

## TEM Study on the Formation Process of TiO<sub>2</sub> Nanotubes

Jing Wei ZHANG, Xin Yong GUO, Zhen Sheng JIN\*, Shun Li ZHANG,  
Jing Fang ZHOU, Zhi Jun ZHANG\*

Lab of Special Functional Materials, Henan University, Kaifeng 475001

**Abstract:** The process, that the polycrystalline TiO<sub>2</sub> powders were converted into TiO<sub>2</sub> nanotubes, was observed with transmission electron microscope. The results obtained indicated that in concentrated NaOH aqueous solution, anisotropic swelling appears on the polycrystalline TiO<sub>2</sub> granula at first, and then the nanotubes are formed.

**Keywords:** TiO<sub>2</sub> nanotubes, anisotropic swelling, TEM.

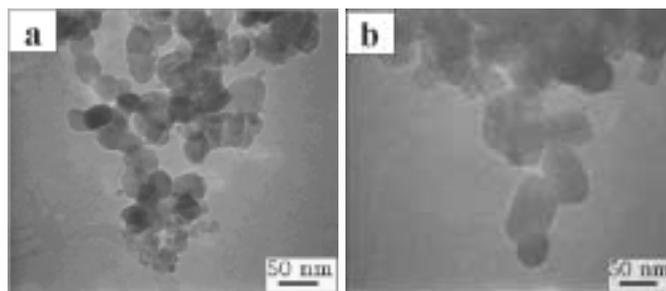
Since the carbon nanotubes were discovered by Iijima<sup>1</sup>, the tube-shaped nano-structured material attracted extensive attention, owing to their novel properties. Various methods, such as electric arc discharging of graphite or pyrolysis of small molecule hydrocarbon was used for the preparation of carbon nanotubes<sup>2-4</sup>. In 1998, Kasuga *et al.* found that the TiO<sub>2</sub> nanotubes can be obtained through the treatment of the powdered polycrystalline TiO<sub>2</sub> in concentrated NaOH solution<sup>5</sup>. Afterwards, we studied its morphological structure and physicochemical properties<sup>6</sup>. Obviously, the formation process and mechanism of TiO<sub>2</sub> nanotube is different from that of carbon nanotubes. Study on its formation process will helpful to understand the mechanism of formation of TiO<sub>2</sub> nanotubes in the solution.

In this paper, using transmission electron microscope (TEM), the formation process of TiO<sub>2</sub> nanotubes in the concentrated NaOH solution was investigated. The results indicated that TiO<sub>2</sub> nanotubes are formed in the stage of alkali treatment of polycrystalline TiO<sub>2</sub>, and not in the stage of the acid treatment following the alkali treatment. This conclusion differs from Kusuga<sup>7</sup>.

100 mL of 9 mol/L NaOH aqueous solution was placed in a PTFE bottle, equipped with a reflux condenser. Then, the bottle was placed in an oil bath. When the aqueous solution was heated up to 110°C, 10 g anatase TiO<sub>2</sub> was added and stirred magnetically. An aliquot of sample was withdrawn after 2, 12, 30 min, and their morphological structures were observed using TEM. After 20 h, the reaction was ceased. When the reaction mass was cooled down to room temperature, the solid was separated and washed with deionized water repeatedly until the conductivity of the supernatant reached 0.8 μs/cm. Then a half of the solid was soaked in 0.1 mol/L HCl solution for 10 min, and

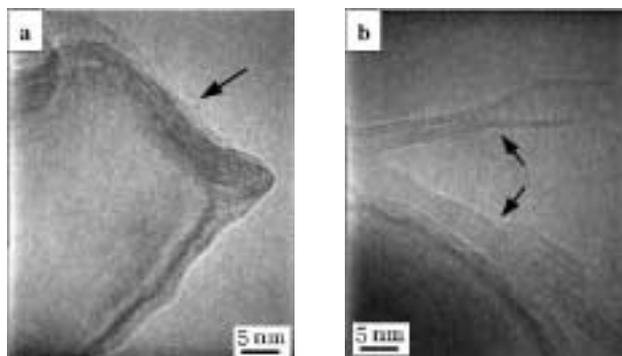
---

\*E-mail: zhenshengjin@henu.edu.cn

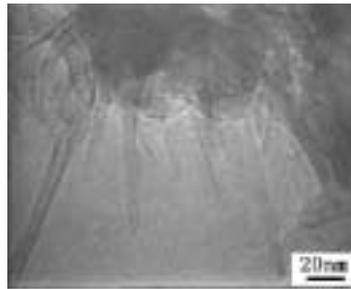
**Figure 1** TEM imagesa) Raw TiO<sub>2</sub>; b) After treatment of alkali reaction for 2min.

washed with deionized water again until the conductivity reached 5.0  $\mu\text{s}/\text{cm}$ . The morphology and Na<sup>+</sup> content were determined by TEM and EDS.

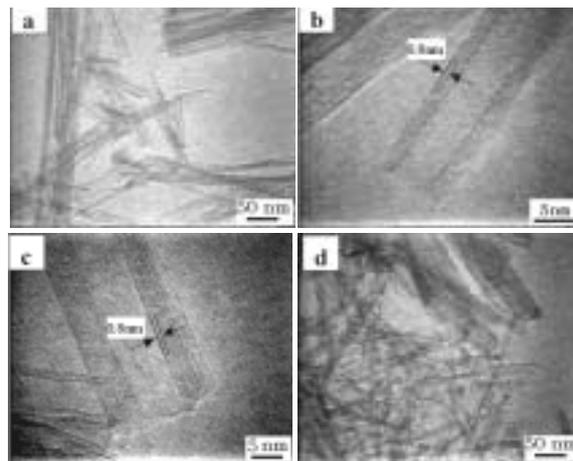
**Figure 1a** and **1b** show the TEM images of the raw TiO<sub>2</sub> and the sample treated with alkali for 2 min respectively. Obviously, they are different in size, the latter is bigger than the former, which reveals that the alkali treatment leads to the granular crystals swelling. **Figure 2a** and **2b** show the high-resolution TEM images of the sample treated with alkali for 12 min. From **Figure 2a**, the swelling stripes can be seen on the side pointed by arrow, but not observed on the side perpendicular to it. This phenomenon hints that the swelling is anisotropic. In **Figure 2b**, there are fragments peeling off from the granular crystal pointed by arrow. After treating for 30 min, the tube-shaped TiO<sub>2</sub> emerges (see **Figure 3**). The TEM images of the sample treated with alkali for 20h and washed with deionized water are shown in **Figure 4a**, **4b** and **4c**. In **Figure 4a**, only TiO<sub>2</sub> nanotubes are present, the particles disappear. In **Figure 4b**, a four-layered nanotube with inner diameter 6.4 nm, outer diameter 9.3 nm and distance

**Figure 2** HRTEM images (After reaction with alkali for 12 min)a) Swelling side (pointed by arrow); b) Fragments peeling off from granular TiO<sub>2</sub>.

**Figure 3** TEM image (After reaction with alkali for 30 min)

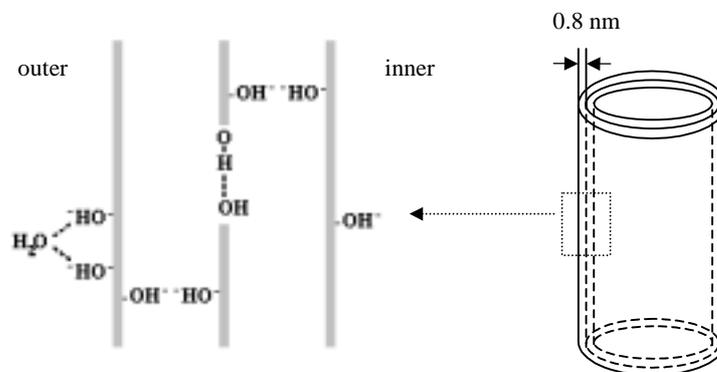


**Figure 4** TEM images (After reaction with alkali for 20 h)



a), b), c) Washed by deionized water;  
 d) Treated by 0.1 mol/L HCl and washed with deionized water.

**Figure 5** The schematic model of nanotube TiO<sub>2</sub>



between adjacent layers 0.8 nm is observed. In **Figure 4c** an eight-layered nanotube with inner and outer diameter 6.4 and 18.6 nm, and distance between adjacent layers 0.8nm is observed. **Figure 4d** shows the image of sample, treated with 0.1mol/L HCl and washed with deionized water again. Comparing **4a** and **4d**, it can be seen that there is no evident morphological difference, but the EDS analysis indicates the sample(**4a**) contains 5.8 atomic percent of Na and the latter(**4d**) contains only trace of Na, it shows that the treatment with HCl solution is helpful for the removing of Na<sup>+</sup> ion from TiO<sub>2</sub> nanotubes.

Why the distance between adjacent layers is 0.8 nm? Because the adjacent layers of nanotube are kept apart by wall of OH<sup>-</sup> groups (shown as **Figure 5**). Theoretically, the distance of the layers of the wall should be  $4\gamma_{OH^-} + 2\gamma_{Ti^{4+}} = 4 \times 0.12 \text{ nm} + 2 \times 0.075 \text{ nm} = 0.63 \text{ nm}$ <sup>8</sup>. Owing to the repulsive force between OH<sup>-</sup> groups, the distance of the layers of the wall broadens to 0.8 nm.

Based on the above results, it can be concluded that the anisotropic swelling took place first, then the structured fragments peeled off from the particles. The TiO<sub>2</sub> nanotubes are assembled with the structured fragments. Further investigations on formation mechanism are now in progress.

### Acknowledgment

This project was supported by the National Natural Science Foundation of China (20071010).

### References

1. S. Iijima, *Nature*, **1991**, 56, 354.
2. S. Iijima, T. Ichihashi, *Nature*, **1993**, 363, 603.
3. M. Endo, H. W. Kroto, *J. Phys. Chem.*, **1992**, 96, 6941.
4. W. Z. Li, S. S. Xie, L. X. Qian *et al.*, *Science*, **1996**, 274, 1701.
5. T. Kasuga, M. Hiramatsu, A. Hoson *et al.*, *Langmuir*, **1998**, 14, 3160.
6. Zhang Shunli, Zhou jingfang, Zhang Zhijun *et al.*, *Chinese Science Bulletin*, **2000**, 45, 1533.
7. T. Kusuga, M. Hiramatsu, A. Hoson *et al.*, *Adv. Mater.*, **1999**, 11, 1307.
8. R. D. Shannon, *Acta Crystallogr. A*, **1976**, 32, 751.

Received 29 October, 2001

Revised 1 November, 2002