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Synthesis and characterisation of nanotubular titanates and titania

L.-Q. Weng [a,*], S.-H. Song [a], S. Hodgson [b], A. Baker [b], J. Yu [a]

[a] *Department of Materials Science and Engineering, Shenzhen Graduate School, Harbin Institute of Technology, Shenzhen University Town, Xili, Shenzhen 518055, China*

[b] *Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK*

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Abstract

Nanotubular titanates and titania, with an external diameter of around 8 nm and a wall thickness of about 1 nm, were synthesised by hydrothermal processing. Their morphological and structural properties were characterised by TEM and XRD, respectively, and their thermal stability was evaluated. The formation of nanotubular products was due to hydrothermal treatment, rather than washing process, but the pH values of washing solutions could determine the composition of the products. Sodium titanates, hydrogen titanates and titania nanotubes could be synthesised, respectively, via changing the pH value of washing solutions and the heat-treatment temperature. The nanotubes remained in their shape at 400 °C, fused together at 600 °C, and completely lost their nanotubular shape to give aggregated anatase nano-particles at 800 °C.

Keywords: Nanotubes; TiO_2; Titanates

1. Introduction

The synthesis of nanotubes has become one of the most important research subjects in nanotechnology, and various nanotubular materials have been produced during the last decades.[1–4] The success of preparing titania nanotubes is one of the examples of such intense research efforts. In general, templates, such as anodic alumina,[5] organogelator[6] and laurylamine hydrochloride surfactant,[7] have been employed to produce titania nanotubes. Nevertheless, Kasuga et al.[8] has synthesised well-developed nanotubes through a more simple hydrothermal approach without using templates. They suggest that washing hydrothermally treated products with acid is a post-synthesis process that is essential for the formation of nanotubes,[8,9] with the support from Sun and Li[10] and Chen et al.[11] However, results published by Du et al.[12] and Yao et al.[13] show that the nanotubes can be formed during the process of hydrothermal treatment process. On the other hand, the composition and structure of the resultant nanotubular products are also in discrepancy in the literature. Yao et al.[13] assumes, following the previous studies by Kasuga et al.,[8] that the nanotubes are composed of TiO_2, while Du et al.[12] first indicated that the composition of the nanotubes is $H_2Ti_nO_{2n+1}$, with which is in agreement with results published by Lin et al.[14] and Ma et al.[15] In this paper, we present our new findings on synthesising titanate nanotubes in an attempt to clarify the discrepancy in the literature on both the formation mechanism and composition of the nanotubes.

2. Experimental procedure

Commercial TiO_2 nanopowder (99.9%, Alfa, Johnson Matthey GmbH)) was used as starting materials. The phase structure was analysed by X-ray diffraction (XRD, Cu Kα radiation) and the morphology observed by transmission electron microscopy (TEM, Jeol 2000 FXII). The TiO_2 nanopowder (1 g) was added to 10 M NaOH solution (10 ml) and the mixture was kept at 110 °C for different durations (6, 14,

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[*] Corresponding author. Tel.: +86 755 26033464; fax: +86 755 26033874.
E-mail address: lqweng@hitsz.edu.cn (L.-Q. Weng).

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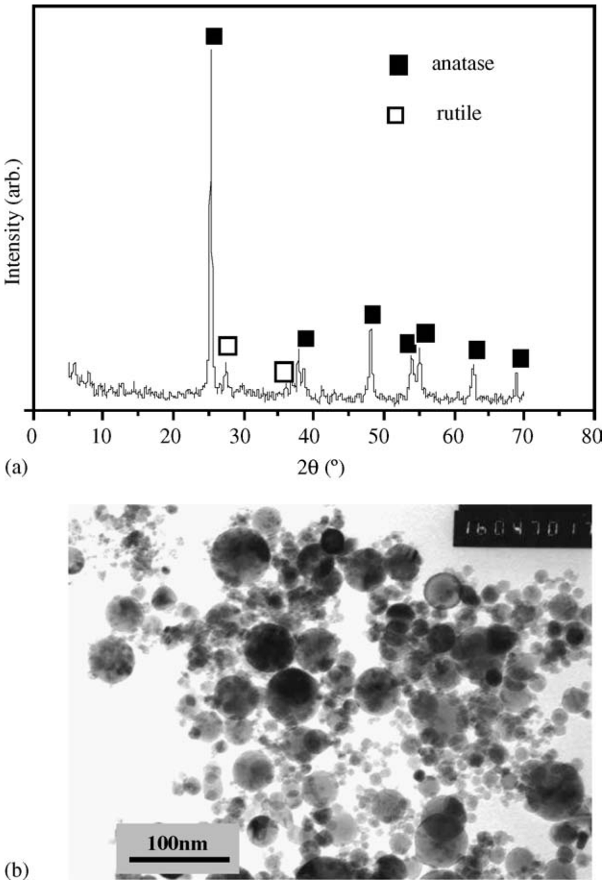

Fig. 1. Phase structure and morphology of the raw material of TiO_2 nanopowder. (a) XRD pattern of TiO_2 nanopowder and (b) TEM micrograph of TiO_2 nanopowder.

24 and 36 h) in a sealed container. The products were later collected by centrifugation and dried in oven at 80 °C. In order to investigate the influence of washing process on the formation mechanism and chemical composition of the nanotubes, the products were thoroughly washed five times with the aqueous solutions of either pH 9.0 or 3.0 with NaOH and HCl, respectively, being used to adjust the pH value of solutions. The products were dried in oven at 80 °C. In order to evaluate the thermal stability a quantity of the products was also isothermally treated in static air for 1 h at 400, 600 and 800 °C, respectively. The structure and morphology of these samples were examined by XRD and TEM.

3. Results and discussion

Fig. 1 shows the structural and morphological properties of TiO_2 nanopowder used as the starting compound. The XRD pattern of the raw nanopowder (Fig. 1a) indicates that the nanoparticles are well-crystallised anatase titania with minor rutile phase. These nanoparticles are spherical and have a broad size distribution ranging from about 2 up to 50 nm with an average size of around 30 nm (Fig. 1b). However, their spherical morphology changes to nanotubular shape after hydrothermal treatment at 110 °C for 1 day, with and without being washed, as observed by TEM (Fig. 2). The well-developed nanotubes have an external diameter of around 8 nm and a wall thickness of around 1 nm. These results indicate that the formation of nanotubes stems directly from the hydrothermal treatment, rather than from the washing process. Consequently, the pH value of a washing solution has no apparent effect on the microstructure of nanotubes, which is different from the mechanism suggested by Kasuga et al.,[9] but is consistent with the results published by Du et al.[12] and Yao et al.[13]

TEM observations on the samples hydrothermally treated at 110 °C for different times (6, 14 and 24 h) (Figs. 2 and 3) suggest the forming mechanism as follows. At the early stage of hydrothermal treatment, titania nanoparticles are partially transformed into nanosheets due to the attack of sodium hydroxide (Fig. 3a), which is well consistent with the previous studies on the hydrothermal synthesis of sodium titanates.[16–19] According to Watts,[16] titania sheets are composed of $[TiO_6]$ octahedra sharing edges with each other, and form a zigzag ribbon structure. With increasing hydrothermal treatment duration, the nanosheets grow, together with the increasing tendency of curling, leading to the formation of short nanotubes (Fig. 3b). Comparing Fig. 3b with Fig. 2a–c exhibits the length increase of the nanotubes with hydrothermal treatment time, probably by a dissolution–reprecipitation mechanism. However, there is no significant further growth in the length of nanotubes when the treatment time extends beyond 24 h.

XRD results of the samples washed in the solutions of different pH values and heat-treated at 400 °C are shown in Fig. 4, illustrating that the crystallinity of the nanotubes is generally poor. However, the influence of the processing parameters, including the pH value of the washing solutions and the temperature of heat treatment, on the composition and phase structure, can be clearly identified. The main difference in the XRD patterns between the crystalline titania (raw material) (Fig. 1a) and the nanotubular samples (Fig. 4) is the appearance of a new and relatively strong broad peak around $2\theta = 10^\circ$ for the nanotube products, which does not exist for the pure titania. The results are consistent with the previous findings by Du et al.,[12] where they attribute the pattern to the layered $H_2Ti_3O_7$ compound, but the Ti/O ratio of titanate nanotubes appears to be different for different nanotubes,[12] which could explain the broadening of XRD peaks. In the present study, the composition of the nanotubular samples is also found to be dependent on the pH value of washing solutions. As shown in Fig. 4, there is a broad peak from $2\theta = 23^\circ$ to 25° when the nanotubular products are washed with a solution of pH 3, which could be assigned to hydrogen titanate compounds according to the standard XRD data. Nevertheless, when the nanotubular sample is washed by the solution of pH 9, there exists a strong diffraction peak around $2\theta = 28^\circ$ besides the weak peak from $2\theta = 23^\circ$ to 25°, which is due to sodium titanate compounds. Heat treatment further exposes

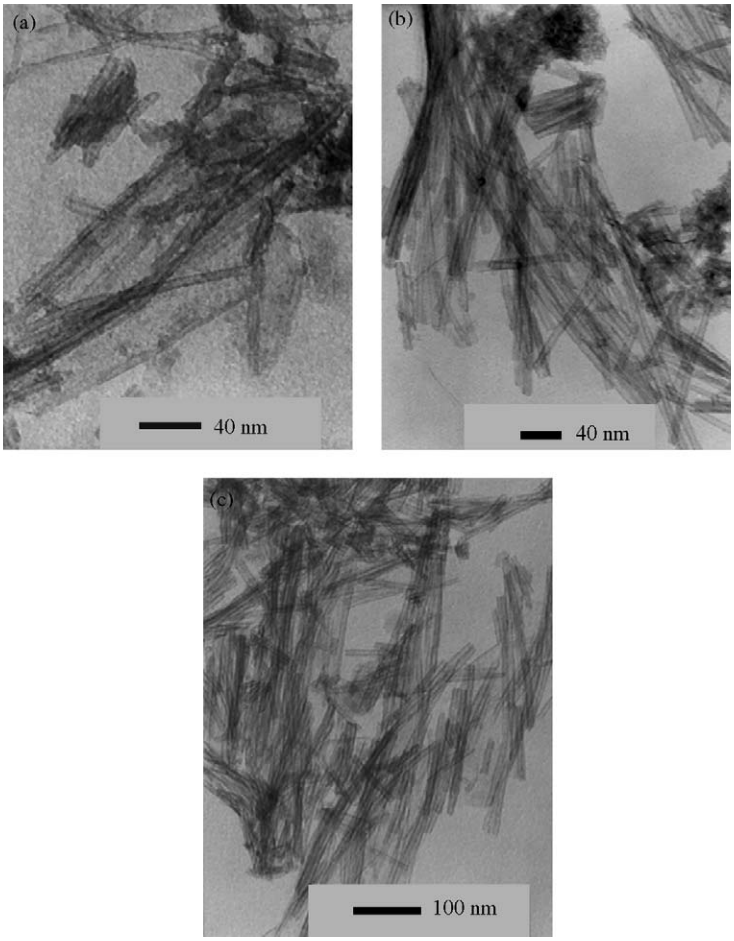

Fig. 2. TEM micrographs of the nanotubular titanate products obtained by hydrothermal processing at 110 °C for 24 h, without being washed (a) and being washed in the solutions of (b) pH 9.0 and (c) pH 3.0.

the compositional difference between these two samples. After the sample washed in the solution of pH 3 is heat-treated at 400 °C, the characteristic peak of titanates around $2\theta = 10°$ almost disappears in the XRD patterns (Fig. 4), which results from the compositional change from hydrogen titanate to titania. However, this peak still remains for the sample washed in the solution of pH 9, suggesting that most of the sample must be composed of sodium titanates because they do not decompose at this temperature. These results indicate that sodium titanates are probably first formed from original

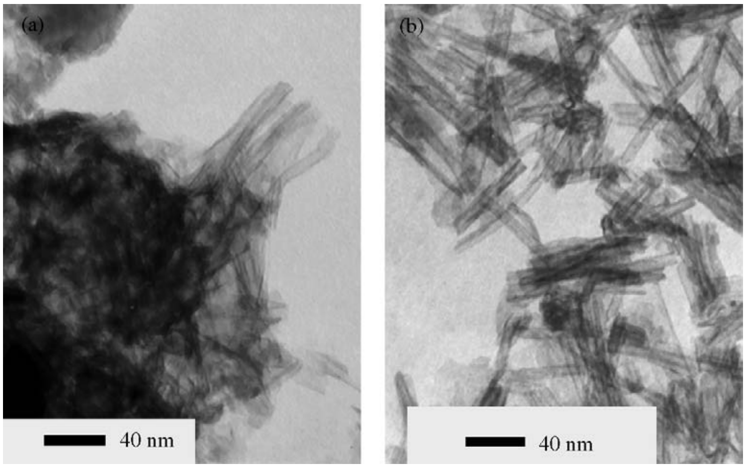

Fig. 3. TEM micrographs of the products hydrothermally treated at 110 °C for (a) 6 h and (b) 14 h.

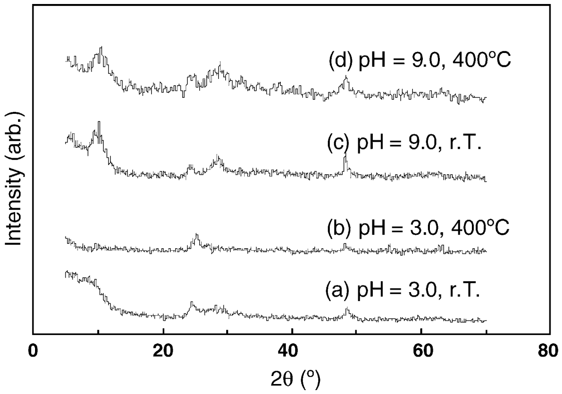

Fig. 4. XRD patterns of the samples treated in the conditions: (a) washed in the solution of pH 3.0 and (b) heat-treated at 400 °C; (c) washed in the solution of pH 9.0 and (d) heat-treated at 400 °C.

titania powder through hydrothermal treatment, which is in agreement with Clearfield and Lehto study,[17] and then the sodium titanate products change to hydrogen titanate after washed in acidic solution through an ion exchange mechanism, as studied by Bunker et al.,[20] The ion exchange process is apparently retarded under basic conditions, therefore the nanotubes mostly retain their sodium titanate composition after washed by the solution of pH 9. The results shown have suggested that the titania nanotubes are formed by heat treating at 400 °C the hydrothermal products that have been washed with a pH 3 solution.

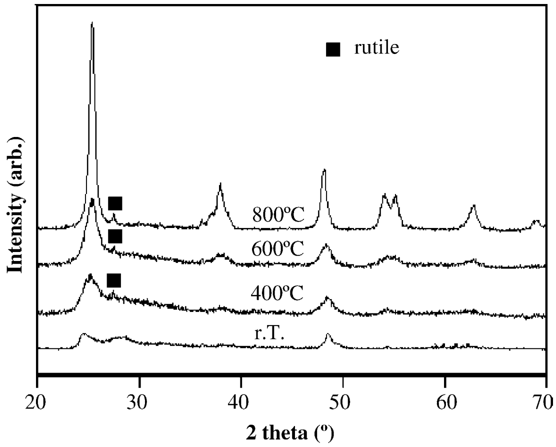

Fig. 5. XRD patterns of the nanotubular products without heat-treatment and those heat-treated at 400, 600 and 800 °C, respectively.

Heat-treatment also affects the microstructure and phase structure of the nanotubular products. XRD results (see

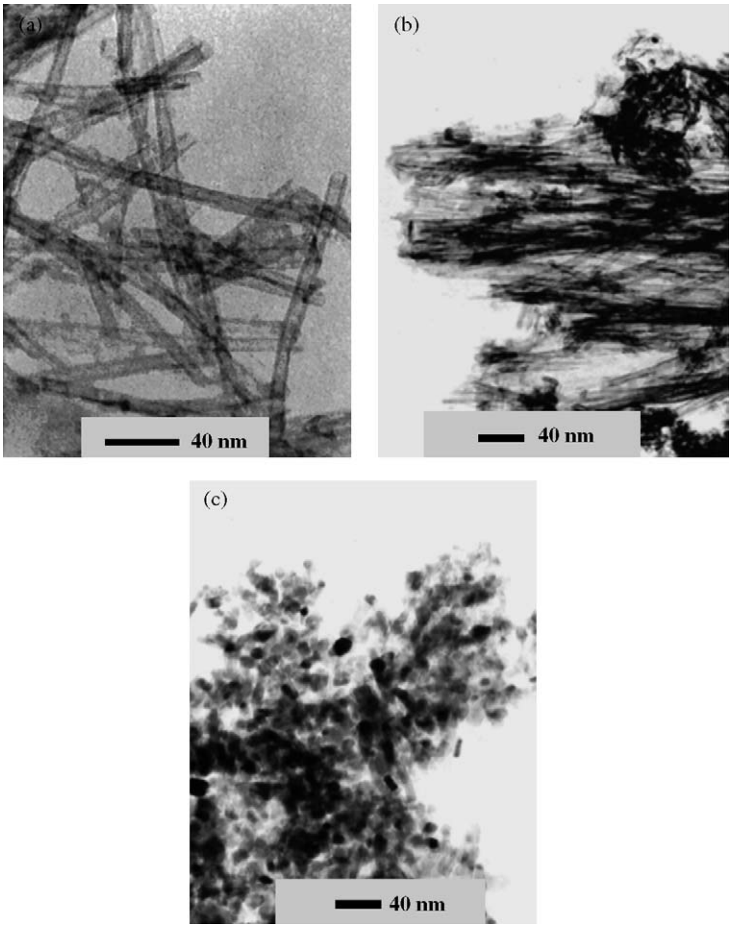

Fig. 6. TEM micrographs of the samples heat-treated at (a) 400 °C, (b) 600 °C and (c) 800 °C, respectively.

Fig. 5) demonstrate that the crystallinity of the resultant nanotubes increases with the increase of heat-treatment temperature. In comparison to the XRD pattern of the starting titania powder (Fig. 1a), the diffraction peaks of the nanotubes heat-treated at 400 °C is considerably broadened due probably to the dimensionality change from powders to nanotubes that are of very thin wall (Fig. 2). Although the microstructure of the nanotubes heat-treated at 400 °C is similar to that of the samples without heat-treatment (Figs. 2 and 6a), the nanotubes are fused together when the temperature of heat treatment is increased to 600 °C (Fig. 6b). The XRD results show that the samples become more crystalline with a dominant anatase phase plus a trace rutile one (Fig. 5). As the temperature is increased to 800 °C, the initial nanotubes completely disappear and are replaced by aggregated nano-particles (Fig. 6c). The aggregated nano-particles possess an anatase phase along with a small amount of rutile phase as marked in Fig. 5.

4. Conclusions

Titanate nanotubes with an external diameter of around 8 nm and a wall thickness of around 1 nm are produced by hydrothermal processing. The formation of titanate nanotubes is in the process of hydrothermal treatment, rather than in the washing process. The nanotubes may be formed from nanosheets through curling in the early stage and growing longer by a dissolution–reprecipitation process with the increase of reaction time. On the other hand, the composition of the resultant products is dependent on the pH value of washing solution and the heat treatment temperature, which result in sodium titanate, hydrogen titanate and titania nanotubes. The nanotubular shape of the products remains at 400 °C and is replaced mainly by the aggregated anatase nano-particles at 800 °C.

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