

## Surface-Mediated Visible-Light Photo-oxidation on Pure TiO<sub>2</sub>(001)

Hiroko Ariga,<sup>†</sup> Toshiaki Taniike,<sup>†</sup> Harumo Morikawa,<sup>†</sup> Mizuki Tada,<sup>†</sup> Byoung Koun Min,<sup>‡</sup>  
Kazuya Watanabe,<sup>§</sup> Yoshiyasu Matsumoto,<sup>§</sup> Susumu Ikeda,<sup>||</sup> Koichiro Saiki,<sup>||</sup> and  
Yasuhiro Iwasawa<sup>\*,†</sup>

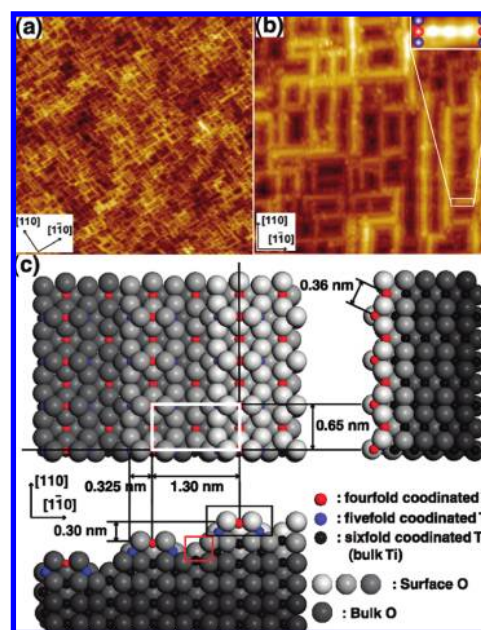
Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Tokyo 113-0033, Japan,  
Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012, Department of Chemistry,  
Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan, and Department of Chemistry, Graduate School of Frontier  
Science, The University of Tokyo, Kashiwa, Chiba 277-8561, Japan

Received August 6, 2009; E-mail: iwasawa@chem.s.u-tokyo.ac.jp

Usually only ultraviolet light must be used for photochemical reactions on TiO<sub>2</sub> because of its bulk band gap (3.0–3.2 eV). However, we used scanning tunneling microscopy (STM) to observe visible light photo-oxidation reactions of formic acid on the new ordered lattice-work structure of a TiO<sub>2</sub>(001) surface for the first time. Two photon photoelectron and electron energy loss spectroscopies and density functional theory calculations revealed that the nanostructured surface makes the band gap significantly smaller than 3.0 eV only at the surface layer and that the surface state of the crystal enables a visible light response. We report the first example of pure TiO<sub>2</sub> that shows visible light photochemical activity at the surface.

Photochemical materials have become important from an environmental viewpoint because they have the ability to decompose toxic substances in air and water,<sup>1</sup> and their ability to self-clean has been used in commercial products.<sup>2</sup> Understanding and controlling the electronic structure of the material is key to making photochemical materials a reality.<sup>3</sup> TiO<sub>2</sub> is one of the most intensively studied photochemical materials because it is stable, nontoxic, and inexpensive.<sup>4</sup> With a band gap of more than 3.0 eV, its photochemical properties appear in the near-ultraviolet region. However, since the major component of the solar light lies in the visible light region, research has been trying to extend the photoactivity of TiO<sub>2</sub>-based materials from 3.0 eV down to the visible light range to utilize solar light more efficiently. Several methods such as dye sensitization,<sup>5</sup> metal or nonmetal doping,<sup>6</sup> and oxygen defect doping<sup>7</sup> have been used, and recently, powder TiO<sub>2</sub> has been converted into vis light photocatalysts by doping. The basic strategy of these methods is to create impurity/defect states in the bulk band gap to enable low energy photo excitation.

Previous photochemical studies have mainly focused on the bulk states, and almost no attention has been paid to the surface state because powder materials with inhomogeneous surfaces, in which the surface states are not controllable, have been used. In the present study, we investigated the effect of the unique “lattice-work structure” of a TiO<sub>2</sub>(001) surface on the photochemistry of the surface, particularly the vis light responsible photo-oxidation by using formic acid as a probe molecule. The reaction using UV irradiation has already been studied on a powder TiO<sub>2</sub> catalyst, on which formic acid decomposes to CO<sub>2</sub> and H<sub>2</sub>O without any long-lived intermediate.<sup>8,9</sup> To our knowledge, however, there are no reports for a single crystal TiO<sub>2</sub> surface to date. We found through scanning tunneling microscopy (STM) that the nanostructured



**Figure 1.** STM images (constant current topograph, (a) 200 × 200 nm<sup>2</sup>, (b) 40 × 40 nm<sup>2</sup>, V<sub>s</sub>: 2.00 V, I<sub>t</sub>: 0.05 nA) of TiO<sub>2</sub>(001) after Ar<sup>+</sup>-sputtering followed by annealing at 1050 K in a UHV. (Inset of (b)) Magnified image of the topmost terrace (red circle: 4-fold coordinated Ti row, blue circle: 5-fold coordinated Ti rows). (c) Top and side views of a structural model of the lattice-work structure on TiO<sub>2</sub>(001). Both side views are cut with black line in the top view. The black squares are “hill part”, and the red squares are “valley part”.

surface was photochemically active toward vis light (~2.3 eV) in spite of the bulk band gap of 3.0 eV. Combined electronic and theoretical studies also revealed that the photochemical reaction proceeds through the surface state created from the ordered lattice-work structured surface.

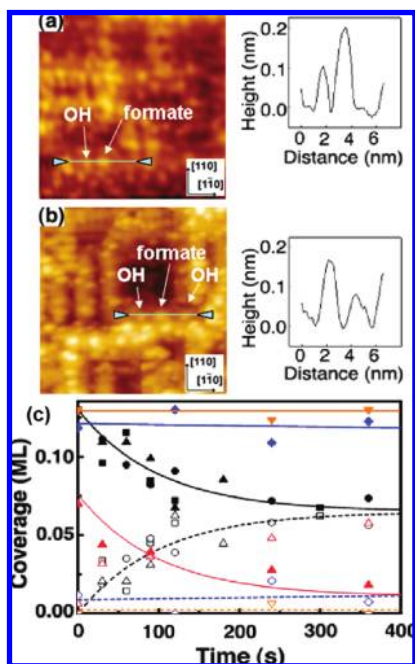
A typical empty-state STM image of the TiO<sub>2</sub>(001) lattice-work structured surface is shown in Figure 1a and b. The details of all the experiments and the lattice-work structure are described in Supporting Information (SI) 1 and 2.<sup>10</sup> The ordered lattice-work structure has been characterized by STM topographic analysis, adsorption of probe molecules, and DFT calculations in the previous study.<sup>10</sup> This surface has cross-linked and stacked rows running in the [110] and  $\bar{1}\bar{1}0$  directions. Each row of the hill part (black square in Figure 1c) consists of three lines of bright protrusions as shown in the inset of Figure 1b. There is ambiguity for the valley part (red square in Figure 1c) in the surface structure. However, the electronic and atomic structure of the hill part, where the visible-light oxidation of formic acid was observed with STM, fortunately,

<sup>†</sup> The University of Tokyo, Tokyo.

<sup>‡</sup> Texas A&M University.

<sup>§</sup> Kyoto University.

<sup>||</sup> The University of Tokyo, Chiba.



**Figure 2.** STM image (constant current topograph,  $20 \times 20 \text{ nm}^2$ ,  $V_t$ : 2.00 V,  $I_t$ : 0.05 nA, recorded at RT) of the TiO<sub>2</sub>(001) surface after exposure to formic acid, followed by (a) UV light ( $5 \times 10^{17} \text{ photon cm}^{-2} \text{ s}^{-1}$ ) and (b) vis light ( $2 \times 10^{18} \text{ photon cm}^{-2} \text{ s}^{-1}$ ) irradiation in the presence of O<sub>2</sub>. Line profiles between white arrowheads in the images are shown in the right panels. (c) Time dependence of formate (solid) and hydroxyl (open) coverages under 3.4 eV (square), 2.1–2.8 eV (circle), 2.3 eV (triangle), and 2.1 eV (diamond) light irradiation in the presence of O<sub>2</sub> (black, blue, and red). The same plots under UV light irradiation but without O<sub>2</sub> are also shown with orange markers. The time profile was almost independent of the initial formate coverages. The photo-oxidation was performed under the flux intensity of UV and vis light at saturation. The dependency of the rate constant on the photon intensity is shown in SI 4. The surface temperature is estimated to be below 320 K under prolonged irradiation because no formates on TiO<sub>2</sub>(110) desorb under similar irradiation conditions to the case of TiO<sub>2</sub>(001).

was not affected by the valley part in the DFT calculation.<sup>10</sup> The side rows consisted of 5-fold coordinated Ti<sup>4+</sup> ions, while the center row was formed by a zigzag chain of 4-fold coordinated Ti<sup>4+</sup> ions as illustrated in Figure 1c.

On the TiO<sub>2</sub>(001) surface, formic acid dissociatively adsorbed as a formate ion onto the 4- and 5-fold coordinated Ti<sup>4+</sup> ions at room temperature. These formate ions were visualized by STM as bright protrusions with an  $\sim 0.17 \text{ nm}$  height. Formic acid also dissociatively adsorbs on a TiO<sub>2</sub>(110) surface with only 5-fold coordinated Ti<sup>4+</sup> ions, which is most stable among low-index TiO<sub>2</sub> surfaces;<sup>8,11</sup> however, no report can be found concerning the photo-oxidation of formic acid on the surface even under UV irradiation (SI 3). The lack of reactivity is probably caused by the local geometry around the Ti<sup>4+</sup> cations because the band gap of the TiO<sub>2</sub>(110) surface is almost the same as the bulk one.<sup>8</sup> On the other hand, UV light (3.4 eV) irradiation of the TiO<sub>2</sub>(001) in the presence of oxygen ( $1.0 \times 10^{-6} \text{ Pa}$ ) changed formate ions to smaller species with a height of  $\sim 0.10 \text{ nm}$  on the Ti<sup>4+</sup> ions (Figure 2a). Black solid squares and black open squares in Figure 2c show the coverages of formates and small species as a function of the light irradiation time, respectively. The amount of formates and small species gradually decreased and increased, respectively, with the irradiation time, where the total amount of the formates and the small species is always constant, which indicates that the formates transform directly to the small species. The coverage decrease is not due to thermal desorption of the formates caused by light

irradiation because no change in the amount of formates occurred by light irradiation of formates/TiO<sub>2</sub>(110) in the presence of O<sub>2</sub> (SI 3) and the small species did not appear by irradiation without oxygen (Figure 2c orange squares). Thus, the nanostructured surface is photoreactive toward the oxidation of formate anions, and the small species are concluded to be products of the photo-oxidation of formates. As a result, the small species are assigned as OH groups on the basis that the same reaction as that on the powder TiO<sub>2</sub> catalyst occurs. The bright contrasts produced by dissociative adsorption of H<sub>2</sub>O at room temperature show almost the same protrusion as the product protrusion in Figure 2b. The height of the on-top OH groups is a little higher than that reported for bridging OH groups on TiO<sub>2</sub>(110) prepared by atomic H adsorption.<sup>12</sup>

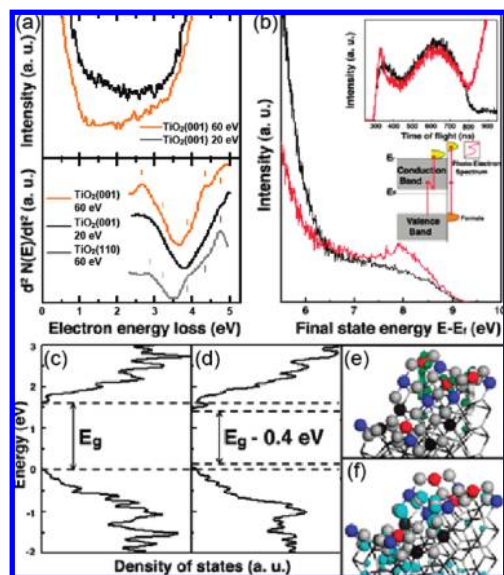
The time dependences of the open and solid black squares were well fitted with the exponential curves, shown as black lines in Figure 2c, which indicates that the reaction was of first order to the formate coverage. We also examined oxygen pressure dependence of the reaction rate and found that the reaction rate was almost proportional to the O<sub>2</sub> pressure. The TiO<sub>2</sub>(001) surface is geometrically suitable for the photo-oxidation of formic acid, and the same UV light caused the same reaction as that on the powder TiO<sub>2</sub> catalyst.<sup>9</sup> However, the most striking result was obtained under broad-band vis light (2.1–2.8 eV) irradiation under the same conditions. The formates gradually changed to OH groups even under irradiation with vis light (Figure 2c). OH formation by irradiation of the formate with vis light was also suggested by reflection–absorption infrared spectroscopy (RAIRS); a new peak at  $3215 \text{ cm}^{-1}$  due to hydrogen-bonded OH groups developed with the irradiation time.

We examined the reaction by changing the light energy and found that it proceeded in the same way under 2.3 eV light (black open/solid triangles) but did not proceed under 2.1 eV light (blue open/solid triangles) in Figure 2c (O<sub>2</sub>:  $1.0 \times 10^{-6} \text{ Pa}$ ). This result goes against the common knowledge of photocatalysts because the bulk band gap of TiO<sub>2</sub>, which determines the light energy threshold for the photoreactivity, is 3.05 eV and is significantly larger than the threshold energy (2.1–2.3 eV). The quantum yield defined by reaction rate/irradiated photon intensity was 23 times higher for UV irradiation than for vis irradiation. The rate constant was proportional to the intensity of photons and reached the maximum rate constant (SI 4).

The mechanism of the visible light excitation was investigated by electron energy loss spectroscopy (EELS) and DFT calculations (SI 1). Figure 3a shows EELS spectra and their second derivatives at the incident beam energies of 60 and 20 eV. The spectrum of the electron injection energy of 60 eV had a peak at 2.6 eV, while that at 20 eV did not have a distinct peak, which was consistent with the second-derivative spectra. The spectrum taken at 60 eV is more surface sensitive than that of 20 eV.<sup>13</sup> The existence of the peak at 2.6 eV in the spectrum means that the electron excitation of 2.6 eV is possible around the surface. Because the electron energy loss process includes indirect excitation of the electron and overestimates the gap value, the value 2.6 eV is consistent with the observed photo-oxidation of formates under vis irradiation. No peak was observed on a TiO<sub>2</sub>(110) surface (Figure 3a).

The DFT calculations in Figure 3c and d revealed the density of states for the TiO<sub>2</sub>(110)-(1 × 1) and the TiO<sub>2</sub>(001) lattice-work structure, respectively. Generally, the DFT underestimates band gaps of semiconductors,<sup>14</sup> and the absolute values of the calculated band gaps are not reliable. However the relative value is reliable in the calculation, and we can compare the difference in the band gap between the TiO<sub>2</sub>(110) surface and the TiO<sub>2</sub>(001) lattice-work structured surface. It is obvious from Figure 3c and d that the band

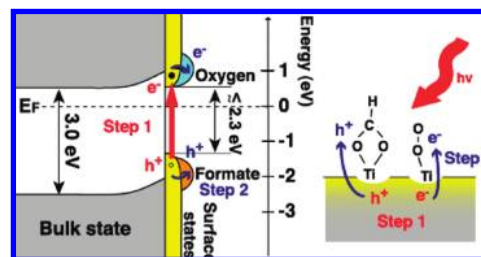




**Figure 3.** (a) EELS spectra for the lattice-work structure. A spectrum at a beam energy of 60 eV is surface sensitive. (b) 2PPE spectra ( $h\nu = 4.66$  eV) for the lattice-work structure before (black) and after (red) exposure to formic acid. (c) DFT-calculated density of states of  $\text{TiO}_2(110)-1 \times 1$  structure. (d) DFT-calculated density of states of  $\text{TiO}_2(001)$  lattice-work structure. (e) Orbitals of the conduction band minimum (upper) and the valence band maximum (lower).

gap of the  $\text{TiO}_2(001)$  surface is significantly narrower than that of the  $\text{TiO}_2(110)$  structure, which is consistent with the EELS. Orbital calculations showed that the energy levels near the conduction band minimum and near the valence band maximum originated from a one-dimensional row of 4-fold coordinated  $\text{Ti}^{4+}$  and surface oxygen orbitals, respectively (Figure 3e). Thus, the band gap narrowing is caused by the low coordinated atoms on the topmost surface. In other words, the creation of the electron and hole for the present photochemical reaction is mediated by the surface state of the  $\text{TiO}_2(001)$  lattice-work structure.

We also examined the transport path of the created hole into the adsorbed formate by acquiring the two photon photoelectron (2PPE) spectra for the  $\text{TiO}_2(001)$  surface with a 4.66 eV laser (Figure 3b) (SI 1). The 2PPE intensity of the clean surface plotted as a function of time-of-flight (TOF; inset) had a distinct peak at a flight time of 340 ns which is converted into a final state energy value of 8.2 eV. The initial energy of this electronic state was estimated to be 1.1 eV ( $= 2 \times 4.66 - 8.2$ ) below the Fermi level ( $E_F$ ). The peak shifted twice the change in the irradiation energy. Thus, there should be an electronic state at  $\sim 1.1$  eV below  $E_F$  on the clean surface. This position is closer to  $E_F$  than that of the  $\text{TiO}_2(001)$  surface, of which the valence band maximum is 2.2 eV below the  $E_F$ . Importantly, in the 2PPE spectrum, after exposure to formic acid, the intensity of the peak around 340 ns became significantly larger. The result indicated that the formate anions on the surface also have an electronic state  $\sim 1.1$  eV below  $E_F$ , making it easy for a photo-created hole to hop to the adsorbed formate. Based on the experimental and theoretical results, we drew a schematic energy diagram in Figure 4. The  $\text{TiO}_2(001)$  lattice-work structured surface has a surface state that penetrates into the bulk band gap, and the electronic state of the formate is at the top of the valence band of the surface state.



**Figure 4.** Schematic diagram showing electron transport triggered by light.

Questions still remain for the present reaction. For example, the reaction did not go to completion (Figure 2c), which may be explained several ways, including a blocking effect by the product.<sup>15</sup> Actually, we found that the reaction saturated not at a certain coverage of formates but at that of OH groups. However, the details of such a blocking mechanism are still not clear and are beyond the scope of this study. The surface state mixed with formates may also be excited by vis light. EELS and DFT results show the band gap narrowing to the region of vis light by the surface state, which suggests the potential for the  $\text{TiO}_2(001)$  surface for the vis light induced reactions. Further studies of the electron/hole transfer process are necessary to explain them.

In summary, we investigated the photo-oxidation of formic acid on a  $\text{TiO}_2(001)$  surface. Contrary to the conventional knowledge of the photon threshold energy, which is determined by the bulk band gap of photochemical materials, we showed for the first time experimental and theoretical evidence for a surface state (the smaller band gap)-mediated photochemical reaction on  $\text{TiO}_2(001)$  with vis light. The present finding shows the critical importance of the atomic-scale design of the surface of such a material.

**Supporting Information Available:** Description of experiments, STM topographic analysis of  $\text{TiO}_2(001)$ , photo-oxidation of formate ions on  $\text{TiO}_2(110)$ , and “apparent” quantum yields of the reaction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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