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One-pot, rapid synthesis of chalcopyrite $CuInSe_2$ nanoparticles for low-cost thin film solar cell

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ABSTRACT

In this work, highly dispersed and near stoichiometric chalcopyrite $CuInSe_2$ nanoparticles were successfully synthesized via a facile and rapid one-pot method. The effects of reaction temperature and reaction time on the crystal phase, morphology, element composition and the absorption spectrum of the as-synthesized $CuInSe_2$ nanoparticles were investigated by x-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX) and UV-Vis-IR spectrophotometer, respectively. The XRD patterns showed that the as-synthesized nanoparticles had pure chalcopyrite phase with the particle size in the range of 50–300 nm confirmed by FE-SEM images. The Vis-IR absorption spectra showed strong absorption in the entire visible light to near-infrared region, the estimated band gap of the as-synthesized nanoparticles matched very well with that of the bulk $CuInSe_2$ material. All results suggested that the as-synthesized $CuInSe_2$ nanoparticles were good light absorber layer material for thin film solar cell.

1. Introduction

$CuInSe_2$ (CISe) and its related alloys with gallium and sulfur $Cu(In_xGa_{1-x})(S,Se)_2$ (CIGS) have attracted much attention as solar cell absorber layer materials because of their high absorption coefficient (10^5 cm^{-1}), good photostability and demonstrated high solar cell conversion efficiency of 20.3% [1–3]. However, the absorber layer of high efficiency solar cell is usually prepared by vacuum processes, which have several limitations such as high production cost, complex process and difficulty in scaling up production [4,5]. Additionally, highly toxic H_2Se is commonly used during selenization. In recent years, nanoparticle-based printing technology has been developed as alternative for the fabrication of solar cell absorber layer to reduce production costs, which is a very promising technology for the fabrication of low-cost absorber layer due to its important advantages, e.g., simple, non-vacuum, low-temperature, high material utilization efficiency (close to 100%) and compatibility with roll-to-roll production process. For the nanoparticle-based printing technology, the synthesis of ordered chalcopyrite and near stoichiometric CISe nanoparticles is a key step to have a good photovoltaic conversion.

By using CISe nanoparticles with fixed composition and crystalline structures, high temperature selenization processes under a selenium or H_2Se environment can be minimized or even eliminated. Furthermore, the composition of the printed film can be easily controlled on all scales by controlling the composition of the nanoparticles. Several techniques have been reported for the synthesis of CISe and related nanoparticles, such as solvothermal [6–8], thermal decomposition [9], hot injection [10,11], ball milling [12] and polyol reflux method [13]. However, most of the above-mentioned techniques cannot sufficiently control the size, shape, crystallinity or purity of the nanoparticles. Moreover, the synthesized nanoparticles generally agglomerate seriously. So far, the rapid hot injection method is the most successful and widely used technology in the nanoparticles synthesis, which can synthesize smaller, uniform and dispersed nanoparticles. However, it is difficult to mass production because the injection rate of monomers and mass transfer are limited in large quantities [14]. To overcome this difficulty, a one-pot strategy has been used to synthesize highly dispersed nanoparticles. One-pot solution process, which features easy handling and high reproducibility, has been used for the synthesis of many binary sulfides such as CdS [15]. However, this mild and facile method has rarely been applied in the synthesis of ternary or quaternary chalcogenide nanoparticles.

In this paper, we reported the facile and rapid synthesis of CISe nanoparticles by one-pot method. The effects of reaction temperature and time on the crystal phase, morphology, element composition and the absorption spectrum of the as-synthesized CISe nanoparticles were investigated.

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2. Experiment

2.1. Materials

Copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, AR), indium (III) chloride tetrahydrate ($InCl_3 \cdot 4H_2O$, 99.99%), selenium powder (Se, 99.95%), hexane (AR) and ethanol (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Oleylamine (OLA, 80–90%) was the product of Aladdin. All reagents were used without further purification.

2.2. Synthesis of CISe nanoparticles

Copper (II) chloride dihydrate, indium (III) chloride tetrahydrate and selenium powder were used as reagents, and OLA acted as both solvent and capping agent in the study. In a typical experimental procedure, 1 mmol copper (II) chloride dihydrate, 1 mmol indium (III) chloride tetrahydrate and 10 ml OLA were successively added to a 50-ml three-neck ground bottom flask and magnetic stirred at 60 °C. The solution color changed from sky blue to blue-green and then to brown as the reaction proceeded. Then the solution was cooled down to room temperature and the selenium suspension in OLA (2 mmol selenium powder dissolved in 10 ml OLA) was quickly added into the three-neck flask. The flask was attached to a Schlenk line and degassed at room temperature for several minutes. Then the mixture was heated to 130 °C and purged with N_2 gas for three times. The temperature of the mixture was slowly raised to 265 °C, which took about 45 min. The temperature was then kept for 1 h to let the particles grow. After the reaction finished, the mixture was cooled down to room temperature. Non-polar hexane (10 ml) and polar ethanol (10 ml) were successively added into the flask to disperse and flocculate the nanoparticles. The obtained mixture was centrifuged with the rate of 8000 rpm for 10 min without size-selective precipitation and then washed with ethanol for several times to remove the by-products. Finally, the dark precipitate was collected and dried at 60 °C for several hours for the characterizations.

2.3. Characterizations of CISe nanoparticles

The phases and crystallographic structures of the as-synthesized nanoparticles were characterized by x-ray diffraction (XRD; D8 ADVANCE, Bruker). The morphology of the as-synthesized nanoparticles was observed by field emission scanning electron microscopy (FE-SEM; QUANTA FEG450, FEI). Element composition of the as-synthesized nanoparticles was also analyzed by energy dispersive X-ray spectroscopy (EDX; FT/IR-4200, JASCO). The absorption spectra of the as-synthesized nanoparticles were measured with an UV-Vis-IR double beam spectrophotometer (Lambda 1050, Perkin-Elmer). The structure and morphology were further examined by dispersive Raman spectroscopy (Raman Station 400/400 F, Perkin-Elmer) and transmission electron microscopy (TEM; Tecnai F30, FEI). All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Effects of reaction temperature

To understand the effects of reaction temperature on the properties of the as-synthesized CISe nanoparticles, several experiments were designed and carried out by one-pot method on the basis of temperature variable. The experimental parameters for the synthesis of CISe nanoparticles are shown in Table 1.

XRD patterns as shown in Fig. 1(a) reveal the effects of reaction temperature on the structure of the as-synthesized CISe nanoparticles. All samples exhibited high crystalline quality with a polycrystalline chalcopyrite crystal structure of CISe. The major diffraction peaks observed at 26.58°, 44.23°, 52.39°, 64.38°, 70.78°, 81.34° and 87.39°, which match very well with the reference JCPD data (PDF card no. 40-1487) for chalcopyrite CISe, are indexed to the (112), (204)/(220), (116)/(312), (008)/(400), (316)/(332), (228)/(424) and (336)/(512) of the tetragonal chalcopyrite crystal structure, respectively. However, these major diffraction peaks are common to both the disordered sphalerite and the ordered chalcopyrite structures. In order to ascertain that the as-synthesized nanoparticles are chalcopyrite, it is critical to be able to observe the (101), (103) and (211) minor peaks that are unique to the chalcopyrite structure [10]. With the reaction temperature increasing, the diffraction peaks become sharper, indicating that grains grew. These minor peaks at 17.12°, 27.68° and 35.48° corresponding to the (101), (103) and (211) diffraction peaks, respectively, appear in the samples when the reaction temperature is over 200 °C (as shown in Fig. 1(b)), indicating that the as-synthesized nanoparticles are chalcopyrite when the reaction temperature is higher than 200 °C. Moreover, the minor peaks gradually increase with the increase of reaction temperature. It was found that adding the Se suspension at low temperature (from room temperature to 130 °C) and controlling the temperature rise slowly could easily form the ordered chalcopyrite phase. However, disordered sphalerite phase was formed either adding the Se suspension at higher temperature (over 200 °C) or adding the Se solution. The reasons may be that adding the Se suspension at low temperature can prevent large supersaturation (Se powder is difficult to dissolve in OLA at low temperature) and allow the atoms to form the thermodynamically favored chalcopyrite phase. However, either adding the Se suspension at higher temperature or adding the Se solution can lead to large supersaturation and tend to form sphalerite phase caused by disordering of the cation lattice.

The average crystalline size of the nanoparticles synthesized at 200 °C, 230 °C, 265 °C and 285 °C, calculated by Scherrer equation based on the (112) peak is about 44 nm, 75 nm, 78 nm and 98 nm, respectively.

Some other peaks also appear in Fig. 1. These peaks do not correspond to the diffraction peaks of any materials by comparing to the standard cards, but match very well with the diffraction peaks of the sample stage. Therefore, these peaks should be the diffraction peaks of the sample stage, instead of the diffraction peaks of impurities, indicating the high phase purity of the as-synthesized CISe nanoparticles.

To understand the reaction mechanism of one-pot method, the products obtained at different stages of CISe nanoparticles synthesis process were investigated. Fig. 2 shows the XRD patterns of the products obtained at different stages. The XRD results exhibit that the phase formation sequence is from CuSe to $CuInSe_2$. Surprisingly, the diffraction peaks of In-containing secondary phase, such as In_2Se_3, are not observed, the similar result has been reported by Olejnicek et al. [16]. Olejnicek et al. thought that the In-containing species must be amorphous, as no XRD signals were observed. Raman-active phonon frequencies for amorphous $In_{1-x}Se$ alloys have been reported [17], but it was not exhibited by the samples of Olejnicek et al. Therefore, we speculate that In-containing secondary phase has not been formation independently in the reaction process. The possible reaction mechanism is as follows. OLA acted as both high boiling point solvent and reducing agent during the reaction. Firstly, Cu^{2+} ion was reduced to Cu^{+} ion, Se powder dissolved partially and was reduced to Se_x^{2-} ion by OLA at a lower reaction temperature. OLA can also behave as a complex ligand and form stable complexes with $CuCl_2$, $InCl_3$ and Se powder. The

Table 1
Experimental parameters and chemical composition of the CISe nanoparticles.

Reaction temperature (°C)	Reaction time (h)	Mole ratio of reagents ($CuCl_2$:$InCl_3$:Se)	Chemical composition (Cu:In:Se)
200	1	1:1:2	23.7:29.6:46.7
230	1	1:1:2	29.0:23.5:47.5
265	1	1:1:2	25.6:23.6:50.9
285	1	1:1:2	24.7:26.0:36.1