A Simple Route for the Synthesis of Rutile TiO_2 Nanorods

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(Received March 25, 2003; CL-030257)

The monodispersed rutile TiO_2 nanorods in diameter 4–6 nm and in length up to 50–150 nm were prepared by the hydrolysis of $TiCl_4$ solution in the concerntrated HNO_3 under ambient condition in air and required no complex apparatus.

One-dimensional nanoscale building blocks, such as nanotubes,[1,2] nanowires,[3] nanobelts,[4] and nanorods,[5,6] have attracted intensive interest because of their unique optical, magnetic and electronic properties. TiO_2 is an n-type semiconductor and typical photocatalyst for environmental purification.[7] Three main crystallography forms exist in the TiO_2 material including anatase, rutile, and brookite. Rutile TiO_2 material has very important applications in the fields of solar cell,[8] gas sensing,[9] and catalysis[9,10] owing to its higher dielectric constant, refractive index, ultraviolet ray absorption rate. However, synthesis of nanosize rutile TiO_2 powder is much challengeable because the traditional methods, either annealing anatase powder at elevated temperature or directly flame oxidizing of the $TiCl_4$, inevitably result in large particles. So far, many groups have carried out significant works to explore novel methods for preparation of rutile TiO_2 with controllable nanoscale size and morphology as well as related properties.[11–16] Recently, Li et al. reported that the crystallization of rutile TiO_2 is accelerated by the use of small amounts of nano rutile TiO_2 as crystal seed,[14] but the yield of product decreases dramatically when the concentration of $TiCl_4$ solution is above 0.28 M and the anatase TiO_2 is formed no mater whether there is crystal seed or not when increasing the reaction temperature. Pedraza et al. used $TiCl_3$ as titanium source and directly oxidized it at room temperature to prepare rutile TiO_2,[15] but the anatase TiO_2 also exists in the products. Cheng et al. found that the mineralizer $SnCl_4$ and NaCl reduce markedly the grain size and favor the formation of rutile TiO_2,[11] but as the concentration is increased to 1.4 M, rod-like rutile TiO_2 grains agglomerated orientationally to form a broom-like aggregate. Furthermore, the mineralizer maybe exists in the products as contaminant and affects the properties. Zaban et al. directly synthesized pure rutile TiO_2 without mineralizer by hydrothermal synthesis and found that stirring will influence the colloid size contribution and the formation of anatase structure.[16] Here, we report a novel and simple one-step wet chemical route without mineralizer and surfactant for preparation of well-dispersed uniform rutile TiO_2 nanorods. In addition, the process is carried out under ambient condition in air and required no complex apparatus.

The procedure employed here is described as following. Titanium tetrachloride (98%, $TiCl_4$, Shanghai Chemical Agent Co.) was used as a starting material without further purification. The appropriate amount of $TiCl_4$ was dissolved in distilled water within an ice-water bath to get the 3 M $TiCl_4$ solution. In a typical experiment, a 35 mL aliquot of concentrated nitric acid (15 M, HNO_3) was refluxed in a silicone oil bath maintained at desired temperature (range from 100 °C to 250 °C), and then 20 mL 3 M titanium tetrachloride solution was rapidly injected into vigorously stirred nitric acid solution. After several hours' reaction (6, 12, and 24 h were selected), the final products were filtered out, washed with distilled water and ethanol in subsequence, and later dried at 100 °C for 12 h.

The morphologies of the samples were observed through TEM (JEM200CX) with an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) images were taken on TEM (JEM-2010) with EDX attachment. The products were characterised by using X-ray powder diffraction (XRD, D/max 2550V) with Cu Kα radiation ($\lambda = 0.15406$ nm).

Figure 1 is the TEM images of as-prepared samples showing large quantity of rod materials with narrow size distribution. The diameters of the rods are ca. 4–6 nm and lengths range from 50 nm to 150 nm. The rods are close to monodispersed with an aspect ratio of 10 (±5%) (Figures 1a–1d) and their sizes appear to be independent of temperature (Figures 1a and 1c). We also prolonged the reaction time to 24 h and shortened to 6 h, but found that the products' morphology and size have little change (Figures 1b and 1d). Spherical particles are seldom found in our sample. The X-ray diffraction (XRD) pattern of the rod materials can be indexed to rutile TiO_2 with strong (110), (211) and (101) refractions according to JCPDS 21-1276 (Figure 2). The (110) peak is obviously broadened compared with other characteristic diffraction peaks, which denote the products grow anisotrophically. The average grain size is 8 nm determined from the broadening of the (110) peak by the Scherrer formula: $L = 0.89\lambda/\beta\cos\theta$, which is close to the diameter of nanorods. Increasing the reaction temperature promotes the crystallization of TiO_2 as indicated by the sharpness of (110) peak. No characteristic peak of anatase phase was observed in all samples, even

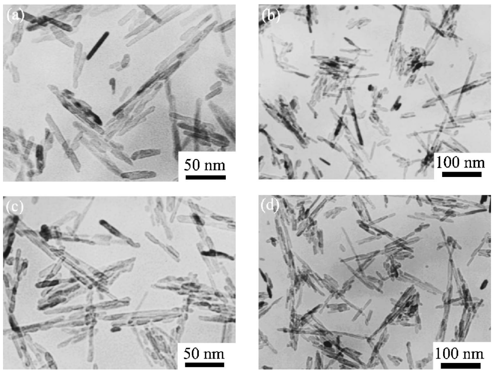

Figure 1. TEM micrographs of the TiO_2 nanorods prepared at different temperature and time: (a) 110 °C for 12 h, (b) 140 °C for 12 h, (c) 240 °C for 12 h, and (d) 140 °C for 6 h.

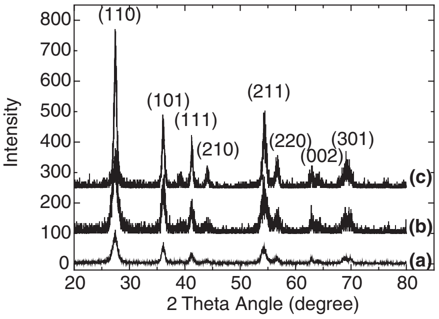

Figure 2. XRD pattern of TiO_2 nanorods, (a) 110 °C for 12 h (b) 240 °C for 12 h, and (c) annealing at 500 °C of sample (a).

in the sample annealed at 500 °C for 2 h, indicating that the reaction produces the rutile TiO_2 without anatase and amorphous TiO_2.

The high resolution TEM image of single TiO_2 nanorod (Figure 3) corroborates the XRD results. The fringe spacing paralleling to the nanorod is estimated to be 0.32 nm, which is close to the (110) lattice spacing of rutile TiO_2, indicating that the crystal growth is preferential in the [110] direction. The inset SAD pattern, taken from the correspondent nanorod, is consistent with the crystalline nature of rutile TiO_2.

The synthesis process employing simply concentrated nitric acid and highly concentrated titanium tetrachloride solutions as the reactants was not reported before. The exact reaction mechanism is hard to elucidate because of lacking information on the essential solute complexation at elevated temperature. When 3 M $TiCl_4$ solution was abruptly injected into hot HNO_3 solution, oxolation of the Ti (IV) complex ion $[TiO(OH_2)_5]^{2+}$ occurrs and leads to linear growth along the equatorial plane of the cation, which results in the rutile TiO_2 formation.[17,18] Although some groups have observed the needle-like or rod-like rutile TiO_2,[11,14] these products tend to agglomerate and form broom-like cluster. The crystal growth mechanism of rutile TiO_2 nanorods is hardly clarified yet. From our previous work on the preparation of TiO_2 powder,[13,19] combined with the XRD, TEM, HRTEM results, we deem that the selective adsorption of anions on the (110) surface of rutile TiO_2 plays an important role in controlling the crystal growth direction. According to the acid–base surface properties of metal oxides, by decreasing the pH of solution from the point of zero charge (PZC) and increasing ionic strength the surface charge density increases by adsorption of protons and consequently gives rise to the reduction of the interfacial tension of the system.[20] Thus the nucleation of rutile TiO_2 is promoted thermodynamically and kinetically through enhanced corner-shared bonding of $[TiO(OH_2)_5]^{2+}$ nuclei in the excess acid solution and the ripening processes are considerably lowered,[20] which account for the as-prepared superfine rutile TiO_2 (the diameter is about 4–6 nm). Moreover, high surface charge density may obstruct the agglomeration of as-prepared nanorods through electrostatic repulsion and well disperse it. Since the TiO_2 (110) surface possesses the lowest energy[21] and has abundant five-fold coordinated Ti^{4+} atoms, two-fold coordinated O^{2-} atoms and oxygen vacancies, it may be the favorite source of the selective adsorption of the chloride ion and nitric ion, which form the ‘screening layer’ and resist the further oxolation of $[TiO(OH_2)_5]^{2+}$ complex on the (110) surface. On the contrary, the two cusps of rod consist of other higher surface energy crystal surface (such as (111)) and can adsorb more $[TiO(OH_2)_5]^{2+}$ complex to decrease the surface energy. Thus, the crystal grows anisotropically along the (110) surface and form rod-like morphology.

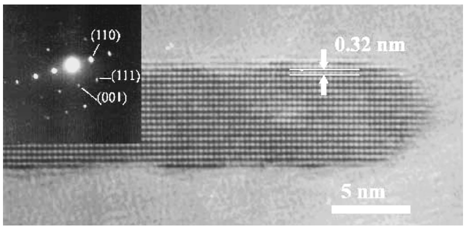

Figure 3. High-resolution TEM image of TiO_2 nanorod. Inset shows the corresponding selected area electron diffraction pattern (SAD).

The whole process, with a product yield repeatedly about 98% (based on Ti, and neglected the loss during the wash process), may be hopeful adjusted to prepare rutile TiO_2 nanorod materials on a large scale. As the diameter of the as-prepared rutile nanorods is less than 10 nm (ca. 4–6 nm), it has potential applications for the quantum size effect. Also, this simple method may be extended to other transition metal oxide, such as Fe_2O_3, ZrO_2, and V_2O_5, etc.

We acknowledge Meiling Ruan and Jing wei Feng for their guidance and help with the TEM work.

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Published on the web (Advance View) June 24, 2003; DOI 10.1246/cl.2003.638