Low-temperature Synthesis of Crystalline TiO_2 Nanorods: Mass Production Assisted by Surfactant

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Crystalline and dispersed rutile TiO_2 nanorods with diameters of ≈6–8 nm and lengths of 40–100 nm were synthesized via a low-temperature solution process in the presence of nonionic surfactant P123.

The design and synthesis of one-dimensional (1D) nanostructural inorganic materials (nanorods, nanowires, nanotubes, nanobelts, and nanoribbons) have recently attracted considerable attention because of their potential applications in electronics, optoelectronics, catalysis, biomedicine, and others. TiO_2, a functionally important material, mainly has three crystal phases: anatase, rutile and brookite. Owing to its advantages, such as high chemical stability, high refractive index and cheap production cost, rutile TiO_2 has attracted more and more attention in the extension of its application scope very recently.[1,2] However, the synthesis of nanostructured rutile TiO_2 is more challenging than that of anatase. Conventionally, rutile TiO_2 is prepared through annealing anatase powders at elevated temperature or directly flame oxidizing of $TiCl_4$, which can inevitably cause the increase of grains. Direct synthesis of nanostructured rutile via a wet chemistry route has attracted much attention recently.[3–7] During these preparative processes, rutile TiO_2 favors to form the morphology of broom-like aggregates or spherical aggregations with needle-like surfaces, and mineralizer such as $SnCl_4$, or NaCl is added to tune the morphology of nanosized rutile TiO_2. The mineralizer, however, can exist in the products as impurity and damage the further application of the products.[8] Our previous work presented the preparation of free-standing rutile nanorods in the absence of mineralizer at a relatively high temperature (110–250 °C).[9] Synthesis of rutile nanorods in the absence of mineralizer at a low temperature (<80 °C) has seldom been reported so far.[10,11] Therefore, new strategies should be desirable for the synthesis of dispersed rutile nanorods via a facile wet chemical route. Herein, we have developed a low-temperature process for the synthesis of dispersed and crystalline rutile nanorod in the presence of triblock copolymer Pluronic P123. This preparative process has the characteristic of facility, generality, low cost, and mass production for the preparation of thin nanorods.

The typical preparation procedure was as follows: 2.0 g of triblock copolymer, $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, BASF) was added to a mixture of 15.0 g of water and 120.0 g of 2 M HCl aqueous solution with stirring at 40 °C overnight. Then, 6.95 g of tetrabutyl titanate was added to this solution, followed by further stirring for 2 h. The transparent solution was transferred into a Teflon-lined stainless steel autoclave and kept at 75 °C for 5 days under static conditions. For comparison, the experiment with the absence of surfactant of P123 was also carried out. The products were filtered, carefully washed with ethanol repeatedly, and finally dried in a vacuum oven at 60 °C overnight. The products were characterized with transmission electron microscopy, selected area electron diffraction (TEM/HRTEM/SAED, JEOL-2100F), powder X-Ray diffraction (XRD, D/max 2550V, Cu Kα radiation), and nitrogen adsorption analysis (Micromeritics ASAP 2010).

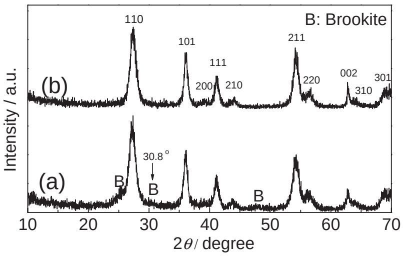

Figure 1. XRD patterns of the products derived from (a) the absence of P123, capital B designates brookite phase; (b) the presence of P123.

Figure 1 shows the XRD patterns of the products derived from the absence and presence of the surfactant of P123. It can be seen that there exists a small amount of brookite phase in the product without the surfactant of P123. The weight fraction of brookite in the product, 2.5%, is estimated from the formula $\chi = (1 + I_R/2.721 I_B)^{-1}$,[12] where χ is the weight fraction of brookite in the powder, and I_B and I_R are the respective peak intensities of the brookite (121) and rutile (110) peaks. The product derived in the presence of P123 can be exclusively indexed as rutile phase of TiO_2 (S. G.: $P4_2/mnm$; $a_0 = b_0 = 4.593$ Å, $c_0 = 2.959$ Å; JCPDS No. 21-1276). The diffraction peaks of the two products are broadened, which shows the small crystallite size according to the Scherrer formula.

Figure 2 depicts the morphological and structural characteristic of the product derived from the present preparative method through TEM, HRTEM, and SAED techniques. Figure 2a reveals the low-magnification TEM image of the product, and a large amount of nanorods could be seen clearly. Estimated by the TEM observation, the yield of rodlike morphology is above 80%. The diameters of the nanorods are ≈6–8 nm, and the lengths of them are 40–100 nm. Because of the small diameters of the nanorods, it is impossible to take the SAED pattern of an individual nanorod in the present product. Figure 2b shows the SAED pattern taken from an area containing several nanorods, whose diffraction rings from inside to outside can be clearly indexed as (110), (101), (111), (210), (211), (220), (002), and (301) planes of rutile TiO_2 as the XRD pattern (Figure 1b) has confirmed, revealing the crystalline nature of the gained nanorods. The edges of the nanorod are not smoothly straight and

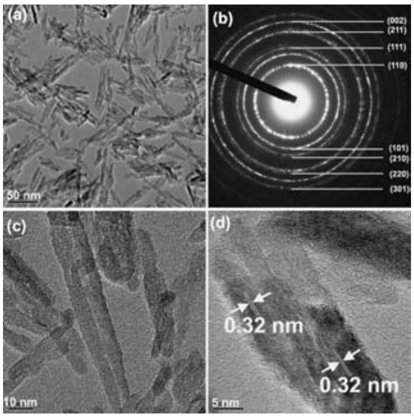

Figure 2. (a) Low-magnification TEM image of TiO_2 nanorods, an overview of the large-scale nanorods; (b) SAED pattern taken from a domain containing several nanorods; (c) High-magnification TEM image of the nanorods; (d) HRTEM image of the coplanar aggregation of two individual nanorods.

the diameter of the nanorod is not constant throughout its length, as can be seen from Figure 2c. More interestingly, the oriented aggregation between the nanorods in a coplanar fashion occurs in the present preparative method as shown in the HRTEM image of Figure 2d. The fringe spacing is $\approx$0.32 nm, which corresponds to the lattice spacing for the (110) faces. Low contrast between crystalline regions of two nanorods indicates that space separates the two nanorods, while the parallelism of lattice fringes demonstrates that the crystallographic axes of the two nanorods are parallel. This phenomenon has also been observed in the preparation of ZnO nanorod with small diameters via a solution-based method.[13] N_2 adsorption/desorption analysis also shows that the synthesized single-crystalline rutile nanorods have a relatively high specific surface area, 118.4 m^2/g.

The surfactant P123 plays an important role in the formation of the dispersed rutile nanorods at a low temperature. Spherical aggregations of needle-like surfaces with the mixed phases of rutile and brookite were gained when the surfactant P123 is absent (Figure 3). High-magnification TEM image (Figure 3b) shows that the needle-like surface is of rod-like morphology with the diameter of $\approx$7 nm. In fact, the $\{110\}$ planes are the most stable low-index crystal plane for rutile, and the rutile TiO_2 favors to form elongated nanocrystals along the crystallographic c axis and enclosed by the stable $\{110\}$ planes.[14] It is apparent that c axis-elongated anisotropic rutile TiO_2 nanocrystals are favored to generate even though the surfactant P123 is absent, whereas dispersed nanorods can fail to be gained because of the presence of heavy aggregation. The absorption of nonionic surfactant P123 on the surfaces of TiO_2 nanocrystallites can change the surface energies of some specific planes, which may influence the final morphology of nanocrystals. More importantly, the steric effect of the surfactant capsule[15] plays the role of interstitial filler to avoid the aggregation of nanorods, which makes the final morphology of the nanorods dispersed rather than agglomerated.

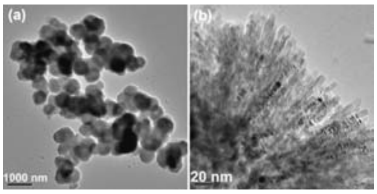

Figure 3. (a) Low-magnification TEM image of the product derived from the absence of P123; (b) High-magnification TEM image of the brim of an aggregation of the product.

The presence of surfactant P123 may have an effect on the stabilization of the rutile phase in the solution condition at low temperature (Figure 1). To the best of our knowledge, the rutile–brookite phase transformation in solution condition has not been reported. Recent research results demonstrate that the stability of phase of nanocrystallites is related to their surface energy.[16] The adsorption of surfactant on the surfaces of the nanocrystals can alter the surface energy, which may be the reason that the presence of surfactant favors the stabilization of rutile phase nanorods. The effect of the presence of surfactant on the phase transformation of nanocrystalline TiO_2 in solution condition at low temperature is currently in progress in our laboratory.

In summary, crystalline rutile nanorods have been synthesized at a low temperature via a wet chemical method. Dispersed rutile nanorods with the diameters of $\approx$6–8 nm, and lengths of 40–100 nm are formed in the presence of surfactant P123. The nonionic surfactant P123 plays an important role in the present method. It not only favors the formation of the dispersed nanorods, but also favors the formation of phase-pure rutile nanorods at a low temperature. This facile and low-cost preparative method promises to pave the way for the diversely important applications of rutile TiO_2 in various fields of nanotechnology.

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