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Preparation and characterization of CuO nanorods by thermal decomposition of CuC_2O_4 precursor

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Abstract

Synthesis of copper oxide (CuO) nanorods was achieved by thermal decomposition of the precursor of CuC_2O_4 obtained via chemical reaction between $Cu(CH_3COO)_2{\cdot}H_2O$ and $H_2C_2O_4{\cdot}2H_2O$ in the presence of surfactant nonyl phenyl ether (9)/(5) (NP-9/5) and NaCl flux. Transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), selected-area electron diffraction (SAED) and high-resolution TEM (HRTEM) were used to characterize the structure features and chemical compositions of the as-made nanorods. The results showed that the as-prepared nanorods is composed of CuO with diameter of 30–100 nm, and lengths ranging from 1 to 3 μm. The mechanism of formation of CuO nanorods was also discussed.

Keywords: A. Nanostructure; A. Oxides; C. X-ray diffraction

1. Introduction

In recent years, quasi one-dimensional (1-D) solid nanostructures (nanowires or nanorods) have stimulated considerable interest for scientific research because of their importance in mesoscopic physics and their potential applications. Compared with micrometer-diameter whiskers and fibers, these nanostructures are expected to have remarkable optical, electrical, magnetic, and mechanical properties. Different

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approaches have been used for the preparations of quasi 1-D solid nanostructures, e.g. the vapor–liquid–solid (VLS) growth [1–11], solution–liquid–solid (SLS) method [12], template-mediated growth method [13–15], electron-beam lithography (EBL) [16] and scanning tunneling microscopy (STM) techniques [17], and other methods [14–18] of nanowire production. Exploration of novel methods for the large-scale synthesis of 1-D nanostructures is a challenging research area. As a p-type semiconductor with a narrow band gap and the basis of several high-T_c superconductors, copper oxide (CuO), has received a considerable attention over last few years because of many applications in various field, especially, CuO nanostructured materials are expected to possess properties having photothermal, photoconductive, and gas sensors applications [19–22]. However, up to now, many methods have been developed to synthesize CuO nanoparticles and films, few attempts have been made to prepare CuO nanorods. In this work, we report a simple and novel approach to the fabrication of CuO nanorods by thermal decomposition of the precursor of CuC_2O_4 obtained via chemical reaction between $Cu(CH_3COO)_2\cdot H_2O$ and $H_2C_2O_4\cdot 2H_2O$ in the presence of surfactant nonyl phenyl ether (9)/(5) (NP-9/5) and NaCl flux.

2. Sample preparation and experimental procedure

Staring materials are copper acetate $Cu(CH_3COO)_2\cdot H_2O$, oxalic acid $H_2C_2O_4\cdot 2H_2O$, nonyl phenyl ether (9)/(5)(NP-9/5), and NaCl. Among them, $Cu(CH_3COO)_2\cdot H_2O$, $H_2C_2O_4\cdot 2H_2O$, and NaCl are of analytical purity, NP-9/5 is up to 99.0%. A total of 3.99 g of $Cu(CH_3COO)_2\cdot H_2O$ and 2.53 g of $H_2C_2O_4\cdot 2H_2O$ according to 1:1 molar rate were mixed with 5 ml of NP-9/5 in a mortar, ground for several minutes and kept in a thermostat oven at 50–60°C for 6 h to prepare the precursor, the product was washed several times with distilled water and acetone to remove remaining reactants, NP-9/5 and by-product, and then dried in an oven at 70–80°C for 12 h. The obtained product was collected for the fabrication of CuO nanorods. Two grams of CuC_2O_4, was simultaneously mixed with 8 g of NaCl powder, and then ground for several minutes. The ground mixture was annealed at 950°C for 2 h in a porcelain crucible that was placed in the middle of the alumina tube; the reaction chamber is of alumina tube with a length of 1500 mm and a diameter of 60 mm. After heat treatment, it was gradually cooled to room temperature (5 °C/min), the as-prepared product was washed with distilled water one time, ethanol three times and then ethyl ether one time using an ultrasonic bath and a centrifuge.

The as-prepared product was identified by X-ray powder diffraction (XRD) employing a scanning rate of 0.02°/s in a 2θ range from 30 to 75°, using a Japanese Rigaku D/max-γA K_{II} X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation. The morphologies and dimensions of the products were observed by transmission electron microscopy (TEM), which were taken on a JEOL-2010 transmission electron microscope using an accelerating voltage of 200 kV. Meanwhile, the as-made products were also characterized by X-ray photoelectron spectroscopy (XPS), which was carried out on an ESCALAB M K_{II} X-ray photoelectron spectrometer, using Mg Kα X-ray as the excitation source; Raman spectroscopy was obtained using a RFS 100 spectrometer from 100 to 700 cm^{-1} at room temperature. The 1064 nm line of the laser was used as the excitation source, with the capability of supplying 200 mW. For high-resolution TEM (HRTEM) and TEM observation, the as-prepared product was ground in a mortar and suspended in ethanol using an ultrasonic bath for half an hour. A drop was then placed on a holey-carbon copper grid.

3. Results and discussion

The general TEM morphologies of the as-synthesized product are shown in Fig. 1. It can be seen that the product mainly consists of solid rod-like structures. The length of the rods, as shown in Fig. 1a, can be up to several micrometers. The typical nanorod, as can be seen in Fig. 1b, are around 30 nm in diameter.

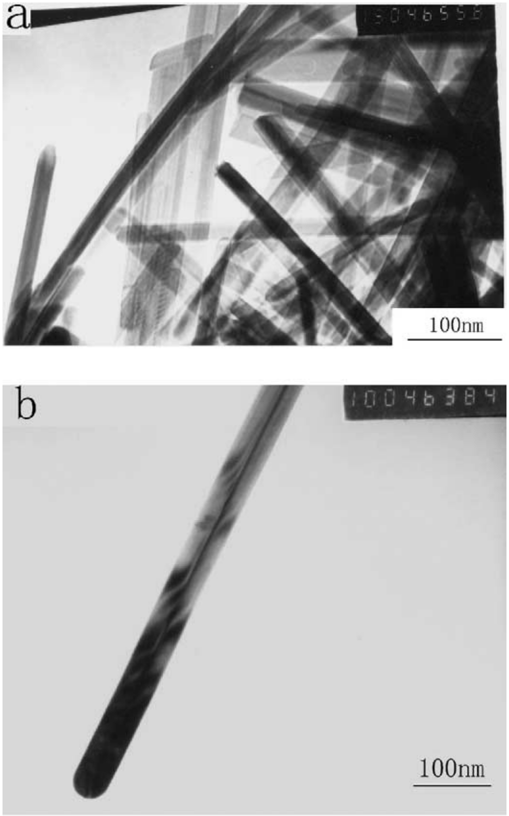

Fig. 1. TEM image of the as-prepared CuO nanorods. (a) Morphologies of the as-prepared CuO nanorods. (b) Morphologies of the as-prepared single CuO nanorod.

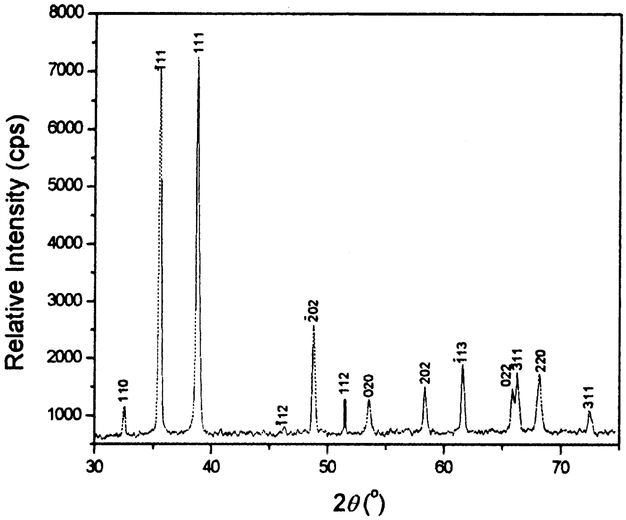

Fig. 2. The XRD pattern of the as-prepared CuO nanorods.

Fig. 2 shows the XRD of the as-prepared products obtained by thermal decomposition of the precursor of CuC_2O_4.

The reaction is as follows:

$$C_2O_4{}^{2-} + Cu^{2+} \rightarrow CuC_2O_4, \quad (1)$$

$$CuC_2O_4 \rightarrow CuO + CO + CO_2. \quad (2)$$

Its diffraction peaks were quite identical to those of pure CuO, which can be indexed as the monoclinic structure CuO ($a = 4.68$ Å, $b = 3.42$ Å, $c = 5.12$ Å) and diffraction data were in agreement with JCPDS card of CuO (JCPDS 5-0661). No characteristic peaks of impurities such as NaCl, CuC_2O_4, Cu_2O, and other precursor compounds were observed. Thus, the results clearly showed that the as-prepared product is single phase monoclinic CuO.

Fig. 3 presents Raman spectra of the as-prepared products. CuO belongs to the C_{2h}^6space group with two molecules per primitive cell. One can find for the zone center normal modes:

$$\Gamma = 4Au + 5Bu + Ag + 2Bg.$$

There are three acoustic modes (Au + 2Bu), six infrared active modes (3Au + 3Bu), and three Raman active modes (Ag + 2Bg).

As Fig. 3 shown, three Raman peaks at 621.4, 339.8, and 295.4 cm^{-1} were observed, with first one being broad and the second one being weakest. In comparison with the vibrational spectra of a CuO single crystal [23], the peak at 295.4 cm^{-1} is assigned to the Ag mode and the peak at 339.8, and 621.4 cm^{-1} to the Bg modes. The results are in agreement with the literature reference value for nanocrystal CuO [24]. As a consequence, the Raman spectra showed that the as-made product is composed of single phase CuO with monoclinic structure.

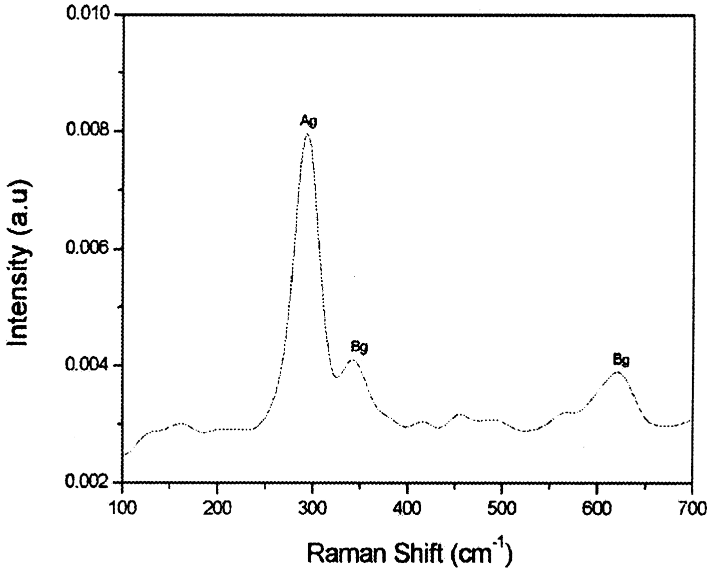

Fig. 3. The Raman spectra of the as-prepared CuO nanorods.

Fig. 4a and b shows XPS spectra taken from the Cu and O regions of the sample. The peaks at about 933.1 and 952.9 eV are attributed to Cu $2p_{3/2}$ and $2p_{1/2}$ (Fig. 4a), respectively, which are close to the data for Cu (2p) in CuO; the gap between the Cu $2p_{1/2}$ and $2p_{3/2}$ level is 19.8 eV that is approximately the same as in the standard spectrum of Cu. On the other hand, Cu (2p) peak is sharp, as implying the existence of Cu^{2+}, the peak at 933.1 eV with two shake-up satellites at about 9 and 10.1 eV higher in binding energy than that of the main peak. The existence of strong satellite features for Cu (2p) rules out the possibility of the presence of Cu_2O phase. From Fig. 4b, it is seen that the O (1s) XPS is asymmetric, indicating that at least two oxygen species are present in the nearby region. The peak at about 530 eV is due to oxygen in the CuO crystal lattice, which corresponds to O–Cu bonds, whereas the peak at about 532 eV is due to chemisorbed oxygen caused by surface hydroxyl, which corresponds to O–H bonds. The atomic composition of Cu and O were calculated by using the integrated peak area and sensitivity factors, the atomic ration of Cu:O is nearly 1:1. Thus the XPS results clearly proved that the sample is composed of CuO.

Fig. 5 exhibits the selected-area electron diffraction (SAED) patterns, taken from the same nanorod shown in Fig. 1b, can be indexed to the reflection of monoclinic CuO structure, which is consistent with the above XRD result. Clearly, it also demonstrates that the nanorod is single crystal.

As a rule, the chemical route often uses direct, very simple, chemical reactions to produce a product in powder form. These techniques have in common the fact that they do not offer underlying of physical or chemical principles. Thus, the generalization of the processes involved must require the understanding of the formation mechanism of nanorods. There usually exist two models that explain the mechanism of growth for nanorods [18]. One is the VLS growth mechanism; the other is the

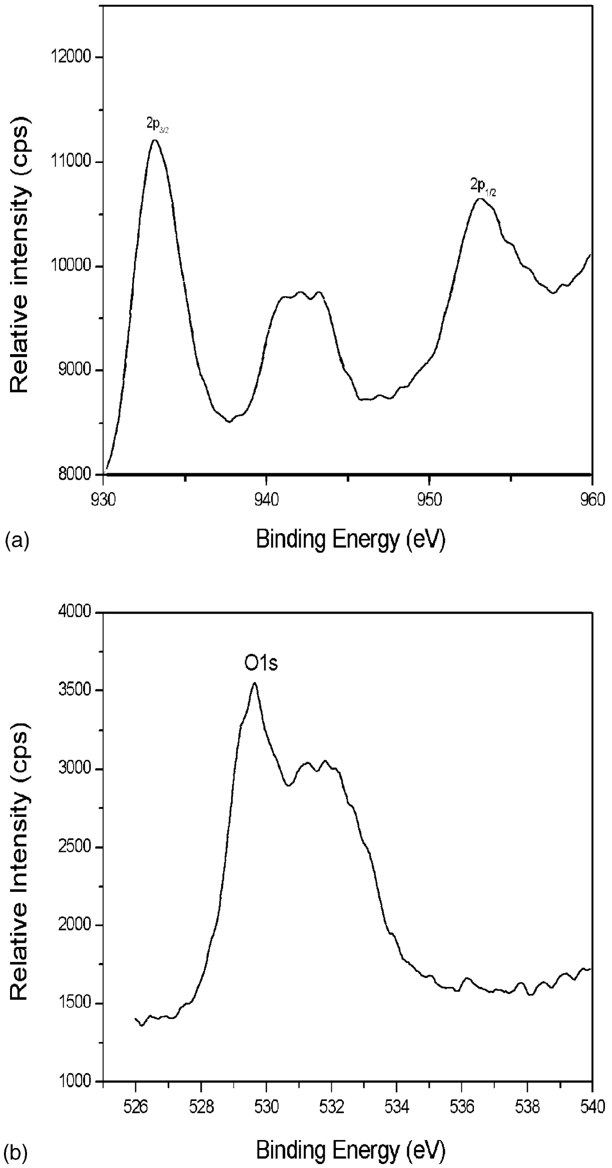

Fig. 4. The XPS analysis of the as-prepared CuO nanorods. (a) Cu region. (b) O region.

conventional spiral mechanism, that is, VS mechanism. In our product, because no droplets were observed on any end of the nanorods, which is the most remarkable sign of the VLS mechanism, no evidence indicated that the CuO nanorod growth matches VLS mechanism. On the contrary, there exists a conical tip at the end of nanorod (Fig. 1b), which is evidence of the spiral growth mechanism, hence, the growth mechanism of the CuO nanorods is most likely controlled by the VS growth mechanism.

Apparently, the formation of the nanorods must be affected by the character of the starting material, such as, the particle size and/or chemical activity in that the

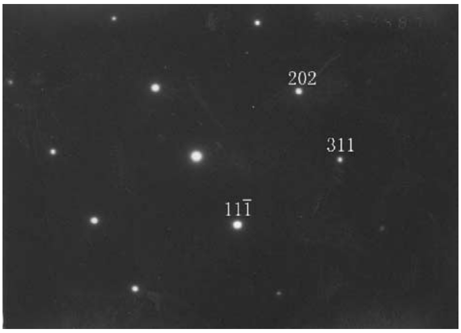

Fig. 5. SAED of one single crystalline CuO nanorods.

dissolution rate of the material depend upon these characters. The viscosity of the flux during calcination and the eutectic temperature of the system also affect the formation of the nanorods. We found that the CuO nanorods fail to form in the absence of NaCl and surfactant NP-9/5 or either of them. Only in this way can the CuO nanorods be formed in the presence of surfactant NP-9/5 and NaCl flux. We speculated that NaCl may significantly decrease the viscosity of the melt, and thus make mobility of components in the flux become easier, i.e. provide a favorable environment for the growth of nanorods, the surfactant NP-9/5 is favorable to form fine particle and make a ‘‘shell’’ surrounding the particles to prevent them from aggregating to larger particles during the grinding process of the precursor, on the other hand, during the formation of CuO nanorods, surfactant was thought to be able to act as a template, with the template action resulting in the expitaxial growth of the product. It is interesting to note that the precursor takes the shape of rod-like structure if the surfactant NP-9/5 is sufficient. A detailed study of mechanism of CuO nanorods is in progress.

4. Conclusions

In summary, CuO nanorods with diameters of 30–100 nm and lengths of several micrometers have been successfully prepared by a simple and novel method. The as-prepared CuO nanorods are structurally uniform, single crystalline. The growth mechanism of the CuO nanorods is most likely controlled by the VS growth mechanism. Particularly, surfactant NP-9/5 is of critically importance for the formation of CuO nanorods, if surfactant is chosen properly, this method may be extended to other oxide nanorods.

Acknowledgments

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