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Synthesis and characterizations of nanoribbons and monodispersed nanocrystals of CuBr

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Abstract

Nanoribbons and monodispersed nanocrystals of CuBr have been prepared by a simple reaction between CuO suspension, $NH_2OH{\cdot}HCl$ and KBr in the presence of deionized gelatin at 10 °C. The products were characterized by X-ray powder diffraction, transmission electron microscopy and UV–vis absorption spectroscopy. The sizes of the monodispersed nanocrystals of CuBr were estimated by Debye-Scherrer formula according to XRD spectrum.

Keywords: A. Nanostructures; B. Crystal growth; B. Sol–gel chemistry; C. X-ray diffraction

1. Introduction

Nanoscales materials, such as monodispersed nanoparticles, nanowires, nanorods nanoribbobs and nanotubes, have attracted extensive synthetic attention as a result of their novel size-dependent properties [1–6]. It is well known that CuBr is a good Cu^+ ion conductor [7,8] through its three polymorphisms, the γ-phase with the zincblende structure below 385 °C, the β-phase with the wurtzite structure at 385 °C $< T >$ 469 °C and the α-phase with the fcc structure in a disordered distribution of Cu^+ ions between 469 °C and the melting temperature 488 °C [9]. In the γ-phase, the magnitude of electrical conductivity depends strongly on a small deviation from the ideal stoichiometric composition and on a

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small amount of impurity element included unavoidably in preparing specimens, while in the β-phase and α-phase the conductivity shows the intrinsic value almost independent of the way of the sample preparation. The copper(I) bromide is a candidate material for realization of electrochemical microsensors, because the Cu^+ ion conductivity permits in principle a fast adaptation to chemical potential variations in the environment and, furthermore, a non-negligible electron hole conductivity makes integration into microelectronic circuitry possible [10–12]. CuBr has been prepared by several different methods, such as laser deposition technique [13], vacuum evaporation [14], electrodeposition [15], sol–gel process [16] and liquid phase reaction [17]. In this paper, we report a method to synthesize CuBr nanoribbobs and monodispersed nanocrystals by a very simple reaction between $Cu(CH_3COO)_2$, NaOH, $NH_2OH{\cdot}HCl$ and KBr in the presence of deionized gelatin agents at 10 °C. The nanoribbobs and monodispersed nanocrystals of CuBr were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and UV–vis absorption spectroscopy. The sizes of the monodispersed nanocrystals of CuBr were estimated by Debye-Scherrer formula according to XRD spectrum.

2. Experimental procedure

2.1. Materials

All the reagents used in the experiment were of the analytical purity. $Cu(CH_3COO)_2$, NaOH, $NH_2OH{\cdot}HCl$, KBr, HCl, C_2H_5OH and deionized gelatin were purchased from Shanghai Chemical Reagent Factory (China). Distilled water was used throughout.

2.2. Instruments

Powder XRD patterns were recorded on a Shimadzu X-ray diffractometer XD-3A (Cu Kα radiation, $\lambda = 0.15418$ nm). TEM was performed using a JEOL-JEM 200CX instrument. The samples used for TEM observations were prepared by dispersing some products in ethanol followed by ultrasonic vibration for 10 min using a ultrasonic washing machine (50 W, 20 KHZ), then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon. A shimadzu UV-3100 photospectrometer was used to record the UV–vis absorption spectra of the as-prepared nanoribbobs and monodispersed nanocrystals.

2.3. Standard procedure for the preparation of CuBr

Synthesis of CuO suspension. CuO powder was prepared by adding 100 ml of 1.0 mol L^{-1} NaOH to the same volume of 0.5 mol L^{-1} $Cu(CH_3COO)_2$, aging the precipitated $Cu(OH)_2$ gel at 80 °C for 2 days in a laboratory oven, thoroughly washing with doubly distilled water and freeze drying. 0.5 mol L^{-1} CuO suspension was prepared in which 4% deionized gelatin was contained.

Preparation of CuBr nanoribborns. The same volume of the 0.5 mol L^{-1} CuO suspension stabilized, 0.3 mol L^{-1} $NH_2OH{\cdot}HCl$ and 0.5 mol L^{-1} KBr were added rapidly with stirring for 8 h under agitation at 10 °C. The pH values were adjusted to 4–6 with HCl in the course of the reaction. The products obtained were washed thoroughly with absolute ethanol in an inert glove box ($O_2 < 2$ ppm) and vacuum dried at room temperature overnight.

Synthesis of monodispersed CuBr nanocrystals. The same volume of the 0.5 mol L^{-1} CuO suspension stabilized and 0.3 mol L^{-1} $NH_2OH \cdot HCl$ were added rapidly with stirring for 10 h under agitation at 10 °C. The pH values were adjusted to 4–6 with HCl in the course of the reaction. The CuCl as intermediate product was separated using centrifuge machine. The same volume of the 0.5 mol L^{-1} CuCl suspension and 0.5 mol L^{-1} KBr were added rapidly with stirring for 10 min under agitation at 10 °C. After reaction, the nanoparticles of CuBr were rapidly separated from the solutions by centrifugation at 10,000 rpm for 8 min. The CuBr nanocrystals obtained were washed thoroughly with absolute ethanol in an inert glove box ($O_2 < 2$ ppm) and vacuum dried at room temperature overnight.

3. Results and discussion

3.1. XRD study

XRD patterns of the as-prepared CuBr were given in Fig. 1. Every XRD spectrum contains five peaks that are clearly distinguishable as shown in Fig. 1a and b. All of them can be perfectly indexed to crystalline γ-CuBr, not only in peak position, but also in their relative intensity. The peak positions are in good agreement with those for CuBr powder obtained from the International Center of Diffraction Data card (ICDD, formerly JCPDS, 06–0292). The size of the monodispersed nanocrystals of CuBr was calculated to be about 10 nm according to half-width of the diffraction peaks using Debye-Scherer equation.

3.2. TEM measurements

The morphology of the as prepared CuBr was studied by TEM. Fig. 2a shows the as prepared CuBr with nanoribborns by direct reaction. In indirect reaction, the CuCl as intermediate products exhibited fabric of flakes as shown in Fig. 2b. The monodispersed nanocrystals of CuBr with diameters range from 6 to 15 nm can clearly observe in Fig. 2c. This result is in good agreement with XRD result.

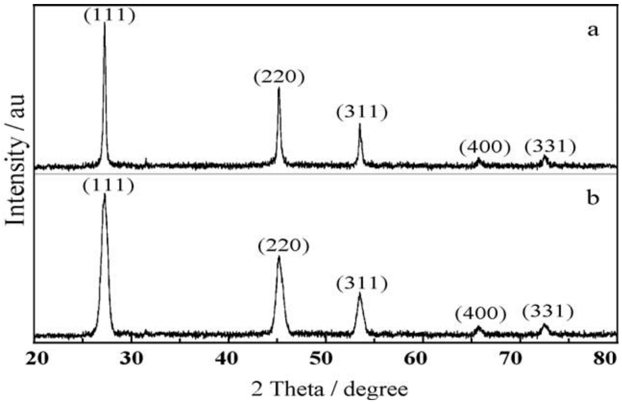

Fig. 1. Powder X-ray diffraction pattern of (a) the nanoribbons of CuBr and (b) monodispersed nanocrystals of CuBr.

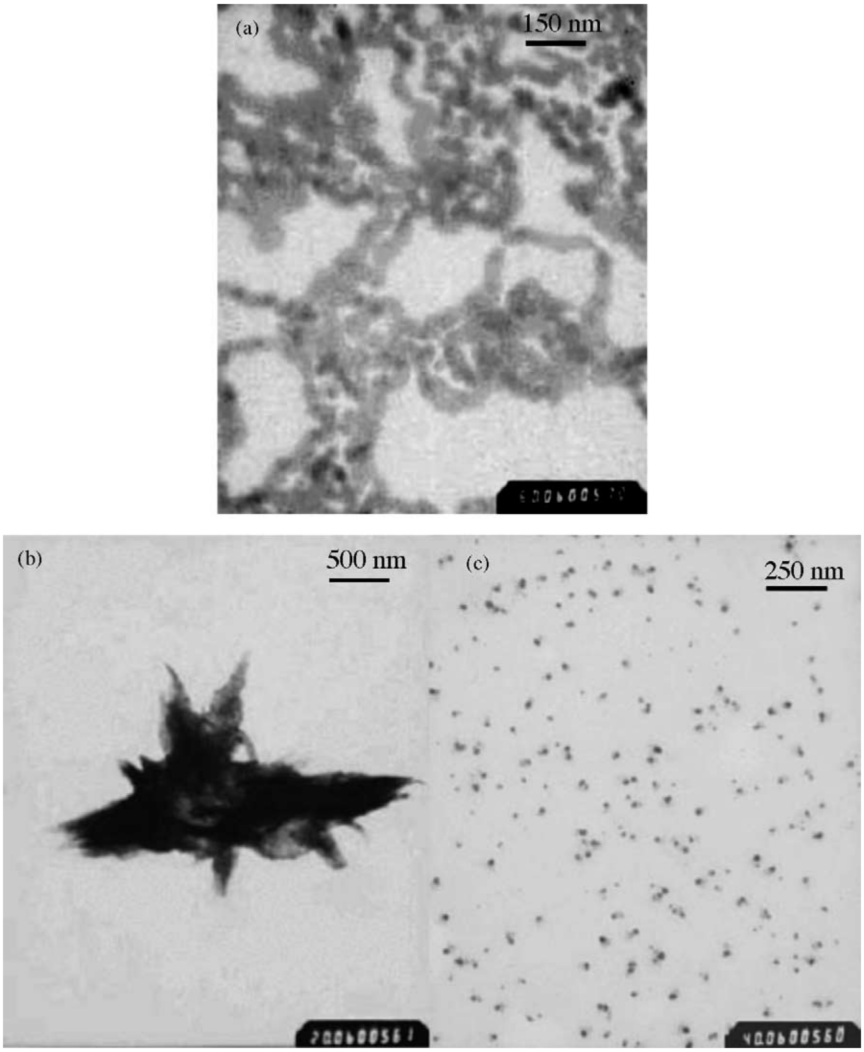

Fig. 2. TEM micrograph of (a) nanoribbons of CuBr; (b) the CuCl as intermediate products and (c) monodispersed nanocrystals of CuBr.

3.3. Proposed reaction path

Based on the investigation on the formation of CuBr, the possible mechanism may be summarized as below:

$$Cu(CH_3COO)_2 + 2NaOH \rightarrow Cu(OH)_2 + 2NaCH_3COO$$

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

The directed reaction as below:

$$4CuO + 2NH_2OH \cdot HCl + 2HCl + 4KBr \rightarrow 4CuBr + N_2O + 5H_2O + 4KCl$$

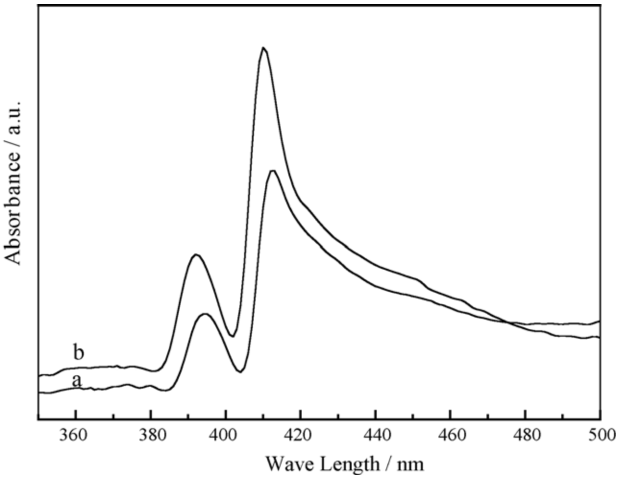

Fig. 3. The UV–vis absorption spectrum of (a) the nanoribbons of CuBr and (b) monodispersed nanocrystals of CuBr dispersed in ethanol solution.

The indirected reaction as below:

$$4CuO + 2NH_2OH \cdot HCl + 2HCl \rightarrow 4CuCl + N_2O + 5H_2O$$

$$CuCl + KBr \rightarrow CuBr + KCl$$

In the experiment, we employed hydroxylamine hydrochloride as the reducing agent. The gelatin on the surfaces of CuO particles may form an adsorption layer to control the diffusion of NH_2OH, Br ions and Cl ions. The reaction may occur mainly in a balanced region of the reagent flux and counter flux of the released mental ions, more or less away from the surface of each solid precursor particle. As a result, the obtained CuBr particles possess the nanoribborns structure and the CuCl as exhibited fabric of flakes. The gelation works as an inhibitor of both the direct reaction of NH_2OH with CuO and coagulation of the produced CuBr and CuCl particles. The reaction of CuCl with Br^- may rapidly occur in each region of the surface of CuCl flakes. A lot of CuBr nanoparticles was produced with stirring for 10 min under agitation at low temperature. After reaction, the nanoparticles were rapidly separated from the solutions by centrifugation. The monodispersed nanocrystals of CuBr were produced.

3.4. Optical properties

The as-prepared CuBr were well dispersed in ethanol to form a transparent solution (the concentration is 0.1200 mg/ml) by ultrasonic vibration for 10 min. UV–vis absorption spectrums of the CuBr nanoribbons shows two absorption peaks at 394 and 412 nm in Fig. 3a. As shown in Fig. 3b, the Peaks of the monodispersed nanocrystals of CuBr at 390 and 410 nm are in good agreement with the reported value for the CuBr nanoparticles with diameters ranging from 2 to 28 nm (exhibited peaks at 391 and 410 nm) [18].

4. Conclusion

The nanoribbons of CuBr have been successfully prepared by a sol–gel/emulsion technique at 10 °C. The monodispersed nanocrystals of CuBr have been successfully prepared by a reaction of the CuCl flakes with KBr at 10 °C. The possible mechanism was summarized. It is expected that the method can be extended to prepare other nanoribbons and monodispersed nanomaterials.

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