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 (Ovac), 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 annealing11 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 Ovac 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].\textsuperscript{17–19} Also, heating by electrons causes reaction in electron excitation [3, manipulation by local heating].\textsuperscript{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]\textsuperscript{21} or electric field to reduce the height of the reaction barrier [5, electric field excitation]\textsuperscript{22–24} have been utilized to manipulate atoms/molecules. Here, we provide insight into such reaction mechanisms for manipulation of defects on TiO\textsubscript{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.\textsuperscript{16–19} H desorption on TiO\textsubscript{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,\textsuperscript{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\textsubscript{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\textsubscript{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\textsubscript{b}), respectively.\textsuperscript{1–8,14,15} After applying a $V_{t} = +1.7$ 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.\textsuperscript{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 $V_{t} = +1.0$ 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\textsubscript{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 shift of the threshold energy originally at $V_{s} = +1.7$ V to $V_{s} = +2.0$ V (red filled circles and curve).\textsuperscript{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,\textsuperscript{16} [2] multiple vibrational state excitation for overcoming the reaction barrier,\textsuperscript{17–19,25,26} [3] thermal reaction caused by local heating,\textsuperscript{20} [4] direct manipulation by means of van der Waals/chemical forces,\textsuperscript{21} and [5] electric field excitation for reduction of the reaction barrier.\textsuperscript{22–24} To assess the possibility of electronic state excitation of antibonding states, $d/dV$ measurements were performed on H/TiO\textsubscript{2}(110) as a function of TD. No electronic states were observed in $d/dV$ curves that correspond with the threshold energies observed in STM-AS (Figure S1). Also, the shift of the threshold energies ($\approx$3.0 V/nm in $-0.1$ to $+0.1$ nm of TD) in STM-AS did not match with the shift in $d/dV$ spectra ($\approx$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\textsubscript{2}(110) is 0.457 eV (3690 cm\textsuperscript{-1}).\textsuperscript{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.\textsuperscript{32} In addition, the possibility of local heating and direct manipulation by means of van der Waals/chemical
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 with the SEMTIP program developed by Feenstra. The electric field for the threshold energies of the shifted region ($0.1 < \Delta D < 0.1$ 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 $1 \times 10^{12}$ s$^{-1}$, respectively). 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$_6$ of TiO$_2$ is positively charged, with the hydrogen being attached to the O site through a bond with some ionic character. The hydrogen feels an electric potential $-\varepsilon E_\text{tip}$ from the STM tip when the sample voltage is positive, where $\varepsilon$ is an 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 5a. We assume that the hydrogen receives energy, $\varepsilon$, from the tunneling electrons flowing from the STM tip to the

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., $\Delta D = 0$ nm). All other spectra have the same start parameters but with different $\Delta D$. Red filled circles: $\Delta D = 0.1$ nm. Green filled triangles: $\Delta D = 0.04$ nm. Orange filled circles: $\Delta D = 0.10$ nm. Purple filled squares: $\Delta D = 0.14$ nm. Black filled triangles: $\Delta D = 0.20$ nm. (b) Threshold energy observed in STM--AS depending on $\Delta D$.

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.
sample. Using the Wentzel–Kramers–Brillouin (WKB) approximation, the tunneling probability for the hydrogen desorption denoted by $T$ is expressed by

$$T = \exp \left\{ -\frac{8\pi \sqrt{2m}}{3\hbar E} (V_0 - \Phi)^{3/2} \right\} \quad (1)$$

where $\hbar$ 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 $s$, 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. 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 $\approx 1.7$, 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 $V_t = +1.7$ V and $I_t = 0.5$–$5$ nA. In our experiments, the tunneling reaction was observed with $V_t = +1.0$ V and $I_t = 0.001$–$0.5$ nA (TD = $-0.1$ to $-0.1$ nm). Thus, in the earlier work, 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.$^1$–$^3$,$^{41}$–$^{43}$

**METHODS**

The experiments were performed with a low temperature STM (Omicron GmbH) housed in an ultrahigh vacuum chamber (base pressure: $4 \times 10^{-9}$ Pa). The TiO$_2$(110) samples (Shinkosha, Co. Ltd.) were cleaned by cycles of Ar$^+$ sputtering (1 keV, 10 $\mu$A for 10 min) and annealing (900 K for 10 min). The density of O$_{\text{vac}}$. 

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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 $V_t = +1.0$ V, $I_t = 0.02$ nA. (b) Schematic energy diagram for H desorption on TiO$_2$(110).
on pristine TiO$_2$(110) was 9%. After cleaning, a small amount (1 × 10$^{14}$ Pa for 3 s) of H$_2$O (or D$_2$O) 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 adsorption 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$^{46,47}$). We employed the Perdew–Burke–Ernzerhof (PBE) functional as the exchange correlation term,$^{48}$ ultrsoft 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 repeated (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.

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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/acs.nano.5b01607.

REFERENCES AND NOTES


30. An additional threshold at lower energy could not be observed because of the low tunneling current.


32. DFT calculations using the GGA functional underestimate the energy barrier.$^{33,34}$ The true energy barrier should be higher than 3.5 eV.


Supplemental Information for

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§1. Experimental details and theoretical methods

The experiments were performed using a low-temperature STM system (Omicron GmbH) consisting of two chambers separated by a gate valve. TiO$_2$(110) single crystals (Shinkosha Co. Ltd.) were transferred to the preparation chamber without any pre-treatment. The TiO$_2$(110) samples were cleaned in the preparation chamber (base pressure: $7 \times 10^{-7}$ Pa) via cycles of Ar$^+$ sputtering (at 1 keV and 10 μA for 10 min) and annealing (at 900 K for 10 min). After cleaning, the TiO$_2$(110) was transferred to the STM chamber (base pressure: $4 \times 10^{-9}$ Pa), where it was placed on a gas-dosing stage. A small amount ($1 \times 10^{-8}$ Pa for 3 sec) of H$_2$O (or D$_2$O) was introduced to the dosing stage at room temperature to allow H (or D) to form on the surface. After H$_2$O (or D$_2$O) exposure, the TiO$_2$(110) was transferred to the STM stage, which was maintained at 78 K. All STM results were obtained using electrochemically etched tungsten tips.

To record the action spectroscopy measured via STM (STM-AS), the STM tip was placed above the H (or D) on the TiO$_2$(110) surface while an electrical bias was applied. The tunneling current ($I$) was monitored using an oscilloscope while the bias was applied. The I signal decreased rapidly when desorption of H (or D) from the TiO$_2$(110) surface occurred. The reaction yields ($Y$) and reaction rates ($R$) were calculated as follows:

$$Y = \frac{e}{I \times t}$$

$$R = \frac{1}{t}$$

where $e$ is the elementary charge and $t$ is the duration of the applied electric bias, calculated from the onset of the applied bias until desorption. The error bars of $Y$ ($Y_{error}$), $R$ ($R_{error}$) and $I$ ($I_{error}$) in Figure 2 and Figure S2 were calculated as follows:

$$Y_{error} = \pm \sqrt{\frac{1}{N} \sum_{i=1}^{N} (Y_i - Y_{av.})^2}$$

$$R_{error} = \pm \sqrt{\frac{1}{N} \sum_{i=1}^{N} (R_i - R_{av.})^2}$$

$$I_{error} = \pm \sqrt{\frac{1}{N} \sum_{i=1}^{N} (I_i - I_{av.})^2}$$

where $N$ is the total number of data; $Y_i$, $R_i$, and $I_i$ are the values of $Y$, $R$, and $I$ in each measurement; and $Y_{av.}$, $R_{av.}$, and $I_{av.}$ are the average values of $Y$, $R$, and $I$.

DFT calculations were performed using the Tokyo Ab-initio Program Package (TAPP)$^1$. We employed the Perdew-Burke-Ernzerhof (PBE) functional as the exchange-correlation term$^2$, ultrasoft pseudopotentials to describe the ionic cores$^3$ and a plane-wave basis set with a cut-off energy of 25 Ryd to expand the wave functions of the valence electrons. The TiO$_2$(110) surface was modeled using a repeated (1 × 2) slab composed of five TiO$_2$ trilayers separated by a vacuum space equivalent to 1.3 nm. A single H was adsorbed onto the surface O site of the slab. A $(4 \times 4 \times$...
1) Monkhorst-Pack mesh was used for k-point sampling in the Brillouin zone\(^4\). The slab was relaxed until the force on each atom was below 0.005 Hartree/a.u. with the center trilayer of the slab held frozen in the optimized geometry. The reliability of the parameters was confirmed by evaluating the lattice parameters, and the discrepancy with respect to the experimental values was found to be less than 3\%. The field-induced charge-sheets (FICS) method was implemented in the DFT calculations to examine the effect of an applied electric field\(^5\). In this method, electrons are subtracted from the slab to model positively charged surfaces, and negatively charged counter sheets are inserted into the vacuum regions to maintain overall charge neutrality. Unrealistic interactions between the repeated charged slabs are effectively removed by artificially inserting counter sheets into vacuum regions because the density of the counter sheets varies to screen the electric field of the charged slab. Thus, one can accurately calculate the total energy and electronic states of charged surfaces. The FICS method offers several advantages in terms of the stability of the convergence in the electronic states, its ease of implementation and its accuracy compared with other methods of charged-surface calculation\(^6\)\(^-\)\(^8\). We set a parameter of width of the counter sheets at 0.5 Bohr.
§2. Electronic structure of H/TiO$_2$(110)

Figure S1 presents scanning tunneling spectra (STS) of H/TiO$_2$(110) for a range of different sample-tip distances. On TiO$_2$(110), which is an n-type semiconductor, STS spectra acquired with positive sample bias exhibit an energy shift as a function of the sample-tip distance because of tip-induced band bending$^{9-12}$. No electronic states corresponding to the threshold energies observed in the STM-AS results (Fig. 2) are observable. This finding demonstrates that the STM-tip-induced H desorption from TiO$_2$(110) is not caused by the excitation of an anti-bonding state.

Figure S1. Scanning tunneling spectra obtained on H/TiO$_2$(110) for various tip-sample distances. Blue curve: tip displacement (TD) = 0 nm ($V_s$ = +1.0 V and $I_t$ = 0.02 nA); green curve: TD = -0.04 nm; yellow curve: TD = -0.10 nm; gray curve: TD = -0.14 nm; purple curve: TD = -0.20 nm. All spectra were normalized by dividing by I/V.
§3. Reaction order of H desorption on TiO$_2$(110)

The reaction barrier for H desorption on TiO$_2$(110) is 3.7 eV (Fig. 3). Multiple excitations are necessary to overcome the reaction barrier *via* vibrational excitation because no single vibrational excitation is higher than 3.7 eV (*e.g.*, the OH stretching vibration of H/TiO$_2$(110) is only 0.457 eV$^{12}$). Figure S2 presents the reaction rates and reaction yields of hydrogen desorption from the TiO$_2$(110) surface at $V_\text{s} = +1.6$ V. From these results, the reaction order ($N$) of this reaction was found to be 1.057. This means that the reaction occurs *via* single-electron excitation and that the desorption of H from TiO$_2$(110) is not induced by multiple vibrational excitations.

![Figure S2](image_url)

*Figure S2.* (a) Reaction rates and (b) reaction yields of H desorption from the TiO$_2$(110) surface obtained at $V_\text{s} = +1.6$ eV.
§4. Reduction of the barrier width for H desorption on TiO$_2$(110)

When an electric field (positive sample bias) is applied to TiO$_2$(110), the width of the reaction barrier for H desorption is reduced, as indicated by the arrows in Fig. 3. These features can be explained by the following mechanisms due to the two effects of the electronic field on the potential curve.

In the neutral state of the hydrogenated TiO$_2$(110) surface, the H on the O$_b$ site forms (H-O$_b$)$^-$, which indicates an excess electron associated with the H is provided to the surface. Based on charge-distribution analysis (Fig. S3a), this excess electron redistributes onto Ti sites beneath the O$_b$ sites, and consequently it weakens the ionic bonds between Ti$^{4+}$ and O$_b$$^2$. In the process of the H desorption, the O$_b$ is also displaced toward the vacuum to keep the form (H-O$_b$) unit.

When a positive electric field is applied on the surface, in the region around the +0.30 nm (or larger than +0.30 nm) displacement of the H in Fig. 3, the protonated H is completely separated from the O$_b$$^2$. The desorption H takes an energy gain by the positive electrostatic filed. This energy gain accounts for the reduction of the barrier width in this region. In the region around the +0.15 nm (or shorter than +0.15 nm) displacement of the H, the positively charged surface decreases the amount of the excess electron on the Ti sites, because the excess electron lies nearest to the Fermi level of the H/TiO$_2$(110) system (as a typical example, in case of no displacement of H is indicated in Fig. S3b). This decrease of the excess electrons causes a recovery in the stiffness of the weakened O$_b$-Ti ion bond; that is, the Ti sites are able to stretch more to follow the desorbing (H-O$_b$) unit. Indeed, Fig. S4 presents that the elongation of bond length between Ti and O$_b$ of O$_b$H in the H desorption process is suppressed by the positively charged effect. The flexibility of the Ti sites in the desorption process enhances the electrostatic energy gain because the Ti$^{4+}$ sites is close to the counter STM tip that is charged up negatively. Thus, the barrier width is reduced by applying a positive charge on the TiO$_2$ surface.

Fig. S3. Distribution of excess electron (a) in the neutral state and (b) in applying 4.5 V/nm electric field on H/TiO$_2$(110). In (b), the density of the excess electron is decreased. These figures are obtained by subtraction of the electron distribution of the clean TiO$_2$ surface from that of the H/TiO$_2$ surface. The cross section in (a) and (b) go along the O$_b$ line in the surface normal direction, that is denoted by the horizontal line in (c).
Fig. S4. Variations of the bond length between Ti and O₈ of O₈H in the H desorption process. Open circles: 0.0 V/nm; filled circles: 4.5 V/nm.
§5. Effects of the STM tip on the desorption of H from TiO$_2$(110)

The H that desorbs from the TiO$_2$(110) adsorbs on the STM tip. Therefore, the effects of the tip on the potential curve for H desorption must be considered. As the tip approaches the TiO$_2$(110) surface, the potential curves for H on TiO$_2$ and on the tip begin to cross. The crossing of the potential curves decreases the height of the reaction barrier for H desorption, thus increasing the tunneling probability for H desorption. However, if the effect of the tip on the potential curve only determines the reaction barrier, then the threshold energies observed in the STM-AS measurements (Fig. 2) at a fixed tip-sample distance should be triggered by the excitation of electronic or vibrational states by the tunneling electrons. As shown in Fig. S1, no electronic states were observed in the STS results at the STM-AS threshold energies. As for vibrational excitation, the observed threshold energies (1.2 – 2.0 eV = 9679 – 16131 cm$^{-1}$) are too large for the vibrational states of H/TiO$_2$(110). These results indicate that the reaction barrier is not only determined by the effects of STM tip on the potential curve of the H desorption on TiO$_2$(110).
§6. Tunneling probability of H desorption

The model from which Eq. 1 is derived is explained in detail here. For an isotopic analysis of the tunneling desorption, we used a simple energy-potential well model under an applied electric field, as illustrated in Fig. S5. In this model, the hydrogen on TiO$_2$(110) is a positive ion. We assume that the protonated hydrogen has a charge of $+\alpha e$ and is bound within a potential well, in which the potential inside the TiO$_2$(110) is represented by an infinite wall and there is an energy barrier of $V_0$, representing the desorption energy, at $x = 0$. In the region of $x > 0$, an electric field, $E$, is applied between the TiO$_2$(110) and the STM tip. We assume that the hydrogen receives energy, $\epsilon$, from the tunneling electrons from the STM tip and that the received energy is converted into the excitation of hydrogen vibrations. Here, we use a classical limit of quantum theory called the Wentzel-Kramers-Brillouin (WKB) approximation\(^\text{13}\). The probability of the hydrogen tunneling toward $x > 0$ can be written as follows:

$$T = \exp \left[-\frac{4\pi}{\hbar} \int_0^a dx \sqrt{2m(-\alpha eEx + V_0 - \epsilon)} \right] - (S1)$$

where $\hbar$ is the Planck constant, $m$ is the mass of hydrogen, and $a$ is its position after the tunneling reaction. Equation S1 can be solved analytically as follows:

$$T = \exp \left\{ -\frac{8\pi\sqrt{2m}(V_0 - \epsilon)}{3\alpha eE(V_0 - \epsilon)^2} \right\}.$$  

This equation is the same as Eq. 1 in the main text.

![Figure S5](image-url)  
**Figure S5.** Schematic potential-energy diagram used in the estimation of the tunneling probability for hydrogen desorption. The yellow ball represents the terminal hydrogen on TiO$_2$(110).
§7. Saturation of the energy shift and the origin of the threshold energies in the STM-AS measurements

The saturation of the shift in the STM-AS threshold energies as the tip approaches the surface (Fig. 2) cannot be completely understood thus far. One possible explanation is that as the STM tip (tungsten (W)) approaches the sample, the tip makes a chemical bond with the H on the TiO$_2$(110). As the tip continues to draw closer, the W-H-O bond distorts. This distortion may not affect the H desorption behavior. Therefore, the STM-AS measurements do not shift as the tip continues to approach.

Moreover, the origins of the two threshold energies observed in the STM-AS results also remain unclear. The threshold energies observed at a fixed tip-sample distance (Fig. 2) are not directly related to electronic or vibrational states. The reduction of the width of the reaction barrier by electric field would be related to the two threshold energies.
References
13 Bohm, D.; Quantum Theory, Dover New York, **1989**.