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# Hollow Anatase TiO<sub>2</sub> Octahedrons with Exposed High-Index {102} Facets for Improved Dye-Sensitized Photoredox Catalysis Activity

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S Supporting Information

ABSTRACT: The high activity of exposed facets and large surface area have significant effects on the performance of photocatalysts because most of the photoreactivity properties of materials are related to surface processes. The strategy of combining high-index facets and a hollow structure into one material will provide a new way for designing effective photocatalysts, possessing active exposed facets and a large surface area at the same time. However, fabricating one material with both high-index facets and a hollow structure is still a great challenge due to their thermodynamic instability. Here, hollow anatase TiO<sub>2</sub> octahedrons exposed with high-index (102) facets (HTO-102)



were successfully fabricated for the first time by a facile hydrothermal method using HF and  $H_2O_2$  as morphology controlling agents. Compared with two other catalysts (a solid sharp octahedron with (101) facets (SSO-101) and a hollow sharp octahedron with (101) facets (HSO-101)), HTO-102 particles exhibit a better photochemical activity for the selective aerobic oxidation of organic sulfides under visible-light irradiation. Experimental results and theoretical calculations indicate that the excellent photocatalytic activity of HTO-102 particles is mainly due to the synergistic effects of its hollow structure and exposed high-index (102) facets.

# INTRODUCTION

Photoredox catalysis has great potential in converting solar energy to chemical energy, which can environmentally facilitate organic transformations to valuable products.<sup>1-4</sup> Although significant achievements in photocatalytic semiconductor materials have been realized in recent years, the photocatalytic efficiency for solar energy is still quite low for practical applications.<sup>5-7</sup> The catalysts with exposed high-index crystal facets usually show chemical activities higher than those of catalysts with exposed low-index crystal facets, as the high-index crystal surfaces possess a high density of kinks, edges, steps, and low-coordinated atoms within the structures which usually serve as active sites in chemical reactions.<sup>8–10</sup> During the current decade, many noble metals and metal oxides with exposed high-index crystal facets have been fabricated by different synthesized strategies. At present, the already reported metal oxide nanoparticles exposed with high-index crystal facets usually present microscale solid bulk structures with large sizes and low surface areas, which greatly limit their practical application in the field of photocatalysis.

The hollow structures provide a large surface area and low diffusion resistance for improving accessibility, which can offer some new opportunities that can make up for the lack of particles with high-index facets.<sup>11,12</sup> The hollow cavity can also serve as a reactor and support efficient diffusion of the reactants, solvent, and products in and out of the inside

chamber through a porous hull. Meanwhile, the hollow structure can enhance the utilization efficiency of incident light by multiple reflections of light in an internal cavity.<sup>13–15</sup> Therefore, combining the high-index facets and hollow structure into one material will be a new way to design highly efficient photocatalysts. However, most of the synthesized hollow structures are exposed without specific crystal facets, and a few parts are exposed with low-index crystal facets.<sup>16</sup> Thus, fabricating one material that has both high-index facets and a hollow structure is still a great challenge, owing to the thermodynamic instability of high-index crystal facets and hollow structures.

Titanium dioxide (TiO<sub>2</sub>), an n-type metal oxide semiconductor (bandgap about 3.2 eV), is a promising prospect in applications of solar cells,<sup>17</sup> photocatalysis,<sup>18</sup> and photosplitting of water.<sup>19-22</sup> To date, different morphologies of TiO<sub>2</sub> nanomaterials with exposed various crystal facets have been fabricated via different synthesized methods.<sup>23,24</sup> However, the hollow structure TiO<sub>2</sub> with exposed high-index facets has not been reported. In this article, we first fabricate the hollow anatase TiO<sub>2</sub> octahedron exposed with high-index {102} crystal facets by a simple hydrothermal route. Due to the synergistic effects of the hollow strucuture and exposed high-index (102)

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facets, HTO-102 particles exhibit excellent photochemical activity for selective aerobic oxidation of organic sulfides under visible-light irradiation.

#### EXPERIMENTAL SECTION

**Preparation of Anatase Hollow TiO<sub>2</sub> Nanoparticles with** {102} Facets (HTO-102). Hollow TiO<sub>2</sub> nanoparticles with {102} facets were fabricated through a one step hydrothermal method by utilizing a potassium titanate nanowires (KTNWs) precursor (for the synthetic method see the Supporting Information or ref 25). Typically, a KTNWs precursor (0.025 g) was dissolved in a solution that contained deionized water (27 mL),  $H_2O_2$  (3 mL, 30%), and HF (0.02 mL, 40 wt %). The solution was loaded into a Teflon-lined autoclave and was heated at 180 °C for 12 h in the oven. After the autoclave was cooled to room temperature, the products were obtained after being washed, centrifuged, and then dried at 60 °C in an oven.

**Photocatalytic Test for the Oxidation of Sulfide.** Typically, ARS-TiO<sub>2</sub> (10 mg), thioanisole (0.3 mmol), and TEMPO (0.02 mmol) were added to CH<sub>3</sub>OH (3 mL). The solution was illuminated by blue LED light (3W, 450 nm) for 12 h while being constantly stirred in an air atmosphere. The product yield was determined by <sup>1</sup>H NMR analysis. The recycle experiments were conducted by centrifuging the catalytic solution and washing it with CH<sub>2</sub>Cl<sub>2</sub> three times. Finally, the recycled catalysts were dried at 50 °C in a vacuum for 24 h.

# RESULTS AND DISCUSSION

The hollow anatase  $TiO_2$  with exposed (102) facets (HTO-102) was synthesized by direct hydrolysis of KTNWs with a certain proportion of HF and H<sub>2</sub>O<sub>2</sub> in a hydrothermal system at 180 °C for 12 h (detailed experimental process provided in ESI). The X-ray powder diffraction (XRD) pattern of HTO-102 is shown in Figure 1a. All diffraction peaks could be indexed to be the anatase phase  $TiO_2$  with lattice parameters a = b = 3.775 Å and c = 9.49 Å (JCPDF no. 00-002-0387), indicating the high purity of the product. The morphology and size of the product were first examined by a SEM technique. A typical low magnification SEM image of the product is shown in Figure 1b, from which large quantities of the TiO<sub>2</sub> particles with a porous polyhedral morphology and an average edge length of about 90-120 nm can be found (Figure S1). Closer observations (inset of Figure 1b) indicated that they have a well-defined hollow octahedral structure.

In order to collect details of the morphology and structural information on the hollow octahedral TiO<sub>2</sub> particles, transmission electron microscopy (TEM) observations were carried out. The low-magnification TEM image of a single TiO<sub>2</sub> octahedron is shown in Figure 1c, where the hollow structure was further confirmed by the obvious contrast of the dark edges and the pale center. The relevant selected-area electron diffraction pattern (SAED) can be indexed to the [111] crystal zone axis of single-crystal tetragonal TiO<sub>2</sub> (inset Figure 1c). Under electron beam illumation, the octahedron shows a rhombic shape with a length/width proportion of about 1.15 and a vertex angle between two lateral faces of approximately 84°. The profile and angles correspond well with the anatase TiO<sub>2</sub> octahedral model with exposed (102) crystal facets viewed from the [111] direction (Figure 1d). The highresolution transmission electron microscopy (HRTEM) image of HTO-102 is shown in Figure 1e. The lattice spacing is 0.351 nm, corresponding to the (101) lattice spacing of the anatase phase of TiO2. To further identify the enclosed facets of the HTO-102, another octahedral particle viewed from the [001] crystal zone axis was detected by TEM image (Figure 1f) and SAED pattern analyses (inset of Figure 1f). Both the vertex



**Figure 1.** (a) XRD pattern. (b) SEM image of as-synthesized hollow  $TiO_2$  octahedral nanocrystals. (c) TEM image of an individual hollow  $TiO_2$  octahedron projected from the  $[\overline{111}]$  direction, where the inset shows the corresponding SAED pattern. (d) Schematic model of an ideal  $TiO_2$  octahedron enclosed within {102} facets viewed along the  $[\overline{111}]$  direction. (e) The corresponding HRTEM image. (f) TEM image of the  $TiO_2$  octahedron viewed along the [001] direction, inset: the corresponding SAED pattern. (g) Schematic model of an ideal  $TiO_2$  octahedron enclosed within {102} facets viewed along the [001] direction, inset: the corresponding SAED pattern. (g) Schematic model of an ideal  $TiO_2$  octahedron enclosed within {102} facets viewed along the [001] direction. (h) The corresponding HRTEM image.

angle and the outline of the octahedral particle still coincide well with the anatase  $TiO_2$  octahedral model with exposed (102) facets viewed from the same direction (Figure 1g). Figure 1h shows that the *d*-spacing is about 0.19 nm, which corresponds well with the (200) facet of anatase  $TiO_2$ . The above TEM result and corresponding structural analysis indicate HTO-102 particles have a hollow structure with exposed high-index (102) facets. The nitrogen adsorption–desorption isotherms show that the specific surface area of HTO-102 is about 64.1 m<sup>2</sup> g<sup>-1</sup>, and the pore size distribution indicates a porous structure (Figure S2), which corresponds well with the SEM and TEM observations. In other words, the obtained HTO-102 particles possess high-index facets, a hollow structure, and a large BET surface area, all of which are favorable for catalysis.

Their catalytic activities were evaluated by using selective aerobic oxidation of thioanisole in methanol solvent. In order to broaden the HTO-102 visible-light adsorption range, the dye (alizarin red S (ARS)) was anchored onto HTO-102. In addition, TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) was adopted as a redox mediator for preserving the anchored dye's stability.<sup>26</sup> The catalytic reaction was performed in a Schlenk tube by using blue-light emitting diodes (LEDs, *hv* 450 nm, 3 W) as the light source (Figure 2a). As shown in Figure 2b, the conversions of thioanisole for only HTO-102 as a catalyst are merely 3% under the visible-light irradiation. The inclusion of the dye could lead to a dramatic increase in yield (53%) owing to the extended visible-light adsorption range (Figure S3, UV– vis spectrum). However, after a few minutes of visible-light irradiation, the color of the solution had changed markedly



Figure 2. (a) Photocatalytic equation and reaction conditions. (b) Conversion of thioanisole with different experimental conditions, inset: photograph of before (I) and after (II) with TMMPO and (III) without TEMPO visible-light reaction. (c) Conversion of thioanisole irradiated by different light sources. (d) Product yield with respect to reaction time in the selective oxidation of sulfides into sulfoxides by various catalysts. (e) Recycling experiments using various catalysts.

(inset of Figure 2bII and Figure S4), which indicated the oxidation of ARS itself rather than the oxidation of thioanisole.

With the addition of the TEMPO redox mediator, the stability and catalytic efficiency of dispersed ARS-TiO<sub>2</sub> could be substantially increased. The above contrast experiments revealed that dye sensitivity and having a TEMPO redox mediator were two basic conditions for this catalytic reaction. When the light source was switched to yellow light (590 nm, 3 W) and green light (530 nm, 3 W), the catalytic conversion was able to achieve a low conversion of only 13% and 56%, respectively (Figure 2c). Therefore, suitable experimental conditions for this catalysis used blue LEDs as the light source in the presence of ARS and TEMPO. The catalytic reaction result is shown in Figure 2d. Compared with sharp octahedrons with (101) facets (SSO-101) (Figure S5), hollow sharp octahedrons with (101) facets (HSO-101) (Figure S6) show better reactivity after 12 h irradiation, indicating that the existence of having hollow structures could enhance the catalytic activity under the same reaction conditions. The hollow structures have three advantages for improving the photocatalytic activity of catalysts: (1) the inner cavity can enlarge the surface area (the specific surface areas of HSO-101 and SSO-101 are about 59.9 and 26.7 m<sup>2</sup> g<sup>-1</sup>, respectively, as the BET measurement shows in Figure S7), which increases the active sites of the catalyst; (2) the hollow structure can increase the multiple light reflections, which can enhance the utilization efficiency of incident light; and (3) the hollow structure can shorten the diffusion length of photogenerated electrons and holes. High-index facets, defined as a series of Miller index  $\{hkl\}$  with not less than one index greater than unity, can generally provide more catalytic active sites (e.g., more atomic steps and dangling bonds) than low-index facets can. Therefore, synergistic effects of a hollow structure and high-index plane in one material will further improve the catalytic activity of catalysts. As shown in Figure 2d, the photocatalytic activity of HTO-102 particles (hollow structure and enclosed by highindex (102) facets) is better than that of SSO-101 (solid structure and enclosed by low-index (101) facets) and HSO-101 (hollow structure and enclosed by low-index (101) facets). In order to demonstrate the generality for this reaction, various thioanisole derivatives were used to evaluate HTO-102 catalysts, and the yields and selectivity of the desired oxidized product were 77–96% and 78–98%, respectively (Table 1). In

Table 1. Scope of Visible-Light-Induced Selective Oxidation of Sulfides to Sulfoxides in Air on ARS-Sensitized HTO-102 with TEMPO as a Redox Mediator

R		<u> </u>	3 W Blue Light CH,OH, Air	LED R <sub>1</sub>	
	R1	R2	R3	conv. (%)	select. (%)
1	[Cl]	[H]	[H]	90	98
2	[F]	[H]	[H]	92	98
3	[Br]	[H]	[H]	93	98
4	[Me]	[H]	[H]	90	96
5	[MeO]	[H]	[H]	96	97
6	$[NO_2]$	[H]	[H]	77	78
7	[H]	[MeO]	[H]	82	98
8	[H]	[H]	[MeO]	94	98

order to evaluate the catalytic stability, we carried out the cycle performance of SSO-101, HSO-101, and HTO-102 catalysts for the selective aerobic oxidation of thioanisole (Figure 2e). The results reveal that the HTO-102 catalyst possesses an outstanding catalytic stability and maintains an above 90% conversion rate for the selective aerobic oxidation of thioanisole within 12 h even after four cycles. The above results suggested that the HTO-102 possessed outstanding catalytic activity and stability.

All catalytic experiments were performed as follows: photocatalyst (10 mg), sulfide (0.3 mmol), and TEMPO (0.02 mmol) were added to  $CH_3OH$  (3 mL). The mixture was stirred and then irradiated by blue LEDs (450 nm, 3 W) for 12 h under an air atmosphere at room temperature. <sup>1</sup>H NMR analysis was employed to determine the yield.

Based on the control experiments and others' previous findings, a probable reaction mechanism for visible-light photoredox catalysis by ARS-sensitized TiO<sub>2</sub> with TEMPO as a redox mediator is proposed and illustrated in Scheme 1. Under blue-light irradiation, dye molecules (ARS) were excited to an excited state (ARS\*) and the generated electrons were injected into the conduction band of TiO2. These electrons travel through the conduction band of TiO<sub>2</sub> to react with chemisorbed oxygen on the TiO<sub>2</sub> surface, thereby forming  $O_2^{\bullet-}$ , which prefers to react with an S-centered free-radical cation for the evolution of sulfide peroxide. Therefore, the amount of photogenerated electrons played a key role in determining photocatalytic efficiency. In theory, the two characteristics of hollow structure and high-index facets will contribute to more effective contact between HTO-102 and the dye molecules, resulting in the production of a large number of photogenerated electrons.

To prove this, the photocurrent density of three ARSsensitized  $TiO_2$  samples was measured by using a 0.2 V potential under light (i.e., illuminated) and dark (i.e., nonScheme 1. Proposed Mechanism of Selective Aerobic Oxidation of Thioanisole by ARS-HTO-102 under Blue-Light Irradiation



illuminated) conditions with 20 s intervals. Figure 3a shows that the sequence of average photocurrent densities was HTO-



Figure 3. (a) Photocurrent density of three ARS-sensitized  $TiO_2$  samples measured at 0.2 V versus  $Hg/Hg_2Cl_2$  under non-illuminated (i.e., dark) and visible-light illuminated (xenon lamp with an optical filter UVCUT-420) conditions. (b) UV–vis adsorption spectra of the cationic radical of TMPD generated by three ARS-sensitized  $TiO_2$  samples in the presence of light and oxygen.

102 > HSO-101 > SSO-101. Electrochemical impedance spectroscopy (EIS) results (Figure S8) further demonstrated that a high separation efficiency of photogenerated electronhole pairs and fast interfacial electron and hole transfers occurred for HTO-102. The above results show that the amount of effective photogenerated electrons increases due to the existence of hollow structures and high-index facets. The molecular oxygen was reduced by separated electrons to obtain superoxide radical  $(O_2^{\bullet-})$ , which was confirmed as generated by the cationic radical species of N,N,N',N'-tetramethylphenylenediamine (TMPD) (Figure 3b). Under irradiation with a blue LED, blue color species with absorption bands at 563 and 612 nm were formed by ARS-TiO<sub>2</sub> mediating the abstraction of an electron from TMPD. Compared with those of ARS-SSO-101 and ARS-HSO-101, the solution after ARS-HTO-102 reaction had stronger absorption peaks at 563 and 612 nm, which demonstrated ARS-HTO-102 could produce more  $O_2^{\bullet-}$ . The above results were consistent with the photoredox catalysis activity of the three different catalysts.

In the whole photocatalytic process, the amount of chemisorbed oxygen on the  $TiO_2$  surface, which is determined by the surface structure of the catalyst, also plays a key role in the improvement of forming  $O_2^{\bullet-}$ . In order to obtain useful information about chemisorbed oxygen on the  $TiO_2$  surface, X-

ray photoelectron spectroscopy (XPS) analyses were used. The fully scanned spectra (Figure S9) showed that Ti and O element signals existed in the SSO-101, HSO-101, and HTO-102 samples. Figure 4a shows the high-resolution XPS spectra



Figure 4. (a) High-resolution XPS spectra of  $Ti_{2p}$ . (b) XPS spectra and curve fitting of O 1s in SSO-101, HSO-101, and HTO-102.

of Ti<sub>2p</sub>, in which the peak located at 464.4 eV corresponds to  $Ti_{2p1/2}$  and the other peak located at 458.6 eV was assigned to  $Ti_{2p3/2}$ . This indicated that the distribution and position of the Ti<sub>2p</sub> XPS peaks of the three samples were basically analogous. However, the high-resolution  $O_{1s}$  XPS peaks of the three TiO<sub>2</sub> samples had some slight differences. The O<sub>1s</sub> core level peaks could be resolved into three centered Gaussian components (Figure 4b). The O<sub>L</sub> component (529.6  $\pm$  0.1 eV) was associated with the lattice oxygen in the anatase TiO<sub>2</sub> phase. The O<sub>V</sub> peak at the medium binding energy (530.2  $\pm$  0.1 eV) was usually assigned to the O<sup>2-</sup> ions in the oxygen-deficient region, and the  $O_C$  component (531.8 ± 0.1 eV) was associated with the dissociated and chemisorbed oxygen species  $(O^-, O_2^-, O_2^-)$ and  $O^{2-}$ ). Therefore, the peak area of the  $O_{C}$  constituents in the O<sub>1s</sub> XPS spectrum can be used to estimate the oxygenchemisorbed amount of the three various materials.<sup>27</sup> Table 2

Table 2. Results of Curve Fitting of O 1s Spectra in Three Different  $TiO_2$  Samples

TiO <sub>2</sub> samples	Ti 2p3/2	Ti 2p1/2	O <sub>L</sub> (Ti–O)	O <sub>V</sub> (vacancy)	O <sub>C</sub> (chemisorbed)
SSO-101	710.2	723.5	529.7 57.6%	530.2 37.6%	531.8 4.8%
HSO-101	710.7	724.1	529.7 65.3%	530.2 25.6%	531.8 9.1%
HTO-102	710.2	723.8	529.6 62.1%	530.1 24.1%	531.7 13.8%

shows that the relative proportions of the  $O_C$  component in the three various materials are about 4.8% (SSO-101), 9.1% (HSO-101), and 13.8% (HTO-102). Obviously, HTO-102 samples could absorb a quantity of oxygen species higher than that of the HSO-101 and SSO-101 samples. The above comparison of XPS experimental results confirms that the two factors of hollow structure and high-index facets play a key role in the enhancement of capacity for surface oxygen adsorption.

In addition to the large surface area, the structure of the exposed surface also plays an important role in oxygen adsorption, because HTO-102 can absorb oxygen species in an amount greater than that of HSO-101, as the results of XPS analysis show. In order to further explore the influences of surface structures on oxygen adsorption, the surface structures of anatase  $TiO_2$  (102) and (101) surfaces were calculated, and the optimized structures are shown in Figure 5a and 5b, respectively. By comparing Figure 5a and 5b, we find that the



**Figure 5.** Optimized surface structure of anatase  $TiO_2$  (102) (a) and (101) (b). The optimized stable configurations for  $O_2$  adsorption on  $TiO_2$  (102) (c) and (101) (d). The projected density of states (PDOSs) of  $O_2$  adsorbed  $TiO_2$  (102) (e) and (101) (f).

(102) surface possesses more wrinkles than the (101) surface, which is beneficial to oxygen adsorption. Ti sites are the main active sites for oxygen adsorption on TiO<sub>2</sub> surfaces. The anatase  $TiO_2$  (102) surface is composed of  $Ti_{4c}$  (four-coordination Ti), while the (101) surface consists of  $Ti_{5c}$  (five-coordination Ti). The  $Ti_{4c}$  on the (102) surface can provide electrons to oxygen more easily than the  $Ti_{5c}$  on the (101) surface, resulting in a greater oxygen adsorption on the  $TiO_2$  (102) surface. The optimized stable configurations of oxygen adsorbed on anatase  $TiO_2$  (102) and (101) surfaces are shown in Figure 5c and 5d, respectively. The calculated adsorption energies of these two configurations are -8.65 and 5.17 eV, respectively. The oxygen adsorption on the  $TiO_2$  (102) surface is an exothermic process, while the process of oxygen adsorbed on the (101) surface is endothermic, indicating that the adsorption of oxygen is favored on the TiO<sub>2</sub> (102) surface. This result is in accordance with the above structure analysis. From the projected density of states (PDOSs) of oxygen adsorbed on anatase  $TiO_2$  (102) and (101) surfaces (Figure 5e and 5f), it can be found that, for the  $TiO_2$  (102) surface, the adsorbed  $O_2$  2p states have an overlap with the surface  $Ti_{4c}$  3d states greater than that for the (101) surface, meaning that there are stronger electronic effects between adsorbed oxygen and  $TiO_2$  (102) than between adsorbed oxygen and the  $TiO_2$  (101) surface. These results explain the reason for more oxygen being adsorbed on the TiO<sub>2</sub> (102) surface than on the (101) surface from electronic structures.

# CONCLUSION

In conclusion, the hollow anatase  $\text{TiO}_2$  octahedrons with exposed high-index (102) facets have been successfully synthesized by a facile hydrothermal method with HF and  $H_2O_2$  as morphology controlling agents. Experimental results and theoretical calculations indicate that HTO-102 easily absorbed sensitized dye molecules and oxygen species, which resulted in the production of a large amount of photogenerated electrons and superoxide radicals ( $O_2^{\bullet-}$ ). Due to the synergistic influence of exposed high-index crystal facets and its hollow structure, HTO-102 exhibits a photochemical activity for the selective aerobic oxidation of organic sulfides under visible-light irradiation better than that of SSO-101 and HSO-101. This result can be used as a new strategy for designing highly efficient photocatalysts for catalyzing many organic reactions.

#### ASSOCIATED CONTENT

# **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b00307.

Experiment details; size distribution, BET, and UV-vis absorption of HTO-102 (Figures S1–S3); and XRD, SEM, BET, and XPS of SSO-101 and HSO-101 (Figures S4–S8) (PDF)

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#### Notes

The authors declare no competing financial interest.

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