Synthesis of $Cu_2ZnSnSe_4$ Nanoparticles via Solvothermal Route

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Keywords: $Cu_2ZnSnSe_4$, Nanoparticles, Solvothermal synthesis

Abstract. Solvothermal synthesis was investigated as a viable method for the fabrication of quaternary $Cu_2ZnSnSe_4$ (CZTSe) semiconductor compound. With metal salts and selenium powder as starting materials, single-phase CZTSe nanoparticles, as determined by X-ray diffraction and Raman analysis, were obtained in a quantitative yield after solvothermal reaction at 200°C for 24 h. Transmission electron microscopy (TEM) further revealed that the CZTSe were nanoflakes formed by aggregation of nanoparticles. The average particle size estimated from X-ray diffraction data was 49 nm. Furthermore, the metal ratio of CZTSe was precisely tunable by varying the molar ratio of starting metal salts in the solvothermal synthesis.

Introduction

Recently, it has been of great interest in the quaternary Cu_2ZnSnS_4 (CZTS) semiconductor compound, due to its desirable optoelectronic properties and its potential to serve as low-cost absorber layers in thin film solar cells [1]. CZTS is cost efficient for practical applications because its constituent elements are all earth abundant. The selenide analogues of CZTS, $Cu_2ZnSnSe_4$ (CZTSe), as well as their substitution mixture, $Cu_2ZnSn(S,Se)_4$ (CZTSSe), have also been studied extensively due to their similarities to CZTS in structure and properties [2]. Among the three semiconductor compounds, $Cu_2ZnSn(S,Se)_4$ based cells have so far achieved the highest power conversion efficiency, due to S/Se ratio-mediated band gap and improved grain structure as a result of Se incorporation. The reported band gap is typically 1.5 eV for CZTS and 1.0 eV for CZTSe. The band gap of CZTSSe thin films may be mediated from 1.0 to 1.5 eV by adjusting the S/Se ratio, and a favorable band gap gradient across the film thickness may also be realized for better optical absorption and conversion. This is analogous to the band gap mediation mechanism through intentional Ga gradient in CIGS thin film solar cells [3]. In CZTSSe, the presence of Se may lead to the formation of Cu_xSe phases that become liquid during annealing to facilitate grain growth, as seen in CIGS thin films [4].

To better understand how Se brings improvement of properties in CZTSSe, it is worth studying the methods of synthesizing materials with tunable S/Se ratio. Recently, it has been reported that CZTSSe nanoparticles can be synthesized by hot-injection of sulfur and selenium precursors simultaneously into the solution of metal salts [5], and the S/Se ratio in CZTSSe can be adjusted by varying the ratio of starting materials. From this point of view, solvothermal method, another convenient and cost efficient route, seems promising for the synthesis of $Cu_2ZnSn(S,Se)_4$, as it has demonstrated to be applicable to the preparation of CZTS nanoparticles [6, 7]and $Cu(In,Ga)Se_2$ [8], another semiconductor selenide. There have been only scarce reports regarding the solvothermal synthesis of CZTSe nanowires so far [9]. In this study, we report an efficient solvothermal route for syntheizing $Cu_2ZnSnSe_4$ nanoparticles, in which the chemical composition of the semiconductor compound can be tuned by varying the amounts of metal precursors.

Experimental

Typically, $CuCl_2{\cdot}2H_2O$ (271 mg, 1.60 mmol), $ZnSO_4{\cdot}7H_2O$ (229 mg, 0.80 mmol), and $SnSO_4$ (171 mg, 0.79 mmol) were dissolved in 10 ml deionized water, added into the Teflon container of a 25 ml autoclave preloaded with the suspension of 302 mg (3.82 mmol) selenium powder in 10 ml ethylenediamine (en). The autoclave was closed and heated in an oven, the temperature of which was ramped from room temperature to 200 °C and held for 24 h. The oven was subsequently cooled down and the reaction products were collected by centrifugation and rinsed 3 times with deionized water, resulting in 506 mg dark red particles (100% yield). CZTSe nanoparticles with Cu-rich and Zn-poor compositions were also synthesized by adjusting the molar ratio of the starting metal salts such that Cu/(Zn + Sn) = 0.8, Zn/Sn = 1.2, and Se is 5% excessive. All as-synthesized nanoparticles were characterized using X-ray Diffraction (XRD), Raman Spectroscopy, Transmission Electron Microscopy (TEM), and Electron Dispersive X-ray Spectroscopy (EDX).

Results and discussion

The XRD peaks of the synthesized nanoparticles in Figure 1a are characteristic of CZTSe [10]. The average nanoparticle size is estimated to be 49 nm using the Scherrer equation and the FWHM of the (112) and (220) peaks. The calculated lattice parameters, a = 5.6643 Å and c = 11.3888 Å, agree well with the solution-fusion synthesized CZTSe (a = 5.6882 Å and c = 11.3378 Å) [11].

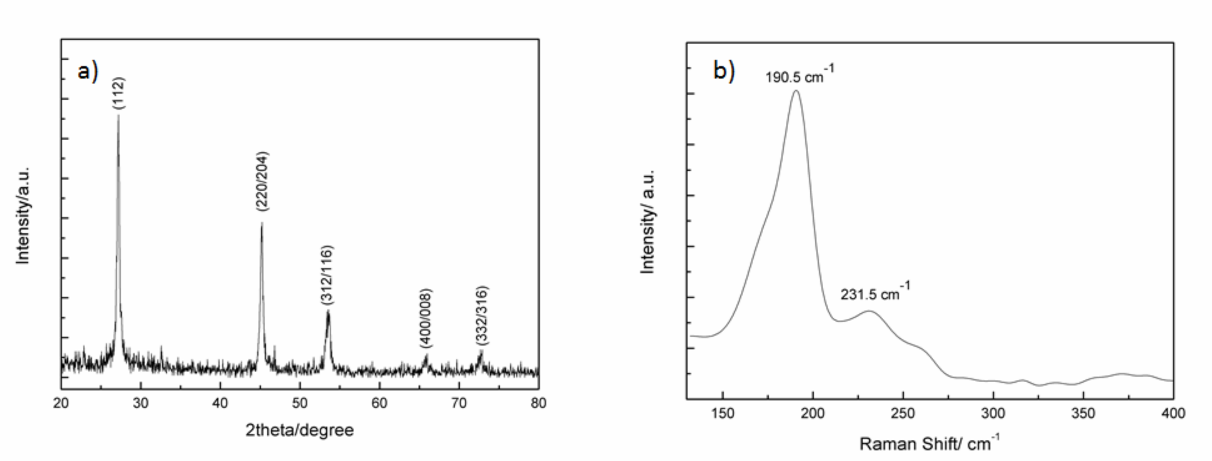

Figure 1. XRD pattern of $Cu_2ZnSnSe_4$ nanoparticles (a) and Raman spectra of $Cu_2ZnSnSe_4$ nanoparticles synthesized by solvothermal method (b)

Although the XRD peaks in Figure 1a are all characteristic of CZTSe, the existence of ZnSe and Cu_2SnSe_3 phases cannot be ruled out because their characteristic diffraction peaks overlap with those of CZTSe [12]. Therefore, Raman spectrometry was used to further identify the phase status of nanoparticles, as shown in Figure 1b. The peaks of 190.5 cm^{-1} and 231.5 cm^{-1} are consistent with reported Raman signals of CZTSe, while ZnSe and Cu_2SnSe_3 peaks were absent. The Raman result, together with the XRD data, unambiguously confirms the phase purity of the CZTSe nanoparticles synthesized by solvothermal method.

EDS analysis indicates that the composition of the synthesized CZTSe is Cu:Zn:Sn:Se = 2:1.04:1.09:4.47, close to the elemental ratio of the starting materials as well as the stoichiometry of $Cu_2ZnSnSe_4$. For solar cells based on CZTS type of absorber materials, Cu-poor and Zn-rich compositions have demonstrated to be superior to stoichiometric compositions in terms of resulting cell efficiency. Therefore, we also synthesized CZTSe particles with Cu-poor and Zn-rich compositions by adjusting the molar ratio of the precursor metal salts such that Cu/(Zn+Sn) = 0.8 and Zn/Sn = 1.2, *i.e.*, $CuCl_2$:$ZnSO_4$:$SnSO_4$ = 2:1.36:1.14. The synthesized particles were characterized to be $Cu_2Zn_{1.4}1Sn_{1.04}Se_{4.83}$, with Cu/(Zn + Sn) = 0.82 and Zn/Sn = 1.36, close to the designed formula. In addition, XRD and Raman analysis together identified pure CZTSe phase of these particles. This demonstrates that the metal ratio in CZTSe compounds can be tuned precisely and conveniently by varying the quantity of starting metal precursors in solvothermal synthesis.

The TEM image in Figure 2a exhibits nanoflake morphology of the synthesized CZTSe. A close-up view of the nanoflakes in Figure 3b further reveals that they were formed through aggregation of nanoparticles, the average size of which was estimated earlier from the XRD data to be 49 nm.

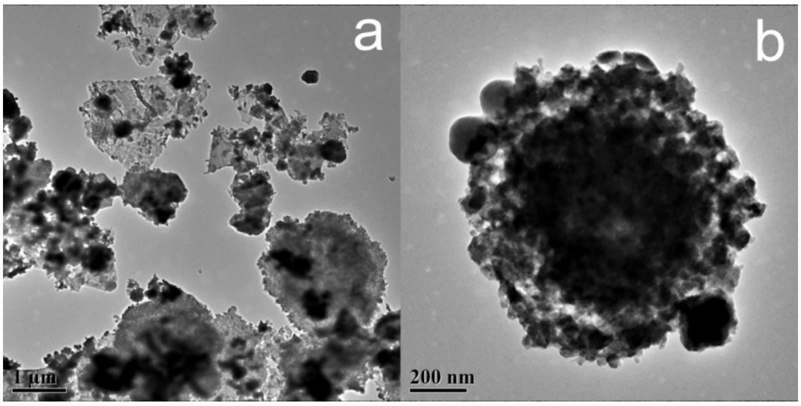

Figure 2. TEM imagies of $Cu_2ZnSnSe_4$ nanoparticles synthesized by solvothermal method

On the basis of the solvothermal reaction mechanism of Cu(In,Ga)Se_2, the possible solvothermal reaction pathway of CZTSe was proposed as follows:

$$Se_8 + en \rightarrow Se^{2-} + (enSe_7)^{2+} \text{ (en = ethylenediamine)} \quad (1)$$

$$Se^{2-} + Cu^{2+} \rightarrow CuSe, \quad Se^{2-} + Zn^{2+} \rightarrow ZnSe, \quad Se^{2-} + Sn^{2+} \rightarrow ZnSe \quad (2)$$

$$2CuSe + ZnSe + SnSe \rightarrow Cu_2ZnSnSe_4 (3)$$

In reaction (1), selenium dissolves in en and gives S^{2-} by opening the Se_8 ring as a result of nucleophilic attack by the amine. Se^{2-} and metal ions (or en coordinated complex ions) react to form binary selenides in reaction (2). The binary selenides further react to form CZTSe in reaction (3), in which the reduction of Cu(II) to Cu(I) and oxidation of Sn(II) to Sn(IV) also take place. Under typical solvothermal conditions, the aforementioned reactions occur homogeneously at molecular scales, resulting in nanosized products. Improvement of the synthesis method based on a better understanding of the reaction mechanism and applications of the solvothermal method to the synthesis of $Cu_2ZnSn(S,Se)_4$ are currently undergoing.

Summary

In this study, CZTSe nanoparticles were synthesized with quantitative yield through a solvothermal reaction at 200 °C for 24 h. The metal ratio in CZTSe could be conveniently tuned by varying the quantity of starting metal salts. XRD and Raman results confirmed that the reaction produced single-phase CZTSe and no ZnSe and Cu_2SnSe_3 impurities were observed. TEM showed that the resulting CZTSe were nanoflakes formed through aggregation of nanoparticles.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China [grant number 51472044].

References

[1] D.B. Mitzi, O. Gunawan, T.K. Todorov, et al, The path towards a high-performance solution-processed kesterite solar cell, Sol.Energ. Mat. Sol. C.95 (2011) 1421-1436.

[2] G. Zoppi, I. Forbes, R.W. Miles, et al, $Cu_2ZnSnSe_4$ thin film solar cells produced by selenisation of magnetron sputtered precursors, Prog. Photovoltaics.17 (2009) 315-319.

[3] O. Lundberg, M. Edoff, L. Stolt, The effect of Ga-grading in CIGS thin film solar cells, Thin Solid Films. 480 (2005) 520-525.

[4] J.R. Tuttle, M. Contreras, M.H. Bode, et al, Structure chemistry and growth mechanisms of photovoltaic quality thin-film Cu(In,Ga)Se_2 grown from a mixed-phase precursor, J. Appl. Phys. 77 (1995) 153-161.

[5] S.C. Riha, B.A. Parkinson, A.L. Prieto, Compositionally tunable $Cu_2ZnSn(S_{1-x}Se_x)_4$nanocrystals: probing the effect of Se-inclusion in mixed chalcogenidethin films, J. Am. Chem. Soc.133 (2011) 15272-15275.

[6] Y.L. Zhou, W.H. Zhou, Y.F. Du, et al, Sphere-like kesterite Cu_2ZnSnS_4 nanoparticles synthesized by a facile solvothermal method, Mater. Lett. 65 (2011) 1535-1537.

[7] M. Cao, Y. Shen, A mild solvothermal route to kesterite quaternary Cu_2ZnSnS_4 nanoparticles, J. Cryst. Growth. 318 (2011) 1117-1120.

[8] Y.G. Chun, K.H. Kim, K.H. Yoon, Synthesis of $CuInGaSe_2$ nanoparticles by solvothermal route, Thin solid films. 480-481 (2005) 46-49.

[9] L. Shi, C. Pei, Y. Xu, et al, Template-Directed synthesis of ordered single-crystalline nanowires arrays of $Cu_2ZnSnS_4$and $Cu_2ZnSnSe_4$, J. Am. Chem. Soc. 133 (2011)10328-10331.

[10] H. Matsushita, T. Maeda, A. Katsui, et al, Thermal analysis and synthesis from the melts of Cu-based quaternary compounds Cu-III-IV-VI_4 and Cu_2-II-IV-VI_4 (II=Zn, Cd; III=Ga, In; IV=Ge, Sn; VI=Se), J. Cryst. Growth. 208 (2000) 416-422.

[11] I.D. Olekseyuk, L.D. Gulay, I.V. Dydchak, et al, Single crystal preparation and crystal structure of the Cu_2Zn/Cd, Hg/$SnSe_4$ compounds, J. Alloy Compd. 340 (2002) 141-145.

[12] S. Ahn, S. Jung, J. Gwak, et al, Determination of band gap energy (Eg) of $Cu_2ZnSnSe_4$ thin films: On the discrepancies of reported band gap values, Appl. Phys. Lett. 97 (2010) 021905.