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Flower-like CuO synthesized by CTAB-assisted hydrothermal method

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Abstract. Flower-like CuO nanostructures have been synthesized by cetyltrimethylammonium bromide (CTAB)-assisted hydrothermal method. Here, $CuCl_2 \cdot 2H_2O$ was used as copper raw material, and sodium hydroxide was used as precipitate. The resulting CuO powders were characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). X-ray diffraction (XRD) pattern exhibited the nanocrystalline nature with monoclinic structure for the as-synthesized nanostructures. FESEM images indicated that the flower-like CuO nanostructures are composed of many interconnected nanosheets in size of several micrometres in length and width and 60–80 nm in thickness. The possible formation mechanism of flower-like CuO nanostructures was discussed.

Keywords. CuO; flower; nanostructures; CTAB; hydrothermal method.

1. Introduction

Copper oxide (CuO) is a narrow band gap (E = 1·2 eV) p-type semiconductor and has received considerable attention due to its potential applications in many fields, such as solar cells (Musa *et al* 1998), magnetic storage media (Dar *et al* 2008), superconductors (MacDonald 2001), lithium batteries (Morales *et al* 2005), heterogeneous catalysts (Chen *et al* 2008), and so on. For the properties of semiconductors depending on their size, shape and crystalline structure, the control of the shape and size of the semiconductors has become more important. Recently, much effort has been devoted to synthesizing unique CuO nanostructures, such as rods (Xu *et al* 2002), robbons (Liu and Zeng 2004; Gao *et al* 2009), wires (Su *et al* 2007), belts (Zhang *et al* 2008b), sheets (Zheng *et al* 2007), platelets (Zarate *et al* 2007), needles (Dar *et al* 2008), and tubes (Cho and Huh 2008). As one of the novel structures, flower-like CuO was expected to offer some exciting opportunities for some potential applications on electrochemistry (Pan *et al* 2007), sensors (Teng *et al* 2008), catalysis (Vaseem *et al* 2008), and field emission (Yu *et al* 2008). So far, a variety of approaches to fabricating flower-like CuO nanostructures have been developed, such as hydrothermal (Yang *et al* 2007; Teng *et al* 2008), solution-immersion (Pan *et al* 2007), hydrolysis (Zhu *et al* 2007), microwave-hydrothermal (Volanti *et al* 2007; Xia *et al* 2009), chemical precipitation (Zhang *et al* 2008a), thermal oxidation (Yu *et al* 2008) and solution-phase route (Yu *et al* 2009). Teng *et al* (2008) synthesized the flower-like CuO nanostructures by hydrothermal process using copper threads as precursor and pointed out that the flower-like CuO nanostructures are made of three structures: the nanocrystals, the petals, and the assembly of the petals. Zhu *et al* (2007) reported a facile route for synthesis of the flower-like CuO nanostructures composed of many interconnected needle-like crystallites by hydrolyzing of $Cu(OAc)_2$ solution without any surfactants. Rose-like nanoarchitectures CuO composed of wide nanosheets have been prepared by a mild solution-phase route without the utility of the templates, additives or external magnetic field (Yu *et al* 2009).

Surfactant is conventionally used as morphology-directing agent to obtain nanostructural-conducting polymers due to its ability to form thermodynamically stable aggregates of inherently nanoscale dimensions (Jang and Oh 2002; Andrew *et al* 2003). CTAB is a useful surfactant that has been widely used in fabricating the nanomaterials to control the morphology. Recently CTAB-assisted hydrothermal technique has emerged as an attractive technique to investigate the synthesis of zinc oxide nanostructures. There are also some reports about the preparation of CuO nanostructures by using CTAB assisted hydrothermal technique. Cao and co-workers (Cao *et al* 2003) reported CTAB-assisted hydrothermal synthesis of CuO of various morphologies such as rod-like spheroidal, hexahedron structures, and other irregular structures. CuO shuttle-like nanocrystals were synthesized by the hydrolysis of cupric acetate ($Cu(CH_3COO)_2 \cdot H_2O$) via a CTAB-assisted hydrothermal route at low temperature (Zhang *et al* 2006). In this work, we reported the fabrication of flower-like CuO nanostructures by CTAB-assisted hydrothermal method and its characterization by X-ray diffraction (XRD). The morphology of flower-like CuO nanostructures was observed by field

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emission scanning electron microscopy (FESEM). The possible formation mechanism of flower-like CuO nanostructures was discussed.

2. Experimental

2.1 *Chemicals*

Analytical grade copper chloride dihydrate $CuCl_2 \cdot 2H_2O$ and sodium hydroxide NaOH were used as precursors, purchased from Tianjin Tianda Chemical Experiment Factory. Cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$) of analytical grade was purchased from Kewei Company of the Tianjin University. All the chemicals were directly used without further purification. Deionized water was used throughout.

2.2 *Sample preparation*

In a typical synthesis, the starting solution of copper (0·25 mol l^{-1}) was prepared by dissolving 0·8524 g (5 mmol) $CuCl_2 \cdot 2H_2O$ in 20 ml deionized water. Subsequently, the $CuCl_2$ solution was slowly dropped into the 50 ml of NaOH solution (3 mol l^{-1}) under vigorous stirring, and a blue-coloured precursor was obtained. 1 g CTAB (3 mmol) was added to the blue-coloured precursor and stirred vigorously for 30 min at 50°C to ensure complete dissolution of CTAB. This reaction solution was then transferred to a 100 ml Teflon-lined stainless steel autoclave and heated at 150°C for 12 h in an electric oven. After reaction, the autoclave was allowed to cool to room temperature. The obtained black precipitate was centrifuged and washed thoroughly with deionized water and ethanol. Then, the precipitate was dried in drying oven at 60°C for 24 h. Finally, the products were calcined in a furnace with an air atmosphere at 500°C for 2 h.

2.3 *Instrumentation*

Power X-ray diffraction (XRD) was measured on a DX-2000 X-ray diffractometer with CuKα radiation (λ = 0·1542 nm), and the tests were under accelerated voltage of 30 kV and current of 25 mA. Field emission scanning electron microscopy (FESEM) images and energy dispersive spectrum (EDS) were obtained by FEI Nanosem 430 FESEM and Genesis XM2 APEX 60SEM respectively.

3. Results and discussion

3.1 *The structural characterization of CuO*

The structure and chemical composition of the sample were confirmed by an X-ray diffraction. The typical XRD patterns of the samples synthesized via CTAB-assisted hydrothermal method at 150°C for 12 h are shown in figure 1. In the XRD pattern, compared with the standard diffraction peaks from JCPDS card no. 80-1917, the peaks located at 2θ values of 30–80° can be indexed to the characteristic diffractions of monoclinic phase CuO (a = 4·689 Å, c = 5·132 Å). The peak intensities and widths clearly indicated that the sample was highly crystalline in nature. Compared with the standard diffraction patterns, there are no other characteristic peaks observed belonging to impurities indicating that all the products were phase-pure.

Energy dispersive analysis of X-ray (EDAX) on the obtained as-prepared CuO sample was performed using the field emission scanning electron microscope (FESEM). EDAX spectra (shown in figure 2) clearly demonstrates

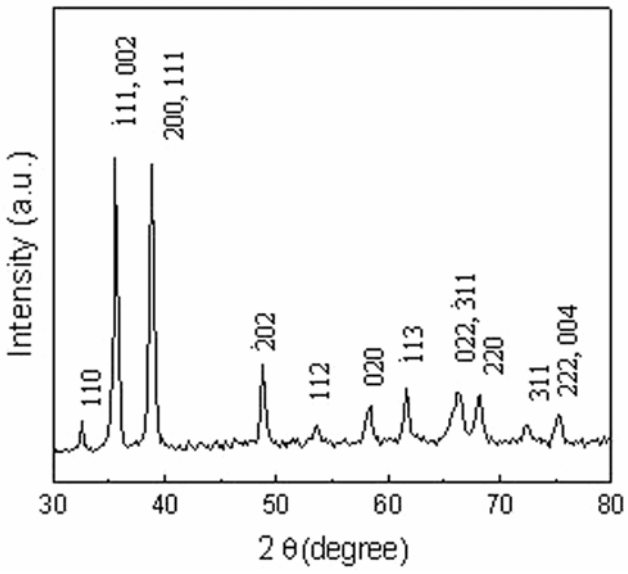

Figure 1. XRD pattern of flower-like CuO nanostructures synthesized at 150°C for 12 h.

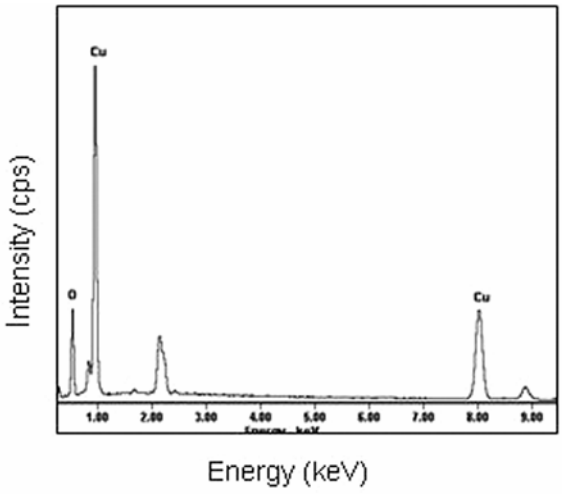

Figure 2. EDS spectra of flower-like CuO nanostructures.

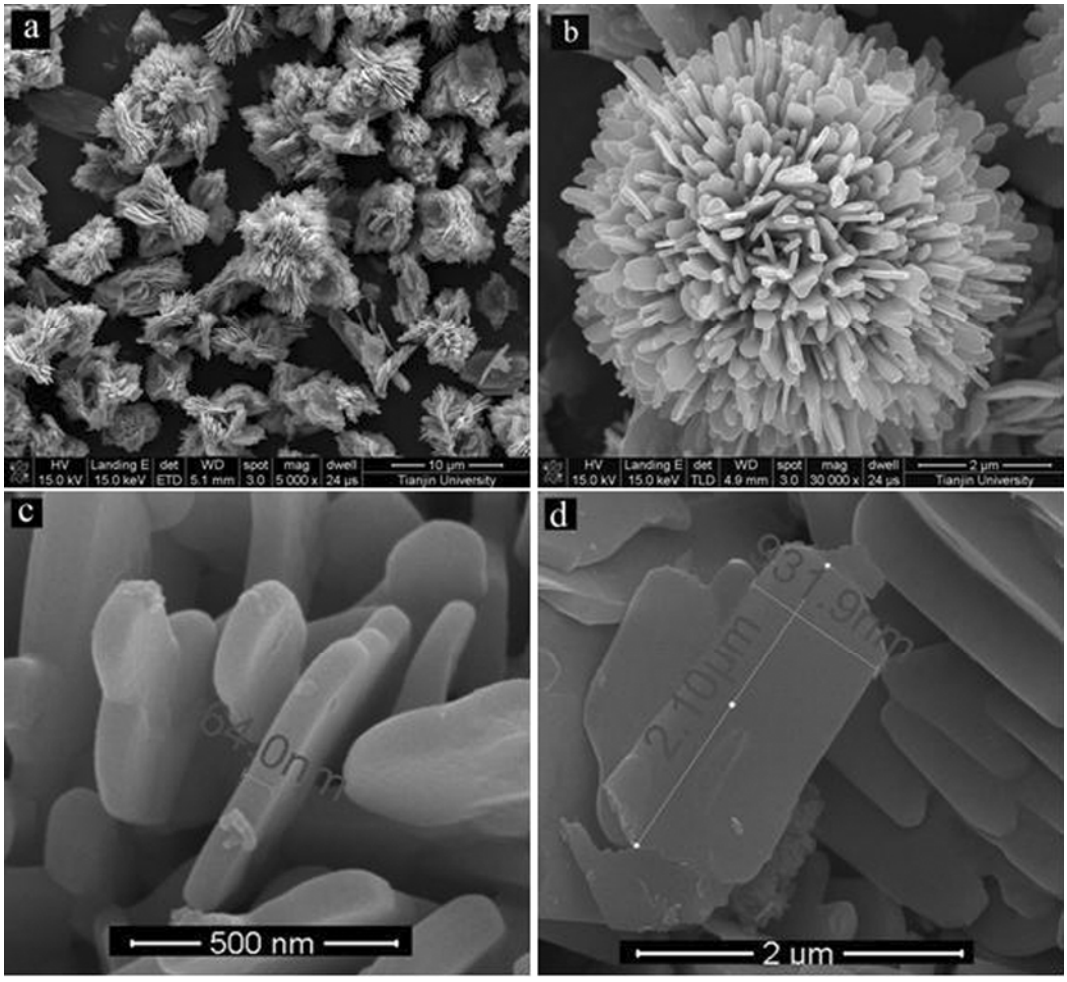

Figure 3. FESEM images of flower-like CuO nanostructures.

the presence of Cu and O peaks and quantitative analysis reveals that Cu and O are in a stoichiometry with 1 : 1 ratio. Therefore, it was obvious that the sample is composed of a pure monoclinic phase CuO, which is consistent with the XRD pattern.

3.2 *The morphology of product and formation mechanism*

The morphology of the as-prepared CuO sample was analysed by the FESEM as shown in figure 3. The lower magnification image in figure 3a indicates that the obtained CuO is composed of flower-like structure. The diameter of the micro-flower is about 6 μm. A detailed side view on the individual flower-like CuO particle can be observed from the higher magnification image (figure 3b), which clearly shows that the CuO flowers with spherical symmetry are composed of many interconnected wide nanosheets. The thickness of the nanosheets is in average of 60–80 nm (shown in figure 3c). Figure 3d shows a typical image of a piece of the leaves forming the flower-like structures, which clearly shows that the width of the nanosheets is about 932 nm and the length is about 2·10 μm at the higher magnification. FESEM images in figures 3b–d indicate that the nanosheets were first formed in the beginning and then they interconnect each other to form the flower-like CuO nanostructures. From figure 3b, we can also see that the nanosheets are aligned perpendicularly to the flower surface pointing toward a common centre.

According to references, the formation mechanisms of the flower-like CuO nanostructures were different when different preparation methods were used. Zhu *et al* (2007) obtained the flower-like CuO nanostructures composed of many interconnected needle-like crystallites by hydrolysing of $Cu(OAc)_2$ solution without any surfactants. They analyzed that the morphology of CuO crystallites is depended on different growing rates of various crystal facets. The coordination number of Cu^{2+} generally keeps six in the hydrolysis reaction. Each Cu^{2+} would be surrounded by six water molecules due to the solvating action when copper salt dissolved in water, in which four water molecules surrounded Cu^{2+} to form square structure, and other two water molecules located at its axis.

Teng *et al* (2008) synthesized the flower-like CuO nanostructures by hydrothermal process using copper threads as precursor. They investigated the influences of hydrothermal temperature and hydrothermal time on the nanostructures and reported that the formation of the flower-like structure was controlled not only by the growth thermodynamics, but also by the growth kinetics. Yu *et al* (2008) prepared the flower-like CuO nanostructures by reaction between a Cu plate and a KOH solution at room temperature. They speculated that the nanoflower was a representative morphology of spherulite formed by radiating growth from a centre or a number of centres and the $[Cu(OH)_4]^{2-}$ complexes played a key role in the growth of nanoflowers.

In our work, we reported the preparation of by cetyltrimethylammonium bromide (CTAB)-assisted hydrothermal method. CTAB has been systematically studied in the synthesis of mesostructured materials and may form spherical, cylindrical micelle, or even higher-order phases depending on the solution conditions (Fendler and Fendler 1975). Here, we think that CTAB serves as a template in the formation of flower-like CuO nanostructures. The formation of flower-like CuO nanostructures in the reaction system could be represented by the following reactions

$$Cu^{2+} + 4OH^- \leftrightarrow [Cu(OH)_4]^{2-}, \quad (1)$$

$$Cu(OH)_4^{2-} \leftrightarrow CuO + H_2O + 2OH^-. \quad (2)$$

The $[Cu(OH)_4]^{2-}$ anion can be considered as a precursor entity for the formation of CuO in this study. We believe that inorganic precursor $Cu(OH)_4^{2-}$ and cationic surfactant CTAB form CTA^+-$[Cu(OH)_4]^{2-}$ ion pairs at the beginning of the CTAB-assisted hydrothermal process. Since CTAB is a kind of strong-acid-weak-base salt, it can accelerate the ionization of $[Cu(OH)_4]^{2-}$. The CTA^+-$[Cu(OH)_4]^{2-}$ ion pairs form combination of CTAB and CuO. In addition to the general confirmation of CuO phase, the XRD patterns also provide information on crystal orientations (Chang and Zeng 2004). From the XRD pattern of figure 1, we know that low miller-indexed ((002) and (200)) reflections are the strongest. It indicated that the CuO nanosheets were first formed with the oriented growth of the $[Cu(OH)_4]^{2-}$ along (002) and (200) direction in the beginning (shown in figure 3d). Therefore a possible formation process of the flower-like CuO nanostructures could be purposely divided into several processes: (1) formation of CTA^+–$[Cu(OH)_4]^{2-}$ ion pairs; (2) growth of the CuO nanosheets (shown in figure 3d); and (3) formation of the flower-like nanostructures (shown in figure 3b).

4. Conclusions

Flower-like CuO nanostructures have been synthesized by cetyltrimethylammonium bromide (CTAB)-assisted hydrothermal method with $CuCl_2{\cdot}2H_2O$ and sodium hydroxide as raw materials. X-ray diffraction (XRD) pattern exhibited the nanocrystalline nature with monoclinic structure for the as-synthesized nanostructures. FESEM images indicated that the flower-like CuO nanostructures are composed of many interconnected nanosheets in size of several micrometres in length and width and 60–80 nm in thickness. The nanosheets were aligned perpendicularly to the flower surface pointing toward a common centre. A possible formation mechanism is proposed: the nanosheets were first formed in the beginning and then the nanosheets interconnect each other to form the flower-like CuO nanostructures.

Acknowledgements

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