

Acid transformation of TiO₂ nanotubes to nanoparticles

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ABSTRACT

The long-term stability of TiO₂ nanotubes in acid, neutral and basic water suspensions was studied at room temperature. In neutral and basic (0.1 M NaOH) solutions, the TiO₂ nanotubes are stable and undergo minimal morphological changes. In dilute solutions of 0.1M H₂SO₄, suspended TiO₂ nanotubes slowly transform to rutile nanoparticles having an ellipsoid shape. The porosity and crystal structure of TiO₂ are also changed during the transformation. The rate of conversion of nanotubes to nanoparticles depends on the nature of the acid and is high in the case of sulfuric acid. Thermodynamic and kinetic aspects of the acid transformation are discussed.

Keywords: TiO₂ nanostructures, dissolution, crystallisation

1 INTRODUCTION

Nanotubular titanium dioxide, produced by alkali hydrothermal treatment, is a relatively novel [1] and intensively studied material [2,3] which is characterized by nano-sized diameter morphology and unique physico-chemical properties. The material shows promise for applications including hydrogen sensors [4], photocatalysts [5], catalyst supports [6], solar cell photosensitisers [7], ion-exchange materials [8,9] and a new generation of lithium electrodes [10,11]. In all of these applications, except optoelectronic devices, nanotubes of TiO₂ can be exposed to chemically aggressive media. Titanium dioxide nanotubes are relatively fragile and can be easily broken under ultrasonic treatment [12] resulting in shorter nanotubes. During hydrothermal treatment in 0.1M HNO₃ at 100°C for 7 h TiO₂, the nanotubes completely transform to anatase [8]. Annealing of the protonated form of TiO₂ nanotubes in air at temperatures higher than 500°C results in transformation of the nanotubes and formation of anatase [13]. Sodium saturated form of TiO₂ nanotubes is stable up to 850°C [8].

For the successful application of TiO₂ nanotubes it is necessary to determine the range of operational conditions under which nanotubes are stable. In this work, the long-term stability of multilayered wall TiO₂ nanotubes in the presence of bases and acid was studied. During the acid transformation of nanotubes all intermediate states were characterised.

2 EXPERIMENTAL DETAILS

The alkali hydrothermal method of preparing TiO₂ nanotubes was based on studies by Kasuga et al.. 9 g of titanium dioxide (anatase) was added to 300 mL of 10M NaOH solution in a PTFE (Teflon) beaker under vigorous stirring. The solution was placed in a PTFE-lined autoclave and heated for 22 hours at 140°C. The white, powdery TiO₂ produced was thoroughly washed with water until the washing solution achieved pH 7, then it was washed with 0.05M H₂SO₄ on a glass filter for over 30 min then washed with water to pH 7. The sample was dried in vacuum at 50°C.

The surface area and BJH pore distribution of the synthesised TiO₂ were measured using a Micromeritics ASAP 2010 instrument. SEM images were obtained with a JOEL 6500 FEG-SEM scanning electron microscope. XRD patterns were recorded using a Bruker AXS D8 Discover x-ray diffractometer, with Cu-K_α radiation $\lambda = 0.154$ nm and a graphite monochromator in the 2θ range of 20° - 50°.

For the long-term TiO₂ nanotube suspension ageing studies, 0.2 g of TiO₂ nanotubes were placed to the 9 vials and 10 mL of decimolar solution of NaOH, HCl and HNO₃ was added. 10 mL of 0.1M sulfuric acid was added to the five other vials. One vial was filled with 10 mL of water. All vials were closed, ultrasonicated for 10 min and kept at room temperature (22°C). The samples were washed with water and dried in vacuum at 50°C

3 RESULTS AND DISCUSSION

Acids and bases typically react with the surface of metal oxide powders resulting in their modification. For example, in the case of photoactive anatase, TiO₂ particles treatment with sulfuric acid improves the activity of this photocatalyst [14] without changing the crystal structure of particles and only modifies the surface properties. In contrast, long-term treatment of TiO₂ nanotubes in diluted sulfuric acid results in a complete change of morphology of particles. In Figure 1, pore size distributions produced from a N₂ desorption curve using the BJH algorithm are shown for samples of nanotubular TiO₂ treated with 0.1 M H₂SO₄ for controlled times. The average pore size increases at longer there is a significant fall of BJH pore volume (see Table 1), but the BET surface area remains unchanged.

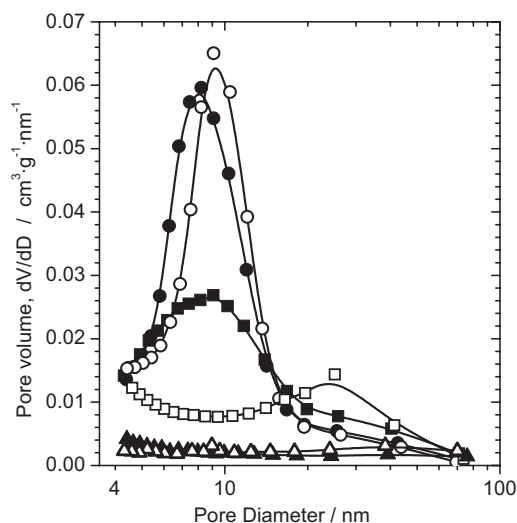


Figure 1. Pore volume distribution (BJH desorption) of TiO_2 nanotubes soaked in 0.1M H_2SO_4 for controlled time at room temperature: (■) – initial powder, (●) – 5 days, (○) – 15 days, (□) – 32 days, (▲) – 2 months, (△) – 5 months

In Figure 2, high resolution SEM micrographs of the initial TiO_2 nanotubes and rutile produced by ageing of nanotubes in 0.1M H_2SO_4 for 5 months are presented. Initial nanotubes having an internal tube diameter *ca.* 3-5 nm, external diameter *ca.* 7-10 nm, and length more than several hundreds of nanometers slowly transform to ellipsoid particles having typical dimensions of 50x200 nm. These particles consist of smaller particles of rutile nanocrystallites.

Despite some debate over the crystal structure of TiO_2 nanotubes [15, 16] we denote the apparent pattern of initial nanotubes (see Figure 3a) to the trititanic acid $\text{H}_2\text{Ti}_3\text{O}_7$ having followed characteristic reflections of 24.38, 28.98, 37.95 and 48.4 degree. Long-term washing of the nanotubes with sulfuric acid results in complete disappearance of the trititanic acid phase accompanied by appearance of the rutile phase having characteristic reflections 27.46, 36.10, 41.25 and 44.07 degree. The coherence area for the rutile crystals was calculated from the half-width at half-height of the (110) plane diffraction peak ($2\theta = 27.65^\circ$) using the Scherrer equation and was found to be approximately 3.9 nm for samples e) and f) in Figure 3. The sample produced after 32 days of washing in sulfuric acid is an approximately equimolar mixture of nanotubular $\text{H}_2\text{Ti}_3\text{O}_7$ and rutile. In all of the samples, the amount of anatase phase is negligible. Previously, it has been reported [17] that SO_4^{2-} ions in solution stimulate the preferential formation of the anatase phase of TiO_2 during hydrolysis reactions. In our case, the presence of sulfate ions during the transformation of nanotubes does not promote the

anatase phase. Generally speaking, the formation of the rutile phase at room temperatures is relatively rare. Adding relatively concentrated 1M HCl or HNO_3 can promote recrystallization of amorphous TiO_2 to rutile at room temperature [18]. Addition of sulfuric acid, however, results in formation of anatase. Phase transformation of protonic layered titanates $\text{H}_2\text{Ti}_4\text{O}_9$ to the anatase TiO_2 in water suspension begins at 225°C without the formation of a rutile phase [19].

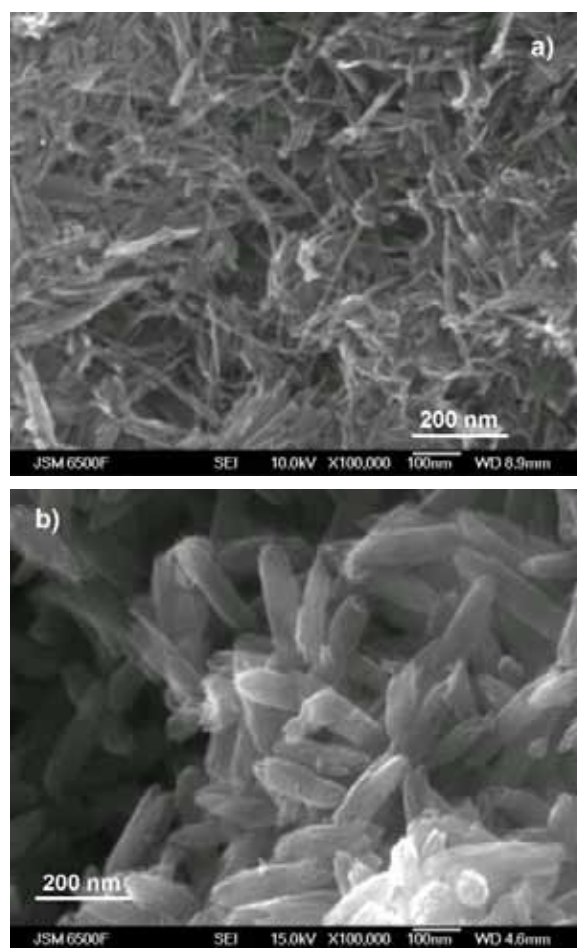


Figure 2. HRSEM pictures of TiO_2 a) initial nanotubes, b) nanotubes transformed to rutile nanoparticles after 5 months ageing in 0.1M H_2SO_4 at room temperature

Data on the stability of a suspension of TiO_2 nanotubes in 0.1M solutions of NaOH, HCl, or HNO_3 are presented in Figure 4 and Table 1. There is no significant change in pore size distribution, surface area or pore volume for samples aged for 5 months in NaOH solution. Probably, the high pH and high sodium ion level in the solution stabilise the nanotubular TiO_2 . Ageing of TiO_2 nanotubes for 2 months in HCl and HNO_3 results in the partial transformation of nanotubes.

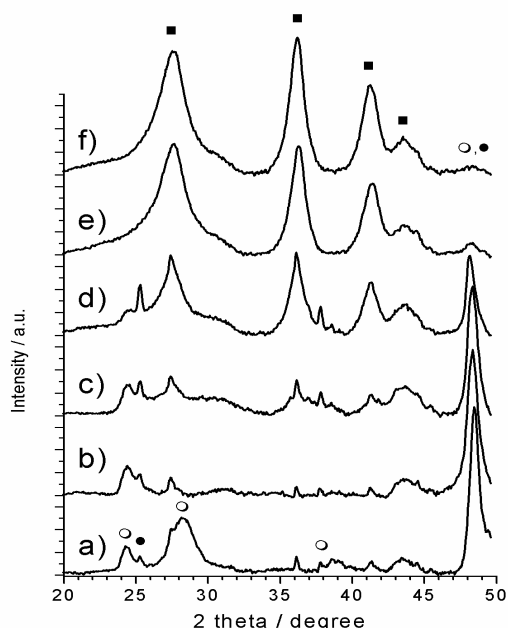


Figure 3. XRD patterns of TiO₂ nanotubes and acid washed samples for different time at room temperature: a) initial sample; b) 5 days; c) 15 days; d) 32 days; e) 2 months; f) 5 months. (■) rutile, (●) anatase and (○) H₂Ti₃O₇ reflections

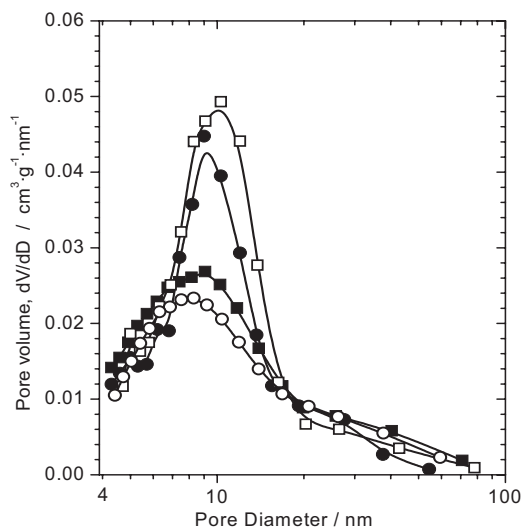
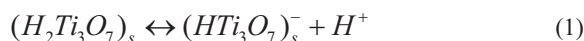


Figure 4. Pore volume distribution (BJH desorption) of TiO₂ nanotubes soaked in 0.1M solutions at room temperature: (■) – initial powder, (●) – 2 months in HNO₃, (○) – 5 months in NaOH, (□) – 2 months in HCl.

The pore size distribution of nanotubes aged for 2 months in HNO₃ and HCl is similar to the pore size distribution of nanotubes aged in H₂SO₄ for 5 and 15 days, respectively.. Thus, it can be estimated that the rate of TiO₂ nanotube transformation in HCl is 4 times (and in HNO₃ 12 times) less than the rate of transformation in H₂SO₄. Such a difference in reaction rate may be attributable to the differences in TiO₂ solubility in different acids which decreases in the order: H₂SO₄ > HCl > HNO₃. The value of pH could also be a key factor that initiates the process of transformation. Since trititanic acid is a weak acid in water, the following dissociation occurs:



This results in a negative zeta potential in water (see Table 1). Addition of NaOH slightly increases the potential due to the adsorption of sodium ions [8,9]. In contrast, addition of 0.1M sulfuric acid significantly increases the zeta potential, resulting in a change of sign for the surface charge, the zeta potential having a small positive value. Probably, excess adsorption of protons from solution onto the surface of nanotubular TiO₂ destabilises the crystal structure of the multilayered trititanic acid, resulting in leaching of the surface TiO₆ octahedrons. A very slow, recrystallization of titania over several months results in formation of the most stable (rutile) phase of TiO₂.

Solution	Time of treatment	S _{BET} / m ² g ⁻¹	V _{BJH} / cm ³ g ⁻¹	Zeta potential / mV
H ₂ O	0 day	199	0.70	-42.69
0.1M H ₂ SO ₄	5 day	240	0.69	6.59
0.1M H ₂ SO ₄	15 day	251	0.69	6.59
0.1M H ₂ SO ₄	32 day	235	0.64	n/a
0.1M H ₂ SO ₄	2 month	184	0.25	n/a
0.1 MH ₂ SO ₄	5 month	246	0.30	n/a
0.1M NaOH	5 month	161	0.56	-36.71
0.1M HCl	2 month	247	0.73	n/a
0.1M HNO ₃	2 month	199	0.55	n/a

Table 1 Change of TiO₂ nanotubes properties during slow transformation in acids and alkali.

4 CONCLUSIONS

The long-term stability of TiO₂ nanotubes in acid, neutral and basic water suspensions was studied. It was found in water and basic (0.1M NaOH) solutions that the TiO₂ nanotubes are stable and undergo minimal morphological changes. In dilute sulfuric acid (0.1M H₂SO₄) suspended TiO₂ nanotubes slowly transform to rutile nanoparticles having an ellipsoid morphology. In 0.1M solutions of HCl and HNO₃ the process of

transformation is several times slower due to the lower solubility of TiO₂ in these acids. Slow recrystallization of TiO₂ nanotubes in acids results in the formation of a rutile phase having a very high surface area (BET N₂ adsorption) of 246 m² g⁻¹.

REFERENCES

- 1 T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Langmuir* **1998**, *14*, 3160-3163
- 2 C.C. Tsai, H. Teng, *Chem. Mater.* **2004**, *16*, 4352-4358
- 3 Z.Y. Yuan, B.L. Su, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **2004**, *241*, 173-183
- 4 O.K. Varghese, D.Gong, M. Paulose, K.G. Ong, C.A. Grimes, *Sensors and Actuators B*, **2003**, *93*, 338-344
- 5 C.H. Lin, C.H. Lee, J.H. Chao, C.Y. Kuo, Y.C. Cheng, W.N. Huang, H.W. Chang, Y.M. Huang and M.K. Shih, *Catalysis Letters*, **2004**, *98*, 61-66
- 6 J. Cao, J.-Z. Sun, H.-Y. Li, J. Hong, M. Wang, *J. Mater. Chem.* **2004**, *14*, 1203-1206
- 7 M. Adachi, Y. Murata, I. Okada, S. Yoshikawa, *J. Electrochemical Society*, **2003**, *150* (8), G488-G493
- 8 X. Sun, Y. Li, *Chem. Eur. J.*, **2003**, *9*, 2229-2238
- 9 J.J. Yang, Z.S. Jin, X.D. Wang, W. Li, J.W. Zhang, S.L. Zhang, X.Y. Guo, Z.J. Zhang, *Dalton Transactions*, **2003**, *20*, 3898-3901
- 10 J. Li, Z. Tang, Z. Zhang, *Electrochemistry Communications*, **2005**, *7*, 62-67
- 11 L. Kavan, M. Kalbac, M. Zikalova, I. Exnar, V. Lorenzen, R. Nesper, M. Graetzel, *Chem. Mater.* **2004**, *16*, 477-485
- 12 D.V. Bavykin, V.N. Parmon, A.A. Lapkin, F.C. Walsh, *J. Mater. Chem.*, **2004**, *14*, 3370
- 13 M. Zhang, Z. Jin, J. Zhang, X. Guo, J. Yang, W. Li, X. Wang, Z. Zhang, *Journal of Molecular Catalysis A: Chemical*, **2004**, *217*, 203-210
- 14 D.V. Kozlov, D.V. Bavykin, E.N. Savinov, *Catalysis Letters*, **2003**, Vol. 86, No. 4, 169-172.
- 15 Q. Chen, G.H. Du, S. L.-M. Zhang Peng, *Acta Cryst. B*, **2002**, *58*, 587-593
- 16 J.J. Yang, Z.S. Jin, X.D. Wang, W. Li, J.W. Zhang, S.L. Zhang, X.Y. Guo, Z.J. Zhang, *Dalton Transactions*, **2003**, *20*, 3898-3901
- 17 M. Yan, F. Chen, J. Zhang, *Chemistry Letters*, **2004**, Vol.33, No.10, 1352-1353
- 18 S. Yin, R. Li, Q. He, T. Sato, *Materials Chemistry and Physics*, **2002**, *75*, 76-80
- 19 S. Yin, S. Uchida, Y. Fujishiro, M. Akib, T. Sato, *J. Mater. Chem.*, **1999**, *9*, 1191-1195