Morphological structure and physicochemical properties of nanotube TiO_2

ZHANG Shunli[1], ZHOU Jingfang[1], ZHANG Zhijun[1], DU Zuliang[1], A.V. Vorontsov[2] & JIN Zhensheng[1]

1. Labaratory of Lubrication and Functional Materials, Henan University, Kaifeng 475001, China;
2. Boreskov Institute of Catalysis, Novosibirsk 630090, Russia
Correspondence should be addressed to Zhang Zhijun or Jin Zhensheng

Abstract Morphological structure and physicochemical properties of nanotube TiO_2 were investigated. It was found that the TiO_2 nanotube consisted of 2—5 monolayers of TiO_2 molecules, and its inner diameter was between 4.2 and 5.9 nm. The nanotube TiO_2 powder had high specific surface area and pore volume (379 m^2/g and 1.431 cm^3/g respectively) and its decolorization activity for Reactive Brilliant Red X-3B was 2 times higher than that of raw TiO_2 (p-25). This new type of TiO_2 was hopeful for application in photocatalysis and composite nanomaterial.

Keywords: nanomaterial, nanotube, titania, photocatalyst, decolorization of reactive dye.

TiO_2 has widely drawn increasing attention in its use as a catalyst or as a support in environmental photocatalysis. A main limitation to the use of TiO_2 obtained by conventional methods is its low surface area. There are some ways to be studied for obtaining TiO_2 with larger surface area, e.g. using surfactant tetradecylphosphate[1] and biopolymer chistosan[2] as template to synthesize mesoporous TiO_2, and using the supercritical drying method to prepare aerogel TiO_2[3]. Recently, some people developed methods to deposit titania sol within the pores of template membrane (such as alumina membrane) to produce tube type of TiO_2, but the tube diameter is larger (ca. 200 nm). In this note, the morphological structure and physicochemical properties of nanotube TiO_2, synthesized after Kasuga's work[4], were investigated. The results showed that this type of nanotube TiO_2 had larger surface area and smaller size than those of mesoporous and tube type TiO_2, synthesized by Hoyer[5] and Lakshmi et al.[6].

1 Experiment

Degussa TiO_2 was used as the raw material for preparation of nanotube TiO_2. Transmission electron microscopy (TEM), energy dispersion spectroscopy (EDS) analysis, and electron diffraction (ED) of raw TiO_2 and nanotube TiO_2 were carried out with JEM 1200EX/S apparatus. High resolution transmission electron microscopy (HRTEM) patterns (1.25×10^6) of nanotube TiO_2 were taken in Boreskov Institute of Catalysis, Russia. BET surface area and BJH pore volume were determined with ASAP 2010 apparatus (produced by Micromeritics). Fourier transform infrared spectra (FTIR) and UV-visible diffuse reflectance spectra (DRS) were obtained on Nicolet Avatar 360 and Hitachi 2010, respectively.

2 Results and discussion

TEM photographs of raw TiO_2 and nanotube TiO_2 are shown in fig 1. Nanotube sample A was calcined at 500℃ for 5 h in air (fig.1(b)), nanotube sample B was dried at ~100℃ (fig. 1(c)). The nanotube length of sample B is ca. 500 nm (fig.1(d)), its observed layer number is less than that of sample A and its picture contrast is not so striking as that of sample A (fig. 1(b, c)). It can be seen that the nanotube structure of sample A calcined at 500℃ is not destroyed, but the local sintering and twisting has happened (fig. 1(b)). All of the nanotubes are open and consist of 2—5 monolayers of TiO_2 molecule, and their schematic diagrams are shown in fig. 2. The parameters of the morphological structure of TiO_2 nanotube calculated according to fig. 1(b, c) are listed in table 1. The thickness of one monolayer equals 0.2— 0.3 nm, and it closes to the diameter of anion O^{2-}, which indicates that each monolayer represents a TiO_2 molecular layer. The nano tube inner diameter varies with the monolayer number: 5.9 nm for double layer nanotube and 4.2 nm for five layer nanotube (fig. 2). Therefore, this

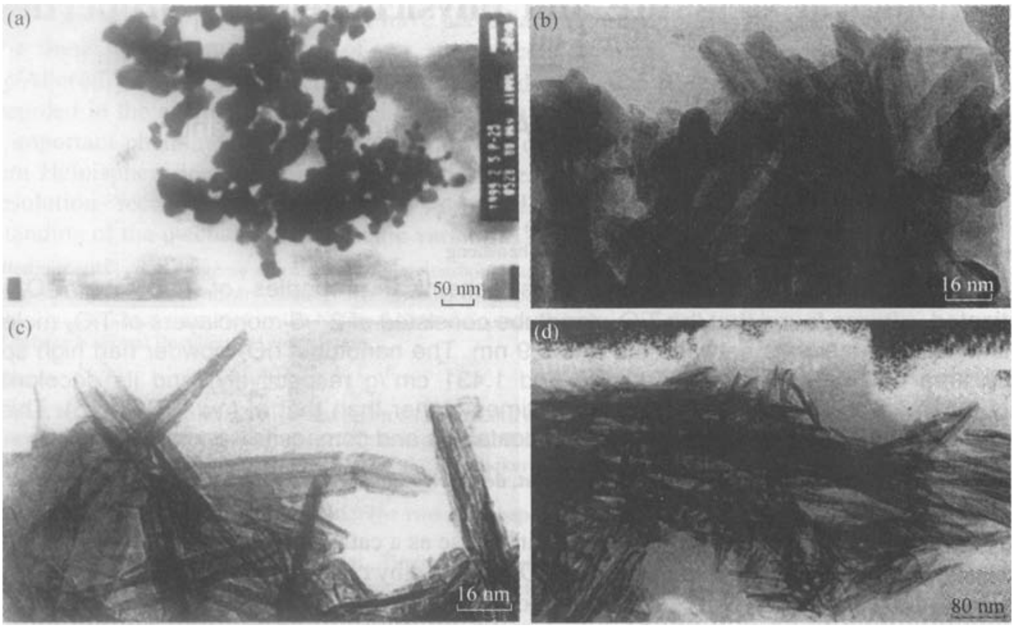

Fig. 1. TEM pictures of (a) raw TiO_2 (×10^5), (b) sample A (×1.25×10^6), (c) sample B (×1.25×10^6) and (d) sample B (×2.5×10^5).

type of TiO_2 provided a new precursor for assembling composite materials, i.e. some nanosized metal particle or inorganic particle could be inserted in it. XRD patterns show that the crystalline form of raw TiO_2 was anatase-rutile (ratio of content of anatase and rutile form was ca. 4 : 1) (fig. 3-1) and nanotube TiO_2 dried at ca.100℃ was converted into amorphous (fig. 3-3). However, when calcined at 500℃, nanotube TiO_2 was turned into anatase-rutile form again while the ratio was 5 : 1 (fig. 3-2), insert figure was the ED pattern of sample A.) Generally, atoms can deviate from their natural positions when some microstress exists in crystalline[7, 8]. Thus, the formation of TiO_2 nanotube resulted from the alteration of TiO_2 microstucture. When calcined at 500℃, the deviated atoms relaxed further and formed a new structure. It is noted that comparing to raw TiO_2, all diffractive peaks of sample A were broadened obviously and the best strong peak representing anatase structure varied from 0.3525 to 0.3509 nm while some peaks did not move, which indicated that some crystal plane change caused TiO_2 to be turned from nanoparticle to nanotube.

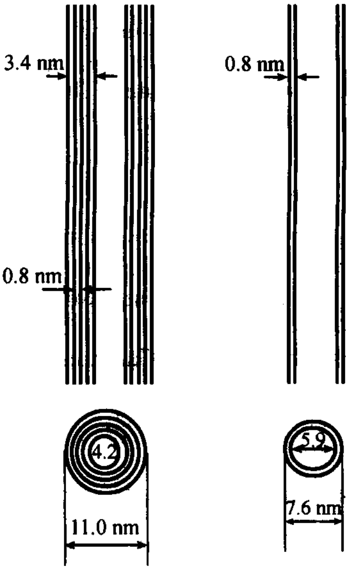

Fig. 2. Schematic diagrams of five and two layers of TiO_2 tube.

Table 1 Morphological structure of TiO_2 nanotube

	Double-layer tube/nm	Five-layer tube/nm
Outside diameter	7.6	11.0
Inner diameter	5.9	4.2
Thickness of tube	0.8	3.4
Distance between two layers	0.8	0.8
Thickness of monolayer	0.2—0.3	0.2—0.3

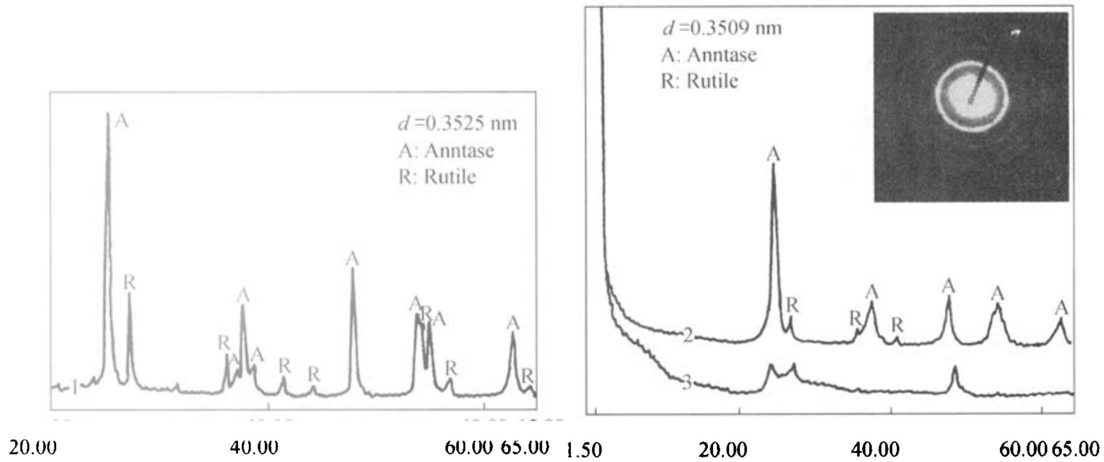

Fig. 3. XRD patterns of raw TiO_2(1), sample A (2) and sample B (3) (insert is ED pattern of sample A).

After being transformed from nanoparticle into nanotube, the surface area of TiO_2 was greatly increased (table 2). The surface area of sample A and sample B was 3.2 and 7.6 times larger than that of raw TiO_2 respectively, while EDS analysis showed that their atomic composition was identical (table 2). In addition, the FTIR spectra of raw TiO_2 (with two Ti-O-Ti stretching vibration bands 660 cm^{-1} and 500 cm^{-1}) (fig. 4-1) also changed. 660 cm^{-1} band became a shoulder and 500 cm^{-1} band protruded for sample B (fig. 4-3); 660 cm^{-1} and 500 cm^{-1} bands connected with each other and red-shifted for sample A (fig. 4-2). This showed that the Ti-O bond length changed with the morphological structure of TiO_2. DRS spectra are shown in fig 5, λ_{onset} of sample A and raw TiO_2 was the same, but the absorption of <405 nm slightly red-shifted, and the absorption curve of sample B blue-shifted relative to that of raw TiO_2. All the above results revealed that the electronic interaction between atoms of TiO_2 was influenced while the morphological structure changed.

Table 2 Specific surface area, pore volumes, atomic composition of raw TiO_2 and samples A and B

	Raw TiO_2	Sample A	Sample B
BET surface area, m^2/g	50	159	379
BJH pore volume, cm^3/g		0.798	1.431
EDS analysis (oxygen free base)	Ti 99.0 Si 0.7 others 0.3	Ti 98.2 Si 0.4 Ca 0.9* others 0.5	

* Possibly introduced during preparation.

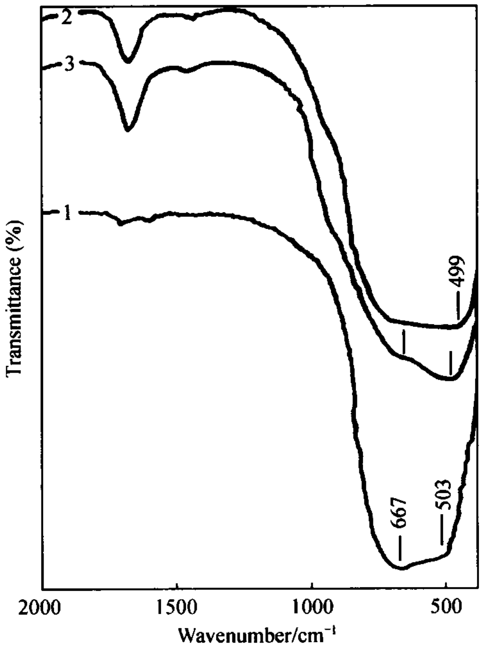

Fig. 4. FT-IR spectra of (1) raw TiO_2, (2) sample A, and (3) sample B.

So far, the mechanism of the formation of TiO_2 nanotube is unknown yet. However, the properties of this new type of TiO_2 in photocatalysis, photoelectronics, absorption and

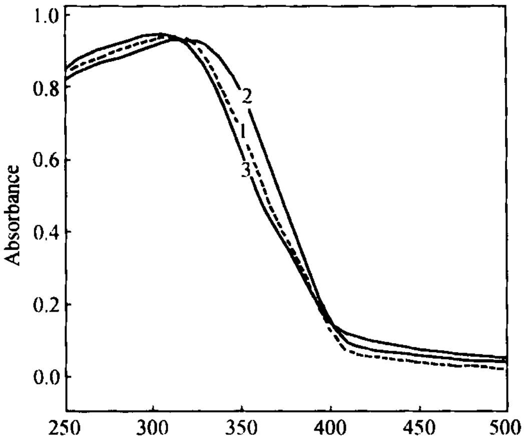

Fig. 5. UV-Vis diffuse reflective spectra of raw TiO_2 (1), sample A (2) and sample B (3).

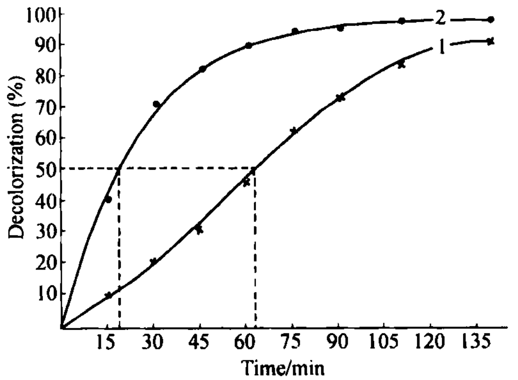

Fig. 6. Photocatalyze-decolorization comparison of raw TiO_2 (1) and sample A for active Reactive Brilliant Red X-3B (2) (50 mL dye solution, 100 mg photocatalyst and 250 W mercury lamp were used; The distance between the light source and reaction bottle was 15 cm, kept on stirring).

composite material are worth studying at first. Fig. 6 indicates the preliminary results of its photocatalytic decolorization activity for dye Reactive Brilliant Red X-3B, which showed that the activity of nanotube TiO_2 increased ca. 3-fold higher than that of raw TiO_2 (half life period: 20 and 62 min for sample A and raw TiO_2 respectively).

3 Conclusion

Nanotube TiO_2, provided by College of Chemistry and Chemical Engineering, Henan University, consisted of 2—5 monolayers of TiO_2 molecules, its inner diameter was 4.2—5.9 nm and its surface area was 3.2—7.6 times larger than that of raw TiO_2. Before calcined at 500℃, the length of TiO_2 nanotube was ca. 500 nm.

After transformation from solid particle to nanotube, the crystalline form of TiO_2 changed from anatase-rutile into amorphous, then turned again into anatase-rutile after calcined at 500℃ in air.

Nanotube TiO_2 —— a new type of material is worth studying further for its fundamental basis and practical applications.

Acknowledgements The authors would like to express their thanks to Prof. Zhao Jiazheng, Associate Prof. He Li, Engineer Li Meiyi, Dr. Yu. L. Chuvilin, Master Sun Fuxia for their help with the measurements and discussion on some results.

References

1. Antonelli, D. M., Ying, J. Y., Synthesis of hexagonally packed mesoporous TiO_2 by a modified sol-gel method, Angew. Chem. Int. Ed. Engl., 1995, 34(18): 2014.
2. Retuert, J., Quijada, R., Arias, V., Porous titania obtained through polymer incorporated composites, Chem. Mater., 1998, 10: 3923.
3. Gesser, H. D., Goswami, P. C., Aerogels and related porous materials, Chem. Rev., 1989, 89: 765.
4. Kasuga, T., Hiramatsu, M., Hoson, A. et al., Formation of titanium oxide nanotube, Langmuir, 1998, 14: 3160.
5. Hoyer, P., Formation of titanium dioxide nanotube array, Langmuir, 1996, 12: 1411.
6. Lakshmi, B. B., Dorhout, P. K., Martin, C. R., Sol-gel template synthesis of semiconductor nanostructures, Chem. Mater., 1997, 9: 857.
7. Cong Qiuzhi, Two dimensional X-ray Diffraction of Polycrystals, Beijing: Science Press, 1997, 211.
8. Langford, J. I., Delhez, R., de Keijser, Th. H. et al., Profile analysis for microcrystalline properties by the Fourier and other methods, Aust. J. Phys. 1988, 41: 173.
9. Yamashita, H., Kawasaki, S., Ichihashi, Y. et al., Characterization of titanium-silicon binary oxide catalysts prepared by the sol-gel method and their photocatalytic reactivity for the liquid-phase oxidation of 1-octanol, J. Phys. Chem. B., 1998, B102: 5870.

(Received February 15, 2000)