Notes

Synthesis of Nanorods of Crystalline Co_3O_4 Using Carbon Nanotubes as Templates

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Synthesis of cobalt oxide (Co_3O_4) nanorods was achieved by templating against carbon nanotubes via wet chemical technique. The products with crystalline structure were mainly composed of Co_3O_4 nanorods with diameters in the range of *ca*. 75—100 nm and lengths in the range of 0.12—1 μm, and were characterized by XRD, TEM, SAED and HRTEM.

Keywords Co_3O_4, nanorods, carbon nanotubes

Introduction

Materials based on cobalt oxides have attracted a great interest in view of their potential applications in scientific and technological fields.[1] They have been used for the production of solid-state sensors,[2] heterogeneous catalysts,[3] electrochromic devices (ECDs)[4] and as intercalation compounds for energy storage.[5] Co_3O_4, the most stable phase in the Co—O system, a mixed valence compound $[Co^{II}Co_2^{III}O_4]$ with a normal spinel structure, has been used as an active material with relatively high electrochromic efficiency for its color change from brown to light yellow when Li^+ ions were inserted.[6] Furthermore, the dilute Co_3O_4 nanocrystals are a new and ideally suitable material for the study of macroscopic magnetic quantum effects.[7] Recently there were some reports for the preparation of cobalt oxide nanoparticles by liquid-control-precipitation method,[8] solid state oxidation of a metallic colloid precursor,[9] chemical vapor deposition[10] and thermal decomposition of the hydroxide.[11] However, one-dimensional nanostructures of cobalt oxide have been unreported.

It is well known that one-dimensional nanostructural materials are currently the focus of considerable interest, because they often possess unique chemical, mechanical and physical properties, and may prove to be key components in the next generation of nano-optical and electronic devices.[12-15] One successful route leading to one-dimensional nanostructures is template-mediated growth using zeolites, membranes or nanotubes.[16-18] Carbon nanotubes have been used as templates for preparing zirconia nanotubes[19] and nanowires of metal,[20-23] fullerene[24] and nanorods of carbide,[25] nitride[16,26] and phosphide,[27] the d-block and f-block transition metal oxides.[20,28,29] In this paper the crystalline Co_3O_4 nanorods with diameters in the range of 75—100 nm and length in the range of 0.12—1 μm were obtained by templating against carbon nanotubes.

Experimental

Transmission electron microscopy (TEM) micrographs were taken using a Hitachi Model H-800 transmission electron microscope, with an accelerating voltage of 200 kV. X-ray powder diffraction (XRD) was carried out on a Rigaku (Japan) D/max γ_A X-ray diffractometer with Cu Kα radiation ($\lambda = 0.154178$ nm) at a scanning rate of $0.02° s^{-1}$ in the 2θ range of 10°—70°. High-

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resolution transmission electron microscopy (HRTEM) was performed using a JEOL 2010 microcopes operated at optimum defocus with accelerating voltages of 200 kV.

The multi-walled carbon nanotubes (MWNTs) were gifts from Chengdu Institute of Organic Chemistry (China), which was prepared by the thermal catalytic decomposition of hydrocarbon.[30]

The procedure of preparing cobalt oxide Co_3O_4 nanorods is as follows. In a typical synthesis, the multi-walled carbon nanotubes (1 g) were suspended in 200 mL of nitric acid (68%) and refluxed for 24 h, then washed with redistilled water and dried in an oven at 60 ℃ for 24 h. The acid-treated carbon nanotubes (400 mg) were stirred with 100 mL of saturated cobalt nitrate solution for 20 h, filtered and washed with redistilled water, then dried at 60 ℃ for 10 h, followed by calcining at 400 ℃ for 6 h under argon atmosphere. The calcined samples were then heated at 700 ℃ in air for 6 h to burn off the carbon nanotubes.

Results and discussion

The carbon nanotubes used had an inner diameter in the range of 3—10 nm and an outer diameter in the range of 20—50 nm (length up to a few microns). The nanotubes are almost open and contain considerable number of acidic sites on the surface[31,32] after being treated with nitric acid for 24 h. The calcined samples of the cobalt nitrate-coated carbon nanotubes revealed the presence of Co_3O_4 which was filled satisfactorily as shown in the typical TEM image in Fig. 1(a). It could be seen that the cobalt oxide consists of solid rod-like structures. The length of the rods could be up to several hundreds nanometers. The selected area electron diffraction (SAED) pattern shows the presence of (311) and (422) planes (between three diffraction rings of carbon nanotubes) as shown in Fig. 1(b), signifying the crystalline nature of Co_3O_4. HRTEM image of Co_3O_4 inside the carbon nanotube, shown in Fig. 2, reveals lattice fringes with an observed fringe separation of 0.244 nm, which is consistent with the interlayer separation of the (311) crystal plane of Co_3O_4. It is interesting to note that the (311) Co_3O_4 plane is always parallel to the graphite layer (002) of the tube. Most of diameters of the Co_3O_4 crystallites almost equal to the internal cross-section of the tubes (~ 10 nm). It could be envisaged that cobalt nitrate solution was sucked into the tubes[20] as they were opened and crystalline cobalt oxide was formed inside the tubes during calcination at 400 ℃ for 6 h under argon atmosphere. The cobalt nitrate was decomposited at 400 ℃ in inert atmosphere as follows:

$$MWNTs/Co(NO_3)_2 \rightarrow MWNTs/Co_3O_4 + NO_2(g) + O_2(g)$$

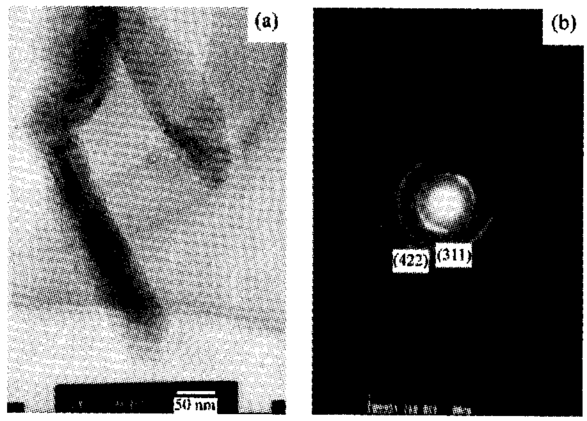

Fig. 1 TEM image of Co_3O_4 filled in carbon nanotubes on calcinations at 400 ℃ for 6 h under argon atmosphere (a) and selected area electron diffraction (SAED) pattern (b).

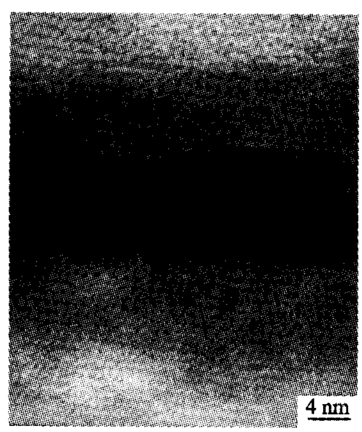

Fig. 2 HRTEM image of Co_3O_4 filled in carbon nanotube on calcinations at 400 ℃ for 6 h under argon atmosphere.

On the removal of the nanotube templates, the resulting oxidic species showed the presence of interesting nanostructures. Fig. 3 shows the XRD pattern of a sample of the cobalt oxide nanorods prepared by templating against carbon nanotubes. Powder XRD peaks of the cobalt oxide are consistent with the data of the JCPDS file of Co_3O_4 with cubic phase.[33] The peaks at 2θ values of 18.9°, 31.2°, 36.9°, 38.6°, 44.8°, 55.6°, 59.3° and 65.2° correspond to the crystal planes of (111), (220), (311), (222), (400), (422), (511) and (440) of crystalline Co_3O_4, respectively.

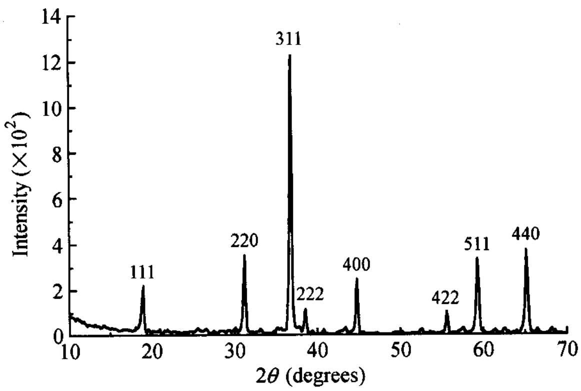

Fig. 3 XRD pattern of a cobalt oxide nanorod sample obtained by removal of carbon nanotubes on calcination at 700 ℃ in air for 6 h.

The TEM image of the cobalt oxide sample mentional above, is shown in Fig. 4, which reveals that the cobalt oxide powders consist of uniform nanorods. It can be seen that the diameters of nanorods are in the range of *ca*. 75—100 nm and their lengths are in the ranges of 0.12—1 μm. So, the calcination of Co_3O_4 inside carbon nanotubes at 700 ℃ in air follows the reaction equation:

$$\text{MWNTs}/Co_3O_4 + O_2(g) \rightarrow Co_3O_4(\text{nanorods}) + CO_2(g)\ [CO(g)]$$

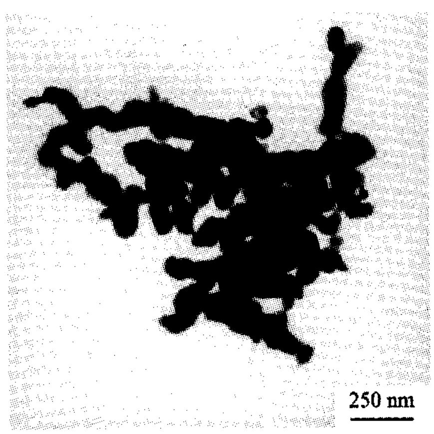

Fig. 4 TEM image of the cobalt oxide nanorods sample shown in Fig. 3.

The formation of crystalline nanorods of Co_3O_4 in the present study is noteworthy. A possible mechanism of formation[29] of such nanorods is that the decomposition of the oxide precursor in the hot combustion zone of the nanotubes gives rise to the crystals *in situ*. The crystals could get elongated because of the evolution of gases during the transformation. The form of the growth of Co_3O_4 crystallites may be influenced by the surface structure of the inner tube and the elongated shape of the Co_3O_4 crystallites may reflect surface-wetting properties. Furthermore, the nanorods are generally much larger than the starting nanotube template since Co_3O_4 are prone to merge into large particles at high temperature to reduce surface energy.

Conclusion

A novel and facile method has been developed to synthesize cobalt oxide nanorods. The nanorods of Co_3O_4 with diameters in the range of 75—100 nm and lengths in the range of 0.12—1 μm can be readily prepared by using carbon nanotubes as templates via wet chemical technique. The method also offers certain advantages, such as yielding crystalline nanorods of fairly large dimensions and good yields.

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