Imaging Water Dissociation on $TiO_2(110)$

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Scanning tunneling microscopy has been used to identify the adsorption site of H_2O on $TiO_2(110)$-(1×1) at 150 K, and to monitor the site of the dissociation products at 290 K. Water adsorbs onto the rows of fivefold coordinated Ti atoms at 150 K, dissociating by 290 K to form bridging but not terminal hydroxyls. This points to the involvement of bridging O vacancies in the dissociation pathway.

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Molecular processes on oxide surfaces are important in a number of applications, including catalysis and environmental control. The interaction of water with TiO_2 surfaces, the subject of this Letter, has particular relevance to photocatalysis.

Oxide surface reactivity has long been thought to be dominated by minority sites in the form of defects [1], although a detailed understanding of these processes still has to be achieved. The principal experimental obstacle to this goal has been associated with the spatially averaging nature of nonimaging techniques. Experience with prototype surfaces, particularly $TiO_2(110)$ indicates that a mixture of minority sites is often present [2]. The effect produced by each type of minority site will be summed in a nonimaging measurement. In principle, scanning tunneling microscopy (STM) offers the possibility to focus on the behavior of one type of minority site. Here we employ STM to study the reactivity to H_2O of a $TiO_2(110)$-(1×1) surface with point defects in the form of bridging O vacancies. As judged by scanning probe microscopy images, a typical $TiO_2(110)$-(1×1) surface contains about 3% monolayer (ML) of bridging O vacancies, where 1 ML is defined as the number of fivefold coordinate Ti^{4+} atoms at the surface [3].

Temperature programmed desorption (TPD) spectra from $TiO_2(110)$-(1×1) after exposure to water contain four peaks centered at 155, 190, 295, and 490–540 K [4]. The first three have been assigned to molecular desorption from multilayer, second layer, and first layer states. As for the higher temperature feature, this has been assigned to recombinative desorption. The corresponding adsorbate coverage was in the region of that of the bridging-O vacancies [4]. This implicates these vacancies in the H_2O dissociation process, a suggestion that is further supported by isotope substitution measurements [4].

Although there is general agreement that the maximum coverage of OH species on $TiO_2(110)$ resulting from H_2O dissociation is in the region of 0.1 ML [5–7], a consensus still has to be reached regarding the temperature at which H_2O dissociates. A photoemission study concluded that water adsorbs molecularly at 160 K, with some dissociation associated with O vacancies as the temperature is increased to 200 K [5]. In contrast, a high resolution electron energy loss spectroscopy (HREELS) study found that water dissociates at 130 K at defect sites to give a coverage of about 0.1 ML, while subsequent adsorption is molecular [7]. This apparent discrepancy may reflect a difference in the O vacancy density.

A first principles density functional theory calculation and molecular dynamics simulations of water adsorption on $TiO_2(110)$ have been reported for a defect free surface [8]. This was based on a substrate structure determined by surface x-ray diffraction [9]. The calculations predict dissociative adsorption below 0.5 ML, and mixed dissociative and molecular adsorption with H bonding above this coverage [8].

In this Letter we describe a variable temperature STM study of water adsorption on $TiO_2(110)$ at $\leq$150 K and the effect of increasing the substrate temperature to 290 K. Adsorbate fingerprinting is provided by complementary photoemission measurements. The results point to molecular adsorption on fivefold coordinated Ti atoms at 150 K with thermally activated dissociation at bridging O vacancy sites to form only bridging OH species.

STM images were recorded using an Omicron Variable Temperature UHV STM. Images of $TiO_2(110)$ were recorded in the constant current mode with the sample positively biased with respect to the tip. As in earlier studies we were unable to image the sample at negative bias [10]. A 1.5 V sample bias and a tunneling current of 1 nA were used to record all of the images reported here. Photoemission measurements employed a VSW HA100 MCD electron energy analyzer and VG He lamp. Both the photoemission and STM instruments had base pressures of $\leq 2 \times 10^{-10}$ mbar during this work.

The $TiO_2(110)$ samples (Pi-Kem) were cleaned by repeated Ar^+ sputtering (1 kV) and annealing to 900 K until judged clean and ordered by Auger electron spectroscopy, low energy electron diffraction, and STM. The sample was exposed to the vapor of distilled H_2O after further purification of the liquid using freeze-pump-thaw cycles. An *in situ* mass spectrometer was used to confirm the absence of significant impurity levels in the water vapor. The doser inlet on the photoemission chamber was in direct line of sight to the sample, which explains the smaller exposures to give the same coverage of H_2O.

STM images of the clean $TiO_2(110)$-(1×1) surface recorded in the range 150–300 K resemble the room temperature images reported in the literature [2,3]. These contain bright [001] direction rows that arise from tunneling into fivefold coordinated Ti atoms, with the dark rows corresponding to the positions of bridging O atoms [2,3].

A representative STM image of $TiO_2(110)$ after exposure to 0.5 L (1 Langmuir = 1.32 mbar · s) of water at 120 K and warming to 150 K is shown in Fig. 1. It is clear that adsorbate induced features are situated on the bright Ti rows. Although individual Ti atoms in the row can be discerned, it is not possible from the data recorded thus far to determine whether the adsorbate induced features lie atop Ti. The line profile in Fig. 1 shows that the adsorbates have an apparent height of about 1 Å above the Ti rows with intermolecular separations between molecules 1 and 2, 2 and 3, and 3 and 3′ of about 9, 12, and 3 Å, respectively. These separations are integer multiples of the 2.96 Å unit cell length along [001].

The upper photoemission difference spectrum in Fig. 2 was recorded from the STM sample, after recleaning and reexposing to 0.2 L at 150 K. This spectrum can be seen to be characteristic of molecular water by comparison with the gas phase spectrum of water that is shown in Fig. 2 for comparison. The 0.4 eV bonding shift of the $3a_1$ peak is consistent with chemisorbed H_2O [5]. On the basis

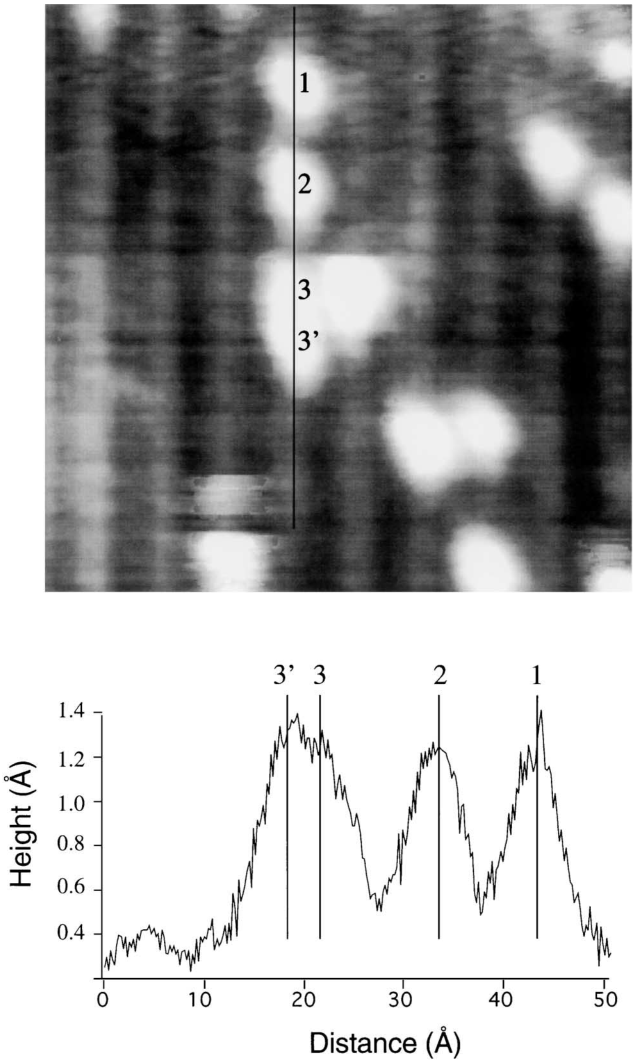

FIG. 1. A 60 Å × 60 Å STM image of $TiO_2(110)$-(1×1) after exposure to 0.5 L H_2O at 120 K and subsequent heating to the measurement temperature of 150 K. The line within the image shows the path of the line profile. Features identified in the image and line profile are discussed in the text.

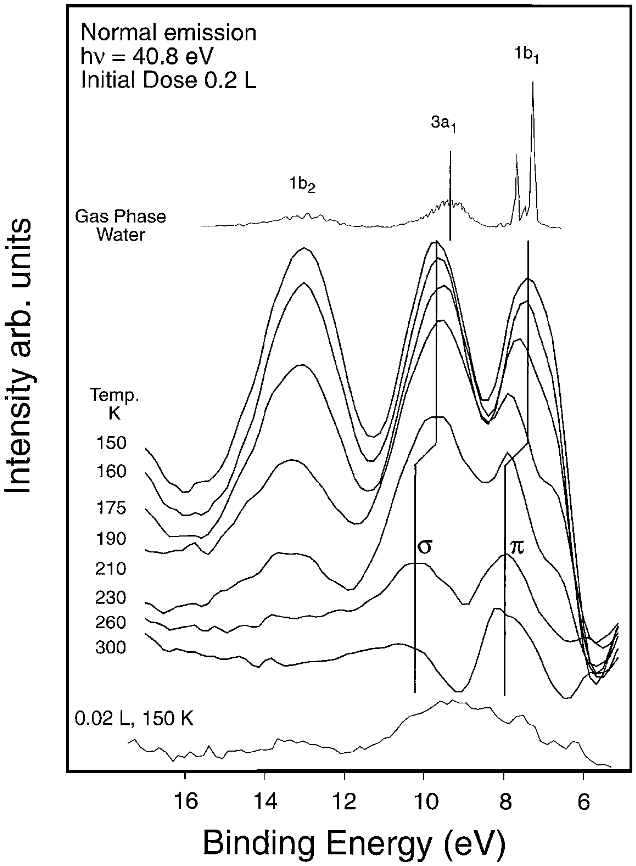

FIG. 2. He II ($h\nu = 40.8$ eV) photoemission difference spectra of $TiO_2(110)$-(1×1) recorded at normal emission. Difference spectra were obtained by subtracting a clean surface spectrum from spectra recorded after exposing the surface to 0.2 L H_2O at 150 K and subsequently warming in steps to 300 K. The binding energy scale was aligned to the Fermi level recorded from the Ta sample holder. For comparison, a gas phase spectra of water [12] has been included, aligned at the $1b_1$ orbital, as well as the relative positions of the $OH\sigma$ and $OH\pi$ features [11]. We can estimate the H_2O coverage corresponding to the 150 K spectrum if we assume that the OH and H_2O valence band intensity is proportional to the number of adsorbate O atoms. On the basis of an 0.08 ML coverage of OH in the 290 K spectrum (see text), the H_2O coverage at 150 K is 0.7 ML. For comparison, a difference spectrum is included which was recorded following an exposure to 0.02 L H_2O at 150 K.

of the photoemission results, features in the STM image in Fig. 1 can be associated with chemisorbed H_2O. The molecules are expected to be bonded atop Ti atoms on the basis of theoretical calculations [8]. A small but discernible $1b_2$ feature is observed in the photoemission difference spectrum at the lowest H_2O exposure studied, namely 0.02 L (see Fig. 2), suggesting that on this surface there may be little dissociation at 150 K.

The STM image in Fig. 3(a) indicates that an H_2O exposure of 3.5 L at 150 K results in a coverage of about 0.7 ML, with the features remaining above the Ti rows. The STM images in Figs. 3(b) and 3(c) show the effect of warming the sample imaged in Fig. 3(a) from 150 K. At 190 K [Fig. 3(b)] the apparent coverage of water decreases to about 0.3 ML.

Increasing the temperature of the overlayer to 290 K results in a quite different signature in the photoemission difference spectrum (see Fig. 2). Now only two features are observed, which appear at binding energies consistent with photoemission from the σ and π orbitals of OH [11]. The integrated adsorbate valence region intensity has decreased by a factor of about 10, consistent with water desorption. In the STM image, water dissociation is reflected by the appearance of adsorbate induced features on the dark rows, which correspond to the position of bridging O atoms. The apparent height of the adsorbates is about 1.2 Å above Ti rows, and they appear at a coverage of 0.08 ML. This is close to the density of bridging OH species observed (0.07 ML) on an as-prepared sample of $TiO_2(110)$-(1×1) [3], presumably because of adventitious reaction with water in the vacuum system.

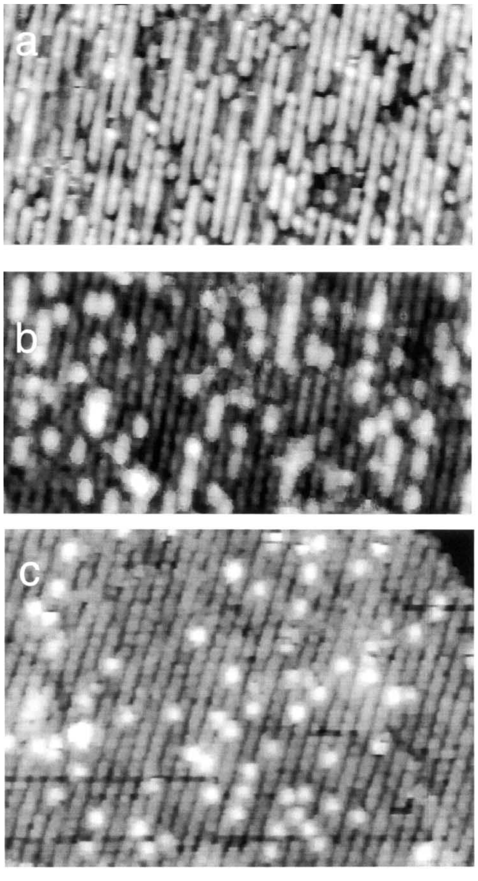

FIG. 3. STM images of $TiO_2(110)$-(1×1) exposed to 3.5 L of H_2O at 150 K, and consecutively heated to the measurement temperatures of the following: (a) 150 K (240 Å × 120 Å); (b) 195 K (240 Å × 120 Å); and (c) 290 K (200 Å × 145 Å).

As in the photoemission spectra, the STM images reflect desorption of water on increasing the temperature to 290 K. Annealing to above 500 K is sufficient to remove all adsorbate contributions to the STM image, leaving a clean 1 × 1 substrate.

The observation of what have been termed bridging hydroxyl species [8] resulting from thermally activated dissociation of chemisorbed water is significant. On the basis of the calculations for water interacting with the perfect surface, dissociation on regular lattice sites should give rise to both terminal and bridging hydroxyl species, where terminal OH groups lie atop fivefold coordinated Ti atoms [8]. That only bridging OH species are observed points to water dissociation to fill a bridging O vacancy with a bridging OH and releases a H atom to form an additional bridging OH. An autocorrelation analysis of the position of OH species reveals no evidence of pairing, suggesting a certain mobility of the H atoms. This is in line with the isotope substitution measurements [4]. The behavior described above is summarized in the model shown in Fig. 4. Implicit in the description above is the absence of terminal OH groups which are invisible to STM. This is discounted on two grounds. First, the reasonable argument that if bridging OH groups are STM visible then it is likely that

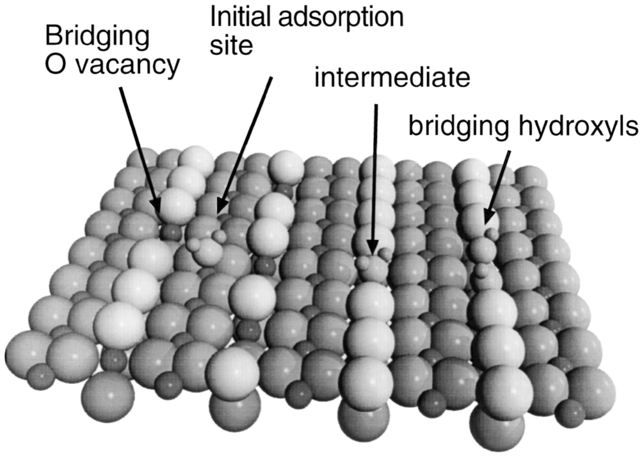

FIG. 4. Schematic diagram showing the mechanism deduced from our STM and photoemission measurements for the interaction of H_2O with $TiO_2(110)$ at 150 K and its thermally activated dissociation. "Temperature" increases from left to right in the diagram. The mechanism takes into account the predictions of theoretical calculations which point to molecular adsorption on Ti atoms [8]. Water initially adsorbs on Ti atoms with dissociation at bridging O vacancies to form bridging hydroxyl species. Small spheres are Ti atoms, while large spheres are O atoms.

terminal OH would also be visible. Second, the HREELS data are consistent with only one type of OH (see below).

If we now inspect the results of nonimaging techniques in light of our STM work, we find a number of features which provide a consistent picture with the model in Fig. 4. First, the TPD results [4], which have a desorption peak at 270 K for molecular desorption and recombinative peak at 490–540 K, are broadly in line with our expectations. Our observation of molecular adsorption at 150 K is in agreement with previous photoemission work [5] but not with HREELS [7]. However, the observation of a sharp single ν_{OH} loss in HREELS spectra recorded from a surface exposed to H_2O at 130 K and heated to 275 K [7] is consistent with the presence of only one type of OH species.

In summary, we have used STM to follow the reaction of water with $TiO_2(110)$-(1×1), using photoemission spectroscopy to identify the adsorbates. Molecular water adsorbed at 150 K occupies sites on the Ti rows of the substrate. Theoretical studies indicate that water will sit atop the Ti atoms in the row. Heating an 0.7 ML H_2O overlayer to 290 K results in the formation of 0.08 ML of bridging OH, with no adsorbate species on the Ti rows of the substrate. On the basis of theoretical studies that indicate that dissociation on regular lattice sites will result in both terminal and bridging OH, this result indicates that water dissociates at bridging-O vacancy sites.

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