

Formation and Splitting of Paired Hydroxyl Groups on Reduced TiO₂(110)

S. Wendt, J. Matthiesen, R. Schaub, E. K. Vestergaard, E. Lægsgaard, F. Besenbacher, and B. Hammer
*Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, University of Aarhus,
DK 8000 Aarhus C, Denmark*

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A combination of high-resolution scanning tunneling microscopy and density functional theory is utilized to study the interaction of water with the reduced TiO₂(110)-(1 × 1) surface. As the direct product of water dissociation in oxygen vacancies, paired hydroxyl groups are formed. These pairs are immobile and stable unless they interact with adsorbed water molecules. As a result of these interactions, protons are transferred to adjacent oxygen rows, thereby forming single hydroxyl groups. Additionally, we show that hydroxyl groups facilitate the diffusion of water molecules over the oxygen rows.

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TiO₂ is important in the fields of gas sensors, biocompatible materials, and photocatalysis [1]. In addition, TiO₂ shows interesting properties in photochemical hydrogen production from water [2,3], the photogeneration of hydrophilic oxide films [4], and as a support of Au nano-clusters [5].

Among countless investigations addressing TiO₂, many studies have been undertaken under ultrahigh vacuum (UHV) conditions [1,3,6]. Here the anisotropic rutile TiO₂(110) surface is preferred, since this surface is the thermodynamically most stable one. The (110) face of TiO₂ is composed of alternating rows of fivefold-coordinated Ti atoms (5f-Ti) and twofold coordinated bridging oxygen (O_{br}) atoms [for details, see Ref. [7]]. The most discussed point defects on the TiO₂(110) surface are missing single O_{br} atoms—O_{br} vacancies [1].

Many previous studies addressing TiO₂(110) have assumed perfectly clean surfaces with O_{br} vacancies, but without hydroxyls. However, even in UHV this crucial assumption is not always justified [8,9]. The reason is twofold: first, even in UHV, a water background cannot be completely avoided, and second, water reacts very efficiently with O_{br} vacancies in a wide temperature range [9]. It should be emphasized that the stabilization of hydroxyls on metal oxides can drastically change the surface chemistry [10]. The knowledge of how an oxide surface undergoes hydroxylation helps in characterizing the state of the oxide more precisely. Furthermore, the hydroxylation process itself is of broad interest for a better understanding of the chemistry on oxide surfaces. Note that in many applications the natural state of an oxide is such that hydroxyls are present at the surface [10].

In this Letter, the hydroxylation of the reduced TiO₂(110)-(1 × 1) surface is described by means of scanning tunneling microscopy (STM) movies [11] and density functional theory (DFT) calculations. We present the first STM images showing the dissociation of a single water molecule in an oxygen vacancy on an oxide surface. As a result, stable pairs of hydroxyl groups (OH_{br}) are formed in the O_{br} rows. Spontaneous splitting of the OH_{br} pairs is not

observed at any investigated temperature. However, the interaction with water molecules provides a path for the splitting of the OH_{br} pairs into two single OH_{br} that reside in adjacent O_{br} rows. Utilizing DFT calculations, we explain the splitting of an OH_{br} pair as a sequence of proton transfers in the [1 $\bar{1}$ 0] direction. Finally, we show that water diffusion in the [1 $\bar{1}$ 0] direction is facilitated by OH_{br} groups in the O_{br} rows. Based on these results, a previous STM study is reinterpreted [Ref. [12]].

The experimental setup and the sample preparation are described elsewhere [9]. The color of the TiO₂(110) crystal is dark blue, indicating an O-deficient, bulk-reduced sample [1]. Using the STM, the O_{br} vacancy concentration is estimated to be $5.1 \pm 0.2\%$ ML, where 1 ML (monolayer) is defined as the density of the (1 × 1) units, $5.2 \times 10^{14}/\text{cm}^2$. The STM images presented in this work are acquired in the constant current mode using a tunneling voltage of +1.25 V and a tunneling current of ~ 0.1 nA. For the purpose of cleaning the water, several freeze-pump-thaw cycles are performed.

The DFT calculations are done using the DACAPO package [13]. We employ ultrasoft pseudopotentials, a plane wave basis (orbital cutoff: 25 Ry, density cutoff: 35 Ry), and the revised Perdew-Burke-Ernzerhof (RPBE) exchange-correlation functional [14]. The TiO₂(110) surface is modeled using (3 × 2) periodic slabs of four trilayers, i.e., 48 TiO₂ units (144 atoms), half of which are relaxed. We use the theoretically derived lattice constants ($a = 4.69$ Å, $c = 2.99$ Å, and $u = 0.305$). Estimates of energy barriers are obtained by constrained relaxation.

Figure 1 shows snapshots from an STM movie (“dissociation”) recorded on the water-exposed, reduced TiO₂(110) surface [15]. When imaging the TiO₂(110) surface with the STM, dark rows correspond to geometrically protruding O_{br} atoms, whereas Ti atoms in the troughs appear bright [1]. In Fig. 1 various kinds of bright features on the dark rows, so-called type A defects, are discernible. Among the type A defects, O_{br} vacancies show up as faint spots, single OH_{br} are imaged brighter, and OH_{br} pairs are seen with even brighter contrast than single

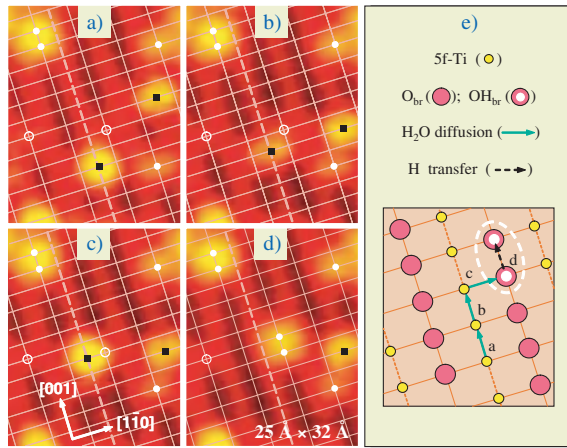


FIG. 1 (color). (a)–(d) Dissociation of water in an O_{br} vacancy on $TiO_2(110)$ at ~ 187 K [STM movie dissociation [15]]. Protrusions are labeled as follows: O_{br} vacancies (open white circles), OH_{br} groups (filled white circles), water on 5f-Ti sites (filled black squares). (e) Schematic: letters (a)–(d) mark oxygen positions of the water.

OH_{br} [9]. Besides the type A defects on the dark O_{br} rows, a protruding species is seen in Fig. 1(a) on the bright Ti troughs. Its identity is revealed when tracking the dynamics of this species. Focusing on the Ti trough marked by a dashed line, it is evident that this species is adsorbed on 5f-Ti sites, and diffuses along the Ti trough [Figs. 1(a)–1(c)]. When this species reaches a 5f-Ti site next to an O_{br} vacancy [Fig. 1(c)], both the species on the Ti trough as well as the vacancy in the O_{br} row disappear, and are replaced by an OH_{br} pair [Fig. 1(d)]. The reaction monitored in movie “dissociation” (Fig. 1) is explained straightforwardly when ascribing the species in the Ti trough to an isolated water molecule that dissociates in the vacancy [Fig. 1(e)]. This interpretation is consistent with temperature programmed desorption data in the literature [6,16], since the species in the Ti troughs is absent after flashing the sample to 350 K. In addition, our DFT calculations presented below strongly support this interpretation.

The atomistic mechanism of water dissociation in O_{br} vacancies, which explains the formation of OH_{br} pairs, has been suggested previously [17–19], but movie “dissociation” (Fig. 1) represents the first real-space images of this reaction. We observe water dissociation in O_{br} vacancies at ~ 180 K, which is in line with recent vibrational data [16]. The OH_{br} pairs are stable under the given experimental conditions, as, e.g., illustrated by the static appearance of the pair in the upper left corner of all images in Fig. 1. In fact, the OH_{br} pairs are stable even at 300 K [9].

However, the OH_{br} pairs split into two single OH_{br} groups when interacting with water [Fig. 2, movie “splitting” [15]]. After a water molecule has diffused to a 5f-Ti site next to an OH_{br} pair [Figs. 2(a) and 2(b)], several changes are discernible when comparing with the subsequent image [Fig. 2(c)]. Instead of the OH_{br} pair in the

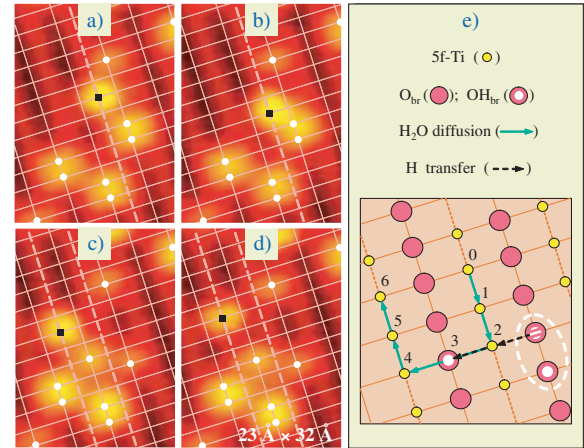


FIG. 2 (color). (a)–(d) Splitting of an OH_{br} pair mediated by a water molecule at ~ 187 K [STM movie splitting [15]]. Protrusions are labeled as in Fig. 1. (e) Schematic: numerals 0–6 mark oxygen positions of the water for selected configurations that we will discuss in the DFT section. The hatched white disk indicates the proton of the pair that is transferred.

center of Figs. 2(a) and 2(b), two single OH_{br} groups are now seen, one residing at the same place as in Fig. 2(b), but the other in the adjacent O_{br} row on the left. In addition, the water molecule also appears on a different adsorption site, namely, shifted one Ti trough to the left. The changes seen in STM movie “splitting” suggest that water molecules mediate proton transfer from one O_{br} row to another, and further that water molecules can easily diffuse over the OH_{br} groups in the O_{br} rows. In Fig. 2(e) we show a schematic denoting likely intermediate configurations corresponding to STM movie “splitting.”

We also observe diffusion of single OH_{br} mediated by water molecules. However, the reverse reaction as compared to Fig. 2, i.e., the formation of OH_{br} pairs from two single OH_{br} , is found very rarely and only for high OH_{br} coverages. This result indicates that water dissociation in O_{br} vacancies is the major channel for producing the OH_{br} pairs. Also notably, we observe water diffusion over the ~ 1.1 Å protruding O_{br} atoms at OH_{br} groups, but not at regular O_{br} atoms.

The series of STM images showing the diffusion of single OH_{br} in the $[1\bar{1}0]$ direction (not shown) is indistinguishable from the STM movies previously published by some of us [12]. In Ref. [12], the dynamics of the $TiO_2(110)$ surface after oxygen exposure is described, and the STM movies have been interpreted as diffusion of O_2 molecules on a surface with O_{br} vacancies. However, according to our recent results discussed in Ref. [9], it is evident that the type A defects in Ref. [12] were single OH_{br} and not vacancies. The species diffusing in the Ti troughs in Ref. [12] is therefore reassigned to water molecules [20].

We now turn to our DFT calculations, starting with the case of an isolated water molecule on the *stoichiometric* $TiO_2(110)$ surface. Previous calculations addressing this

issue indicate that the adsorption energies for water being adsorbed either molecularly or dissociatively depend critically on the water coverage [1,6,21]. In accordance with Ref. [21], our calculations predict dissociation of an isolated water molecule on the stoichiometric $\text{TiO}_2(110)$ surface at low coverages to be preferred by 0.13 eV [9]. In the dissociated configuration, a terminal hydroxyl group (OH_t) resides in the Ti trough, and an adjacent OH_{br} is formed. The dissociation reaction would be completed if these two OH groups were able to separate from each other. However, high barriers for the diffusion processes in the [001] direction inhibit the separation of the two OH groups. For the diffusion of the OH_t group, the barrier is 1.17 eV, while the diffusion of the proton along the O_{br} rows is hindered by a barrier as high as ~ 1.5 eV. Therefore, the state of an isolated water molecule on the stoichiometric $\text{TiO}_2(110)$ surface is “pseudo-dissociated,” since the two OH groups remain neighbors. As we calculate only a small barrier (~ 0.4 eV) for the transition from the pseudo-dissociated to the molecular state of adsorbed water, we anticipate rapid dynamics of the protons. At the time scale of the STM experiments, the OH_{br} may thus be formed many times at the O_{br} rows on alternating sides of the 5f-Ti site. Therefore, pseudo-dissociated water molecules appear in STM images as features which are symmetrical about the Ti troughs.

With the aim of modeling the *reduced* $\text{TiO}_2(110)$ surface, we calculate the energy profile for a water molecule diffusing from the Ti trough (Fig. 3, $s = 0$ Å; $s \sim 2.7$ Å) into an adjacent O_{br} vacancy ($s \sim 10.6$ Å), where it dissociates ($s \sim 14.3$ Å). In agreement with our STM results, we find low barriers for all diffusion and transfer processes (Fig. 3). The pseudo-dissociated water absorbed in the Ti

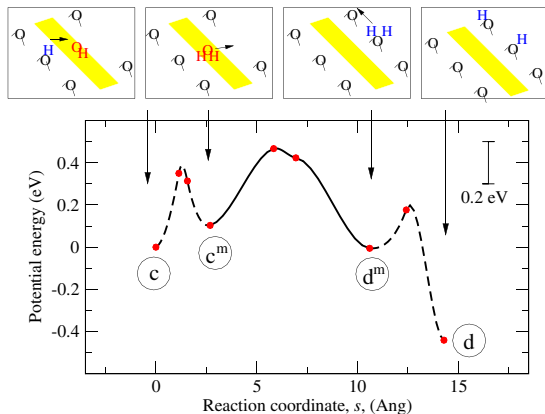


FIG. 3 (color online). Potential energy profile for water diffusion into an O_{br} vacancy and subsequent dissociation. Dashed lines are used for proton transfers and solid lines for water diffusion. Encircled characters refer to the positions as indicated in Fig. 1(e). The superscript “m” indicates that the water is in its molecular state. The reaction coordinate, s , is defined as $s_j = \sum_{i=1}^{j-1} \sqrt{|\Delta \vec{R}_{i,i+1}|^2}$, where $\Delta \vec{R}_{i,i+1}$ connects the i 'th and the $i+1$ 'th configurations in $3N$ space, N being the number of atoms.

trough ($s = 0$ Å) is comparable in energy to molecular adsorption of water in the O_{br} vacancy ($s \sim 10.6$ Å). However, upon dissociation in the O_{br} vacancy, more than 0.4 eV is gained. In addition, the barrier for this proton transfer is only 0.2 eV ($s \sim 12.4$ Å). As a result of the dissociation, an OH_{br} pair is created, which is exactly what we observe with STM (Fig. 1).

Guided by our STM results in Fig. 2, we further use the DFT approach to study the splitting of OH_{br} pairs mediated by an adsorbed water molecule. In Fig. 4, the energy profile and selected configurations are shown for the case when a water molecule diffuses to a position in the trough right next to an OH_{br} pair. As in the case of the stoichiometric surface, the pseudo-dissociated state ($s = 0$ Å) is slightly preferred (here by 0.12 eV). After diffusion of the water in its molecular state to the Ti site next to one of the two OH_{br} in a pair ($s \sim 9.8$ Å), one proton of the water molecule is transferred to the adjacent, bare O_{br} row; i.e., the water molecule pseudo-dissociates. In this configuration ($s \sim 12.5$ Å), the OH_t group left behind in the Ti trough is surrounded by OH_{br} groups on both sides. The diffusion of the water molecule may proceed when the OH_t group takes a proton from either of the surrounding OH_{br} . Splitting of the OH_{br} pair occurs, because transferring a proton from an OH_{br} pair is favored by 0.12 eV compared to the case where a proton is taken from the single OH_{br} . Thus, in total a proton is transferred to the adjacent O_{br} row ($s \sim 15.3$ Å). Such a sequence of proton transfers is calculated to be possible also when a water molecule passes a single OH_{br} . Accordingly, water molecules mediate the splitting of OH_{br} pairs as well as the net OH_{br} diffusion in the $[1\bar{1}0]$ direction.

Finally, we utilize DFT to study the diffusion in the $[1\bar{1}0]$ direction (from one Ti trough to another) of the water molecule left after the splitting of the OH_{br} pair. The

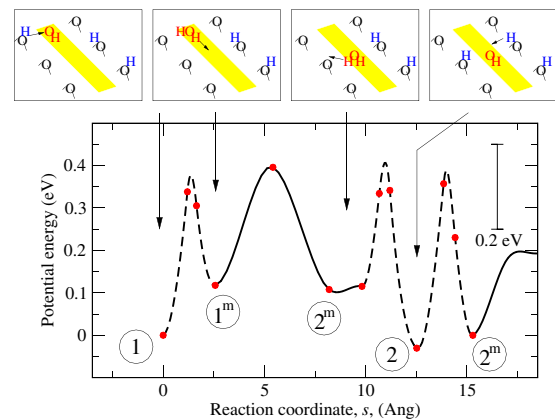


FIG. 4 (color online). Potential energy profile for the water mediated splitting of an OH_{br} pair. As in Fig. 3, dashed lines indicate proton transfers and solid lines water diffusion. Encircled numbers refer to the positions that are labeled in Fig. 2(e). At $s \sim 15.3$ Å, the OH_t group in the Ti trough has taken one of the protons from the OH_{br} pair.

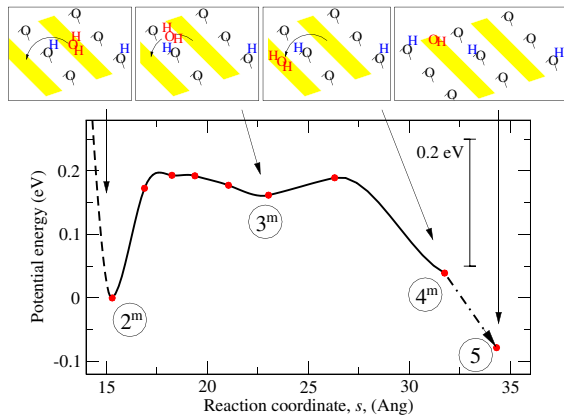


FIG. 5 (color online). Potential energy profile for the water diffusion in the $[1\bar{1}0]$ direction over the O_{br} row at an OH_{br} group. Labels as in Fig. 4. The reaction coordinate of Fig. 4 is continued. To avoid falsifications through interaction of species over the periodic boundaries, the configurations ④ and ⑤ are calculated in a (3×3) supercell.

diffusion energy profile is shown in Fig. 5 for the direction, where the water passes over the adjacent OH_{br} group and ultimately pseudo-dissociates at some distance to the OH_{br} . The diffusion event is surprisingly facile, the barrier being only 0.19 eV, which we attribute to the formation of a strong hydrogen bond between the proton of the OH_{br} group and the oxygen of the water molecule (bond length: 1.79 Å at $s \sim 23.0$ Å). In the absence of the OH_{br} group, we calculate a barrier as high as 0.6 eV (profile not shown) for the diffusion of water across the O_{br} row. This barrier is almost as high as the desorption energy on the stoichiometric surface, which amounts to 0.79 eV. In this hypothetical configuration where a water molecule diffuses over a bare O_{br} atom, only a weak hydrogen bond can be formed (length: 2.07 Å).

In summary, the hydroxylation process of the reduced $TiO_2(110)$ surface is elucidated by STM and DFT on the atomic scale. As a result of water dissociation in O_{br} vacancies, stable pairs of OH_{br} groups are formed. However, the OH_{br} pairs split into single OH_{br} groups when interacting with adsorbed water molecules. The splitting reaction consists of several proton transfers with the result of net OH_{br} diffusion in the $[1\bar{1}0]$ direction. In analogy, also the diffusion of single OH_{br} groups is mediated by water molecules. Furthermore, it is shown that OH_{br} groups facilitate the diffusion of isolated water molecules in the $[1\bar{1}0]$ direction.

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- [15] The freshly prepared $TiO_2(110)$ sample was quenched to ~ 110 K and exposed to water corresponding to ~ 0.1 ML. Subsequently, the sample was slowly warmed up while recording STM movies. Both movies “dissociation” and “splitting” (2.7 s/image) are acquired within the same experiment at ~ 187 K (see additional information at www.phys.au.dk/spm). See EPAPS Document No. E-PRLTAO-96-016607 for STM movies “dissociation” and “splitting.” For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.
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