Synthesis and characterization of CuInSe₂ nanoparticles via a solution method

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Abstract

Pure CuInSe₂ nanoparticles have been successfully synthesized via a solution method in the solvent of oleylamine. Anhydrous InCl₃, CuCl, and Se powder were used as the starting materials. The CuInSe₂ samples were characterized by XRD, TEM, and XPS techniques. It was found that tetragonal chalcopyrite structured CuInSe₂ nanoparticles were obtained with temperature above 230 °C. Sample prepared at 200 °C possesses triangular morphology and a minute amount of In₂Se₃ coexists as intermediate. CuInSe₂ nanoparticles with size of 20.2 ± 0.4 nm were prepared at 230 °C and the narrow size distribution was ascribed to the employment of hot injection, which was better for homogeneous nucleation. Stable “ink” can be formed when the as-synthesized CuInSe₂ nanoparticles were dispersed in organic solvents such as hexane and toluene, and such “ink” might have a practical application in CuInSe₂-based solar cells.

1. Introduction

As an important ternary I–III–VI₂ semiconductor, copper indium diselenide (CuInSe₂) has attracted wide attention in recent years because it is considered as a promising photovoltaic material for thin film solar cells [1–3]. CuInSe₂ has band gap that matches well with the solar spectrum, has large absorption coefficient and high radiation stability [4,5]. Interestingly, both p- and n-type of CuInSe₂ can be obtained under excess of Se and In, respectively [6]. However, the fabrication of CuInSe₂ thin film for the application in solar cells with high efficiency is laborious. It requires precisely control the co-evaporation of several elements under high vacuum and high temperature conditions. In addition, the post-treatment procedure often involves use of toxic reagent such as H₂Se. Therefore, it is desired to make CuInSe₂ film using CuInSe₂ nanoparticles as the starting materials and the solution derived CuInSe₂ nanocrystal suspensions can be easily deposited via spin-coating or printing technique. This method might lead to control the stoichiometry over large device areas and thus commercialization of this type of solar cell is currently underway.

Until now, several methods have been employed to prepare CuInSe₂ nanostructures. Typically, CuInSe₂ nanowhiskers and nanoparticles were successfully synthesized via solvothermal route using anhydrous ethylenediamine as solvent [7,8]. Korgel and coworkers reported that CuInSe₂ nanocrystals with trigonal pyramidal shape were prepared with the assistance of selenourea as Se source [9]. CuInSe₂ nanoparticles and nanorings were also fabricated in the solvent of oleylamine [10–12], and the “ink” formed by dispersing these nanostructures in some organic solvents could be used in CuInSe₂-based solar cells. One-dimensional CuInSe₂ nanorings were obtained by electrodeposition approach using porous anodized aluminum oxide template [13,14], or via a Au-catalyzed vapor–liquid–solid growth route [15], or by solvothermal method without any assistance of surfactant [16,17]. Most of the above reported work was involved in the complicated synthetic process or use of expensive instruments. Considering that the optoelectronic properties are closely related to elemental stoichiometry, phase purity, size, and size distribution of semiconductor nanocrystals, it is expected to synthesize CuInSe₂ with high phase purity, excellent crystallinity, and colloidal stability for their practical applications.

Herein, we report the synthesis of chalcopyrite CuInSe₂ nanoparticles in the presence of oleylamine as solvent. Temperature was found to be a key role for controlling the shape and phase of these nanoparticles. The “ink” was formed when CuInSe₂ nanoparticles were dispersed in nonpolar organic solvents such as hexane and toluene, and such “ink” could be preserved for more than 3 months without any sedimentation. Therefore, the as-obtained “ink” may serve as an important material for the fabrication of device.
2. Experimental

2.1. Materials

All chemical reagents were purchased from Sigma–Aldrich and used as received without further purification. Copper (I) chloride (CuCl; anhydrous >99.9%), indium (III) chloride (InCl₃; anhydrous 99.99%), elemental selenium (99.5%) and oleylamine were used as starting materials.

2.2. Synthesis of CuInSe₂ nanoparticles

In a typical synthesis, 0.25 mmol of InCl₃ and 0.25 mmol of CuCl were firstly added to 5 mL of oleylamine, and heated at 80 °C for more than 10 h accompanied by magnetic stirring, in order that the salts could be completely dissolved. Later on, 0.5 mmol of Se powder was loaded into 30 mL of oleylamine and heated to 270 °C with stirring. The InCl₃ and CuCl solution was injected into the hot Se-based solution (hot injection) 30 min later, then let the temperature of the whole mixed solution cool down to 70 °C naturally. After that, the temperature was quickly increased to 230 °C within 15 min. After 1 h reaction, the product was collected, rinsed, and finally was dispersed into hexane to form “ink”. The controlled experiments were carried out by changing the temperature and reaction time, respectively, while kept other synthetic parameters and procedures constant.

2.3. Characterizations

The crystal structure of the obtained product was examined by X-ray powder diffraction (XRD) with a Bruker D8 focus diffractometer at a voltage of 40 kV and a current of 40 mA with a Cu Kα radiation (λ = 0.15406 nm), employing a scanning rate of 4°/min in the 2θ range from 20° to 80°. The transmission electron microscopy (TEM and HRTEM) images and the corresponding selected area electron diffraction (SAED) patterns were taken on a JEOL JEM-2100F transmission electron microscope at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCA 2000 spectrometer using an Al Kα X-ray as the excitation source.

3. Results and discussion

The crystal structure of the synthesized product was first characterized by X-ray diffraction (XRD). Fig. 1a shows a typical XRD pattern of the as-obtained CuInSe₂ sample synthesized at 230 °C for 1 h. All the peaks can be indexed to the tetragonal chalcopyrite structured CuInSe₂ (JCPDS No.: 40-1487) and no other impurities can be detected. In the inset shows a digital camera image of the sample dispersed in hexane, the black “ink” could be preserved for more than 3 months without any sedimentation indicating the stable status of the CuInSe₂ nanoparticles in nonpolar organic solvent. There are few reports that CuInSe₂ nanoparticles can be preserved over such long duration and the stable “ink” is crucial for the fabrication of solar cell device.

Fig. 1b is a representative TEM image of the resultant CuInSe₂ nanoparticles synthesized at 230 °C for 1 h. It can be clearly observed that the CuInSe₂ nanoparticles exhibit irregular shapes and have uniform size of about 20 nm. The high-resolution TEM (HRTEM) image of CuInSe₂ nanoparticle is displayed in Fig. 1c, from which the observed d-spacing is about 0.33 nm and is complied with the (1 1 2) lattice spacing of chalcopyrite CuInSe₂ nanoparticles. The corresponding selected area electron diffraction (SAED) pattern (Fig. 1d) possesses several rings composed many discrete spots, and the rings match well with (1 1 2), (2 2 0)/(2 0 4), and (1 1 6)/(3 1 2) reflections of the tetragonal CuInSe₂. In order to obtain small size of CuInSe₂ nanoparticles with narrow size distribution, it is necessary to employ hot injection and to form homogeneous nucleation. As described in typical synthesis, InCl₃ and CuCl salts were initially completely dissolved in oleylamine by magnetic stirring and heating. At 270 °C, this mixture was injected into Se²⁻-based oleylamine solution by syringe, and then stopped heating to cool down to 70 °C for better homogeneous nucleation.
The purity and composition of the obtained CuInSe$_2$ nanoparticles were further examined by X-ray photoelectron spectrum (XPS) technique, and Al K$_\alpha$ X-ray was used as the excitation source. Fig. 1e and f shows the XPS survey spectrum and Cu 2p core level spectrum, respectively. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C$_{1s}$ to 284.60 eV. The binding energies for Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ (Fig. 1f) are located at 932.6 eV and 952.5 eV, respectively, which are in agreement with the literature report [8]. In addition, the Cu 2p$_{3/2}$ satellite peak at about 942 eV characterizing Cu$^{2+}$ does not emerge in the spectrum [7,8]. Therefore, we can conclude that only Cu$^+$ exists in this compound. The In 3d and Se 3d core level spectra (not shown here) were also consistent with those reported in literature for CuInSe$_2$ [18].

Temperature was found to be a key role for controlling the size, size distribution, and phase purity of CuInSe$_2$ products. Fig. 2 shows the TEM images of the CuInSe$_2$ nanoparticles synthesized at different temperature with reaction time of 1 h. The average size increased with reaction temperature increasing, some particles with size larger than 50 nm existed in the final products when the temperature was higher than 260 °C (Fig. 2c and d). Meanwhile, the particles do not show uniformity as those obtained at lower temperature (≤245 °C). These CuInSe$_2$ nanoparticles exhibit a variety of shapes. It seemed that the size and size distribution could be less effectively controlled in the higher temperature region in this work. It was reported that oleylamine can etch CuInSe$_2$ nanocrystals even in the room temperature [9]. Similar etching of Cu–In–Se nanocrystals was observed in TOP/oleylamine by Allen and Bawendi [19]. Its etching ability could be greatly enhanced by heating at high temperature. Guo et al. also reported the formation of hollow CuInSe$_2$ nanorings when TOP/oleylamine was used as a reaction solvent [10]. In our work, the etching may be strengthened when the chemical reactions occurred with temperature above 260 °C, which destroyed some facets of minute CuInSe$_2$ nanocrystals in the initial stage. Thus, CuInSe$_2$ nanocrystals with various size and shapes could be produced in the subsequent process. Probably, other factors including the types of starting materials, rate of temperature increasing, and so on, might also influence it. The detailed reasons need more investigations and the related work is currently underway. It is interesting to find in Fig. 2a that some triangular CuInSe$_2$ nanoparticles emerged in the product which was prepared at 215 °C. As a matter of fact, a large amount of such CuInSe$_2$ nanoparticles with narrow size distribution were produced at 200 °C with time of 1 h (Fig. 3a). It is clearly seen from a randomly selected triangular CuInSe$_2$ nanocrystal (Fig. 3b) that the edge length is about 18.6 ± 0.7 nm. The fast Fourier transform of the nanoparticle in the inset reveals the single crystalline. The measured d-spacings of 0.205 nm correspond to the (2 2 0) lattice planes of tetragonal (chalcopyrite) CuInSe$_2$, which is investigated by the magnified TEM image (Fig. 3c) of the position circled with white box in Fig. 3b. The XRD pattern (Fig. 3d) demonstrates that minute impurities of In$_2$Se$_3$ coexisted in the final product and it implied that the temperature of 200 °C was not high enough to transform intermediate into pure CuInSe$_2$. The CuInSe$_2$ nanoparticles synthesized at 200 and 215 °C did not show obvious difference in size, but the morphology changed to some extent. It indicated that some crystal facets tended to preferentially grow at 200 °C and it resulted in the formation of triangular shape. CuInSe$_2$ nanoparticles with such novel morphology were not reported previously. Fig. 4 displays the evolution
process of triangular shape by investigating the samples prepared with different reaction time. When the time was about 20 min, the product contained large quantity of small nanoparticles with average size smaller than 10 nm (Fig. 4a). We could clearly find that these nanoparticles have various irregular shapes. Particles with size of 12.4 ± 2.1 nm were produced when the time was prolonged to 40 min, the triangular shape begins to form at this stage and as viewed by the TEM image in Fig. 4b. A small amount of irregular CuInSe₂ nanoparticles with very large size of 30–40 nm appeared in the final product when we continued to increase the reaction time to 2 h (Fig. 4c). In our synthesis, oleylamine provided a solvating medium for CuCl and InCl₃ and served as an effective capping ligand. The powder Se was reduced to Se²⁻ in oleylamine solvent, and the amine group in the molecule was oxidized into a nitroso group [12]. The detailed reaction pathway needs further elucidation.

4. Conclusions

In summary, tetragonal chalcopyrite structured CuInSe₂ nanoparticles with high purity were prepared via a solution route using anhydrous InCl₃, CuCl, and Se powder as the starting materials. Oleylamine acted as both solvent and reducing reagent. Temperature was found to be a key role for controlling the morphology and phase of CuInSe₂ samples. Triangular CuInSe₂ nanocrystals with edge length of about 18 nm were produced at 200 °C and nearly monodisperse nanoparticles could be produced at 200–245 °C. Broad size distribution exists for CuInSe₂ synthesized at or above
260 °C probably due to the fact that oleyamine can etch the originally formed CuInSe₂ nanocrystals. The as-obtained CuInSe₂ samples are dispersed in hexane to form stable “ink” and can be preserved for more than 3 months without any sedimentation, which is significant for fabricating the CuInSe₂-based solar cells.

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References