The Phase and Morphology of Cu$_2$ZnSnSe$_4$ Nanopowders by Hydrothermal Method

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Quaternary compound Cu$_2$ZnSnSe$_4$ (CTZSe) which belonged to I$_2$-II-IV-VI$_4$ group, without rare elements, can be considered as the perfect material for absorbing layer in eco-friendly solar cells due to low cost and high efficiency. The CTZSe powders were synthesized by hydrothermal coreduction method from metal chlorides and SeO$_2$ with reducing agent hydrazine hydrate at 160–200°C. The phases of obtained products were analyzed by X-ray diffraction (XRD) and the size and morphology were observed by field emission scanning electron microscope (FESEM). Experimental results show that well crystallized Cu$_2$ZnSnSe$_4$ powders without Se impurities can be obtained by reacting at 200°C for 90h. The three strong XRD peaks of these products are corresponding to (112), (204), and (312) crystal planes, respectively. The morphologies of these products mostly show irregular polygon flakes with about 30–40 nm thickness and 50–200 nm diameters.

1. Introduction

As the bellwether of the new generation of solar cells, the conversion efficiency of Cu(InGa)Se$_2$ (CIGS) cell has been as high as 20.3% [1]. So a crucial position has been taken by the thin film solar cells of CuInSe$_2$ (CIS) in the photovoltaic market. Since rare and costly elements such as In and Ga are contained in above compounds. The new cheap elements have been consistently researched for their alternatives. It greatly reduced the cost of raw materials by replacing In and Ga in CIGS with cheap Zn and Sn atoms in quaternary compound semiconductors Cu$_2$ZnSnS$_4$ (CZTS) or Cu$_2$ZnSnSe$_4$ (CTZSe).

As a p-semiconductor with optical band within 1.0 eV–1.56 eV and absorption coefficient $10^4$ cm$^{-1}$ [2], CTZSe is the ideal absorber layer material in solar cells and becomes one research focus of photoelectric materials. A dramatic progress has been made in the efficiency of these solar cells. During the past three years, two conversion efficiencies of 9.6%, 10.1% for the liquid processed CTZSe batteries have been reported by the Todorov group successively [3, 4].

The methods for preparing CZTSe thin film mainly include coevaporation [5], sputtering [6], and electrochemical deposition [7]. All of these techniques must be performed under restrictive fabrication conditions, such as vacuum or conductive substrates. In addition, solution based synthesis of CZTS nanoparticles and selenization in the layer after coating is a very common method to prepare CZTSe layers. Cu$_2$ZnSnSe$_4$ films have been fabricated by vacuum evaporation onto soda-lime glass substrates covered with molybdenum [8]. It indicated that nearly single-phase Cu$_2$ZnSnSe$_4$ films were deposited through the use of binary precursors and highly crystalline, P-type Cu$_2$ZnSnSe$_4$ films with an optical band gap of 1.14 eV were produced via SnSe$_2$ selenization. Cu$_2$ZnSnSe$_4$ thin film with large grains of 1–8 μm was prepared through sputtering with a metallic Cu-Zn-Sn target and a subsequent selenization procedure at 550–650°C under the existence of SnSe$_2$ and CuSe$_3$ pellets [9]. This method requires the specific conditions of high vacuum and large equipment.

Wet chemical methods such as solvothermal method were mostly used in preparation of CZTSe powders.
Nanocrystalline CZTSe prepared by wet chemical method was first reported by Alexey Shavel group [10]. Nanocrystalline CZTSe was synthesized through the process of dissolving single-substance Se and metal salts, respectively, in a solution of triethanolamine and heating at 200°C, where triethanolamine acts as reaction solvent, reducing agent, and complexing agent [11]. The CZTSe particles were synthesized in different solvents; the morphology of the particles is hexagon sheet-like when ethylene glycol was used as solvent; the sphere-like rough surface was observed with ethylenediamine as solvent [12]. The CZTSe nanoparticles with sizes of 7–35 nm were prepared through the process of dissolving corresponding metal salts in oleylamine at 170°C and heating for 30 min, then pouring into oleylamine solution of single substance Se, and heating at 230°C for 90 min [2]. CZTSe nanoparticles were synthesized in an organic solution under nitrogen atmosphere at 235°C via thermal reaction of elemental Cu, Zn, Sn, and Se powders in an IPDA chelated solution [13]. However, it is easy to produce a series of adverse reactions with this method whose reaction factors are not easy to be mastered. Previous studies have reported the synthesis of CZTSe nanocrystals via these methods; however, it still needs to develop a simple and practical synthesis route that expands the practicality of these.
materials in commercial products. This work provides a simple and easy-to-handle way to produce low-price and eco-friendly $\text{Cu}_2\text{ZnSnSe}_4$. 

2. Experimental Details

For preparing CZTSe powder, $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, $\text{ZnCl}_2$, $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$, and $\text{SeO}_2$ with a ratio of 2:1:1:4 were added into a stainless steel autoclave with a teflon liner of 20 mL capacity. The autoclave was filled with absolute ethyl alcohol and deionized water (1:2) up to 80% of the total volume. After ultrasonic agitation for about 30 min, 1 mL HCl and 2 mL hydrazine hydrate (N$_2$H$_4\cdot$HzO) were poured into the reactants. The autoclave was sealed and heated at different temperatures (160°C, 180°C, and 200°C) for 10–90 h in an electric furnace. After heating, it was cooled down to room temperature naturally. The black products were collected by filtration, washed with deionized water and absolute ethanol, and then dried at 70°C.

The phases of product samples were analyzed by X-ray diffraction (XRD) on a model of Bruker D8 Advance XRD system with Nifiltered Cu-Kα ($λ = 1.5059$ Å). The size and morphology of the products were observed using a model of Hitachi S-4800 field emission scanning electron microscope (FESEM). The compositions of $\text{Cu}_2\text{ZnSnSe}_4$ powder were analyzed by energy dispersive spectrometer (EDS) as the attachment of Hitachi S-4800 FESEM.

3. Results and Discussion

3.1. Synthesis of $\text{Cu}_2\text{ZnSnSe}_4$ by Hydrothermal Coreduction. Figure 1 shows XRD patterns of CZTSe nanometer powders synthesized under different conditions. According to the standard pdf card of $\text{Cu}_2\text{ZnSnSe}_4$ (No. 52-0868), it indicates that the major phase $\text{Cu}_2\text{ZnSnSe}_4$ can be synthesized in the products obtained at 160, 180, and 200°C as shown in Figure 1. The diffraction peaks at the 2θ angles of 27.1°, 45.1°, and 53.4° were corresponding to (112), (204), and (312) crystal planes, respectively. These results are in good agreement with those Liu et al. [11] and Wei et al. [14] reported. From Figure 1(a) it can be seen that Se impurity was produced at each temperature with the same reaction time 22h. Figure 1(b) shows that impurity Se was only produced at lower temperature 160°C with reaction time 45 h. It can be clearly seen, at 200°C with different reaction time, Se impurity was produced at 10 h and 22 h in Figure 1(c). An X-ray diffraction peak corresponding to (200) crystal plane appeared at 2θ = 31.1° of samples with reaction time 90 h. Therefore, well-crystallinity $\text{Cu}_2\text{ZnSnSe}_4$ nanopowder can be produced under the conditions of higher temperature and longer time.

3.2. Discussion about Identification of $\text{Cu}_2\text{ZnSnSe}_4$ Phase. For distinguishing the CZTSe phase from other three phases of $\text{Cu}_2\text{SnSe}_4$, ZnSe, and Cu$_3$Se, Figure 2 shows the standard pdf cards of CZTSe, $\text{Cu}_2\text{ZnSnSe}_4$, ZnSe, and Cu$_3$Se. According to Figure 2, Figure 1(c) indicates that the product powder is not $\text{Cu}_2\text{SnSe}_4$ phase because the XRD peak at (200) crystal plane of the product powder prepared at 200°C for 90 h appeared. Authors have prepared $\text{Cu}_4\text{Se}$ [15] and ZnSe powders using the same method. ZnSe powder is yellow, so it is easily to be distinguished from black CZTSe powder. Therefore, it is the most difficult to distinguish between $\text{Cu}_2\text{Se}$ and CZTSe. Figure 3 shows the EDS results of the product powders prepared at 200°C for 45 h and 90 h; it can be seen that the products also consist of four elements of Cu, Zn, Sn, and Se. By comparing carefully the standard XRD pdf cards in Figure 2, it can be found that the strength ratios of $\text{Cu}_4\text{Se}$ and CZTSe have difference for three strong characteristic XRD peaks. In three strong peaks of standard XRD pdf cards of $\text{Cu}_4\text{Se}$, the strength ratio of the second strong peak for (220) or the third strong peak (311) with the first strong peak for (311) is relatively small, while those of CZTSe are relatively greater. From the XRD results of the CZTSe and $\text{Cu}_4\text{Se}$ powders prepared by authors, it is clearly seen that their strength ratios are different, which are similar to the difference for their standard XRD pdf cards. Figure 1 shows the strength ratios of the three strong peaks are similar to those of standard XRD pdf card of CZTSe. Combined the composition results by EDS, it can be considered that the product powders in this word are CZTSe powders.

3.3. The Morphology of $\text{Cu}_2\text{ZnSnSe}_4$ Powders. The morphologies of samples prepared under the conditions of 180°C for 45 h (Figures 4(a) and 4(b)), 200°C for 45 h (Figures 4(c) and 4(d)), and 200°C for 90 h (Figures 4(e) and 4(f)) were observed. It demonstrates that the microstructures of $\text{Cu}_2\text{ZnSnSe}_4$ nanopowders synthesized by chemical coreduction show flakes; the shape and size of the nanosheets also vary with the reaction condition changing. From Figures 4(a) and 4(b) it can be seen that the sample shows irregular polygons with about 30–40 nm sheet thickness and approximately 150–200 nm diameters. Figures 4(c) and 4(d) indicate that the nanosheets are approximately circular with about 30–40 nm sheet thickness and 150–200 nm diameters. From Figures 4(e) and 4(f) it can be seen that many small particles with different sizes exist in the sample prepared by reacting...
Figure 3: The EDS results of Cu$_2$ZnSnSe$_4$ powders prepared at 200°C for different time. (a) 200°C for 45 h, (b) 200°C for 90 h.

Figure 4: FESEM images of CZTSe powders synthesized under different conditions. (a) and (b): 180°C for 45 h; (c) and (d): 200°C for 45 h; (e) and (f): 200°C for 90 h.
at 200°C for 90 h. It shows clearly more regular hexagonal flakes with 30–40 nm thickness under high magnification, which are similar to the nanoparticle of CZTSe prepared by Du et al. in shape while smaller than the latter in diameters of 50–70 nm [12].

4. Conclusions

The CTZSe powders were synthesized by hydrothermal coreduction method from metal chlorides and SeO₂ with hydrazine hydrate as reducing agent at 160–200°C. It indicates that well crystallized Cu₂ZnSnSe₄ powders can be obtained by reacting at 200°C for 90 h. It provides a simple and easy-to-handle way to produce low-price and eco-friendly Cu₂ZnSnSe₄ powders. The CTZSe powders grow mainly along (112), (204), and (312) crystal planes, respectively. The FESEM results showed that the nanoparticles obtained are flaky with about 30–40 nm thickness and 50–200 nm diameters.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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