

Synthesis of CuInSe_2 nanoparticles by phase transformation of In_2Se_3 via wet chemical process in low temperature

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Chalcopyrite-type CuInSe_2 nanoparticles are successfully prepared by using In_2Se_3 nanoparticles as a precursor reacted with copper chloride (CuCl) solution via a phase transformation process in low temperature. The reaction time is a key parameter. After the reaction time increasing from 0.5 h to 8 h, In_2Se_3 and CuCl react with each other gradually via phase transformation into CuInSe_2 without any intermediate phase. The crystalline structure and morphology of the CuInSe_2 nanoparticles are characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). The diameter of CuInSe_2 nanoparticles with good dispersibility ranges from 10 nm to 20 nm. The band gap of the CuInSe_2 nanoparticles is 1.04 eV calculated from the ultraviolet-visible (UV-VIS) spectrum.

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Copper indium diselenide (CIS) and related materials are one kind of the most promising candidates for thin film photovoltaic applications due to their unique structural and electrical properties, such as high absorption coefficient, suitable band gap and good radiation stability^[1-3]. The low fabricating cost of CIS is a key aspect in the development of low-cost solar cells. In recent years, many methods for the synthesis of CIS have been reported, such as solid-state reaction^[4], mechanochemical process (MCP)^[5,6], solvothermal methods^[7-9], microwave method^[10], molecular single-source precursors^[11] and hot-injection method^[12-14]. The above mentioned methods need either high processing temperature or special apparatus, and some of them even use toxic agents such as organ-metallic compounds.

Fu et al^[15,16] reported the synthesis of CIS by using Cu_{2-x}Se as precursor to react with InCl_3 in ethylenediamine. However, in this paper, we obtain CIS nanoparticles by using the as-prepared precursor In_2Se_3 nanoparticles reacted with CuCl in deionized water at 0 °C. In this process, there is no organic solvent and mild fabrication condition, which can be much beneficial to decrease the production cost, and it is a most important aspects in the development of low-cost solar cells. Meanwhile, the process is much easier. To the best of our knowledge, this method is used to prepare CIS nanoparticles for the first time.

All chemicals were of analytical grade and used as re-

ceived without further purification. CIS nanoparticles were prepared by employing selenium powder, copper (I) chloride and indium (III) chloride. Selenium ions were fabricated by dissolving selenium powder into sodium borohydride (NaBH_4) solution under Ar gas atmosphere.

In a typical synthesis process of In_2Se_3 nanoparticles, 0.15 mol NaHSe_4 was slowly dripped into 0.1 mol InCl_3 with the pH value of 7.5–8.0 and with mechanical stirring under Ar atmosphere. After that, the resulting In_2Se_3 precipitates was centrifuged and washed several times with deionized water, and then dried at 6 °C for 6 h in vacuum.

CuCl (0.225 mol) was first dissolved in 100 mL deionized water, and the pH value is adjusted to 7.0. Then 0.15 mol as-prepared In_2Se_3 nanoparticles were distracted in deionized water with magnetic stirring for 10 min. The CuCl was slowly dripped into the suspension liquid of as-prepared In_2Se_3 nanoparticles at 0 °C in an ice bath with mechanical stirring. The CIS precipitates were then centrifuged and washed with deionized water several times to remove the solvent and by-products, and then dried in an oven at 60 °C for 6 h.

The obtained products were characterized with X-ray diffraction (XRD) with Cu $K\alpha$ radiation ($\lambda=0.154178$ nm). Scanning electron microscopy (SEM) images were taken with a field emission scanning electron microscopy (FESEM, JEOL, JSM-6340F) operated at an accelerating voltage of 200 kV. Then, the adsorption ultraviolet-visi-

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ble (UV-VIS) spectrum of the centrifuged solution was recorded using a UV-VIS spectrophotometer (Perkin Elmer Lambda 850).

The XRD pattern and SEM image of the as-prepared In_2Se_3 powders are shown in Fig.1. Fig.1(a) indicates that the α -phase In_2Se_3 can be obtained by the reaction of $\text{InCl}_3 + \text{NaHSe}_4 \rightarrow \text{In}_2\text{Se}_3$, and the as-prepared In_2Se_3 is less crystallized. As shown in Fig.1(b), it is clear that the size of the as-prepared In_2Se_3 nanoparticles is less than 100 nm.

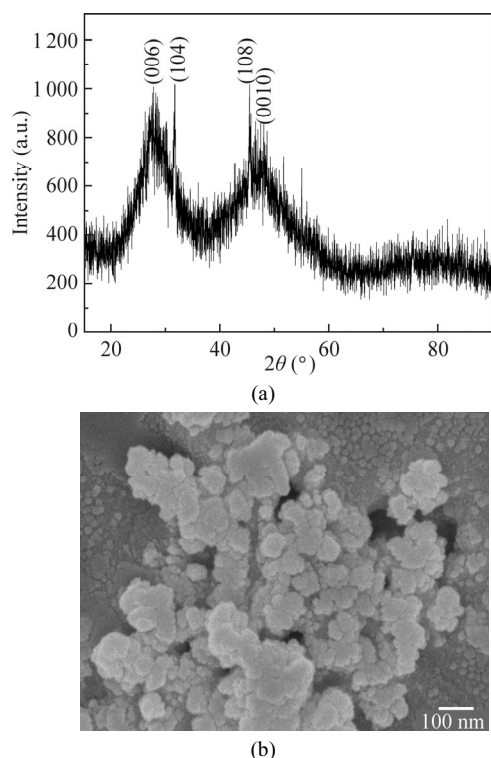


Fig.1 (a) XRD pattern and (b) SEM image of In_2Se_3 nanoparticles

Fig.2 shows the XRD pattern of CIS nanoparticles synthesised by using the In_2Se_3 as precursors reacted for 8 h. The broadening peaks are presumably due to the small size and not well developed crystalline structure of the particles. The three relatively broad diffraction peaks are detected around $2\theta=27.1^\circ$, 45.8° and 52.92° . These diffraction peaks correspond to the (112), (204/220) and (116/312) planes of the chalcopyrite structure^[18], respectively. The characteristic peaks of other impurities, such as Se, CuSe and In_2Se_3 , are not detected.

The typical FESEM micrograph of the CIS nanoparticles is reacted for 8 h as shown in Fig.3(a). It can be seen that the diameter of as-prepared CuInSe_2 nanoparticles is in the range from 10 nm to 20 nm, and the CIS nanoparticles have good dispersibility compared with those in our previous work^[17]. According to the qualification of the peaks in the energy dispersive spectroscopy (EDS) shown in Fig.3(b), the molar ratio of Cu/In/Se is 1.00:1.01:1.96, which is close to the stoichiometric result of CuInSe_2 shown in Fig.3(b).

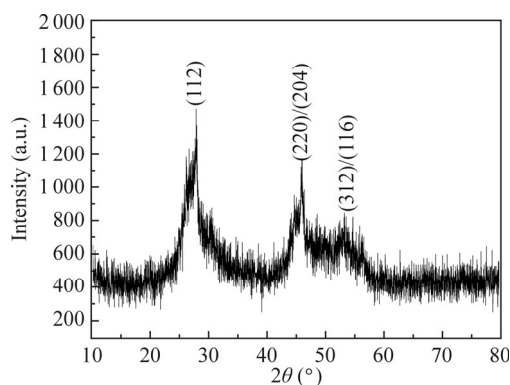


Fig.2 XRD pattern of CIS nanoparticles

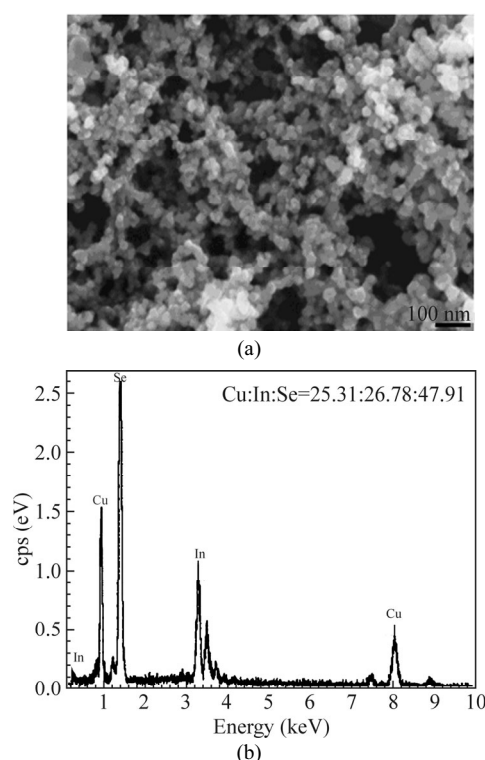


Fig.3 (a) FESEM micrograph and (b) EDS result of CIS nanoparticles

Fig.4(a) shows the UV-VIS absorption spectrum for the as-prepared CIS nanoparticles at room temperature, and it exhibits a broad absorption in the visible region with a tail in the long wavelength direction, which indicates a potential application for solar cells. $(ah\nu)^{1/2}$ as a function of photon energy $h\nu$ is shown in Fig.4(b), where α is the absorption coefficient, h is Planck's constant, and ν is the frequency. According to Fig.4(b), the optical band gap for CIS nanoparticles is calculated as 1.04 eV, which is consistent with the value reported in Ref.[17].

The XRD patterns of CIS nanoparticles obtained by phase transformation with different reaction time are shown in Fig.5. It demonstrates that the In_2Se_3 powder and CuCl solution can react and directly transform into CIS without any intermediate phase. As reaction time increasing, the In_2Se_3 phase gradually disappears, while the CIS phase gradually increases.

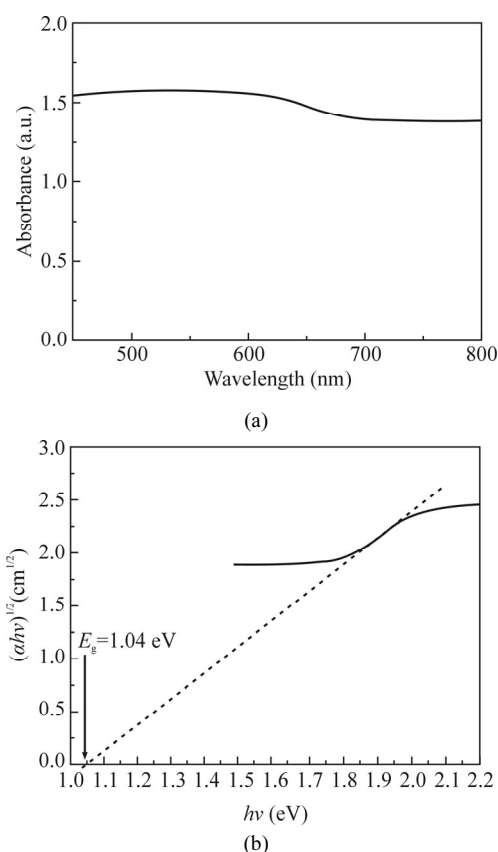


Fig.4 (a) UV-VIS spectrum of CIS nanoparticles and (b) $(\alpha hv)^{1/2}$ as a function of photon energy hv

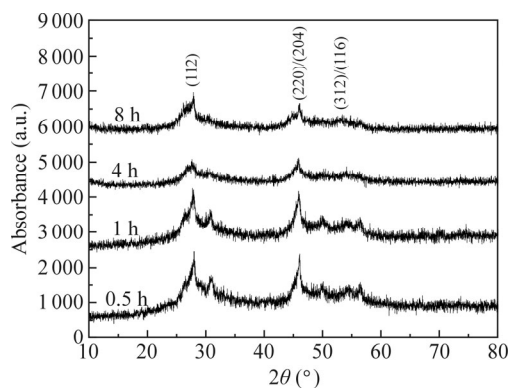


Fig.5 XRD patterns of the CIS nanoparticles obtained via phase transformation with different reaction time

CIS nanoparticles with a chalcopyrite-type structure are successfully prepared by using low temperature phase transformation of In_2Se_3 via wet chemical process which is a relatively simple and environment friendly process. The results show that the CIS nanoparticles with diameters in the range of 10–20 nm are obtained by the reactions of CuCl solution and In_2Se_3 powder at 0 °C for 8 h. EDS results of the CIS particles reveal that the chemical composition is well transferred to that of the

synthesized CIS particles. The reaction time is a key factor in controlling the phase conversion. As the reaction time increases from 0 h to 8 h, Cu^+ gradually displaces In^{3+} , while $\text{In}_2\text{Se}_3\text{:Cu}$ transforms into chalcopyrite CIS nanoparticles. The absorption spectra show that the band gap of the obtained CIS is 1.04 eV.

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