One-step Hydrothermal Synthesis of Suprastructural Rutile (α-TiO_2) with Controllable Morphology in Microemulsions at Low Temperature

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Suprastructural nanorutile crystals were synthesized by thermal hydrolysis of $TiCl_4$ in reverse microemulsion solutions at a relatively low temperature. Furthermore, the morphology of resulting materials could be controlled easily by changing the concentration of surfactant in reverse microemulsions. It also confirms the diversity of micelles in microemulsions.

Size- and shape-controlled synthesis of nanocrystals has naturally become one of the major subjects in the nanosynthesis field because of the intimately morphology-dependent characteristic of their properties.[1] Among them, the application of surfactants as reverse micelles or microemulsions for the synthesis of nanoscale structures is one of the most widely adopted methods in the literature. So far, it has been successfully used to prepare and control the size and shape of various nanostructures with different chemical compositions, such as Prussian blue analogue,[2] cadmium sulfide,[3] titania,[4] etc. Nanosized titania 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.[5] On the basis of the above observation, we planned to create a novel method to synthesize the rutile nanocrystals in reverse microemulsions. In fact, many studies have been conducted on the synthesis and morphology control of TiO_2 nanoparticles. TiO_2 nanoparticles are obtained via the hydrolysis of titanium salts, such as titanium(III) chloride ($TiCl_3$),[6] titanium(IV) sulfate ($Ti(SO_4)_2$),[7] titanium alkyloxide ($Ti(OR)_4$),[8] and titanium(IV) chloride ($TiCl_4$) in solution,[9] but one-step synthesis of monomineralic and well-shaped rutile nanocrystals in reverse microemulsions at low temperature were never reported. In this communication, we present a novel method not only to synthesize suprastructural rutile nanocrystals by thermal hydrolysis of $TiCl_4$ in reverse microemulsion solutions at a relatively low temperature but also to control the morphology of rutile crystals by changing the shape of micelles in reverse microemulsions.

In a typical synthesis, 4 g of cetyltrimethylammonium bromide (CTAB), 8 mL of *n*-hexanol, and 45 mL of *n*-heptane were mixed under magnetic stirring, and 300 μL of $TiCl_4$ was dissolved in 700 μL of 4.8 M hydrochloric acid solution, making up the aqueous phase. Then, the aqueous phase was added dropwise to the oil phase, forming the clear microemulsion. The microemulsion was transferred into a 100-mL flask which was kept at 85 °C for 6 h, and then cooled to room temperature on standing. The precipitate was filtered and washed several times with distilled water and absolute ethanol, and finally dried in a vacuum oven at 40 °C for 12 h. The experiments were repeated under the same condition, while the mass of CTAB grew into 2.5, 1.5, and 1.0 g, respectively. The composition of the as-synthesized product was determined from the X-ray diffraction pattern (Figure 1). All the reflections can be readily indexed to rutile, no other phases of TiO_2, such as anatase or brookite, could be detected via XRD.

The morphology and the microstructure of the rutile nanocrystals were investigated by TEM (H-800). Figure 2 shows the TEM images and their corresponding SAED patterns of the obtained samples prepared in reverse microemulsions with various mass of CTAB at 85 °C (we scanned the negative directly in order to improve the contrast). Thermal hydrolysis of $TiCl_4$ in microemulsion with 1.0 g of CTAB produced some nanoclusters with diameter about 600 nm (Figures 2a and 2b). By increasing the concentration of CTAB, we found the rodlike crystals with a diameter of 100 nm and a length of 500 nm (Figures 2c and 2d) and the corncob-like nanostructural rutile about 100 nm in width and 300–400 nm in length on which some irregular nanoparticles grew (Figures 2e and 2f). When the mass of CTAB became 4.0 g, the morphology of product turned into flower with a diameter of 500 nm (Figures 2g and 2h). The corresponding SAED patterns are given in Figures 2b, 2d, 2f, and 2h, respectively. It can be observed that only the rodlike rutile is single crystalline which grows along the [001] axis.

Figure 3 shows a high-resolution transmission electron microscope (HR-TEM) image of the rutile nanorod (JEOL-2010). The surface observed in the image corresponds to the rod as indicated in an image at a low magnification (inset of Figure 3). 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), which is $d_{110} = 3.25$ Å. The rods have therefore grown along the [001] axis that is perpendicular to the [110] axis, which is consistent with the SAED pattern of the rod (inset of Figure 2d). Meanwhile, the adjacent lattice fringes can also be assigned to the (101) which is $d_{101} = 2.49$ Å.

In order to get more detailed microstructure of the surface,

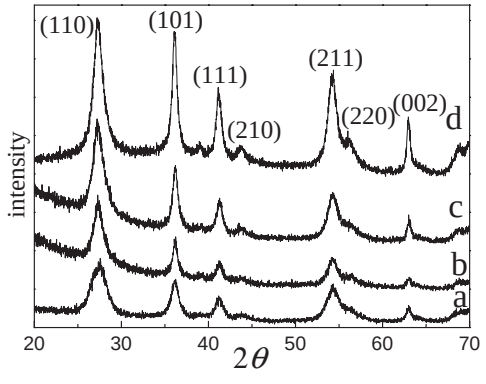

Figure 1. XRD patterns of TiO_2 nanocrystals prepared in reverse microemulsions with various mass of CTAB at 85 °C. (a) 1.0 g, (b) 1.5 g, (c) 2.5 g, and (d) 4.0 g.

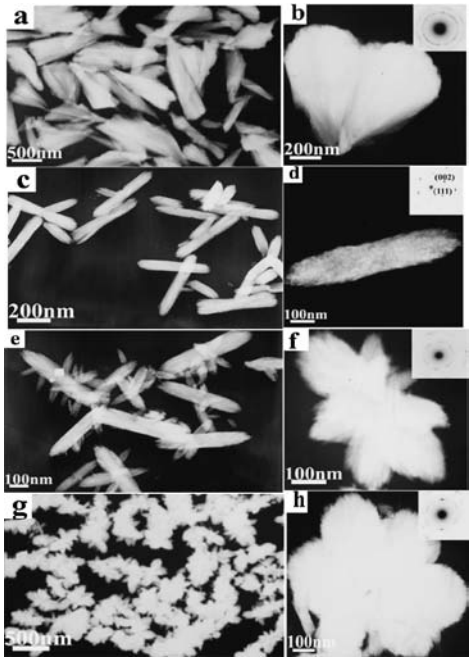

Figure 2. TEM images of TiO_2 synthesized in reverse microemulsions with various masses of CTAB at 85 °C (inset is its corresponding SAED pattern). (a, b) 1.0 g, (c, d) 1.5 g, (e, f) 2.5 g, and (g, h) 4.0 g.

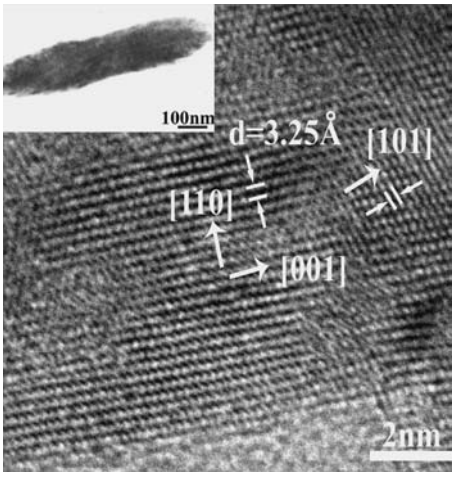

Figure 3. HR-TEM image of one of the TiO_2 nanorods prepared in reverse microemulsion with 1.5 g of CTAB at 85 °C.

as-synthesized products were analyzed using field emission scanning electron microscopy (FE-SEM) (JEOL-6700F). The FE-SEM images of the samples that were prepared in micro emulsions with various masses of CTAB at 85 °C are obtained (Figure 4). We could observe the variation of the morphologies of the samples clearly, which is in accordance with the TEM images (Figure 2).

In microemulsion solutions, surfactant molecules tend to self-assemble to form aggregates. With the difference of the ways that surfactant molecules aggregate, the various micelles will form. Usually, the spherical droplets will form in reverse microemulsion, but the shape of micelles in microemulsion will turn from sphere to cylinder if the concentration of surfactact is very high. If the concentration of surfactant continues to increase, the redundant surfactant will assemble on the surface of micelles, which will lead to the formation of corncob-like and flowerlike nanoparticles.

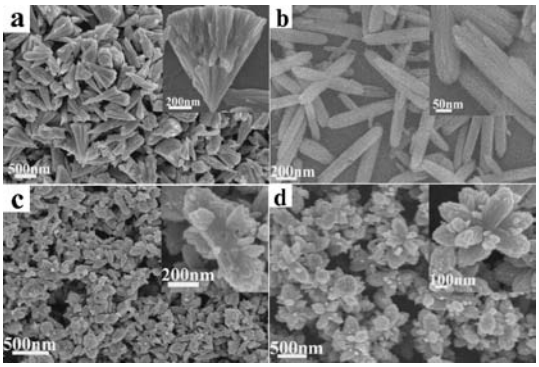

Figure 4. FE-SEM images of TiO_2 synthesized in reverse microemulsions with various masses of CTAB at 85 °C. (a) 1.0 g, (b) 1.5 g, (c) 2.5 g, and (d) 4.0 g.

We have demonstrated a novel method to prepare the rutile nanocrystallites with suprastructure in reverse microemulsions at 85 °C. By changing the concentration of surfactant in reverse microemulsions, the different micelles formed. It provides a convenient route to synthesize some special nanostructures in microemulsions, even in a predictable manner.

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