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Sonochemical synthesis of copper selenides nanocrystals with different phases

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Abstract

A series of copper selenides ($Cu_{2-x}Se$, Cu_3Se_2 and CuSe) nanocrystals were prepared by a sonochemical method based on the reaction of copper acetate and sodium selenosulfate in an aqueous system. The phases and sizes of the nanocrystals could be controlled by changing the ratio of $[Cu^{2+}]/[SeSO_3^{2-}]$ and complexing agents. X-ray powder diffraction and transmission electron microscopy were used to determine the phase, purity, size and morphology of the products.

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1. Introduction

In recent years, there has been considerable interest in the study of copper selenides due to their composition's complexity [1] and wide applications as solar cell materials and superionic conductors [2–5]. The works are mainly concentrated on the chemical deposition and phase transformation of copper selenide thin films [6–10]. As reported, the phase transition in thin film is possible at room temperature by controlling the selenium concentration [7]. During the past years, a number of methods for the preparation of copper selenide nanocrystals of single phase have been reported including mechanical alloying (MA) method [11], gamma-irradiation [12], microwave-assisted heating [13], sonochemical method [14,15] and hydrothermal method [16,17]. It is recently reported [14] that Cu_3Se_2 and $Cu_{2-x}Se$ could be prepared by a sonochemical method. However, the products are not nanosized and the reactions lasted 4–8 h. Li et al. [15] reported the preparation of CuSe. They used the element Se as the selenium source and the reactions lasted for 10 h.

In this paper, we report a novel sonochemical route for the preparation of a series of copper selenides nanocrystals with average sizes ranging from 20 to 60 nm in an aqueous solution of copper acetate and sodium selenosulfate. It only

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needs 30 min to obtain the products, which include pure $Cu_{2-x}Se$, Cu_3Se_2, CuSe phases and the mix-phased particles of $Cu_{2-x}Se$ and Cu_3Se_2. In this system, *copper senelides* with different phases could be obtained by changing the ratio between Cu^{2+} and $SeSO_3^{2-}$ concentrations. Different complexing agents were used to control the sizes of the $Cu_{2-x}Se$ nanocrystals.

2. Experimental

All the reagents used were of analytical purity. 0.2 M Na_2SeSO_3 solution was prepared by stirring 0.2 M Se and 0.5 M Na_2SO_3 at ca. 70°C for 24 h [18]. In a typical procedure, an aqueous solution of $Cu(CH_3COO)_2$ was mixed with 0.2 M Na_2SeSO_3 solution in a 150 ml round-bottom flask to give a final concentration of 10 mM $Cu(CH_3COO)_2$ and 5–40 mM Na_2SeSO_3 and the total volume of the solution was 100 ml. To prepare $Cu_{2-x}Se$ with different sizes, trisodium citrate (TSC) and triethanolamine (TEA) was introduced into an aqueous solution containing 10 mM $Cu(CH_3COO)_2$ and 5 mM Na_2SeSO_3. Then, the solutions were irradiated with a high-intensity ultrasonic horn (Xinzhi Co., China, Ti-horn, 20 kHz, 60 W/cm^2) under ambient air for 30 min and black precipitates were obtained. After cooling to room temperature, the precipitates were centrifuged, washed by distilled water and acetone in sequence, and dried in air. The products were characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM).

The XRD patterns were recorded on Shimadzu XD-3A X-ray diffractometer (Cu K_α radiation, $\lambda = 0.15418$ nm). The TEM examinations were carried out on a JEOL JEM-200CX transmission electron microscope, using an accelerating voltage of 200 kV.

3. Results and discussion

Fig. 1 shows the XRD patterns of copper selenides with different phases. When the ratio of $[Cu^{2+}]/[SeSO_3^{2-}]$ was changed, copper selenides with different phases could be obtained. The results are shown in Table 1.

The TEM images (Fig. 2) show the sizes and morphologies of the copper selenide nanocrystals with different phases. The average sizes of the $Cu_{2-x}Se$ and Cu_3Se_2 particles are in the range of 20–25 nm and the sizes of the CuSe particles are in the range of 50–60 nm.

We found that the ratio between Cu^{2+} and $SeSO_3^{2-}$ concentrations played an important role in the phase transformation of copper selenides.

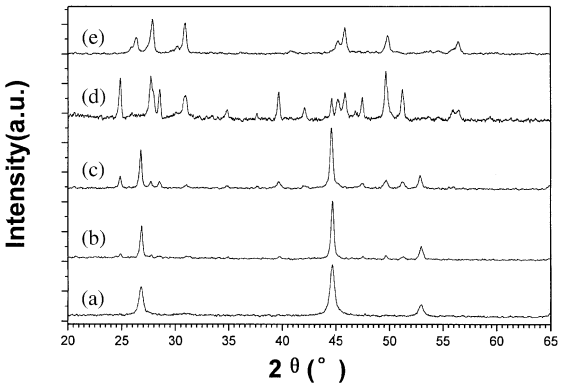

Fig. 1. Powdered XRD patterns of copper selenides: (a) $Cu_{2-x}Se$; (b,c) mix-phased $Cu_{2-x}Se$ and Cu_3Se_2; (d) Cu_3Se_2; and (e) CuSe.

Table 1
The XRD results of the as-prepared copper selenides nanocrystals

Sample No.	Phase from the XRD patterns	Ratio of $[Cu^{2+}]/[SeSO_3^{2-}]$
a	$Cu_{2-x}Se$ (JCPDS 5-667)	2
b,c	Mixed $Cu_{2-x}Se$ and Cu_3Se_2	From 2 to 0.5
d	Cu_3Se_2 (JCPDS 19-402)	0.5
e	CuSe (JCPDS 34-171)	0.25

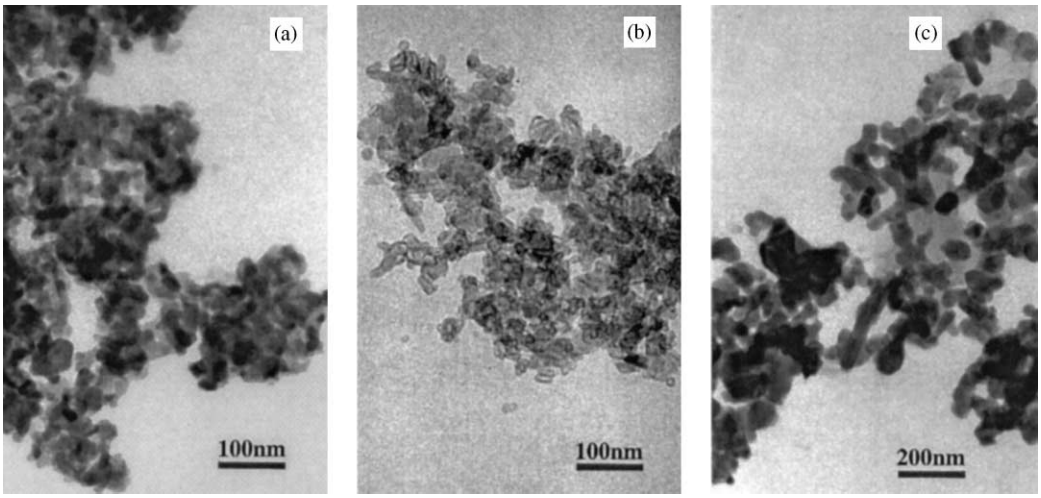

Fig. 2. TEM images of copper selenides: (a) $Cu_{2-x}Se$; (b) Cu_3Se_2; and (c) CuSe.

The reaction mechanism can be explained as follows:

$$H_2O \rightarrow H\cdot + OH\cdot, \quad (1)$$

$$2H\cdot + SeSO_3^{2-} \rightarrow Se^{2-} + H_2SO_3, \quad (2)$$

$$2OH\cdot + H_2SO_3 \rightarrow SO_4^{2-} + 2H^+ + H_2O, \quad (3)$$

$$2Cu^{2+} + SO_3^{2-} + 2OH^{2-} \rightarrow 2Cu^+ + SO_4^{2-} + H_2O, \quad (4)$$

$$Cu^{2+} + Se^{2-} \rightarrow CuSe, \quad (5)$$

$$Cu^{2+} + 2Cu^{2+} + 2Se^{2-} \rightarrow Cu_3Se_2, \quad (6)$$

$$(2-x)Cu^{2+} + Se^{2-} \rightarrow Cu_{2-x}Se, \quad (7)$$

$$n(\text{CuSe or } Cu_3Se_2 \text{ or } Cu_{2-x}Se) \rightarrow (\text{CuSe or } Cu_3Se_2 \text{ or } Cu_{2-x}Se)_n. \quad (8)$$

The ultrasound irradiation can promote the formation of copper selenides nanocrystals. According to the research by Suslick et al. [19,20], the effects of high-intensity of ultrasound result from acoustic cavitation: the formation, growth and implosive collapse of bubbles in liquids which generate transient temperatures of ~ 5000 K, pressures of ~ 1800 atm and cooling rates of 10^{10} K/s. The extreme conditions of sonification were favorable for many reactions in liquid and liquid–solid mixture [21]. During sonochemical processes, $H\cdot$ and $OH\cdot$ radicals are formed [22]. The situ-generated $H\cdot$ radicals can react with $SeSO_3^{2-}$ to give Se^{2-} via reactions (2) and (3). Meanwhile, Cu^{2+} can be reduced by SO_3^{2-} to generate Cu^+ via reaction (4). When $[SeSO_3^{2-}]$ was high enough, reaction (2) may be the main reaction so that the product is CuSe. The rate of reaction (2) decreased sharply with the decrease of the concentration of $SeSO_3^{2-}$. When the $[SeSO_3^{2-}]$ was decreased, the reaction (4) changed gradually to be the main reaction so that the Cu^+ and Cu^{2+} react with Se^-, leading to the formation of Cu_3Se_2 and $Cu_{2-x}Se$, as shown in reactions (6) and (7). The freshly generated nuclei have the tendency to grow into larger particles via reaction (8). The release of Se^{2-} is a continuous process, which makes the gradual growth of copper selenides nanocrystals.

We also found that the sizes of the products would be changed when adding complexing agents in the system. Fig. 3 shows the XRD patterns of $Cu_{2-x}Se$ nanocrystals obtained by using different complexing agents. We selected $Cu_{2-x}Se$ as a sample to investigate the effect of the complexing agents. The products obtained have the different average sizes from 20 to 60 nm estimated by Debye-Scherrer formula. The complexing strength of different complexing agents has influence on the nucleation rate of copper selenides, which leads to

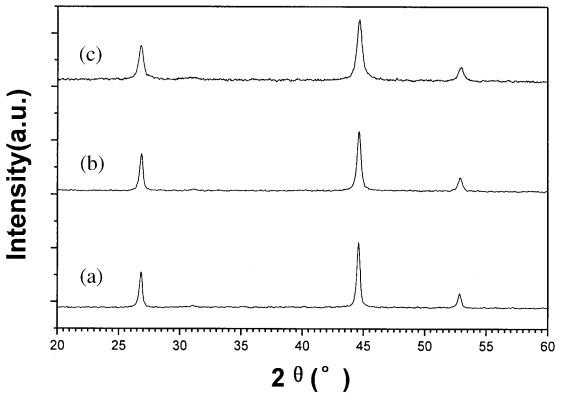

Fig. 3. Powdered XRD patterns of $Cu_{2-x}Se$ prepared in the presence of different complexing agents: (a) TSC; (b) TEA; and (c) without any complexing agent.

the formation of $Cu_{2-x}Se$ nanocrystals with different sizes.

4. Conclusions

In summary, a convenient sonochemical route has been successfully established to prepare copper selenides nanocrystals with different phases. It is found that the ratio of $[Cu^{2+}]/[SeSO_3^{2-}]$ determines the phases of the products. The size of $Cu_{2-x}Se$ nanocrystals can be controlled by using different complexing agents. This route is proved to be a convenient, mild and energy-efficient route for the preparation of copper selenides nanocrystals with different phases.

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