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Synthesis of Anatase TiO_2 Tubular Structures Microcrystallites with a High Percentage of {001} Facets by a Simple One-Step Hydrothermal Template Process

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Since the discovery of carbon nanotubes in 1991,[1] tubular structures have received much attention.[2–4] Owing to their special structures and outstanding mechanical/electrical properties, tubular structures have been widely used for the fabrication of microfluidics and optical devices, biomedical instruments, chemical microreactors, and composite materials.[5–12] So far, various tubular structures have been produced by using vapor phase deposition, lamella structure scroll, template-assisted, metal-catalyst-assisted, and thermal solution methods.[7,13–18] High-aspect-ratio TiO_2 nanotubular layers possess significantly stronger photocatalytic properties than nanoparticulate layers do.[19] Thus, TiO_2 tubular materials are particularly interesting for their potential applications in photocatalysis and photovoltaic cells. TiO_2 crystals with {001} facets, which have a high surface energy and hence exhibit enhanced reactivity, are attractive as photocatalysts.[20] Recently, a method to synthesize anatase TiO_2 single crystals with a high percentage of {001} facets has been developed,[21] and has been used to prepare several morphologically different anatase TiO_2 materials with a high percentage of {001} facets and hence with high photocatalytic activities.[22–24] So far, however, there has been no report on TiO_2 tubular materials exposing highly reactive {001} facets. In this work, we report a simple one-step hydrothermal method for preparing anatase TiO_2 tubular structures made up of microscrystallites with a high percentage of {001} facets by using ZrO_2 fibers as a template. This process may provide a facile way to produce TiO_2 with special structures, which may have promising applications in photocatalysis and photoelectronics. Our analysis of the structures, morphologies, and growth procedures of the as-grown TiO_2 microtubes provides a plausible growth mechanism.

Figure 1 shows the XRD patterns of the as-grown samples obtained after hydrothermal processing at 200 °C with a ZrO_2 template for various reaction times *t*. The products obtained with $t = 6$ h exhibit a mixed phase of anatase TiO_2 (JCPDS card 21-1272) and tetragonal ZrO_2 (JCPDS card 79-1764, Figure 1 b). The peaks corresponding to tetragonal ZrO_2 gradually decreases with increasing the reaction time *t*.

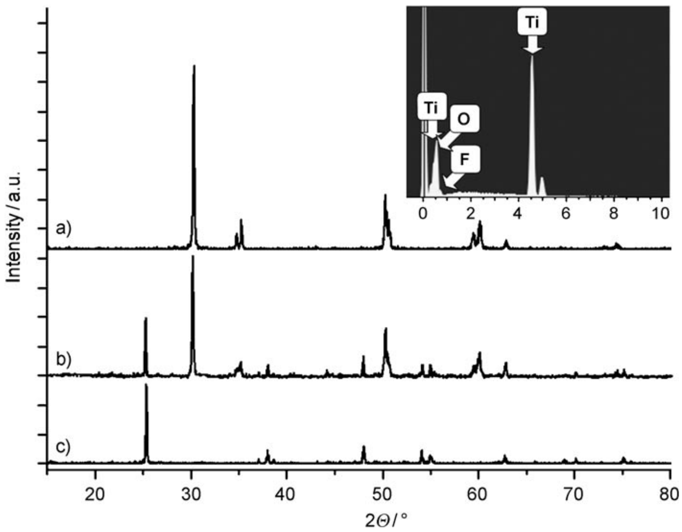

Figure 1. XRD patterns of a) the ZrO_2 template, b) the TiO_2 tubular structures obtained from hydrothermal processing at 200 °C for $t = 6$ h, and c) the TiO_2 tubular structures obtained from hydrothermal processing at 200 °C for $t = 24$ h. The inset shows the EDS of as-grown TiO_2 tubular structures obtained with $t = 24$ h.

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When $t=24$ h, the tetragonal ZrO_2 phase completely disappears, and all the diffraction peaks of the as-grown samples can be indexed to pure anatase TiO_2 (Figure 1 c). This observation is further confirmed by the energy dispersive spectrum (EDS) of the as-grown TiO_2 tubular structures (see the inset of Figure 1); only Ti, O, and F atoms are detected from the as-grown TiO_2 samples with the [Ti]/[O] ratio of 1:2.35, which is close to the expected stoichiometry. The presence of F is attributed to the presence of $(NH_4)TiF_6$ in the hydrothermal process.

Polycrystalline ZrO_2 fibers are long with smooth surfaces (Figure 2 a), whereas the as-grown TiO_2 tubular structures are short (70–150 μm) with rough surfaces (shown in Figure 2 b). The SEM images in Figure 3 show zoomed-in views

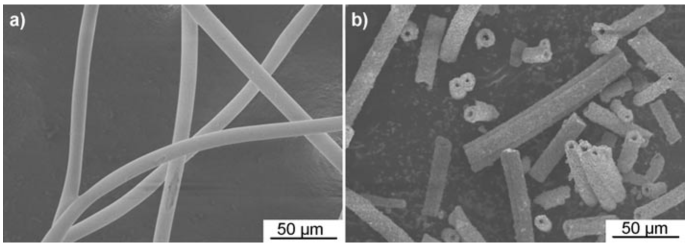

Figure 2. SEM images of a) ZrO_2 fibers and b) the as-grown TiO_2 tublar structures obtained from hydrothermal processing at 200 °C for 24 h.

of the open ends and the surfaces of the as-prepared TiO_2 tubular structures. The latter are composed of many TiO_2 microcrystals and have external diameters of about 10–15 μm and a wall thickness of approximately 3 μm. The high-magnification SEM image (Figure 3 c) shows that the tubular structures consist of plate-shaped rectangular structures with side lengths of approximately 3 μm and thickness of approximately 1 μm. High-resolution transmission electron microscopy (HR-TEM) shows the (200) and (020) atomic planes with a lattice spacing of 0.19 nm (Figure 3 d). The selected-area electron diffraction (SAED) patterns further confirm the single-crystalline characteristics, and the SAED pattern can be indexed as a (001) zone (insert of Figure 3 d). In contrast to the case of regular anatase TiO_2 crystals, which are usually dominated by the thermodynamically stable {101} facets,[21] both {101} and {001} facets are clearly observed in the microcrystallites of as-prepared TiO_2 tubular structures. The appearance of highly reactive {001} facets, which is thermodynamically unstable due to its higher surface energy, is due most probably to the F^- ions generated during the hydrothermal procedure, because F^- ions are known to preferentially stabilize the (001) rather than the (101) surface.[20,21] The existence of F in the EDS (the inset of Figure 1) indicates that some F atoms are adsorbed on the TiO_2 microcrystal surfaces, thereby stabilizing the {001} facets. Based on the SEM image of the rectangular TiO_2 microcrystals, the percentage of the highly reactive {001} facets is estimated to be approximately 46 %.

The synthesis of TiO_2 tubular structures by the hydrothermal process can be explained in terms of two reactions

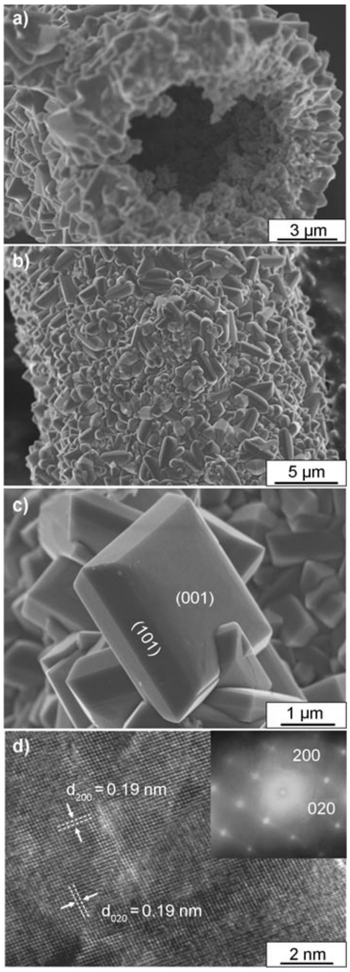

Figure 3. SEM images of anatase TiO_2 tubular structures: a) The end of one tube, b) the surface of a tube, and c) the faces of microcrystals. d) HR-TEM images of a TiO_2 sheet (the inset shows the corresponding SAED patten).

shown in [Eq. (1)] and [Eq. (2)]. First, $(NH_4)_2TiF_6$ is hydrolyzed to form TiO_2 nanoparticles, HF and NH_4F [Eq. (1)]. Second, ZrO_2 fibers are gradually corroded away by the resulting HF and NH_4F and are transformed to water-soluble $(NH_4)_2ZrF_6$ [Eq. (2)].

$$(NH_4)_2TiF_6 + 2H_2O \rightarrow TiO_2 + 2NH_4F + 4HF \quad (1)$$

$$ZrO_2 + 4HF + 2NH_4F \rightarrow (NH_4)_2ZrF_6 + 2H_2O \quad (2)$$

In this way, TiO_2 nanoparticles are deposited and grow on the surfaces of ZrO_2 fibers, whereas the ZrO_2 fibers are gradually corroded as the reaction time t increases. Figure 4 illustrates the schematic diagram of a plausible growth mechanism, along with the cross-sectional SEM images of TiO_2 tubular structures obtained after hydrothermal processing at 200 °C at various reaction times t. At $t=1$ h (Figure 4 b), a dense layer of TiO_2 nanocrystals are randomly deposited on the smooth surfaces of ZrO_2 fibers. At $t=6$ h (Figure 4 c), the TiO_2 layer grows thicker and the ZrO_2 tem-

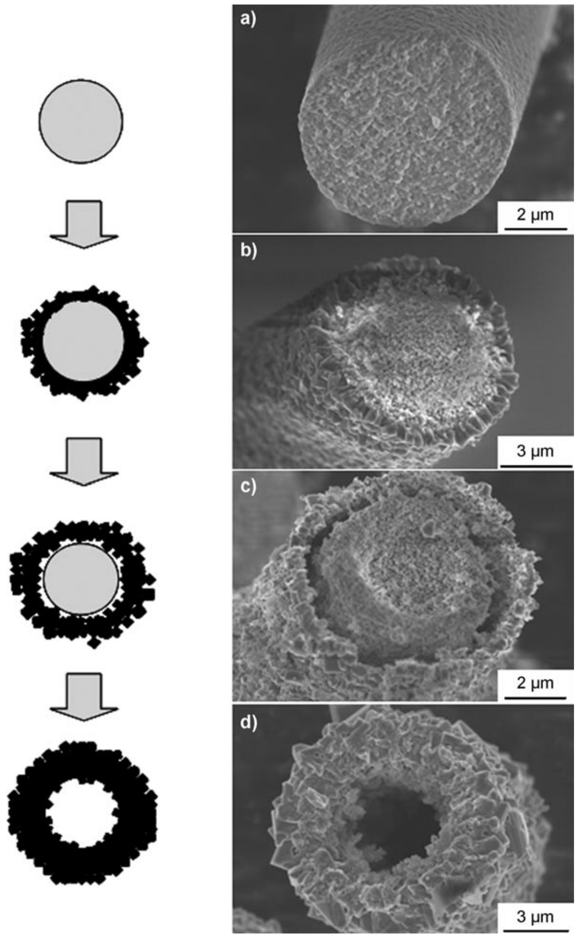

Figure 4. Schematic diagrams (left) illustrating the growth mechanism, which are consistent with the SEM images of TiO_2 microtubes obtained in a $(NH_4)_2TiF_6$ solution at 200 °C for a) $t=0$ h, b) $t=1$ h, c) $t=6$ h, and d) $t=24$ h.

plates begin to corrode (Figure 4c). When t reaches 24 h (Figure 4d), the ZrO_2 templates are completely corroded away and only a TiO_2 tubular structure remains. Our analysis suggests that by controlling the morphologies and sizes of ZrO_2 templates a variety of anatase TiO_2 tubular or hollow spherical materials consisting of microcrystallites with high percentage of {001} facets can be obtained.

In summary, we have developed a simple one-step hydrothermal template process for preparing TiO_2 tubular materials made up of microcrystallites with a high percentage of reactive {001} facets, and have formulated a plausible growth mechanism for this process. The modification of the morphologies and sizes of ZrO_2 templates can lead to various anatase TiO_2 tubular or spherical materials made up of microcrystallites with a high percentage of {001} facets, which can be of potential use in many fields.

Experimental Section

For the fabrication of anatase TiO_2 tubular structures composed of microcrystallites, tetragonal ZrO_2 polycrystalline fibers (5–10 μm in diameter and longer than ≈50 mm) were employed as a template in our experiments (as shown in Figure 1a). The fibers were pretreated by dipping them in dilute HNO_3 solution for about 12 h. Then they were filtered, rinsed with distilled water and ethanol three times, and dried at 80 °C for 12 h in air prior to use. 1.23 g of pretreated ZrO_2 fibers was immersed in 40 mL aqueous solutions containing $(NH_4)_2TiF_6$ (2.97 g, 0.015 mol). The mixture was then transferred into 60 mL Teflon-lined stainless-steel autoclaves and maintained at 200 °C for 24 h. After the reaction, the products were filtered, rinsed with distilled water and ethanol several times, and dried in an oven at 80 °C.

The XRD patterns were taken on a Bruker AXS D8 advance powder diffractometer with a $Cu_{K\alpha}$ X-ray tube, using filtered $Cu_{K\alpha}$ radiation over a 2θ range from 15 to 80° with a step size of 0.02° and a counting time of 0.1 s step^{-1}. The EDS was taken on a HORIBA EMAX Energy EX-350 energy dispersive X-ray microanalyzer. The morphologies and structure were observed by SEM (Hitachi S-4800 microscopy) and HRTEM (JEOL JEM-2100).

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Keywords: anatase · hydrothermal synthesis · titanium · tubular structures · zirconium

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