

# Study on composition, structure and formation process of nanotube $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$

Jianjun Yang, Zhensheng Jin,\* Xiaodong Wang, Wei Li, Jingwei Zhang, Shunli Zhang, Xinyong Guo and Zhijun Zhang\*

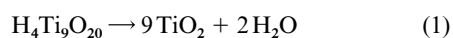
Key Lab of Special Functional Materials, Henan University, Kaifeng, 475001, China.  
E-mail: zhenshengjin@henu.edu.cn

Received 19th May 2003, Accepted 20th August 2003  
First published as an Advance Article on the web 3rd September 2003

A nanotube material is obtained by the reaction of polycrystalline  $\text{TiO}_2$  with concentrated NaOH solution for 20 h at 110 °C. From the contents of Na, Ti and the structural water determined, it is concluded that the nanotube material is  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ , rather than  $\text{TiO}_2$ ,  $\text{TiO}_x$  or  $\text{H}_2\text{Ti}_3\text{O}_7$ . After treating with an HCl solution of pH 1, nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  can be converted to nanotube  $\text{H}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ . The crystalline structure of such nanotube materials belongs to an orthorhombic crystalline system. TEM results indicate that nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  is formed in the reaction stage of  $\text{TiO}_2$  with concentrated NaOH solution. The formation process is discussed.

## Introduction

Metal (Na, K, Ba, etc.) titanates can be prepared by three different methods: flux method, solution method and self-propagating high-temperature synthesis (SHS). By changing both the preparation method and the experimental conditions titanates with different compositions and morphologies can be obtained. In the early 1960s, Andersson obtained the tunnel structured  $\text{Na}_2\text{Ti}_6\text{O}_{13}$  and zigzag structured  $\text{Na}_2\text{Ti}_3\text{O}_7$  by heating  $\text{Na}_2\text{CO}_3$  and  $\text{TiO}_2$  (anatase) in different molar ratios at 950–1300 °C.<sup>1</sup> Izawa *et al.* reported that when  $\text{Na}_2\text{Ti}_3\text{O}_7$  was treated with 0.5 M HCl at 60 °C, it was completely hydrolyzed to  $\text{H}_2\text{Ti}_3\text{O}_7$ .<sup>2,3</sup> In the late 1970s, Lunch *et al.* prepared a new product of sodium titanate with a proposed formula of  $\text{NaTi}_2\text{O}_5\text{H}$  by mixing NaOH with  $(i\text{-C}_3\text{H}_7\text{O})_4\text{Ti}$  in a methanol solution and the product precipitated by the addition of water.<sup>4</sup> In the 1980s, Clearfield and Lehto synthesized layered  $\text{Na}_4\text{Ti}_9\text{O}_{20}\cdot x\text{H}_2\text{O}$  according to the following procedure:<sup>5</sup> a fixed amount of 10 M NaOH solution was added to an anatase  $\text{TiO}_2$  slurry (with a Na to Ti reactant ratio of 2 : 1), boiled for 2–3 h under stirring, and then treated hydrothermally for 20 h at 200–300 °C. The Ti/Na atomic ratio of the needle shaped  $\text{Na}_4\text{Ti}_9\text{O}_{20}\cdot x\text{H}_2\text{O}$  determined by neutron activation analysis was  $2.16 \pm 0.03$ , with an inter-layer distance of 8.6 Å for the semi-hydrous phase, and 6.9 Å for the anhydrous phase. The anhydrous  $\text{Na}_4\text{Ti}_9\text{O}_{20}$ , when treated with 0.1 M HCl, converted to  $\text{H}_4\text{Ti}_9\text{O}_{20}$ . At 700 °C,  $\text{H}_4\text{Ti}_9\text{O}_{20}$  thermally decomposed to  $\text{TiO}_2$  (eqn. (1)):



Sugita *et al.* hydrothermally synthesized a layered hydrous lithium titanate  $(\text{Li}_{1.81}\text{H}_{0.19})\text{Ti}_2\text{O}_5\cdot 2.2\text{H}_2\text{O}$ , which showed a C-base-centered orthorhombic system with the lattice constants  $a_0 = 16.66 \pm 0.02$  Å,  $b_0 = 3.797 \pm 0.002$  Å and  $c_0 = 3.007 \pm 0.003$  Å. Upon conversion to the hydrogen form the lattice constants changed to  $a_0 = 18.08 \pm 0.03$  Å,  $b_0 = 3.784 \pm 0.003$  Å and  $c_0 = 2.998 \pm 0.002$  Å, respectively.<sup>6</sup> Sasaki *et al.* obtained a layered titanate  $\text{H}_2\text{Ti}_4\text{O}_9\cdot 1.2\text{H}_2\text{O}$  by extracting the interlayered  $\text{K}^+$  ions of  $\text{K}_2\text{Ti}_4\text{O}_9$  with a 1 M HCl solution.  $\text{K}_2\text{Ti}_4\text{O}_9$  in fibrous form was grown from a  $\text{K}_2\text{MoO}_4$  flux melt containing a 3 : 1  $\text{K}_2\text{O}$ – $\text{TiO}_2$  mixture by a slow-cooling method.<sup>7</sup> The photocatalytic properties of  $\text{RuO}_2$ -dispersed  $\text{M}_2\text{Ti}_6\text{O}_{13}$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) for water decomposition were investigated by Inoue *et al.*<sup>8,9</sup> The photocatalytic activity depends on the nature of the alkaline metal atom and increases in the order of  $\text{Na} > \text{K} > \text{Rb} > \text{Cs}$ . Komarov and Parkin prepared  $\text{BaTiO}_3$  with a grain size of 1.5 µm (a major component of high dielectric constant ceramics) by the reaction of  $\text{TiCl}_3$  or titanium metal with  $\text{BaO}_2$  via self-propagating high-temperature synthesis.<sup>10</sup>

In 1998, by treating anatase  $\text{TiO}_2$  powder with a 5–10 M NaOH aqueous solution at 110 °C for 20 h, Kasuga *et al.*<sup>11</sup> obtained a nanotube material; Jin *et al.* repeated their work in 2000.<sup>12</sup> Both of them considered that this nanotube material was nanotube  $\text{TiO}_2$ . Afterwards, Du *et al.* suggested that it was nanotube  $\text{TiO}_x$ <sup>13</sup> or  $\text{H}_2\text{Ti}_3\text{O}_7$ .<sup>14</sup> Recently, we investigated the composition and structure of this nanotube material and found that it is nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ , which can be converted to nanotube  $\text{H}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  in a pH 1 HCl solution, and its crystalline form belongs to an orthorhombic system. The formation process of nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  was also studied by us.

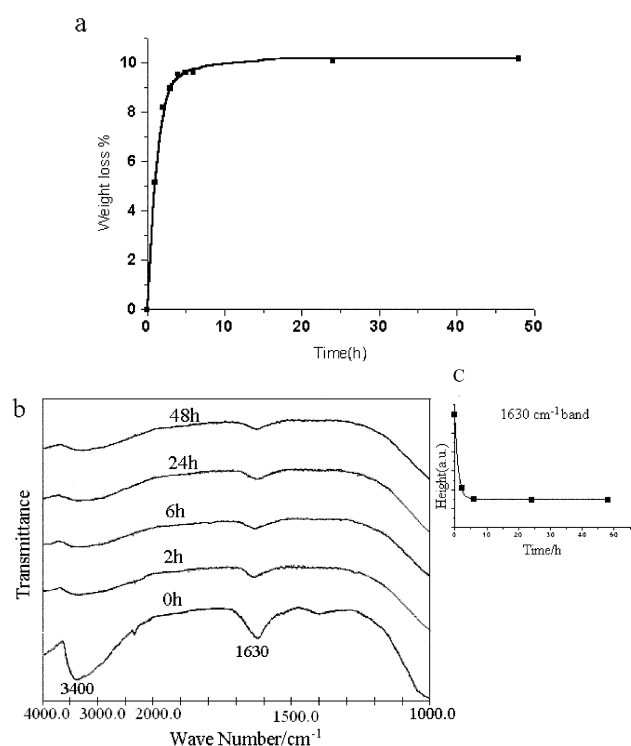
## Experimental

### 1 Preparation of samples

300 ml of 40% (w/w) NaOH aqueous solution was put in a PTFE bottle equipped with a reflux condenser which was placed in an oil-bath. After the temperature of the NaOH solution reached 110 °C, 6 g  $\text{TiO}_2$  powder was added and stirred magnetically for 20 h, then the reaction was stopped. The dispersion was cooled to room temperature and diluted with distilled water to a pH of 13.5. The solid which settled from the dispersion was divided into seven parts. The first part was washed with anhydrous ethanol to remove free NaOH adsorbed on both the outside and inside surfaces of the nanotube material, then it was filtered and dried at room temperature (sample A). The second to sixth parts were treated with distilled water or dilute HCl to pH 12.0, 10.0, 8.0, 5.5 and 3.5, respectively, being immersed for 5 h, and then were filtered off and dried at room temperature (samples B–F). The seventh part was first washed with distilled water to *ca.* neutral pH, then immersed in a pH 1.0 HCl solution for 72 h and washed again with distilled water to remove  $\text{Cl}^-$ , and dried under vacuum (–0.1 MPa) at room temperature till constant weight (Fig. 1(a)). Fig. 1(b) shows the variation in IR spectra during vacuum drying at room temperature; at  $t > 6$  h the intensities of the the deformation and stretching vibrations of water at 1630 and 3400  $\text{cm}^{-1}$ , respectively, decreased to constant values (*i.e.* only the adsorbed water of the KBr matrix remained, see Fig. 1(c)), which demonstrates that the adsorbed water on both outside and inside nanotube surfaces has been removed (sample G).

### 2 Na,Ti analysis and structural water analysis

Ti contents of samples A–G were determined by means of colorimetric method using a UNICAM  $\lambda\text{HEI}10\text{S } \alpha\text{UV-Vis}$  absorption spectrometer. Na contents were analyzed on a Hitachi 180–60 atomic absorption spectrometer. The structural



**Fig. 1** Vacuum-drying ( $-0.1$  MPa) at room temperature of sample G: (a) weight-loss curve; (b) IR spectra at different times of drying; (c) curve of height vs. time for the  $1630\text{ cm}^{-1}$  band.

water of sample G was measured according to the following procedure: an accurately weighed amount of sample G in a crucible was put in a muffle furnace, which was raised to  $700\text{ }^{\circ}\text{C}$  and kept for 4 h, then cooled to room temperature with the sample then weighed immediately. The weight lost was considered to correspond to the structural water of sample G.

### 3 Characterization

Transmission electron microscopic (TEM) images and electron diffraction (ED) patterns were taken on a JEM-2010 electron microscope. X-Ray diffraction (XRD) patterns were measured on a Philips X'Pert Pro X-ray diffractometer. A Shimadzu IR-460 spectrometer was used for the infrared (IR) determination of samples in KBr pellets in an *in-situ* IR cell which can be evacuated.

### 4 Reagents

NaOH, analytically pure, a product of Tianjin Chemical Reagents Factory; HCl, analytically pure, a product of Kaifeng Chemical Reagents Factory;  $\text{TiO}_2$  (anatase), was purchased from Jiangsu Hehai Nano Sci-Tech Company; anhydrous ethanol, analytically pure, was produced by Tianjin Hongyan Reagents Factory.

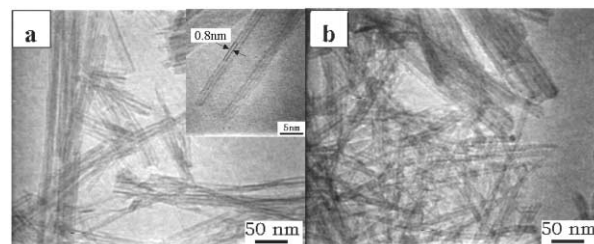
## Results and discussion

Fig. 2(a) shows the TEM image of the reaction product taken from concentrated NaOH solution, while the insert shows a four-layered nanotube with inner and outer diameters of 6.4 and 9.3 nm, respectively, the distance between two adjacent layers is *ca.* 0.8 nm. After treating with a HCl solution of pH 1, the morphology of the nanotube remains unchanged (see Fig. 2(b)), indicating that the nanotube material is formed in the reaction stage of  $\text{TiO}_2$  with concentrated NaOH solution, but not in the post-treatment stage by 0.1 M HCl or 0.1 M  $\text{HNO}_3$ .<sup>15,16</sup>

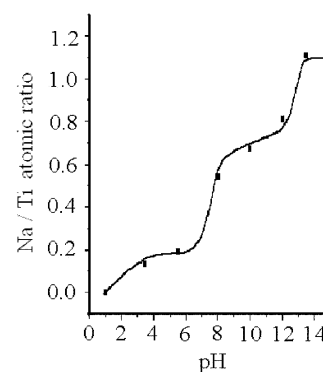
The results of Na/Ti atomic ratios for samples A–G are shown in Table 1. The dependence of Na/Ti atomic ratio on pH (Fig. 3) has two equivalent points, *i.e.* two plateau regions at

**Table 1** Na/Ti atomic ratio of nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  at different pH values

Sample	pH	Na/Ti atomic ratio
A	13.5	$1.11 \pm 0.02$
B	12.0	$0.81 \pm 0.06$
C	10.0	$0.67 \pm 0.07$
D	8.0	$0.54 \pm 0.02$
E	5.5	$0.19 \pm 0.02$
F	3.5	$0.13 \pm 0.02$
G	1.0	$0.00 \pm 0.02$



**Fig. 2** TEM images of nanotube materials: (a) as-prepared from concentrated NaOH; insert is a four-layered nanotube with inner and outer diameters of 6.4 and 9.3 nm respectively, the distance between two adjacent layers is *ca.* 0.8 nm; (b) after treating with a HCl solution of pH 1.



**Fig. 3** Dependence of Na/Ti atomic ratio on pH value of solution.

*ca.* 20 and 80%  $\text{Na}^+/\text{H}^+$  exchange suggesting that these two particular compositions have some inherent stability. Fig. 3 corresponds to a hydrolytic curve of a divalent sodium salt, the Na/Ti atomic ratio of which is *ca.* 1 (a positive deviation of *ca.* 0.1). According to the balancing rule of oxidation value, the radical ion of this divalent salt may be  $(\text{Ti}_2\text{O}_3)^{2-}$  or  $(\text{Ti}_2\text{O}_4(\text{OH})_2)^{2-}$ . From the ignition loss of weight for sample G, in which the  $\text{Na}^+$  ions contained were all replaced by  $\text{H}^+$ , we obtained a  $\text{H}_2\text{O}/\text{TiO}_2$  mole ratio close to 1, which indicates that the thermal decomposition formula of sample G is:  $\text{H}_2\text{Ti}_2\text{O}_4(\text{OH})_2 \rightarrow 2\text{H}_2\text{O} + 2\text{TiO}_2$ , rather than  $\text{H}_2\text{Ti}_2\text{O}_5 \rightarrow \text{H}_2\text{O} + 2\text{TiO}_2$ . Based on the above results, we conclude that the product (*i.e.* nanotube material) for anatase  $\text{TiO}_2$  reacted with concentrated NaOH at  $110\text{ }^{\circ}\text{C}$  is  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ , not  $\text{TiO}_2$  or  $\text{TiO}_x$ ,<sup>11–13,17,18</sup> and also not  $\text{H}_2\text{Ti}_3\text{O}_7$ ,<sup>14</sup> because in concentrated NaOH solution, the existence of the weak acid  $\text{H}_2\text{Ti}_3\text{O}_7$  is impossible. A question needed to be answered is why does the Na/Ti atomic ratio for sample A have a  $\approx 0.1$  positive deviation from the theoretical value of 1.0 (Table 1)? It is well known that  $\text{CO}_2$  in air can easily be absorbed by concentrated NaOH solution to form  $\text{Na}_2\text{CO}_3$ , which is also insoluble in ethanol. In the washing process of sample A with anhydrous ethanol, which was conducted in ambient air, it seems that the formation of  $\text{Na}_2\text{CO}_3$  is unavoidable so leading to a positive deviation of the Na/Ti atomic ratio from the theoretical value.

From the composition of nanotube material stated above, the reaction formula of  $\text{TiO}_2$  (anatase) with concentrated NaOH can be written as follows (eqn. (2)):

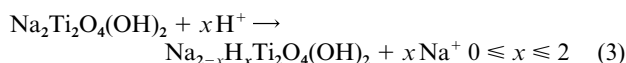
**Table 2** XRD Data of nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ 

$2\theta/^\circ$	$d/\text{\AA}$	$hkl$	$I/I_0$
9.18	9.63	200 <sup>a</sup>	100
24.30	3.66	110	32
28.14	3.17	600	60
34.24	2.62 (?)	301	8
38.06	2.36 (?)	501	10
48.14	1.89	020	69
61.76	1.50 (?)	002	8

<sup>a</sup>  $d_{200}$  corresponds to the distance between adjacent layers,  $\sim 0.8$  nm, see Fig. 2(a).

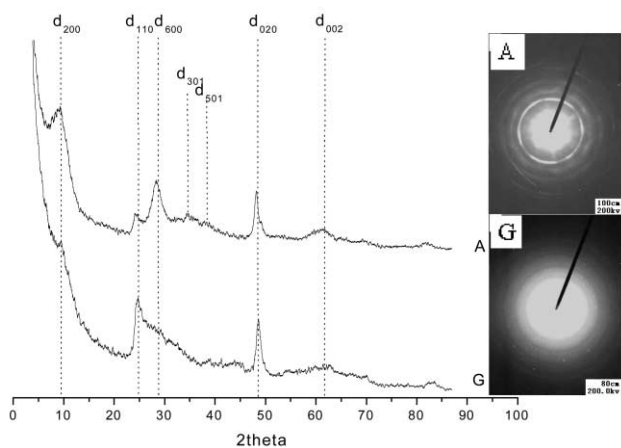
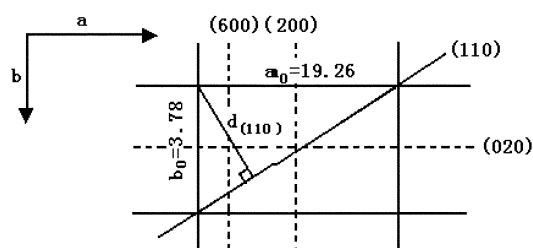


In  $1 \leq \text{pH} \leq 13.5$  aqueous solution,  $\text{Na}^+$  can exchange with  $\text{H}^+$  (eqn. (3)):



Based on the above results and discussion, the material, which has been previously denoted as “nanotube  $\text{TiO}_2$ , nanotube  $\text{TiO}_x$  or nanotube  $\text{H}_2\text{Ti}_3\text{O}_7$ ”,<sup>11–18</sup> is actually nanotube  $\text{Na}_{2-x}\text{H}_x\text{Ti}_2\text{O}_4(\text{OH})_2$ , where  $x$  depends on the pH of the post-treatment solution.

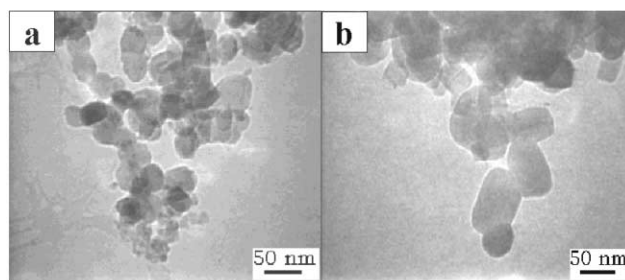
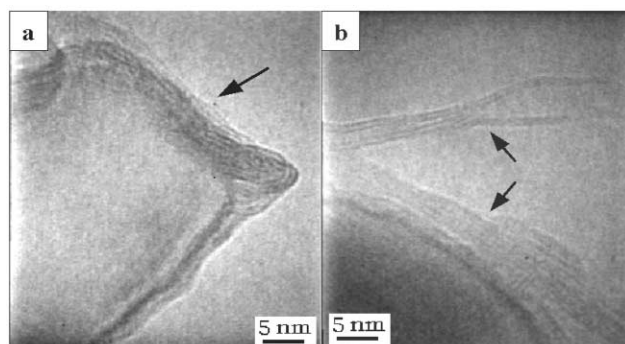
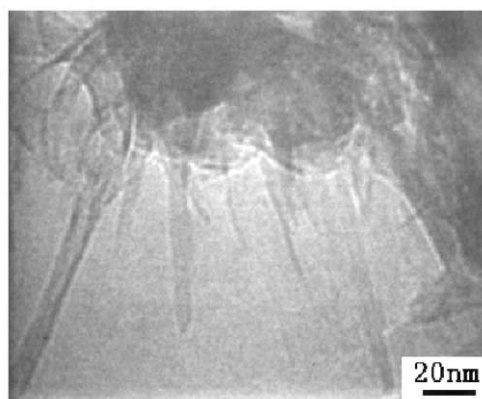
Fig. 4(a) shows the XRD pattern of sample A (insert is its ED pattern). Referring to the XRD patterns of flat layered  $\text{Li}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ <sup>7</sup> and  $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ ,<sup>19</sup> the crystal form of sample A belongs to an orthorhombic system; its diffraction data are shown in Table 2. The hypothetical schematic view ( $X$ – $Y$  section, Fig. 5) of nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  may be deduced from the data in Table 2, the lattice constants are:  $a_0 = 19.26$  Å,  $b_0 = 3.78$  Å and  $c_0 = 3.00$  Å. Since the layers of nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  are curved, the diffraction peaks related to the  $Z$  axis (e.g. 301, 501, 002) are much weaker than the peaks 200, 110, 600 and 020 (Fig. 4, curve A). Comparing the lattice constant  $a_0$  of nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  ( $a_0 = 19.26$  Å) with that of flat layered  $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$  ( $a_0 = 17.2$  Å)<sup>6</sup> and  $\text{Li}_{1.81}\text{H}_{0.19}\text{Ti}_2\text{O}_5 \cdot$

**Fig. 4** XRD spectra of samples A and G.**Fig. 5** Schematic view of the orthorhombic layered-nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ .

$2.2\text{H}_2\text{O}$  ( $a_0 = 16.66$  Å),<sup>7</sup> the distance between the adjacent layers ( $a_0 = 2 \times d_{200}$ ) for the former is larger than that for the other two.

Fig. 4, curve G shows the XRD pattern of sample G. Although the diffraction peak positions of sample A and G are the same, the shape and intensity of some of the peaks change markedly, especially for peak 600. This may be a result of the replacement of  $\text{Na}^+$  in  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  by  $\text{H}^+$ .

To investigate how crystalline  $\text{TiO}_2$  powder (e.g. anatase  $\text{TiO}_2$ ) converts to layered nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  in concentrated  $\text{NaOH}$  solution, we carried out TEM observations at different reaction times. Fig. 6(a) and (b) show the TEM images of raw  $\text{TiO}_2$  and the sample reacted for 2 min in concentrated  $\text{NaOH}$  solution, respectively. It is evident that the samples are different in size, i.e., the mean diameter is *ca.* 30 nm for the former and *ca.* 60 nm for the latter, which indicates that a 2 min treatment has already made the raw  $\text{TiO}_2$  particles swell. Fig. 7(a) and (b) show the HRTEM images of the sample reacted for 12 min. From Fig. 7(a), swelling stripes can be seen on the side pointed by an arrow, but they can not be clearly observed on the side perpendicular to it. In Fig. 7(b) there are fragments peeling off from the granular crystal as indicated by arrows. After  $\text{TiO}_2$  reacted with concentrated  $\text{NaOH}$  for 30 min, tube shaped material formed (Fig. 8). The TEM image of the product

**Fig. 6** TEM images of (a) raw  $\text{TiO}_2$  and (b) the sample reacted for 2 min in concentrated  $\text{NaOH}$  solution.**Fig. 7** HRTEM images of the sample reacted for 12 min: (a) swelling side indicated by the arrow; (b) fragments peeling off from granule.**Fig. 8** TEM image of the sample reacted for 30 min.

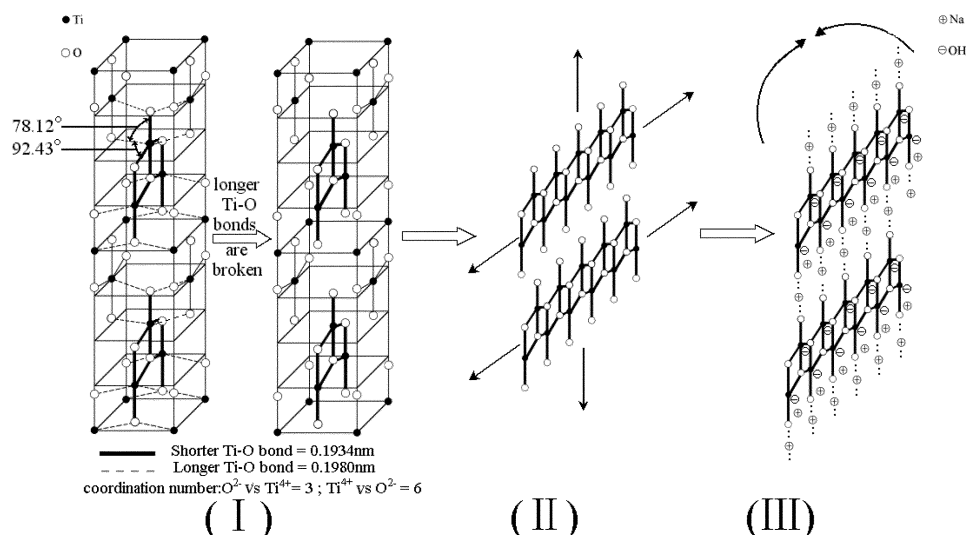


Fig. 9 Schematic diagram of formation process for nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ .

reacted for 20 h is the same as that shown in Fig. 2(a). From the above observations, we can propose a formation mechanism for the nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  as detailed below.

It is well known that the structure of anatase  $\text{TiO}_2$  can be described in terms of chains of distorted  $\text{TiO}_6$  octahedra<sup>20,21</sup> (Fig. 9-I). Each  $\text{Ti}^{4+}$  is surrounded by an octahedron of six  $\text{O}^{2-}$  ions. Two Ti–O bonds are longer (0.1980 nm), while the other four are shorter (0.1934 nm). The coordination number of  $\text{O}^{2-}$  with  $\text{Ti}^{4+}$  is three. Treating with concentrated NaOH, the longer Ti–O bonds might be attacked by  $\text{OH}^-$  ions and break, but the shorter ones would not, so irregular swelling occurs (see Fig. 7(a) and Fig. 9-I). Then, linear fragments are formed and peel off from the  $\text{TiO}_2$  crystalline particles (Fig. 9-II). The linear fragments link with each other to form planar fragments through  $\text{O}^- \text{Na}^+ \text{O}^-$  ionic bonds (Fig. 9-III). According to the nomenclature in supramolecular chemistry,<sup>22</sup> the planar fragments may be denoted the kinetic product in the formation process of the nanotube material. The  $(-\text{Ti}-\text{O}-\text{Ti}-\text{O}-\text{Ti}-\text{O}-)_x$  chains included in a planar fragment are flexible and the thermodynamic product (*i.e.* solid nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ ) could be obtained through the covalent bonding of their end groups (Fig. 9-III); the monolayer nanotube may then play the role of template for a multilayer nanotube.  $\text{Na}^+$  and  $\text{OH}^-$  groups exist between the adjacent layers of a multilayer nanotube. Such a structure of multilayer nanotube will possess the chemical composition  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ . The overall formation process may be expressed as: anatase  $\text{TiO}_2$  particles  $\rightarrow$  planar fragments (dissolved, kinetic product)  $\rightarrow$  solid nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  (thermodynamic product) (Fig. 9).

## Conclusions

The nanotube material obtained by anatase  $\text{TiO}_2$  powder reacted with concentrated NaOH solution at 110 °C for 20 h is  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ . Nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  is formed in the reaction stage, not in the post-treatment stage; its formation process may be expressed as follows: anatase  $\text{TiO}_2$  particles  $\rightarrow$  planar fragments (dissolved, kinetic product)  $\rightarrow$  solid nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  (thermodynamic product). After treating with a HCl solution of pH 1, nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  can be converted to nanotube  $\text{H}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ . The crystalline structure of both nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  and nanotube  $\text{H}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  belongs to an orthorhombic system.

## Acknowledgements

This work was supported by National Natural Science Foundation of China. (No. 20071010). The authors express their gratitude to Dr. Yu Li for recording the IR spectra.

## References

- 1 S. Andersson, *Acta. Crystallogr.*, 1962, **15**, 194–201.
- 2 H. Izawa, S. Kikkawa and M. Koizumi, *J. Phys. Chem.*, 1982, **86**, 5023–5026.
- 3 H. Izawa, S. Kikkawa and M. Koizumi, *J. Solid State Chem.*, 1985, **60**, 264–267.
- 4 R. W. Lurch, R. G. Dosch, B. T. Kenna, J. K. Johnstone and E. J. Nowak, in International Atomic Energy Agency SM-207/75, P. 361, Vienna 1975.
- 5 A. Clearfield and J. Lehto, *J. Solid State Chem.*, 1988, **73**, 98–106.
- 6 M. Sugita, M. Tsuji and M. Abe, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1978–1984.
- 7 T. Sasaki, M. Watanabe, Y. Komatsu and Y. Fujiki, *Inorg. Chem.*, 1985, **24**, 2265–2271.
- 8 S. Ogura, M. Kohno, K. Sato and Y. Inoue, *Phys. Chem. Chem. Phys.*, 1999, **1**, 179–183.
- 9 Y. Inoue, T. Kubokawa and K. Sato, *J. Phys. Chem.*, 1991, **95**, 4059–4063.
- 10 A. V. Komarov and I. P. Parkin, *Polyhedron*, 1996, **15**, 1349–1353.
- 11 T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino and K. Niihara, *Langmuir*, 1998, **14**, 3160–3163.
- 12 S. Zhang, J. Zhou, Z. Zhang, A. V. Vorontsov and Z. Jin, *Chin. Sci. Bull.*, 2000, **45**(16), 1533–1536.
- 13 G. H. Du, Q. Chen, R. C. Che, Z. Y. Yuan and L. M. Peng, *Appl. Phys. Lett.*, 2001, **79**, 3702–3704.
- 14 Q. Chen, G. H. Du and L. M. Peng, *J. Chin. Electron Microsc. Soc.*, 2002, **21**, 265–269.
- 15 T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino and K. Niihara, *Adv. Mater.*, 1999, **11**, 1307–1311.
- 16 Y. Zhu, H. Li, Y. Koltylpin, Y. R. Hacohen and A. Gedanken, *Chem. Commun.*, 2001, 2616–2617.
- 17 B. D. Yao, Y. F. Chan, X. Y. Zhang, W. F. Zhang, Z. Y. Yang and N. Wang, *Appl. Phys. Lett.*, 2003, **82**, 281–283.
- 18 J. Zhang, X. Guo, Z. Jin, S. Zhang, J. Zhou and Z. Zhang, *Chin. Chem. Lett.*, 2003, **14**, 419–422.
- 19 Joint Committee on Powder Diffraction Standard, 47–0124.
- 20 J. K. Burdett, T. Hughbanks, J. Miller, J. W. Richardson, Jr. and J. V. Smith, *J. Am. Chem. Soc.*, 1987, **109**, 3639–3646.
- 21 A. Fahmi and C. Minot, *Phys. Rev. B*, 1993, **47**, 11717–11724.
- 22 J.-M. Lehn, *Supramolecular Chemistry—Concepts and Perspectives*, VCH, Weinheim/New York, 2001.