

Preparation and characterisation of $\text{Cu}_2\text{FeSnS}_4$ micro/nano particles by a liquid reflux method

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Published in Micro & Nano Letters; Received on 15th November 2015; Revised on 24th February 2016; Accepted on 23rd March 2016

Quaternary compounds $\text{Cu}_2\text{FeSnS}_4$ (CFTS), a promising alternative material for solar cell absorber layer, were successfully synthesised by a liquid reflux method in a mixture solvent of triethylenetetramine-ethylene glycol (TETA-EG, 1:1, v/v) at 230°C for 3 h under the atmospheric pressure condition. The phase, micro-structure, morphology, chemical composition and optical properties of the as-synthesised CFTS micro/nano particles were characterised using X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectrometry and ultraviolet-visible absorption spectrophotometer. The results showed that the stannite structured CFTS micro/nano particles with close to theoretical stoichiometric ratio were pure and well-crystallised, the particle size ranged from 70 to 240 nm and the particles were well-distributed, the band gap was about 1.25 eV which indicated its suitable application as the absorption layer of thin film solar cells.

1. Introduction: Recently, quaternary chalcogenides attract increasing attention due to their excellent optoelectronic properties which are suitable for a light absorber in thin film solar cells. Among them, $\text{CuIn}_x\text{Ga}_{1-x}(\text{S,Se})_2$ (CIGS) has been studied extensively and achieved rapid development. The laboratory conversion efficiency of CIGS solar cell has been beyond 20% [1]. However, the production cost increases due to the scarcity of indium and gallium which restricts the large-scale application of CIGS thin film solar cells [2].

The quaternary stannite structured $\text{Cu}_2\text{FeSnS}_4$ (CFTS), with a direct band gap of 1.1–1.54 eV, higher optical absorption efficient ($>10^4 \text{ cm}^{-1}$), abundant and non-toxic elements, is an ideal alternative material for CIGS [3–5]. Several methods have been used to prepare CFTS particles. Guan *et al.* [6] prepared flower-like CFTS particles with sphere structure by a microwave irradiation method and its band gap was $\sim 1.52 \text{ eV}$; Jiang *et al.* [7] successfully prepared CFTS particles with the composition closing to the stoichiometry by solvothermal method under 250°C using N, N-dimethyl formamide (DMF) as reaction solvent, the average size of the CFTS particles was about 200 nm and it had a band gap of $\sim 1.28 \text{ eV}$. Moreover, some other methods were also developed to the preparation of CFTS particles, such as hot-injection method [8], solution-based method [9], chemical method [4] etc. In this Letter, an easy-to-operate and low-cost liquid reflux method was developed, the structure, morphology and optical properties of the CFTS particles were also studied.

2. Experimental details: The initial materials used for the experiment were copper (II) chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), iron(III)chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), tin (IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$), thiourea ($\text{CH}_4\text{N}_2\text{S}$, Tu), precipitated sulphur (S), triethylenetetramine (TETA), ethylene glycol (EG), triethanolamine (TEA), DMF. All reagents were of analytical grade and used without any further purification.

First, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (4 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2 mmol), $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (2 mmol), $\text{CH}_4\text{N}_2\text{S}$ (8 mmol) or S (8 mmol) were dissolved in 30 ml reaction solutions in a three-necked round bottomed flask equipped with a reflux condenser which was fixed on the magnetic stirrer. The high purity nitrogen was inlet as protected gas. Then the temperature was maintained at 200°C–250°C for 30 min–5 h. After the reaction completed and cooled down to room temperature naturally, the products were cleaned by deionised

water and ethanol for several times, respectively. Finally, the black precipitate was dried in air at 60°C for 3 h.

All tests were conducted at room temperature. The micro-structure of CFTS particles was carried out using a Y-2000 automated X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). The morphology of the products was investigated using scanning electron microscope (FEI, Sirion 200). The chemical composition was measured from energy disperse spectroscopy (EDX-GENESIS 60S). The optical property was characterised using a ultraviolet-visible absorption spectrophotometer (UV-vis)-NIR spectrophotometer (TU-1800PC).

3. Results and discussion: In the reaction process, the decomposition of the precursors at a particular temperature mainly depends on the reducibility of the reaction solvent and sulphur source. As shown in Fig. 1, when TETA-EG (1:1, v/v) was used as reaction solvent and thiourea was used as sulphur source, the diffraction peaks appeared at $2\theta = 28.4^\circ, 32.8^\circ, 47.1^\circ, 47.3^\circ, 56.0^\circ$,

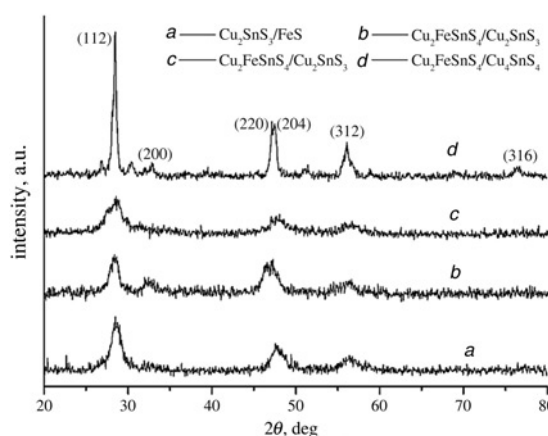


Fig. 1 XRD patterns of CFTS particles synthesised using different sulphur source in different reaction solution at 200°C for 3 h

a DMF/ $\text{CH}_4\text{N}_2\text{S}$

b TEA/ $\text{CH}_4\text{N}_2\text{S}$

c TETA-EG/S

d TETA-EG/ $\text{CH}_4\text{N}_2\text{S}$

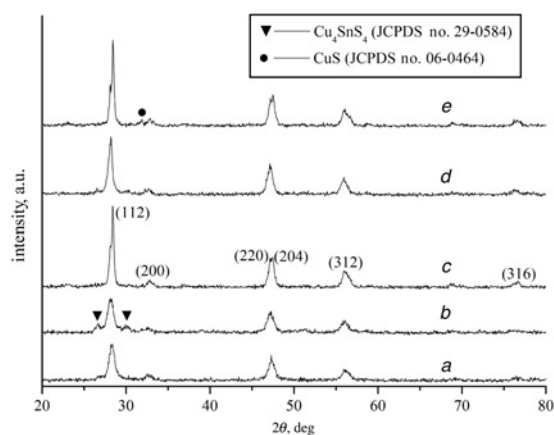


Fig. 2 XRD patterns of CFTS particles synthesised in TETA-EG (1:1, v/v) a 230°C/30 min b 230°C/1 h c 230°C/3 h d 230°C/5 h e 250°C/3 h

76.6° corresponded well with (112), (200), (220), (204), (312) and (316) planes of the stannite structured CFTS (JCPDS Card No. 44-1476) in the tetragonal space group I-42 m, the crystallinity was better than CFTS particles synthesised in other conditions, but the impurity of Cu_4SnS_4 (JCPDS Card No. 29-0584) was also appeared in the product.

The XRD patterns of CFTS particles synthesised in TETA-EG (1:1, v/v) at 230°C–250°C for 30 min–5 h were shown in Fig. 2. For the sample synthesised at 230°C for 3 h, no impurity peaks were detected in the XRD patterns, which indicated a high purity of CFTS phase. The lattice parameters were calculated to be $a = b = 5.442 \text{ \AA}$, $c = 10.764 \text{ \AA}$ which had slight deviation with the standard values ($a = b = 5.450 \text{ \AA}$, $c = 10.739 \text{ \AA}$, JCPDS Card No. 44-1476), indicating that there exist longitudinal tensile stress in the unit cell of CFTS particles. When the temperature increased to 250°C, the impurity of CuS (JCPDS Card No. 06-0464) appeared, which was due to the decomposition of CFTS particles at high temperature. When the temperature was 230°C and the reaction time was less or longer than 3 h, the diffraction peaks of the products were weaker, and the impurity peak could be indexed to Cu_4SnS_4 (JCPDS Card No. 29-0584). The average grain sizes calculated from the FWHM of the (112) plane using Debye Scherrer formula were 12.8, 13.0, 21.9 and 17.2 nm for the CFTS particles synthesised for 30 min, 1 h, 3 h and 5 h, respectively.

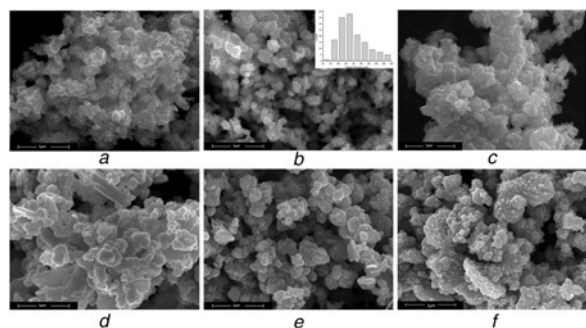


Fig. 3 Scanning electron microscopy images of CFTS micro/nano particles synthesised in TETA-EG (1:1, v/v) a 200°C/3 h b 230°C/3 h c 250°C/3 h d 230°C/30 min e 230°C/1 h f 230°C/5 h

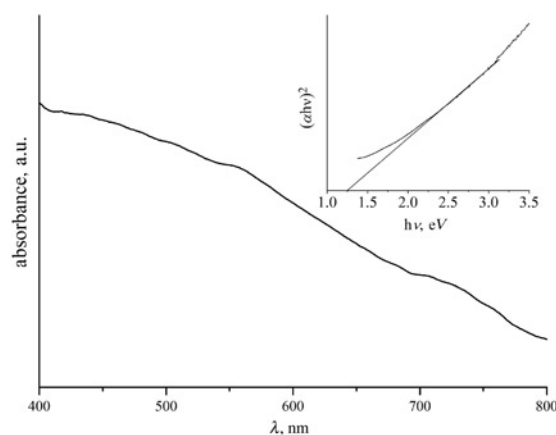


Fig. 4 Absorption spectra of CFTS particles synthesised in TETA-EG (1:1, v/v) at 230°C for 3 h. The inset shows the band gap value to be 1.25 eV

The morphology analysis of CFTS particles was shown in Fig. 3. At the temperature of 230°C, the CFTS particles in Fig. 3b were well-dispersed and the particle size was about 70–240 nm. However, when the temperature were 200°C and 250°C, the CFTS particles were aggregated remarkably, it may be due to EG acted as dispersion agent and capping agent during the reaction which slowed down the nucleation rate and the crystal growth rate and decreased the agglomeration effect of the particles [10, 11]. However, at the temperature of 250°C, some EG in the solvent evaporated which decreased the dispersion of the particles. When CFTS particles synthesised at 230°C for less than 3 h, the products showed layered structure. The formation of layered structure was due to EG in the solvent could adsorb on certain crystal surface and inhibited the growth of corresponding surface. When the reaction time increased to 3 h, the products showed blocky structure, the reason may be EG in the solvent had been consumed out and atoms in the layered structure rearranged under the action of TETA. When the reaction time increased continually, as shown in Fig. 2f, the morphology of CFTS particles was destroyed which corresponded well with the XRD pattern in Fig. 2. For the samples synthesised at 230°C for 3 h, the composition of Cu:Fe:Sn:S was 2:0.75:0.98:3.71 which was closed to the theoretical value of 2:1:1:4, and the composition ratio of Fe/Sn was less than 1 due to their different chemical reactivity in the reaction solvents.

During the reaction process, metal cations in the solvent complexed with TETA and Tu to form metal-TETA and metal-Tu complexes. When the temperature reached above 180°C, the melted thiourea decomposed to NH_2CN and H_2S [12]. Due to the reducibility of reaction solvent and H_2S , Fe^{3+} and Cu^{2+} in the metal-complexes were reduced to Fe^{2+} and Cu^+ . With the temperature and reaction time increased, the metal-complexes decomposed rapidly and released the metal ions of Cu^+ , Fe^{2+} and Sn^{4+} . The crystal nucleus were formed spontaneously at the same time. Based on the results above, the first generated products of Cu_2S and SnS_2 led to the formation of Cu_4SnS_4 . Finally, Cu_4SnS_4 reacted with FeS and formed stable black powders of CFTS.

Fig. 4 showed the UV-vis absorption spectra of the CFTS particles synthesised at 230°C for 3 h. CFTS particles exhibit a broad optical absorption in the UV-visible region. The optical bandgap was estimated using the following equation [13]

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

where α is the optical absorption coefficient, h is Planck's constant, ν is frequency, A is a constant and E_g is the band-gap energy. As shown in the inset, the bandgap value was estimated to be 1.25 eV which matched well the references report [4, 14].

4. Conclusion: In summary, the pure stannite structured CFTS micro/nano particles which was well-crystallised were successfully synthesised in TETA-EG (1:1, v/v) at 230°C for 3 h by a liquid reflux method. The particle size ranged from 70 to 240 nm and the particles were well-dispersed. The chemical ratio of Cu:Fe:Sn:S was 2:0.75:0.98:3.71 which was closed to the theoretical value. The band gap was about 1.25 eV, indicating it was promising for the application of solar cells.

5. Acknowledgments: This work was supported by the Fundamental Research Funds for the Central Universities of Central South University (grant no. 2014zzts037). We acknowledge senior engineer Dihui Huang for his assistance during the XRD patterns analysis.

6 References

- [1] Jackson P., Hariskos D., Lotter E., *ET AL.*: 'New world record efficiency for Cu(In,Ga)Se₂ thin-film solar cells beyond 20%', *Prog. Photovoltaics Res. Appl.*, 2011, **19**, pp. 894–897
- [2] Zuser A., Rechberger H.: 'Considerations of resource availability in technology development strategies: the case study of photovoltaics', *Resour. Conserv. Recy.*, 2011, **56**, pp. 56–65
- [3] Ai L.H., Jiang J.: 'Hierarchical porous quaternary Cu-Fe-Sn-S hollow chain microspheres: rapid microwave nonaqueous synthesis, growth mechanism, and their efficient removal of organic dye pollutant in water', *J. Mater. Chem.*, 2012, **22**, pp. 20586–20592
- [4] Guan H., Shen H.L., Jiao B.X., *ET AL.*: 'Structural and optical properties of Cu₂FeSnS₄ thin film synthesized via a simple chemical method', *Mat. Sci. Semicon. Proc.*, 2014, **25**, pp. 159–162
- [5] Fontané X., Izquierdo-Roca V., Saucedo E., *ET AL.*: 'Vibrational properties of stannite and kesterite type compounds: Raman scattering analysis of Cu₂(Fe,Zn)SnS₄', *J. Alloy Compd.*, 2012, **539**, pp. 190–194
- [6] Guan H., Shi Y.F., Jiao B.X., *ET AL.*: 'Flower-like Cu₂FeSnS₄ particles synthesized by microwave irradiation method', *Chalcogenide Lett.*, 2014, **11**, pp. 9–12
- [7] Jiang X., Xu W., Tan R.Q., *ET AL.*: 'Solvothelmal synthesis of highly crystallized quaternary chalcogenide Cu₂FeSnS₄ particles', *Mater. Lett.*, 2013, **102–103**, pp. 39–42
- [8] Liang X.L., Wei X.H., Pan D.C.: 'Dilute Magnetic Semiconductor Cu₂FeSnS₄ Nanocrystals with a Novel Zincblende Structure', *J. Nanomater.*, 2012, **2012**, p. 708648
- [9] Li L., Liu X.Y., Huang J., *ET AL.*: 'Solution-based synthesis and characterization of Cu₂FeSnS₄ nanocrystals', *Mater. Chem. Phys.*, 2012, **133**, pp. 688–691
- [10] Pan D.C., An L.J., Sun Z.M., *ET AL.*: 'Synthesis of Cu-In-S Ternary Nanocrystals with Tunable Structure and Composition', *J. Am. Chem. Soc.*, 2008, **130**, pp. 5620–5621
- [11] Zhou J.C., Li S.W., Gong X.L., *ET AL.*: 'Preparation of CuInS₂ microspheres via a facile solution-chemical method', *Mater. Lett.*, 2011, **65**, pp. 2001–2003
- [12] Yu S.H., Shu L., Yang J., *ET AL.*: 'A solvothelmal decomposition process for fabrication and particle sizes control of Bi₂S₃ nanowires', *J. Mater. Res.*, 1999, **14**, pp. 4157–4162
- [13] Hiroyasu N., Takahito N., Susumu K., *ET AL.*: 'Controllable electronic energy structure of size-controlled Cu₂ZnSnS₄ nanoparticles prepared by a solution-based approach', *Phys. Chem. Chem. Phys.*, 2014, **16**, pp. 672–675
- [14] Yan C., Huang C., Yang J., *ET AL.*: 'Synthesis and characterizations of quaternary Cu₂FeSnS₄ nanocrystals', *Chem. Commun.*, 2012, **48**, pp. 2603–2605