Microwave-assisted Preparation of Titanate Nanotubes

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Titanate nanotubes were successfully prepared for the first time by using microwave irradiation as the heating resource. The process is mild, quick, and easy to control. The morphology and structure of the product were checked by TEM, HRTEM and XRD.

Nanostructured materials have been attracted much attention because of their novel properties. Recently, there has been great interest in controlling the shapes of materials, including the size, shape, and surface. One-dimensional (1D) materials, such as nanobelts and nanoribbons, have been widely studied.[1–5] The nanotublar materials include metal, metal sulfide, metal oxide, and carbon, such as Au, SiO_2, MoS_2, Al_2O_3, and TiO_2. Among them, TiO_2-based nanotubes is one of the most extensively studied materials for the potential applications in many areas such as photocatalysis,[6] photo-voltaic cell,[7,8] ion exchange,[9,10] sensing,[11] etc.

Many attempts have been made to get titania nanotubes and titanate nanotubes. The methods include mainly template synthesis,[8,12] supramolecular assemble,[13] hydrothermal synthesis,[14,15] and inductive synthesis.[16] Zhu[17] and his co-workers reported a new method of sonochemical synthesis. Since the first report about the hydrothermal synthesis of titania (TiO_2) nanotubes, there have been many studies on the growth process, the structure, the mechanism,[18–22] and the materials derived from the nanotubes, such as oriented array,[23] Ag- or Au-loaded nanotubes,[24] layer-by-layer assembled multiplayer film,[24,25] CdS-inserted nanotubes,[26] RuO_2/TiO_2 nanotubes composites,[27] and nanotube aggregates.[28] The products synthesized by hydrothermal method show high quality but the process needs 20–72 h reaction time and/or high pressure.

Microwave irradiation is an efficient and distinct heating method, and has attracted chemists' attention because of very short reaction time and low energy consumption needed for the reactions, compared with conventional methods.[29,30] Synthesis via microwave heating is a relatively new technique in chemistry, especially in the preparation of inorganic materials. Recently, the applications of microwave-assisted synthetic procedures are extending for preparation of nanostructural materials. However, there are few reports about microwave-assisted reactions for preparation of one-dimensional materials, such as ZnO rods,[31] carbon nanotubes,[32] CdS nanotubes,[33] and ZnS nanoribbons,[34] Au[35] and Ag[36] nanowires.

In this paper, microwave-assisted preparation of titanate nanotubes using NaOH aqueous and TiO_2 powder under normal pressure is reported for the first time. The process was mild and short. The products were highly pure with the size of the length up to tens of micrometer and the diameter about 7 nm.

The preparation was carried out in a domestic microwave oven (Haier, HR-7751M, 750W). A window was opened on the top of the oven in order to connect the mechanical stirrer and reflex condenser. The system was equipped with Teflon PFA vessels that were transparent for microwave irradiation. The power of the microwave oven can be set to the mode of high (continuous irradiation), high-mid (irradiation 17 s, stop 5 s), mid (irradiation 12 s, stop 10 s), mid-low (irradiation 10 s, stop 12 s), or low (irradiation 4 s, stop 12 s). The reaction was taken in water under normal pressure. In a typical synthesis, 2.5 g of TiO_2 (anatase, purchased from Zhejiang Zhoushan) was mixed with 100 mL of 40% (w/w) aqueous NaOH solution in the Teflon vessels and then put them in the microwave oven for 6 h under mid-low model of power. The reaction mixture was cooled to room temperature and washed with distilled water and ethanol to a pH of 6–8, and then dried at 60 °C for 24 h. The reaction process is simple and easy to control.

The TEM image (Figure 1a) shows that the starting material of TiO_2 is a kind of particles with a size range of 20 to 30 nm. When the reaction finished, a large quantity of one-dimensional materials with about several to tens of micrometers in the length were obtained (Figure 1b). The yield is pretty high (>90%) and almost none of particles can be observed. The HRTEM images (Figures 1c and 1d) show that the one-dimensional materials are all tubular structure with multiple shells of 2–4 layers and a shell space is about 0.8 nm, and the inner diameter of the open end is about 5–9 nm. It can be seen from the HRTEM image that the products show a well crystalline structure, which fits well to our report before.[20]

Figure 2 shows the XRD patterns of the starting material and the product (after reacting 6 h). It shows that the raw material is anatase TiO_2. The product shows an orthorhombic system with the lattice constants, $a_0 = 19.26$ Å, $b_0 = 3.18$ Å, and $c_0 = 3.00$ Å, which fit well to the titanate nanotubes obtained via hydrothermal method.[20]

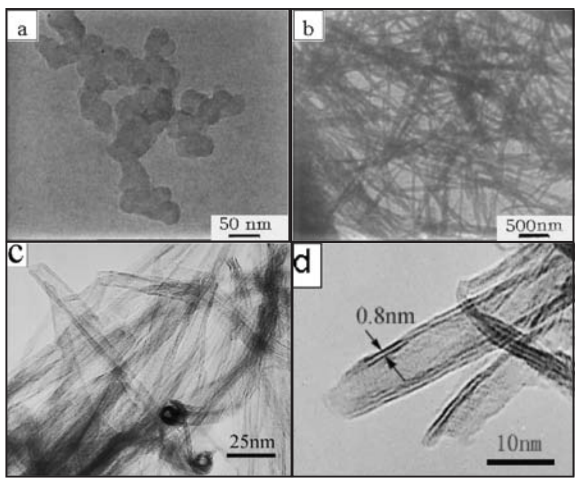

Figure 1. The TEM image of the raw material and the products after 6 h, a) the raw materials, b) low magnification TEM image of the products, and c) and d) the HRTEM of the products.

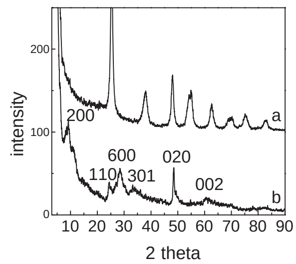

Figure 2. XRD patterns of the raw materials (a) and the products after 6 h (b).

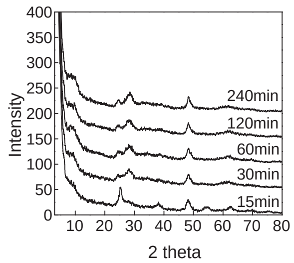

Figure 3. XRD patterns of the products at different reaction time.

The reacting process was investigated by XRD (as shown in Figure 3) and TEM. From XRD results, it can be seen that after reacting for 15 min, the peak intensity of anatase decreased remarkably and some new peaks, could be ascribed to titanate nanotubes, occurred. After reacting for 2–4 h, the peaks belonging to anatase disappeared, most of the product were nanotubes. However, at this stage, some short nanotubes could been found from TEM images (shown as Supporting Informantion). For this method, 6 h is suitable to fabricate titanate nanotubes with a length in range of several micrometer.

It is well-known that it would take 20–72 h to prepare the nanotubes from the raw materials of TiO_2 and NaOH via conventional hydrothermal method even when the raw materials TiO_2 powder is so small to nanoscale (5–21 nm).[9,25,29] However, the reaction can be accomplished within 6 h or less by using microwave. The temperature during the reaction is not higher than 110 °C, which is equal to or less than the temperature in the conventional hydrothermal method. Some lamellar products were found and the formation mechanism of the titanate nanotubes was discussed in our former report.[20] It is suggested that there is nonirradiation effect of microwave during the synthesis process of titanate nanotubes which contributes to make the particles swelled. Microwave is an electromagnetic wave composed of both electronic and magnetic field components, which give both the irradiation effects and the nonirradiation effects.[37] They both can attract the long Ti–O bond (0.1980 nm) and make the bond broken, but the short one (0.1934 nm) is surviving. Then linear fragments are formed and peeled off from the bulky TiO_2 particles. Finally, the nanoscale tubular structures are achieved by rolling further and the one-dimensional nanotubes are formed. Such process can be explained as 3D $\rightarrow$ 2D $\rightarrow$ 1D. The further study on the mechanism is still in discussion.

In summary, by using microwave irradiation as the heating method, titanate nanotubes can be prepared easily via hydrothermal procedure within a short time. The process is simple, easy to control, and the products are of high quality with high yield. There is likely nonirradiation effect of microwave during the preparation process which could enhance the reaction. Such result not only makes a possibility of the industrialization of titanate nanotubes, but also gives a new effective opportunity for the preparation of other materials which can be made in conventional hydrothermal method.

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