Controllable Nanocarving of Anatase TiO₂ Single Crystals with Reactive {001} Facets

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Owing to its wide applications in photocatalysis, photoelectrochromics, solar cells, sensors, and smart surface coatings, anatase titanium dioxide (TiO₂) has attracted intensive research interests during the past decades.^[1–4] Most available and stable anatase TiO₂ single crystals have truncated octahedral-bipyramid shapes, in which the majority of the surface area is normally surrounded by thermodynamically stable {101} facets, rather than the more reactive {001} facets.^[5–7] For a long period, tailored synthesis of {001}-faceted anatase TiO₂ single crystals has been a great challenge. Recently, we made a breakthrough in the hydrothermal synthesis of anatase TiO₂ single crystals with a large percentage (35–47 %) of highly reactive {001} facets by using hydrofluoric acid (HF) as a specific morphology-controlling agent.^[8] Later, with the assistant of isopropanol (*i*PrOH)—a synergistic capping agent together with HF, anatase TiO₂ single crystals with a higher ratio of {001} facets were prepared through a water–isopropanol solvothermal synthetic route.^[9] During these processes, HF was reported to act as a capping agent by reversing the relative stability of {001} and {101} facets and therefore promoting the growth of {001}-faceted surfaces of anatase TiO₂. By using similar strategies, a series of studies by research groups worldwide have demonstrated the syntheses and applications of anatase TiO₂ with exposed reactive {001} facets.^[10–18] Unfortunately, few researchers have explored the etching effect of HF, which was traditionally considered a strong etching agent for metal oxides.^[19–24] Thus studying the chemical stability of {001}-faceted anatase TiO₂ in the presence of HF is quite important and can help to understand the real function of HF during these important chemical processes. Herein, the dual role of HF—as capping agent and etching agent—is revealed through the controllable nanocarving of {001}-faceted anatase TiO₂ single crystals. This process was realized through thermal treatment of anatase TiO₂ single crystals with 35 % of {001} facets by using HF-containing solutions or just by

one-step solvothermal reactions of aqueous titanium tetrafluoride (TiF₄) solutions in mixed solvents containing HF. In addition, a feasible mechanism is proposed to clarify the etching process involving HF and the growth process of the anatase TiO₂ products with diverse morphologies.

Figure 1a presents a typical SEM image of anatase TiO₂ single crystals with 35 % of reactive {001} facets, which was synthesized according to the method described in our earlier

Figure 1. a) SEM image of anatase TiO₂ single crystals with 35 % of {001} facets synthesized with an aqueous TiF₄ solution (5.33×10^{-3} M) at 180 °C for 14 h. b,c) Typical SEM images of the samples prepared through hydrothermal treatment of the product with H₂O (25 g) containing HF (10 wt %, 0.4 mL) at 180 °C for 6 and 9 h, respectively. d) Corresponding TEM image of an individual particle in (c).

report.^[8] It can be observed that the as-obtained product consists of well-faceted truncated octahedra, in which the two square surfaces and the other eight isosceles have been confirmed to be {001} and {101} facets, respectively.^[8] Moreover, all of the crystal surfaces are extremely smooth without any impurities. When the as-synthesized anatase TiO₂ single crystals were treated with deionized water containing HF (10 wt %) at 180 °C for 6 h, uniform truncated octahedra with specific surface topography were obtained, as shown in Figure 1b. Compared with the original anatase TiO₂ with perfect crystal surfaces, it can be clearly observed that very significant etching traces appeared on {001} surfaces and inverted pyramidal pits were generated at the center of the {001} facets after the hydrothermal treatment, which can be

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201100134>.

attributed to the etching effect of HF in aqueous solutions. Simultaneously, new crystal faces were formed on the surfaces of the particles. These faces can be identified as {112} facets of anatase TiO₂.^[21] By prolonging the treating time to 9 h, the initial exposed {001} surfaces nearly disappeared and button-like particles were obtained. Viewed from the crystallographic direction that corresponds to the {001} facets, small holes can be observed at the center of the {001} facets as well (Figure 1c,d). When the treatment time was further extended to 14 h, the original anatase TiO₂ crystals would dissolve in the aqueous HF solution completely and no solid product could be obtained. These experimental results revealed a strong etching effect of HF on {001}-faceted anatase TiO₂ under hydrothermal conditions.

To investigate the influence of solvent on the etching process of {001}-faceted anatase TiO₂, a series of experiments were carried out by replacing deionized water with mixed solvents. Figure 2a–f presents the SEM images of the sam-

Figure 2. SEM images of the samples prepared by treating anatase TiO₂ single crystals with 35% of {001} facets at 180 °C for 22 h with mixed solvents containing an aqueous HF solution (10 wt %, 0.4 mL, a–f). The mixed solvents consist of a) *i*PrOH (25 g), b) H₂O (5 g) + *i*PrOH (20 g), c) H₂O (10 g) + *i*PrOH (15 g), d) H₂O (15 g) + *i*PrOH (10 g), and e,f) H₂O (20 g) + *i*PrOH (5 g).

ples derived from treatment of the as-synthesized TiO₂ crystals in a mixture of isopropanol and deionized water in various mass ratios. When the process was performed in nonaqueous solvent (i.e., isopropanol), the obtained product exhibits an identical structure to the starting material without any etching traces detected on the crystal surfaces, as seen in Figure 2a. Nevertheless, when mixed solvents were adopted in the treatment, significant etching phenomena on the

surfaces of the resulting products can be observed. Furthermore, the facial etching gradually intensified as the content of deionized water in the mixed solvents increased, which can be deduced from the SEM images shown in Figure 2b–f. In addition, the etching activity on {001} facets is very uniform on the whole crystal surface, showing a dramatic difference from the etching process that originates from the center of the {001} facets. Figure 2e,f show that many newly formed tiny TiO₂ pits, which exhibit the same characteristics as the pits shown in Figure 1b, are distributed uniformly on the etched surface area. The XRD pattern (Figure S1a in the Supporting Information) evidenced the pure anatase phase of the typical sample synthesized by this method. On the whole, {001}-faceted anatase TiO₂ single crystals treated with nonaqueous and water–isopropanol mixed solvents exhibit milder etching than the crystals treated with pure deionized water. We believe that isopropanol can be deemed as a stabilizer of {001}-faceted surfaces of anatase TiO₂,^[9] hindering the nanocarving processes, whereas water provides a desirable environment for the etching of anatase TiO₂ by HF.

In addition to the posttreatment strategies mentioned above, which can be used to realize facial etching of the as-synthesized {001} faceted anatase TiO₂, a one-pot synthetic method was also applied to investigate the HF etching behavior during the synthetic process of {001}-faceted anatase TiO₂. This process was conducted by simply modifying the experimental parameters of the synthetic method for anatase TiO₂ single crystals with 64% of {001} facets.^[9] The XRD pattern (Figure S1b in the Supporting Information) indicates the pure anatase phase of the resulting product. The SEM images shown in Figure 3a,b reveal that the uniform, single particle-composed product have a truncated octahedral-bipyramid morphology similar to the {001}-faceted anatase TiO₂, except for two etched square surfaces. The TEM image (Figure 3c) and the corresponding selected-area elec-

Figure 3. a,b) SEM images of the product fabricated from the one-step solvothermal reaction at 180 °C for 12 h with a mixture containing TiF₄ solution (0.04 M, 2 mL), H₂O (3 g), *i*PrOH (20 g), and HF (10 wt %, 0.4 mL). c) Typical TEM image of a single particle and d) the corresponding SAED pattern.

tron-diffraction (SAED) pattern (Figure 3d) indicate single-crystalline characteristics and the [001] direction perpendicular to the flat square surfaces. Thus, the perfect eight isosceles trapezoidal surfaces can be identified as {101} facets, whereas the other two surfaces are {001} facets of anatase TiO₂ single crystals. A stamp-like pattern can be observed from the [001] crystallographic direction, which is remarkably different from the products derived from posttreatment processes. To address the growing process of this product, experiments with different reaction time were carried out under similar conditions.

From TEM images of the resulting products derived from solvothermal reactions with different reaction time, ranging from 3 to 31 h (Figure 4a–f), it can be suggested that the etched anatase single crystals shown in Figure 3 were devel-

Figure 4. TEM images of the products synthesized through the solvothermal reaction with a mixture containing TiF₄ solution (0.04 M, 2 mL), H₂O (3 g), *i*PrOH (20 g), and HF (10 wt %, 0.4 mL) at 180 °C for a) 3, b–e) 22, and f) 31 h.

oped from the selective etching of the perfect {001}-faceted anatase TiO₂, which was produced at the initial stage of the reaction (Figure 4a). Due to the etching effect of the excess HF in the reaction system, numerous tiny pits were generated simultaneously at the central region and edges of the {001}-faceted anatase TiO₂ in the early stages (Figure 4b,c). These pits were then enlarged gradually and finally combined to form hollow channels or holes. Thus, complex nanostructures with hollow core-shell morphology were generated (Figure 4d,e). Interestingly, when the reaction time was prolonged to 31 h, more complex structures with a

double-hollow core-shell morphology was obtained (Figure 4f). The related formation process can be considered as the result of the continuous etching of the original hollow structures and the backfilling process through TiF₄ hydrolysis that occurred at the same time.

Based on the results discussed, it can be readily concluded that HF has an etching effect on the {001}-faceted anatase TiO₂ in the presence of water and the etching phenomena normally occurs on the {001}-faceted surfaces. Moreover, the degree of etching and the morphology of the resulting products varied remarkably under different reaction conditions. Herein, a plausible mechanism is developed to help understand these phenomena.

Generally, the surface of TiO₂ is readily hydroxylated in an aqueous solution. When anatase TiO₂ is dispersed in an aqueous medium, Ti atoms on the surfaces usually exist in one out of three possible species, that is, TiOH₂⁺, TiO[−], or TiOH, as depicted in Equation (1) and (2).^[22] When F ions were introduced into the system at a pH value of 3, nearly 99.2% of the previous dominant TiOH₂⁺ would be replaced by Ti–F through ligand exchange between surface hydroxyl (–OH) groups on TiO₂ and fluoride ions (F[−]) in the aqueous solution, as illustrated by Equation (3).^[23]

With respect to the {001}-faceted anatase TiO₂ single crystals synthesized by using HF as the capping agent, all of the (001) and (101) surfaces were capped by F atoms, as illustrated by our earlier research.^[8] When anatase TiO₂ with F-terminated surfaces is dispersed in an aqueous HF solution, the surfaces would be hydroxylated and form species, such as TiOH, TiO[−], and TiOH₂⁺ under acidic conditions. Then, these species would be further replaced by Ti–F units. With the consecutive substitution of hydroxyl groups, the surface Ti atoms would dissolve into the aqueous solution in the form of Ti^{IV} complexes,^[25] such as TiF₆^{2−}, and finally result in the etching of anatase TiO₂. After the hydroxylation of surface Ti atoms, each –OH group on the (001) surfaces connects with two adjacent surface Ti atoms, whereas each –OH group on (101) surfaces is linked to two uncoordinated atoms, one surface Ti atom and one subsurface Ti atom. The constraints by subsurface Ti atoms and the thermodynamically lower surface energy of {101} facets would promote further displacement of Ti–OH by Ti–F to preferably occur on (001) surfaces of anatase TiO₂.

Furthermore, when {001}-faceted anatase TiO₂ is present in the mixed water–isopropanol solvent containing HF, Ti atoms on the surfaces would partially bind to isopropoxy ions (*i*PrO[−], (CH₃)₂CHO[−]) and subsequently result in more stable (001) surfaces, as illustrated previously.^[9] Accordingly, with treatment in pure isopropanol, as observed in Figure 2a, the resulting product can maintain a perfect truncat-

ed octahedral structure similar to the starting material. If exposed to the mixed solvents including water and isopropanol, some tiny areas of the {001} surface can also be preserved even under the strong etching effect of HF. Therefore, the formation of the discontinuous surface topography might be reasonable for the {001}-faceted anatase TiO_2 during the etching process in mixed solvents. Besides, the fact that the etching degree gradually increased with the reduction of the isopropanol content in the mixture can also be attributed to the preserving effect on the grown {001} facets exerted by isopropanol together with F atoms. Similarly, the channeled or stamp-like etching of {001}-faceted anatase TiO_2 synthesized by a one-step solvothermal method might be illustrated by using this mechanism as well. The difference is that the etching and refilling reaction are coexisting due to the presence of TiF_4 in reaction medium.^[23]

In summary, controllable nanocarving of {001}-faceted anatase TiO_2 single crystals was realized through various chemical processes involving HF. In the posttreatment method, HF merely acted as an etching agent, which finally led to the formation of anatase single crystals with controlled facial etching. Nevertheless, in the one-step synthesis, HF not only acted as a stabilizer to promote the growth of {001}-faceted anatase single crystals at the early stage of the reaction but also worked as an etching agent that finally gave the etched stamp-like anatase particles, which implies a dual role of HF. Moreover, isopropanol used in these experiments retarded the etching rate by working as a synergistic stabilizer of {001}-faceted surfaces of anatase TiO_2 . Furthermore, due to the differences in surface energy and atomic arrangement between (001) and (101) crystal surfaces of anatase TiO_2 , the etching was mainly observed on high-energy {001} facets and proceeded along the [001] crystallographic direction. In addition, the etching mechanism is suggested to be the replacement of $-\text{OH}$ groups on the crystal surfaces of anatase TiO_2 with F ions and the subsequent dissolution of Ti atoms in the form of Ti^{IV} complexes, such as TiF_6^{2-} . These findings are expected to be useful for the fundamental research of inorganic semiconductors with exposed high-reactive facets and provide effective strategies for the fabrication of complex structures with special morphologies on nano- or micrometer scales.

Experimental Section

Controllable nanocarving of anatase TiO_2 single crystals with reactive {001} facets was achieved by using the different chemical processes described below. All of the chemicals were used as received.

Posttreatment with solvents containing HF: In a typical procedure, deionized water (25 g) containing HF (10 wt %, 0.4 mL)^[8] was added into a Teflon-lined, stainless steel autoclave with a capacity of 50 mL. The as-synthesized TiO_2 single crystals with 35 % of {001} facets were then dispersed into the mixture under vigorous stirring. The autoclave was sealed and kept at 180 °C for 6 h in an electric oven. Under similar conditions, a series of experiments were carried out by prolonging the treatment time or replacing deionized water with mixed solvents, that is, deionized water

and *i*PrOH. All of the solvents used in these processes contained an aqueous HF solution (10 wt %, 0.4 mL).^[8] Detailed experimental parameters and the corresponding products are presented in the Supporting Information (Table S1).

One-pot solvothermal synthesis: For a typical experiment, an aqueous TiF_4 (Aldrich) solution (0.04 M, 2 mL), ^[8] H_2O (23 g), *i*PrOH (20 g), and an aqueous HF solution (10 wt %, 0.4 mL) were added into a Teflon-lined stainless steel autoclave. Then, the autoclave was sealed and heated at 180 °C for 12 h in an electric oven. Under similar conditions, more experiments were performed with different reaction time, that is, 3, 22, and 31 h.

For all experiments, after the reactions, the precipitates on the bottom of the reactor were collected by centrifugation, washed with deionized water three times, and then dried at 80 °C in vacuum overnight.

Material characterization: The crystallographic phases of the samples were examined by XRD (Shimadzu XRD-6000, $\text{Cu K}\alpha$ radiation). Morphology and crystal structure were determined by using a scanning electron microscope (JSM-5600 LV) and a transmission electron microscope (JEM 2010, 200 kV). For TEM or SEM analyses, samples were dispersed in ethanol and then dropped on a carbon-coated copper grid or a conductive SEM sample holder, respectively.

Acknowledgements

This work was financially supported by Scientific Research Foundation of East China University of Science and Technology (YD0142125), Pujiang Talents Programme and Major Basic Research Programme of Science and Technology Commission of Shanghai Municipality (09J1402800, 10JC1403200), Shuguang Talents Programme of Education Commission of Shanghai Municipality (09SG27), National Natural Science Foundation of China (20925621, 20973059, 91022023, 21076076), Fundamental Research Funds for the Central Universities (WJ0913001), and Program for New Century Excellent Talents in University (NCET-09-0347).

Keywords: etching • hydrofluoric acid • nanocarving • reactive facets • titanium dioxide

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Received: January 14, 2011

Published online: ■ ■ ■, 0000

Nanostructures

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**Controllable Nanocarving of Anatase
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{001} Facets**

The dual role of HF: Controllable nanocarving of {001} faceted anatase TiO₂ single crystals was achieved through various chemical processes involving HF, which was revealed to predominantly act as an etching agent during the process. The etching activity preferably occurred on the highly reactive {001} facets (see figure). Moreover, isopropanol can retard the etching of {001} faceted surfaces effectively.