Synthesis of Bamboo-shaped TiO_2 Nanotubes in Nanochannels of Porous Aluminum Oxide Membrane

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The bamboo-shaped TiO_2 nanotubes with diameters of ca. 100 nm have been fabricated in nanochannels of PAO membranes by upright dipping manner. The bamboo-shaped nanotubes consist of many hollow compartments that are separated by TiO_2 layers.

Recently, there has been growing interest in the preparation of bamboo-shaped carbon,[1,2] BN,[3,4] and MoS_2[5] nanotubes since the report of carbon nanobamboos in 1993.[1] Compared with cylindrical hollow tubes, bamboo-shaped tubes may have some specific applications as both structural and functional materials.[2,5] Therefore, different methods including arc discharge and catalytic pyrolysis as well as the thermal decomposition of infiltrated precursor solution in nanochannels of porous anodic aluminum oxide (PAO) membrane, have been developed to synthesize bamboo-shaped nanotubes.[1–5] It is worth noting that the matrix materials of those bamboo-shaped nanotubes have layered structures. On the other hand, although without layered structures, many transition metal oxides have been developed to fabricate hollow nanotubes over the past decade.[6–10] PAO membranes possess uniform and porous structures, which are controllable. Hence, they are used as an ideal template to fabricate metal oxide tubes and/or fibrils with a narrow diameter distribution.[2,5–8] Martin et al. have fabricated tubes of metal oxide and composite materials in nanochannels of PAO membranes by electrodeposition and sol–gel method.[6–8] Among metal oxide nanotubes, TiO_2 is one of the most investigated oxide materials because of its potential applications. And that, bamboo-shaped nanotubes may potentially find application in nanoscale electronic devices, nanofunctional materials, and as protective shields for encapsulated species, for example, in the nanocrystal photoelectrochemical cell, this special morphology of TiO_2 may provide protective shield from photocorrosive of some narrow-band semiconductor such as WO_3 etc., and enhances the efficiency of photoelectrochemical cell. To the best of our knowledge, the literature on the existence of metal oxide bamboo-shaped nanotubes is still deficient. Herein, we report the first synthesis of bamboo-shaped TiO_2 nanotubes in the nanochannels of PAO membranes.

TiO_2 nanotubes were prepared as following.[7] Titanium isopropoxide (TIPO, 5 mL) was added to 25 mL of ethanol, and the resulting solution was stirred in an ice bath. A second 25-mL portion of ethanol containing 0.5 mL of H_2O and 0.5 mL of 0.1 M HCl was slowly added under stirring. After ca. 60 s, the resulting mixture turned milky white (sol formation). The PAO membranes were dipped into this sol for 10 s. The PAO membranes (Whatman) have nanochannels with diameters range from 100 to 120 nm. The face of PAO membranes is perpendicular (upright manner) or parallel to the solution level (horizontal manner). For comparing, TIPO sol was replaced by titanium *n*-butoxide (TNBO) sol or 20% $TiCl_3$ sol (containing dilute HCl solution, pH 1.6, heated at 60 °C for 1 h). In all cases, the membranes were removed from the sol, dried 24 h at room temperature, and then heated at 400 °C for 18 h. Samples were characterized by scanning electronic microscopy (SEM, Hitachi S-510) and transmission electronic microscopy (TEM, JEM-100CX). The crystallinity of samples was characterized by powder X-ray diffractometry (XRD, Rigaku Rint-1400). Specimens for TEM, SEM, and XRD were obtained after dissolving template in 1 M NaOH for 1 h.

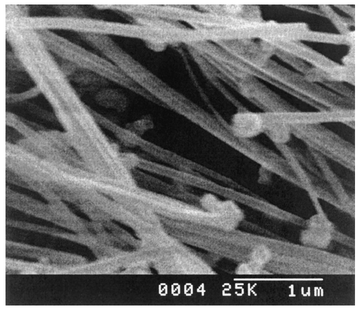

Figure 1. SEM image of bamboo-shaped TiO_2 nanotubes produced from TIPO sol by upright dipping manner.

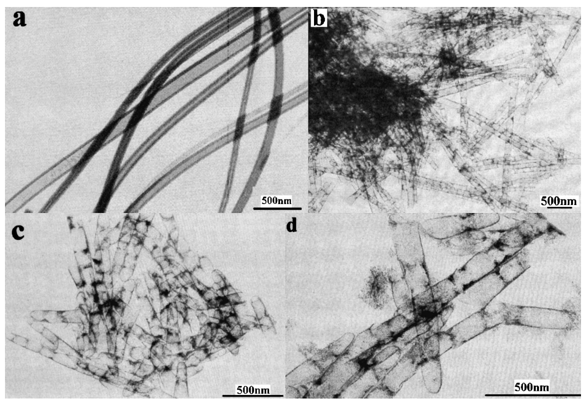

Figure 2. TEM images of cylindrical nanotubes (a) derived from TIPO sol by horizontal dipping manner and bamboo-shaped TiO_2 nanotubes derived from (b) TIPO sol. (c) TNBO sol. (d) $TiCl_3$ sol by upright dipping manner.

SEM images of samples show similar morphologies regardless of the precursor kinds and the dipping manner. Figure 1 shows the SEM image of samples obtained from TIPO sol by upright dipping manner. Some particles together with the fibers may be attributed to the incomplete dissolving. The fibers in

Figure 1 are ca. 100-nm wide and do not stand erect as bristles of a brush but appear more flexible, which is similar to the previous report.[5] However, imaging of TEM revealed that the microscopic feature of those fibers changed with the dipping manner. Figure 2a shows a typical TEM image of well-developed cylindrical nanotubes derived from TIPO sol by horizontal dipping manner. Most of the tubes have an outer diameter of ca. 100 nm with wall thickness ranged from 15 to 40 nm. An interesting observation about the morphologies of nanotubes derived from the same sol but by upright dipping manner is also illustrated in Figure 2b. It can be clearly seen that the sample shows voids and knots in the tubular structures, which made the nanotubes looks like bamboo. The regions of high electron density appear along the tubes and transect the hollow regions at intervals ranged from 80 to 300 nm. Moreover, most of bamboo-shaped TiO_2 nanotubes have thinner wall relative to hollow nanotubes by the same dipping duration.

Figures 2b–2d show TEM images of bamboo-shaped nanotubes resulted from different precursor sol by upright dipping manner. As can be seen, these nanotubes produced by upright dipping manner have similar morphologies as shown in Figure 2b, the samples only consist of bamboo-shaped TiO_2 nanotubes and their outer diameter is almost the same as the nanochannel diameter of the PAO membrane. No other morphologies were observed in the TEM observation. On the other hand, TEM observation (not shown) also indicated that samples obtained by horizontal dipping manner only formed cylindrical nanotubes with characteristics similar to Figure 2a, and there are no any bamboo-shaped nanotubes regardless of different titanium source, which is consistent with the previous reports.[6–9] Apparently, the formation of the specific bamboo-shaped structures do not depend on the precursor kinds but do depend on the dipping manner. It was noticed that the bamboo-shaped nanotubes resulted from TNBO and $TiCl_3$ sol were more brittle and broke into short pieces, and the bamboo-shaped nanotubes resulted from TIPO sol tend to form larger hollow compartment. Nevertheless, plugs transecting along the nanotubes were formed in all of those cases. XRD pattern of bamboo-shaped tubes (Figure 3) shows that all the diffraction peaks can be readily indexed to anatase titania. The XRD patterns of the other nanotubes obtained from different titanium sources are consistent with this observation.

Dorhout et al. have pointed that the formations of bamboo-shaped MoS_2 nanotubes were resulted from the evaporation dynamics of the solvent–precursor mixture rather than any annealing process of the MoS_2 that had been formed.[5] Thus, they think that the unique shapes of MoS_2 produced by their reactions likely reflect the shape of the thiomolybdate precursor left behind in the nanochannels after the solvent evaporated. It is well known that the evaporation of solvent on wettable surface is a complex process. Along with the solvent evaporated, complex 2-D patterns formed by the remaing have also been observed.[11,12] In our systems, the evaporation of precursor sol filled in the nanochannels of PAO membrane was more complex than that of pure solvents, and the nanochannels promoted the formation of three-dimensional patterns as the solvent evaporated in contrast to the evaporation from flat surfaces. Taking into account that no evidence was reported for the large-scale rearrangement or annealing of TiO_2 solid during the reaction at 400 °C in the previous preparation of TiO_2 tubes in PAO membrane,[6–9] and the press difference between the two ends of nanochannels in the upright manner is less than that in the horizontal manner owing to the two ends of nanochannels located at the same liquid level, we think that those less press differences in upright dipping manner play an important role in the promoting or maintaining a meniscus created by wetting of sol at points along the nanochannels which, when fired, creates the transecting region of the tubes, therefore form bamboo-shaped nanotubes rather than hollow nanotubes. Furthermore, the results of repeating experimental on the upright dipping manner indicated that the morphologies of bamboo-shaped nanotubes have not obvious changes despite the dip–dry–dip–fire step for 4 times. Perhaps, this is related to that the transecting region of nanotubes may prevent other sol particles from entering nanochannels during the following dipping step. However, we cannot suppose a definitive formation mechanism of bamboo-shaped nanotubes because of the complexity in our system.

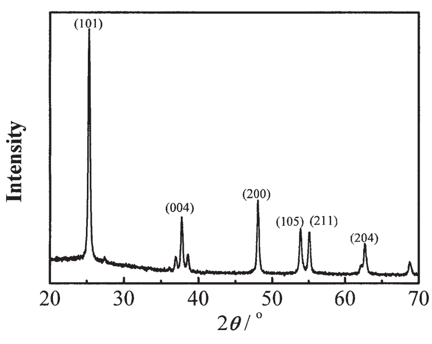

Figure 3. Powder X-ray diffraction pattern of bamboo-shaped TiO_2 nanotubes derived from TIPO sol by upright dipping manner.

In summary, bamboo-shaped TiO_2 nanotubes have been fabricated in nanochannels of PAO membranes from different titanium precursor sols by upright dipping manner. The formation of bamboo-shaped morphologies appears to be independent of the precursor kind, but to be closely connected with the dipping manner. It is unclear why our routine resulted in bamboo-shaped nanotubes yet, but this synthesis routine is easily controllable and feasible, and may be applied to the fabrication of bamboo-shaped nanostructure of other metal oxide materials. However, the forces that generated these patterns are not yet well understood.

References

1 Y. Saito and T. Yoshikawa, *J. Cryst. Growth*, **134**, 154 (1993).
2 T. Kyotani, L. F. Tsai, and A. Tomita, *Chem. Mater.*, **8**, 2109 (1996).
3 Y. Chem, L. T. Chadderton, J. F. Gerald, and J. S. William, *Appl. Phys. Lett.*, **74**, 2960 (1999).
4 J. L. Chemol, H. P. Jung, and P. Jeunghee, *Chem. Phys. Lett.*, **323**, 560 (2000).
5 C. M. Zelenski and P. K. Dorhout, *J. Am. Chem. Soc.*, **120**, 734 (1998).
6 C. J. Brumlik and C. R. Matrin, *J. Am. Chem. Soc.*, **113**, 3174 (1991).
7 C. R. Martin, *Chem. Mater.*, **8**, 1739 (1996).
8 J. C. Hulteen and C. R. Matrin, *J. Mater. Chem.*, **7**, 1705 (1997).
9 M. Zhang, Y. Bando, and K. Wada, *J. Mater. Sci. Lett.*, **20**, 167 (2001).
10 W. Shenton, T. Douglas, M. Young, G. Stubbs, and S. Mann, *Adv. Mater.*, **11**, 253 (1999).
11 C. Redon, F. Bouchard-Wyart, and F. Rondelez, *Phys. Rev. Lett.*, **66**, 715 (1991).
12 M. Elbaum and S. G. Lipsom, *Phys. Rev. Lett.*, **72**, 3562 (1994).

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