Anatase TiO₂ Single Crystals Exposed with High-Reactive {111} Facets Toward Efficient H₂ Evolution

Hua Xu, Pakpoom Reunchan, Shuxin Ouyang, Hua Tong, Naoto Umezawa, Tetsuya Kako, and Jinhua Ye

ABSTRACT: In this study, for the first time, {111} facet exposed anatase TiO₂ single crystals are prepared via both F⁻ and ammonia as the capping reagents. In comparison with the most investigated {001}, {010}, and {101} facets for anatase TiO₂, the density functional theory (DFT) calculations predict that {111} facet owns a much higher surface energy of 1.61 J/m², which is partially attributed to the large percentage of undercoordinated Ti atoms and O atoms existed on the {111} surface. These undercoordinated atoms can act as active sites in the photoreaction. Experimentally, it is revealed that this material exhibits the superior electronic band structure which can produce more reductive electrons in the photocatalytic reaction than those of the TiO₂ samples exposed with majority {010}, {101}, and {001} facets. More importantly, we demonstrate that this material is an excellent photocatalyst with much higher photocatalytic activity (405.2 μmol h⁻¹), about 5, 9, and 13 times that of the TiO₂ samples exposed with dominant {010}, {101}, and {001} facets, respectively. Both the superior surface atomic structure and electronic band structure significantly contribute to the enhanced photocatalytic activity. This work exemplifies that the surface engineering of semiconductors is one of the most effective strategies to achieve advanced and excellent performance over photofunctional materials for solar energy conversion.

KEYWORDS: anatase TiO₂, {111} facet, photocatalysis, surface chemistry

INTRODUCTION

Photocatalysis is an environmentally friendly and promising technology to convert solar energy into chemical energy.¹–⁶ The discovery of water photolysis on TiO₂ electrode by Fujishima and Honda in 1972 was recognized as the landmark event in photocatalysis;⁷ since then, large amounts of research have been carried out on TiO₂ photocatalysis to achieve a higher solar-to-energy conversion efficiency, such as modification of the electronic structure of TiO₂ to extend its light-absorption region via doping,⁸–¹² and fabrication of TiO₂-based heterojunction materials to enhance the charge separation efficiency.¹³–¹⁵ Recently, special attention has been paid on the surface chemistry of TiO₂, since many physical and chemical processes (e.g., adsorption of reactant molecules, surface transfer of photoexcited electrons to reactant molecules, and desorption of product molecules) happened on the surface during the photocatalytic reaction.¹⁶–¹⁸

In the case of anatase TiO₂, the shape of this material under equilibrium conditions is a slightly truncated tetragonal bipyramid enclosed with 94% of {101} surfaces (the most thermodynamically stable) and minor {001} surfaces based on the Wulff construction and theoretically calculated surface energy (⟨{101}⟩ 0.44 J/m² < ⟨{010}⟩ 0.53 J/m² < ⟨{001}⟩ 0.90 J/m²).¹⁶ Nevertheless, in the real experimental process, the facet control of anatase TiO₂ can be effectively achieved.¹⁹ A significant breakthrough was carried out by Yang and his co-workers, who experimentally obtained the anatase TiO₂ single crystals with majority of {001} facets.²⁰ Moreover, in spite of that no {010} facet can be observed in the Wulff construction model, the latest investigations have confirmed the existence of chemical properties.¹⁷ Therefore, tailored synthesis of TiO₂ single crystals with optimized reactive facets is highly desirable for promoting the photocatalytic activity.

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Supporting Information
{010} facet existed as the ‘belt’ at the center of TiO\textsubscript{2} particle.\textsuperscript{21–24} Among these three crystal facets \{010\}, \{011\}, and \{001\} facets, \{011\} facet was ever been considered to be the active facets in the photocatalysis because of its highest surface energy (0.90 J/m\textsuperscript{2}) and superior surface atomic structure (100\% five-coordinated Ti atoms (Ti\textsubscript{5c}) on its surface). However, in 2011, Pan et al. reported that \{010\} facet owns the superior electronic structure than that of \{011\} and \{010\} facets, and TiO\textsubscript{2} single crystals exposed with more \{010\} facets exhibited superior electronic band structure than that of TiO\textsubscript{2} exposed with more \{001\} facets, thus resulted into a much higher photocatalytic activity in the H\textsubscript{2} evolution.\textsuperscript{17} Those above findings indicated that both the surface atomic structure and electronic structure play important roles in the photocatalytic reaction, thus inspire us to make TiO\textsubscript{2} expose new active crystal facet with superior properties in both atomic structure and electronic configuration. We expect that those unique properties can endow TiO\textsubscript{2} with high photocatalytic activity, hence promoting their potential applications in the clean energy and environmental remediation.

To date, compared with the previously investigated \{001\}, \{011\}, and \{010\} facets for anatase TiO\textsubscript{2}, few studies have been concerned on the \{111\} facet, as illustrated in Scheme 1.

**Scheme 1. Schematic Illustration of \{011\}, \{010\}, \{001\}, and \{111\} Facets of Anatase TiO\textsubscript{2} (a) Molecular Simulation Model; (b) Crystal Model**

Herein, we report a facile process to prepare well-defined anatase TiO\textsubscript{2} single crystals exposed with \{111\} facets (T\textsubscript{111}) which have never been realized experimentally before. The DFT theoretical calculations predict that the surface energy of \{111\} facet is up to 1.61 J/m\textsuperscript{2} and large percentages of undercoordinated Ti atoms and O atoms existed on the surface. Experimentally, it is discovered that the conduction band minimum of this material is much higher than those of TiO\textsubscript{2} samples exposed with dominant \{010\}, \{011\}, and \{001\} facets (denoted as T\textsubscript{010}, T\textsubscript{101}, and T\textsubscript{001}), indicating that more undercoordinated Ti atoms and O atoms existed on the surface. Furthermore, the photocatalytic properties of T\textsubscript{111} are evaluated, it is revealed that T\textsubscript{111} is an excellent photocatalyst with much higher photocatalytic activity, about 5, 9, and 13 times that of T\textsubscript{010}, T\textsubscript{101}, and T\textsubscript{001}, respectively. Both the superior surface atomic structure and electronic band structure significantly contribute to the enhanced photocatalytic performance. The previous research reported that \{010\} facet was the most active facet for anatase TiO\textsubscript{2}, which owns 100\% Ti\textsubscript{5c} atoms on its surface and superior electronic structure compared to that of \{011\} and \{010\} facets.\textsuperscript{17} However, in this study, \{111\} facet is proved to be the more active crystal facet than \{010\} facet, which exhibits excellent properties in both the surface atomic structure and electronic structure. To the best of our knowledge, it is the first report about the \{111\} facet exposed anatase TiO\textsubscript{2}.

### EXPERIMENTAL SECTION

**Synthesis.** In a typical synthesis procedure of TiO\textsubscript{2} single crystals exposed with \{111\} facet, first, 3 mmol of Ti\textsubscript{4+} (Aldrich) was added into the 100 mL of mixed solution of ethanol (Wako) and acetonitrile (Wako); then 0.6 mL of ammonia (Wako) was added slowly into the above solution. After being stirred at room temperature for 48 h, the white suspension was centrifuged and the followed precipitation was dried at 60°C for 3 h to get the gel-like precursor (denoted as TFN). To get the final single-crystalline TiO\textsubscript{2}, we heated the Ti precursor (TFN) at 500°C for 2 h with a temperature ramping rate of 1°C/min in the air atmosphere. After the combustion process, loosely TiO\textsubscript{2} powder was obtained. Furthermore, the obtained samples need to be calcined in the air atmosphere at 600°C for 2 h to clean the surface for the photocatalytic test. This as-prepared TiO\textsubscript{2} sample was denoted as T\textsubscript{111}.

In comparison with T\textsubscript{111}, TiO\textsubscript{2} samples with exposed \{001\}, \{010\}, and \{011\} facets were prepared via solvothermal method reported in the literature as following: 64, 32, 32 mg of titanium oxysulfate (TiOSO\textsubscript{4}·3H\textsubscript{2}O) (Aldrich) was dissolved in the HF solution (Aldrich) with concentrations of 120, 40, and 80 mM to prepare the precursors of TiO\textsubscript{2} with \{001\}, \{010\}, and \{011\} facet exposed, respectively. Then 40 mL of the TiOSO\textsubscript{4} solution were transferred to the Teflon-lined autoclave and heated at 180°C for 12, 2, and 12 h for the \{001\}, \{010\}, and \{011\} facet exposed TiO\textsubscript{2}, respectively. After reaction, the products were collected by centrifugation and washed with deionized water then dried at 80°C in air for 12 h. To remove the surface fluorine, all the products were calcined in the air atmosphere at 600°C for 2 h. The samples with \{001\}, \{010\}, and \{011\} facets exposed were denoted as T\textsubscript{001}, T\textsubscript{010} and T\textsubscript{111} respectively.

**Characterization.** The X-ray diffraction (XRD) patterns of the prepared samples were conducted on a Rigaku Multilux diffractometer (RINT 2000; Rigaku Corp., Japan) with monochromatized Cu K\textsubscript{α} radiation (λ=1.54178 Å). Raman measurement was carried out using a Raman spectroscopy (NRS-1000; Jasco Corp, Japan). The size and morphology of the samples were observed with a scanning electron microscope (SEM, JSM-6701F, JEOL Co., Japan) and transmission electron microscope (TEM, JEM-200 CX, JEOL) operating at 200 kV. The low temperature Electron Paramagnetic Resonance (EPR) spectra of the TiO\textsubscript{2} samples were recorded for 4 K to confirm the presence of oxygen vacancy on JEOl JES-FA200 Electron Spin Resonance Spectrometer. UV-visible absorption spectra were measured on a UV-visible spectrophotometer (UV-2500PC, Shimadzu Co., Japan). X-ray Photoelectron Spectroscopy (XPS) were performed on Thermo ESCALAB250 using monochromatized Al K\textsubscript{α} radiation (λ=1.4866 eV). The binding energies were calibrated to the C\textsubscript{1s} peak by 284.6 eV. The Brunauer—Emmett—Teller (BET) surface areas were recorded by a surface area analyzer (BEL Sorp-II mini, BEL Japan Co., Japan) with nitrogen absorption at 77 K.

**Theoretical Calculations.** The calculations of the surface structure were based on the density-functional theory (DFT), as implemented in the VASP code.\textsuperscript{25} The exchange-correlation energy was represented by the generalized-gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE).\textsuperscript{26} The Ti 3s\textsuperscript{2}3p\textsuperscript{6}3d\textsuperscript{2}4s\textsuperscript{2} and O 2s\textsuperscript{2}2p\textsuperscript{4} were treated as valence electrons. The energy cutoff for the plane-wave basis set was 400 eV. The calculated crystal parameters for bulk anatase TiO\textsubscript{2} were a = 3.786 Å and c/a = 2.556, which were in good agreement with the experimental values.\textsuperscript{27} A 6 × 6 × 6 Monkhorst—K-point mesh was used for the Brillouin-zone integrations of the unit cell. For each surface, the supercells which were constructed from the relaxed unit cell of TiO\textsubscript{2} were periodically repeated along the surface normal and separated by vacuum layers. The constructed slabs with a vacuum thickness of ~10 Å can sufficiently suppress the interaction between adjacent slabs. The surface models were consisted of 144 atoms (24 unit cells of bulk TiO\textsubscript{2}) for \{111\} and \{001\} planes,
and 96 atoms (16 unit cells) for {010} and {101} planes, respectively. All atoms in the slabs were relaxed until the residual force was less than 0.02 eV/Å.

To further investigate the possibility of the oxygen vacancy existed on each surface, we also calculated the surface energies of the reduced surfaces. In the model structure, one oxygen atom was removed from each side of the {101}, {010}, {001}, and {111} slabs mentioned above. The geometries of the reduced surfaces were fully relaxed. The surface energy $\gamma$ of the reduced surface was given by

$$\gamma = \frac{E_{\text{reduced}} - nE_{\text{bulk}} + \mu_O}{A}$$

where $E_{\text{reduced}}$ is the total energy of the reduced slab, and $\mu_O$ is the chemical potential of oxygen, which is directly related to the O$_2$ partial pressure in ambient.

Photocatalytic Test. Photocatalytic reactions of H$_2$ evolution were carried out in a closed glass circulation system with an external-irradiation type of a glass reactor. The light source was a 300 W xenon lamp. The intensity of the light at 300~800 nm was measured to be 240 mW/cm$^2$ by using a spectroradiometer (USR-40; Ushio Inc., Japan). The cocatalyst Pt was loaded by an in situ photodeposition method. The 0.5 wt % Pt-loaded catalyst (60 mg) was dispersed with a magnetic stirrer in an aqueous methanol solution (50 mL of CH$_3$OH and 220 mL of H$_2$O). The evolved gas including H$_2$ was analyzed by online gas chromatograph (GC-8A; Shimadzu) equipped with a thermal conductivity detector.

RESULTS AND DISCUSSION

As shown in Figure 1, the XRD patterns of the as-prepared TiO$_2$ samples (T$_{001}$, T$_{101}$, T$_{010}$ and T$_{111}$) can be indexed to the anatase TiO$_2$, respectively.$^{28}$ Obviously, the peak positions of all the four prepared TiO$_2$ samples (T$_{111}$, T$_{101}$, T$_{010}$, and T$_{001}$) are similar, no other additional peaks indexed to rutile can be found. Therefore, we can prove that all the four prepared TiO$_2$ samples (T$_{111}$, T$_{101}$, T$_{010}$, and T$_{001}$) are pure anatase.

The morphology of the TiO$_2$ sample (T$_{111}$) was observed by the SEM image (Figure 2a), which was consisted of some square-like plates. As shown in Figure 2b, a square-shaped plate (400 $\times$ 400 nm$^2$) with a thickness of 50 nm in high-magnification was observed. Furthermore, a detailed study was carried out to verify the crystal facet of the square-shaped nanoplates via TEM (Figure 2c). The corresponding electron diffraction (SAED) pattern (inset in Figure 2c) confirms that the square-shaped crystalline is single crystal, and the zone axis is indexed to be [111]. Additionally, based on the analysis of the high-resolution TEM (HRTEM) image (Figure 2d), the interfacial angle between the (101) and (011) atomic planes (the same lattice spacing of 0.351 nm) of anatase TiO$_2$ is 82°, we can confirm that the exposed crystal plane is {111} facet. To the best of our knowledge, this is the first report about the single crystalline TiO$_2$ with {111} facet exposed. According to the SEM and TEM images, the percentage of the {111} facets on T$_{111}$ is calculated to be about 72% in average. For the morphology observation of other TiO$_2$ samples (T$_{001}$, T$_{101}$, and T$_{010}$), the SEM images are shown in Figure S2 in the Supporting Information.

On the basis of the above experimental findings, the surface structure of the {111} crystal facet was further theoretically studied via the density functional theory (DFT) calculation in comparison with the reported {001}, {010}, and {101} facets. The representative relaxed atomic geometries of each slab are shown in Figure 3. Accounting from the slab models, the surface atomic structures of each facets are described as following. On the {111} surface, all the Ti and O atoms on the top layer are undercoordinated: Ti atoms are 5-fold and 3-fold coordinated ($T_{1x}$ and $T_{3x}$) with the ratio of $T_{1x}$ to $T_{3x}$ is 1:3, and O atoms are 2-fold coordinated ($O_{2c}$). On the {001} surface, only $T_{3x}$ atoms are present as well as $O_{2c}$ and $O_{3c}$ atoms. On the {010} surface, we note that besides the outmost $T_{1x}$ atoms on the top layer, the fully (6-fold)-coordinated Ti atoms on the side layer...
cells contained in the slab, and energy of the bulk per unit cell, as $O_2c$ and $O_3c$ atoms. Apparently, {111} surface has favorable accordance with the values reported in the literature (as listed respectively; the latter three surface energies are in well

Table 1. Surface Energies of Each Crystal Facet for Anatase TiO$_2$

<table>
<thead>
<tr>
<th>crystal facet</th>
<th>surface energy ($J/m^2$) this work</th>
<th>surface energy ($J/m^2$) GGA-PBE$^{18}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>1.61</td>
<td>0.94</td>
</tr>
<tr>
<td>(010)</td>
<td>0.57</td>
<td>0.53</td>
</tr>
<tr>
<td>(001)</td>
<td>0.95</td>
<td>0.90</td>
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<tr>
<td>(101)</td>
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surface energy of {111} facet has never been reported. Compared with {001}, {010}, and {101} facets, the surface energy of {111} facet is much higher. The higher surface energy of {111} facet is partially attributed to the large percentage of undercoordinated Ti and O atoms, of which the ground state energy is higher in contrast with the fully coordinated atoms.

Generally, the facet with high surface energy will vanish rapidly during the crystal growth process to minimize the total crystal energy. In order to stabilize the reactive surface during the crystal growth process, the TiO$_2$ samples with exposed high-energy {001} and {010} facets were prepared by using HF$^{17,20,31-40}$ NH$_4F^{19,41,42}$ or any other capping reagents (such as 1-butyl-3-methylimidazolium tetrafluoroborate$^{43}$ disodii

um ethylenediaminetetraacetate$^{44}$ and diethylenetriamine$^{45}$ as stabilizers to lower the surface energy for certain crystallographic crystal facets in the previous report$^{46}$ Herein, anatase TiO$_2$ single crystals with high-surface-energy {111} facet exposed is obtained, which could be ascribed to the synergetic effect of the F$^-$ and ammonia as the capping reagents. The crystal growth mechanism was also investigated in detail as described in the Supporting Information (Figures S3 and S4).

In addition, the numerous undercoordinated O atoms (100% $O_2c$) existed on the {111} surface can facilitates the formation of oxygen vacancy, which will affect the photocatalytic performance via acting as active sites in the photoreaction. $^{47}$ In order to verify the possibility of the existence of oxygen vacancy existed on the TiO$_2$ surface, the surface energy of the reduced {111} surface was theoretically calculated in comparison with other crystal facets such as {001}, {010}, and {101}. As shown in Figure S5a in the Supporting Information, the intersection of the ideal and reduced surface curves gives the transition value of $\sim -1.61$ eV for the (111) facet, which is much higher than that of the {001} (approximately $-3.76$ eV), {010} (approximately $-4.25$ eV), and {101} (approximately $-4.52$ eV) facets. These results indicate that the oxygen vacancies can be more easily created on the {111} surface than that on the {001}, {010}, and {101} surfaces, and oxygen vacancies start to form on the {111} surface even under a relatively high O$_2$ pressure.$^{15}$ Later, to get a more convincing experimental evidence, we also adopted the low temperature electron paramagnetic resonance (EPR) spectra to check the existence of the oxygen vacancies on the TiO$_2$ surface. As shown in Figure S5b in the Supporting Information, the signal observed at $g = 2.002$ is the characteristics of a paramagnetic Ti$^{3+}$ existed on the surface of TiO$_2$. It is reported that the surface Ti$^{3+}$ would tend to adsorb atmospheric O$_2$ and reduce the O$_2$ into O$_2^-$, which shows an EPR signal at $g = 2.002$. The intensity of the signal appeared in $T_{111}$ is much stronger than that of $T_{010}$, $T_{101}$, and $T_{001}$, indicating that more oxygen vacancies are existed on the surface of $T_{111}$. These oxygen vacancies can act as active sites in the photocatalytic reaction, which are beneficial for the enhancement of the photocatalytic efficiency.

In parallel, the electronic band structures of the four TiO$_2$ samples, which will also affect their photocatalytic efficiencies, were deduced from the UV–visible absorption spectra and valence band XPS spectra. As shown in Figure 4a, the UV–visible absorption spectra demonstrate that, the absorption edges of $T_{111}$, $T_{010}$, $T_{101}$, and $T_{001}$ are nearly 371, 385, 388, and 392 nm, respectively. TiO$_2$ is known as an indirect semiconductor, for which the relation between the absorption coefficient ($\alpha$) and incident photon energy ($hv$) can be written as $\alpha = B(hv - E_g)^2/h$ where $E_g$ is the absorption constant for indirect transitions.$^{49}$ The band gaps of the TiO$_2$ samples are calculated to be 3.01, 3.04, 3.08, and 3.17 eV for $T_{111}$, $T_{010}$, $T_{101}$, and $T_{111}$, respectively (Figure 4b). Because each facet owns its own unique surface atomic arrangement, which will result in different electronic configuration from other facet, thus TiO$_2$ single crystals exposed with various crystal facets will exhibit different electronic band structures.$^{17,23}$ As shown in Figure 4c, the valence band XPS spectra reveal that the VB maxima of all the four TiO$_2$ samples are similar. Consequently, the order of the potential of the conduction band minimum are $T_{111} > T_{010} > T_{101} > T_{001}$ (Figure 4d). In the photocatalytic reaction, considering the effect of the electronic band structure, the TiO$_2$ sample with a higher conduction band minimum which can generate more reductive electrons to take part in the

Figure 3. Surface structures of the relaxed stoichiometric {111}, {001}, {010}, and {101} facets.
the photocatalytic property of T111 as well as the other TiO2 aqueous methanol solution was employed for evaluation of Δ327.5 nm (ΔE18.5 nm) were also studied. Their corresponding plots of transformed Kubelka–Munk function versus the energy of photon. (c) Valence-band XPS spectra of the four TiO2 samples. (d) Schematic illustration of the determined valence-band (VB) and conduction-band (CB) edges of T001, T101, T010, and T111.

Figure 4. (a) UV–visible absorption spectra of the TiO2 samples. (b) Comparison of photocatalytic activities between T111 and T010 with the same surface area (ca. 0.23 m2) under the monochromatic light centered at a wavelength of 327.5 nm (ΔE18.5 nm) (gray curve). (d) Comparison of photocatalytic activities between T111 and T010, respectively, via the method reported in our previous study.52 It is apparent that the absorbed photons for T010 are higher than that of T010 (1.2 μmol h−1 m−2) for T111 and T010 respectively, see Table S1 in the Supporting Information). Taking the surface areas into account, based on the data from Figure 5a, the photocatalytic activities are calculated to be 582.1 and 341.3 μmol h−1 m−2) for T111 and T010 respectively. In addition, we also experimentally tested the photocatalytic performance of the two photocatalysts (T111 and T010) in the same surface area of ca. 0.23 m2 (Figure 5b). In this case, the photocatalytic activity of T111 is about 3 times that of T010 as shown in Figure 5b. Therefore, on the basis of the above analysis, both the calculation and experimental results confirm that T111 exhibits higher specific activity than that of T010.

Moreover, we should consider that the light absorption abilities for the two photocatalysts (T111 and T010) under the UV–visible light irradiation are different (Figure 5c). The number of the absorbed photons between 300 and 400 nm were calculated to be 0.254 μmol/s and 0.367 μmol/s for T111 and T010 respectively, via the method reported in our previous study.52 It is apparent that the absorbed photons for T010 are approximately 1.5 times that of T111. Hence, their photocatalytic performances under monochromatic light centered at a wavelength of 327.5 nm (ΔE18.5 nm) were also studied. As shown in Figure 5c, the light-absorption difference between T111 and T010 can be eliminated under this condition. In this way, it is worthy of note that T111 still exhibits a significantly higher photocatalytic activity (8.2 μmol h−1), more than 6 times that of T010 (1.2 μmol h−1) (Figure 5d).

Finally, to investigate the contribution of oxygen vacancy worked on the enhancement of the photocatalytic activity, control experiments related to the oxygen vacancy on T111 surface have been done. Instead of treating T111 into air atmosphere at 600 °C to clean the surface, we treated T111 into the pure O2 atmosphere at 600 °C to obtain the oxygen-vacancy-free sample (denoted as T010). The EPR spectra confirm that there is almost no oxygen vacancy existed on the TiO2 surface (see Figure 6a in the Supporting Information). T010 exhibits a slightly better crystallinity (see Figure 6b in the Supporting Information) and similar light absorption edge (see Figure 6c in the Supporting Information) to that of T111. However, as shown in Figure 6d in the Supporting...
Information, it is revealed that the photocatalytic activity of $T_{111}$ without oxygen vacancy is only 0.75 times of $T_{111}$ with small amount of oxygen vacancies, proving that the suitable amounts of oxygen vacancy existed on the $T_{111}$ surface is indeed beneficial for the promotion of the photocatalytic performance. On the basis of the above theoretical analysis and experimental results, we can address that the vital factor for the higher photocatalytic performance of $T_{111}$ is the superior surface properties owned by $\{111\}$ facet. Because of its particular surface structure, the surface atomic coordination and arrangement of $\{111\}$ facet are obviously different from other facets (Figure 3). Accordingly, TiO$_2$ sample with dominant $\{111\}$ facet exposed exhibited good candidate characters in both surface atomic structure (the density of undercoordinated atoms) and electronic band structure for the excellent photoreactivity, which can be explained in detail as following.

The first property relevant to the photocatalytic activity is the surface atomic structure. It is reported that a facet with a higher percentage of undercoordinated atoms are usually more reactive in the heterogeneous reactions. These undercoordinated Ti atoms on the TiO$_2$ surface can act as the catalytically active sites for the photoreaction.3,5,4 On the $\{111\}$ surface, all Ti atoms are undercoordinated (25% Ti$_3$c and 75% Ti$_5$c). Compared with $\{010\}$ (100% Ti$_3$c), $\{001\}$ (100% Ti$_3$c), and $\{101\}$ (50% Ti$_3$c and 50% Ti$_5$c), the photoreactivity of $\{111\}$ surface is thus expected to be higher than those of other facets. What’s more, the formation of oxygen vacancies on the $\{111\}$ surface, which is facilitated by the presence of numerous undercoordinated O atoms (100% O$_2$c), can also offer more active sites on the $\{111\}$ surface, thus enhance the photocatalytic activity.4,7 Another key issue influencing the photocatalytic efficiency is the electronic band structure. On the basis of the deduced electronic band structures of the four TiO$_2$ samples ($T_{111}$, $T_{010}$, $T_{101}$, and $T_{001}$), the conduction band minimum of $T_{111}$ is the highest, hence the more strongly reductive electrons can be produced then transferred to the surface Pt sites to reduce $H^+$ into $H_2$.5,6 Thereby, compared with the previous report in which the photoreactivity only can be promoted by one or two times via facet control,6 herein, via optimizing both the surface atomic structure and electronic band structure, $T_{111}$ exhibits the obviously higher photocatalytic activity, about five times that of $T_{010}$ (Figure 5a).

**CONCLUSIONS**

The well-defined $\{111\}$ facet exposed TiO$_2$ single crystals are synthesized via both F$^-$ and ammonia as the capping reagents. This TiO$_2$ sample exhibits an obviously higher photocatalytic activity in comparison to TiO$_2$ samples exposed with majority $\{001\}$, $\{101\}$, and $\{010\}$ facets. The largely enhanced photocatalytic activity can be attributed to its superior surface atomic structure (large percentage of undercoordinated atoms on the TiO$_2$ surface to act as the active sites for the photoreaction) and electronic band structure (higher conduction band minimum on which more reductive electrons can be generated). This fundamental understanding shows that the facet control of semiconductors allows the optimization of both the surface atomic structure and electronic band structure, thus largely promotes the photocatalytic efficiency. This study evidence that the surface-structural engineering of semiconductors is an effective approach to achieve advanced and excellent performance over photocatalysts.