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氏名：久保 敬

所属：大阪府立大学 大学院工学研究科

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“Structural evaluation of fibrous titania with tubular structure prepared by modified hydrothermal method”

### Introduction

The syntheses of materials with various nanoscale spaces are currently under intensive investigation. Since carbon nanotubes, which have novel properties unlike those of either graphite or fullence, were discovered by Iijima,<sup>1</sup> various syntheses of micro- and nanotubes of TiO<sub>2</sub> have been attempted by various method such as template methods.<sup>2-4</sup> Recently, Kasuga et al. treated TiO<sub>2</sub> in the 10 M NaOH aqueous solution for 20 h at 383 K without the need for molds for replication or template and nanotubes with 8 nm in diameter and 100 nm in length<sup>5</sup> were obtained by their experiments. These titania-derived nanotubes are notable nanoscale-materials because of their nanotubular structures and high surface areas.<sup>6-13</sup> Therefore, several application studies on such as electrochromism,<sup>14</sup> bone regeneration,<sup>15</sup> proton conduction,<sup>16</sup> photoinduced hydrophilicity,<sup>17</sup> photocatalysts,<sup>18-21</sup> and dye-sensitizing solar batteries<sup>22</sup> have been conducted by many researchers. This simple and low-cost synthetic method may be applied in the fabrication of other oxide nanotubes. After this report, many groups have investigated about the structure, formation mechanism, or synthetic condition for the nanotubular product. Recently, the products with various morphologies were obtained by modifying synthetic conditions for this hydrothermal process. Nanowires was obtained by hydrothermal process from anatase and successively post heat-treatment.<sup>23</sup> Yuan and co-workers found that the nanofiber was prepared when anatase was prepared by static hydrothermal treatment at 523 K.<sup>24</sup>

In this study, a rotary-hydrothermal method as a novel synthetic process was used to synthesize a new type of nanotube. Commercial anatase-type titania were conventional static or rotary-hydrothermally treated in 10 M NaOH aqueous solution at 383 to 473 K. The structural investigation of obtained products by various processes was analyzed by various methods, such as a scanning electron microscopy (SEM), a transmission electron microscopy (TEM), and high energy X-ray diffraction (HEXRD).

### Experimental

As a starting material, two grams of anatase-type titania (Kojundo Chem., Japan) were used. They were added in a NaOH aqueous solution (15 ml) with the concentration of 10 M. Then the specimens were treated under conventional static-hydrothermal reaction or rotary-hydrothermal reaction at 383 to 423 K for 48 h to 96 h. The speed of rotation for a

rotary-hydrothermal treatment was 20 revolutions per minute (rpm). Obtained products after these treatments were washed with de-ionized water, filtered, and dried at temperatures above 323 K in an oven for 12 h.

Various microstructural analyses were performed by a scanning electron microscopy (FE-SEM: S-4500, Hitachi, Japan) with accelerating voltage of 15 kV and a transmission electron microscopy (TEM: JEM2010/SP, JEOL) with accelerating voltage of 200 kV.

The HEXRD experiments were carried out at the bending magnet beamline, BL04B2 of SPring-8 with a two-axis diffractometer for disordered materials. Incident photon energy of 61.6 keV ( $\lambda = 0.20 \text{ \AA}$ ) was obtained from a bent Si (220) crystal. Diffraction runs were conducted at room temperature under vacuum conditions. The recorded data were normalized for flux, corrected for background, Compton scattering, and absorption, and then converted to total structure factor,  $s(Q)$ . The  $Q$  value is determined by the following equation:

$$Q = \frac{4\pi \sin \theta}{\lambda}$$

To get information in real space, total correction functions,  $T(r)$ , were calculated from the weighted interference functions,  $Q[s(Q)-1]$ , by Fourier transformation up to  $Q_{\max} = 25 \text{ \AA}^{-1}$

$$T(r) = 4\pi\rho r + \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} M(Q)Q[s(Q)-1]\sin(Qr)dQ$$

where  $\rho$  is the total number density and  $M(Q)$  is a Lorch modification function to reduce termination effects arising from the finite upper limit of  $Q$ .

## Results and discussion

Fig 1 show typical TEM images of the product prepared by a static-hydrothermal treatment of commercial anatase-type titania at 383 K for 96 h in 10 M NaOH aqueous solution. As shown in Fig. 1 (a), the obtained product possessed nanotubular structures with about 10 nm in outer diameter and 5 nm in inner diameter and a few hundred nm in length, and they were open-end with several wall layers on both sides. The measured interlayer spacing was about 0.90 nm. Moreover, it was found that the obtained nanotubular product had a scroll structure as shown in Fig. 1 (b). Thus, titania-derived nanotubes were prepared by the static-hydrothermal treatment of commercial anatase-type titania at 383 K for 96 h in 10 M NaOH aqueous solution.

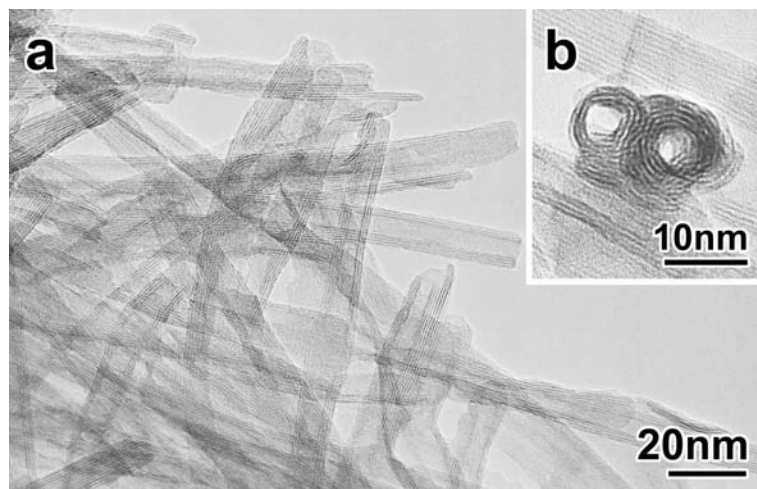


Fig. 1 TEM images of the product prepared by the hydrothermal treatment of commercial anatase-type  $\text{TiO}_2$  powder at 383 K for 96 h and the subsequent washing treatment.

Fig. 2 shows SEM and TEM images of the products prepared by rotary-hydrothermal treatments of anatase with 10 M-NaOH aqueous solution for 48 h at 383 and 423 K. From SEM observation, it was found that the nanowhisker-shaped product and the nanofiber-shaped product were obtained when anatase was prepared by rotary hydrothermal treatment at 383 K. In the case of rotary hydrothermal treatment at 423 K, the morphologies of obtained products completely were nanofiber-like. According to TEM observation, this fiber-shaped product had tubular structures with 10-50 nm in width and several hundreds micron in length. Thus, fibrous titania with tubular structures were successfully synthesized by the rotary-hydrothermal process.

Fig. 3 shows the total correlation functions,  $T(r)$ , of titania derived nanotubes prepared by the static-hydrothermal treatment, fibrous titania with tubular structures prepared by the rotary-hydrothermal treatment, and anatase as a starting material. As shown in Fig. 3,  $T(r)$  of titania nanotubes was obviously different from that of anatase as a starting materials. In particular, the nearest Ti-O peak for anatase was sharp, and the Ti-O distance and its average coordination number of anatase were approximately 1.96 Å, respectively. On the other hand, the nearest Ti-O peak for the nanotubular product was broad, and its distance was 1.93 Å. It is considered that the shift of the nearest Ti-O peak toward smaller distances and the difference of the peak geometry are due to highly distorted  $\text{TiO}_6$  octahedra. On the other hand,  $T(r)$  of fibrous titania with tubular structures prepared by the rotary-hydrothermal process was very similar to that of titania nanotubes. This result showed that these fibrous titania with tubular structures prepared by the rotary-hydrothermal process could have the almost same crystalline structure as titania derived nanotubes prepared by the static-hydrothermal process.

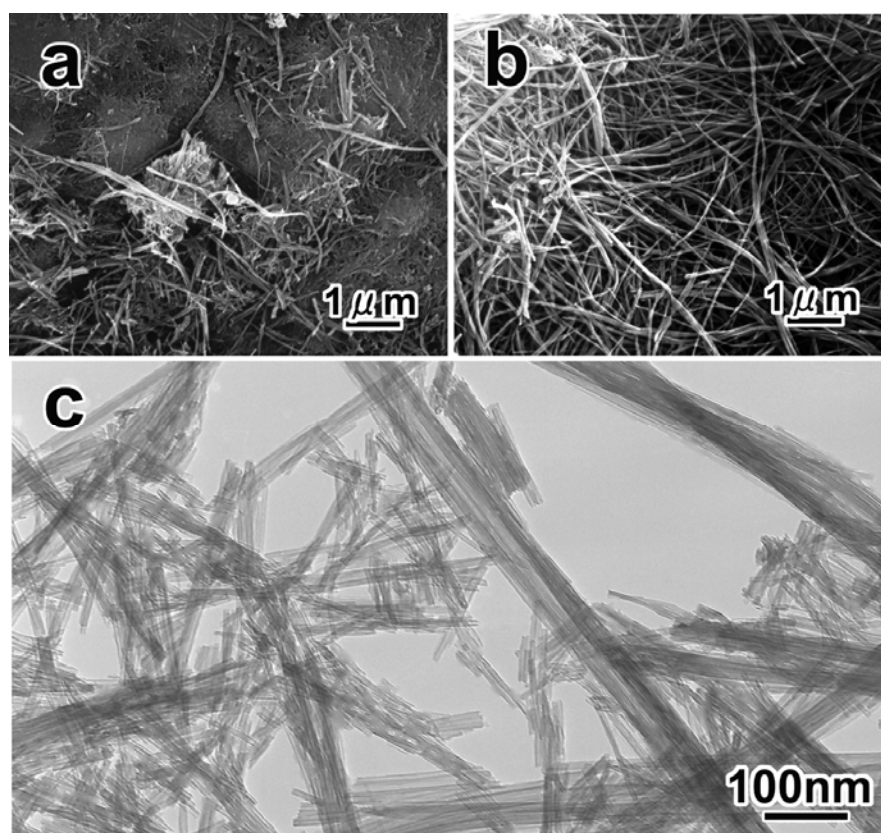


Fig. 2 SEM images of products prepared by rotary-hydrothermal treatments of anatase-type  $\text{TiO}_2$  for 48 h at (a) 383 and (b) 423 K. (c) shows TEM image of (b)

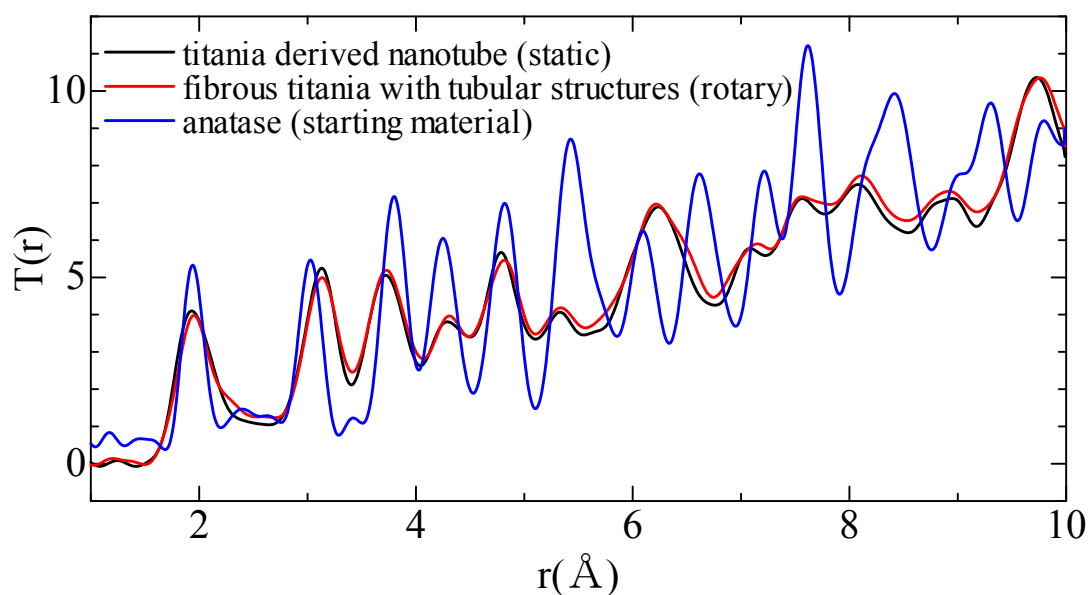


Fig. 3  $T(r)$  of titania derived nanotubes prepared by the static-hydrothermal treatment, fibrous titania with tubular structures prepared by the rotary-hydrothermal treatment, and anatase as a starting material.

### Summary

Titania derived products with various morphologies were synthesized by the hydrothermal method for anatase-type titania in NaOH aqueous solution systems at low temperatures and for short time in this study. The titania derived nanotubular product with approximately 10 nm in outer diameter and approximately 5 nm in inner diameter was obtained by the static-hydrothermal treatment of anatase. In the case of the rotary hydrothermal process, the obtained product had fiber-like morphology. According to TEM observation, this fiber-shaped product possessed tubular structures with 10-50 nm in width and several hundreds micron in length. Moreover, HEXRD result showed that these fibrous titania derived products with tubular structures prepared by the rotary-hydrothermal process could have the almost same crystalline structure as titania derived nanotubes prepared by the static-hydrothermal process. Thus, these results suggested that the diameter and length of nanotubes and the morphology could be controlled by this process, leading to development of useful materials for several applications.

### References

1. S. Iijima, *Nature*, **354** (1991) 56.
2. P. M. Ajayan, O. Stephan, P. Redlich, and C. Colliex, *Nature*, **375** (1995) 564.
3. P. Hoyer, *Langmuir*, **12** (1996) 1411.
4. H. Imai, Y. Takei, K. Shimizu, M. Matsuda, and H. Hirashima, *J. Mater. Chem.*, **9** (1999) 2971.
5. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, and K. Niihara, *Langmuir*, **14** (1998) 3160.

6. Q. Chen, G. H. Du, S. Zhang, and L. M. Peng, *Acta Crystallogr. B*, **58** (2002) 587.
7. Q. Chen, W. Zhou, G. Du, and L. M. Peng, *Adv. Mater.* **14** (2002) 1208.
8. X. Sun and Y. Li, *Chem. Eur. J.* **9** (2003) 2229.
9. A. Nakahira, W. Kato, M. Tamai, T. Isshiki, K. Nishio, and H. Aritani, *J. Mater. Sci.* **39**(2004) 4239.
10. T. Kubo, W. Kato, Y. Yamasaki, and A. Nakahira, *Key Eng. Mater.* **317&318** (2006) 247.
11. T. Kubo, Y. Yamasaki, and A. Nakahira, *J. Ion Exchange* **18** (2007) 310.
12. T. Kubo, Y. Yamasaki, and A. Nakahira, *J. Mater. Res.* **22** (2007) 1286.
13. T. Kubo and A. Nakahira, *J. Phys. Chem. C* **112** (2008) 1658.
14. H. Tokudome and M. Miyauchi, *Angew. Chem. Int. Ed.* **44** (2005) 1974.
15. S. Kubota, K. Johkura, K. Asanuma, Y. Okouchi, N. Ogiwara, K. Sasaki, and T. Kasuga, *J. Mater. Sci.: Mater. Med.* **15** (2004) 1031.
16. A. Thorne, A. Kruth, D. Tunstall, J. T. S. Irvine, and W. Zhou, *J. Phys. Chem. B* **109** (2005) 5439.
17. H. Tokudome and M. Miyauchi, *Chem. Comm.* 958 (2004).
18. M. Adachi, Y. Murata, M. Harada, and S. Yoshikawa, *Chem. Lett.* **29** (2000) 942.
19. T. Akita, M. Okumura, K. Tanaka, K. Ohkuma, M. Kohyama, T. Koyanagi, M. Date, S. Tsubota, and M. Haruta, *Surf. Interface. Anal.* **37** (2005) 265.
20. A. Nakahira, T. Kubo, Y. Yamasaki, T. Suzuki, and Y. Ikuhara, *Jpn. J. Appl. Phys.* **44** (2005) 690.
21. T. Kubo, H. Nagata, M. Takeuchi, M. Matsuoka, M. Anpo, and A. Nakahira, *Res. Chem. Intermed.* **34** (2008) 339.
22. S. Uchida, R. Chiba, M. Tomiha, N. Masaki, and M. Shirai, *Electrochemistry* **70** (2002) 418.
23. M. Zhang, Z. S. Jin, J. J. Yung, and Z. J. Zhang, *J. Molec. Catal. A: Chem.*, **217** (2004) 203.
24. Z. Y. Yung and B. L. Su, *Colloids Surf. A*, **241** (2004) 173.