A Noninjection Reaction Route to CuInSe₂ Nanocrystals with Triethanolamine as the Complexing Agent

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The chalcopyrite-type CuInSe₂ is a remarkable material for thin film solar cells owing to its electronic structure and optical response. Single-phase sphere-like CuInSe₂ nanocrystallite particles were prepared by a facile noninjection method with triethanolamine as the complexing agent and the solvent simultaneously. The period of the reaction was the key to form single-phase CuInSe₂ nanocrystals at 240 °C. TEM, XRD, XPS, EDX investigations were performed to characterize the morphology and the detailed structure of as-synthesized CuInSe₂ nanocrystals. All of the analysis results proved that the synthesized nanocrystals were pure phase and close to the stoichiometric ratio rather than a simple mixture. The band gap of the obtained CuInSe₂ nanocrystals was 1.03 ± 0.03 eV.

Key Words: CuInSe₂, Nanocrystals, CIGS solar cells, Triethanolamine

Introduction

Copper indium diselenide (CuInSe₂)-based solar cells have often been considered as one of the most promising ones for cost-effective power generation due to the high-efficiency. In fact, devices based on this optical material and produced by three-stage co-evaporation with a modied surface termination under high vacuum have achieved a conversion efficiency up to around 20%. However, the high costs of widespread utilization of CuInSe₂-based solar cells, using high-vacuum deposition techniques, have become a substantial hurdle to the thin film PV market. Meanwhile, non-vacuum methods for formation of CuInₓGa₁₋ₓSe₂ (0 ≤ x ≤ 1) (CIGS) thin film photovoltaic absorbers can obviously reduce the cost of the fabrication and installation, which is necessary to compete with the traditionally generated power. What’s more, the quality of CIGS layers obtained under non-vacuum are close to those made by vacuum methods, and some non-vacuum methods have been widely adopted. There are currently several interesting ways to form high-quality CIGS films under non-vacuum condition. Particularly, one approach is to chemically synthesize corresponding nanocrystals with tunable size and crystal phase, and then mixing these nanocrystals with suitable organic solvents so as to create a good dispersive and air-stable paint or ink. The particulate paint or ink can be assembled on both rigid and exible substrates using roll-to-roll process, which have the potential to make them cheap enough to large-scale manufacture. To obtain high-quality CIGS films, a key challenge is the synthetize of single-phase and nearly monodisperse semiconductor compounds nanocrystals. Therefore, developing facile routes that enable low-cost fabrication of inorganic colloidal nanocrystals ink to be used in a scalable coating process has attracted a great deal of attention.

To date, CuInSe₂ and related nanocrystals, a class of optical materials suitable for high-efficiency solar cell fabrication, have been synthesized by solid-state reaction, solvothermal, and hot-injection techniques. In a common sense, however, the nanocrystals synthesized by solvothermal techniques, which are conducted under the high temperature and pressure, are highly polydispersed, and generally require above 15 hours or even a few days to perform. Meanwhile, the hot-injection methods need complex devices with protective atmosphere and a rapid injection of precursors into a hot organic reaction medium. Furthermore, expensive oleylamine is needed as solvent and complexing agent via hot-injection technique to synthesize such multiple chalcopyrite nanocrystals. It is rarely reported that CuInSe₂ nanocrystals with a band gap greater than 1.03 eV are synthesized by hot-injection solution method, due to the fact that high-temperature is benefical to nanocrystals growing in hot-injection processes.

Here, we report a facile noninjection route to prepare high-quality chalcopyrite CuInSe₂ nanocrystals. A similar non-injection thermal decomposition method has also been successfully used in the synthesis of monodisperse pyramidal CuInSe₂ nanocrystals. However, some toxic chemical, such as n-dodecanethiol and 1-octadecene, were used during the reaction process. In this work, the synthesis was carried out in triethanolamine (tEA). tEA was considered as the reaction medium and the complexing agent. The mechanism showed that the period of the reaction was the key to form single-phase CuInSe₂ nanocrystals at a fixed temperature. The structure, composition, morphology and absorption spectra of CuInSe₂ nanocrystals were investigated. This approach will allow low-cost fabrication of solar cell devices through these methods such as drop casting, spin coating, and printing.
Experimental

**Chemicals.** Copper (I) chloride (CuCl, 99.99%), indium (III) chloride (InCl₃·4H₂O, 99.99%), selenium (Se, 99.99%), and triethanolamine (tEA, 99%) were purchased from Sigma Aldrich and used without further purification.

**Characterization.** Phase purity and crystal structure of the samples were analyzed by powder X-ray diffraction (XRD; Rigaku D/max-Ra) using Cu Kα radiation. The morphology and element composition were characterized by Scanning electron microscopy (SEM; FEI Inspect F) equipped with an energy dispersive X-ray spectrometer (EDS; Oxford INCA Penta FET×3). The average size (P = 95%) of the nanocrystals was measured by SigmaScan Pro 2.0 software based on 5 different SEM images with a magnification rate of 80000. The microstructure and morphology were characterized by Transmission electron microscopy (TEM; Tecnai G2 F20 S-TWIN)) with an accelerating voltage of 200 kV. The X-ray photoelectron spectra (XPS) were collected on an XSAM 800 XPS, using non-monochromatized Mg Kα X-ray as the excitation source. UV-vis-NIR absorption spectra were carried out to evaluate the optical properties of CuInSe₂ nanocrystals by using a Perkin Elmer Lambda 750 UV-vis spectrometer.

**Sample Preparation.** In a typical synthesis, two precursor solutions were prepared. For the preparation of a Cu-tEA and In-tEA precursor solution, stoichiometric amounts of copper (I) chloride, indium (III) chloride, and selenium (Se) in tEA at a high temperature. When the two precursor solutions were mixed, associative Se²⁻ might combine with Cu or In ions to form Cu₂Se or In₂Se₃ in the tEA solution. Cu₂Se and In₂Se₃ could react, and CuInSe₂ nanocrystals were produced. A similar phenomenon had also been reported, which was considered as a solid-liquid reaction mechanism. On the other hand, the chelating ability of tEA is attributed to the interaction of oxygen atoms on hydroxyl groups with metal ions. As the complexing constant of (Cu-tEA₂)²⁻ is 1 × 10⁶, tEA is a good candidate for the chelating agent. As the metal ion-tEA is a chelate, a steady stream of metal ions was provided for the reaction process, and then CuInSe₂ nanocrystals were consistently deposited.

The morphology of the obtained nanocrystals was investigated by TEM observation. Figure 2(a) shows the TEM image of the CuInSe₂ synthesized at 240 °C for 10 h, indicating that the outward appearance of the as-prepared CuInSe₂ nanocrystals seems like spheroid. The size of the CuInSe₂ nanocrystals ranges from 27.2 nm to 53.1 nm, which can be attributed to the different growth time at a high temperature.

The high-resolution TEM (HRTEM) image (Figure 2(b)) of the as-synthesized nanocrystals shows that the lattice fringe gives an interplanar spacing of 0.33 nm, which matches well with the distance of the (112) plane of the standard...
tetragonal CuInSe₂. Both HRTEM and XRD confirmed that pure-phase CuInSe₂ nanocrystals with a tetragonal chalcopyrite structure were obtained. The formation of such nanocrystals may involve the reactions of Cu₂Se with In₂Se₃, decomposed from CuCl and InCl₃ respectively, in the presence of tEA.

Additionally, the energy dispersive X-ray spectrum (EDS) of the nanocrystals (Figure 2(c)) microanalysis was performed by randomly selecting single particles in the TEM image. No appreciable impurity is observed in the spectra. A very small C peak and a significant Au peak, which come from the metallization process, were detected in the EDX spectrum. The results show that the atomic ratio of Cu:In:Se is 1.05:0.97:1.86, which further demonstrates that these nanocrystals are single phase and close to stoichiometric. The nanocrystals are slightly copper-rich and selenium-deficient. The lower Se content may be attributed to the oxidation of the samples during the analysis.

X-ray photoelectron spectroscopy (XPS) analysis was used to confirm the valence states of the CuInSe₂ nanocrystals as shown in Figure 3. The Cu 2p, In 3d, and Se 2p core levels were examined respectively. The binding energies obtained in the XPS analysis were corrected for
A facile noninjection reaction route is developed for the synthesis of single-phase CuInSe$_2$ nanocrystals, by using tEA as the complexing agent and the solvent. This route is low-cost and based on green chemistry with a large-scale capability. This noninjection synthesis foretells an easy handling with high reproducibility, low-cost but high-yield (about 85%).

XRD, XPS, EDS, HR-TEM analyses confirm that the structure and composition of the nanocrystals, prepared by this method, correspond to those of pure phase CuInSe$_2$.

The UV-vis-NIR data show that the band gap of the obtained CuInSe$_2$ nanocrystals are in the range of 1.03-1.09 eV, which is of interest for its photovoltaic applications.

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References


Conclusion

A facile noninjection reaction route is developed for the synthesis of single-phase CuInSe$_2$ nanocrystals, by using tEA as the complexing agent and the solvent. This route is low-cost and based on green chemistry with a large-scale capability. This noninjection synthesis foretells an easy handling with high reproducibility, low-cost but high-yield (about 85%).
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