Controllable Synthesis of One-dimensional Single-crystalline TiO_2 Nanostructures

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One-dimensional (1-D) TiO_2 nanostructures (nanoribbons, nanorods, nanotubes) were obtained by a simple solvothermal process in the presence of organic solvents in which the resulting products were basically single crystals. Morphologies of single crystalline TiO_2 were successfully controlled through the optimization of various solvents.

Controlling the shape and dimension of nanostructures during their preparation has become a new and interesting research area. In fact it has been demonstrated that physical and chemical properties are strongly related to the shape and dimension of the nanostructures. Moreover, the architectural control of nanosized materials with well-defined crystal shape is important for the success of "bottom-up" approaches toward future nanodevice.[1,2] Over the past decade, 1-D nanostructured materials such as nanowires, nanotubes, nanorods, and nanobelts have particularly attracted extensive attention because of their potential use as active components or interconnects in constructing nanoscale electronic, optical, optoelectronic, and electrochemical devices.[3,4] Generally, 1-D nanostructures have been fabricated by template-directed growth methods, the vapor–liquid–solid (VLS) mechanism, and solution approaches. Recently, a solvothermal process has been developed for the synthesis of various nanostructures at relatively low temperature and in soft experimental conditions. Chalcogenides, SiC, and $CdWO_4$ nanorods and nanowires, InAs nanofibers, and carbon nanotubes have all been synthesized solvothermally.[5–9]

TiO_2 has many potential applications in photocatalysis,[10] solar energy conversion,[11] and gas sensors.[12] 1-D TiO_2 nanostructures have been synthesized by chemical vapor deposition (CVD), thermal evaporation and high-temperature vapor transport process. All these methods need either high temperatures or special equipment. To explore novel approaches for the nanostructured TiO_2 of various natures by controlling their nanoscale size and morphology is of great interest for both theoretical and practical research. Though a facile solution-phase synthesis for 1-D TiO_2 nanostructures has recently been reported,[13–16] the synthesis of single-crystal TiO_2 with well-defined structures and controllable morphology is still a challenge. In the present work, we have synthesized a series of single crystalline TiO_2 with 1-D nanostructures (nanoribbons, nanorods, nanotubes) by a simple, economical solvothermal process. Morphologies of 1-D single crystalline TiO_2 are successfully controlled only through varying solvents without the use of the membrane and templates.

A certain amount of commercial Degussa P25 powders was added into the mixed solvents of NaOH aqueous solution of 10 M and an organic reagent (ethanol, diethanolamine, and glycerol), the volume ratio of NaOH aqueous solution to organic reagent was 1:1. Then 20 mL of the mixed solution was transferred into a Teflon-lined stainless steel autoclave. The autoclave was maintained at 170–200 °C under autogeneous pressure for 12–24 h and then cooled to room temperature naturally. The resulting products were collected and washed with dilute HCl aqueous solution of 0.1 M and deionized water for several times until the pH value of the washing solution was about 7, and dried at 60 °C for 12 h in air.

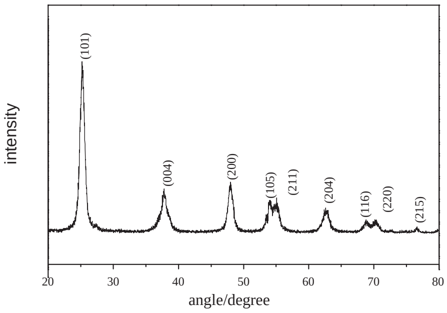

Figure 1. XRD pattern of titania nanoribbons when ethanol was used.

X-ray powder diffraction (XRD) analysis was used to determine the phases of the products. Figure 1 shows XRD pattern from final products prepared when ethanol is used. All of the peaks of the XRD pattern can be readily indexed to the pure anatase TiO_2 according to the XRD standard spectrum of anatase-type TiO_2 crystal. No characteristic peaks of other impurities were observed, which indicated that the product had high purity.

Figure 2 shows low-magnification TEM images of as-synthesized nanostructures. Solvents greatly influence the morphology of the finial products. When ethanol was used, we obtained the ribbon-like structures with lengths of up to a few millimeters and the width ranging from 20 to 100 nm (Figure 2a). The nanoribbons with a layered end consist of very thin flake with less a few nanometers (Figure 2b). When diethanolamine was used instead of ethanol, we synthesized ultralong TiO_2 nanorods with diameters of 50–100 nm and lengths ranging from several micrometers to several tens of micrometers (Figure 2c). Figure 2d shows an individual nanorod with a round end. The geometry of the nanorod is very uniform. We obtained TiO_2 nanotubes when glycerol replaced ethanol. As shown in Figure 2e, the tubules are flexible and open. The outer diameters are about 10–20 nm while the inner diameters are round 5–8 nm for most of the nanotubes. The single-crystalline structural details of the synthesized nanostructures were revealed by HRTEM and the corresponding electron diffraction patterns.

Figure 3 shows HRTEM images and the electron diffraction (ED) spots of the TiO_2 nanostructures in Figures 2a, 2c, and 2e, respectively. Figures 3a and 3b indicate that the synthesized nanoribbons and nanorods are structurally uniform with an interplanar spacing of about 0.35 nm, which corresponds to the dis-

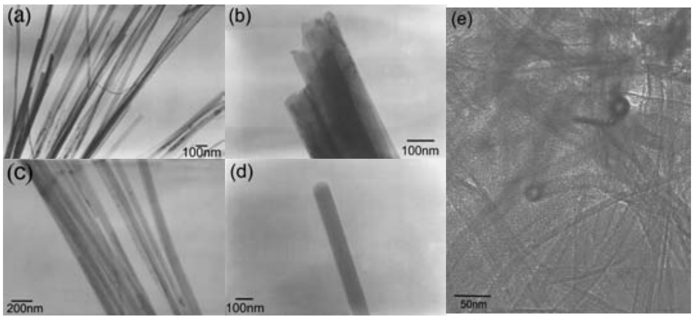

Figure 2. Low-magnification TEM images of as-synthesized titania nanostructures. (a), (b), nanoribbons, (c), (d), nanorods, and (e) nanotubes.

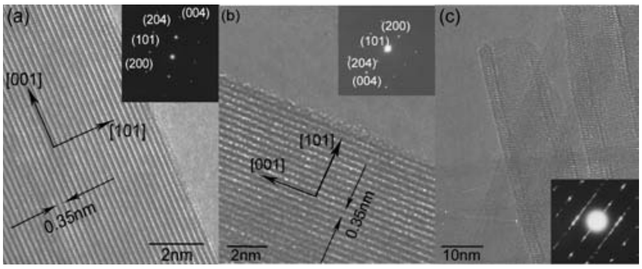

Figure 3. High-magnification TEM and ED images of as-synthesized titania nanostructures. (a) nanoribbons, (b) nanorods, and (c) nanotubes.

tance between two (101) planes of anatase phase TiO_2. The electron diffraction patterns taken from the [010] zone axis reveals the single-crystalline nature of the products with a preferential growth direction along the [001] direction. Figure 3c shows that the synthesized nanotube is a layer structure similar to a carbon nanotube and usually three to six layers in the wall thickness. The layer numbers on either side are not always equal, indicating that they are likely to be scrolls. The interlayer spacing in the tube walls is about 0.35 nm, which corresponds to the (101) planes of the anatase phase.[17] It is expected that a flat plane of (101) rolls into a cylindrical tubule. This agrees well with the experimental results. The electron diffraction pattern shows its single-crystal nature.

Regarding the growth process, it is believed that the solvent is of a very important role. The "solid-solution–solid transformation"[18,19] may be employed to elucidate the growth mechanism of TiO_2 nanostructures in the present study. We could suppose that the raw materials reacted with NaOH to produce a thin titanate nanosheets intermediate in the initial stage.[20,21] With the process of reaction, more nanosheets would be formed with the growth. This titanate nanosheets intermediate was not stable in the present reaction conditions, and had a tendency to decompose into resulting products. The presence of the ethanol, diethanolamine, and glycerol with a high concentration caused the properties of solvents, such as dielectric constant to change, which might greatly influence the morphologies and the crystallization behavior of the finial products. The more detailed and exact formation mechanism currently is not very clear and need to further research.

In summary, we have synthesized a series of single crystalline TiO_2 nanostructures of various morphologies by a simple solvothermal process. Morphologies of TiO_2 nanostructures could be controlled by the optimization of various solvents. This simple approach could be expected to use in the synthesis of nanostructures of other metal oxides.

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