



Synthesis of copper oxide nanoparticles using carbon nanotubes as templates

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Abstract

The filling of carbon nanotubes with copper oxide via wet chemical techniques is presented. Crystalline copper oxide nanoparticles, mostly shaped like bamboo shoots, with diameters in the range of ca. 20–90 nm and length of 250–700 nm, have been prepared by templating with carbon nanotubes. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Copper oxide nanoparticles have been of considerable interest due to the role of CuO in catalysis, in high-Tc superconductors [1–4], and in gas sensors [5–7]. There have been various methods to prepare ultrafine CuO, such as sol–gel [8], precipitation-stripping method [9], solid-state reaction [10] and alkoxide-based synthesis [11]. However, there has been limited work on copper oxide nanowires and nanorods [12].

As is well known, one-dimensional nanostructured 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 [13–16]. One successful route leading to one-dimensional nanostructures is the template-mediated growth using zeolites, membranes, or nanotubes [17–19]. Carbon nanotubes have been used as templates for preparing zirconia nanotubes [20], metal nanowires [21–24] and carbide- [25], nitride- [17,26], phosphide- [27], and d-block and f-block transition metal oxides nanorods [21,28–30]. In this Letter we describe the generation of rod-like crystalline CuO nanoparticles, with diameters in the range of 20–90 nm and length in the 250–700 nm range, by templating against carbon nanotubes.

2. Experimental

Multi-walled carbon nanotubes (MWNTs) were prepared by the thermal catalytic decomposition

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of hydrocarbon [31]. The procedure employed by us for preparing CuO nanoparticles was as follows. In a typical synthesis, the multi-walled carbon nanotubes (0.5 g) were treated with boiling HNO₃ (68%, 100 ml) for 24 h, then washed with water and dried in an oven at 60 °C for 24 h. The acid-treated carbon nanotubes (250 mg) were stirred with 50 ml of saturated copper nitrate solution for 48 h, filtered and washed with water, then dried at 60 °C for 12 h, followed by calcination at 450 °C for 5 h under argon. The calcined samples were then heated at 750 °C in air for 1 h to burn off the carbon nanotubes.

X-ray powder diffraction (XRD) was carried out on a Rigaku (Japan) D/max γ_A X-ray diffractometer with Cu-K α radiation ($\lambda = 0.154178$ nm) at a scanning rate of $0.02^\circ \text{ s}^{-1}$ in the 2θ range from 10° to 70° . Transmission electron microscopy (TEM) micrographs were taken using a Hitachi Model H-800 transmission electron microscope, with an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) was performed using JEOL 2010 microscopes operated at 200 kV.

3. Results and discussion

3.1. Filling of MWNTs with CuO

The carbon nanotubes used had an inner diameter in the range 3–10 nm and an outer diameter in the range of 20–50 nm (with lengths of up to a few microns), which were checked by HRTEM. The nanotubes were almost open after being treated with nitric acid for 24 h.

The calcined samples of copper nitrate coated carbon nanotubes were shown to have been satisfactorily filled with the copper material from the typical TEM images presented in Figs. 1a,b. About 50% of the open nanotubes contained copper material inside. Some copper-containing material was observed on the exterior of the nanotubes. Close examination of the copper material inside the tubes (Fig. 1b) showed lattice fringes with an observed fringe separation of 4.64 Å, consistent with the interlayer separation of the (100) crystal plane of copper oxide (CuO). The

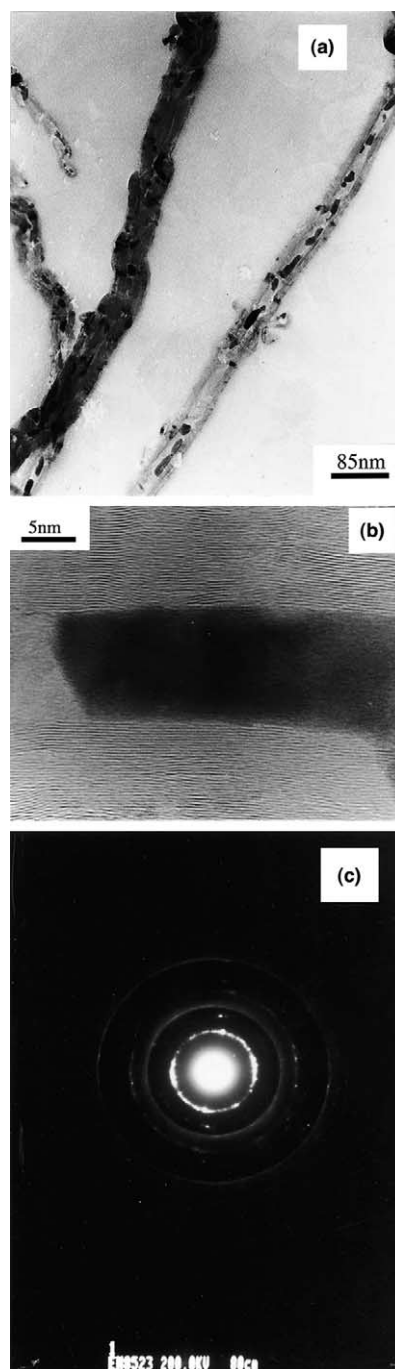


Fig. 1. (a) TEM, (b) HRTEM images and (c) selected-area electron diffraction (SAED) pattern of carbon nanotubes filled with copper oxide.

selected-area electron diffraction (SAED) pattern shows the presence of two diffraction spots (between diffraction rings of carbon nanotube) due to the (1 1 1) plane, as shown in Fig. 1c, signifying the crystalline nature of CuO. Most of the CuO crystallites have diameters less than or nearly equal to the internal cross-section of the tubes (~ 10 nm) and have lengths of 10–35 nm. These crystallites are also found at a considerable distance from the opened ends of the tubes, due possibly to the copper nitrate solution being sucked into the tubes as they were opened, with crystalline CuO being formed during calcination. The growth of the CuO crystallites may be influenced by the surface structure of the inner tube, and the elongated shape of the CuO crystallites may reflect their surface-wetting properties.

3.2. Rod-like nanoparticles of CuO

On the removal of the nanotube template, the resulting oxidic species showed the presence of interesting nanostructures. Fig. 2 shows the XRD pattern of a sample of the copper oxide powders so obtained. From the powder XRD peaks, the unit cell parameters can be calculated as $a = 4.6969$ Å, $b = 3.4254$ Å, $c = 5.1301$ Å, $\beta = 99.67^\circ$, which are consistent with the JCPDS (5-0661) data of the

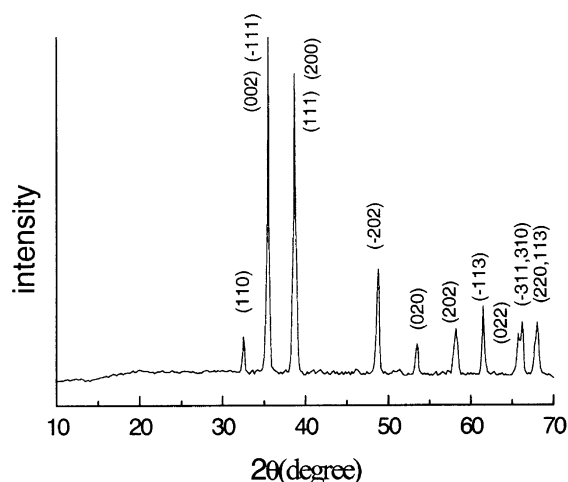


Fig. 2. XRD pattern of a copper oxide sample produced by removal of carbon nanotubes on calcination at 700°C in air for 1 h.

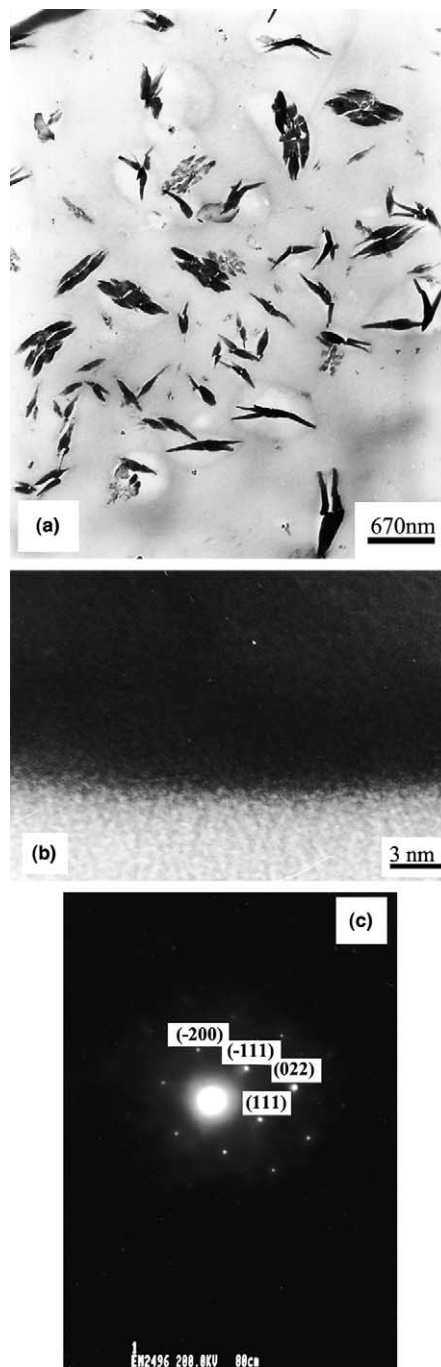


Fig. 3. (a) TEM, (b) HRTEM images and (c) selected-area electron diffraction pattern of the copper oxide sample shown in Fig. 2.

copper oxide with monoclinic phase [32] ($a = 4.684 \text{ \AA}$, $b = 3.425 \text{ \AA}$, $c = 5.129 \text{ \AA}$, $\beta = 99.28^\circ$). The peaks at 2θ values of 32.6° , 35.5° , 38.7° , 48.8° , 53.5° , 58.2° , 61.5° , 65.8° , 66.2° and 68.0° correspond to the crystal planes of (110), (002), (-111), (111), (200), (-202), (020), (202), (-113), (022), (-311), (310), (220), (113), respectively, of the crystalline copper oxide. Planes (-311)/(310), and (220)/(113) are superimposed peaks; both planes (002)/(-111), and (111)/(200) are too close to be identifiable. There is a much stronger (-202) peak in the XRD pattern than expected from the powder pattern, which indicates a preferential orientation of $[-101]$ in the CuO crystal. The average size of the as-synthesized crystalline CuO, calculated from the half-width of the (110) diffraction peak using the Scherrer formula [33], is 37.2 nm.

The TEM image of the copper oxide sample of Fig. 2 is shown in Fig. 3a, which reveals that the copper oxide powders consist of mainly rod-like nanoparticles with shapes resembling bamboo shoots, confirming the preferential orientation of $[-101]$ in the XRD pattern. It can be seen that the rod-like nanoparticles have diameters of ca. 20–90 nm and lengths of 250–700 nm. This result accords with the XRD results for the particle diameter.

An HRTEM image (Fig. 3b) of a part of a nanorod displayed that the distance between parallel lattice fringes is equal to the spacing of the (200) planes (2.32 Å) of CuO. The SAED pattern of the nanorod (Fig. 3c) can also be indexed to the reflection of monoclinic CuO structure.

The formation of crystalline nanoparticles of CuO in the present study is noteworthy. A possible mechanism [29] of formation of the nanoparticles is that the decomposition of the oxide precursor $[\text{Cu}(\text{NO}_3)_2]$ in the hot combustion zone of the nanotubes gives rise to the CuO crystals in situ. The crystals could become elongated as a result of the evolution of gases (NO_2 , H_2O) during the transformation. Furthermore, the rod-like CuO nanoparticles are generally much larger than the starting nanotube template attributable to merging at high temperature of smaller particles of CuO into larger ones in order to reduce the surface energy. Another possibility is that the copper oxides in neighboring carbon nanotubes or in the

same nanotube coalesce to form the rod-like nanostructures during the course of the template removal.

4. Conclusions

The present study establishes that rod-like nanoparticles of CuO, having diameters in the range of ca. 20–90 nm and lengths of up to 700 nm, can be prepared readily via wet chemistry by using carbon nanotubes as a template. The method offers certain advantages, such as providing rod-like crystalline nanoparticles in fairly large dimensions and good yields.

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