Cubic assembly composed of CuBr nanoparticles

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Abstract

Cubes of CuBr with an average dimensions of 0.3–0.8 \( \mu \text{m} \) have been prepared by a simple reaction between CuO suspension, NH\(_2\)OH and KBr in the presence of deionized gelatin at 40°C. Gelatin played a decisive role as an inhibitor of the direct attack of NH\(_2\)OH, KBr to CuO surfaces and coagulation of the growing CuBr in producing the cubes. The products were characterized by X-ray powder diffraction, transmission electron microscopy, X-ray photoelectron spectra techniques and UV-visible absorption spectroscopy. The sizes of the subunits of the polycrystalline CuBr particles were estimated by Debye–Scherrer formula according to XRD spectrum.

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1. Introduction

Cubes of nanometer to micrometer dimensions are being pursued with great interest because of several possible technical applications in development of new generation optical, electronic, magnetic and catalytic materials [1–6]. It is well known that CuBr is a good Cu\textsuperscript{+} ion conductor [7,8] through its three polymorphisms, the \( \gamma \)-phase with the zincblende structure below 385°C, the \( \beta \)-phase with the wurtzite structure at 385°C < \( T < \) 469°C and the \( \alpha \)-phase with the fcc structure in a disordered distribution of Cu\textsuperscript{+} ions between 469°C and the melting temperature 488°C [9]. In the \( \gamma \)-phase, the magnitude of electrical conductivity depends strongly on a small deviation from the ideal stoichiometric composition and on a small amount of impurity element included unavoidably in preparing specimens, while in the \( \beta \)- and \( \alpha \)-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\textsuperscript{+} ion conductivity permits in principle a fast adaptation to chemical potential variations in the environment and, furthermore, a nonnegligible 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 at 40°C by a very simple reaction between Cu(CH$_3$COO)$_2$, NaOH, NH$_2$OH·HCl and KBr in the presence of deionized gelatin agents. The CuBr cubes were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS) and UV-visible absorption spectroscopy. The sizes of the subunits of the polycrystalline CuBr particles were estimated by Debye–Scherrer formula according to XRD spectrum.

2. Experimental procedure

2.1. Materials

All the reagents used in the experiments were of the analytical purity. Cu(CH$_3$COO)$_2$, NaOH, NH$_2$OH·HCl, KBr, HCl, C$_2$H$_5$OH 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 K$_\alpha$ 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, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon. XPS were recorded on ESCALAB MK II instrument. A shimadzu UV-3100 photospectrometer was used to record the UV-visible absorption spectra of the as-prepared particles.

2.3. Standard procedure for the preparation of CuBr particles

The standard conditions for the synthesis of CuBr are as follows. First, CuO powder was prepared by adding 100 ml of 2.0 mol l$^{-1}$ NaOH to the same volume of 1.0 mol l$^{-1}$ Cu(CH$_3$COO)$_2$, 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. Then 1.0 mol l$^{-1}$ CuO suspension and 0.5 mol l$^{-1}$ NH$_2$OH·HCl were prepared, respectively, in which 4% deionized gelatin was contained. The same volume of the 1.0 mol l$^{-1}$ CuO suspension stabilized, 0.5 mol l$^{-1}$ NH$_2$OH·HCl and 1.0 mol l$^{-1}$ KBr were added rapidly with stirring for 8 h under agitation at 40°C. The pH values were adjusted to 5–7 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.

3. Results and discussion

3.1. XRD study

An XRD pattern of the CuBr cubes was given in Fig. 1. The XRD spectrum contains five peaks that are clearly distinguishable. All of them can be perfectly indexed to crystalline $\gamma$-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
subunits of the polycrystalline CuBr particles was calculated to be about 9 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 technique. Fig. 2 shows the as prepared CuBr with the shape of cubes and the average dimensions is about 0.3–0.8 μm. Although the aggregation is found in the image, we still can observe single particle in the image and these cubes appear to be hollow. The grain sizes from the TEM images are 6–10 nm. This result is in good agreement with XRD result.

3.3. XPS measurements

The wide XPS picture of the product is shown in Fig. 3. Fig. 4a shows the photoelectron spectrum of Cu$_{2p}$. The peak at 932.0 eV, which was corrected with reference to C$_{1s}$ (284.6 eV), corresponding to the binding energy of Cu$_{2p}^{	ext{3/2}}$, is in good agreement with data observed for CuBr [18]. As shown in Fig. 4b, the peak of Br$_{3d}$ at 69.3 eV is in good agreement with Br$^-\text{in CuBr}$. Thus, the XPS results prove that the sample is composed of CuBr.

3.4. Proposed reaction path

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

\[
\text{Cu(CH}_3\text{COO)}_2 + 2 \text{NaOH} \rightarrow \text{Cu(OH)}_2 + 2 \text{NaCH}_3\text{COO},
\]

\[
4 \text{CuO} + 2 \text{NH}_2\text{OH} \cdot \text{HCl} + 2 \text{HCl} + 4 \text{KBr} \rightarrow 4 \text{CuBr} + 5 \text{H}_2\text{O} + 4 \text{KCl}.
\]

In the experiments, we employed hydroxylamine hydrochloride as the reducing agent. The gelation works as an inhibitor of both the direct reaction of NH$_2$OH, KBr with CuO and coagulation of the produced CuBr particles.

3.5. Optical properties

UV-Visible absorption spectrum of the as-prepared CuBr particles dispersed in ethanol
solution shows two absorption peaks at 392 and 410 nm. The CuBr particles were well dispersed in ethanol to form a transparent solution by ultrasonic vibration for 10 min. As shown in Fig. 5, the peak of the as-prepared CuBr particles is 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) [19].

3.6. Roles of gelatin

The gelatin in the bulk and on the surfaces of CuO particles in the form of an adsorption layer may control the diffusion of NH₂OH, KBr molecules. As a result, the reaction may occur mainly in a balanced region of the reagent flux and counter flux of the released metal ions, more or less away from the surface of each solid precursor particle. In the absence of gelatin, the reaction may take place on the surfaces of the solid precursor, because of the too rapid diffusion of the reagent. The gelation works as an inhibitor of both the direct reaction of NH₂OH, KBr with CuO and coagulation of the produced CuBr particles.

4. Conclusion

CuBr cubes of with size of 0.3–0.8 μm have been successfully prepared by a sol–gel/emulsion technique at 40°C. The role of gelatin in the growing

Fig. 3. Wide X-ray photoelectron spectrum of the as-prepared cubic assembly composed of CuBr nanoparticles.

Fig. 4. High-resolution XPS spectra taken for the Cu and Br region of the as-prepared CuBr cubes: (a) Cu₂p and (b) Br₃d.

Fig. 5. The UV-visible absorption spectrum of the cubic assembly composed of CuBr nanoparticles dispersed in ethanol solution.
CuBr cubes was discussed. It is expected that the method can be extended to prepare other sub-micrometer cubes materials.

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References