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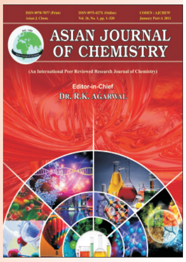

Synthesis and Characterization of Leaf-Like CuO Nanostructures†

AIQIN DING, CHONGHAI DENG*, CHENGLIANG HAN, JINSONG XIE and BENHONG YANG

Department of Chemical and Materials Engineering, Hefei University, Hefei, P.R. China

*Corresponding author: Tel: +86 551 2158436; E-mail: chdeng@hfuu.edu.cn

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Using copper chloride and triethylamine as starting reactants, uniform two dimensional (2D) leaf-like CuO nanostructures have been successfully prepared *via* a convenient microwave-assisted chemical route. The synthesized products were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and UV-visible absorption spectrum. The widths of the central parts for shuttle-like CuO nanoleaves are estimated to be 100-160 nm and the lengths are 0.8-1.4 μm. The growth process of leaf-like CuO nanostructures was investigated in detail. The band-gap energy of as-prepared CuO nanoleaves was estimated to be 2.56 eV from the optical absorption spectrum, showing a good quantum size effect.

Keywords: Oxides, Leaf-like, Crystal growth, UV-visible absorption.

INTRODUCTION

Cupric oxide (CuO) is an important *p*-type transition-metal-oxide semiconductor. Owing to its photoconductive and photochemical properties, CuO has many potential applications, such as solar cell[1], gas sensors[2], lithium ion electrode materials[3], catalysts[4] and superconductor[5]. The morphology and sizes of nanomaterials have been proved to have a significant influence on their properties and applications. Over the past years, various methods have been applied to prepare CuO with special morphologies, such as nanofibers[6], hollow nanospheres[7], rose-like nanoarchitectures[8], urchin-nanostructures[9], sheaf-like nanostructures[10], hollow submicrospheres[11] and nanowires [12]. In this work, a convenient microwave-assisted chemical route was applied to prepare leaf-like CuO nanocrystals using $CuCl_2·2H_2O$ and triethylamine as starting reactants. According to the optical absorption spectrum, the band-gap energy of as-prepared CuO nanoleaves was estimated to be 2.56 eV, showing a good quantum size effect.

EXPERIMENTAL

All chemicals (analytical grade reagents) were purchased from Shanghai Chemical Reagents Co. and used without further purification. Microwave-heating was carried out by a domestic microwave oven (Galanz WG800SL23-K6, 2.45 GHz, maximum power 800 W).

General procedure: 1 mmol $CuCl_2·2H_2O$ was dissolved in 30 mL deionized water under magnetic stirring. Then, 30 mL aqueous solution containing 0.4 mL triethylamine was added into the above solution. After stirring for 10-15 min, the obtained reaction solution was covered with a piece of PE film, then transferred to a domestic microwave oven and irradiated for 0.5 h at low power grade. After cooling down to room temperature, the back precipitate was filtered out, washed several times with anhydrous ethanol and deionized water and then dried in a vacuum at 60 ºC for 6-8 h for characterization.

Detection method: The phase purity of as-synthesized products was examined by X-ray diffraction (XRD) using a Dandong Y-2000 X-ray diffractometer equipped with graphite monochromatized CuK$_\alpha$ radiation (λ = 1.54178 Å). Field-emission scanning electron microscope (FESEM) images of the samples were recorded on a field-emission microscope (Sirion 200, 15 kV). The optical absorption spectrum was analyzed by a UV-VIS spectrophotometer (UV-5500PC).

RESULTS AND DISCUSSION

Fig. 1 presents a typical XRD pattern of as-prepared CuO nanoleaves. All diffraction peaks can be readily indexed to the monoclinic structured CuO (JCPDS No. 05-0661). The strong and sharp reflection peaks suggest that the CuO products obtained through microwave-assisted chemical route are highly crystalline. It is noteworthy that the peak intensity ratio of

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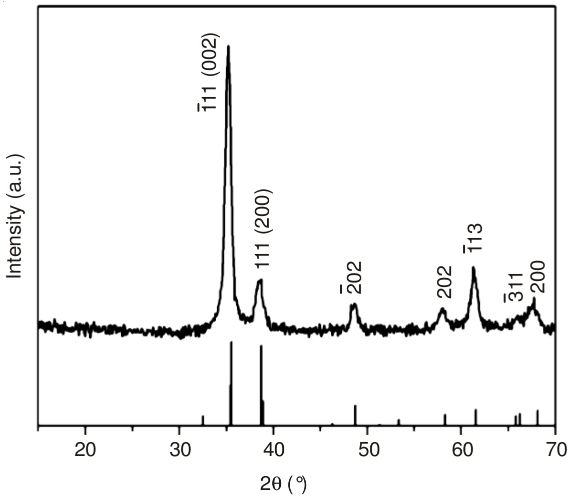

Fig. 1. XRD pattern of as-prepared leaf-like CuO nanostructures

$I_{-111(002)}/I_{111(200)}$ increase from 1.04 for standard CuO to 2.60 for the prepared CuO nanoleaves, indicating that the CuO nanocrystals may have an highly anisotropic growth.

Fig. 2 shows the morphologies of the as-synthesized CuO products. Fig. 2(a) is the low magnification FESEM image, demonstrating that large quantities of two dimensional (2D) leaf-like CuO nanocrystals are existed in the products. The high magnification FESEM image is given in Fig. 2(b), which distinctly reveals that both ends of each CuO nanoleaf are needle-shaped, that is, shuttle-like leaf. The widths of the central parts for leaf-like CuO nanostructures are estimated to be 100-160 nm and the lengths are 0.8-1.4 μm.

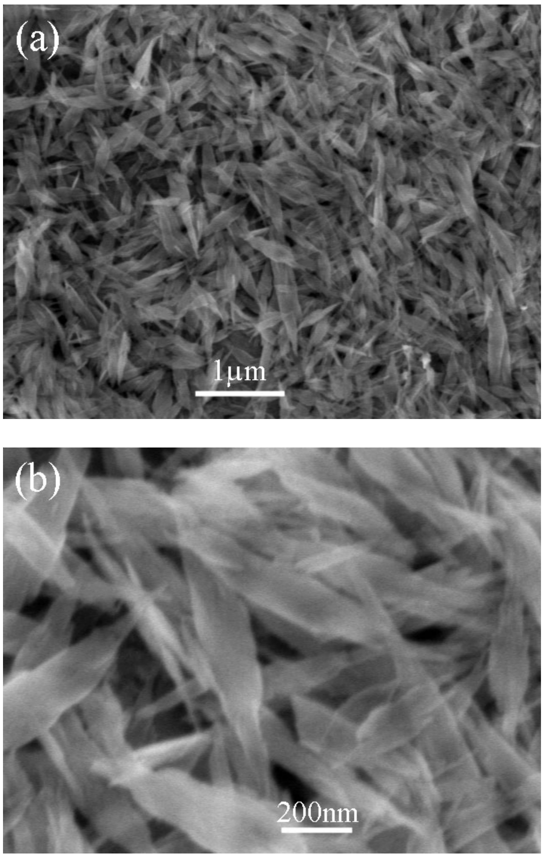

Fig. 2. Morphologies of as-prepared leaf-like CuO nanostructures

Time-dependent experiments were carried out to investigate the formation of leaf-like CuO nanostructures. Fig. 3(a) presents the XRD patterns of the products obtained at 5 min and 10 min keeping other conditions unchanged. When the microwave irradiating time is 5 min, the main phase of the products is CuO and a handful of $Cu(OH)_2$ with orthorhombic structure is also found (Marked by "*" in Fig. 3(a), JCPDS No. 13-0420). Pure monoclinic CuO can be generated when the irradiating time is added up to 10 min. In addition, it is detected that the peak intensity ratio of $I_{-111(002)}/I_{111(200)}$ increase from 1.67 for CuO nanocrystals obtained at 5 min to 1.84 for CuO nanocrystals obtained at 10 min, suggesting that the orientation growth of leaf-like CuO nanostructures gradually increase with the prolongation of reaction time. Fig. 3(b) give

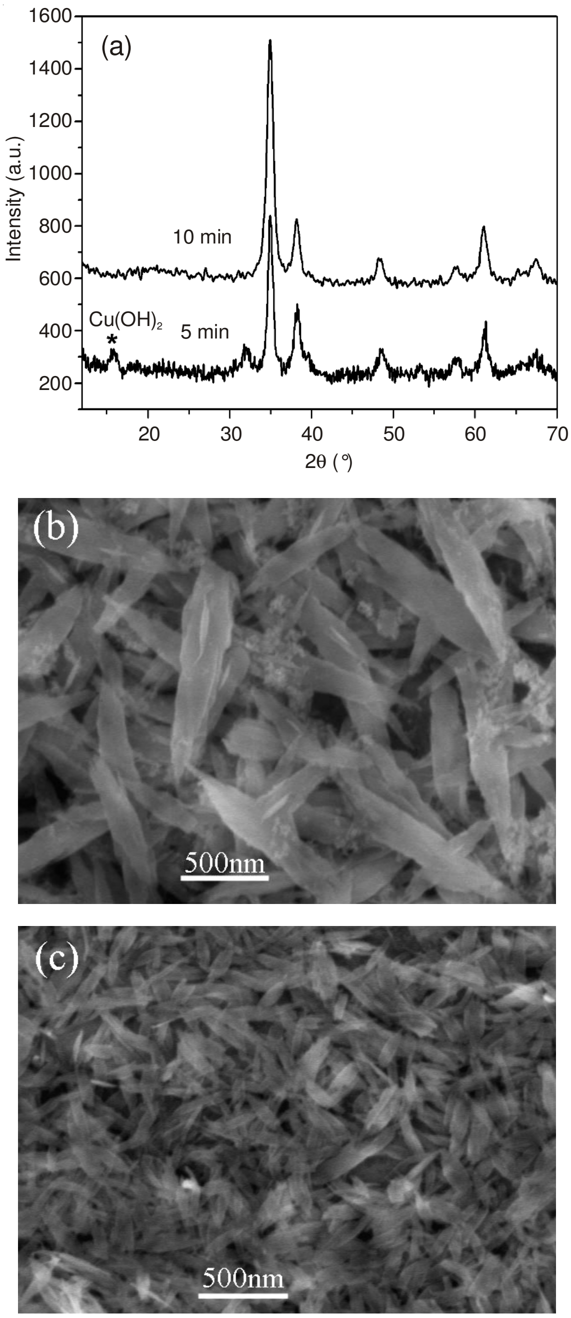

Fig. 3. (a) XRD patterns of the products obtained with different irradiating time, (b) FESEM image of CuO products obtained at 5 min, (c) FESEM image of CuO obtained with 1.6 mL triethylamine

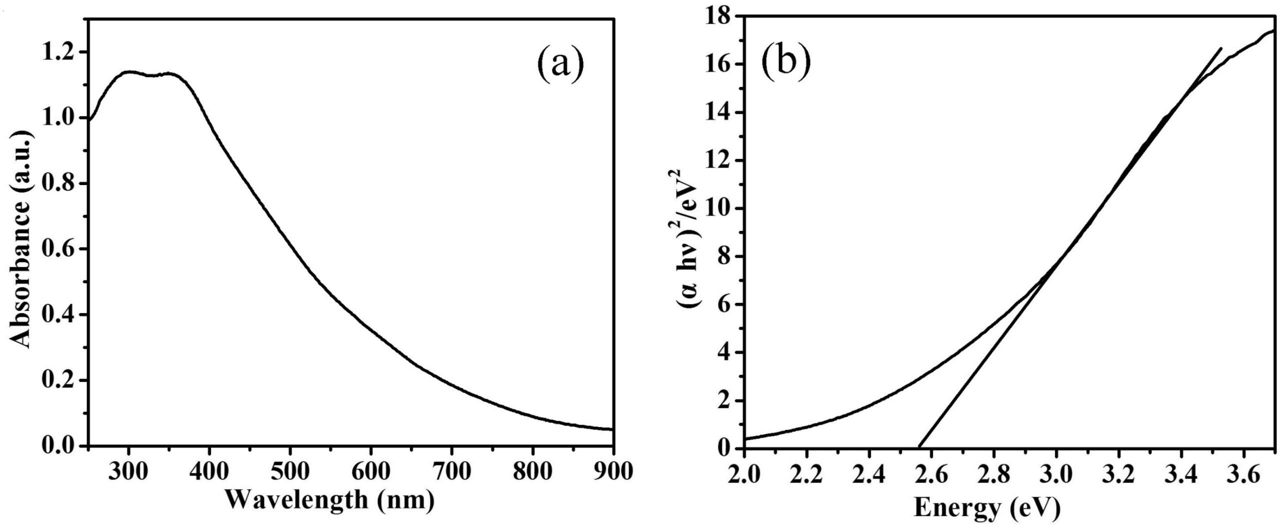

Fig. 4. (a) Optical absorption spectrum and (b) $(\alpha E_{photon})^2$ ~ E_{photon} curve of CuO nanostructures

the picture of the products obtained at 5 min, confirming that the products are composed of CuO nanoleaves and a small number of $Cu(OH)_2$ nanoparticles. In the process of experiments, we discovered that the dosage of triethylamine basically did not affect the morphology of CuO products. Fig. 3(c) is the FESEM image of CuO products obtained with the adding amount of 1.6 mL triethylamine while maintaining other parameter constant, indicating that leaf-like nanocrystals are still produced.

Based on the above experimental results, the formation process of leaf-like CuO nanostructures is proposed as follows. First, as a weak organic amine, the hydrolysis reaction for triethylamine could occur in the solution and produce OH^- ions (eqn. 1). Second, metal Cu^{2+} ions in the solution reacted with OH^- ions to form $Cu(OH)_2$ intermediate products (eqn. 2). Third, the newly-produced $Cu(OH)_2$ quickly dehydrolyze to generate CuO nuclei under microwave irradiating (eqn. 3). Then, the CuO nuclei rapidly grew along 2D direction possibly due to its internal crystal structure. Finally, elegant leaf-like CuO nanocrystallites were successfully achieved in the process of crystal growing and Ostwald ripening.

$$(CH_3CH_2)_3N + H_2O \rightarrow (CH_3CH_2)_3NH^+ + OH^- \quad (1)$$

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \quad (2)$$

$$Cu(OH)_2 \rightarrow CuO + H_2O \quad (3)$$

The optical absorption spectrum was shown in Fig. 4a. There is a wide absorption band in the ultraviolet region. Moreover, the $(\alpha E_{photon})^2$ ~ E_{photon} curve was used to estimate the band gap of as-prepared CuO sample, as indicated in Fig. 4b. By plotting and extrapolating to zero, the band gap E_g of as-preparfed leaf-like CuO nanostructures was estimated to be 2.56 eV, which is larger than that of bulk CuO (1.85eV). The blue shift phenomenon may be attributed to quantum size effects.

Conclusion

Two dimensional (2D) leaf-like CuO nanostructures were successfully prepared by employing a microwave-assisted chemical route by using triethylamine as an organic base and a morphology-controlled agent. The widths of the central parts for shuttle-like CuO nanoleaves are estimated to be 100-160 nm and the lengths are 0.8-1.4 mm. The band-gap energy of as-prepared leaf-like CuO nanostructures was estimated to be 2.56 eV, showing a good quantum size effect. The synthetic route is simple, manipulative and economical in the industrialized production in future.

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