# Tunneling Desorption of Single Hydrogen on the Surface of Titanium Dioxide

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ABSTRACT We investigated the reaction mechanism of the desorption of single hydrogen from a titanium dioxide surface excited by the tip of a scanning tunneling microscope (STM). Analysis of the desorption yield, in combination with theoretical calculations, indicates the crucial role played by the applied electric field. Instead of facilitating desorption by reducing the barrier height, the applied electric field causes a reduction in the barrier width, which, when coupled with the electron excitation induced by the STM tip, leads to the tunneling desorption of the hydrogen. A significant reduction in the desorption yield was observed when deuterium was used instead of hydrogen, providing further support for the tunneling-desorption mechanism.
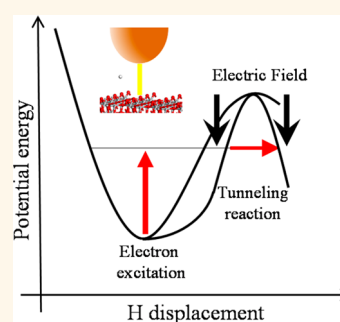
KEYWORDS: defect · manipulation · scanning tunneling microscopy · titanium dioxide

Electric conductivity, photophysical properties, magnetic properties, and catalytic activity can be produced by introduction of defects onto inert materials.[1−8] Clarifying the fundamental properties of such defects is therefore of extraordinary interest in developing new materials. Typical defects on titanium dioxide (TiO₂) include hydrogen (H) adatoms, oxygen vacancies (O$_{vac}$), and Ti interstitials, each of which confer new properties absent in the perfect material. TiO₂ is a transition metal oxide showing a number of characteristic functions that can be exploited in processes such as heterogeneous catalysis, photocatalysis, sensing, and light-induced switching, among others.[1−10]

Defects have been created at TiO₂ surfaces by thermal annealing[11] as well as by photo- and electron-stimulated desorption (PSD and ESD).[1,12,13] The principles of these methods are based on thermal reaction to produce O₂ in the former case and interionic Auger decay processes in the latter two examples.[1,11−13] While these methods have

been successfully used to introduce defects on the TiO₂ surface, precise control of the defect arrangement is not possible. The control of the defect arrangement on TiO₂ has been reported by applying specific voltages with a scanning tunneling microscope (STM). For example, Suzuki et al. found that hydrogen atoms on TiO₂ can be removed by scanning at a raised bias,[14] and we have recently reported the introduction of an individual O$_{vac}$ by applying a single voltage pulse.[15] While manipulation of defects by STM methods allows for ideal spatial control of the defect, the mechanisms are still unclear.

In the manipulation of atoms/molecules by STM, the mechanisms can be categorized into electron excitation and nonelectron excitation processes. In electron excitation reactions, tunneling electrons excite electronic states that are related to chemical bonds [1, electronic state excitation][16] or vibrational states (including translational, rotational, and conformational change states) to overcome reaction barriers by exciting

reaction coordinate modes [2, vibrational state excitation].[17−19] Also, heating by electrons causes reaction in electron excitation [3, manipulation by local heating].[20] In nonelectron excitation reactions, direct interaction between the STM tip and atoms/molecules by means of van der Waals/chemical forces [4, direct manipulation][21] or electric field to reduce the height of the reaction barrier [5, electric field excitation][22−24] have been utilized to manipulate atoms/molecules. Here, we provide insight into such reaction mechanisms for manipulation of defects on TiO_2 by using action spectroscopy measured by STM (STM-AS), whereby the response of a molecule is recorded as a function of applied bias voltage.[16−19] H desorption on TiO_2 was chosen as a model system because it is the simplest reaction. We found that H desorption induced by the STM is a tunneling reaction facilitated by the reduction of the barrier width by the applied electric field together with excitation by the tunneling electrons. Although tunneling reactions of atoms/molecules induced by STM tips are reported,[25,26] this reaction mechanism whereby the barrier width is reduced by the applied electric field has not been observed previously. Apart from being an important reaction mechanism in other H/TiO_2 systems, such reaction mechanisms are also likely to be important in other atomic scale reactions as well.

RESULTS AND DISCUSSION

Figure 1a shows a typical STM image of H on $TiO_2(110)$ obtained with sample bias (V_s) = +1.5 V. The bright rows and the spot at the center of the image are the Ti ions and H on bridging oxygen (O_b), respectively.[1−8,14,15] After applying a V_s = +1.7 V pulse to the H for 1 s, the spot corresponding to H disappeared due to desorption of H (Figure 1b). In contrast, no change occurred when voltage pulses were applied with negative sample bias (up to V_s = −5.0 V). These observations are in line with previous reports.[1−8,14,15,27−29]

In order to investigate the reaction mechanism for H desorption, STM-AS was measured. When the tip was fixed at V_s = +1.0 V and I_t = 0.02 nA (with no additional tip displacement (TD = 0 nm)), the obtained spectrum showed two clear threshold energies at V_s = +1.4 and +1.7 V (blue filled squares and curve in Figure 2a). Displacing the tip closer to the TiO_2 surface leads to a shift of the thresholds toward lower energy. For example, when the tip was moved toward the surface (TD = −0.04 nm), the threshold energies were shifted to V_s = +1.3 and +1.6 V (green filled triangles and curve in Figure 2a), and with further displacement of the tip to −0.10 nm, the threshold energies were also further shifted to V_s = +1.2 and +1.5 V (purple filled circles and curve in Figure 2a). Further shifts of the threshold energies were not observed for displacements of −0.14 and −0.20 nm (orange filled squares and black filled triangles in Figure 2a). In contrast, displacement of the tip away from the surface to +0.1 nm led to a
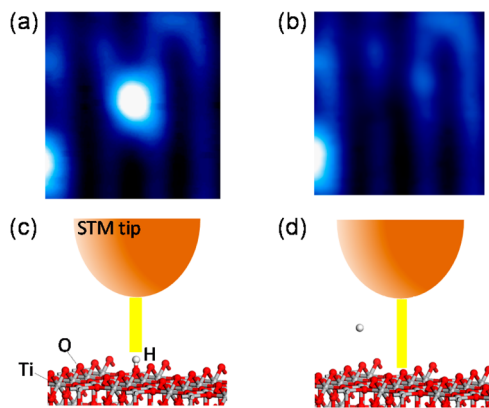

Figure 1. STM images of $TiO_2(110)$ (a) before and (b) after H desorption (2.7 nm × 3.0 nm, V_s = +1.5 V, I_t = 0.3 nA). (c, d) Schematic images of H desorption on $TiO_2(110)$.

shift of the threshold energy originally at V_s = +1.7 V to V_s = +2.0 V (red filled circles and curve).[30] Figure 2b summarizes the threshold energy shifts as a function of tip displacement. Clearly, the shift of the threshold energies depends on the tip displacement (TD between +0.1 and −0.1 nm) with saturation of the shift in the closer region (TD less than −0.1 nm).

Based on our STM-AS results, we consider possible mechanisms for the voltage pulse-induced desorption of H: [1] electronic state excitation of reaction coordinate modes,[16] [2] multiple vibrational state excitation for overcoming the reaction barrier,[17−19,25,26] [3] thermal reaction caused by local heating,[20] [4] direct manipulation by means of van der Waals/chemical forces,[21] and [5] electric field excitation for reduction of the reaction barrier.[22−24] To assess the possibility of electronic state excitation of antibonding states, dI/dV measurements were performed on $H/TiO_2(110)$ as a function of TD. No electronic states were observed in dI/dV curves that correspond with the threshold energies observed in STM-AS (Figure S1). Also, the shift of the threshold energies (≈3.0 V/nm in −0.1 to +0.1 nm of TD) in STM-AS did not match with the shift in dI/dV spectra (≈6.0 V/nm) that is caused by tip induced band bending (TIBB) (Figure S1). This implies that the reaction cannot be caused by electronic state excitation. Next, we consider the possibility of multiple vibrational excitation to overcome the reaction barrier. From density functional theory (DFT) calculations, the energy barrier of H desorption was obtained as 3.7 eV (open circles in Figure 3). To overcome the reaction barrier by vibrational state excitation, multiple excitation is necessary (for example, the vibrational energy of stretching mode of OH on $TiO_2(110)$ is 0.457 eV (3690 cm^{-1})[31]). However, the tunneling current dependence of the reaction yield indicates a one-electron process (Figure S2). Therefore, this reaction cannot be explained by multiple vibrational state excitation.[32] In addition, the possibility of local heating and direct manipulation by means of van der Waals/chemical
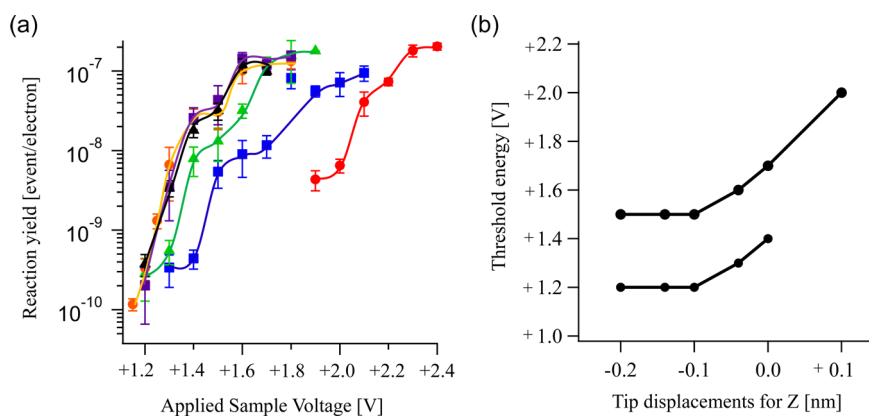
Figure 2. (a) STM-AS of H desorption on TiO$_2$(110). Spectrum with blue filled squares is obtained with start parameters $V_s = +1.0$ V, $I_t = 0.02$ nA and with no tip displacement (i.e., TD = 0 nm). All other spectra have the same start parameters but with different TD. Red filled circles: TD = +0.1 nm. Green filled triangles: TD = −0.04 nm. Orange filled circles: TD = −0.10 nm. Purple filled squares: TD = −0.14 nm. Black filled triangles: TD = −0.20 nm. (b) Threshold energy observed in STM-AS depending on TD.
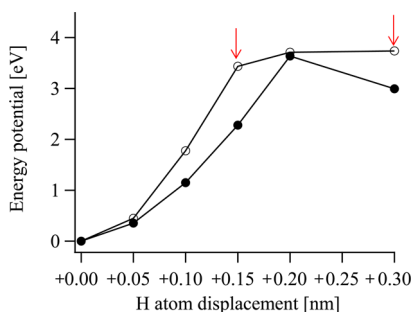

Figure 3. Potential energy of H as a function of the displacement from the surface of TiO$_2$(110) under an electric field as calculated using DFT. Open circles, 0.0 V/nm; filled circles, 4.5 V/nm.

forces can be eliminated because the thermal energy is not changed by tip position and the van der Waals/chemical forces are not dependent on the applied electric field. Finally, the possibility of electric field excitation was considered. We estimated the electric field generated in our experimental condition by carrying out simulations using a tip−sample distance of 0.4 nm at $V_s = +1.0$ V,[35] with the SEMTIP program developed by Feenstra.[36] The electric field for the threshold energies of the shifted region (−0.1 < TD < +0.1 nm) was estimated to be 3.25−4.00 V/nm. However, the reaction barrier obtained by the DFT calculation under the electric field (3.6 eV at 4.5 V/nm; black filled circles in Figure 3) is not lower than the thermal activation energy estimated from the Arrhenius equation using the experimental condition (0.15−0.19 eV at 78 K assuming that reaction rates and frequency factor are 1−100 s^{-1} and 1×10^{12} s^{-1}, respectively[37]). We conclude therefore that the reaction cannot be caused by electric field excitation. Based on the above discussion, we conclude that the reaction cannot be caused by any one of these excitation processes.

Then, how does this reaction proceed? From the calculated potential curve under an electric field, it was found that while the *height* of the reaction barrier does

not change significantly, either side of the maximum point (i.e., the points indicated by red arrows in Figure 3) decreases as a result of the applied field. The energy gain in the potential curve is caused by ionization of the desorbed H and variability of the valence state and bond distance of Ti and O in the applied electric field (Supporting Information section 4). This means the barrier *width* is reduced by the electric field and this may open up a tunneling channel for the desorption of H. In addition to this, the tunneling electrons injected by the STM tip also excite the adsorbed hydrogen into electronic or vibrational states part way up the energy barrier at which point the barrier width is narrower, thereby further increasing the tunneling probability. From the calculation of potential curves with and without applied electric field, therefore it is suggested that STM tip-induced H desorption is caused by a H tunneling reaction (for the effects of the tip on the reaction barrier, see Supporting Information section 5).

To test this tunneling desorption mechanism further, we used STM-AS to measure any isotope effect on the reaction yield. STM-AS of D desorption from TiO$_2$(110) showed a significant decrease ($\approx 10^{-4}$) in the reaction yield at $V_s = +1.8$ V (black filled square and curve in Figure 4a) compared with H desorption (blue filled square and curve in Figure 4a). A theoretical model was used to quantitatively explain the isotopic shift of the tunneling desorption. H on the O$_b$ of TiO$_2$ is positively charged, with the hydrogen being attached to the O site through a bond with some ionic character.[37,38] The hydrogen feels an electric potential $-\alpha eEx$ from the STM tip when the sample voltage is positive, where α is a constant showing the valency of hydrogen, e is the elementary charge, E is the electric field, and x is the position of the hydrogen. We modeled the system as an energy-potential well represented by the potential curve shown in Figure S4. We assume that the hydrogen receives energy, ε, from the tunneling electrons flowing from the STM tip to the
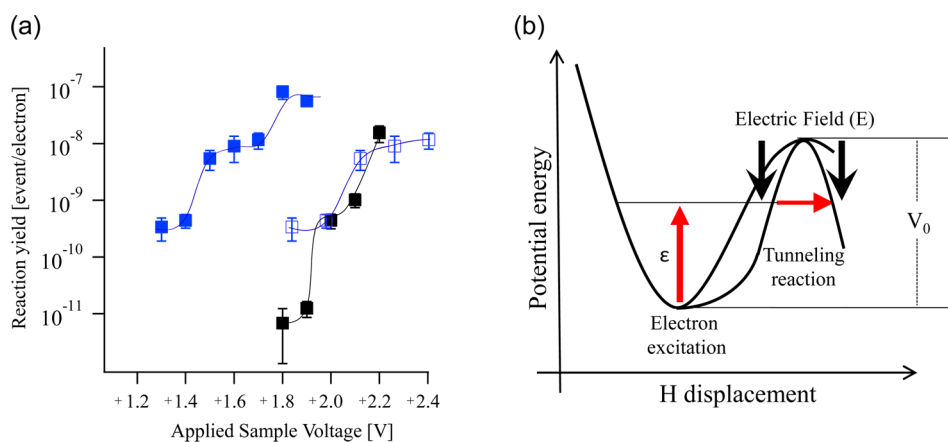
Figure 4. (a) STM-AS measurements of the desorption of single H (blue filled squares) and single D (black filled squares) from TiO$_2$(110). STM-AS results for H are also replotted with the applied electric field multiplied by $\sqrt{2}$ (blue open squares). Initial tip position was V_s = +1.0 V, I_t = 0.02 nA. (b) Schematic energy diagram for H desorption on TiO$_2$(110).

sample. Using the Wentzel−Kramers−Brillouin (WKB) approximation,[39] the tunneling probability for the hydrogen desorption denoted by T is expressed by

$$T = \exp\left\{ -\frac{8\pi\sqrt{2m}}{3heE}(V_0 - \varepsilon)^{3/2} \right\} \qquad (1)$$

where h is the Planck constant, m is the mass of hydrogen, V_0 is the reaction barrier (for detail, see Supporting Information section 6). Equation 1 gives the dependence of T on m, so that with the mass of D being twice that of H, the multiplier factor of the exponential will increase by $\sqrt{2}$ given that the isotopic element does not change electronic properties such as V_0. Figure 4a shows the H desorption yield spectrum together with the same spectrum replotted with the electric field multiplied by $\sqrt{2}$. The replotted spectrum (blue open squares and curve in Figure 4a) appears to reproduce that obtained for D desorption (black filled squares and curve in Figure 4a), thus confirming that STM tip-induced H desorption on TiO$_2$(110) is indeed due to the proposed tunneling reaction which results from the narrowing of the barrier width by the electric field together with excitation by the tunneling electron (Figure 4b).

Previously, Acharya et al. reported a vibrational excitation mechanism for H desorption on TiO$_2$(110) based on their STM-AS measurements.[40] They observed (A) no threshold energy, (B) no isotope effects on the reaction yield, (C) no tip position dependence of the reaction yield, and (D) a reaction order ≈1.7, which we did not observe in our experiments. Observation (A) might be caused by different energy resolutions between the different experiments (current detection circuit, vibration and scanner noise, etc.), whereas

observations (B)−(D) are probably caused by different tip positions in our experiments. The STM-AS experiments in ref 40 were measured with V_s = +1.7 V and I_t = 0.5−5 nA. In our experiments, the tunneling reaction was observed with V_s = +1.0 V and I_t = 0.001−0.5 nA (TD = +0.1 to −0.1 nm). Thus, in the earlier work,[40] a much closer tip sample distance was used and in that regime, H desorption is caused by vibrational state excitation leading to observations (B)−(D) in ref 40. We note that when we displace the tip toward the sample by more than −0.1 nm (TD = −0.1 to −0.2 nm, Figure 2), we also did not observe any further shift of STM-AS.

The saturation of the shift as the tip approaches closer to the surface and the origin of the two threshold energies in STM-AS (Figure 2) are not completely understood so far. The former is probably related to the formation of a chemical bond of the tip with H on TiO$_2$(110) and the latter probably related to the electric field that narrows the width of the desorption barrier (see Supporting Information section 7).

CONCLUSION

We have investigated the reaction mechanism of the desorption of single hydrogen on the surface of TiO$_2$(110) by STM-AS and DFT calculation under an electric field. Our results clearly shows the new reaction mechanism of defect control on TiO$_2$(110) by a narrowing of the desorption barrier due to the electric field, together with electron excitation. Understanding the role of the tunneling reactions of H may be important for the application of TiO$_2$ and related materials in electronic devices.[1−8,41−43]

METHODS

The experiments were performed with a low temperature STM (Omicron GmbH) housed in an ultrahigh vacuum chamber

(base pressure: 4×10^{-9} Pa). The TiO$_2$(110) samples (Shinkosha, Co. Ltd.) were cleaned by cycles of Ar$^+$ sputtering (1 keV, 10 μA for 10 min) and annealing (900 K for 10 min). The density of O$_{vac}$

on pristine TiO_2(110) was 9%. After cleaning, a small amount (1×10^{-8} Pa for 3 s) of H_2O (or D_2O) was dosed in the chamber to form H (or D) on the surface. All STM results were obtained at 78 K with electrochemically etched tungsten tips.

To analyze the reaction mechanism, we used DFT calculations of the charged surface under an electric field. The DFT calculations were performed using the Tokyo *ab initio* program package (TAPP).[44] We employed the Perdew–Burke–Ernzefhof (PBE) functional as the exchange correlation term,[45] ultrasoft pseudopotentials,[46] and a plane wave basis set. In order to examine the effect of an electric field, the field-induced charge-sheets method was implemented in the DFT calculations.[47] In this method, electrons are subtracted from the slab to realize the positively charged surfaces, and negatively charged counter sheets are inserted in the vacuum regions to maintain overall charge neutrality. The TiO_2(110) surface is modeled by a re-peated (1×2) slab made of five TiO_2 trilayers. Single H adsorbs on the surface O site of the slab.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Experimental details and theoretical methods, electronic structure of H/TiO_2(110), reaction order of H desorption on TiO_2(110), reduction of the barrier width for H desorption on TiO_2(110), effects of the STM tip on the desorption of H from TiO_2(110), tunneling probability of H desorption and saturation of the energy shift, and the origin of the threshold energies in the STM-AS measurements. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b01607.

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