A Facile and One-pot Synthesis of High Aspect Ratio Anatase Nanorods Based on Aqueous Solution

Songwang Yang[†,††] and Lian Gao*[†]
[†]*State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, P. R. China*
[††]*Graduate School of the Chinese Academy of Sciences, Shanghai 200050, P. R. China*

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Single-crystalline anatase nanorods with high aspect ratios have been synthesized through a facile and one-pot method based on an aqueous solution. The synthesized anatase nanorods have pits, crevices, and dislocations on the surfaces besides the steps, kinks, and terraces on the side walls.

Considerable efforts have been devoted to the design and synthesis of low-dimensionally nanostructured materials because of their morphology-dependent distinguished performance manifested in nanoelectronics,[1] optoelectronics,[2] biomedicine,[3] and catalysis.[4] Titanium dioxide (TiO_2), as a typical oxide material, mainly has three crystal phases: anatase, rutile, and brookite. Unlike rutile, anatase is not easily favored to form rodlike morphologies with high aspect ratios in an aqueous solution because of the surface energy property of the truncated octagonal bipyramid seeds,[5] while anatase nanorods with high aspect ratio are considered to have many advantages over nearly spherical particles.[6] The "gel–sol" method developed by Sugimoto is an effective approach to the control over the anatase shape.[7] Very recently, shape-controlled synthesis of anisotropic inorganic nanostructures in liquid media has been successfully applied to the control over the shape of anatase TiO_2.[5,6] However, it would also be desirable for new strategies to gain surface-clean and highly single-crystalline anatase nanorods in a facile fashion for their further important diverse applications. Herein, we have presented a facile route to the fabrication of single-crystalline anatase nanorods in an aqueous solution under the one-pot condition. More interestingly, the anatase nanorods prepared by the present method have rough surface structures and zigzag rodlike shape.

In our preparative method, $TiCl_4$ was used as a titanium source, diluted with doubly distilled water into 3.0 M under stirring in an ice-water bath as the stock, and further diluted into 0.03 M immediatly before use. In a typical synthesis, 0.03 M fresh aqueous $TiCl_4$ solution was mixed with isopropanol in an ice-water bath with magnetic stirring, and then ethylenediamine (EDA, Shanghai Chemical Reagent Co.) was added (the volume ratio of 0.03 M $TiCl_4$:isopropanol:ethylenediamine equaling to 3:6:1). The gained suspension was loaded into a stainless steel autoclave lined with Teflon. The autoclave was kept at 180 °C for 30 h in an oven. The white precipitates were washed with ethanol for several times, collected from the solution by filtration, and dried at 60 °C in a vacuum oven overnight.

The gained anatase TiO_2 was characterized with transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAED) on a field emission electron microscope (JEOL-2100F); and scanning electron microscopy (SEM) on a field emission electron microscope (JSM-6700F). The phase of the products was identified by powder X-ray diffraction (XRD) analysis using a D/max 2550V diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å).

As shown in scanning electron microscopic (SEM) and transmission electron microscopic (TEM) images (Figures 1a–1d), the morphology of the synthesized TiO_2 is free-standing "zigzag" nanorods with corrugated sides and the diameter of the rod is not constant throughout its length. Although the lengths of the rods have a wide distribution from 60 to 420 nm (Figure 1e), the morphology of the observed nanoparticles is exclusively rodlike and few single nanoparticles are observed. Therefore, this method has morphologically a high rodlike yield. The average aspect ratio of the nanorods is up to around 9.

On the basis of powder X-ray diffraction (XRD) (Figure 1f),

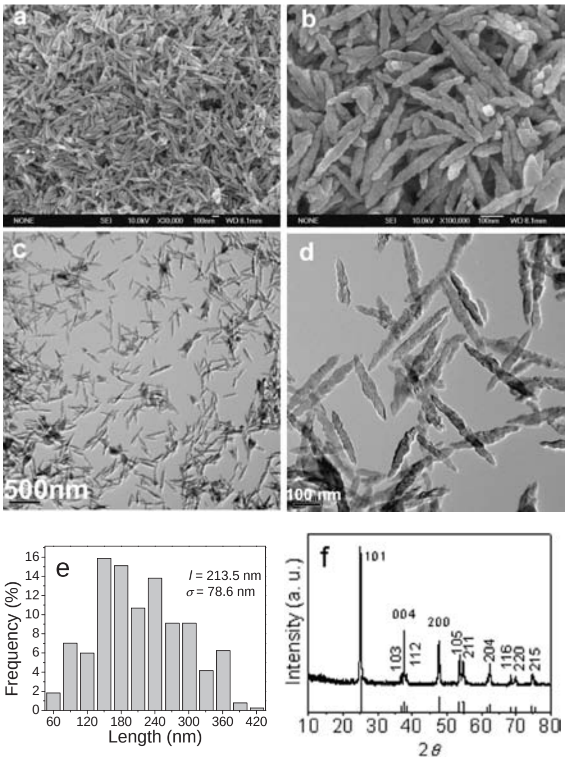

Figure 1. (a, b) SEM and (c, d) TEM images of anatase nanorods synthesized in the present work with different magnifications, (e) histogram of the nanorod length distribution (nearly 500 anatase nanorods were measured), and (f) XRD pattern of the synthesized nanorods, vertical bars indicate peak position and intensity of anatase TiO_2 (JCPDS No. 21-1272).

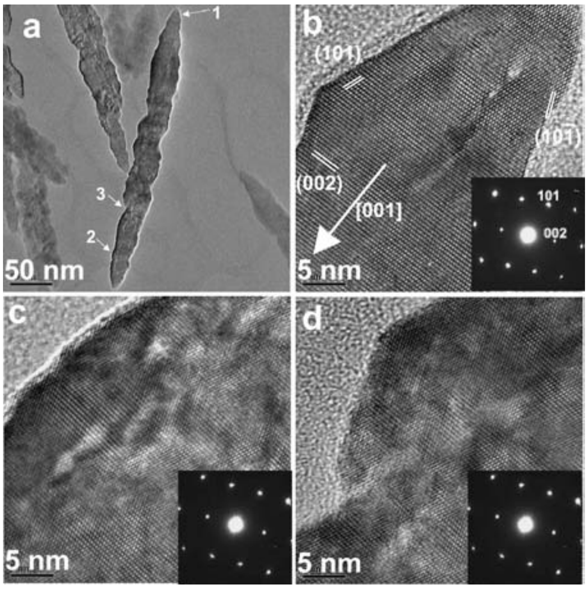

Figure 2. (a) TEM image of a typical individual anatase nanorod; HRTEM images and SAED patterns of (b) one end of the nanorod (**1**), (c) a typical body part of the nanorod (**2**), and (d) an indentation of the nanorod (**3**).

the synthesized TiO_2 belongs to anatase phase. All the recorded peaks can be clearly shown and assigned to the anatase phase of TiO_2 (S. G.: $I4_1/amd$; $a_0 = b_0 = 3.785\,\text{Å}$, $c_0 = 9.513\,\text{Å}$; JCPDS No. 21-1272). In particular, the narrowing of the full width of half maximum (FWHM) of the XRD peaks demonstrates the high quality of crystallites of the gained nanorods.

Detailed investigations on the nanorods through the high-resolution transmission electron microscopic (HRTEM) technique reveal some important characteristics of the nanorods. Figure 2a depicts a typical individual nanorod gained from the present method with the average value of diameter of $\approx$28.8 nm, length of 336.5 nm, and the aspect ratio of $\approx$11.7. It can be seen that the nanorod has irregular steps, kinks and terraces on its side walls. Figures 2b–2d are the HRTEM images of the three typical parts in the nanorod, the end, the typical body part, and the indentation, respectively. The selected area electron diffraction (SAED) patterns of the three parts can be indexed as the same diffraction spot pattern and their lattice fringes are clear as well, which demonstrate that the whole nanorod is highly single-crystalline. The SAED pattern can be indexed as [010] zone spots, which indicates that the nanorod is preferential in the [001] direction (Figure 2b). However, the surface structure of the nanorod is rough because there exist pits, crevices and dislocations in the nanorod.

Although the formation mechanism of this kind of nanorods is complex, the alcohol–water mixture phase and the surface controller, ethylenediamine (EDA), may play a decisive role in the formation of the anatase nanorods. The experimental results show that no anatase nanorods are formed without ethylenediamine or isopropanol (Figure S1). Ethylenediamine can be adsorbed onto the specific planes parallel to the *c* axis of TiO_2 nuclei, leaving (002) plane exposed to the alcohol–water mixture media. The preferential adsorption of EDA on the specific planes can result in the anisotropic growth of the primary particulates. At the same time, the presence of long homogeneous hydrogen-bonded chains in the isopropanol–water mixture phase[8] may provide the long-distance interaction which can drive the initial orientated arrangements of the primary particulates, and then aggregation-based growth[9,10] occurs along the crystallographically specific direction (*c* axes). This growth process results in the formation of irregular steps, kinks, terraces, and rough surface structures of the fabricated nanorods. A similar growth process may have been observed in the formation of α-Fe_2O_3 ellipsoidal particles in solution.[11] Also a more detailed investigation on the precursor solution chemistry is currently in progress.

In summary, a facile and aqueous solution-based method has been developed for the synthesis of free-standing and high aspect ratio single-crystalline anatase nanorods with rough surface structures (pits, crevices, and dislocations). This simple method should promise the large-scale fabrication of high aspect ratio anatase nanorods and this kind of nanorods should be expected to have an important application in photocatalysis.

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