Brookite-type TiO_2 nanotubes

Qixin Deng,[a] Mingdeng Wei,*[ab] Xiaokun Ding,[a] Lilong Jiang,[a] Binghuo Ye[b] and Kemei Wei[b]

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Brookite-type TiO_2 nanotubes with crystalline multilayer walls have been synthesized for the first time *via* a simple hydrothermal route.

Recently, one-dimensional (1D) TiO_2 nanomaterials have attracted great attention because of their interesting properties and widespread applications in the photovoltaic, photocatalytic, electrochemical, and gas sensing fields. As is well known, TiO_2 is a semiconductor that crystallizes in eight polymorphic forms: anatase ($I4_1/amd$), rutile ($P4_2/mnm$), brookite ($Pbca$), TiO_2-B ($C2/m$), TiO_2-R ($Pbnm$), TiO_2-H ($I4/m$), TiO_2-II ($Pbcn$), and TiO_2-III ($P2_1/c$). Rutile is the only stable form, whereas the others are metastable phases and transform to the rutile phase when they are heated to high temperatures. Anatase and rutile are the most common phases and much more research has been done on their syntheses and applications.[1–10] In contrast, brookite is the rarest of the natural TiO_2 polymorphs, and it is the most difficult phase to synthesize in the laboratory. For this reason the properties of pure brookite TiO_2 are little known. Ohtani *et al.*[11] have reported the markedly high photocatalytic activity of brookite nanocrystals as compared to those of rutile and anatase. Koelsch *et al.*[12] considered that brookite TiO_2 would be a good candidate for photovoltaic devices. In fact, few studies have reported the synthesis of pure brookite TiO_2 with the absence of a mixture of rutile and anatase phases, as revealed from the X-ray powder diffraction (XRD) measurements. Kominami *et al.*[13] reported the synthesis of nanocrystalline brookite TiO_2 of ~ 50 nm crystal size in organic media. Nanocrystalline particles of brookite TiO_2 were also synthesized using hydrolysis of a $TiCl_3$ or $TiCl_4$ solution as a precursor.[14–16] To the best of our knowledge, however, 1D nanostructural single phase brookite TiO_2 has not been synthesized other than by Tomita *et al.*[17] They reported the synthesis of short nanorods of brookite using an aqueous-solution of a titanium complex. In this study, we first develop a simple synthetic route for the synthesis of pure brookite nanotubes. In this route, the precursor is titanate nanotubes, which are prepared using TiO_2 powder and NaOH (10 M) as the starting materials. The titanate nanotubes are then transformed into pure brookite nanotubes under hydrothermal conditions. The mechanism of formation of the brookite TiO_2 nanotubes is discussed based on our measurements.

In a typical synthetic procedure, 2.5 g of anatase TiO_2 powder was dispersed into 20 ml of 10 M NaOH solution, and then transferred into a 75 ml Teflon container, which was then kept in an oil bath at 120 °C for 20 h. The white product was washed with dilute HCl, centrifuged several times until pH values of the final products ranged from 5 to 12, and then was used as a precursor in the next reaction. 50 ml of the precursor was then transferred into a 75 ml Teflon-lined autoclave, and kept in an oven at 200 °C for 1 day. The white product was washed with deionized water and filtered, and then dried at 100 °C for 3 h. XRD patterns were recorded on a PANalytical X'Pert spectrometer using Co Kα radiation (λ = 1.79 Å), and the data would be changed to Cu Kα data. Scanning electron microscope (SEM) and transmission electron micrographs (TEM) were taken on a Philip-XL30 instrument, Hitachi S-4800 and a JEOL 2010 instrument, respectively.

Fig. 1 shows the XRD pattern, SEM and TEM images of the precursor synthesized at 120 °C for 20 h in a Teflon container in an oil bath. A peak at about $2\theta = 10°$ was observed (Fig. 1a). This is characteristic of a layered structure.[18] According to current structural investigations, it can be indexed to a layered titanate $Na_xH_{2-x}Ti_3O_7$.[18–23] As depicted in Fig. 1b, numerous fiber-like products are observed whose lengths typically range from several hundreds of nanometres to several tens of micrometres. Also, the fiber-like products lie close to each other to form a bundle-like morphology.

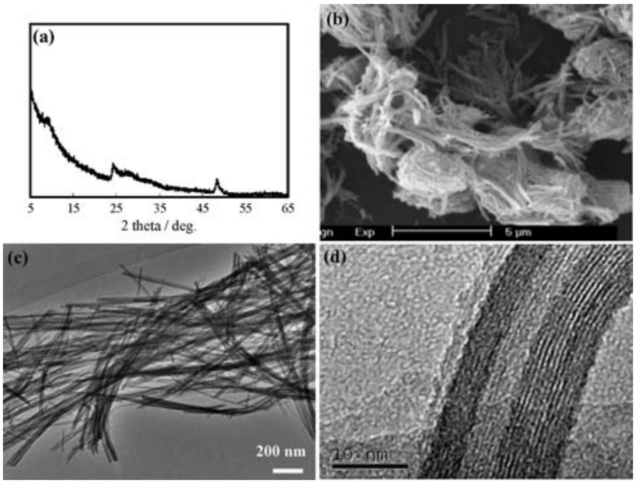

Fig. 1 XRD pattern, SEM and TEM images of the precursor synthesized at 120 °C for 20 h in a Teflon container in an oil bath: (a) XRD pattern, (b) SEM image, (c) low-magnification TEM image, and (d) high-magnification TEM image of a single nanotube.

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[a] *Institute of New Energy Technology and Nano-Materials, Fuzhou University, Fuzhou, Fujian 350002, China. E-mail: wei-mingdeng@fzu.edu.cn; Fax: +86-591-83753180*
[b] *National Engineering Research Center for Fertilizer Catalyst, Fuzhou University, Fuzhou, Fujian 350002, China*

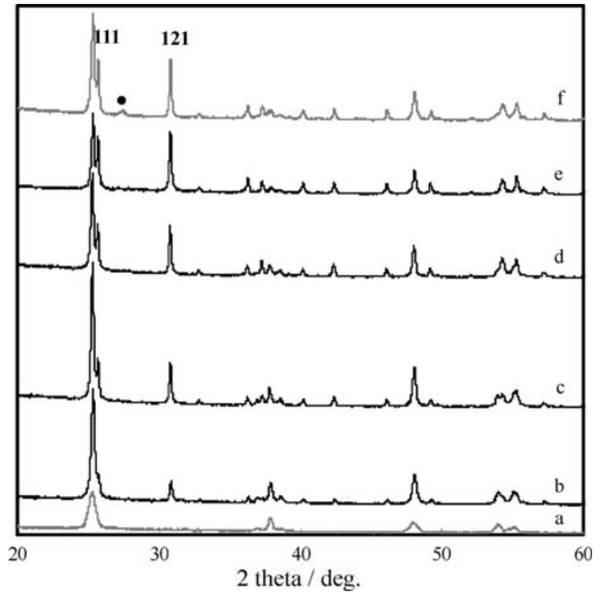


Fig. 2 XRD patterns of products synthesized at 200 °C for 20 h under different pH values: (a) 6.0, (b) 7.6, (c) 8.8, (d) 9.6, (e) 10.9, and (f) calcined at 600 °C for 4 h (●: rutile).

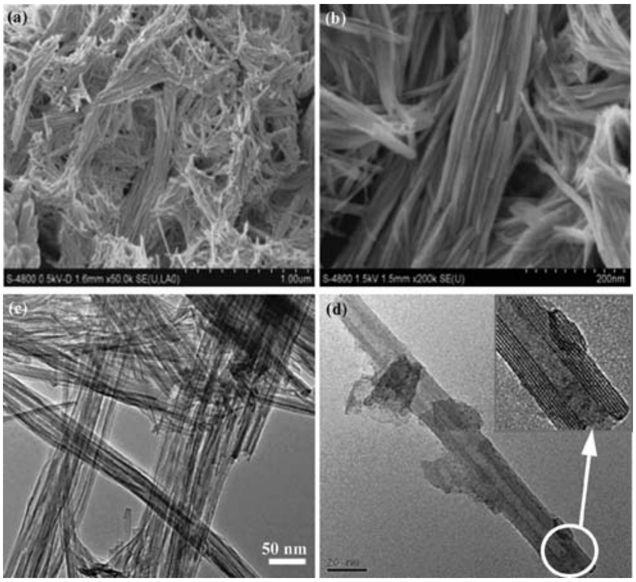


Fig. 3 SEM (a, b) and TEM (c, d) images of the brookite nanotubes synthesized at 200 °C for 20 h under pH = 10.9.

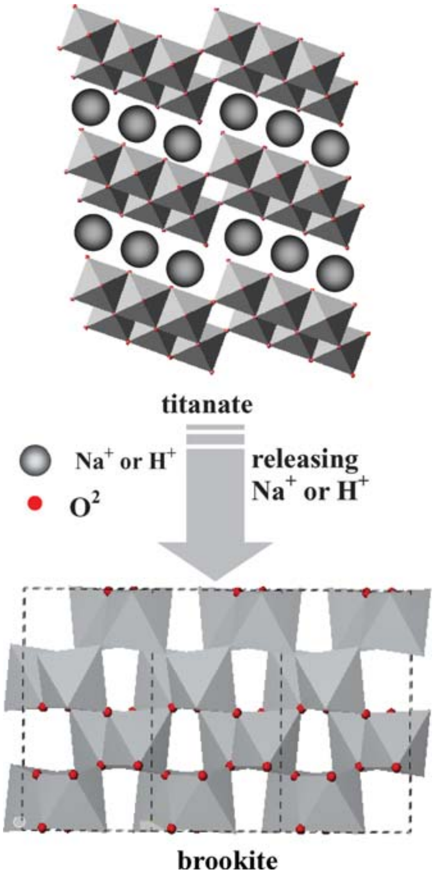
The diameter of the fibers is found to be *ca.* ~20 nm. The morphology of the precursor can be further confirmed by TEM measurements. As shown in Fig. 1c, the hollow nature of the tubes is clearly visible. Fig. 1d shows a high-magnification image of a single nanotube. The nanotubes are composed of crystalline multilayer walls, in which the interspaces between the layers and inner diameter are found to be about 0.7 and 5 nm, respectively. The morphologies of our synthesized titanate nanotubes are similar to those of other reports.[18–23]

Fig. 2 shows the XRD patterns of the products synthesized at 200 °C for 20 h at different pH values in an autoclave. The XRD patterns of the products are very different from those of the precursor. As depicted in Fig. 2a, a typical profile of anatase TiO_2 was observed (JCPDS 21-1272) when the reaction was executed under acidic conditions (pH < 7). When the reaction was performed under basic conditions, the brookite phase of TiO_2 (JCPDS 29-1360) was obtained, as shown in Fig. 2b–e. The patterns show that the purity of brookite TiO_2 increased with increasing pH, and neither anatase nor rutile phases were detected when the pH value was controlled at 10.9. Thus, pure brookite TiO_2 can be obtained at this high pH value. This is in agreement with the report by Li *et al.*[24] They concluded that a quantity of sodium cations in the reaction system seem necessary for the formation of pure brookite TiO_2. After the brookite TiO_2 was calcined at 600 °C for 4 h, a small amount of the rutile phase was detected, as shown in Fig. 2f, indicating that the brookite phase can be stabilized at higher temperatures.

Fig. 3 depicts the SEM and TEM images of brookite TiO_2. It can be seen from Fig. 3a and b that the morphology of the product did not change after the precursor was treated at 200 °C for 20 h at pH = 10.9. The TEM images also confirmed that the morphology of the product is a nanotube with a crystalline multiwall structure, as depicted in Fig. 3c and d. The high magnification image indicates that the inner diameter of the nanotubes is ~5 nm and that the interspace of the layers is ~0.78 nm. The interspace of the brookite nanotubes is larger than that of the precursor; this must be attributed to the fact that H_2O molecules were inserted into the interspaces of layers which subsequently expanded. It can also be seen that brookite TiO_2 nanotubes are more crystalline than titanate nanotubes; this might be due to the fact that brookite TiO_2 nanotubes were prepared at 200 °C in an autoclave. In general, the crystallinity of the product can be increased at a higher synthetic temperature.

In this study, the precursor, titanate $Na_2H_{2-x}Ti_3O_7$ nanotubes, was synthesized using Kasuga's method,[26,27] which has been widely used to synthesize titanate nanotubes, titanate nanowires, and titanate nanosheets over the past decade.[22,28–30] It is well known that titanates are composed of edge-sharing $[TiO_6]$ octahedral layers,[19,31,32] and the interspaces between the layers are occupied by Na^+ or H^+, as depicted in Scheme 1. Nagase *et al.*[25] reported the hydrothermal synthesis of brookite TiO_2 as an almost single phase at 200 °C with a TiO_2/NaOH mole ratio ≈ 1. They considered that the brookite phase can be formed from sodium titanate by releasing Na^+ and H^+ from the surface accompanied by oxidation of Ti in the structure. Thus, in the present study, we believe that Na^+ and H^+ located in the interlayer spaces of titanate can be released and consequently the brookite TiO_2 phase is formed. The release of Na^+ cations from titanates changes the pH value of the solution, which can be confirmed by the measured pH data. In our study, the pH value of the solution taken from the autoclave was measured and was found to have increased from 10.9 to 12 after reaction.

Brookite-type TiO_2 nanotubes, with a ~5 nm inner diameter and a ~0.78 nm interlayer space, were synthesized for the first time using a simple two-step hydrothermal process. Firstly, titanate nanotubes were prepared and used as a



Scheme 1 A possible model for the transformation of titanate nanotubes to brookite-type TiO_2 nanotubes by releasing Na^+ and H^+ cations under a hydrothermal condition.

precursor. Secondly, the titanate nanotubes were transformed into pure brookite nanotubes under hydrothermal conditions. The synthesized products were characterized by XRD, SEM and TEM measurements, and it was found from XRD that the brookite-type TiO_2 nanotubes consist of a pure phase. High magnification TEM observations show that they are composed of crystalline multilayer walls. A formation mechanism for the brookite-type TiO_2 nanotubes is discussed based on our experimental results. We believe that this kind of simple synthetic route, with no catalysts or templates and requiring no expensive and precise equipment, will greatly reduce the production cost, and thus offer great opportunity for scaling up the synthesis of 1D nanoscale materials.

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