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Hierarchical TiO₂ Nanospheres with Dominant {001} Facets: Facile Synthesis, Growth Mechanism, and Photocatalytic Activity

Hongmei Li,^[a] Yangsu Zeng,^[a] Tongcheng Huang,^[a] Lingyu Piao,^{*[b]} Zijie Yan,^[c] and Min Liu^{*[a]}

Abstract: Hierarchical TiO₂ nanospheres with controlled surface morphologies and dominant {001} facets were directly synthesized from Ti powder by a facile, one-pot, hydrothermal method. The obtained hierarchical TiO₂ nanospheres have a uniform size of 400–500 nm and remarkable 78 % fraction of {001} facets. The influence of the reaction temperature, amount of HF, and reaction time on the morphology and the exposed facets was systematically studied. A possible growth mechanism speculates that Ti powder first dissolves in HF solution, and then flowerlike TiO₂ nanostructures are formed by assembly of TiO₂ nanocrystals. Because of the high concentration of HF in the early stage, these TiO₂

nanostructures were etched, and hollow structures formed on the surface. After the F[−] ions were effectively absorbed on the crystal surfaces, {001} facets appear and grow steadily. At the same time, the {101} facets also grow and meet the {101} facets from adjacent truncated tetragonal pyramids, causing coalescence of these facets and formation of nanospheres with dominant {001} facets. With further extension of the reaction time, single-crystal {001} facets of hierarchical TiO₂ nanospheres are dissolved and TiO₂ nanospheres

with dominant {101} facets are obtained. The photocatalytic activities of the hierarchical TiO₂ nanospheres were evaluated and found to be closely related to the exposed {001} facets. Owing to the special hierarchical architecture and high percentage of exposed {001} facets, the TiO₂ nanospheres exhibit much enhanced photocatalytic efficiency (almost fourfold) compared to P25 TiO₂ as a benchmark material. This study provides new insight into crystal-facet engineering of anatase TiO₂ nanostructures with high percentage of {001} facets as well as opportunities for controllable synthesis of 3D hierarchical nanostructures.

Keywords: hydrothermal synthesis • nanostructures • photocatalysis • titanium dioxide

Introduction

Titanium dioxide (TiO₂), as one of the most important transition metal oxides, has been widely used in catalysis, photovoltaic cells, self-cleaning devices, sensors, Li-ion battery materials, optical emission, water splitting, paints, paper, cosmetics, and so forth.^[1–5] These applications originate from

the unique physical and chemical properties of TiO₂, which depend not only on the crystal phase and particle size but also on the exposed facet.^[6–10] For anatase TiO₂, both theoretical and experimental studies have found that minority {001} facets are much more reactive than {101} facets.^[8–11] Therefore, interest in controlled synthesis of TiO₂ particles with exposed {001} facets has increased.^[11–27] Although anatase TiO₂ with exposed {001} facets is highly desirable for photocatalysis applications, synthesized anatase TiO₂ is often dominated by {101} facets, which are thermodynamically stable due to their lower surface energy (0.44 J m^{−2}).^[7,9,10] The {001} facets, which have a higher surface energy (0.90 J m^{−2}), quickly diminish during the crystal growth process for minimization of surface energy.^[7,9,10] An important breakthrough in the preparation of anatase TiO₂ single crystals with exposed {001} facets was achieved by Yang et al.^[11] They reported the synthesis of anatase TiO₂ single crystals with 47 % exposed {001} facets using titanium tetrafluoride as raw material and hydrofluoric acid as a shape-controlling agent. Following this breakthrough, anatase TiO₂ crystals with exposed {001} facets have led to an upsurge in interest, whereby most of the research has been focused on developing synthesis strategies to obtain single crystals with high percentage of exposed {001} facets.^[11–28] Thus, a series of studies have demonstrated syntheses of

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sheetlike anatase TiO_2 single crystals with as high as 89% exposed {001} facets.^[17]

Recently, the design and synthesis of TiO_2 nanomaterials with hierarchical architectures have triggered more and more research in nanoscience and nanotechnology, since they can have a number of attractive properties and a wide range of applications in catalysis, solar cells, Li-ion batteries, and so on.^[29–37] For example, flowerlike TiO_2 nanostructures consisting of many nanorods exhibit enhanced photocatalytic activity in the photodegradation of organic contaminants.^[34] Hierarchical TiO_2 nanorod microspheres have higher reversible capacity, cycling stability, and rate capability than nanosized TiO_2 materials.^[36] Since we first reported the synthesis of hierarchical flowerlike TiO_2 nanostructures with exposed {001} facets from Ti metal powder,^[22] many such advanced hierarchical TiO_2 nanostructures have been reported.^[23–25] However, most of them have small fractions of exposed {001} facets, and the growth mechanism is still unclear.

In this work, hierarchical TiO_2 nanospheres with up to 78% exposed {001} facets were fabricated by a facile, one-pot, hydrothermal process. The possible growth mechanism was elucidated by systematically investigating the influences of the reaction temperature, the amount of HF, and the reaction time on the growth of hierarchical TiO_2 nanospheres. Photocatalytic measurements showed that the photocatalytic activity of the hierarchical nanospheres is closely related to the exposed {001} facets. Owing to its high percentage of {001} facets and hierarchical nanostructure, these TiO_2 nanospheres exhibit greatly enhanced photocatalytic activity. This study can provide new insight into crystal-facet engineering of anatase TiO_2 nanostructures with high percentages of {001} facets as well as opportunities for controllable synthesis of 3D hierarchical nanostructures.

Results and Discussion

Figure 1a shows an FE-SEM image of hierarchical TiO_2 nanospheres synthesized at 180 °C with 0.25 mL of HF solution for 10 h. The product consists of numerous TiO_2 nanospheres with diameters of about 400–500 nm, composed of many thin, truncated tetragonal-pyramidal TiO_2 nanocrystals. The lengths of these truncated tetragonal pyramids are about 10–30 nm and the widths of their top surfaces are about 200–300 nm. Figure 1b shows the XRD pattern of the hierarchical TiO_2 nanospheres. All peaks can be indexed to anatase TiO_2 phase (JCPDS Card No. 21-1272) and no other phases can be detected. Compared with that of the bulk anatase TiO_2 (Figure 1b, bottom, JCPDS No. 21-1272), the remarkably enhanced relative diffraction intensity from the (004) plane indicates that the obtained hierarchical TiO_2 nanospheres are enclosed by {001} facets.^[22,23]

Figure 2 shows TEM images of the hierarchical TiO_2 nanospheres. Figure 2a shows that the TiO_2 nanospheres are composed of many thin, truncated tetragonal-pyramidal TiO_2 nanocrystals. The HRTEM image in Figure 2b, ob-

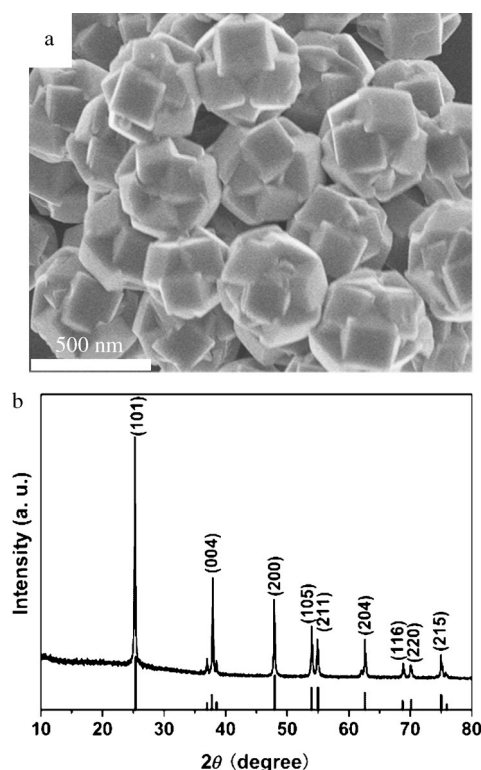


Figure 1. a) FE-SEM image and b) XRD pattern of TiO_2 nanospheres with dominant exposed {001} facets.

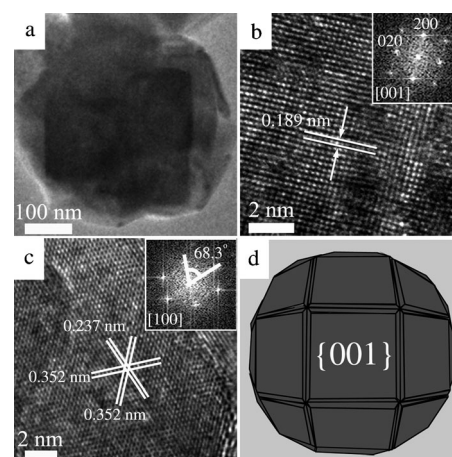


Figure 2. a) TEM image of the TiO_2 nanospheres with dominant exposed {001} facets. b) HRTEM image of a truncated tetragonal-pyramidal TiO_2 nanocrystal recorded along the [001] axis. c) Side-view HRTEM image of a truncated tetragonal-pyramidal TiO_2 nanocrystal. d) Schematic illustration of TiO_2 nanospheres with dominant exposed {001} facets. The insets are the corresponding FFT patterns.

tained from the top of a truncated tetragonal pyramid, clearly shows (200) and (020) atomic planes with a lattice spacing of 0.189 nm and an interfacial angle of 90°. The corresponding fast Fourier transform (FFT) image (inset in Figure 2b) confirms that the obtained anatase TiO_2 nanocrystals are single crystals; the zone axis is [001] and hence the square-faceted surface can be assigned to the {001} surface.^[11,12] Figure 2c shows an HRTEM image from the side of the trun-

cated tetragonal-pyramidal TiO₂ nanocrystals with clear crystalline lattice fringes. The lattice spacing of 0.352 nm corresponds to the (101) planes, while the lattice spacing of 0.237 nm corresponds to the (004) planes, that is, the top surfaces are {001} facets. The angle labeled in the corresponding FFT image (inset in Figure 2c) is 68.3°, identical to the theoretical value for the angle between the {101} and {001} facets.^[20–22] On the basis of the above characterization, we can confirm that the truncated tetragonal pyramidal TiO₂ nanocrystals are single-crystalline, and the top square surfaces and four isosceles trapezoidal surfaces are {001} facets and {101} facets, respectively. Therefore, we estimate the percentage of exposed {001} facets on the hierarchical nanospheres to be about 78% on average. Figure 2d shows a schematic illustration of the hierarchical TiO₂ nanospheres.

Figure 3 shows the results of an investigation into the influence of the reaction temperature. Figure 3a shows XRD patterns, normalized to the (101) reflection, of hierarchical TiO₂ nanospheres synthesized at different temperatures. All of these hierarchical TiO₂ nanospheres can be indexed to anatase TiO₂ phase (JCPDS Card No. 21-1272) and no other phases or residual Ti phase can be detected. The relative diffraction intensity of the (004) plane increased with increasing reaction temperature up to 180 °C. The hierarchical nanospheres synthesized at 180 °C have the highest (004) diffraction intensity and hence the largest fraction of exposed {001} facets. When the reaction temperature reached 200 °C, the (004) diffraction intensity, and thus the percentage of {001} facets, decreased. These results coincide with

the SEM images. Figure 3b–f show FE-SEM images of hierarchical TiO₂ nanospheres synthesized at 120, 140, 160, 180, and 200 °C, respectively. Clearly, hierarchical TiO₂ nanospheres with nearly the same diameter could easily be fabricated at any given temperature, as shown in Table 1. How-

Table 1. Averaged data of hierarchical TiO₂ nanospheres obtained at different temperatures.

Parameter	Reaction temperature [°C]				
	120	140	160	180	200
average size [nm]	420	400	410	430	410
top width of truncated pyramid [nm]	80	100	130	200	–
length of truncated pyramid [nm]	100	70	40	20	–
{001} facets [%]	25.2	32.4	46.9	78.3	–

ever, with increasing reaction temperatures, the widths of the top surfaces of truncated tetragonal pyramids grow steadily, while lengths of truncated tetragonal pyramids decrease steadily. Therefore, the percentage of exposed {001} facets increases steadily (Table 1), which is consistent with the XRD patterns. However, when the reaction temperature was increased to 200 °C, the exposed {001} facets were corroded seriously and irregular shapes appeared on surface of the TiO₂ nanospheres (Figure 3f), that is, the HF etching/dissolution effect was enhanced at high temperature.^[26]

It is well-known that HF has a major influence on the morphology of TiO₂ materials with exposed {001} facets.^[11,12,26] Figure 4 shows FE-SEM images of the hierarchical TiO₂ nanospheres prepared at 180 °C for 10 h with different amounts of HF. As shown in Figure 4a, when 0.2 mL of HF solution was used, hierarchical TiO₂ nanospheres with sizes of about 300–400 nm were obtained. These hierarchical TiO₂ nanospheres are composed of many small nanoparticles and no {001} facets were exposed on the surface. When the amount of HF solution was increased to 0.25 mL, hierarchical TiO₂ nanospheres with dominant exposed {001} facets were obtained (Figure 4b). When the amount of HF solution was further increased to 0.3 mL, hierarchical TiO₂ nanospheres with sizes of about 500–600 nm were produced, as shown in Figure 4c. These hierarchical TiO₂ nanospheres are composed of many thin nanosheets, which were seriously corroded and aggregated. These results indicate that the amount of HF has an enormous influence on the products. It is known that the synergistic functions of fluorine ions can remarkably reduce the surface energy of the {001} facets to a level lower than that of {101} facets.^[11,12] Therefore, when the concentration of HF is low, limited fluorine ions are available to reduce the surface energy of {001} facets, and hierarchical TiO₂ nanospheres with no or few exposed {001} facets were obtained. On the other hand, HF also has a serious corrosive effect on TiO₂.^[25,26] Although thin nanosheets with exposed {001} facets were synthesized at high concentration of HF, they were also seriously corroded by HF.^[25,26] Moreover, without buffer or complexant solution, such as H₂O₂,^[18] hydrolysis of titanium fluoride is very fast and results in serious aggregation of the TiO₂ nanocrystals.

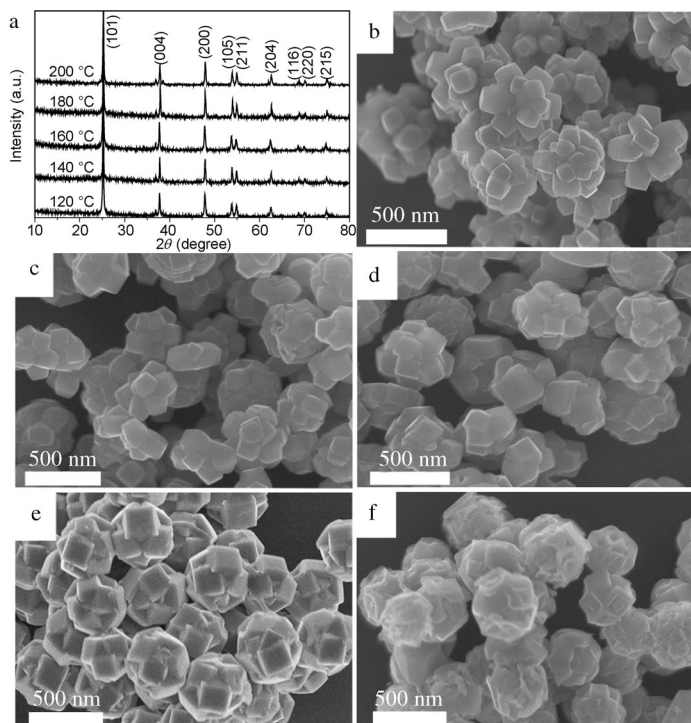


Figure 3. a–f) XRD patterns and FE-SEM images of hierarchical nanospheres obtained at different temperatures. a) XRD patterns. b) 120, c) 140, d) 160, e) 180, and f) 200 °C.

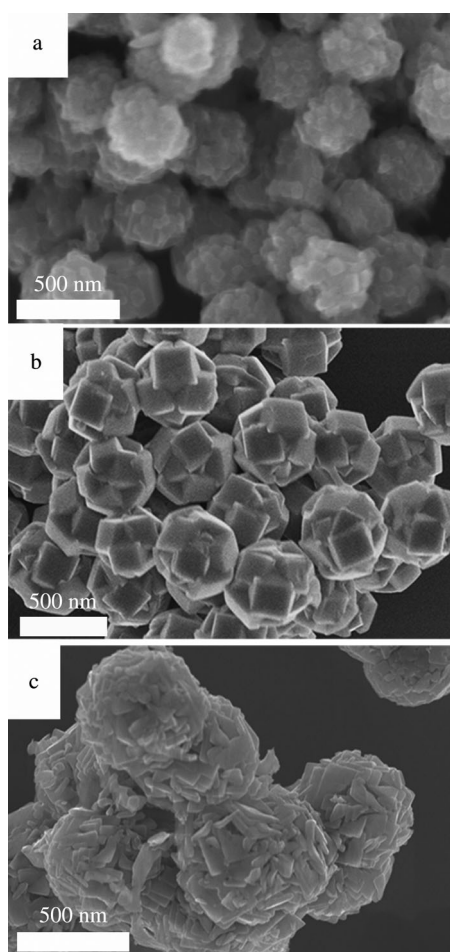


Figure 4. FE-SEM images of hierarchical TiO_2 nanospheres obtained with different amounts of HF. a) 0.2, b) 0.25, and c) 0.3 mL.

Figure 5 shows the XRD patterns, normalized to the (101) reflection, of hierarchical TiO_2 nanospheres obtained at different reaction times. All of these hierarchical TiO_2 nanospheres can be indexed to anatase TiO_2 phase (JCPDS Card No. 21-1272) and no other phases or residual Ti phase can be detected. Thus, Ti powder was completely transformed into TiO_2 , even in the initial stage of the reaction. The relative diffraction intensity of the (004) plane first decreased with increasing reaction time up to 3 h, then increased steadily with reaction time up to 10 h. The highest (004) diffraction intensity indicates that the hierarchical nanospheres obtained at 10 h have the largest fraction of exposed {001} facets. When the reaction time was further extended to 15 h, the (004) diffraction intensity decreased again, that is, the amount of {001} facets would decrease with the further increases in reaction time, which coincides with the SEM images.

Figure 6 shows FE-SEM images of hierarchical TiO_2 nanospheres obtained at different reaction times. With increasing reaction time, the hierarchical nanospheres grew steadily in size and exposed {001} facets, as shown in Table 2, which is consistent with the XRD patterns. It is noteworthy that the

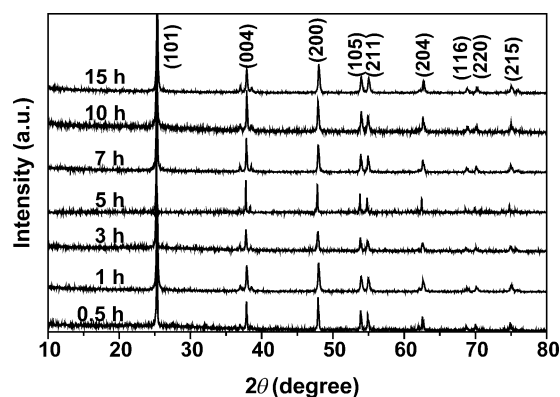


Figure 5. XRD patterns of hierarchical TiO_2 nanospheres obtained at different reaction times.

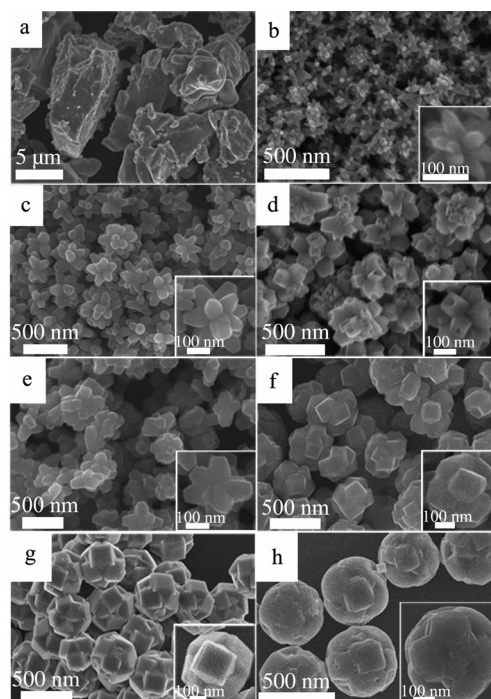


Figure 6. FE-SEM images of hierarchical nanospheres obtained at different reaction times. a) 0, b) 0.5, c) 1, d) 3, e) 5, f) 7, g) 10, and h) 15 h, respectively. The insets are high-magnification SEM images.

particles of the titanium powder starting material are far larger than hierarchical TiO_2 nanospheres, which are always uniform at any given time. In the early growth, hierarchical flowerlike TiO_2 nanospheres, composed of circular cones or

Table 2. Averaged data of hierarchical TiO_2 nanospheres obtained from different reaction times.

Parameter	Reaction time [h]							
	0	0.5	1	3	5	7	10	15
average size [nm]	5000	160	220	280	330	390	430	450
top width of truncated pyramid [nm]	–	–	30	40	50	120	200	–
length of truncated pyramid [nm]	–	50	90	80	70	40	20	–
{001} facets [%]	–	–	–	–	15.5	43.4	78.3	–

truncated circular cones are obtained, as shown in Figure 6b and c. Similar flowerlike TiO₂ nanostructures were also obtained by hydrothermal reaction of Ti metal with HF solution.^[38] The truncated circular cones then grew into truncated pyramids with bowl-like open hollows, which later changed into mirrorlike plane {001} facets, as shown in Figure 6d–g. During these stages, with increasing reaction time, widths of the top surface of truncated tetragonal pyramids grow steadily, while lengths of truncated tetragonal pyramids decrease continuously. Therefore, the percentage of exposed {001} facets increases steadily. However, when the reaction time was further extended to 15 h, truncated pyramids disappeared and spherical surfaces were produced instead, as shown in Figure 6h. Although, the surfaces of nanospheres were corroded by HF, traces of the truncated pyramid nanocrystals can be easily found. This indicates that the mirrorlike planes changed into spherical surfaces. This is consistent with the XRD results.

To investigate the detailed structures of the hierarchical TiO₂ nanospheres, TEM images were recorded. Figure 7 shows TEM images of the hierarchical TiO₂ nanospheres obtained at 0.5, 3, 5, and 15 h. As shown in Figure 7a, hierarchical flowerlike TiO₂ nanospheres, composed of many circular cones, were obtained in the initial reaction stage. An HRTEM image with a clear crystalline lattice spacing of 0.237 nm, which corresponds to the (004) planes, and corre-

sponding FFT image show that these circular cones are single crystals with [001] growth direction (Figure 7b). Figure 7c and d show TEM images of the hierarchical TiO₂ nanospheres obtained at 3 h. Bowl-like open hollows (marked by red arrows) are clearly observed on the surfaces. However, the HRTEM image with clear crystalline lattice spacings of 0.352 and 0.474 nm corresponds to (101) facets and (002) planes, respectively. The angle of 68.3° in the corresponding FFT image (inset of Figure 7d) is identical to the theoretical angle between the {101} and {001} facets in an anatase crystal. These results indicate that these truncated pyramids are single crystals with {001} facets, even though they have bowl-like surfaces. These bowl-like surfaces soon grew into mirrorlike plane surfaces (Figure 6e and f). The HRTEM image and corresponding FFT image show that the truncated pyramids are single crystals and the mirrorlike plane surfaces are {001} facets. However, when the reaction time was extended to 15 h, the mirror-like plane surfaces changed into spherical surfaces (Figure 7g and h). The HRTEM image (Figure 7h) reveals a distance between lattice planes of 0.352 nm, corresponding to the (101) lattice planes of anatase TiO₂. This means that the surface {101} facets became dominant and the surface {001} facets were dissolved during the extended reaction time.

On the basis of the experimental results, a proposed growth mechanism for the formation of the hierarchical TiO₂ nanospheres with dominant {001} facets is given in Figure 8. It was reported that Ti powder could be dissolved in HF acid, forming H₂TiF₆ [Eq. (1)].^[18,22,38]

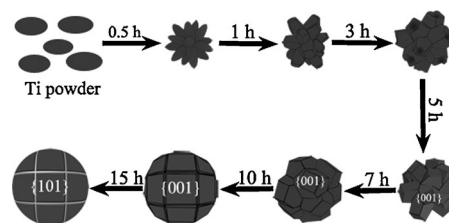
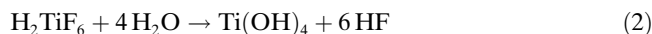


Figure 8. Schematic illustration of the possible growth mechanism of the hierarchical TiO₂ nanospheres.



Under the hydrothermal conditions, H₂TiF₆ is hydrolyzed and TiO₂ nanostructures are formed according to Equations (2) and (3).^[18,22,41]



In the initial reaction stage, without buffer or complexant solution, such as H₂O₂, hydrolysis of H₂TiF₆ is very fast and results in formation of hierarchical flowerlike TiO₂ through the coalescence of randomly oriented TiO₂ circular cones. These single-crystalline TiO₂ circular cones grow along the

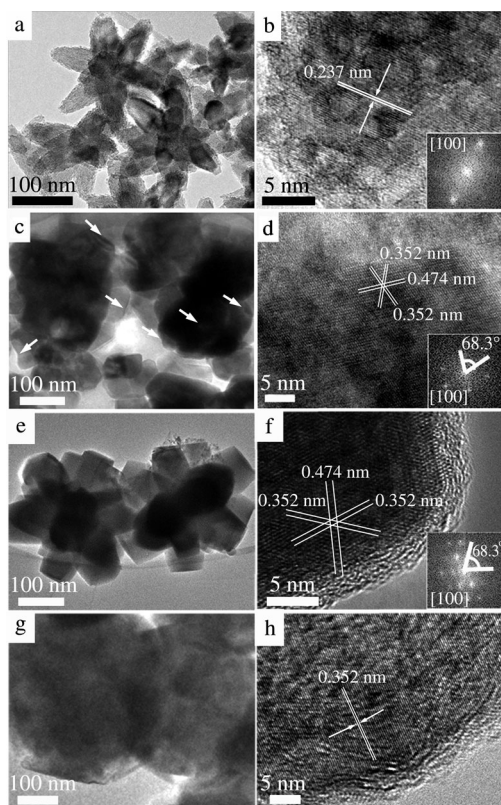
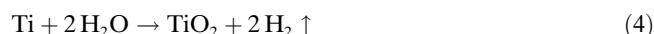


Figure 7. TEM and HRTEM images of hierarchical TiO₂ nanospheres obtained at different reaction times. a) and b) 0.5 h, c) and d) 3 h, e) and f) 5 h, g) and h) 15 h, respectively. The insets are the corresponding FFT patterns. Bowl-like open hollows are marked by arrows in c).

[001] direction, which is the preferential growth direction for anatase crystallites in the presence of HF.^[22–25] Owing to the high concentration of HF, combining the three reactions leads to Equation (4)



that is, the concentration of HF is almost maintained at the beginning, and the cones were etched, forming hollow structures. When the F^- ions are effectively absorbed on the crystal surfaces (Supporting Information Figure S1), the surface energy of {001} facets became lower than that of {101} facets.^[11,12] Therefore, the hollow structures grow into mirrorlike plane {001} facets, which grow steadily with time. At the same time, the {101} facets also grow and finally meet the {101} facets from adjacent truncated tetragonal pyramids, the facets coalesce, and nanospheres with dominant {001} facets are formed. Coalescence releases the F^- ions from the {101} facets, and thus increases the HF concentration again, which could etch the surfaces during the extended reaction time. As a result, single-crystal {001} facets of hierarchical TiO_2 nanospheres were dissolved and TiO_2 nanospheres with {101} facets became dominant.^[25]

The photocatalytic activity of the hierarchical TiO_2 nanospheres was evaluated in terms of the decolorization of methylene blue (MB) under UV irradiation. Figure 9a shows the photocatalytic activities of hierarchical nanospheres prepared with different amounts of HF solution. It clearly shows that the photocatalytic activity of the hierarchical nanospheres with exposed {001} facets is much higher than that of hierarchical nanospheres without exposed {001} facets. Figure 9b shows the photocatalytic activities of hierarchical nanospheres obtained at different reaction times. In the beginning, the photocatalytic activity of the hierarchical nanospheres decreased with increasing reaction time, owing to surface corrosion by HF and the increasing size. Since {001} facets are effectively exposed on the surface at 5 h, the photocatalytic activity of the hierarchical nanospheres was greatly enhanced and increased with increasing percentage of exposed {001} facets. The nanospheres obtained at 10 h show the best photocatalytic activity, owing to the largest fraction of {001} facets. However, when the {001} facets are corroded, the hierarchical nanospheres show only low photocatalytic activity. The results indicate that the photocatalytic activities of the hierarchical TiO_2 nanospheres are closely related to the exposed {001} facets, which can drastically improve the photocatalytic activity of TiO_2 .^[8–11]

Figure 9c compares the photocatalytic activities of hierarchical nanospheres with dominant exposed {001} facets and P25 TiO_2 . The former clearly show that higher activity than the latter. The linear relationship of $\ln(C_0/C)$ versus time (Supporting Information, Figure S2) shows that the photocatalytic degradation of MB follows pseudo-first-order kinetics [Eq. (5)]

$$\ln(C_0/C) = kt \quad (5)$$

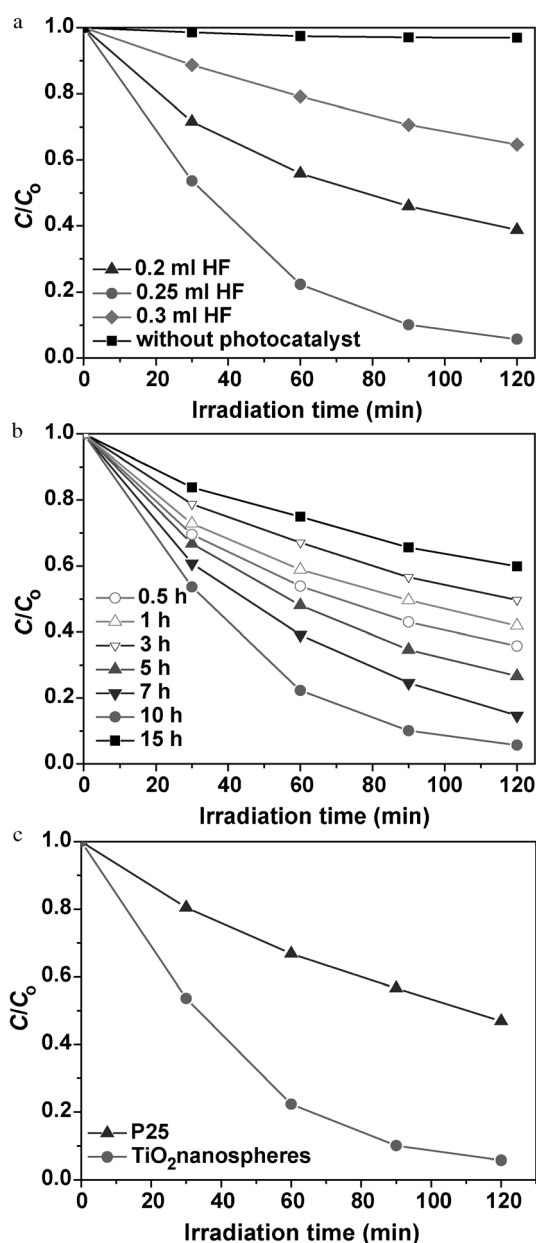


Figure 9. a) Variation of MB concentration in photocatalytic reactions with hierarchical TiO_2 nanospheres obtained with different amounts of HF. b) Variation of MB concentration in photocatalytic reactions with hierarchical TiO_2 nanospheres synthesized for different times. c) Variation of MB concentration in photocatalytic reactions with hierarchical TiO_2 nanospheres and P25.

where C_0/C is the normalized MB concentration, t the reaction time, and k the pseudo-first-order rate constant. The photochemical degradation rate constant for the hierarchical TiO_2 nanospheres is $2.4 \times 10^{-2} \text{ min}^{-1}$, which is almost four times of that of P25 TiO_2 powder ($6.7 \times 10^{-3} \text{ min}^{-1}$). This faster degradation rate further confirms that the hierarchical TiO_2 nanospheres with dominant exposed {001} facets exhibit high photocatalytic efficiency. The enhanced photocatalytic activity of the hierarchical TiO_2 nanospheres can be attributed to their dominated exposed {001} facets and special hierarchi-

cal nanostructure. It was demonstrated that {001} facets are much more reactive than {101} facets.^[8–11] Furthermore, 3D hierarchical nanostructures are regarded as having a greater number of active sites than 1D or 0D architectures.^[39–41] Therefore, the hierarchical TiO₂ nanospheres with dominant exposed {001} facets show high photocatalytic efficiency.

Conclusion

Hierarchical TiO₂ nanospheres with up to 78% {001} facets were synthesized by a facile, one-pot, hydrothermal method. A possible growth mechanism was postulated by systematically investigating the influence of the reaction temperature, amount of HF, and reaction time. Ti powder first dissolves in HF solution and flowerlike TiO₂ nanostructures are formed by assembly of TiO₂ nanocrystals. Due to the high concentration of HF in the early stage, these TiO₂ nanostructures are etched and formed hollow structures. After the F[−] ions are effectively absorbed on the crystal surfaces, {001} facets appear and grow steadily. At the same time, the {101} facets also grow and finally meet the {101} facets from adjacent truncated tetragonal pyramids, these facets coalesce, and nanospheres with dominant {001} facets are formed. With further extension of the reaction time, single-crystal {001} facets of hierarchical TiO₂ nanospheres dissolve and TiO₂ nanospheres with {101} facets are obtained. Photocatalysis studies showed that the photocatalytic activity of the hierarchical nanospheres is closely related to the exposed {001} facets. Owing to the special hierarchical architecture and high percentage of exposed {001} facets, these TiO₂ nanospheres exhibited greatly enhanced photocatalytic efficiency (almost fourfold) compared to P25 TiO₂ as a benchmark material. This study provides new insight into crystal-facet engineering of anatase TiO₂ nanostructures with high percentage of {001} facets as well as opportunities for controllable synthesis of 3D hierarchical nanostructures.

Experimental Section

Preparation: In a typical synthesis, Ti powder (0.1 g, 200 mesh, 99.9% purity, Sinopharm Chemical Reagent Beijing Co., Ltd), H₂O (40 mL) and hydrofluoric acid (0.25 mL, 40 wt%, Sinopharm Chemical Reagent Beijing Co., Ltd) were added to a Teflon-lined autoclave. The autoclave was sealed and heated at 180 °C for 10 h. After allowing the autoclave to cool to room temperature, the samples were collected by centrifugation, thoroughly washed with high-purity water (18 MW), and dried at 80 °C.

Characterization: The crystal structure of the products was determined by XRD (Bruker D8 Advance) with Cu_{Kα} radiation ($\lambda = 1.54056 \text{ \AA}$). SEM images were taken with a field-emission SEM (FE-SEM, Hitachi S-4800). TEM images were obtained on FEI F-20 high-resolution TEM (HRTEM) and JEOL 2010 HRTEM at an accelerating voltage of 200 kV.

Evaluation of photocatalytic properties: Photocatalytic activities of the hierarchical TiO₂ nanospheres were evaluated in terms of the decolorization of methylene blue (MB, Sinopharm Chemical Reagent Beijing Co., Ltd) under UV irradiation. Before photocatalytic testing, the fluorinated surfaces of the crystals were first cleaned by heat treatment at 600 °C in O₂ for 2 h, without altering the morphology.^[18,22] Then, 30 mg of hierarchical TiO₂ nanospheres were dispersed in 100 mL of aqueous solution con-

taining 0.01 M NaOH and 25 ppm MB. Before exposure to UV irradiation, the suspension was stirred in the dark for 1 h to allow it to reach complete adsorption-desorption equilibrium. Then the solution was irradiated with approximately 0.5 mW cm^{−2} UV light (with a wavelength peak at 365 nm) with continuous stirring. The concentration of MB was determined from the absorbance at 665 nm. For comparison, the same procedure was also done for P25 TiO₂ powder (Evonik Degussa (China) Co., Ltd, Shanghai).

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