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Communications

Shape-Controlled Synthesis of ZrO_2, Al_2O_3, and SiO_2 Nanotubes Using Carbon Nanofibers as Templates

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Since the discovery of carbon nanotubes,[1] the design and synthesis of nanoscale materials such as nanotubes, nanowires, nanoparticles, and nanoribbons have been vigorously investigated. In particular, nanotubular materials have drawn increasing attention due to their specific mechanical, electrical, and chemical properties.[2−4] The template approach is a representative synthesis method for oxide nanotubes. Porous anodic alumina,[5] organogels,[6] hydrogels,[7] cholesterol nanotubes,[8] carbon nanotubes,[9−11] and crystalline nanowires[12] have been used as templates. Oxide nanotubes are synthesized by the coating of these templates with oxide, followed by the removal of them.

The advantage of template method is that shapes of formed nanotubes can be controlled by those of templates. For example, SiO_2 nanotubes with various shapes have been synthesized.[13,14] However, except for SiO_2, there have been few investigations in shape-controlled synthesis of oxide nanotubes. One of the reasons for the difficulty in shape-controlled synthesis of various oxide nanotubes would be that there is a limited template with various nanoscale structures. Until now, only organogels were used as templates for the shape-controlled synthesis of oxide nanotubes.

Here, we report a simple shape-controllable synthesis of oxide nanotubes (ZrO_2, Al_2O_3, and SiO_2) using carbon nanofibers as templates. Recently, carbonaceous matareials have been utilized as templates for the preparation of nanoscale materials. For example, mesoporous spheres of metal oxides and zeolite ZSM-5 with unique supermicropores were synthesized using mesoporous carbons,[15,16] and hollow metal oxide fibers with hierarchical architecture were syn-

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(1) Iijima, S. *Nature* **1991**, *354*, 56−58.
(2) Patzke, G. R.; Krumeich, F.; Nesper, R. *Angew. Chem. Ind. Ed.* **2002**, *41*, 2446−2461.
(3) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353−389.
(4) Caruso, R. A.; Antonietti, M. *Chem. Mater.* **2001**, *13*, 3272−3282.
(5) Mitchell, D. T.; Lee, S. B.; Trofin, L.; Li, N.; Nevanen, T. K.; Söderlund, H.; Martin, C. R. *J. Am. Chem. Soc.* **2002**, *124*, 11864−11865.
(6) Ono, Y.; Nakashima, K.; Sano, M.; Kanekiyo, Y.; Inoue, K.; Hojo, J.; Shinkai, S. *Chem. Commun.* **1998**, 1477−1478.
(7) Gundiah, G.; Mukhopadhyay, S.; Tumkurkar, U. G.; Govindaraj, A.; Maitra, U.; Rao, C. N. R. *J. Mater. Chem.* **2003**, *13*, 2118−2122.
(8) Jung, J. H.; Lee, S-H.; Yoo, J. S.; Yoshida, K.; Shimizu, T.; Shinkai, S. *Chem. Eur. J.* **2003**, *9*, 5307−5313.
(9) Rao, C. N. R.; Satishkumar, B. C.; Govindaraj, A. *Chem. Commun.* **1997**, 1581−1582.
(10) Satishkumar, B. C.; Govindaraj, A.; Vogl, E. M.; Basumallick, L.; Rao, C. N. R. *J. Mater. Res.* **1997**, *12*, 604−606.
(11) Satishkumar, B. C.; Govindaraj, A.; Nath, M.; Rao, C. N. R. *J. Mater. Chem.* **2000**, *10*, 2115−2119.
(12) Naito, S.; Ue, M.; Sakai, S.; Miyao, T. *Chem. Commun.* **2005**, 1563−1565.
(13) Bommel, K. J. C.; Friggeri, A.; Shinkai, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 980−999.
(14) Ogihara, H.; Takenaka, S.; Yamanaka, I.; Tanabe, E.; Genseki, A.; Otsuka, K. *Chem. Mater.* **2006**, *18*, 996−1000.
(15) Dong, A.; Ren, N.; Tang, Y.; Wang, Y.; Zhang, Y.; Hua, W.; Gao, Z. *J. Am. Chem. Soc.* **2003**, *125*, 4976−4977.
(16) Yang, Z.; Xia, Y.; Mokaya, R. *Adv. Mater.* **2004**, *16*, 727−732.

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thesiezed using activated carbon fibers as templates.[17] Carbon nanofiber is well-known as one of the nanoscale carbonaceous materials.[18] A large amount of them can be produced by the decomposition of hydrocarbons or carbon monoxide over Ni, Co, or Fe catalysts. In addition, straight, bent, thin, and helical carbon nanofibers can be produced by the control of reaction conditions.[19−21] If these carbon nanofibers with different shapes could be used as templates, oxide nanotubes with a variety of structures would form.

Carbon nanofibers used as templates in the present study are as follows: VGCF (vapor grown carbon fibers, Showa Denko Co.), CNC1 (carbon nanocoils, Microphase Co., Ltd.), CNC2 (carbon nanocoils manufactured in Takikawa Laboratory, Toyohashi Campus Innovation Inc.), and CNT (carbon nanotubes produced through the propane decomposition over Fe/Al_2O_3 catalysts at 973 K, homemade). These templates were placed in a suction filtering unit (Buchner funnel with filter paper), and a precursor diluted with organic solvent ($Zr(O^nPr)_4$ (150 mM) in C_2H_5OH, $Al(O^{sec}Bu)_3$ (150 mM) in CCl_4, or $SiCl_4$ (500 mM) in CCl_4) was dropped into the carbon nanofiber templates. Immediately, precursor solution infiltrated into the space of the fibrous structure. Excess precursor solution was removed by filtration. Obtained samples were dried in air at 393 K (for the synthesis of ZrO_2 and Al_2O_3 nanotubes) or with the air flow at 293 K (for the synthesis of SiO_2 nanotubes). By this drying process, C_2H_5OH or CCl_4 present in the space of the fibrous structure was vaporized. The precursor remained and was adsorbed on the surface of the templates. The precursor adsorbed on the templates was immediately hydrolyzed by the water vapor in air. Consequently, the carbon nanofiber templates were covered with a thin oxide and hydroxide. This coating process was repeated 10−40 times. The carbon nanofiber templates were removed by the calcination in air at 1023 K for 4 h.

First, synthesis of straight nanotubes using VGCF as templates was investigated. Figure 1a shows a TEM image of VGCF templates. The shape of VGCF was straight, and most of their diameters ranged between 100 and 200 nm. Figure 1b−d shows TEM images of ZrO_2, Al_2O_3, and SiO_2 nanotubes formed using VGCF as the template, respectively. TEM images strongly suggested that the shapes of nanotubes were similar to those of VGCF templates. The shapes of formed nanotubes were straight, and their inner diameters were ranged from ca. 100 to 200 nm. Wall thickness of ZrO_2 nanotube was ca. 30 nm, and that of Al_2O_3 and SiO_2 nanotubes was 10−20 nm. Wall thickness of nanotubes could be controlled by the number of coating processes. The yields of ZrO_2, Al_2O_3, and SiO_2 nanotubes (i.e., the weight of obtained of oxide nanotubes normalized to the weight of used VGCF template) were 1.8, 0.58, and 0.98, respectively. In addition, most of the formed oxide had nanotubular structure, indicating that hydrolysis of precursors occurred only on the surface of the VGCF templates.

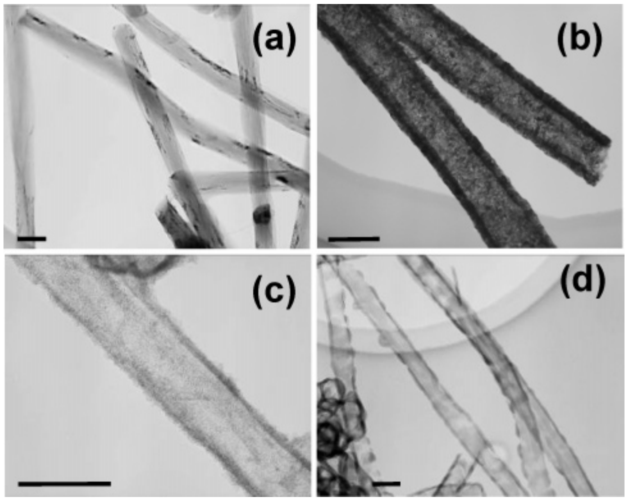

Figure 1. TEM images of (a) VGCF, (b) ZrO_2 nanotubes, (c) Al_2O_3 nanotubes, and (d) SiO_2 nanotubes. The number of coating processes is 20. The scale bars represent 200 nm.

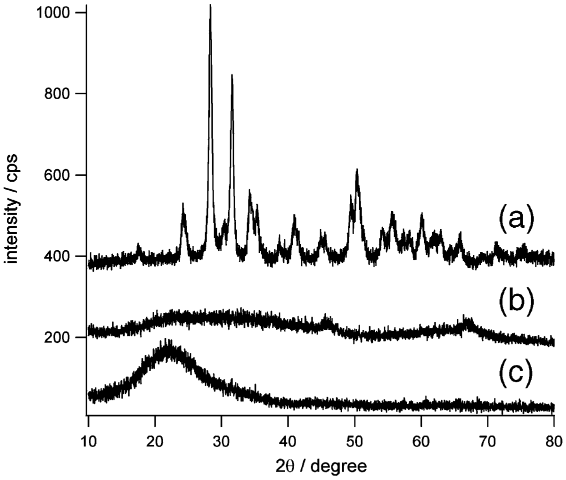

Figure 2. XRD patterns of (a) ZrO_2, (b) Al_2O_3, and (c) SiO_2 nanotubes.

To investigate the crystal structure of nanotubes, X-ray diffraction patterns (XRD) were measured. Figure 2 shows XRD patterns of ZrO_2, Al_2O_3, and SiO_2 nanotubes. From the XRD pattern of ZrO_2 nanotubes, it is clear that most of them are monoclinic structure and that a small amount of them are tetragonal structure.[22,23] In the case of Al_2O_3 nanotubes, very weak diffraction lines corresponding to γ-Al_2O_3 were confirmed,[24] indicating that walls of Al_2O_3 nanotubes consist of small crystallites of γ-Al_2O_3. In the case of SiO_2 nanotubes, clear peaks were not confirmed; that is, their walls are amorphous. Specific surface areas of nanotubes were estimated through nitrogen adsorption at liquid N_2 temperature. Specific surface areas of ZrO_2, Al_2O_3, and SiO_2 nanotubes are 30, 263, and 22 m^2/g, respectively. The crystallite size for ZrO_2 nanotubes calculated using their specific surface area (18 nm) is almost same as that estimated by Scherrer's equation using XRD patterns (20 nm).

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(17) Yuan, R.; Fu, X.; Wang, X.; Liu, P.; Wu, L.; Xu, Y.; Wang, X.; Wang, Z. *Chem. Mater.* **2006**, *18*, 4700−4705.

(18) de Jong, K. P.; Geus, J. W. *Catal. Rev. Sci. Eng.* **2000**, *42*, 481−510.

(19) Takenaka, S.; Shigeta, Y.; Tanabe, E.; Otsuka, K. *J. Phys. Chem. B* **2004**, *108*, 7656−7664.

(20) Yang, S.; Chen, X.; Kusunoki, M.; Yamamoto, K.; Iwanaga, H.; Motojima, S. *Carbon* **2005**, *43*, 916−922.

(21) Otsuka, K.; Kobayashi, S.; Takenaka, S. *Appl. Catal. A* **2001**, *210*, 371−379.

(22) Bhagwat, M.; Ramaswamy, V. *Mater. Res. Bull.* **2004**, *39*, 1627−1640.

(23) Srinivasan, R.; Hubbard, C. R.; Cavin, O. B.; Davis, B. H. *Chem. Mater.* **1993**, *5*, 27−31.

(24) Luo, M.-F.; Fang, P.; He, M.; Xie, Y.-L. *Phys. Status Solidi A* **2006**, *203*, 2065−2072.

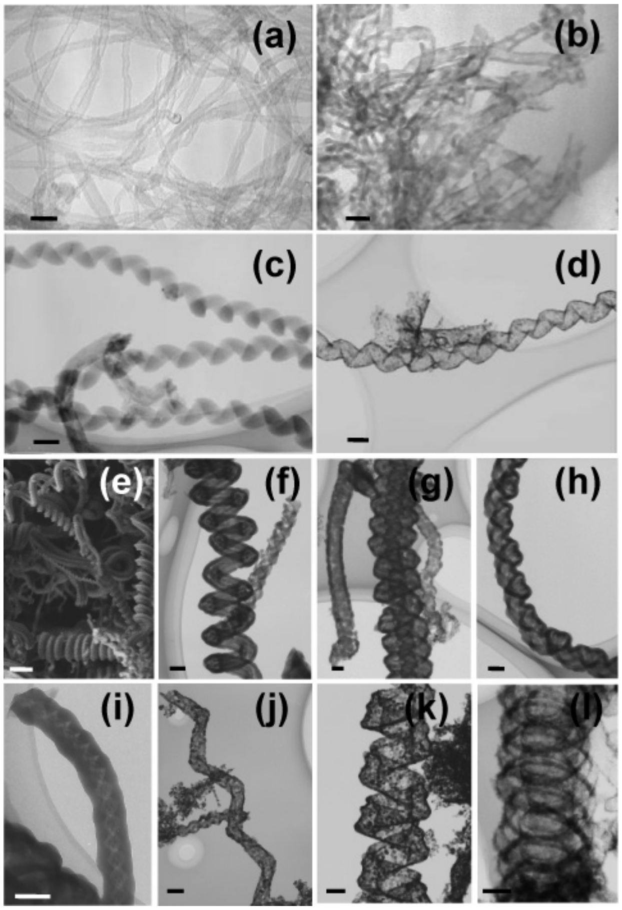

Figure 3. TEM and SEM images of (a) CNT, (b) ZrO_2 nanotubes synthesized using CNT (the number of coating processes is 40), (c) CNC1, (d) ZrO_2 nanotubes synthesized using CNC1 (the number of coating processes is 40), (e) CNC2, (f−i) SiO_2 nanotubes synthesized using CNC2 (the number of coating processes is 20), (j and k) ZrO_2 nanotubes synthesized using CNC2 (the number of coating processes is 10), and (l) Al_2O_3 nanotubes synthesized using CNC2 (the number of coating processes is 20). The scale bars shown in panels a and b; e; and c, d, and f−l represent 30 nm, 1 μm, and 200 nm, respectively.

Figure 3a shows a TEM image of CNT templates. The shapes of CNT were bent, and they were 10−15 nm in diameter. The inner diameters of ZrO_2 nanotubes formed using CNT were 10−15 nm (Figure 3b). As mentioned above, oxide nanotubes formed using VGCF as templates were 100−200 nm in inner diameter. These results strongly suggest that the inner diameter of oxide nanotubes can be controlled by the diameters of carbon nanofiber templates. By the way, the wall thickness of ZrO_2 nanotubes in Figure 3b is smaller than that in Figure 1b. However, the number of coating cycles for the sample in Figure 3b was larger than that in Figure 1b. This could be explained due to the difference of diameter of templates. The proportion of surface to bulk of carbon nanofiber changes as a function of their diameter. Therefore, it is considered that the wall of formed oxide nanotubes would thicken as the diameter of carbon nanofiber becomes larger. CNT templates have a smaller diameter than VGCF templates. This would be the reason why the wall thickness of ZrO_2 nanotubes in Figure 3b is smaller than that in Figure 1b.

A TEM image shown in Figure 3c indicates that CNC1 have a coiled structure as implied by the name. Coil diameters and pitches of CNC1 were uniform. Figure 3d shows a TEM image of ZrO_2 nanotubes formed using CNC1 as templates. Clearly, formed ZrO_2 nanotubes showed a helical structure, reflecting the shapes of CNC1. CNC2 contained carbon nanocoils with different coil diameters and pitches (Figure 3e). Therefore, a variety of helical oxide nanotubes were formed (Figure 3f−l) when CNC2 was used as the template. Helical oxide nanotubes with various inner diameter, coil diameter, and coil pitches were observed. It was the first time that these helical ZrO_2, Al_2O_3, and SiO_2 nanotubes were synthesized. TEM images suggest that a variety of attractive nanotubular materials can be fabricated by using carbon nanofibers as templates.

The formation of helical oxide nanotubes is worth mentioning. A lot of nanotubular materials have been synthesized, but the formation of helical nanotubes was few. As mentioned above, the main reason could be that there is limited template with coiled structure. Until now, only organogels were used as templates for the synthesis of helical nanotubes, and helical SiO_2 and Ta_2O_5 nanotubes were obtained.[25−29] As for microtubes, TiO_2 microtubes were synthesized using carbon microcoils as templates.[30] The present study has demonstrated that carbon nanofibers could act as effective templates for the synthesis of oxide nanotubes with various helical structures.

In the synthesis of oxide nanotubes, coating of templates with oxide is the most important process. In general, templates are coated by the sol−gel polycondensation process using metal alkoxides. A lot of SiO_2 nanotubes have been synthesized through the sol−gel polycondensation process of tetraethyl orthosilicate (TEOS) since the polycondensation of TEOS is moderate and easily controlled. In contrast, investigations in the synthesis of other oxide nanotubes are few, because formation of oxide on the surface of template only is difficult through the sol−gel process. In fact, synthesis of Al_2O_3 and ZrO_2 nanotubes is much less than that of SiO_2 nanotubes. The present study demonstrated that various oxide nanotubes could be synthesized by the adsorption and hydrolysis of precursors on the surface of carbon nanofiber templates only. In addition, our coating process of templates is simple as compared with a previously reported method.

In summary, a shape-controlled fabrication process for oxide nanotubes (ZrO_2, Al_2O_3, and SiO_2) by using carbon nanofiber templates was developed. A variety of oxide nanotubes such as thick, thin, and helical nanotubes reflecting the shapes of carbon nanofibers could be synthesized.

Supporting Information Available: TEM images of VGCF templates coated with ZrO_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Jung, J. H.; Ono, Y.; Hanabusa, K.; Shinkai, S. *J. Am. Chem. Soc.* **2000**, *122*, 5008−5009.
(26) Jung, J. H.; Ono, Y.; Shinkai, S. *Chem. Eur. J.* **2000**, *6*, 4552−4557.
(27) Kobayashi, S.; Hamasaki, N.; Suzuki, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *J. Am. Chem. Soc.* **2002**, *124*, 6550−6551.
(28) Sugiyasu, K.; Tamaru, S.; Takeuchi, M.; Berthier, D.; Huc, I.; Oda, R.; Shinkai, S. *Chem. Commun.* **2002**, 1212−1213.
(29) Jung, J. H.; Yoshida, K.; Shimizu, T. *Langmuir* **2002**, *18*, 8724−8727.
(30) Motojima, S.; Suzuki, T.; Noda, Y.; Hiraga, A.; Iwanaga, H.; Hashishin, T.; Hishikawa, Y.; Yang, S.; Chen, X. *Chem. Phys. Lett.* **2003**, *378*, 111−116.