chemistry.$^{11}$ We show that water on the same material, albeit of a different surface orientation, behaves distinctly different. On the perfect TiO$_2$(011)-2×1 surface, the water−water interaction is stronger than the water−surface interaction that is weak. Surface hydroxyls are needed for wetting on this second-most common crystal face of TiO$_2$. Interestingly, the corrugated geometry of this surface confines the water along one dimension, resulting in the formation of “liquid-like”, H-bonded water chains.

The surface structure of rutile (011) has recently been resolved. A so-called “titanyl” model was originally suggested to account for the experimentally observed 2×1 reconstruction.$^{12}$ Based on SXRD measurements and DFT calculations, a new model with a lower surface energy was proposed by Torrelles et al.$^{13}$ and our group.$^{14}$ Because of its similarity to the brookite (001) surface,$^{15}$ this surface was termed “brookite (001)-like” in ref 14; the present work is undertaken to test its surface chemistry.

All experiments were performed in an ultrahigh-vacuum (UHV) chamber with a variable-temperature Aarhus STM. The rutile TiO$_2$ (011) single crystal (MTI, Inc.) was cleaned by sputtering/annealing cycles in a standard procedure.$^{16}$ Purified water was dosed by backfilling the chamber via a leak valve with the sample in the cold stage of the STM at a T$_{\text{sample}}$ $\sim$ 110−130 K; nominal dosages are given in langmuirs (L, where 1 L equals a dose of $1 \times 10^{-6}$ Torr$	imes$s). Dosing was performed either in situ while STM was scanning or with the tip retracted by $\sim$1 mm from the sample to avoid tip shadowing effects. Empty-states STM images are shown throughout. The DFT calculations were performed using a 2×2 surface supercell ($9.172 \times 10.905 \text{ Å}^2$) for the reconstructed rutile TiO$_2$(011)-2×1 surface and slabs of four TiO$_2$ layers. Molecular species were adsorbed on one side of the slab only while the bottom layer was kept fixed. See ref 14 for further computational details.

The brookite (001)-like TiO$_2$(011)-2×1 surface (Figure 1a) has a corrugated profile along the [100] direction with two inequivalent surface O$_{2c}$ atoms, at the top and either side of hillocks. The O$_{2c}$'s in the valleys show almost bulk-like surroundings. The exposed Ti$_{5c}$ atoms at the top and in the valley are ‘shielded’ by O's, without a clear dangling bond toward the vacuum. This suggests a rather unreactive surface and, indeed, DFT calculations predict that water adsorbs only weakly via H-bonds to surface O$_{2c}$. State $E_{\text{H,O}} = 0.19$ eV, see Figure 1b. Prior photoemission experiments found that water dissociates on rutile (011)-2×1$^{17,18}$ for small exposures, giving rise to the 3σ state that is typical of hydroxyl groups, while states indicative of molecular water appeared with higher coverages. The molecular water desorbed around 200 $\pm$ 20 K; hydroxyls remained on the surface up to $\sim$310 K.$^{17}$ It was then concluded that, after initial water dissociation (at the monocoordinated oxygen sites of the titanyl model), a mixed molecular-dissociated layer formed. For the newly established “brookite (001)-like” model, however, our DFT calculations show that water adsorbs...
in molecular form at the regular surface sites; dissociation can only occur at defect sites, notably at surface oxygen vacancies. The STM image of the clean TiO$_2$(011)-2×1 surface shows rows of bright spots arranged in a zigzag pattern, see Figure 2a. In contrast to TiO$_2$(110), these bright spots are attributed to surface O atoms$^{16,19}$ their appearance in atomically resolved STM depends on the tunneling conditions.$^{14}$ While a pristine TiO$_2$(011)-2×1 surface contains few defects, repeated sputtering/annealing cycles result in a reduced bulk and surface O vacancies,$^{16}$ see inset in Figure 2a. After the surface is exposed to water at room temperature, the STM image (Figure 2b) shows bright spots that occur (almost) exclusively on the zigzag rows with a saturation coverage of $\sim 0.15$ monolayers (ML, where 1 ML refers to all top O atoms on the clean surface). Often, these spots appear in pairs (see Figure 2b and inset in Figure 2c). On the basis of these observations, we identify such bright spots as surface hydroxyls resulting from dissociated water, an interpretation supported also by theoretical STM simulations (see below). Thus we can estimate that the surface O vacancy concentration on our sample is $\sim 0.15/2 = 0.075$ ML, similar to the typical O-vacancy concentrations found on the UHV-annealed rutile (110).$^{20}$

In the DFT calculations a top O$_2$c can be removed more easily than a side O$_2$c (Figure 1a), with vacancy formation energies of 3.77 and 5.65 eV, respectively, relative to gas-phase O$_2$. The calculations also show a large (1.0 eV) energy gain for a water molecule that adsorbs dissociatively at a top O$_2$c vacancy, independent of whether the two resulting H adatoms occupy two nearest or next-nearest oxygen neighbors, see Figure 1c. The O atoms at the side of the hillocks are not only harder to remove, they also hydroxylate less easily: for instance, the binding energy of an H on a top O is by 0.42 eV larger than that of an H on a side oxygen. In STM simulations (see Figure S1 in the Supporting Information, SI) a side OH shows up as a bright spot between rows. In agreement with the computed energetics, this is rarely observed in experimental images (one example is the spot marked in blue in Figure 2c).

Figure 2c shows an STM image taken after a nominal water exposure of 0.4 L at 130 K; the coverage $\theta$ amounts to $\sim 0.08$ ML. As the water dosage is increased to 0.8 L, the number of bright spots increases to $\theta \sim 0.12$ ML and clusters appear (Figure 2d). Consistent with our previous studies indicating that molecular water is stabilized at low temperatures,$^{17,18}$ these clusters are assigned as containing molecular water. Note that few O vacancies are still observable, i.e. molecular water adsorbs before all the vacancies are filled. The clusters preferentially form 1D chains along the [011] direction. They typically consist of three lines of bright spots that span two neighboring hillocks and the black row (the valley in the brookite (001)-like structure) in between. These three lines are of nearly identical length and contain about the same number of bright spots.

The partial water layer is shown in more detail in Figure 3, together with an atomically resolved STM image of a 1D water cluster and line profiles. Three types of isolated spots have corrugations of $\sim 0.4$, 0.8, and 1.3 Å, respectively. Line profiles
taken across 1D water clusters show considerable variation in the apparent height of the water-related features. The water clusters are also dynamic, both the apparent height and position of the bright spots change during consecutive scans (see SI, STM movie S1).

By continuously exposing the surface to low levels of water, the water clusters grow in length, as shown by the sequence of STM images in Figure 4 (for a longer series, see STM movie S2 in the SI). For instance, the cluster marked by a dashed ellipse in Figure 4 triples in length from 15 to 48 Å (∼3 and ∼9 surface unit cells, respectively) over the course of 17 min. The growth is partially due to the adsorption of additional water (the total coverage increases by ∼31%) and partially it occurs at the expense of smaller water clusters and spots. Marked in Figure 4a are features that disappeared during sequential scans. Note that three lines comprising a water cluster always grow at a comparable rate resulting in nearly the same length.

DFT calculations of small water aggregates show the importance of hydroxyls for water adsorption on the “brookite-(001)-like” surface. While weak physisorption is predicted for the perfect surface (Figure 1b), a water molecule can form a H-bond with a top OH group, increasing the binding energy to 0.58 eV/molecule (see Figure 1d). A second H2O forms H-bonds with both the H2O–OH complex of Figure 1d and a neighboring O2c at the side of the hillock (see Figure 1e). Its adsorption energy, 0.57 eV, is nearly identical to that of the first H2O in the H2O–OH complex. Interestingly, the H2O–H2Oδ+ complex in Figure 1f, where an Hδ+ is transferred from the surface hydroxyl to an adsorbed H2O molecule, is energetically more favorable, by ∼0.15 eV, than the cluster in Figure 1(e). The tendency to ‘fill up’ the valley of the 2 × 1 structure with adsorbed water, is also supported by calculated STM images for the H2O–H2Oδ+ complex (see SI, Figure S1). Similarly, STM simulations of single OH and the H2O–OH complexes (Figure S1) suggest that these species may be responsible for the observed isolated spots with corrugations of ∼0.8 and 1.3 Å, respectively.

Temperature-dependent STM provides additional evidence of the importance of surface hydroxyls for water on TiO2(011)-2×1. In the STM image in Figure 5a, with a coverage of ∼0.22 ML and T sample of 170 K, the 1D clusters are ∼100 Å long. When the sample temperature rises to 185 K (Figure 5b), the long water chains disappear. Some small clusters remain and bright spots remain together with some locally ordered, single-line chains on the zigzag rows, all attributable to surface hydroxyls. The coverage decreases by ∼25%, indicating the onset of water desorption. This confirms the previous photoemission study, which concluded that water molecules in the mixed layer desorb from the surface around 200 ± 20 K.

In summary, the STM data, together with DFT calculations based on the “brookite-(001)-like” surface model, clarify the picture of water adsorption on TiO2(011)-2×1. The pristine surface is hydrophobic; surface hydroxyls, introduced via water dissociation at vacancies, are key to water adsorption. This is different from the well-investigated TiO2(110) surface, where water molecules bind rather strongly (∼1 eV according to DFT calculations) to surface Ti5c cations, with their dipole moment oriented away from the surface. The (110) and (011) surfaces of TiO2 exhibit significant differences in their photochemical reactivities; it remains to be tested whether the different structures of the first water layers contribute to this effect.
The growth of the 1D water islands is an interesting observation. The water and hydroxyl molecules in the clusters rearrange within the time scale of the experiment, similar to the fluctuations of the H-bond network in liquid water. The 1D cluster formation is probably related to a higher diffusivity of the water molecules along [011] relative to that along [100]. A precise understanding of the confinement of the growing islands within a single valley between two consecutive ridges will require extensive analysis and simulations; in a plausible scenario the H-bond between a water molecule on the left/right edge of the valley and a top O\textsubscript{2c} atom on the corresponding ridge (see Figure 1f) inhibits the formation of an additional H-bond between this O\textsubscript{2c} and a water molecule at the other side of the ridge. Thus the cluster can only grow along the valley and cannot expand laterally from one valley to the next. Water in nanosized channels is important in different fields, for example, nanofluidics, enzyme catalysis, and biosensors. The 1D water clusters on TiO\textsubscript{2}(011)-2×1 can be readily imaged and could thus represent an useful model system for the study of nanoconfined water.

Acknowledgment. The work was supported by the Department of Energy (DE-FG02-05ER15702) and the NSF (CHE-0715576). The ECUST group thanks the National Natural Science Foundation of China (20703017) and the 111 project (B08021) for financial support.

Supporting Information Available: Simulated STM images for water on rutile TiO\textsubscript{2}(011)-2×1 and STM movies showing dynamics and growth of water clusters on rutile TiO\textsubscript{2}(011)-2×1. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


