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Activating the Single-Crystal TiO_2 Nanoparticle Film with Exposed {001} Facets

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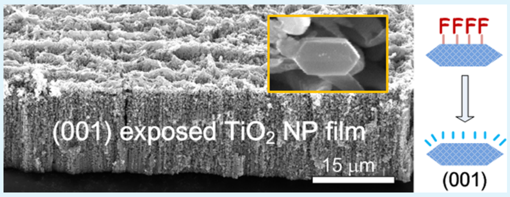
S *Supporting Information*

ABSTRACT: TiO_2 films consisting of single-crystal anatase nanoparticles with exposed {001} facets were fabricated from anodized TiO_2 nanotube arrays. The films' photocatalytic activities were further activated and then enhanced (~2.5 times) by removing F^- from the {001} facets. This study indicates that fluorine-free crystal surfaces are of great importance for the application of such kinds of single-crystal TiO_2 nanoparticle films with exposed {001} facets in related areas.



KEYWORDS: *TiO_2 film, anatase, {001} facets, single crystal, photocatalyst panel*

INTRODUCTION

Titanium dioxide (TiO_2) has attracted worldwide attention because of its promising properties shown in various fields, e.g., solar cell devices, photocatalysis, and sensors.[1−4] Recently, the synthesis and application of anatase TiO_2 particles with exposed higher-surface-energy {001} facets became an ongoing hot research topic. Theoretical studies point out that the (001) surface has much higher chemical activities than the (100) or (101) surface in anatase TiO_2 crystals.[5] Therefore, it is highly desired to obtain anatase TiO_2 nanocrystals with reactive {001} facets exposed in many applications like photocatalysis, catalysis, and dye-sensitized solar cells (DSSCs).

For this reason, great efforts have been made to synthesize TiO_2 crystals with more reactive {001} facets.[6,7] Very recently, an important breakthrough in the preparation of {001}-facet-exposed TiO_2 crystals was achieved by Lu and co-workers.[8−10] They reported the synthesis of micrometer-sized anatase TiO_2 crystallites with highly energetic {001} facets by using hydrofluoric acid as the capping agent under hydrothermal conditions. F ions adsorbed on the TiO_2 surface decrease the surface energy of {001} facets, which then finally leads to the formation of truncated anatase bipyramids with (001) surfaces on the top and bottom. Truncated bipyramidal anatase TiO_2 crystals in powder form were prepared under hydrothermal or solvothermal conditions and have shown excellent performances in various fields.[11−13] For some applications, it is worth noting here that TiO_2 films with exposed reactive (001) surfaces are more favorable, for instance, in electronic related areas (as electrodes) or catalysis (as catalyst panels). However, reports about a TiO_2 film with exposed {001} facets are quite limited so far.

In this study, we prepare a single-crystal TiO_2 nanoparticle (NP) film with exposed {001} facets by using a novel method (not under hydrothermal or solvothermal conditions) raised by Alivov and Fan.[14−16] The successful fabrication of such a TiO_2 film is based on the transformation of electrochemically grown TiO_2 nanotube (NT) arrays into a single-crystal TiO_2 NP film during a special post-thermal annealing process. Further, the as-obtained single-crystal TiO_2 NP films were taken as photocatalyst panels and studied for the first time. Our finding indicates that clean {001} facets are very important for the film's photocatalytic reactivity. This study could benefit the real application of such TiO_2 NP films with exposed {001} facets in various areas.

EXPERIMENTAL SECTION

Briefly, initial TiO_2 NT arrays were grown on titanium substrates by the electrochemical oxidation of metal titanium. The anodic growth was conducted at a constant voltage of 60 V with a water bath at 7 °C. After 3 h of growth, highly ordered TiO_2 NT arrays on titanium substrates were obtained. In order to further get a single-crystal TiO_2 NP film, the obtained TiO_2 NT arrays were annealed in a sealed glass container at 450 °C for 3 h (see Figure S1 in the Supporting Information, SI). The sealed container, full of air at atmospheric pressure, was chosen to keep the residual electrolyte within the as-prepared TiO_2 NTs during the annealing process. After this special post-thermal treatment, single-crystal TiO_2 NP films with exposed

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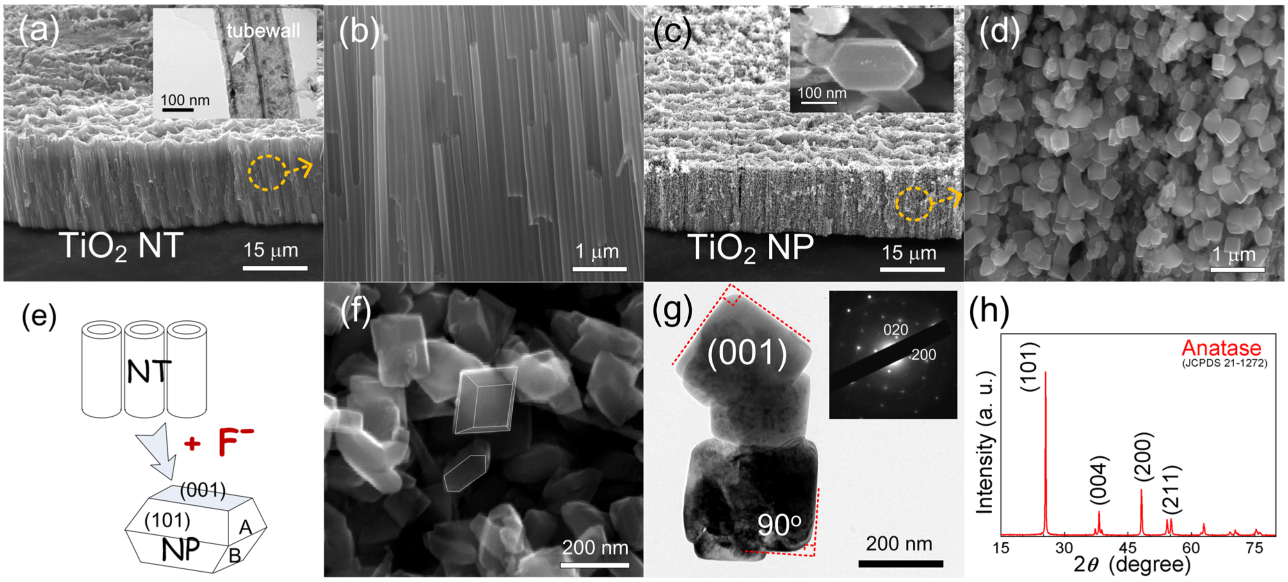

Figure 1. (a and b) SEM images of the as-grown TiO_2 NTs on titanium substrates. (c and d) SEM images of the obtained TiO_2 NP films with exposed {001} facets. (e) Schematic process of the TiO_2 NT to TiO_2 NP transformation. Morphologies of the obtained single-crystal TiO_2 NPs with {001} facets exposed: SEM (f); TEM (g). (h) XRD patterns of the anatase TiO_2 NP films. Insets of parts a, c, and g are a TEM image of two TiO_2 NTs and a zoom-in SEM image and a SEAD image of a single-crystal TiO_2 NP, respectively.

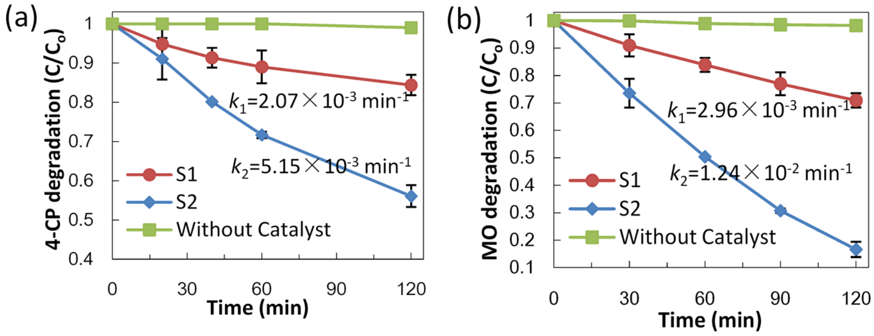

Figure 2. Photocatalytic degradation of 4-chlorophenol (a) and MO (b) kinetics by using the as-obtained TiO_2 NP films (S1) and after further thermal treatment at 600 °C for F^- removal (S2) as photocatalysts.

{001} facets were obtained (for more experimental details, see the SI).

RESULTS AND DISCUSSION

The morphologies of the as-grown TiO_2 NT arrays on titanium substrates are shown in Figure 1a,b. The TiO_2 NTs are highly ordered and grow vertically to the titanium substrate, forming a TiO_2 NT array film with a thickness of up to 25 μm. Each single TiO_2 NT owns very smooth tube walls with an outer diameter of ~120 nm and an inner diameter of ~100 nm. For anodic TiO_2 NTs, the tube length, diameter, and morphology can be tailored by adjusting the anodization protocols. Our earlier studies found that the TiO_2 NT's length could be precisely controlled from 10 to 100 μm.[17] After the special postannealing process, the highly ordered TiO_2 NT arrays disappeared, but a film consisting of numerous TiO_2 NPs with a thickness of about 15 μm was obtained, as shown in Figure 1c,d. Most of the formed TiO_2 NPs have a truncated bipyramidal shape with particle sizes ranging within 100−250 nm. No significant change was observed on the TiO_2 NPs' morphologies after annealing up to 600 °C (see Figure S2 in the SI). Moreover, transmission electron microscopy (TEM) results (see Figure 1g) indicate that those truncated bipyramidal particles are single-crystal TiO_2 NPs with {001} facets on the top and bottom sides (two flat square surfaces). Typical close views of the single-crystal TiO_2 NPs can be seen in the insets of Figure 1c,f, and the outlines of the truncated bipyramids are clearly observed in this case. The transformation from TiO_2 NTs to TiO_2 NPs was attributed to the fluorine residues inside the initial anodic TiO_2 NTs.[15,16] As is schematically shown in Figure 1e, fluorine in this study acted as the catalyst for TiO_2 NT collapse, on the one hand, and also acted as the capping agent for truncated bipyramidal TiO_2 NP formation, on the other hand. The ratio of truncated bipyramidal edge lengths B/A was calculated asabout 0.65, and the percentage of {001} facets exposed on the surface was estimated to be approximately 27.3%. Theoretical calculation predicted that the B/A ratio could reach 1.0 for fully F-terminated surfaces,[8] corresponding to the highest exposed (001) surface areas. The as-obtained single-crystal TiO_2 NP film was further characterized by EDS spectra; signals from the F, Ti, and O elements were clearly observed, suggesting their existence (see Figure S3 in the SI). X-ray photoelectron spectroscopy (XPS) spectra of the as-obtained TiO_2 NP film also indicate the existence of the F, Ti, and O elements on the crystal surface by their characteristic peaks, and the oxidation state of the Ti element in the as-obtained TiO_2 NPs is found to be identical with that of bulk TiO_2 (Ti $2p_{3/2}$, binding energy 458.8 eV; Ti $2p_{1/2}$, binding energy 464.3 eV; see Figure S4 in the SI).[8,18] Figure 1h shows XRD patterns of the as-obtained TiO_2 NP films. All of the diffraction peaks can be indexed to anatase-phase TiO_2 (JCPDS No. 21-1272), which indicates that the as-obtained product is pure anatase TiO_2. For instance, four peaks located at 2θ = 25.3°, 37.8°, 48.05°, and 55.06° could be attributed to the anatase (101), (004), (200), and (211) diffractions, respectively. The crystalline structure of this anatase TiO_2 NP film can be well maintained after an extra post-thermal annealing at 600 °C for 3 h (see Figure S5 in the SI). It can be concluded that well-defined, high-purity anatase single-crystal TiO_2 NP films with exposed {001} facets were successfully fabricated.

As we know, the photocatalytic activity is an important property of TiO_2 materials because TiO_2 remains one of the most widely used photocatalytic materials.[1,2] The TiO_2 NP film with active {001} facets exposed was expected to be a very good photocatalyst candidate without the worry of recycle problems that exist with powder catalysts. Because the {001} surface is more reactive for dissociative adsorption of reactant molecules, a high photocatalytic efficiency is expected for the TiO_2 NPs with {001} facets. However, the as-obtained single-crystal TiO_2 NP films turned out to be not as efficient as people expected at first (sample S1 in Figure 2). The photocatalytic probe used in the testing is a small organic compound, a 4-chlorophenol colorless aqueous solution, but only around 14% was photocatalytically degraded (see Figure 2a). For methyl orange (MO) degradation, a typical organic dye, only around 20% MO was photocatalytically degraded (see Figure 2b). This degradation rate actually refers to an inferior photocatalytic performance, which may explain the missing reports on the application of such kinds of TiO_2 NP films so far.

In order to activate the film's photocatalytic reactivity, we put the as-obtained TiO_2 NP films with exposed {001} facets under further thermal annealing at 600 °C for 3 h again, denoted as S2. It can be seen from Figure 2 that the photocatalytic activity was remarkably enhanced, that is, more 4-chlorophennol or MO was photocatalytically degraded. Figure 2a indicates that the apparent rate constants (k) increased from 2.07×10^{-3} min^{-1} (k_{S1}) to 5.15×10^{-3} min^{-1} (k_{S2}) for 4-chlorophennol, and Figure 2b shows that the k value increased from 2.96×10^{-3} min^{-1} (k_{S1}) to 1.24×10^{-2} min^{-1} (k_{S2}) for MO. The as-obtained TiO_2 NP films had a light-yellow color and could turn into pure white under further sintering in air at 600 °C for 3 h. Actually, UV–vis spectral results reveal that sample S2 has a smaller absorption range than sample S1, as shown in Figure 3. Moreover, considering that thermal annealing up to 600 °C did not significantly change the films' crystal structures or morphologies, this enhancement can be mainly attributed to the post-thermal-treatment-induced F^- removal from the {001} facets. As we discussed earlier, F ions adsorbed on the TiO_2 surface play a key role during the transformation of anodic TiO_2 NT arrays into truncated bipyramidal TiO_2 NP films. Without specific treatment, these F^- ions will continue to adsorb onto the TiO_2 {001} facets and highly passivate the TiO_2 crystal surface, leading to its inferior photocatalytic performance. Jung et al. suggested that the F ions as capping agents must be removed before catalytic applications,[2] and Wang et al. also reported that excess fluorine would cause significant recombination of electron–hole pairs as defect sites and decrease the efficiency.[19]

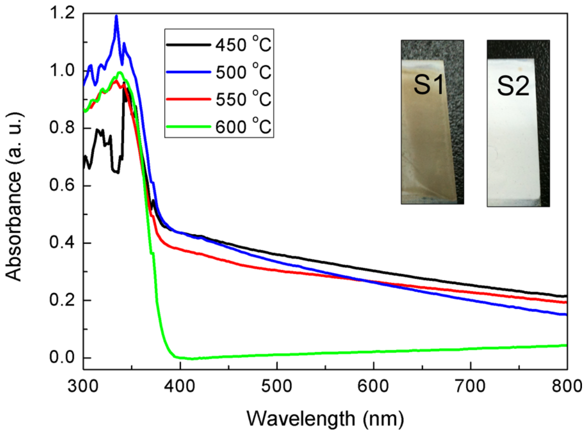

Figure 3. UV–vis spectra of the as-obtained TiO_2 NP films (S1) after further heat treatment at 450, 500, 550, and 600 °C, indicating that only after reheating at 600 °C the TiO_2 NP film (S2) can turn to pure white in color.

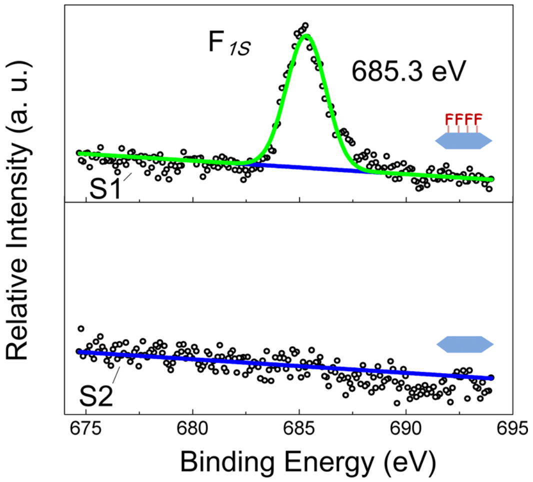

Figure 4. High-resolution XPS spectra of the F element existing on the surfaces of the TiO_2 NP films with {001} facets exposed before (S1) and after (S2) further thermal treatment at 600 °C for F^- removal.

Figure 4 shows the high-resolution XPS spectra of the F element existing on the surfaces of the TiO_2 NP films with {001} facets exposed. The characteristic peak of the F element is evidently found from the as-obtained TiO_2 NP films (sample S1). The measured binding energy is only ~685.3 eV, corresponding to the typical value for the surface Ti–F species.[9] This surface Ti–F bonding is not favorable for photocatalysis because it can change five-coordinated Ti atoms in the exposed {001} facets to six-coordinated ones, which will greatly decrease the surface reactivity.[20] Therefore, it is necessary to clean the crystal surface when using the as-obtained TiO_2 NP film as a photocatalyst panel. Figure 4 shows that, after further thermal treatment at 600 °C (sample S2), no recognizable signal from F 1s core electrons can be found any more, indicating that the F atoms were thoroughly wiped out from the {001} facets. The removal of fluorine by high-temperature sintering was also confirmed by EDS observation (see Figures S3 and S6 in the SI). With clean {001} facets, the TiO_2 NP films' photocatalytic activities were activated and then enhanced by around 2.5 and 4 times for 4-chlorophenol and MO degradation, respectively. We further treated sample S1 in an NaOH solution for 8 h (pH = 12) to remove fluorine, and a similar enhancement of the photocatalytic activity was also observed, as shown in Figure S7 in the SI, confirming that the activity enhancement is due to the removal of surface Ti−F species.[21] Meanwhile, fluorine-free anatase TiO_2 is also important for electrode fabrication;[22] therefore, it would be promising to apply such kinds of single-crystal TiO_2 NP films with exposed clean {001} facets in other areas, such as DSSCs, sensors, and Li^+ batteries.

■ CONCLUSIONS

In summary, TiO_2 films consisting of single-crystal anatase NPs with exposed {001} facets were fabricated by using the initial anodic TiO_2 NT arrays as starting materials. The catalyst and capping agent, F ions, were removed from the {001} facets by an extra post-thermal treatment. The photocatalytic reactivity of the single-crystal TiO_2 NP film with clean {001} facets was further activated and enhanced.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and further characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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