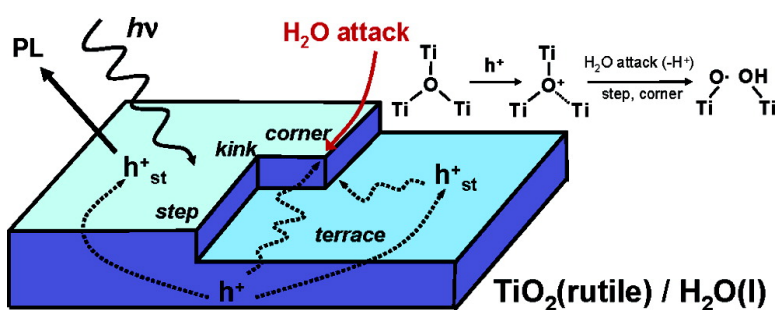


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Molecular Mechanisms of Photoinduced Oxygen Evolution, PL Emission, and Surface Roughening at Atomically Smooth (110) and (100) *n*-TiO₂ (Rutile) Surfaces in Aqueous Acidic Solutions

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Abstract: The success in preparing atomically smooth and stable (110) and (100) TiO₂ (rutile) surfaces, combined with in situ photoluminescence (PL) and photocurrent measurements as well as atomic force microscopic (AFM) inspection, has enabled us to make systematic studies on molecular mechanisms of oxygen photoevolution and related processes on TiO₂ (rutile), which are important for solar water splitting and photocatalytic environmental cleaning. The studies have revealed that various surface processes and properties, such as the flat-band potential (U_{fb}), the spectrum and intensity of the PL from a precursor of the oxygen photoevolution reaction, and photoinduced surface roughening, have all strong dependences on the atomic-level structure of the TiO₂ surface. Importantly, all the results have been explained on the basis of our recently proposed new mechanism that the oxygen photoevolution reaction is initiated by a nucleophilic attack of an H₂O molecule to a surface-trapped hole, thus giving confirmative evidence to it. The molecular mechanisms for photoinduced primary processes at the TiO₂ surface, clarified in the present work, will provide a typical model for photoreactions on metal oxides in contact with aqueous solutions.

Introduction

The oxygen photoevolution (or water-photooxidation) reaction at the surfaces of TiO₂ and related metal oxides^{1–4} has been attracting strong attention from the point of view of solar energy conversion (solar water splitting). This reaction has also attracted much attention in view of photocatalytic environmental cleaning^{5–9} because primary intermediate radicals of this reaction at the surface are believed to play a crucial role in photodecomposition of soiling or harmful organic materials. Much effort has been done to find efficient and stable photoactive reaction systems, including elucidation of the molecular mechanisms, but the present achievements are still far from the final goal.

For clarifying definite molecular-level mechanisms, it is obviously of key importance to use atomically well-defined

metal-oxide surfaces as samples and to adopt in situ spectroscopic techniques for detecting directly reaction intermediates. To date, a large number of studies have been made on the mechanism of the oxygen photoevolution reaction, using various spectroscopic methods, such as ESR,^{10–16} time-resolved laser absorption,^{17–24} FTIR,^{25–29} photoluminescence (PL),^{30–36} sum

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frequency generation (SFG),^{37–39} and ¹H NMR,^{40–42} but it seems that none of them has met both the conditions mentioned above, most probably because of the difficulty in preparing atomically well-defined and stable metal–oxide surfaces. A method of Ar⁺ ion sputtering and thermal annealing under ultrahigh vacuum (UHV) conditions has often been used to prepare the atomically well-defined surfaces,⁴³ but it is reported recently that atomically flat TiO₂ (rutile) (110) surfaces prepared by this method become morphologically rough after exposition to neutral and alkaline aqueous solutions,⁴⁴ indicating that the surfaces of this type are unstable in aqueous solutions.

In a very recent letter,⁴⁵ we have reported that atomically smooth and stable (110) and (100) TiO₂ (rutile) surfaces can be prepared by a novel method of chemical etching and annealing.⁴⁶ This success, combined with in situ spectroscopic methods, has enabled us to elucidate molecular mechanisms of photoinduced surface processes on an atomic level.⁴⁵ In the present work, we have, for the first time, made systematic studies on the molecular mechanism of oxygen photoevolution reaction, using the atomically smooth and stable (110) and (100) *n*-TiO₂ (rutile) surfaces.

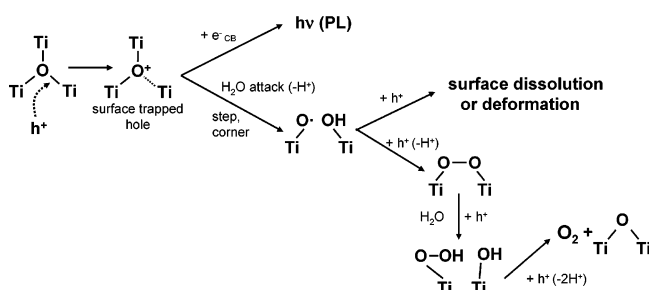
As to the molecular mechanism of the oxygen photoevolution reaction, it has long been assumed^{5–7,10–12,17,47–57} that the reaction is initiated by electron-transfer-type oxidation of either OH[−] (or H₂O) in solution or Ti–OH at the surface by photogenerated holes



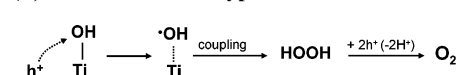
probably by a strong influence of recent prominent progress of electron transfer theory by Marcus, Levich, Gerischer, and others.⁵⁸ The resultant [•]OH or [Ti [•]OH]_s⁺ radicals are usually assumed to recombine with each other, producing H₂O₂, which may further be oxidized by the holes to molecular oxygen.^{48–51} The resultant [•]OH or [Ti [•]OH]_s⁺ radicals have also been regarded as a key intermediate for photocatalytic degradation of organic

Scheme 1. (A) New Mechanism^{59,60} and (B) Conventional Ti–OH Oxidation Mechanism for the Oxygen Photoevolution Reaction at the TiO₂ Surface in Contact with an Aqueous Electrolyte

(A) Lewis acid-base type reaction

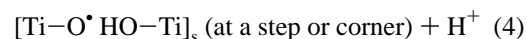
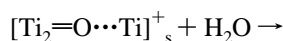
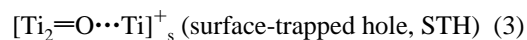
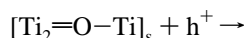


(B) Electron transfer type reaction



compounds at the TiO₂ surface.^{5–7} The [•]OH radical-driven mechanism, in fact, often appears in the literature^{5–7} to explain photodegradation of various organic compounds in TiO₂ photocatalysts.

On the other hand, we have recently reported^{59,60} that the oxygen photoevolution reaction is not initiated by the electron-transfer-type oxidation, but initiated by a nucleophilic attack of an H₂O molecule (Lewis base) to a surface-trapped hole (STH, Lewis acid), accompanied by bond breaking. The processes are schematically represented, including the results of the present work, as follows.



where [Ti₂=O–Ti]_s refers to a triply coordinated O atom in surface crystal lattice. The STH can be regarded as a relaxed hole at the surface. The further details of this mechanism are shown in Scheme 1, compared with the conventional Ti–OH oxidation mechanism.

The presence of the STH was proposed^{30–35,59,60} by observation of a PL band peaked at 840 nm, which was assigned to an electronic transition from the conduction band to a vacant O-2p level of the STH. The assignment of the STH (the PL species) as the precursor of oxygen photoevolution reaction was given³⁵ by experiments on the PL quenching by various reductants added

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to the electrolyte, in which reductants, which quenched the PL efficiently, suppressed efficiently the oxygen photoevolution, as well. The new mechanism (mechanism A of Scheme 1) was verified by many experimental results, such as the crystal-face dependence of the photoetching quantum yield or the selective exposure of the (100) face after photoetching,⁵⁹ in situ detection of surface peroxide intermediates by multiple internal reflection FTIR spectroscopy,^{60,61} and an estimation⁶⁰ of the energy levels for surface Ti–OH and solution OH[−] relative to the valence band by use of ultraviolet photoelectron spectra (UPS).^{62–64} The mechanism was further supported by studies on the water–photooxidation reaction on visible light responsive, nitrogen-containing metal oxides, such as N-doped TiO₂⁶⁵ and TaON.⁶⁶ These materials have a similar band structure, composed of an O-2p valence band and an N-2p valence band located considerably above the O-2p valence band. Visible light illumination will generate holes in the N-2p valence band, and it is quite difficult to assume process 1 or 2 for such N-2p holes with low energies.

The key of the new mechanism is that the oxygen evolution reaction proceeds via a Lewis acid–base mechanism (process 4), not by an electron-transfer mechanism (process 1 or 2).^{59,60} The energetics and kinetics for the former mechanism are quite different from those for the latter. In particular, in the former mechanism, the rate of the oxygen photoevolution has no direct relation with the redox potentials for one-electron-transfer processes such as Ti–OH → Ti•OH⁺ + e[−], H₂O → •OH + H⁺ + e[−], and OH[−] → •OH + e[−], though these quantities play the key role in the latter electron-transfer mechanism.^{65,66} The rate of the oxygen photoevolution reaction in the former Lewis acid–base mechanism is determined by the activation energy (Δ*G*[‡]) for process 4, that is, the formation of an intermediate radical [Ti–O•HO–Ti]_s, which will be governed mainly by the distortion energy in surface lattice for inserting OH into a Ti–O–Ti bond, as well as the atomic and the orientation polarization energies for solvent water molecules and the adsorption energies for the O• and HO[−] species. It is not unreasonable to assume that the Δ*G*[‡] for process 4 can be made much lower by the atomic and the orientation polarization energies and the adsorption energies if the distortion energy in surface lattice is diminished by reaction occurring at a surface step or corner, not at a terrace. We have to note that even in the Lewis acid–base mechanism, the redox level for the surface-trapped hole (STH), which is expected to lie between the STH level estimated from the PL spectrum and the top of the valence band, should be below the equilibrium redox level for the whole water–oxidation reaction, 2H₂O → O₂ + 4H⁺ + 4e[−]. It is to be noted also that the Ti–O• radical in [Ti–O•HO–Ti]_s will still have an ability to initiate decomposition of organic compounds for photocatalytic organic degradation.

The present work has thus been done with an emphasis placed on clarifying how the atomic-level structure of the TiO₂ surface

affects the rate of the oxygen photoevolution reaction, using the atomically smooth and stable (110) and (100) TiO₂ (rutile) surfaces. If mechanism A of Scheme 1 is true, the rate of the oxygen photoevolution reaction (or the intensity of the PL as the competitive process with it) is expected to show strong dependences on the atomic-level structure of the surface because process 4 should be highly sensitive to the atomic-level structure of the surface. This expectation was really proved by experiments.

Experimental Section

Single-crystal TiO₂ (rutile) wafers, 10 mm × 10 mm in area and 1.0 mm thick, doped with 0.05 wt % niobium oxide and having the (100)- and (110)-cut and alkali-polished surfaces, were obtained from Earth Chemical Co., Ltd. The Nb-doped specimens were of n-type, as they were, with no pretreatment, because doped Nb⁴⁺ acted as an electron donor. The atomically smooth surfaces were obtained by a procedure of washing with acetone, immersing in 20% HF for 10 min, washing with water, drying in a nitrogen stream, and then annealing at a temperature from 550 to 900 °C for 1–2 h in air. X-ray photoelectron spectroscopic (XPS) analysis showed that no fluorine atom was left at the surface after the above procedure.

Photocurrent density (*j*) versus potential (*U*) curves for single-crystal *n*-TiO₂ electrodes were measured with a commercial potentiostat and a potential programmer, using a Pt plate as the counter electrode and an Ag/AgCl/KCl_{sat} electrode as the reference electrode. The electrolyte was 0.1 M HClO₄ in all cases. The illumination was carried out by the 365 nm band from a 500 W high-pressure mercury lamp, obtained by use of band-pass filters. The intensity of the UV light was adjusted by a combination of neutral density (metal net) filters and measured with a thermopile (Eppley Laboratory). Photoluminescence (PL) spectra were measured with a multichannel photodiode array detector (Hamamatsu, PMA100) cooled at −20 °C, using the same illumination system as above. The PL intensity (*I*_{PL}) versus *U* and the *I*_{PL} versus time were measured using a photomultiplier (Hamamatsu, R316 or R712) cooled at −20 °C together with a monochromator (Jobin Yvon, H20IR) or cutoff filters. The *I*_{PL} versus *U* was measured simultaneously with the *j*–*U* curve measurements.

The structure of the electrode surface was inspected with an atomic force microscope (AFM, Digital Instruments NanoScope IIIa) at room temperature, the sample being placed in air. All AFM images were obtained in a tapping mode with a silicon tip (Digital Instruments) at a driving frequency of about 280 kHz and a scan rate of 1.5 Hz. The flat-band potential (*U*_{fb}) was determined from Mott–Schottky plots, that is, plots of the inverse square of the differential capacitance (*C*) of the *n*-TiO₂ electrode against the applied electrode potential (*U*). The *C* was measured with a Solartron 1260 impedance analyzer combined with a Solartron 1287 potentiostat at the modulation frequency (*f*) of 10–1000 Hz and the amplitude of 5 mV.

Electrolyte solutions were prepared by use of reagent grade chemicals and pure water, the latter of which was obtained from deionized water with a Milli-Q water purification system. The electrolyte solution was bubbled with N₂ gas to remove dissolved O₂.

Results

Panels a and b of Figure 1 show AFM images of commercially obtained (100)- and (110)-cut *n*-TiO₂ (rutile) surfaces with no surface smoothing treatment, respectively. The surfaces were rough on a scale of a few nanometers, indicating that a variety of crystal faces are exposed at these surfaces with a lot of steps, kinks, and corners. On the other hand, after immersion in 20% HF and annealing at 600 °C for 1 h, both the (100)- and (110)-cut surfaces showed clear step and terrace structures, as shown in panels c and d of Figure 1, respectively. Moreover,

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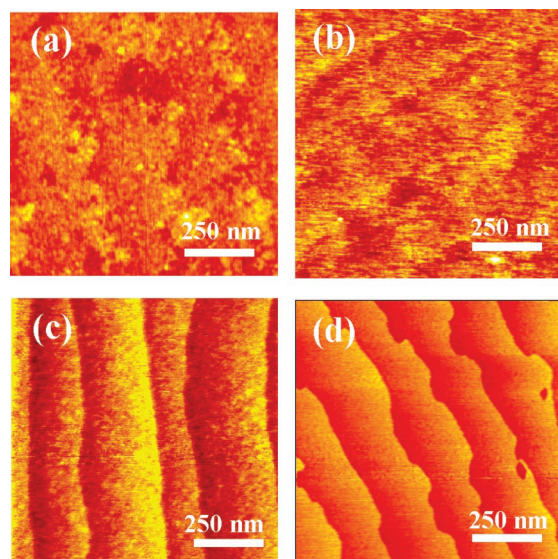


Figure 1. AFM images for commercially obtained (a) (100)- and (b) (110)-cut n -TiO₂ (rutile) surfaces with no surface-smoothing treatment, and those for (c) (100)- and (d) (110)-cut n -TiO₂ (rutile) surfaces after the surface-smoothing treatment of immersion in 20% HF for 10 min and annealing at 600 °C for 1 h in air.

the observed step height was 0.27 nm for the (100) surface and 0.35 nm for the (110) surface, in good agreement with the unit-cell lengths of TiO₂ (100) and (110) faces [0.25 nm for (100) and 0.36 nm for (110)], indicating that atomically smooth (100) and (110) terraces were really prepared.⁴⁵ This conclusion was further supported by LEED (low energy electron diffraction) measurements, in which both the surfaces gave sharp intense (1 × 1) LEED spots indicative of the formation of atomically smooth terraces.⁴⁵ The widths of terraces for the atomically smooth (110) and (100) surfaces in experiments with about 10 samples were nearly the same as those in Figure 1c,d, respectively. The annealing at high temperatures above 900 °C gave AFM images with more regular step lines for both faces, but these surfaces showed low photocurrents compared to the surfaces annealed at 600 °C, suggesting the formation of an inactive (amorphous) surface layer at such a high annealing temperature.⁶⁷

The atomically flat TiO₂ surfaces prepared by the Ar⁺-ion sputtering and thermal annealing under UHV conditions are reported⁴⁴ not to be stable in aqueous solutions, as mentioned in the Introduction. We thus investigated the stability of the atomically smooth surfaces prepared in the present work and confirmed that no change in the surface morphology occurred by exposition to aqueous solutions of pH 1–13. It is likely that the Ar⁺-ion sputtering produces surface damage that cannot be removed by the following annealing treatment.

Figure 2 shows (A) the photocurrent density (j) versus potential (U) and (B) the PL intensity (I_{PL}) versus U for n -TiO₂ electrodes with the atomically smooth (100) and (110) surfaces. The I_{PL} versus U for commercially obtained (110)- and (100)-cut n -TiO₂ electrodes with no surface-smoothing treatment are also included in Figure 2B for comparison. The j versus U for the (110)- and (100)-cut electrodes with no surface-smoothing treatment were nearly the same as that for the atomically smooth (110) electrode. Both the j - U and I_{PL} - U curves were measured

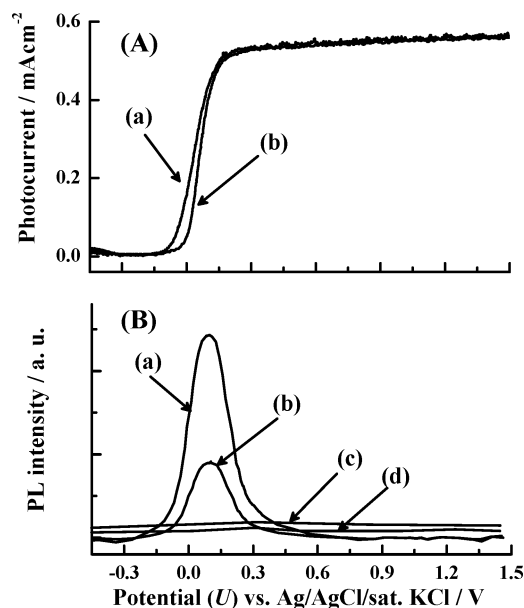


Figure 2. (A) The j versus U and (B) the I_{PL} versus U for n -TiO₂ (rutile) electrodes. The surface morphology: (a) the atomically smooth (100), (b) the atomically smooth (110), (c) the commercially obtained (100)-cut surface with no surface-smoothing treatment, and (d) the commercially obtained (110)-cut surface with no surface-smoothing treatment. The I_{PL} for all of the surfaces was measured by collecting the PL intensities at wavelengths longer than 800 nm (see Figure 3) by use of cutoff filters, under excitation at 365 nm. The electrolyte = 0.1 M HClO₄.

simultaneously in 0.1 M HClO₄ (pH 1.1) in a positive potential scan under UV irradiation with a relatively low intensity of 0.2 mW cm⁻². The low-intensity irradiation was adopted for the following reason. We reported previously⁶⁷ that no photoetching occurred in 0.1 M HClO₄ (or the photoetching occurred only in aqueous H₂SO₄). However, detailed experiments on an atomic level in the present work have revealed that slight surface photoetching (or surface roughening) occurs even in 0.1 M HClO₄ especially under high-intensity illumination, as described in detail later. The surface roughening could be neglected under short-period, low-intensity irradiation.

The onset potential (U_{on}) of the photocurrent for the (100) surface in Figure 2A is about 0.09 V more negative than that for the (110) surface. We reported in a previous letter⁴⁵ that the flat-band potential (U_{fb}) for the (100) surface, determined from Mott–Schottky plots, lay at -0.34 V in 0.1 M HClO₄ (pH 1.0) and about 0.09 V more negative than that for the (110) surface, in agreement with the above U_{on} shift. The positive deviation of the U_{on} from the U_{fb} can be attributed to surface carrier recombination. The parallel shift of the U_{on} from the U_{fb} for the (110) and (100) surfaces implies that the surface carrier recombination is similar for these surfaces.

The PL intensity (I_{PL}) takes the maximum near the onset potential U_{on} of the photocurrent (Figure 2B). This is in harmony with the above argument that the U_{on} is determined by surface carrier recombination because the PL band is assigned to radiative surface carrier recombination, as mentioned earlier (see mechanism A of Scheme 1). The decrease in the I_{PL} at more negative potentials than the U_{on} can be attributed to the formation of reduced surface species, such as Ti³⁺, at these negative potentials,^{31,35} which can trap efficiently the valence-band holes nonradiatively. It is important to note that the I_{PL} from the atomically smooth (100) surface is much higher than

(67) Tsujiko, A.; Kisumi, T.; Magari, Y.; Murakoshi, K.; Nakato, Y. *J. Phys. Chem. B* **2000**, *104*, 4873–4879.

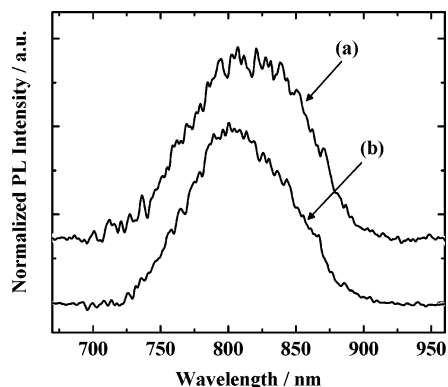


Figure 3. Normalized PL spectra from the atomically smooth (a) (100) and (b) (110) *n*-TiO₂ (rutile) surfaces. The electrolyte = 0.1 M HClO₄.

that from the atomically smooth (110) surface. This difference was reproduced in experiments with about 10 samples. In addition, no PL is observed from the commercially obtained (110)- and (100)-cut surfaces with no surface-smoothing treatment, which have morphologically rough surfaces on an atomic scale (Figure 1a and b). Such a sharp dependence of the I_{PL} on the atomic-level structure of the surface gives strong support to the assignment that the PL band is arising from the STH, as discussed later.

Figure 3 compares the PL spectra from the atomically smooth (100) and (110) *n*-TiO₂ surfaces, as obtained by subtracting the spectral distribution of stray light, measured at 1.5 V, as the background. Both the spectra were observed at 0 V vs Ag/AgCl in 0.1 M HClO₄ under weak illumination at an intensity of 0.2 mW cm⁻². The spectra are normalized to each other at the maximum intensity to see clearly the difference in the spectral shape. They are not corrected for the spectral sensitivity of the multichannel photodiode detector. We can see that the peak of the PL spectrum from the (100) face is at a wavelength somewhat longer than that of the spectrum from the (110) face, indicating that the energy level of the PL emitting species (surface-trapped hole, STH) is different between the (100) and (110) faces. As the energy of the PL spectrum can be regarded to represent the energy difference between the bottom of the conduction band and the energy level for the STH, E_{STH} , the energy level for the STH at the (100) face, $E_{\text{STH}}(100)$, is estimated about 0.14 eV above that at the (110) face, $E_{\text{STH}}(110)$, as shown in Figure 4, by taking into account that the U_{fb} for the (100) face is about 0.09 V more negative than that for the (110) face.⁴⁵

Figure 5 shows how the AFM image of the atomically smooth (110) surface is changed by UV illumination at 1.5 V vs Ag/AgCl in 0.1 M HClO₄ (or by the flow of the water-oxidation photocurrent). The UV illumination was performed at various intensities of 0.04, 1.3, and 50 mW/cm², with the electricity passing across the electrode surface (Q_{p}) being kept constant at 0.5 C/cm². Compared with the atomically smooth (110) surface before illumination (Figure 5a), the surface after illumination with an intensity of 0.04 mW/cm² (Figure 5b) shows a lot of small spots, indicating that the surface is roughened. The surface roughening becomes more and more prominent with increasing the illumination intensity (Figure 5c,d), though the Q_{p} is kept constant, indicating that the illumination intensity (or the flux of photogenerated holes to the surface) is an important factor in causing the surface roughening. It is to be noted, however,

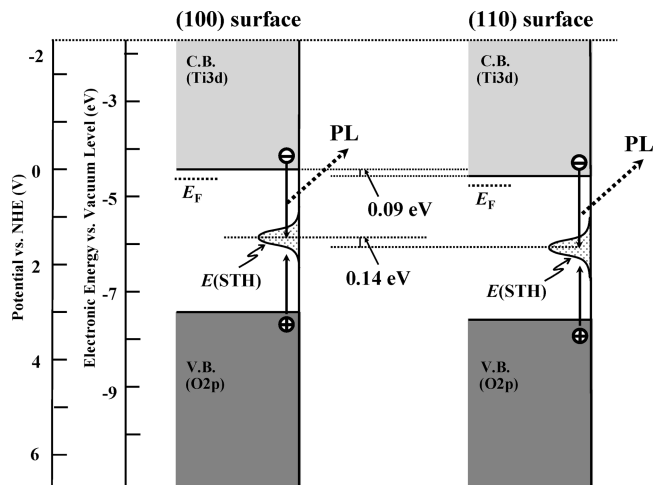


Figure 4. Schematic energy level diagrams for the atomically smooth (100) and (110) surfaces of *n*-TiO₂ (rutile) at pH 0, estimated from the U_{fb} and the PL spectra, with the energy difference between the bottom of the conduction band and the Fermi level in the interior of *n*-TiO₂ being assumed to be 0.2 eV. The potential versus NHE was calculated by use of a relation that 0.00 V vs Ag/AgCl corresponds to 0.20 V vs NHE at 25 °C. C.B. = the conduction band, V.B. = the valence band, - with the circle = electron, and + with the circle = hole, $E(\text{STH})$ = the energy level for the surface-trapped hole.

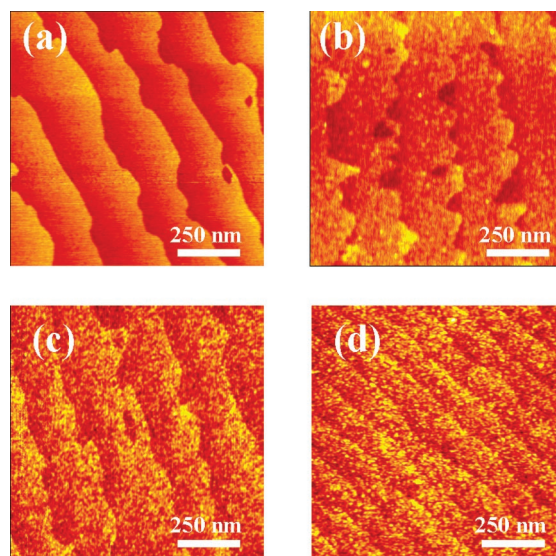


Figure 5. AFM images for the atomically smooth (110) surface (a) before and (b–d) after the flow of the anodic photocurrent in 0.1 M HClO₄. The UV illumination intensity was (b) 0.04, (c) 1.3, and (d) 50 mW/cm², with the electricity passing across the TiO₂ surface (Q_{p}) being kept constant at 0.5 C/cm².

that detailed inspection indicates that the density of the small spots (or the extent of the surface roughening) does not increase in proportion to the illumination intensity and shows a tendency of saturation. The surface roughening did not occur under no anodic bias, indicating that sufficient band bending was another important factor. Essentially the same results were obtained for the atomically smooth (100) surface.

To investigate the influence of the surface roughening on the PL intensity (I_{PL}), we next measured the change in the I_{PL} for the atomically smooth (100) and (110) *n*-TiO₂ surfaces with the illumination time. The I_{PL} was recorded in 0.1 M HClO₄ under continuous illumination, the U being stepped alternately from 0 to 1.5 V and in the inverse direction. The PL is emitted

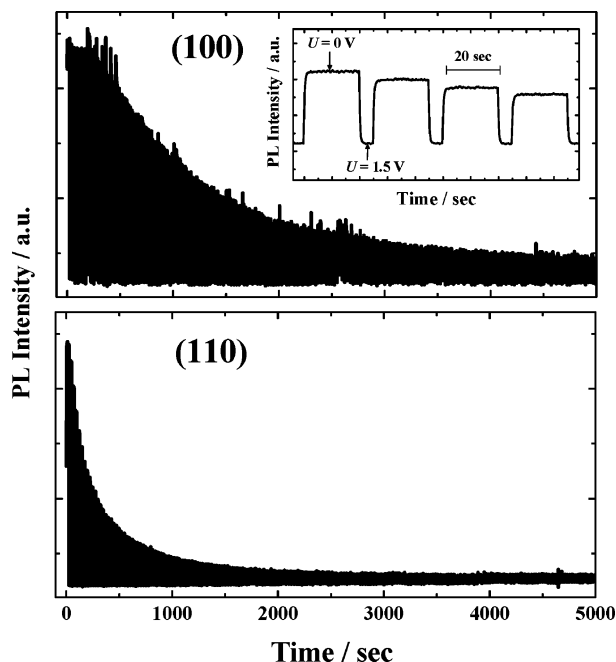


Figure 6. The PL intensity versus the illumination time for the atomically smooth (upper) (100) and (lower) (110) n -TiO₂ (rutile) surfaces under continuous UV illumination at a high intensity of 5.1 mW/cm². The U was stepped alternately from 0.0 to 1.5 V vs Ag/AgCl and in the inverse direction with constant intervals. The inset represents the changes in the PL intensity on an expanded time scale.

at 0 V, whereas no PL is emitted at 1.5 V (see Figure 2), and thus the difference in the observed signal between 0 and 1.5 V gives the PL intensity. On the other hand, the water-oxidation photocurrent flows at 1.5 V but not at 0 V, and thus the surface roughening proceeds while the U is placed at 1.5 V. The interval during which U was at 1.5 V was 5 s, whereas that for $U = 0$ V was 20 s.

Figures 6 and 7 show results of the above experiments, obtained under high (5.1 mW/cm²) and low (0.04 mW/cm²) intensity illumination, respectively. Interestingly, the I_{PL} 's for both the (100) and (110) surfaces show substantial decays with the illumination time under the high-intensity illumination (Figure 6), whereas those under the low-intensity illumination remained nearly constant (Figure 7). The surface roughening occurs under the high-intensity illumination, as mentioned earlier (Figure 5), and therefore, these results clearly indicate that the surface roughening leads to the decrease in the PL intensity. This conclusion is in harmony with the result of Figure 2B, where the PL is observed only for the atomically smooth surfaces and not for commercially obtained rough surfaces.

It is important to note in Figure 6 that the PL intensity from the (110) face decays much faster than that from the (100) face. This implies that the photoinduced surface roughening for the (110) face occurs faster than that for the (100) face. This result is again in harmony with the result of Figure 2B, which shows that the I_{PL} from the (110) face is much lower than that from the (100) face.

We mentioned earlier that the U_{fb} and U_{on} for the atomically smooth (100) surface are about 0.09 V more negative than those for the atomically smooth (110) surface. We also mentioned earlier that the U_{on} for commercially obtained (110)- and (100)-cut n -TiO₂ electrodes with rough surfaces are nearly the same as that for the atomically smooth (110) surface. From these

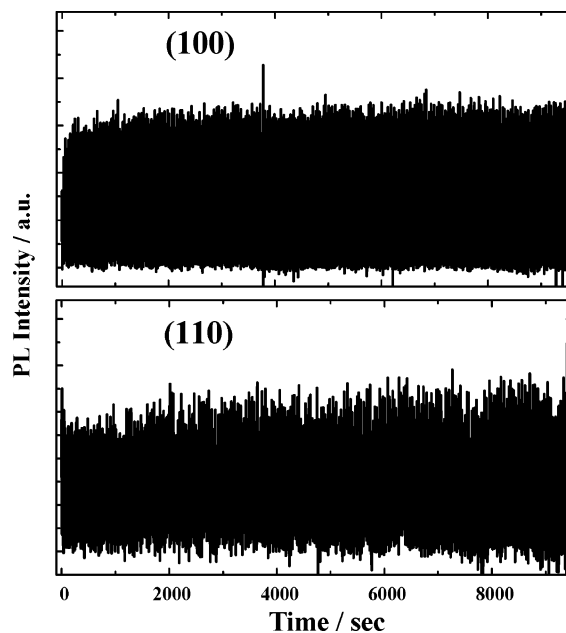


Figure 7. The PL intensity versus the illumination time for the atomically smooth (upper) (100) and (lower) (110) n -TiO₂ (rutile) surfaces under continuous UV illumination at a low intensity of 0.04 mW/cm². The U was stepped from 0.0 to 1.5 V vs Ag/AgCl and inversely with constant intervals.

results, we can expect that the U_{fb} for the atomically smooth (100) surface will shift toward the positive as the surface gets roughened. We thus investigated the influence of the surface roughening on the U_{fb} . Panels A and B of Figure 8 show Mott-Schottky plots for n -TiO₂ electrodes with the atomically smooth (100) and (110) surfaces, respectively. The surface roughening was caused by the flow of the water-oxidation photocurrent under the high-intensity (50 mW/cm²) illumination at 1.5 V vs Ag/AgCl for 30 min. As expected, the U_{fb} for the atomically smooth (100) surface was shifted by about 0.07 V toward the positive by the surface roughening, whereas that for the atomically smooth (110) face was shifted only by about 0.01 V toward the positive.

Discussion

The experimental results described in the preceding section show that photoinduced surface processes, such as oxygen photoevolution, PL emission, and surface roughening, have strong dependences on the atomic-level structure of the TiO₂ (rutile) surface. The main features can be summarized as follows:

- (1) The PL band is emitted only from the atomically smooth (100) and (110) surfaces, and not from morphologically roughened surfaces on an atomic level (Figures 1 and 2B).
- (2) The energy level for the surface-trapped hole (STH) at the (100) face, $E_{\text{STH}}(100)$, is located about 0.14 eV above that at the (110) face, $E_{\text{STH}}(110)$ (Figures 3 and 4).
- (3) The PL intensity from the atomically smooth (100) face is higher than that from the atomically smooth (110) face (Figure 2B).
- (4) The flow of the anodic photocurrent (or the occurrence of the water-photooxidation reaction) by high-intensity illumination causes the surface roughening at both the (110) and (100) TiO₂ (rutile) surfaces, accompanied by the decrease in the PL intensity (Figures 5 and 6). The rate for the surface

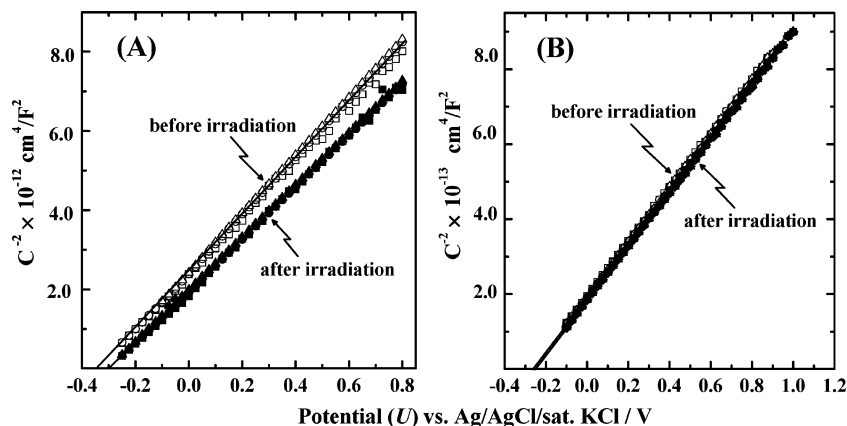


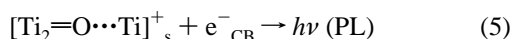
Figure 8. Mott–Schottky plots for *n*-TiO₂ (rutile) electrodes with the atomically smooth (A) (100) and (B) (110) surfaces. The plots represented by white (○, △, and □) and black marks (●, ▲, and ■) are for electrodes before and after the surface roughening, respectively. The modulation frequency was ○(●) 10 Hz, △(▲) 100 Hz, and □(■) 1000 Hz. The electrolyte = 0.1 M HClO₄.

roughening (and the PL intensity decrease) is higher in the (110) face than in the (100) face (Figure 6). On the other hand, the flow of the anodic photocurrent by low-intensity illumination causes little surface roughening (Figure 5), accompanied by no decrease in the PL intensity (Figure 7).

(5) The U_{fb} for the atomically smooth (100) surface is shifted about 0.07 V toward the positive by the surface roughening, whereas that for the atomically smooth (110) surface is shifted only 0.01 V (Figure 8). In other words, the U_{fb} for the atomically smooth (100) face lies at about 0.09 V more negative than the U_{fb} for the atomically smooth (110) surface, which is at nearly the same level as for atomically roughened surfaces.

These strong dependences of the photoinduced surface processes on the atomic-level surface structure can all be explained on the basis of the new mechanism for the water–photooxidation reaction (mechanism A of Scheme 1), as explained below.

Let us first consider that the PL is only observed from the atomically smooth (100) and (110) surfaces and not from morphologically roughened surfaces on an atomic level. According to mechanism A of Scheme 1, the water–photooxidation is initiated by process 4, that is, a nucleophilic attack of a water molecule on a surface-trapped hole (STH), [Ti₂=O••Ti]⁺_s, as described in the Introduction. On the other hand, the PL emission is assigned to an electronic transition from the conduction-band electron to the STH.



Thus, processes 4 and 5 are competitive with each other. This implies that the PL is strong only when process 4 is slow; that is, the STH is chemically stable and has a long lifetime. Accordingly, the sharp morphology dependence of the PL intensity can be explained to be due to the sharp morphology dependence of the rate of process 4.

Figure 9 schematically shows plausible models for the STH existing at the (110) and (100) terraces in contact with an aqueous electrolyte, in which a hole (one-electron deficiency) is located at a triply coordinated O atom (Ti–O=Ti₂) in surface crystal lattice.^{59,60} For such an STH embedded in a rigid surface–lattice framework, the nucleophilic attack of a water molecule (process 4), that is, the insertion of OH into a Ti–O–Ti bond, should be very slow because it should cause a large

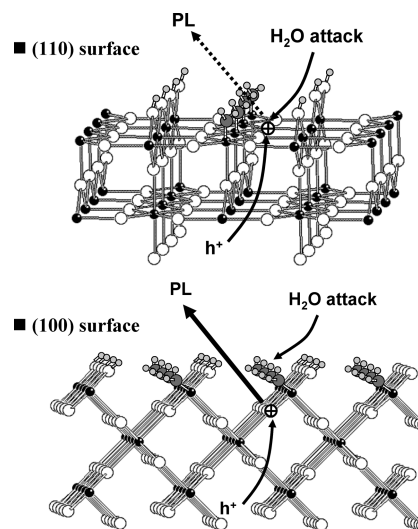


Figure 9. Schematic crystal models for the (110) and (100) terraces of *n*-TiO₂ (rutile) in contact with an aqueous electrolyte after consideration of surface reconstruction, together with some surface electronic processes. Black sphere = Ti atom, white sphere = O atom, small gray sphere = adsorbed H⁺ ion or H atom, and large (dark) gray sphere = O atom of adsorbed H₂O molecule; h⁺ = hole.

distortion energy leading to a large activation energy. The nucleophilic attack may thus occur only when the STH diffuses along a terrace and reaches a certain active site at a surface step or corner where the distortion energy in surface lattice for inserting OH into a Ti–O–Ti bond is much smaller than at a terrace (see Figure 10A). This argument indicates that the PL emission from the atomically smooth (100) and (110) surfaces with wide terraces or low densities of steps and corners, such as Figure 1c,d, is strong, in good agreement with experiments. For an atomically roughened surface, such as in Figure 1a,b, on the other hand, terraces are narrow and high densities of steps and corners exist, as schematically shown in Figure 10B, and hence, the STH can easily reach an active site and undergo the nucleophilic attack of water, thus resulting in a short lifetime of the STH and weak (or no) PL.

The model of the STH in Figure 9 can also explain why the energy level of the STH for the (100) face, $E_{\text{STH}(100)}$, is located about 0.14 eV above that for the (110) face, $E_{\text{STH}(110)}$. The STH can be regarded as a relaxed hole at the surface, as mentioned earlier. The fact that both the $E_{\text{STH}(100)}$ and $E_{\text{STH}(110)}$

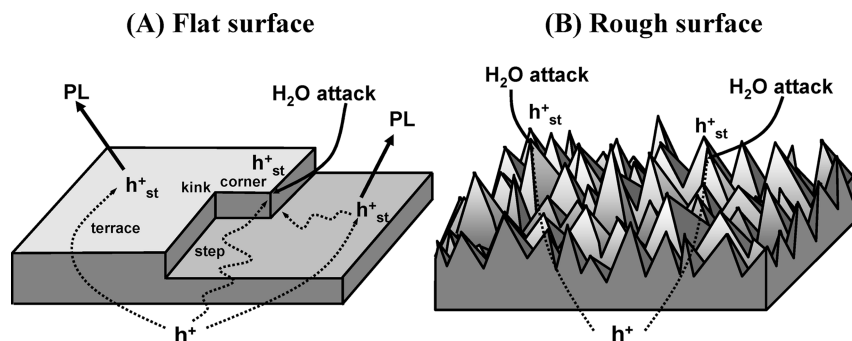


Figure 10. Schematic illustration of the STH formation and its reaction with water on the (A) atomically flat and (B) morphologically roughened surfaces.

(110) are considerably above the top of the valence band at the surface (Figure 4) implies that the STH undergoes fairly large stabilization by surface–lattice relaxation, which occurs to reduce surface–lattice distortion arising from lengthening of Ti–O bonds by hole trapping, together with the atomic and the orientation polarizations for solvent water molecules. The difference in the $E_{STH}(100)$ and $E_{STH}(110)$ will thus come from a difference in this stabilization energy between the (100) and (110) faces. For the (110) terrace, the triply coordinated O atom plane (or $[Ti_2=O-Ti]_s$ plane), where the STH exists, is placed in parallel to the surface and hence rigidly bound to surface crystal lattice on all sides, as seen from Figure 9. On the other hand, the $[Ti_2=O-Ti]_s$ plane at the (100) terrace is placed slantwise to the surface and hence only partially bound to the surface crystal lattice, with the electrolyte side of the plane being left open (Figure 9). This means that the triply coordinated O atom plane at the (100) terrace can be more easily distorted than that at the (110) face, or in other words, the STH at the (100) terrace can be more stabilized by the surface–lattice relaxation than that at the (110) terrace. Thus, the $E_{STH}(100)$ is slightly above the $E_{STH}(110)$, in agreement with the experiment.

The above argument is also in harmony with the fact that the PL intensity from the atomically smooth (100) face is stronger than that from the atomically smooth (110) face (Figure 2B). As discussed earlier, the PL is quenched when the STH diffuses along the terrace and reaches an active site at steps or corners, at which the STH undergoes the nucleophilic attack of a water molecule and disappears (Figure 10A). According to this mechanism, the higher the mobility of the STH along the terrace, the shorter the lifetime of it, and thus the weaker the PL. The mobility of the STH along the terrace will become lower as the aforementioned stabilization energy (by the surface–lattice relaxation) gets larger because the stabilization energy gives rise to an activation energy for the diffusion of the STH. As the stabilization energy in the (100) face is larger than that in the (110) face, as mentioned above, then the lifetime of the STH for the (100) face is longer than that for the (110) face, and thus the PL intensity becomes higher, again in agreement with the experiment.

Now, let us consider another important fact that the flow of the anodic photocurrent (or the occurrence of the water–photooxidation reaction) under high-intensity illumination causes the surface roughening at both the (110) and (100) TiO_2 (rutile) surfaces, accompanied by the decrease in the PL intensity, though the flow of the anodic photocurrent under low-intensity illumination causes little surface roughening, accompanied by no decrease in the PL intensity. This fact can also be explained in terms of the mobility for the STH diffusion. Under low-

intensity illumination, every STH formed at a terrace of the atomically smooth (110) and (100) surfaces will diffuse along the terrace and reach active sites at steps and corners, and then react with water (or undergo the nucleophilic attack of a water molecule), as argued earlier. Such processes cause no surface roughening because no reaction occurs at the terrace, though slight structural changes may occur in steps and corners.

On the other hand, under high-intensity illumination, the flux of photogenerated holes to the TiO_2 surface comes to exceed the rate of the water–oxidation reaction at active sites at steps and corners, in particular, at the surface with a wide terrace or low densities of steps and corners. For such a case, the STH is accumulated at terraces, under large anodic bias, and finally undergoes the nucleophilic attack of a water molecule at the terrace, thus forming intermediate radicals accompanied by bond breaking, such as $[Ti_2=O^{\bullet}HO-Ti]_s^+$ or $[Ti-O^{\bullet}HO-Ti]_s$, at the terrace. It is reasonable to assume that repeated formation of such radicals with broken bonds leads to dissolution or deformation of the terrace, finally causing atomic-level surface roughening. In fact, no surface roughening occurs under no band bending even at a high illumination intensity, as mentioned earlier. It should be emphasized that the occurrence of the surface roughening with the water–photooxidation reaction gives confirmative evidence to the mechanism of the nucleophilic attack of H_2O accompanied by bond breaking (mechanism A of Scheme 1).

The decrease in the PL intensity with the surface roughening can be explained easily in terms of the increases in the densities of steps and corners (i.e., active sites for the nucleophilic attack of water) by the surface roughening. The higher decay rate of the PL intensity at the atomically smooth (110) surface compared to that of the (100) surface thus implies that the rate of the surface roughening is higher at the atomically smooth (110) surface than at the (100) surface. The higher surface roughening at the (110) surface can be explained if we take into account that the STH at the (110) face is directly exposed to the aqueous electrolyte and easily attacked by an H_2O molecule (Figure 9), whereas the STH at the (100) face exists a little inside the surface, covered with outer Ti–OH groups, and hardly attacked by an H_2O molecule owing to steric hindrance.^{59,60,67}

The above arguments are given further support by the following considerations. We mentioned earlier that the surface roughening became more and more prominent with increasing the illumination intensity, but the extent of the surface roughening did not increase in proportion to the illumination intensity and showed a tendency of saturation. This fact indicates that the surface roughening slows down as it proceeds. This is

reasonable if we consider that, as the surface roughening proceeds at a terrace, the density of active sites where the STH can react with water increases, which in turn retards the surface roughening process at the terrace. In relation to this argument, Figure 6 shows that the PL intensity decays with the illumination time, but the decay rate becomes lower as the illumination time gets longer. This fact also shows that the surface roughening slows down as it proceeds.

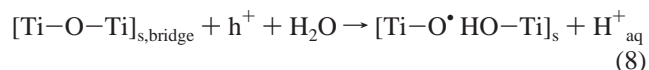
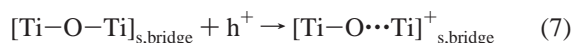
The positive shift in the U_{fb} for the atomically smooth (100) surface by illumination (Figure 8) is in harmony with the occurrence of the surface roughening with the illumination because the U_{fb} for the atomically smooth (100) surface is about 0.09 V more negative than that for the atomically roughened surfaces, as mentioned earlier. Inversely speaking, the positive shift in the U_{fb} for the atomically smooth (100) surface by illumination can be regarded as another evidence for the surface roughening by illumination. The reason the U_{fb} for the atomically smooth (100) surface is more negative than that for the atomically smooth (110) surface or the atomically roughened surface is unknown at present because the U_{fb} (or the Helmholtz layer potential) at metal–oxide electrodes should, in general, be affected by many factors, such as bond dipoles of various surface bonds and ionic adsorption equilibria.

Finally, it is worth noting that the present experimental results are quite hard to explain by the conventional mechanism that the oxygen photoevolution is initiated by the Ti–OH oxidation by photogenerated holes (mechanism B of Scheme 1). In particular, the PL emission only from the atomically smooth (100) and (110) surfaces, or no PL emission from atomically roughened surfaces, is quite hard to explain because the resultant Ti•OH radical, which is expected to be the PL emitting species in this mechanism,⁴⁹ will be formed at any surface since the surface Ti–OH group exists at any face, irrespective of the atomic-level surface morphology. Besides, the occurrence of the surface roughening with the water–photooxidation reaction is also difficult to explain because, in mechanism B of Scheme 1, only the surface Ti–OH reacts and no surface crystal lattice is affected at all.

In relation with the above argument, we have to note also that the strong morphology dependences of the PL emission will exclude the occurrence of other plausible processes, such as the hole oxidation of surface OH group accompanied by release of a hydrated H⁺ ion



and the hole trapping at a doubly coordinated bridging oxygen at the surface



because both the Ti–OH_s and [Ti–O–Ti]_{s,bridge} species exist at high densities at any face, as is expected from Figure 9. Process 7 might be impossible energetically, similar to process 2,⁶⁰ because it is likely that the O-2p electrons in Ti–O–Ti are stabilized by coordination of two Ti⁴⁺ ions, whereas those in Ti–O–H are stabilized by coordination of one Ti⁴⁺ ion and one H⁺ ion, and thus the O-2p electrons in Ti–O–Ti are more stabilized than those in Ti–OH. No occurrence of processes 6 and 8 might arise from the fact that the relaxation of a surface hole (process 3) is very fast^{68,69} and predominates over other processes, and once this process occurs, the resultant STH can no longer cause processes 6 and 8. As an exception, the STH may cause process 8 at a surface step or corner because the distortion energy in surface lattice for inserting OH into a Ti–O–Ti bond is much decreased at such sites, and this leads to process 4. It may be worth noting also that Bocarsly et al. reported⁵² that reaction 2 and release of a hydrated H⁺ ion from resultant [Ti•OH]_s⁺ occurred stepwise, with the latter process as the rate-determining step. This mechanism cannot be accepted as the correct one, as discussed thus far, but this mechanism is interesting as pointing out the significance of the acid–base reaction.

In conclusion, the present work has revealed that photoinduced surface processes on the *n*-TiO₂ (rutile) surfaces, such as the oxygen photoevolution, the PL emission, and the surface roughening (or surface etching), show strong dependences on the atomic-level structure of the TiO₂ surface. Importantly, the strong dependences have all been explained on the basis of our recently proposed new mechanism that the oxygen photoevolution reaction is initiated by a nucleophilic attack of an H₂O molecule to a surface-trapped hole (STH), giving confirmative evidence to the new mechanism. On the other hand, the present results have never been explained by the conventional mechanism that the oxygen photoevolution reaction is initiated by the hole oxidation of surface Ti–OH group. The present work has also shown that the use of atomically smooth surfaces is really a powerful method to elucidate the molecular mechanisms of photoinduced surface reactions.

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