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Short communication

Solvothermal synthesis of TiO_2: anatase nanocrystals and rutile nanofibres from $TiCl_4$ in acetone

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This work reports a new synthetic approach for single-phase TiO_2 nanomaterials by solvothermal treatment of titanium tetrachloride in acetone at 80–110 °C. Small, uniform, and yet size-tunable (5–10 nm) anatase titania nanocrystallites were obtained using a low concentration of $TiCl_4$ in acetone (i.e., at molar ratios of $TiCl_4$/acetone $\leq 1:15$) in the temperature range of 80–110 °C, while rutile nanofibers were synthesized using a high concentration of $TiCl_4$ (e.g., $TiCl_4$/acetone $= 1:10$) at 110 °C. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: single-phase titania; nanomaterials; titania nanofibre; nonaqueous synthesis; acetone

INTRODUCTION

Owing to the importance in many key technologies of titania-based nanomaterials, synthesis of highly crystalline titania nanoparticles with controlled crystal structure, morphology and size has been a very active field in materials chemistry.[1–4] The important discovery of Colvin *et al.*[5] that small anatase nanocrystallites of 3.8–9.2 nm can be prepared by the reaction of titanium halides with titanium alkoxides in a nonaqueous solvent (e.g. heptadecane) in the presence of an additive (e.g. trioctylphosphine, TOPO) has been stimulating increasing interest on nonaqueous approaches to the control of crystal phase, morphology, and size distribution of titania nanoparticles.[6–8] By reacting $TiCl_4$ with various alcohol homologs in solvothermal systems with or without addition of acetic acid, Li *et al.* were successful in generating TiO_2 nanocrystals of different crystal phases (rutile and anatse) and morphologies (spherical, fiber-like and rod-like).[6,7] However, it is unknown whether it is possible to manipulate the crystal phase and morphologies of TiO_2 nanocrystals using a single alcohol source. Very recently, Niederberger *et al.*[8] found that the reactions between titanium tetraisopropoxides and ketones (including acetone) or aldehydes at 130 °C can result in the formation of anatase nanocrystals with relatively large sizes (ca. 15 nm), which extended the nonaqueous approaches mentioned above to non-alcohol/non-ether oxygen-containing organic solutions. The use of ketones or aldehydes as the organic reagents is a significant advance since it enabled the formation of anatase nanocrystals without the aid of any additive as shape-controlling reagent.[7] In this communication, we disclose that the reaction of $TiCl_4$ with acetone at fairly low temperature (80–110 °C) can lead to anatase TiO_2 nanocrystals with small, uniform, and yet tunable sizes between 5 and 10 nm. We show that the reaction system can be easily manipulated to produce needle-like rutile TiO_2 fibers of ca.10 nm width simply by tuning the $TiCl_4$–acetone molar ratio for the synthesis. The method can be easily scaled up for large-scale production of the TiO_2 nanomaterials. To the best of our knowledge, such a feasibility in the manipulation of TiO_2 nanomaterials in such a simple synthesis system was not documented in the open literature. In view of economics, titanium halides are much cheaper than their alkoxides, which makes the present findings more attractive in producing advanced TiO_2 nanomaterials with controllable crystal phase, size and morphology.

EXPERIMENTAL

The procedure for the synthesis of titania nanomaterials is as follows. Typically, a certain volume of $TiCl_4$ (3.0, 6.0 or

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9.0 ml) was quickly dripped into a fixed volume of acetone (60 ml) under vigorous stirring at room temperature. The obtained solution was transferred to and sealed in a Teflon-lined autoclave (ca 100 ml), and the autoclave was then put in an oven for solvothermal treatment at 80 or 110 °C for 12 h. After cooling the autoclave in cold water, the dark red pasty precipitates formed in the autoclave were separated by filtration. Repeated washing of the precipitates with excessive acetone gave dry and loose powder samples, which were used for different characterizations.

RESULTS AND DISCUSSION

One important advantage of the nonaqueous synthesis is the direct formation of titania nanocrystals in the solution, which enables better control of the morphology and size distribution of the nanocrystals.[5–8] The conventional aqueous sol–gel syntheses first produce amorphous precipitates and the nanocrystal formation in the later thermal processing can often induce significant sintering of the nanocrystals. In this work, the reaction of $TiCl_4$ with acetone at 110 °C produced TiO_2 nanocrystals directly, as shown by the powder X-ray diffraction (XRD) patterns of the products (Fig. 1). The crystallites obtained with low concentration of $TiCl_4$, i.e. at molar $TiCl_4$/acetone ratios no higher than 1 : 15, are of an anatase phase. In contrast, a rutile TiO_2 sample was produced in the synthesis with a higher $TiCl_4$ concentration (e.g. $TiCl_4$/acetone = 1 : 10). The anatase or rutile crystallites were also confirmed by the Raman spectra (not shown here). A slight blue shift and broadening was observed for the E_g mode (at 153 cm^{-1}) in the Raman spectra of the anatase samples. The blue shift may be due to a phonon confinement effect and strain applied by carbon residues at the sample surfaces.[9] Thus, these data present a new approach to manipulating the crystal phase of TiO_2 at low temperature (110 °C) simply by changing the concentration of $TiCl_4$ in acetone. We calculated the average crystallite sizes of the samples by using the well-known Debye–Scherrer equation for the diffractions from the anatase (101) and rutile (110) planes, respectively, and found (Table 1) that the averaged crystallite size increases with increasing the concentration of $TiCl_4$ in acetone; e.g. the averaged size of the anatase crystallites was 6.2 nm at $TiCl_4$/acetone = 1 : 30 while it became 8.6 nm at $TiCl_4$/acetone = 1 : 15, demonstrating that the product crystallite sizes can be finely tuned by changing the concentration of $TiCl_4$. In addition, by changing the molar ratio of $TiCl_4$/acetone, the crystallite sizes of anatase nanoparticles can also be tuned with the solvothermal temperature (Table 1). When the solvothermal temperature decreases from 110 to 80 °C, the obtained crystallite sizes decrease from 6.2 to 5.6 nm at $TiCl_4$/acetone = 1 : 30. However, no solid products were detected at 80 °C with $TiCl_4$/acetone = 1 : 10. It is also noteworthy that the anatase crystallites formed in the present acetone–$TiCl_4$ system (<9 nm) are significantly smaller than those obtained in the acetone–titanium tetraisopropoxide system (ca. 15 nm) disclosed by Niederberger *et al.*[8] The yield

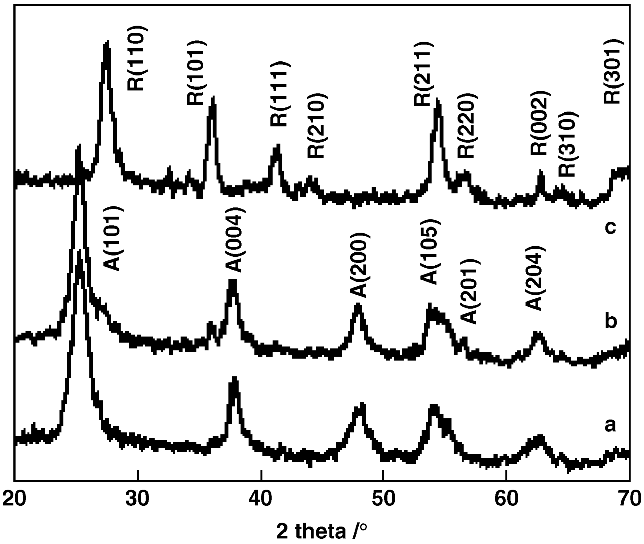

Figure 1. XRD patterns of TiO_2 prepared at 110 °C with different $TiCl_4$/acetone ratios of: (a) 1 : 30 (anatase, 6.2 nm); (b) 1 : 15 (anatase, 8.6 nm); and (c) 1 : 10 (rutile, 9.9 nm).

Table 1. Features and results of investigated systems

$TiCl_4$–acetone	Reaction temperature (°C)	Yield (%)	Crystal structure	Size[a] (nm)	Oxide content[b] (%)	Surface area[c] (m^2/g)
1 : 30	110	92	Anatase	6.2	87.0	174
1 : 15	110	85	Anatase	8.6	88.5	84
1 : 10	110	53	Rutile	9.9	90.0	6
1 : 30	80	90	Anatase	5.6	—	—
1 : 10	80	ND[d]	—	—	—	—

[a] Calculated from the (101) planes of anatase and (110) planes of rutile using the Debye–Scherrer equation; [b] obtained from TG measurements of the samples; [c] measured by nitrogen physisorption using the BET method. [d] No solid product detected.

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of TiO_2 based on titanium tetrachloride used was good for the production of the anatase crystallites (85–100%), but it was as low as 53% for the rutile ones. The low yield for the rutile product might mean that a part of the product is difficult to separate from the reaction media.[7] The contents of residual organics in the samples were evaluated by temperature-programmed oxidation study in flowing air in the thermogravimetric analysis (TGA) mode (not shown here). The measured contents were in the range 10–15%, which is close to the samples reported in Garnweitner *et al.*[8]

The sample powders were characterized with transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) to gain information on the morphology and size distribution of the crystallites. The TEM images showed that the anatase samples appeared as irregular particles with uniform sizes that are comparable to their crystallite sizes in Table 1. A representative TEM image for the anatase sample obtained at the reactant ratio $TiCl_4$/acetone = 1 : 30 is shown as Fig. 2(a); the particles were seen quite uniform and their measured particle sizes were in the range of 4.5–7.0 nm, consistent with the crystallite size (6.2 nm) based on the XRD measurement of the same sample. On the other hand, the TEM images of the rutile sample produced at the reactant ratio $TiCl_4$/acetone = 1 : 10 [Fig. 2(b)] suggest that this sample was composed of bundles of needle-like fibers at sizes of ca. 10 nm × 1 μm, which were probably formed by epitaxial crystal growth. HRTEM images show that the obtained TiO_2 nanoparticles are highly crystallized. Therefore, it is clear that the change of $TiCl_4$ concentration in acetone in the present work is feasible not only for the control of crystal phases and sizes of the titania particles but also for the morphology control of titania nanostructures, enabling a flexible manipulation of TiO_2-based nanomaterials.

We also examined the liquids separated from the solid products with the assistance of GC-MS (see Fig. S1 in supplementary material). The compounds found in the liquids could be considered as the intermolecular condensation products of the acetone molecules, e.g. aldol

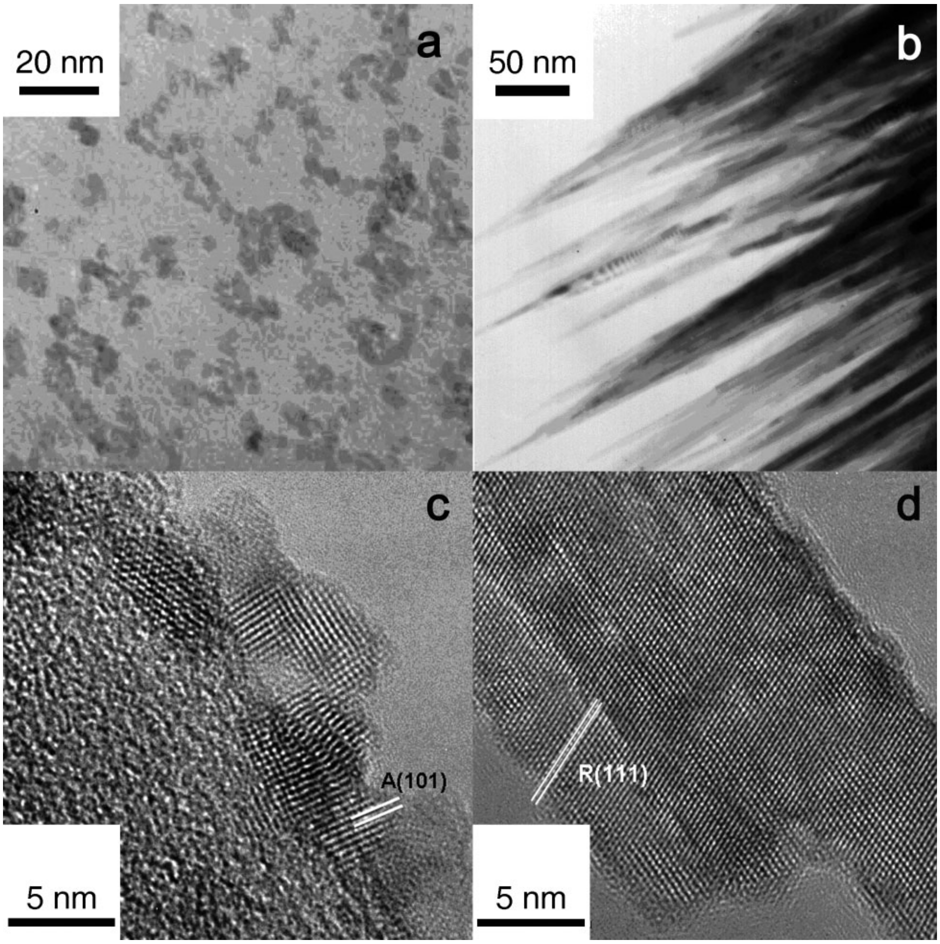

Figure 2. TEM images of samples obtained from reaction of TiCl4 and acetone with the mole ratio of 1 : 30 (a) and 1 : 10 (b) at 110 °C respectively. (c) and (d) High-resolution images of particles in (a) and (b), respectively. A and R denote anatase and rutile, respectively.

condensation.[8] The liquid products are quite different from those in the so-called non-hydrolytic sol–gel synthesis by the reaction of titanium chloride with titanium alkoxide in heptadecane with trioctylphosphine (TOPO) as an additive,[5] in which an alkoxide or ether functioned as an oxygen donor for the titanium chloride and the carbon–oxygen (C–O) bond in the organics could be easily changed to a carbon–chloride (C–Cl) bond to form an alkyl chloride product in the organic phase. Thus, a different mechanism must operate: at the beginning of the reaction, $TiCl_4$ would assume the function of a Lewis acid to catalyze the well-known aldol condensation reaction of acetone to form diacetone alcohol, which can easily dehydrate to produce mesityl oxide and its isomers (as shown in Scheme S1 of the supplementary material). The dehydrated dimers could further condensate with the remaining acetone to produce varying amounts of dehydrated trimers, tetramers, etc.[10] At the same time, water molecules produced from the dehydration of acetone oligomers would induce hydrolysis of $TiCl_4$ to produce Ti–OH species and volatile HCl. The fact that TiO_2 nanocrystals were directly obtained in the reaction system suggests that the dehydration of TiOH species to form the Ti–O–Ti bonds of the nanocrystals would easily happen during the solvothermal treatment at 80–110 °C. According to previous documentations,[11–13] concentration of $TiCl_4$ in aqueous solution could significantly influence crystallization of TiO_2 under hydrothermal conditions, and a higher concentration is in favor of the formation of rutile. However, needle-like rutile nanocrystallites have seldom been reported. It is reasonable that interaction of the condensation products of acetone with the TiO_2 surface would be selective and may have important impact on the morphology and size of the final TiO_2-nanoparticles. A more detailed examination of the organic products in the liquid is underway; the results will be used to gain insight into the mechanism of crystal formation and morphology control of titania.

CONCLUSIONS

In summary, anatase or rutile TiO_2 nanocrystallites are synthesized selectively by solvothermal treatment of the $TiCl_4$–acetone mixture at fairly low temperature (80–110 °C). The key factor determining the crystal phase and morphology is the $TiCl_4$/acetone ratio in the mixture; anatase crystallites with small, uniform, and yet tunable sizes between 5 and 10 nm are obtained when the ratio is no higher than 1 : 15, while rutile TiO_2 nanofibres were produced selectively with higher $TiCl_4$/acetone ratios. These data demonstrate a new nonaqueous approach for the synthesis of TiO_2 nanocrystallites with controlled polymorph and morphology, which could be exploited as a versatile method to synthesize metal oxides.

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