

Hierarchical Structures of Single-Crystalline Anatase TiO₂ Nanosheets Dominated with {001} Facets

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Controllable synthesis of anatase titanium dioxide (TiO₂) have been widely investigated during the past decades due to their important industrial applications such as photovoltaic cells, photo/electrochromics, photonic crystals, smart surface coatings, and sensors.^[1-8] Both theoretical and experimental studies indicated that {001} facets of anatase TiO₂ are extraordinarily reactive.^[9] However, {001} facets usually diminish quickly during the crystal nucleation and growth because of their high surface energy (0.90 Jm⁻²). Therefore, most synthesized anatase TiO₂ crystals, as well as those naturally occurring, are dominated by thermodynamically stable {101} facets. Recently, on the basis of theoretical predictions, we successfully synthesized anatase TiO₂ single crystals with 47% of the highly reactive {001} facets by using hydrofluoric acid (HF) as a capping agent.^[9] Following

this study, various anatase TiO₂ crystals exposed with {001} facets were prepared by different groups using a similar synthetic strategy.^[10-17] Spherical particles containing ultrathin TiO₂ nanosheets exposed with {001} facets were also fabricated.^[18,19] However, to the best of our knowledge, most of these synthesized anatase TiO₂ are micro-sized crystals with two dimensional (2D) sheet-like nanocrystals or spherical particles closely packed by anatase TiO₂ nanosheets (NSs).^[20-24] In order to enhance the photocatalysis/photovoltaic performance further, three dimensional (3D) structures of well-faceted single-crystalline anatase TiO₂ NSs dominated with {001} facets are highly desired because of their excellent incident light scattering within the structures, high organic dye or pollutant adsorption and unique hierarchical characteristics.^[25-27]

Herein, we report a new synthesis method to prepare 3D hierarchical structures of single-crystalline anatase TiO₂ NSs dominated with well-faceted {001} facets. In a typical experiment, 10 mL of isobutyl alcohol (IBA), 2.4×10⁻² mol of deionized (DI) water and 0.16×10⁻³ mol of titanium (IV) butoxide (TNBT) were mixed and stirred constantly for 2 min. Then another 30 mL of IBA and 0.4 mL of HF (10% w/w) were added to the mixture and kept stirring for 2 min. The mixture was heated in a Teflon-lined stainless steel autoclave (50 mL in volume) and kept in an electric oven at 180-200°C for 20 h. The white products were harvested by a centrifugation method and washed by ethanol for 3 times. The surface fluorine was removed by directly cleaning the products with 0.1 M NaOH and DI water.^[14]

As shown in Figure 1a, the crystallographic structure of the resulting products was examined by X-ray diffraction (XRD), which can be indexed to the anatase TiO₂ phase (space group *I4₁/amd*). Notable broadening of (004) can be easily identified in the XRD pattern, indicating the small size along the [001] crystallographic direction. Moreover, along the [100] crystallographic direction the broadening of the diffraction peak does not occur. Compared with that of the bulk anatase TiO₂ in Figure 1c (JCPDS No.21-1272), the relative diffraction intensity (200) is much higher; these results indicate that the as-synthesized anatase TiO₂ has an anisotropic sheet-liked building units. More importantly, obvious asymmetric broadening at the diffraction angle ranging from 54-56° can be detected, which might be caused by the significant and insignificant broadening of (115) and neighboring (211) diffraction peaks, respectively. To reconfirm these experimental findings theoretically, based on general scattering theory and Bragg's Law,^[28,29] the XRD pattern

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of anatase TiO₂ NSs with a 5 nm thickness along the [001] crystallographic direction was calculated. The diffraction intensity is calculated using the scattering equation for single crystals:

$$I(Q) = \sum_j \sum_k f_j(Q) f_k(Q) \exp(i \vec{r}_{jk} \cdot \vec{Q})$$

which has been embedded in the Reflex module of Materials Studio. Where Q is the scattering vector in reciprocal lattice distance unit, k and j indicate different atoms, and $f_j(Q)$ and $f_k(Q)$ are the atomic scattering factors for atom j and k at scattering vector Q , respectively. While r_{jk} is the distance between atom j and atom k . The integration is over all atoms. It should be noted that all the calculations are strictly limited to the slabs of single crystals with a large vacuum space over the slab surface. The calculated results shown in Figure 1b match the experimental data (Figure 1a) well, which illustrates the ultrathin characteristics along the [001] crystallographic direction of the anatase TiO₂.

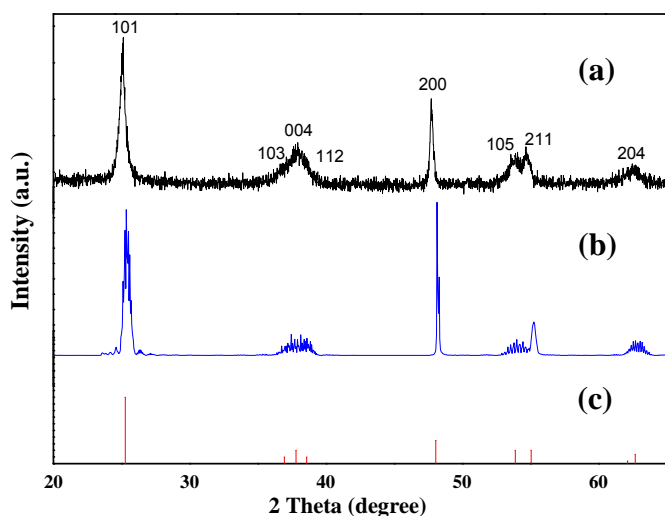


Figure 1. X-ray diffraction (XRD) patterns of the as-synthesized flower-like anatase TiO₂ (a), the calculated results of anatase TiO₂ NSs with a thickness of 5 nm (b) and the bulk anatase TiO₂ (c).

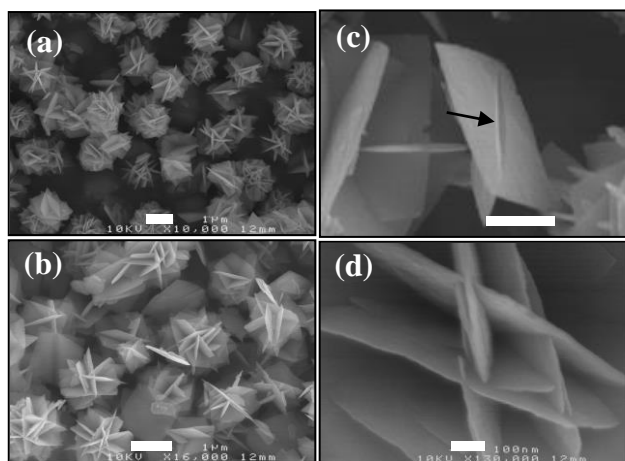


Figure 2. SEM images of flower-like TiO₂ NSs with different magnifications. (Scale bars in (a-d) are 1 μm, 1 μm, 0.5 μm and 100 nm, respectively)

The scanning electron microscopy (SEM) images in Figure 2a,b show the general morphology of the as-prepared TiO₂ products which are entirely composed of flower-like 3D hierarchical structures with a size ~2.0 μm on the average. As shown in Figure 2c,d the hierarchical structures are assembled by 2D NSs of

anatase TiO₂ with a thickness around 10-20 nm and a length about 1.2 μm, which act as the basic building units. From the symmetries of the well-faceted crystal structure of the anatase TiO₂ NSs in Figure 2c, the two exposed flat square surfaces are identified as {001} facets. Thus the percentage of {001} facets of anatase TiO₂ NSs can be derived directly from this regular geometry, which is statistically around 97%. These cross-linked NSs may be the results of the oriented attachment effect during the crystal growth and they can further assemble into flower-like hierarchical structures. The early stage of the oriented attachment was grasped successfully in our experiments, which is evidenced by the trace mark on the surface of the anatase TiO₂ NSs (indicated by a black arrow head in Figure 2c). Furthermore, the internal cross-linked structures revealed in Figure 2d would prevent lamella aggregation occurring along the [001] crystallographic direction, which can help to maintain the long term stability of the 3D hierarchical structures.

The microstructures of 3D hierarchically structured anatase TiO₂ were further investigated by transmission electron microscopy (TEM) (Figure 3a,b), high-resolution TEM (HRTEM) (Figure S1) and selected-area electron diffraction (SAED) (The inset in Figure 3b). TEM image in Figure 3a shows a flower-like hierarchical structure where TiO₂ NSs building units can be easily identified. More importantly, the single-crystalline characteristics of these anatase TiO₂ NSs were evidenced by HRTEM (Figure S1) and SAED. (200) atomic planes with lattice spacing of 0.19 nm are shown in the HRTEM (Figure S1). The SAED pattern can be indexed as [001] zone axis diffraction which indicates that the top and bottom surfaces of the anatase TiO₂ NSs are high-reactive {001} facets.

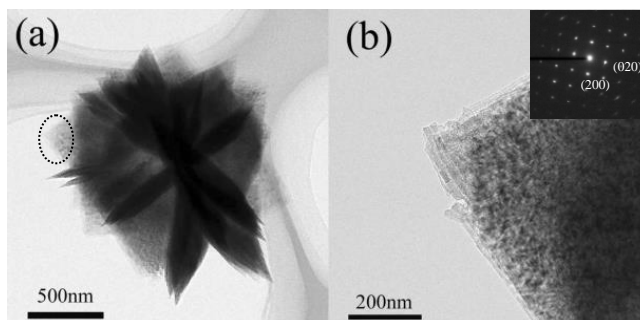


Figure 3. TEM images of a typical flower-like hierarchical structure of anatase TiO₂ (a,b). The image in (b) is the corresponding SAED pattern.

X-ray photoelectron spectroscopy (XPS) was used to verify the surface binding states of the homemade flower-like TiO₂ NSs, and the results are shown in Figure 4. The high-resolution XPS spectra of F 1s indicates that the measured binding energy is 684.3 eV, which is quite close to the fluorinated TiO₂ systems such as TiOF₂ or the surface ≡Ti-F species on the TiO₂ crystal surface.^[30] For Ti 2p, a detectable shoulder peak at 457.1 eV can be found excluding the quadrivalent oxidation state of Ti element (Ti 2p_{3/2}, binding energy 458.6 eV; Ti 2p_{1/2}, binding energy 464.1 eV). This binding energy value which is ~1.5 eV lower than that of Ti⁴⁺ 2p_{3/2} suggests that Ti³⁺ defects were produced during the synthesis.^[31] Regarding the origin of the Ti³⁺ defects in this fluorine-capped system, two possible mechanisms can be proposed. The first one is that the oxygen deficiency leads to transferring the extra electrons to the adjacent Ti⁴⁺ atoms to form trivalent Ti³⁺.^[32] The other one is that the possible presence of fluorine in the lattice induces one extra electron in a 3d orbital of Ti⁴⁺ and thus leads to the formation of Ti³⁺.^[33] It should be noted

that binding energies for all mentioned elements above were referenced to the C 1s peak (284.7 eV) which could be assigned as aliphatic hydrocarbon. The smaller peak at binding energy of 288.1 is due to the presence of carboxylate impurities.

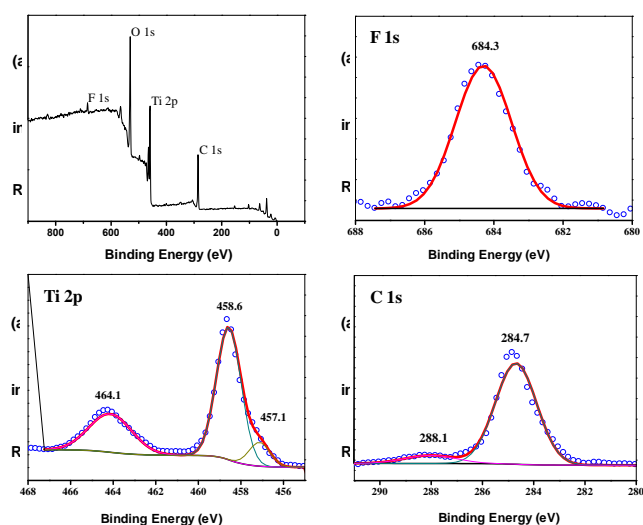


Figure 4. X-ray photoelectron spectra of anatase single crystals, showing three high-resolution characteristic peaks of F 1s, Ti 2p and C 1s. The high resolution characteristic peaks have the same axes as the main panel. The blue open circles are the raw data of the X-ray photoelectron spectra, and the multi-colour lines represent the fitted lines.

To further explore the morphology development and formation mechanism of the 3D hierarchical structures of anatase TiO₂, more systematic experiments were carried out. When the amount of TNBT was increased to 2.4×10^{-4} mol while other reaction parameters were kept unchanged, analogous 3D hierarchical structures of anatase TiO₂ were synthesized (Figure 5a,b). However, in this case, the anatase TiO₂ NSs building units aggregated through a layer-by-layer mode first and then assembled to form flower-like structures, which leads to a 3D expansion. The aggregation of anatase TiO₂ NSs along [001] crystallographic direction may be caused by a strong van der Waals force between the parallel anatase TiO₂ NSs. The average size of the 3D hierarchical structures is 3.5 μm and the thickness of the parallelly aligned TiO₂ NSs is around 500 nm. More interestingly, during the layer-by-layer assembling process, the stacked anatase TiO₂ NSs exposed by {001} facets still demonstrate a Wulff construction principle showing overall highly truncated bipyramidal morphology, as indicated by the white dash line in Figure 5c. Based on these experimental results and corresponding analysis, it can be concluded that the single-crystalline anatase TiO₂ NSs with the high percentage of high-reactive {001} facets which act as the building units of 3D hierarchical structures are controlled by the HF in the reaction media.^[8] That is, the 3D anatase TiO₂ hierarchical structures have a fluorine terminated surface. Moreover, the formation of complex hierarchical structures is due to the reaction media (isobutyl alcohol) used in this work, which might change the growth behavior of initial anatase TiO₂ NSs building units and the interaction between them as well.

In summary, 3D hierarchical structures composed of single-crystalline anatase TiO₂ NSs dominated with well-defined {001} facets were prepared for the first time through a tailored aggregation process. The concentration of Ti precursor has a significant effect on the aggregation behaviors of the TiO₂ NSs

building blocks. Their highly exposed {001} facets and unique 3D hierarchical structures imply their potential applications in dye-sensitized solar cells and photocatalysis areas.^[27, 34-37]

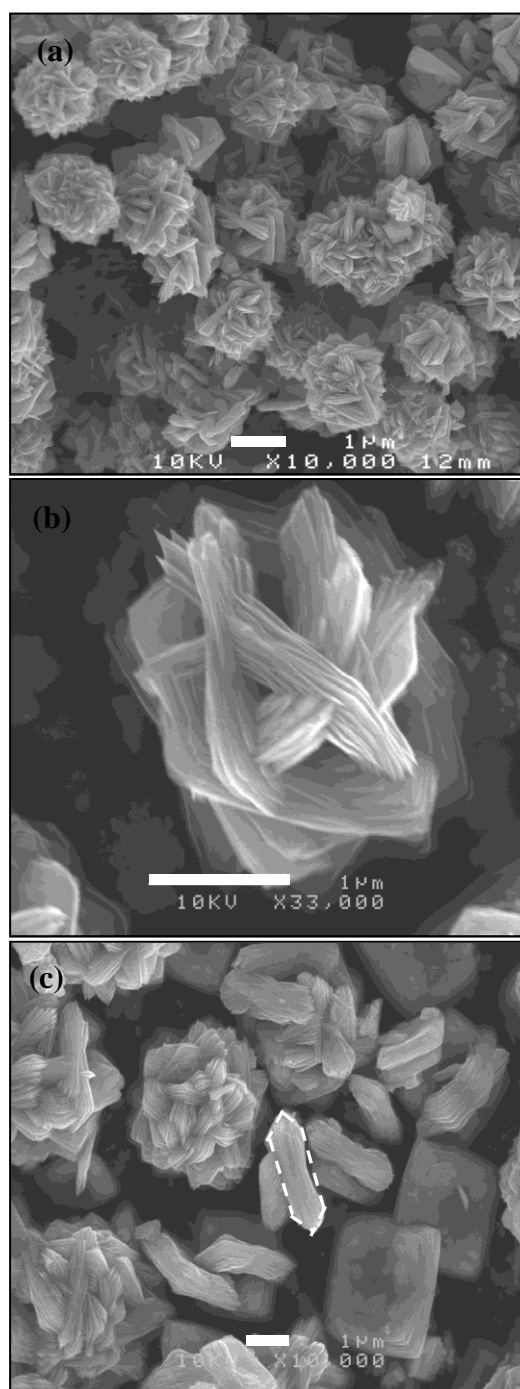


Figure 5. SEM image of 3D hierarchical structures of anatase TiO₂ synthesized at 180°C for 20 h. Scale bars in (a,b and c): 1 μm .

Experimental Section

Hierarchical structures composed of single-crystalline anatase TiO₂ nanosheets dominated with well-defined {001} facets were prepared by a simple water/isobutanol solvothermal reaction of the mixtures containing titanium (IV) butoxide (TNBT, 97% in purity), isobutyl alcohol (IBA, $\geq 98\%$ in purity), and hydrofluoric acid (HF, 47%). In a typical experiment, 10 mL of isobutyl alcohol (IBA) ($\geq 98\%$ in purity), 2.4×10^{-2} mol of deionized (DI) water and $0.16\text{--}0.32 \times 10^{-3}$ mol of titanium (IV) butoxide (TNBT) (97% in purity) were added into a Teflon-lined stainless steel autoclave (50 mL in volume) and the mixture was stirred constantly for 2 min. Then another 30 mL of IBA and 0.4 mL of HF (10% w/w) were added to the mixture and

kept stirring for 2 min. After the reaction at 180-200°C for 20 h in an electric oven, the white products were harvested by a centrifugation method and washed with ethanol for 3 times. The surface fluorine was removed by directly cleaning the products with 0.1 M NaOH and DI water.

Materials characterization: X-ray diffraction (XRD) patterns were obtained by using a Bruker D8 advanced X-ray powder diffractometer with Cu-K α radiation ($\lambda=1.5418$ Å). The morphologies and selected area electron diffraction (SAED) of hierarchically structured anatase TiO $_2$ were examined by using scanning electron microscopy (SEM, JEOL JSM6400F) and transmission electron microscopy (TEM, Philips Tecnai T30F FEG Cryo AEM). Surface composition and binding states were analyzed with X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD). All binding energies were referenced by C1s peak (284.7 eV) arising from surface hydrocarbons (or possible adventitious hydrocarbon). Prior peak deconvolution, X-ray satellites, and inelastic background (Shirley-type) were subtracted for all spectra.

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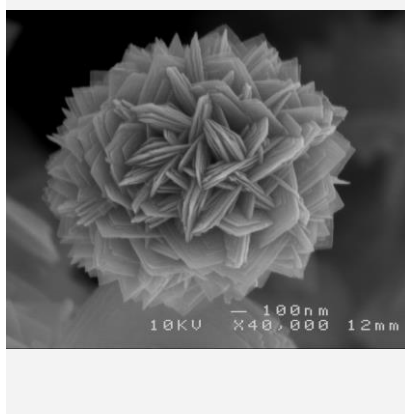
Keywords: hierarchical structures • reactive facets • solvothermal synthesis • titanium dioxide

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Titanium Dioxide

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Hierarchical structures: 3D hierarchically structured single-crystalline anatase TiO₂ nanosheets dominated with well-defined {001} facets were prepared for the first time through a tailored aggregation process. The concentration of Ti precursor has a significant effect on the aggregation behaviors of the TiO₂ nanosheets building blocks.

Supporting Information

Hierarchical Structures of Single-Crystalline Anatase TiO₂ Nanosheets Dominated with {001} Facets

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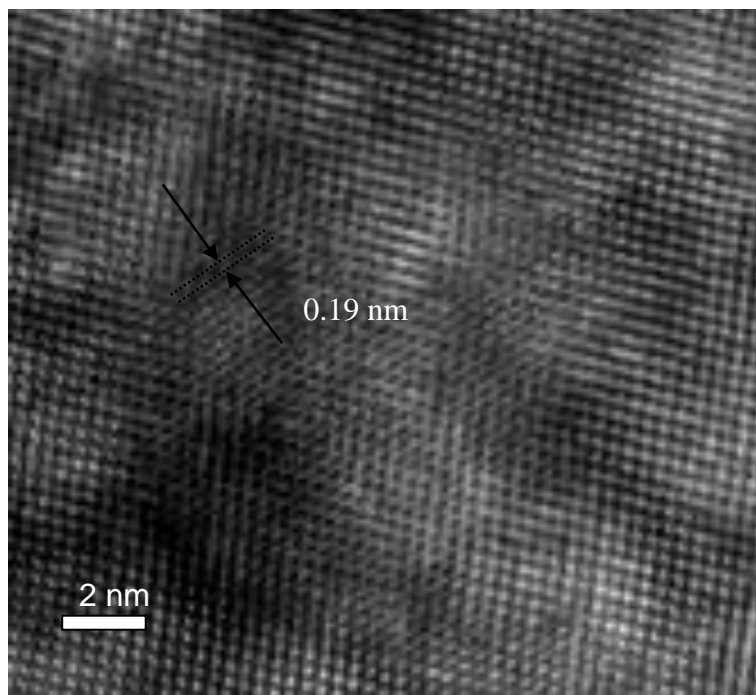


Figure S1. High-resolution TEM image recorded from a single TiO₂ nanosheet.

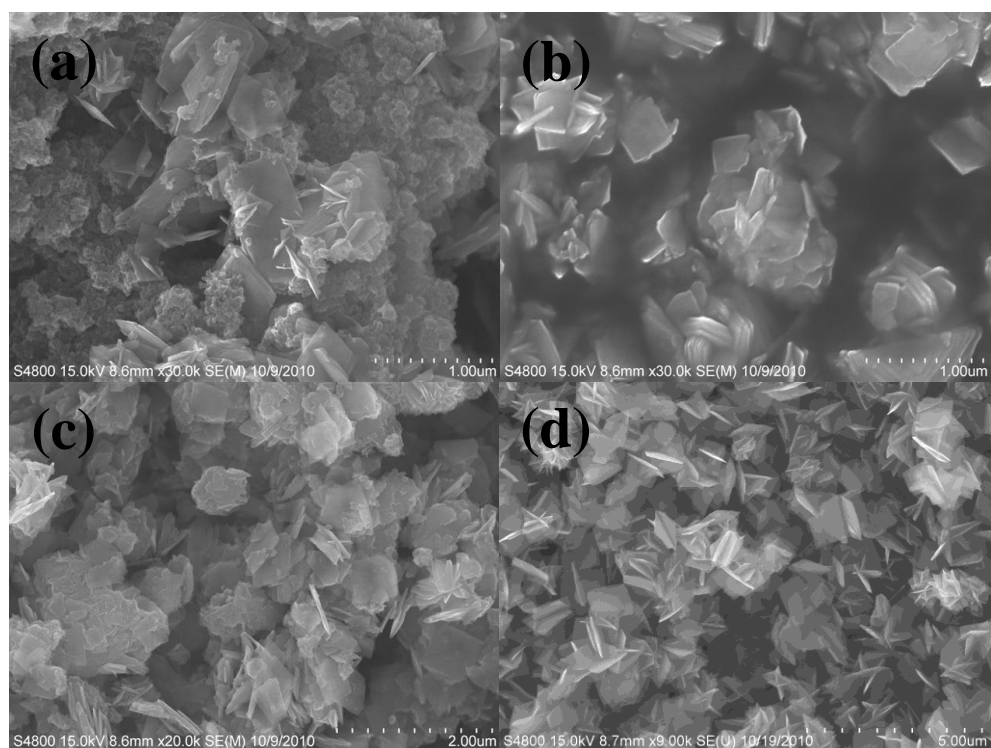


Figure S2. SEM images of the TiO₂ hierarchical structures obtained for the reaction time. a) 14h, b) 16h, c) 18h, and d) 40h.

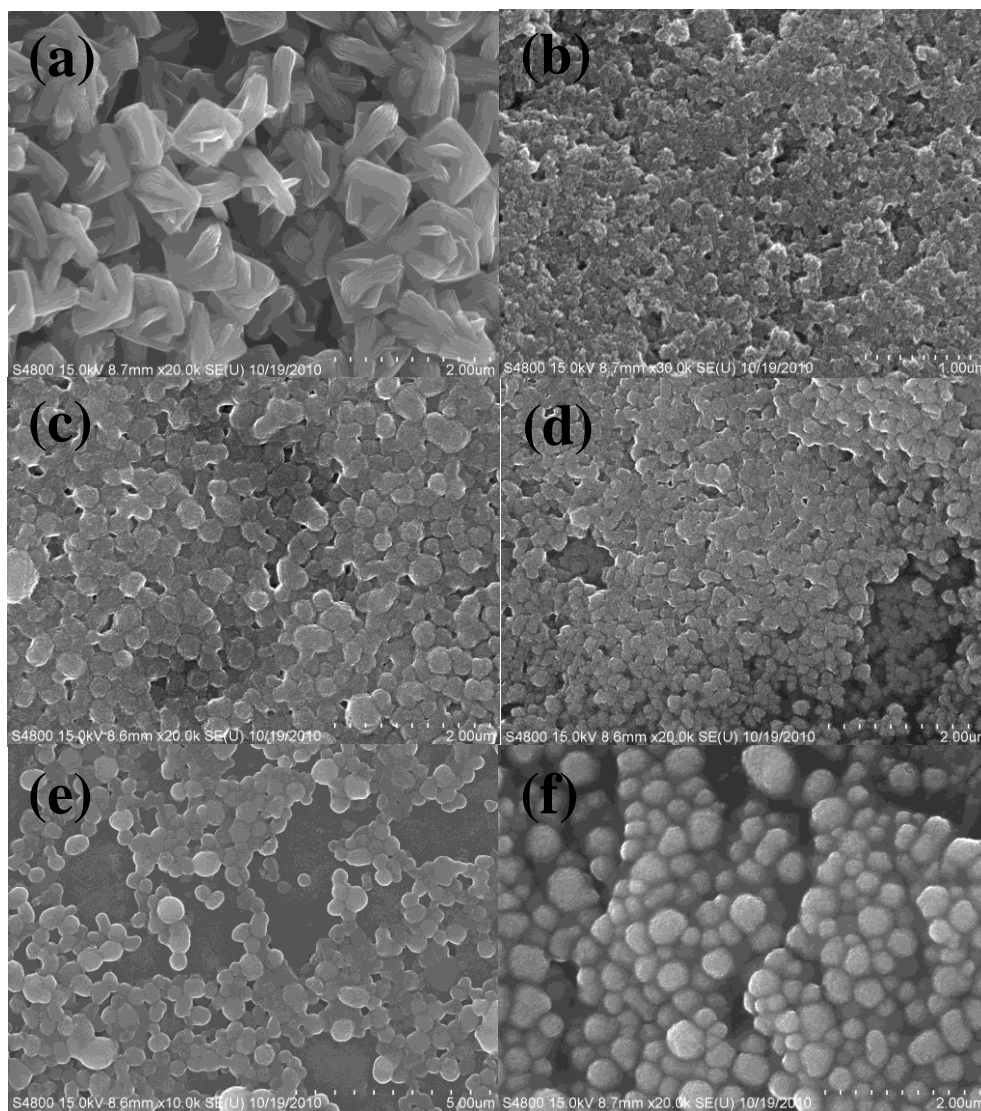


Figure S3. SEM images of the TiO₂ hierarchical structures obtained for different amount of precursor (TNBT) with other conditions unchanged (180°C 20h). a) 0.32 mmol, b) 0.48 mmol, c) 0.64 mmol, d) 0.80 mmol, e) 0.96 mmol, and f) 1.02 mmol.

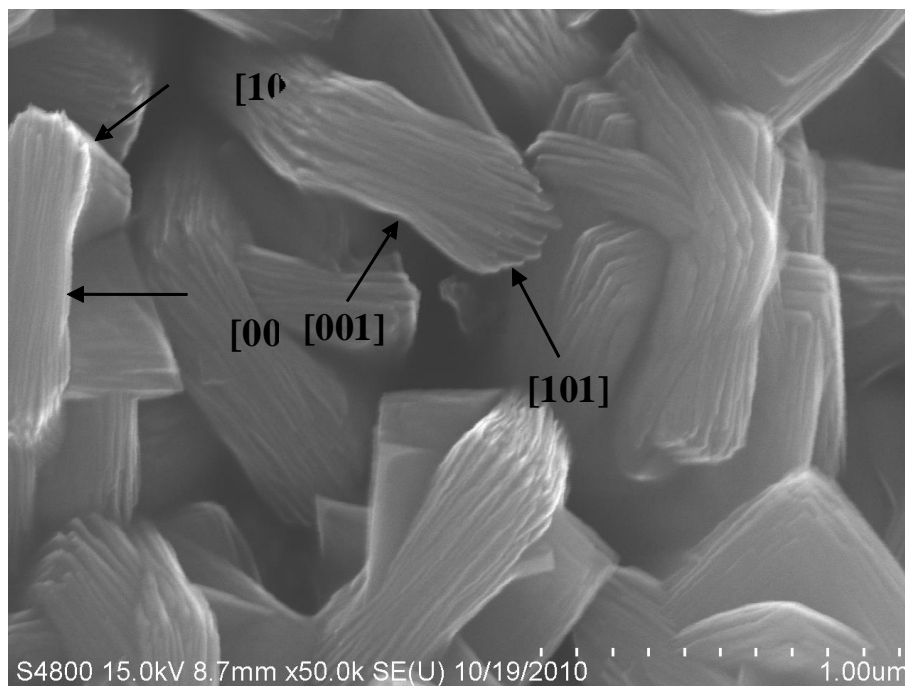


Figure S4. SEM images of the TiO₂ hierarchical structures obtained at 180°C 20h with 0.32 mmol TNBT as precursor.