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Experimental evidence for mixed dissociative and molecular adsorption of water on a rutile $TiO_2(110)$ surface without oxygen vacancies

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We present evidence for mixed molecular and dissociative water adsorption at monolayer coverage on a rutile $TiO_2(110)$ surface free from oxygen vacancies using synchrotron radiation photoemission. At monolayer coverage the $OH:H_2O$ ratio is close to 0.5 and reducing the coverage by heating yields an increased $OH:H_2O$ ratio. At room temperature neither species originating from the monolayer on the defect-free surface can be detected. The OH species of the monolayer hence recombines and leaves the surface at much lower temperatures than OH formed by water dissociation on oxygen vacancies.

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I. INTRODUCTION

Rutile $TiO_2(110)$ has for many years been regarded as the benchmark surface for fundamental studies of metal-oxide surface chemistry.[1,2] TiO_2 is also important in a wide variety of applications, such as photochemical water splitting, solar cells, catalysis, gas sensing, and biomedical implants.[1,3,4] Since water is an integral part of the environment in most of the above-mentioned applications, the $H_2O/TiO_2(110)$ system has received more attention than any other comparable system.[1,2,5] A better understanding of the interaction of water with the rutile $TiO_2(110)$ surface will also broaden our understanding of water chemistry at oxide surfaces in general. While the dissociation of water on the oxygen-deficient $TiO_2(110)$ surface has been characterized in detail,[6–13] there is as of yet no consensus reached between experimentalists and theorists regarding a very fundamental question: does water dissociate upon adsorption on the defect-free $TiO_2(110)$ surface?

Theoretical studies of water adsorption on the defect-free $TiO_2(110)$ surface presented over the years are contradictory. Early studies predicted dissociative adsorption at all coverages.[14,15] More recent studies suggest a delicate balance between dissociated, partial dissociated, and molecular configurations, a balance that most probably depends on the coverage.[16–24] The $TiO_2(110)$-(1×1) surface, shown in Fig. 1, consists of alternating rows of fivefold-coordinated Ti atoms [Ti(5)] and twofold-coordinated bridging oxygen atoms (O_{br}). The situation at a coverage corresponding to one water molecule per Ti(5) site (defined as one monolayer, 1 ML) has been heavily debated. Lindan *et al.* have proposed a mixed molecular-dissociated configuration as the most stable state, emphasizing the importance of intermolecular hydrogen bonding.[16,19] Still, the adsorption energies of the mixed phase and a pure molecular phase were very similar. In a recent quantum molecular-dynamics study it was found that 20% of the water molecules dissociate, supporting the notion of a mixed monolayer.[22] To conclude, available theoretical results do not give a clear-cut answer as to whether water adsorbs associatively or dissociatively on defect-free $TiO_2(110)$.

The most common view expressed in experimental studies is that at all coverages water adsorbs molecularly on the ideal $TiO_2(110)$ surface and dissociation does only take place at defect sites.[1,25–27] One plausible reason for the lack of conclusive experimental proof of dissociation on the defect-free surface can be the elusive nature of the dissociated state. The dissociated state found in the theoretical studies of the defect-free $TiO_2(110)$ surface is depicted in Fig. 1. It consists of one terminal OH (OH_t) at a Ti(5) site and a hydrogen atom adsorbed on a neighboring O_{br}, giving a OH_{br}.[12,16,19,28] Since the two OH groups remain neighbors, the barrier for the transition to a molecular state is low.[12] This state has therefore been denoted as "pseudodissociated." The presence of a pseudodissociated state in scanning tunneling microscopy (STM) images has been controversial. At room temperature (RT), STM fails to image molecular water due to its high mobility at this temperature.[29,30] Neither has there been any record of pseudodissociated water. Structures assigned to OH_{br} and OH_t species have been reported but they vanish as soon as they occupy neighboring sites, leaving

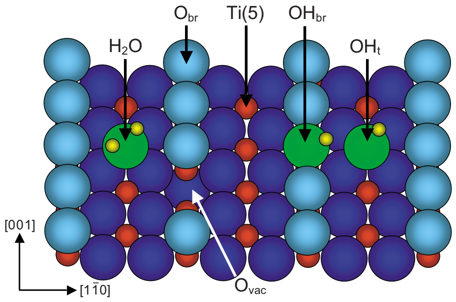

FIG. 1. (Color online) Schematic illustration of the rutile $TiO_2(110)$ surface. Blue and red spheres denote lattice O and Ti, respectively. The light blue spheres are bridging oxygen atoms (O_{br}), which lie in the [001] azimuth of the substrate. One bridging oxygen vacancy is indicated (O_{vac}). Parallel rows that lie between the O_{br} rows are Ti(5) atoms. Green spheres indicate oxygen atoms bonded to H atoms (yellow spheres). Indicated are OH groups on bridging sites (OH_{br}) and on terminal [Ti(5)] sites (OH_t). One water molecule adsorbed on a Ti(5) site is also indicated.

a bridging O atom.[29] Evidently pseudodissociated water is not stable at RT. The presence of pseudodissociated water in STM images recorded below 200 K and at low water coverages has been discussed with the aid of theoretical STM image simulations.[12,28] However, discriminating between pseudodissociated and molecular water using STM has proven to be difficult. Conclusive experimental results that show whether OH is formed or not upon water adsorption on a surface free from O vacancies are therefore much needed.

In this paper, we present a study of the interaction of water with the rutile $TiO_2(110)$ surface using synchrotron radiation photoemission. We demonstrate that O 1*s* spectra recorded at grazing emission angle at optimized photon energy in conjunction with valence spectra allow for the observation of OH on the surface even when substrate oxygen is present. We present clear evidence for mixed molecular and dissociative water adsorption at monolayer coverage on a $TiO_2(110)$ surface free from oxygen vacancies. Reducing the coverage by heating of the monolayer results in an increased $OH:H_2O$ ratio. Importantly, neither species originating from the monolayer is detected at room temperature, which shows that OH in the mixed monolayer is much less stable than OH formed at oxygen vacancies. The detailed nature of OH in the mixed layer is not possible to unveil with present experimental results but they are clearly consistent with the notion of pseudodissociated water on the vacancy-free surface.

II. EXPERIMENTAL

The photoemission measurements were performed at beamline D1011 at the Swedish synchrotron radiation source MAX-II using a Scienta 200 mm hemispherical electron energy analyzer.[31] The rutile $TiO_2(110)$ single crystal (SurfaceNet GmbH) was cleaned by sputtering (Ar^+, 1 keV) and annealing to 900 K until no contaminations could be discerned with photoelectron spectroscopy and a sharp (1×1) low-energy electron diffraction pattern was observed. Pure water was introduced through a leak valve and doses are given in Langmuirs ($1\ \mathrm{L}=1\times10^{-6}$ Torr s). Annealing of the adsorbate layer was performed at a rate of about 1 K per second and with the sample kept at the desired temperature during measurements in order to minimize adsorption of residual water. Spectra for the clean sputtered and annealed surface were measured at elevated temperature (400–550 K). The presented O 1*s* spectra were recorded in 60° off normal emission using 610 eV photons. The valence spectra were recorded in normal emission using 130 eV photons. The binding energy was referenced to the Fermi level of a Pt foil attached to the sample holder. Radiation damage of the overlayer was carefully checked and found to be negligible.[32]

III. RESULTS AND DISCUSSION

A $TiO_2(110)$ surface free from oxygen vacancies was prepared following the recipe in Ref. 33. Sputtering and annealing in vacuum produce a reduced surface, denoted as *r*-$TiO_2(110)$. At room temperature, water dissociates on the O_{br} vacancies on the *r*-$TiO_2(110)$ surface giving a hydrated surface. The capping H atoms can be reacted off by subsequent exposure to O_2 resulting in a surface with perfect O_{br} rows.[33] This is a critical step since O_2 doses exceeding the optimal value yields oxygen adatoms that may affect the surface chemistry.[30] Therefore, the capping hydrogen atoms were titrated away in a stepwise fashion by careful monitoring of the intensity of the OH 3σ peak. Figure 2(a) shows valence photoemission results for such a preparation sequence, performed at RT. Spectra are shown for the clean *r*-TiO_2 surface (green curve), after a subsequent dose of 5 L H_2O (blue curve), after a total dose of 5 L O_2 deposited in three steps (red curve), and finally after another 5 L of H_2O (black curve). An OH 3σ peak at a binding energy of 11.0 eV is evident in the spectrum measured after 5 L H_2O on the *r*-$TiO_2(110)$ surface (blue curve). A much lower OH 3σ intensity is found after O_2 dosing. Consistently, if the surface is subsequently exposed to water at RT there is negligible increase in the OH 3σ peak intensity. Figure 2(b) shows the corresponding O 1*s* spectra with the same color coding as in Fig. 2(a). The green, red, and black curves are identical while the blue curve, measured after 5 L H_2O on the *r*-$TiO_2(110)$ surface, shows an increased intensity at about 532 eV due to surface hydroxyls.[32,34,35] This result is fully consistent with the valence spectra. In agreement with previous STM studies[8,12,28,33] we can therefore conclude that (1) water adsorbs through dissociation on O_{br} vacancies at room temperature, (2) a large fraction of the capping H atoms can be removed through reaction with O_2, and (3) no water adsorption can be detected on the ideal terraces at RT.

A small fraction of OH groups are not possible to dehydrate with O_2. The density of O_{br} vacancies in the RT experiment shown in Figs. 2(a) and 2(b) is estimated to $6\pm1\%$. The O_2 dose needed to reach the limit of surface dehydration (5 L) is consistent with that reported earlier (4 L) for an O_{br} vacancy density of $5.5\pm0.2\%$.[33] In this case, we find that about 75% of the capping H atoms can be reacted off, leaving hydroxylated defects with a density of 1.5%. The *r*-TiO_2 surface of a second sample, cleaned in the same way, was found to exhibit an oxygen-vacancy density of about 12%. The *h*-TiO_2 surface prepared for this sample consequently comprised OH groups of approximately twice the density of the previous sample. Upon O_2 treatment, the limit for dehydration was reached after a dose of about 15 L, consistent with a higher OH density. Approximately 90% of the capping hydrogen atoms were removed, leaving hydroxylated defects with a density of 1.2%. From this follows that there are two types of OH groups on the *h*-TiO_2 surface. A majority type that can be dehydrated with a rather constant proportionality to the O_2 dose and a minority type with a much lower probability for dehydration by O_2. That is the density of the majority type shows a more pronounced variation than the minority type in absolute terms indicating a similar defect concentration of the minority type of defects for the two different samples.

The minority type of OH, the one that cannot be dehydrated, is most likely formed at step edges. A density of species at step edges on a percentage level is in very good agreement with STM images of surfaces prepared in a similar way, showing terrace widths of about 100 Å.[36] The overall stoichiometry for the dominant dehydration reaction mechanism reaction is $1/2O_2+2OH_{br}\rightarrow H_2O+2O_{br}$. The

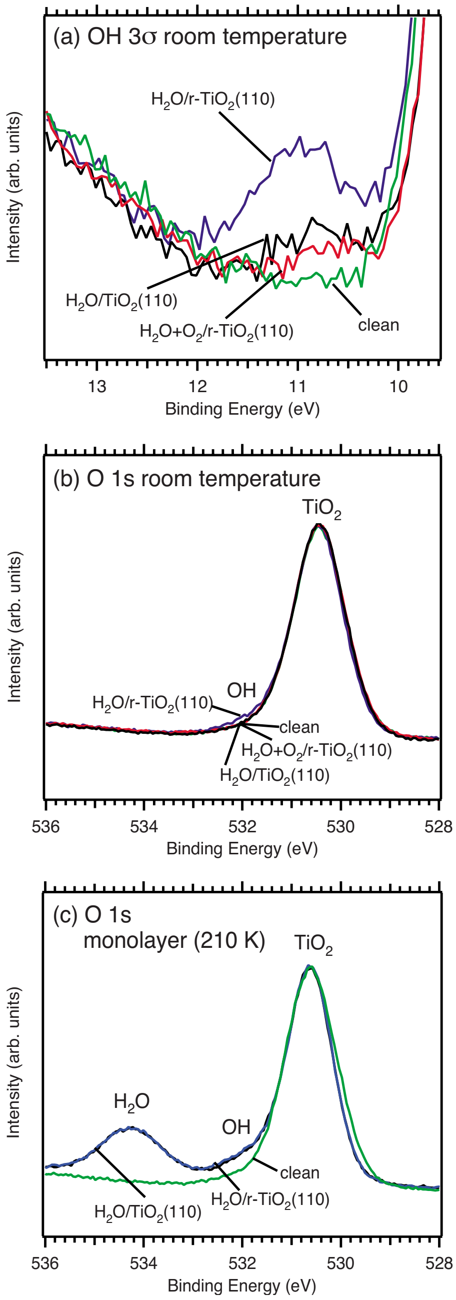

FIG. 2. (Color online) (a) OH 3σ spectra for the clean *r*-TiO_2 surface (green curve, measured at elevated temperature), after 5 L H_2O on the *r*-TiO_2 surface [H_2O/r-$TiO_2(110)$, blue curve], after a subsequent dose of 5 L O_2 [H_2O+O_2/r-$TiO_2(110)$, red curve], and finally after adsorption of another 5 L of H_2O [$H_2O/TiO_2(110)$, black curve]. (b) O 1*s* spectra for the same situations as in (a) and with the same labeling and color coding. (c) O 1*s* spectra for the clean surface (green curve), after annealing of a water multilayer on the *r*-$TiO_2(110)$ surface to 210 K [H_2O/r-$TiO_2(110)$, blue curve] and after annealing of a water multilayer on the oxygen-vacancy-free $TiO_2(110)$ surface to 210 K [$H_2O/TiO_2(110)$, black curve].

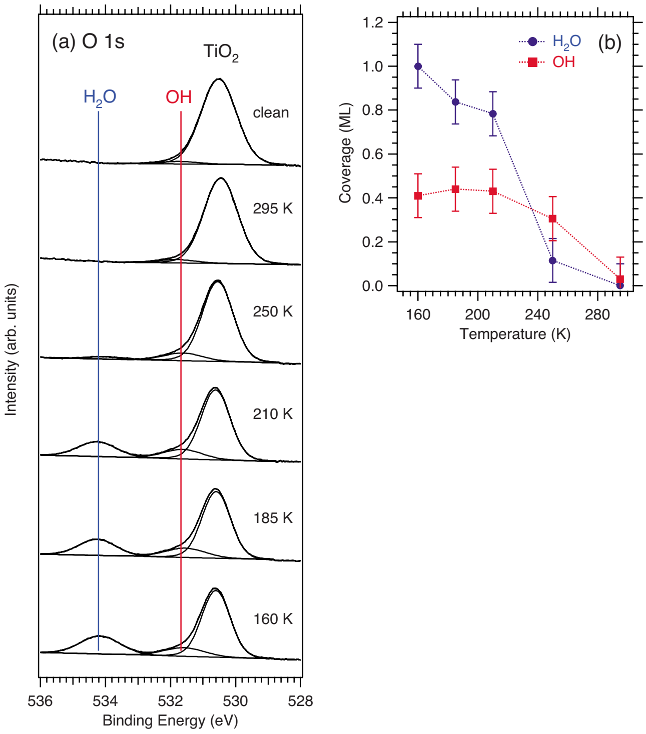

FIG. 3. (Color online) (a) O 1*s* spectra for water adsorption on a rutile $TiO_2(110)$ surface free from oxygen vacancies. The spectra show the results after progressive heating of a multilayer of water and each spectrum has been delineated into individual contributions from the substrate, OH and H_2O. (b) Estimates of the OH and H_2O coverages given in monolayers (ML) where 1 ML corresponds to the density of Ti(5) sites on the surface.

H_2O molecule interacts only very weakly with the surface at RT and is therefore not detectable by photoemission. There are clear indications that the reaction at the terraces involves several intermediate steps that include the formation of surface intermediates and that adsorbate diffusion is critical.[29] It is therefore likely that the dehydration mechanism is quite different at the step edges. Moreover, the STM image of the *h*-TiO_2 surface exposed to an optimal O_2 dose (optimal with respect to defect concentration) shows only a part of a terrace, featuring perfect O_{br} rows.[33] This strongly suggests that ideal terraces are realized in the present experiment and that the remaining traces of OH are exclusively located at step edges. Consequently, water adsorption on a $TiO_2(110)$ surface prepared in this way will occur predominantly at the ideal terraces and reflect the properties of those.

The presence of a mixed OH/H_2O monolayer is demonstrated in Fig. 2(c). The monolayer is prepared by annealing a multilayer of water to 210 K.[26] A pronounced shoulder at 532 eV, related to OH, is observed for both the surface without O_{br} vacancies (denoted as TiO_2) as well as for the *r*-TiO_2 surface with vacancies. The presence of molecular water is evident on both surfaces, giving rise to the O 1*s* peak at 534.2 eV. The OH peak is in both cases clearly more intense than the corresponding peak observed for water adsorption at room temperature on the *r*-TiO_2 surface [Fig. 2(b)]. Clearly there is a mixed layer of dissociative and molecular water on the defect-free $TiO_2(110)$ surface, confirming previous theoretical work.[16,19,22]

O 1*s* spectra monitoring desorption of OH and H_2O from the mixed monolayer on the surface free of O_{br} vacancies are shown in Fig. 3(a). The O 1*s* spectra have been recorded at different temperatures and delineated into individual contributions from TiO_2, OH, and H_2O. Based on the O 1*s* intensities at ML coverage,[37] the coverage of OH and H_2O are estimated for the different temperatures, Fig. 3(b). The OH intensity is compensated for the O 1*s* line profile as well as for the trace amounts of OH that remains after O_2 treatment to produce the surface free of O vacancies (see above). No species originating from the mixed monolayer can be detected on the surface at RT. The absence of water is consistent with previous TPD studies.[6,26] The OH originating from the mixed layer is clearly quite different from the OH formed as OH_{br} at the O vacancies. The latter does not recombine and desorb until about 490 K.[6,26]

The OH coverage stays essentially at 0.43 ML up to 210 K. Assuming that all the OH is in the pseudodissociated state, 0.22 ML will be accommodated on the OH_t sites. The H_2O coverage at the monolayer point (210 K) is 0.78 ML. This means that the Ti rows comprise 0.22 ML OH_t and 0.78 ML H_2O. In the theoretical treatment the energies of a pure water phase and a mixed phase (with a $OH:H_2O$ ratio of 2) were found to be very similar at monolayer coverage.[16,19] Applying this model, we obtain 0.44 ML of the mixed phase and 0.56 ML of the water phase. This suggests rather similar energies with a slightly higher probability for the pure water phase to form. The OH species formed at monolayer coverage is a result of the reduction in the dissociation barrier induced by intermolecular hydrogen bonding.[16,19] Figure 3(b) shows that lowering the coverage by heating results in an increased $OH:H_2O$ ratio. Importantly the $OH:H_2O$ ratio of the layer formed by heating the multilayer to 210 K is identical to that found when exposing the surface to water at 210 K. The barrier is thus reduced as the water coverage is reduced as predicted theoretically. Also, the kinetic effects have to be minor.

Our results can be related to the nature of the wetting layer formed at ambient conditions. The O 1*s* spectrum of a wetting layer on the rutile $TiO_2(110)$ surface was presented recently.[35] Along with molecular water, OH was observed and attributed to vacancy-assisted dissociation. However, assuming a typical amount (5–10 %) of O_{br} vacancies, our results show that the contribution from vacancy-assisted dissociation is much too low to account for the OH peak of the wetting layer. We therefore propose that the OH within the wetting layer stems predominantly from OH within a mixed phase on defect-free areas, similar to the monolayer formed under ultrahigh vacuum (UHV) conditions.

Finally, the chemistry of the $TiO_2(110)$ surface may be influenced by Ti interstitials.[33] Although no water adsorption has been related to Ti interstitials at room temperature,[33] the effect at low temperatures is as of yet unknown and deserves further study.

IV. CONCLUSIONS

We have demonstrated that the formation of a monolayer of water on a rutile $TiO_2(110)$ surface free from oxygen vacancies at low temperature under UHV conditions involves both molecular and dissociative adsorptions. Lower coverages are characterized by an increased $OH:H_2O$ ratio. At room temperature, water adsorption is only possible through dissociation at oxygen vacancies. The mixed nature of the monolayer demonstrates the importance of intermolecular interaction at coverages reached at low temperature in ultrahigh vacuum or under ambient wetting conditions.

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