An Efficient Template Pathway to Synthesis of Ordered Metal Oxide Nanotube Arrays Using Metal Acetylacetonates as Single-Source Molecular Precursors

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α-Fe_2O_3 and CuO nanotube arrays were obtained for the first time within the pores of the porous anodic alumina membranes by pyrolyzing $Fe(acac)_3$ (Hacac = 2,4-pentanedione) at 300 °C and $Cu(acac)_2$ at 330 °C, respectively. These nanotubes with an outer diameter of about 100–300 nm and a length of up to tens of microns were characterized using scanning electron microscopy (SEM), X-ray diffractometer (XRD), and transmission electron microscopy (TEM), respectively.

Since the discovery of carbon nanotubes in 1991,[1] the synthesis and functionalization of nanotubular materials has become one of the most highly energized research areas.[2,3] The development of nanodevices might benefit from the distinct morphology and high aspect ratio of nanotubes. One successful route leading to tubular nanostructures is template-mediated growth using zeolites, membranes, or carbon nanotubes. Porous anodic alumina (PAA) membrane has been demonstrated to be one of the most suitable templates for synthesis of ordered arrays of 1-D nanostructures because of its tunable pore dimensions, narrow pore size distribution, and good mechanical and thermal stability.[4–6] Considering the importance of metal oxides in catalysis, electrochemistry, and functional ceramics and sensors, their fabrication in nanostructured form with anisotropic morphology appears to be a particularly attractive goal and has been pursued in a number of laboratories. Several metal oxides nanotubes such as V_2O_5,[7] TiO_2,[8] ZrO_2,[9] MoO_3, Al_2O_3,[10] In_2O_3, Ga_2O_3,[11] and RuO_2[12] have been successfully synthesized by using a variety of techniques including sol–gel chemistry, vapor–liquid–solid (VLS) process, hydrothermal and surfactant-assisted methods, etc. However, it is still a challenge to develop a general synthetic pathway to a wide variety of metal oxide nanotubes.

α-Fe_2O_3(Hematite), the thermodynamic stable crystallographic phase of iron(III) oxide with a band gap of 2.2 eV, has potential applications in gas sensors, photoanode for photooxidation of water, and for photocatalytic oxidation. Its nontoxicity, low cost, and relatively good stability are definitely very attractive features for these applications. It has been shown that oriented nanorod thin films of hematite improve considerably the collection of the photogenerated electrons.[13] CuO is a p-type semiconductor and it is useful for the preparation of organic catalysts and gas sensors. CuO nanorods have also been obtained by a simple one-step solid-state reaction.[14] However, the nanotubes of these two oxides have been unreported so far. Furthermore, many metal acetylacetonates are known to be volatile complexes at moderate temperatures and have been previously used for chemical vapor deposition (CVD) of thin films of metal oxides.[15] Recently, using metal acetylacetonates as single-source molecular precursors, we have obtained a series of metal oxide nanotube arrays based on the combination of the porous alumina templates with CVD technique. In this paper, we demonstrate the efficient template pathway to synthesis of ordered α-Fe_2O_3 and CuO nanotube arrays.

Previous works[16–19] have demonstrated that PAA membrane is a cheaper and effective template for synthesis of nanowires, nanotubes, and nanocable composite structures. In our present study, α-Fe_2O_3 and CuO nanotube arrays were synthesized within the pores of the PAA membranes (Whatman Ltd., with a nominal pore diameter of 100 nm and thickness of 60 µm) by CVD methods with $Fe(acac)_3$ and $Cu(acac)_2$ as single-source molecular precursors, respectively. The equipment used for synthesis of metal oxide nanotubes is a tube furnace and similar to that reported previously.[20] The organometallic precursors were placed in the low-temperature zone [150 °C for $Fe(acac)_3$ and 160 °C for $Cu(acac)_2$] and their vapors were carried by a O_2 flow to the high-temperature zone, where the PAA templates were placed vertically and the temperatures were 300 °C (α-Fe_2O_3) and 330 °C (CuO), respectively. The deposition reaction lasted for 1 h, and then the template temperatures were elevated to 500 °C (α-Fe_2O_3) and 450 °C (CuO) and maintained for 4 h for annealing. The pressure of the reaction system was maintained at ca. 3 kPa. The as-synthesized products were characterized by X-ray diffractometry (XRD, D/Max-RA), scanning electron microscopy (SEM, JSM-840A for α-Fe_2O_3 and LEO1530VP for CuO) and transmission electron microscopy (TEM, JEM-200CX). Specimens for TEM and SEM were obtained after dissolving the alumina template in 2 M NaOH.

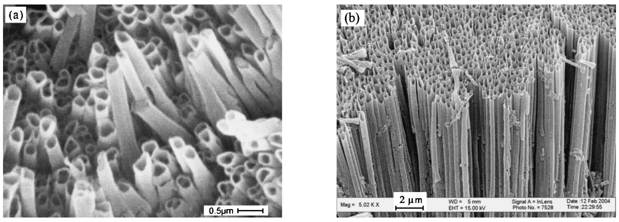

Figure 1. SEM images of the as-prepared nanotubes: (a) α-Fe_2O_3, (b) CuO.

Figure 1 shows the SEM images of the as-prepared α-Fe_2O_3 and CuO nanotubes. It can be seen that the nanotubes have open ends and are arranged in a parallel and well-ordered way. α-Fe_2O_3 nanotubes have smooth and compact walls, while CuO nanotubes have porous walls and are relatively fragile. The lengths of α-Fe_2O_3 and CuO nanotubes are up to tens of microns. The compactness of the nanotubes is quite high of about $1.0 \times 10^9\,cm^{-2}$, corresponding to the pore density of the PAA. Energy-dispersive X-ray spectrometry (EDS) (see Supplemental Information **1**) confirmed the elemental compositions of the

α-Fe_2O_3 and CuO nanotubes and indicated that the as-prepared α-Fe_2O_3 and CuO nanotubes are highly pure and there are no any contaminant of carbon, which could be attributed to the oxidation reaction with oxygen. Figure 2 shows XRD patterns of nanotubes of α-Fe_2O_3 and CuO. The comparison of the diffraction pattern (Figure 2a) with data from JCPDS file 33-664 identifies the iron oxide nanotubes as rhombohedral (Hex) α-Fe_2O_3 (Hematite, syn) with the lattice parameters $a = 5.0356$ and $c = 13.7489$ Å. A similar correlation of the diffraction pattern (Figure 2b) with the JCPDS file 5-0661 confirms that the nanotubes consist of the monoclinic structure of CuO with $a = 4.684$, $b = 3.425$, $c = 5.129$ Å, and $\beta = 99.5°$. The XRD results reveal that both nanotubes are crystalline as anticipated from their respective annealing temperatures. Figure 3 shows the typical TEM images of single nanotube of α-Fe_2O_3 and CuO liberated from the PAA templates. It can be seen that both nanotubes are very straight and the diameters are quite uniform. These nanotubes are composed of the fine particles, whose sizes are around 10 nm for α-Fe_2O_3 and about 10–20 nm for CuO according to the TEM observation ((see Supplemental Information **2**). The outer diameters of the nanotubes are about 200 nm, which reflect the diameter of the pores within the template. The thickness of nanotubular walls of α-Fe_2O_3 and CuO are about 20 and 25 nm, respectively. The selected area electron diffraction (SAED) patterns (Figure 3, inset) reveal that both nanotubes are polycrystalline.

Our preliminary study shows that suitable CVD process conditions such as reaction temperature, precursor evaporating temperature and vacuum etc. are critical to the formation of the nanotubes. The higher deposition rate, which was induced by the higher reaction temperature and the higher precursor-evaporating temperature, will lead to form a cover layer on the PAA membrane and block the pores, which prevents the precursor molecules from entering the pores and therefore, the nanotubes can not be formed in the pores of PAA membranes via the precursor pyrolyzing. A suitable vacuum in the reaction system can greatly improve the CVD efficiency and increase the thickness of nanotubular walls. In addition, as-prepared nanotubes are generally amorphous and the annealing is necessary to obtain crystalline products.

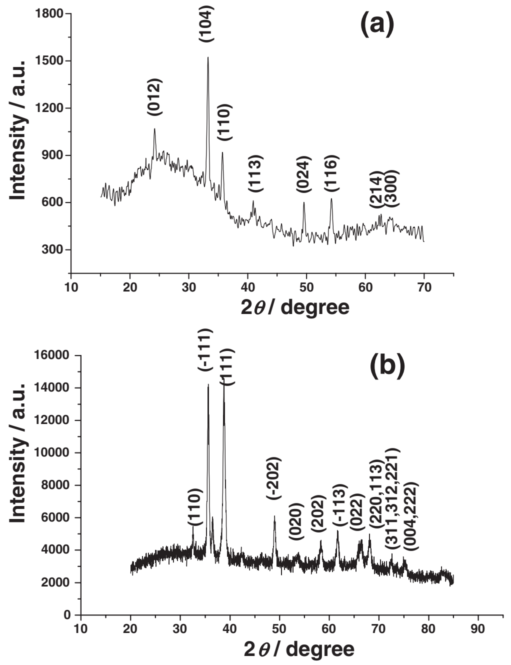

Figure 2. XRD patterns of the nanotube arrays in PAA templates: (a) α-Fe_2O_3, (b) CuO.

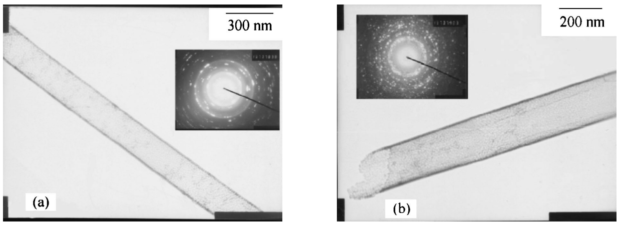

Figure 3. TEM images of the nanotubes of α-Fe_2O_3 (a) and CuO (b), inset is selected area electron diffraction (SAED) patterns.

In summary, we have demonstrated that the single-source molecular precursors for CVD of metal oxide thin films can be extended to growth of 1-D nanostructures. α-Fe_2O_3 and CuO nanotubes with 100–300 nm in outer diameter and several tens of microns in length have been prepared within the pores of the PAA templates using CVD method. The present method possesses a potential for fabricating nanotubes of other various species. Further work on the constructing concentric cable nanostructures is underway by filling the nanotubes with foreign species.

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References

1 S. Iijima, *Nature*, **354**, 56 (1991).
2 G. R. Patzke, F. Krumeich, and R. Nesper, *Angew. Chem., Int. Ed.*, **41**, 2447 (2002).
3 C. N. R. Rao, and M. Nath, *Dalton Trans.*, **2003**, 1.
4 C. R. Martin, *Science*, **266**, 1961 (1994).
5 C. R. Martin, *Chem. Mater.*, **8**, 1739 (1996).
6 J. C. Bao, C. Tie, Z. Xu, Q. Zhou, D. Shen, and Q. Ma, *Adv. Mater.*, **13**, 1631 (2001).
7 P. M. Ajayan, O. Stephan, P. Redlich, and C. Colliex, *Nature*, **375**, 564 (1995).
8 J. H. Jung, H. Kobayashi, K. J. C. van Bommel, S. Shinkai, and T. Shimizu, *Chem. Mater.*, **14**, 1445 (2002).
9 C. N. R. Rao, B. C. Satishkumar, and A. Govindaraj, *Chem. Commun.*, **1997**, 1581.
10 B. C. Satishkumar, A. Govindaraj, E. M. Vogl, L. Basumallick, and C. N. R. Rao, *J. Mater. Res.*, **12**, 604 (1997).
11 B. Cheng and E. T. Samulski, *J. Mater. Chem.*, **11**, 2901 (2001).
12 Y. S. Min, E. J. Bae, K. S. Jeong, Y. J. Cho, J. H. Lee, W. B. Choi, and G. S. Park, *Adv. Mater.*, **15**, 1019 (2003).
13 N. Beermann, L. Vayssieres, S. E. Lindquist, and A. Hagfeldt, *J. Electrochem. Soc.*, **147**, 2456 (2000).
14 W. Wang, Y. Zhan, and G. Wang, *Chem. Commun.*, **2001**, 727.
15 G. Y. Meng, H. Z. Song, H. B. Wang, C. R. Xia, and D. K. Peng, *Thin Solid Films*, **409**, 105 (2002).
16 G. Che, B. B. Lakshmi, C. R. Martin, and E. R. Fisher, *Chem. Mater.*, **10**, 260 (1998).
17 M. J. Pender and L. G. Sneddon, *Chem. Mater.*, **12**, 280 (2000).
18 J. C. Bao, C. Tie, Z. Xu, Q. Ma, J. Hong, H. Sang, and D. Sheng, *Adv. Mater.*, **14**, 44 (2002).
19 H. Q. Cao, Y. Xu, J. M. Hong, H. B. Liu, G. Yin, B. L. Li, C. Y. Tie, and Z. Xu, *Adv. Mater.*, **13**, 1393 (2001).
20 C. C. Chen, C. C. Yeh, C. H. Chen, M. Y. Yu, H. L. Liu, J. J. Wu, K. H. Chen, L. C. Chen, J. Y. Peng, and Y. F. Chen, *J. Am. Chem. Soc.*, **123**, 2791 (2001).

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