Synthesis of 1D Nanorutile (α-TiO_2) by Interfacially Initiating Redox Reaction at Low Temperature

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One-dimensional nanorutile crystals have been synthesized by interfacially initiating redox reaction between titanium trichloride ($TiCl_3$) and benzoyl peroxide (BPO) in a hydrothermal way at a relatively low temperature. It not only produced a large quantity of rutile nanorods but also provided a novel method to synthesize 1D nanomaterials at low temperature.

One-dimensional (1D) nanostructures such as nanowires, nanorods, and nanotubes have attracted special interest in recent years because of their potential application as conducting interconnecters and nanoscale electronic, opto-eletronic, and sensing devices.[1] There has been a surge of research activity related to the synthesis and characterization of nanowires and nanorods of various inorganic materials such as oxides, sulfides, and nitrides.[2] Many strategies have been employed to synthesis (1D) nanostructures such as electrochemistry,[3] template (mesoporous silica, carbon nanotubes, etc.),[4] emulsion or polymermetric system,[5] vapor transport,[6] and organometallic and coordination chemistry methods.[7] Despite these exciting developments, a general route to synthesize 1D nanostructure is still be researched.

TiO_2 has received much research attention because of its unique physicochemical properties in the applications of fine ceramics, photocatalysts for environmental purification, catalyst supports, dielectric materials, etc.[8] In fact, many studies have been conducted on the synthesis and morphology control of TiO_2 nanorods. TiO_2 nanorods are obtained via the hydrolysis of titanium salts, such as titanium alkyloxide ($Ti(OR)_4$)[9] and titanium(IV) chloride ($TiCl_4$) in solution.[10] In these reactions, all reactants are usually in the aqueous phase and the crystals could grow along different directions in solution, so the 3D nanotitania crystals are easily obtained. On the basis of above observation, we used a redox reaction to synthesize 1D nanorutile in solution. In contrast with usual method before, we did not make use of water-soluble oxidant such as $K_2S_2O_8$, H_2O_2, etc. but use an oil-soluble oxidant (BPO), which could ensure that the oxidant and reducing agents are in the different phase in solution.

In a typical synthesis, 2 mL of titanium trichloride ($TiCl_3$) and 20 mL of 1.5 M hydrochloric acid solution were mixed under magnetic stirring, making up the aqueous phase. Then, 2 mmol of BPO was dissolved in 20 mL of benzene, making up the oil phase. Lastly, the oil was added to the aqueous phase without stiring, forming a clear solution which was made up of two phases: oil on the top and water at the bottom. The solution was transferred into a 60-mL autoclave with a Teflon liner which was kept at 80 °C for 6 h, and then cooled to room temperature on standing. The precipitate was filtered, washed several times with distilled water and absolute ethanol, and finally dried in a vacuum oven at 40 °C for 12 h. The experiment was repeated under the same condition without oil phase.

Figure S1 (S is referred to Supporting Information) shows the XRD patterns of the product, in which all the peaks fit well with the literature values (JCPDS No. 21-1276). No other phases of TiO_2, such as anatase or brookite, could be detected by XRD.

The morphology and the microstructure of the rutile nanocrystals were investigated by field emission scanning electron microscopy (FE-SEM) (JSM-6700F). The FE-SEM images of the resulting products are shown in Figure 1. It can be found the morphology of obtained samples is greatly different in two ways: interfacial reaction and noninterfacial reaction. Interfacial reaction between $TiCl_3$ and BPO produces rod-like materials of width around 40 nm and length of about 300 nm (Figure 1a). If there is no oil phase in reaction, only some assembled flower-like crystals are obtained (Figure 1b). From the insert of Figure 1b, it can be observed that the flower-like crystals are actually made up of some rod-like crystals with a diameter of 50 nm and a length of 200 nm. It seems that nucleation of a solid phase initially occurred in the solution and subsequent crystal growth proceeded radially in the direction of the bulk solution.

In order to get more detailed microstructure, the obtained samples were investigated by TEM (H-800). Figure 2 shows the TEM images and their corresponding SAED patterns of the obtained samples. It can be found that the rod-like crystals

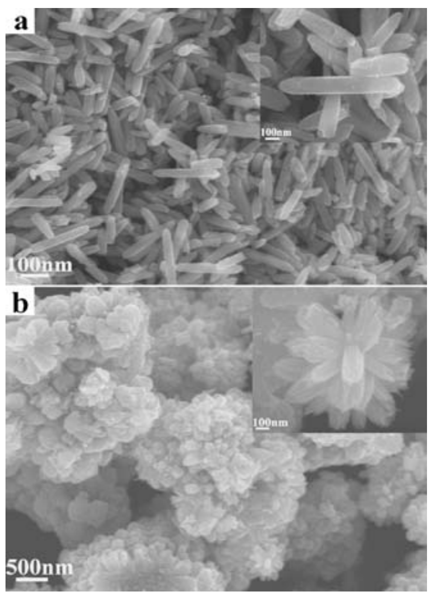

Figure 1. FE-SEM images of TiO_2 synthesized by redox reactions in a hydrothermal way at 80 °C. (a) Interfacial reaction, (b) noninterfacial reaction.

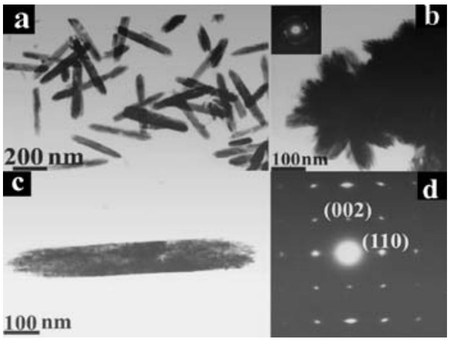

Figure 2. TEM images of TiO_2 synthesized by redox reactions in a hydrothermal way at 80 °C (inset is its corresponding ED pattern). (a, c, and d) Interfacial reaction, (b) noninterfacial reaction.

synthesized by interfacial reaction are single-crystal rutile (Figure 2d). The single-crystal pattern from a rod clearly indicates that crystals grow along [110] axis. Figure 2b shows the diffraction pattern of flower-like crystals prepared hydrothermally from aqueous titanium trichloride. Because the flower-like crystals have 3D structure and grow along different directions, the diffraction pattern shows some smooth rings. Figure S2 shows a high-resolution transmission electron microscope (HRTEM) image of the rutile nanorod (JEOL-2010). The lattice points can be observed clearly. The distance between the adjacent lattice fringes can be assigned to the interplaner distance of rutile $TiO_2(110)$; $d_{110} = 3.25$ Å. The rods have therefore grown along the [110] axis, which is consistent with the SAED pattern of the rod (Figure 2d). At last, the experimental procedures and results for evaluation of the photocatalytic activity of the obtained samples are available in the Supporting Information.

In principle, the crystal growth process includes nucleation and growth. In our experiments, the reaction was controlled to take place at the interface of water and oil successfully by selecting proper solvent. Figure 3 shows the process of the interfacial reaction. When the system was heated, the chemical reactions were invoked as follows:

$$\mathrm{Ph{-}C({=}O){-}O{-}O{-}C({=}O){-}Ph \longrightarrow 2Ph{-}C({=}O){-}O\bullet} \quad (1)$$

$$\mathrm{Ti^{3+} + H_2O \longrightarrow TiOH^{2+} + H^+} \quad (2)$$

$$\mathrm{Ph{-}C({=}O){-}O\bullet + TiOH^{2+} + H_2O \longrightarrow TiO_2 + Ph{-}C({=}O){-}O^- + 3H^+} \quad (3)$$

Reaction 1 only took place in the oil phase while reaction 2 proceeded in the aqueous phase for their solubility. When BPO was heated, it will become radical (PhCOO•) which is easy to turn into anion ($PhCOO^-$) by obtaining an electron. Because oxidant (BPO) only came into contact with reducing agent ($TiOH^{2+}$) at the interface of water and oil, reaction 3 actually occurred at the interface. Meanwhile, the oil would cover the aqueous phase for its lower density, so it insulated the aqueous phase against oxygen in air. That is the reason why we called it interfacial reaction. If there is no oil phase in the system, nucleation and growth of crystals occur in the same aqueous solution. It means that the crystals could grow along different

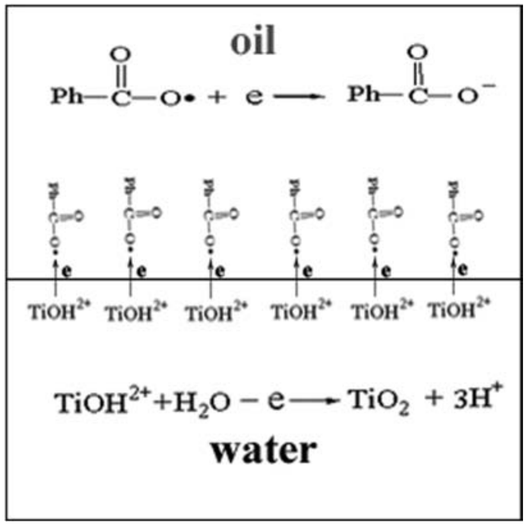

Figure 3. Proposed mechanism for interfacial reaction between BPO and $TiCl_3$ at 80 °C in a hydrothermal way.

directions equally, so assembled flower-like crystals form. This work has been studied before.[11]

In conclusion, a novel method has been presented to synthesize 1D nanorutile by interfacially initiating redox reaction at low temperature. As a very important reaction redox reaction has been used to synthesize a large amount of nanomaterials. So it provides a convenient route to synthesize some 1D nanostructures, especially some metals in predictable manner.

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