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A mild solvothermal route to chalcopyrite quaternary semiconductor $CuIn(Se_xS_{1-x})_2$ nanocrystallites

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Chalcopyrite quaternary semiconductor $CuIn(Se_xS_{1-x})_2$ nanocrystallites ($0 \leqslant x \leqslant 1$) were successfully prepared *via* a relatively simple and convenient solvothermal route. From X-ray data it is found that the cell constants *a* and *c* vary linearly with the composition *x* as: $a(\text{Å}) = 5.5299 + 0.2665x$, $c(\text{Å}) = 11.1004 + 0.5139x$. The sample CuInSeS was characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and infrared spectroscopy (IR). The optical property of $CuIn(Se_xS_{1-x})_2$ nanocrystallites was also recorded by means of UV-Vis absorption spectroscopy. In addition, the effect of different solvents on the formation of the product was studied to indicate that ethylenediamine is the optimal solvent for this reaction. Finally, the reaction mechanism in ethylenediamine was also investigated.

Introduction

In recent years, multinary chalcogenide compounds have attracted much attention due to their interesting physical properties.[1–3] The chalcopyrite quaternary semiconductor $CuIn(Se_xS_{1-x})_2$, which belongs to the I–III–VI_2 family, has been of interest as a polycrystalline thin film material for high-efficiency solar cell applications.[4,5] Preliminary experiments based on $CuInSe_2$ have already demonstrated solar cells with efficiency exceeding 15%.[6] In order to achieve a better match to the solar spectrum, it is necessary to prepare materials with a bandgap 0.2–0.4 eV wider than that of $CuInSe_2$, which can be obtained by two routes: alloying with either $CuGaSe_2$ or $CuInS_2$.[7] In this work, we chose the latter to synthesize $CuIn(Se_xS_{1-x})_2$ nanocrystallites.

The $CuIn(Se_xS_{1-x})_2$ quaternary alloy system can be synthesized by a variety of ways such as solid state reaction at elevated temperature,[8] the Bridgman method,[9] electrodeposition,[10] spray pyrolysis,[11] sputtering,[12] coevaporation,[13] organometallic precursors,[14] chemical transport reaction,[15] chalcogen (S and Se) vapor diffusion into Cu–In alloy,[16] microwave irradiation,[17] and ionized cluster beam techniques.[18] However, these methods require either very high temperature (typically 600–900 °C), high pressure or special apparatus. In addition, these methods are of relatively long reaction time.

It is well known that the device properties of $CuIn(Se_xS_{1-x})_2$-based solar cells are badly affected by their stoichiometric composition, defects, and structure, which are strongly related to the preparation conditions. We have been interested in the use of solvothermal routes, which are carried out at low temperatures and do not require organometallic or toxic precursors, to prepare various kinds of nanocrystalline materials with a wide range of optical and electronic properties accessible in the nanoscale.[19,20]

Jiang *et al.* synthesized $CuInS_2$ nanorods at 280 °C through elemental solvothermal reaction.[21] Li *et al.* prepared $CuInSe_2$ nanowhiskers and nanoparticles at 180 °C using $CuCl_2$, $InCl_3$, and Se as reagents.[22] In this work, we extended the solvothermal pathway to chalcopyrite quaternary semiconductor $CuIn(Se_xS_{1-x})_2$ nanocrystallites with composition *x* ranging from 0 to 1 using $CuCl_2 \cdot 2H_2O$, $InCl_3 \cdot 4H_2O$, Se and S as reagents. In addition, we investigated the effect of different solvents on the formation of the product.

Experimental

In a typical process, appropriate amounts of analytical grade $InCl_3 \cdot 4H_2O$, $CuCl_2 \cdot 2H_2O$, Se and S were added into a stainless steel autoclave with a Teflon liner, which was filled with different solvents such as ethylenediamine (en), diethylamine, pyridine and benzene up to 85% of the total volume. The autoclave was sealed and maintained at 180 °C for 15 h, then allowed to cool to room temperature naturally. The precipitate was filtered off, washed with dilute HNO_3, absolute ethanol and distilled water in sequence, and then dried in vacuum at 50 °C for 4 h. Finally, the products were collected for characterization.

The products were characterized by X-ray powder diffraction (XRD) pattern using a Japan Rigaku D/max-rA X-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). The particle size and morphology were investigated by transmission electron microscopy (TEM) carried out on a Hitachi Model H-800 with an accelerating voltage of 200 kV. The product purity and valence state were detected by X-ray photoelectron spectroscopy (XPS) recorded on an ESCALab MKII X-ray photoelectron spectrometer with Mg Kα X-ray as the excitation source. The results obtained in the XPS analysis were corrected by referencing the C 1s line to 248.6 eV. The infrared spectrum was recorded in the wavenumber range of 4000–400 cm^{-1} with a Nicolet Model 759 Fourier transform infrared (FTIR) spectrometer, using a KBr wafer. UV-Vis absorption spectra was taken on a JGNA Specord 200 PC UV-Vis spectrophotometer when ethanol was used as a reference.

Results and discussion

The obtained products were weighed, and the results show that the yields calculated from the amounts of chalcogens for $CuIn(Se_xS_{1-x})_2$ nanocrystallites are as high as 96%. In addition, excessive $InCl_3 \cdot 4H_2O$ and $CuCl_2 \cdot 2H_2O$ were used to ensure Se and S react completely in our experiment.

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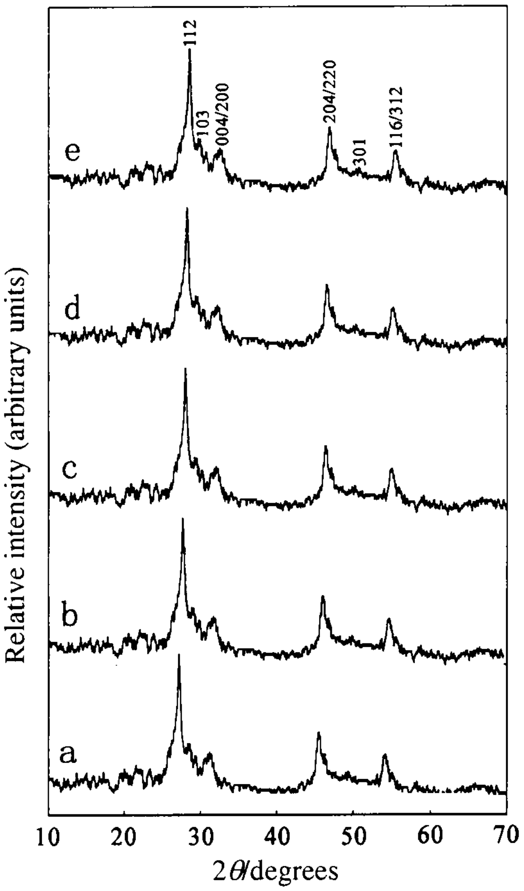

Fig. 1 XRD patterns of the samples prepared in ethylenediamine: (a) $CuInSe_2$, (b) $CuIn(Se_{0.8}S_{0.2})_2$, (c) CuInSeS, (d) $CuIn(Se_{0.2}S_{0.8})_2$, (e) $CuInS_2$.

Therefore, it is considered that the nominal content may denote the practical content. XRD patterns of the samples prepared in ethylenediamine are shown in Fig. 1. Fig. 1c is the typical pattern of CuInSeS, indicating only the chalcopyrite phase with an intense peak at $2\theta = 27.2°$ oriented along the (112) crystal plane. The other prominent peaks correspond to the (204)/(220), (116)/(312) and (004)/(200) planes. In addition to these commonly observed orientations, the weak peaks such as (103) and (301) are also observed in the XRD pattern, distinguishing the chalcopyrite phase from the sphalerite phase. This pattern is consistent with the reported features of CuInSeS in the tetragonal phase, and the cell constants are $a = 5.6625$ Å and $c = 11.3147$ Å, which are in good agreement with the literature values.[23] With the composition x varying from 0 to 1, the diffraction peaks of the (112) crystal plane of $CuIn(Se_xS_{1-x})_2$ range from 27.8° to 26.6°. The measured variation in cell constants a and c as a function of composition, calculated from XRD data, is given in Fig. 2. The relationship is found to obey an empirical formula as follows:

$$a(x) = 5.5299 + 0.2665x \quad (1)$$

$$c(x) = 11.1004 + 0.5139x \quad (2)$$

The variation in cell constants a and c is consistent with the reported values.[24]

The TEM image of $CuIn(Se_xS_{1-x})_2$ nanocrystallites (just taking CuInSeS nanocrystallites as an example) prepared in ethylenediamine, as shown in Fig. 3, indicates that the sample consists of uniform particles with an average size of 15 nm, which is in agreement with the XRD result of 14 nm calculated from the Scherrer formula.[25] Because of the extremely small dimension and high surface energy of the nanocrystallites, it is easy for them to aggregate, as seen in Fig. 3.

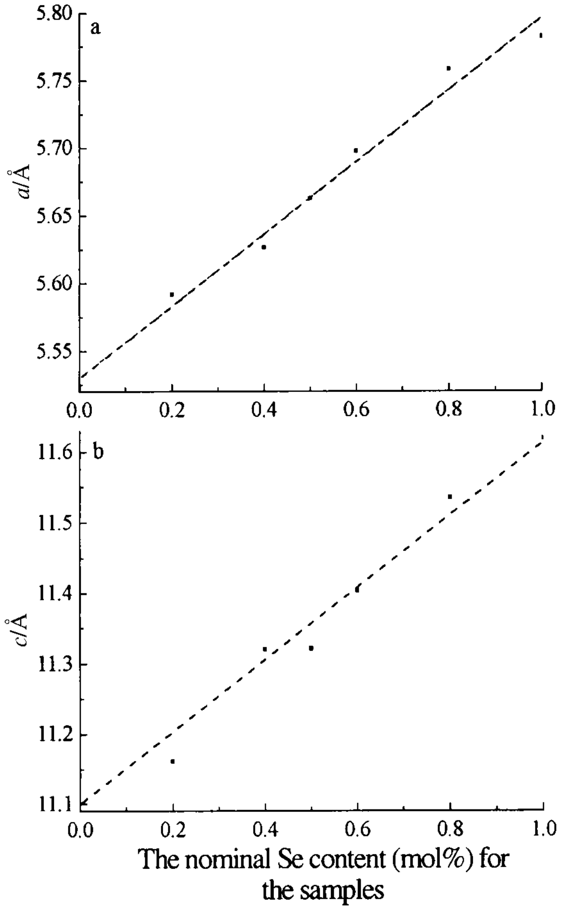

Fig. 2 The dependence of the cell constants a and c on the nominal Se content (mol%): (a) a *vs.* x, (b) c *vs.* x.

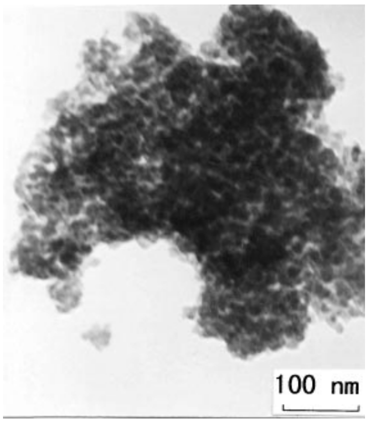

Fig. 3 TEM image of CuInSeS nanocrystallites prepared in ethylenediamine.

The typical survey spectrum of CuInSeS nanocrystallites prepared in ethylenediamine is shown in Fig. 4a, indicating the presence of Cu, In, Se, and S as well as C from the reference and O impurity from absorbed gaseous molecules. The binding energies of Cu $2p_{3/2}$, In $3d_{5/2}$, Se $3d_{5/2}$ and S $2p_{3/2}$ are 932.5, 444.6, 53.9 and 160.9 eV, respectively, and are consistent with the reported data.[26] Fig. 4b shows the Cu 2p core level spectrum. The full width at half maximum values for the Cu $2p_{3/2}$ and $2p_{1/2}$ peaks are 1.8 eV and 2.2 eV, respectively, which are also in good agreement with the literature values for Cu^+.[27] In addition, the Cu $2p_{3/2}$ satellite peak of Cu^{2+}, which is usually centered at 942 eV,[28] does not appear in the spectrum. Therefore, it can be concluded that only Cu^+ exists in the sample, indicating that the Cu^{2+} of the starting material was

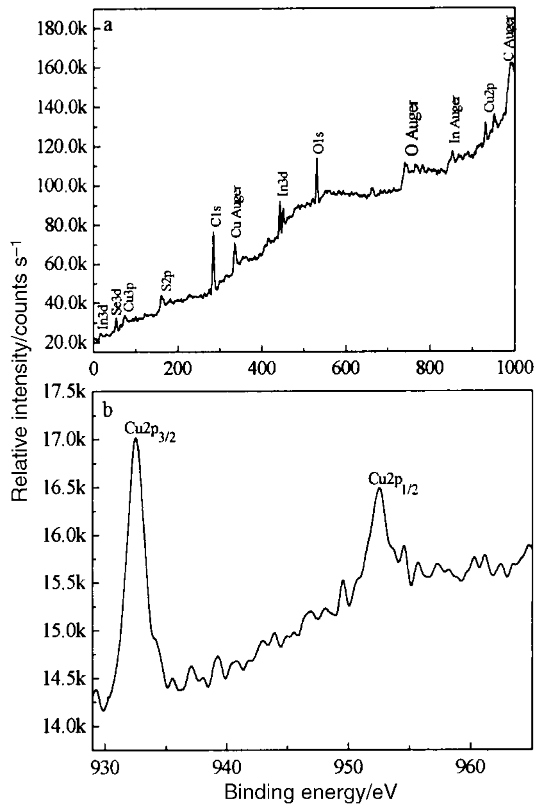

Fig. 4 XPS analysis for CuInSeS nanocrystallites prepared in ethylenediamine: (a) XPS survey spectrum, (b) Cu core level spectrum.

reduced during the course of the reaction. The IR spectrum of as-prepared CuInSeS nanocrystallites is shown in Fig. 5. We can see that there are two weak peaks at 1118 and 619 cm^{-1}, corresponding to the vibration absorption peaks of the Cu–S bond.[29] There are no characteristic peaks of ethylenediamine, indicating that ethylenediamine is not bonded to the surface of the products. This leads to a probable explanation that ethylenediamine can be easily removed during the course of washing, since ethylenediamine can be readily dissolved into water.

In this synthetic process, the solvent plays an important role in the formation of the chalcopyrite quaternary CuIn(Se$_x$S$_{1-x}$)$_2$ nanocrystallites. Ethylenediamine was selected as the solvent due to its strong basic capacity, strong chelation, and its ability to act as an aborber of the excess heat produced in the reaction. As a strongly polar solvent, ethylenediamine can greatly enhance solubility, diffusion and crystallization, but still provide sufficiently mild reaction conditions to enable the molecular building blocks to participate in the formation of a solid-state phase. It is well known that elemental Se and S powders are soluble in ethylenediamine at room temperature, supported by the change in the solution color. In the solvothermal process, a nucleophilic attack by ethylenediamine can activate elemental sulfur and selenium to form S^{2-} and Se^{2-} ions.[30] Since ternary sulfides and selenides commonly have similar crystal structures and properties, it would not be difficult to achieve the coexistent form (InSeS)$^{-}$. Furthermore, in this electron transfer reaction, ethylenediamine, as a reducing solvent, can reduce Cu^{2+} to Cu^{+} ion, then Cu^{+} complexes with ethylenediamine to form [Cu(en)$_2$]$^{+}$. The mechanism of the solvothermal process using ethylenediamine as solvent was proposed as follows (just taking the formation of CuInSeS nanocrystallites as an example).

$$2\mathrm{InCl_3} + 3\mathrm{Se^{2-}} \Rightarrow \mathrm{In_2Se_3} + 6\mathrm{Cl^-} \tag{3}$$

$$\mathrm{In_2Se_3} + \mathrm{Se^{2-}} \Leftrightarrow 2(\mathrm{InSe_2})^- \tag{4}$$

$$2\mathrm{InCl_3} + 3\mathrm{S^{2-}} \Rightarrow \mathrm{In_2S_3} + 6\mathrm{Cl^-} \tag{5}$$

$$\mathrm{In_2S_3} + \mathrm{S^{2-}} \Leftrightarrow 2(\mathrm{InS_2})^- \tag{6}$$

$$(\mathrm{InSe_2})^- + (\mathrm{InS_2})^- \Leftrightarrow 2(\mathrm{InSeS})^- \tag{7}$$

$$\mathrm{Cu^+} + 2\mathrm{en} \Leftrightarrow [\mathrm{Cu(en)_2}]^+ \tag{8}$$

$$(\mathrm{InSeS})^- + [\mathrm{Cu(en)_2}]^+ \Rightarrow \mathrm{CuInSeS} + 2\mathrm{en} \tag{9}$$

In addition, ethylenediamine plays an important role in controlling the nucleation and growth of the product. Because of its N-chelation and special structure, it can easily chelate Cu^{+} (reduced from Cu^{2+}) and form a relatively stable complex [Cu(en)$_2$]$^{+}$. The formation of the complex can effectively prevent the formation of binary copper chalcogenides. To improve our understanding of the above mechanism, experiments were performed under similar conditions when ethylenediamine was replaced by other solvents such as diethylamine, pyridine and benzene. In pyridine or benzene, many diffraction peaks appeared in the XRD patterns which could be indexed to copper sulfide, copper selenide, indium sulfide and indium selenide, but no characteristic peaks of chalcopyrite CuIn(Se$_x$S$_{1-x}$)$_2$ appeared. In diethylamine, a longer reaction time (at least 48 h) was required in order to obtain the product with almost the same morphology as that in ethylenediamine. The above results indicate that ethylenediamine is the optimal solvent for this reaction.

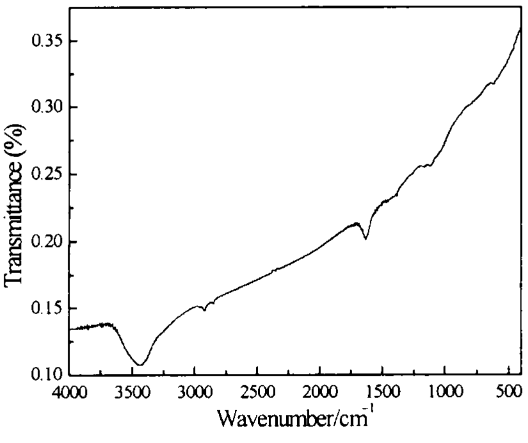

Fig. 5 Typical IR spectrum of as-obtained CuInSeS nanocrystallites.

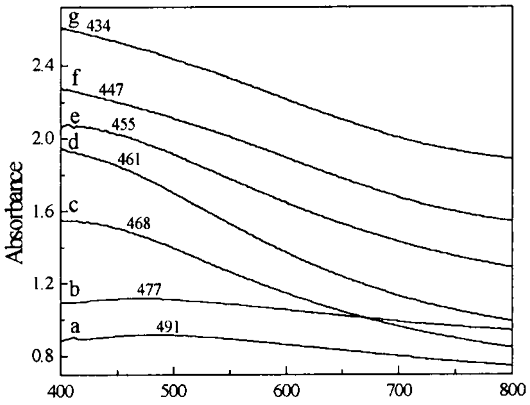

Fig. 6 UV-Vis absorption spectra of (a) CuInSe$_2$, (b) CuIn(Se$_{0.8}$S$_{0.2}$)$_2$, (c) CuIn(Se$_{0.6}$S$_{0.4}$)$_2$, (d) CuInSeS, (e) CuIn(Se$_{0.4}$S$_{0.6}$)$_2$, (f) CuIn(Se$_{0.2}$S$_{0.8}$)$_2$, (g) CuInS$_2$.

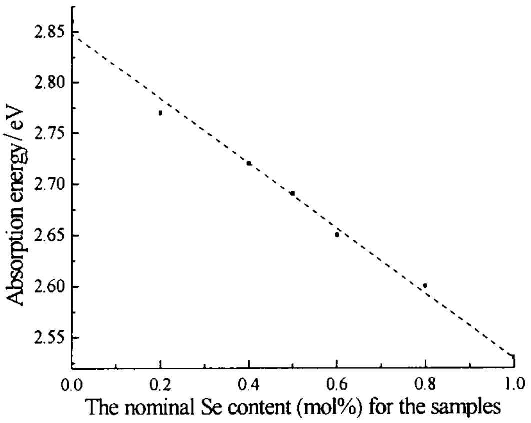

Fig. 7 The dependence of absorption energy on the nominal Se content (mol%) for the samples.

The energy band structure of the end points $CuInSe_2$ and $CuInS_2$ has already been calculated by many authors.[31,32] Generally speaking, the upper valence band of $CuInSe_2$ or $CuInS_2$ consists of nonlocalized and localized states. The nonlocalized states are due to p–d hybridization while the localized ones are due to the d electron states of copper. Fig. 6 shows the absorption spectra of $CuIn(Se_xS_{1-x})_2$ nanocrystallites, which can be generated from the nonbonding Cu d localized states. In addition, the dependence of absorption energy (E) on the nominal Se content is shown in Fig. 7.

$$E = \frac{1240}{\lambda} \qquad (10)$$

In eqn. 10, λ is the wavelength at the absorption peak. The linear evolution of E can be explained as follows. When S displaces Se, the energy levels go down to lower energy. Therefore, the whole valence band is shifted to lower energies, including the Cu d band. Herein, we want to mention two points: one is that we can only measure the wavelength ranging from 400 to 800 nm because of the limits of the apparatus; the other is that there are no reports about quantum size effects of $CuIn(Se_xS_{1-x})_2$ nanocrystallites. Therefore, we can not conclude whether the absorption energy is the ground state absorption energy (namely the bandgap energy) or not. Nevertheless, the result that the absorption energy varies linearly with the composition always exists. Additionally, this phenomenon has also been observed by other authors.[9]

Conclusions

In summary, we have successfully synthesized chalcopyrite quaternary $CuIn(Se_xS_{1-x})_2$ nanocrystallites *via* a relatively mild and convenient solvothermal process. The solvent plays an important role in the formation of the product and ethylenediamine is the optimal solvent for this reaction. UV-Vis absorption spectra indicate that the absorption energy varies linearly with the composition. In addition, the reaction mechanism in ethylenediamine was also studied to indicate that this reaction proceeds with the form $(InSeS)^-$ as the intermediate. We believe that this simple method has potential applications in synthesizing other quaternary chalcogenide compounds such as $CuGa(Se_xS_{1-x})_2$ and $ZnIn_2(Se_xS_{1-x})_2$.

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