Solvothermal synthesis of highly crystallized quaternary chalcogenide 
Cu$_2$FeSnS$_4$ particles

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ABSTRACT

Quaternary chalcogenide Cu$_2$FeSnS$_4$ (CFTS) particles, a potential candidate for application as absorber layer in thin film solar cells, were successfully synthesized by using a convenient solvothermal method. X-ray diffraction (XRD) and transmission electron microscopy (TEM) results revealed that the CFTS particles possessed pure tetragonal structure with high crystallinity. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) results showed that the average size of the CFTS particles was about 200 nm and the composition of products was close to the stoichiometry of CFTS. UV-vis absorption spectrum showed that the CFTS particles had a broad absorption band in the whole visible range with a band gap of 1.28 eV, which are promising for photovoltaic applications.

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1. Introduction

Quaternary chalcogenides such as Cu$_2$ZnSnS$_4$, Cu$_2$ZnSnSe$_4$, and Cu$_2$FeSnS$_4$ have attracted increasing attention recently due to their potential applications in photovoltaics [1–10]. Especially, stannite semiconductor Cu$_2$FeSnS$_4$ is considered to be one of the most promising candidates as a light absorber in thin film solar cells for its suitable optical band gap (1.2–1.5 eV) [8–10] and the abundant and nontoxic constituents. Several vacuum [11–13] and non-vacuum based methods [8–10,14–16] have been developed for fabrication of CFTS materials. Among them, solution-based deposition methods are particularly attractive for their low cost and easy processing [17]. Li et al. prepared CFTS nanocrystals through thermal reactions of metal salts and sulfur in a hot oleylamine solution [8]. Recently, well-dispersed tetragonal CFTS nanocrystals were synthesized using a hot-injection method, which showed notable and stable photoelectrochemical response [9]. Adopting a similar method, Zhang et al. synthesized new wurtzite phase CFTS nanocrystals with the band gap values around 1.5 eV [10]. Ai et al. synthesized CFTS hollow chain microspheres with nanoporous structures by a rapid microwave nonaqueous method [16]. The hydrothermal method was also employed to synthesize CFTS nanocrystals [14,15]. It was reported that the formation of the Cu–thiourea colloid precursor in aqueous solution is crucial for conversion to the final products.

As an important solution-based chemical process, the solvothermal method has been successfully used to prepare quaternary chalcogenides such as Cu$_2$ZnSnS$_4$ [18,19], Cu$_2$CdSnS$_4$ [20], etc. for its low temperature, simplicity and high yield. To the best of authors’ knowledge, the solvothermal synthesis of CFTS has rarely been reported. Here we report a facile solvothermal route for the synthesis of stannite Cu$_2$FeSnS$_4$ particles using N,N-dimethyl formamide as the solvent. The structure, morphology, composition and optical properties of as-synthesized CFTS particles were also investigated.

2. Experimental section

N,N-dimethyl formamide (DMF), copper (II) chloride dehydrate (CuCl$_2$·2H$_2$O), iron (III) chloride trihydrate (FeCl$_3$·3H$_2$O), tin (IV) chloridetetrahydrate (SnCl$_2$·2H$_2$O) and thiourea (CH$_4$N$_2$S) were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were of analytical grade and used without further purification. In a typical process, 2 mmol copper (II) chloride dihydrate, 1 mmol iron (III) chloride trihydrate, 1 mmol tin (IV) chloride tetrahydrate, and 5 mmol thiourea were dissolved in 80 mL DMF under magnetic stirring. The obtained mixture was transferred into a 100 mL Teflon-lined stainless autoclave, sealed, maintained at 250 °C for 24 h, and then cooled down to room temperature. The obtained precipitates were centrifuged and washed six times with deionized water and absolute ethanol successively until Cl-ions could not be detected. The products were finally dried in vacuum at 80 °C for 4 h.
The phase structure of the products was analyzed by a Bruker D8 Advance AXS X-ray diffractometer (XRD) with Cu Kα1 incident radiation in θ−2θ Bragg–Brentano geometry. The morphology and microstructure of the products were characterized by a field emission scanning electron microscope (FE-SEM, Hitachi S-4800, Japan) and a field emission transmission electron microscope (FE-TEM, Tecnai F20, USA) respectively. The chemical composition was analyzed by energy dispersive spectroscopy (EDS) using an EDS spectrometer attached to the microscope. The chemical states of the products were studied using X-ray photoelectron spectroscopy (XPS, Kratos AXIS ULTRADLD, UK). The optical absorption property of the products was measured by using a UV–vis–NIR spectrophotometer (Perkin-Elmer Lambda 950, USA).

3. Results and discussion

The XRD pattern of the as-obtained CFTS particles is shown in Fig. 1a. All the diffraction peaks could be indexed to the stannite structure of CFTS (JCPD no. 44-1476) in the tetragonal space group I-42m. No other characteristic peaks were observed. The lattice parameters calculated from the refined pattern were \(a = b = 5.45\,\text{Å}\) and \(c = 10.74\,\text{Å}\), which matched well with the standard values from the PDF card mentioned above. The main peaks in the pattern showed higher peak intensity and narrower full-width at half-maxima (FWHM) than those of CFTS nanocrystallites synthesized by the hydrothermal method [14,15] and the hot-injection method [9,10]. This indicated that the crystallinity was better and the grain size was larger for our samples. The average grain size estimated using the Scherrer equation was much larger than 100 nm, which was out of the valid range of the equation. Transmission electron microscopy (TEM) images of the as-obtained particles are shown in Fig. 1b. The particles revealed excellent crystallinity with large grain size. The selected area electron diffraction (SAED) pattern in Fig. 1c matched the stannite structure of CFTS, as indicated by the diffraction spots corresponding to the (112), (312), (204) and (116) planes. Meanwhile, the lattice fringes with interplanar d-spacing of 0.31 nm could be observed from the high-resolution TEM image (Fig. 1d), which agreed well with the (112) crystal plane in tetragonal phase CFTS.

The SEM images with EDS results of the Cu2FeSnS4 particles are shown in Fig. 2. It was observed that the particles were aggregated with an average size of about 200 nm, which is consistent with the TEM results. The grain sizes of CFTS synthesized by the solution-based method were usually below 40 nm [8–10,14,15]. Though the size of the nanoparticles grew bigger after annealing process [8], it was still much smaller than that of our untreated samples. It is well known that the grain size is one of the important factors affecting the performance of polycrystalline solar cells [5].


Grain size could increase the carrier diffusion length and reduce the carrier recombination at grain boundaries, which contributes to improving the conversion efficiency of polycrystalline solar cells. Further study is necessary to improve the dispersibility of the CFTS particles. The composition of CFTS particles was determined by EDS. The atomic ratio of the four elements was calculated to be Cu:Fe:Sn:S = 25:12:13:50, which is very close to the Cu$_2$FeSnS$_4$ stoichiometric ratio of 2:1:1:4.

Fig. 3 shows the Cu 2p, Fe 2p, Sn 3d and S 2p XPS peaks of the as-obtained CFTS powders. Fig. 3a shows the Cu 2p core level spectrum. The binding energies for Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ were 932.7 and 952.5 eV, respectively, with a peak splitting of 19.8 eV, in good agreement with the value of Cu(I) [8,16]. The Fe 2p core level spectrum (Fig. 3b) shows the peaks at 710.3 and 724.0 eV with a peak separation of 13.7 eV, corresponding to the Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ of Fe(II) [8,16]. The Sn 3d$_{5/2}$ and Sn 3d$_{3/2}$ peaks were located at 486.5 and 495.0 eV, respectively, and a peak splitting of 8.5 eV indicates Sn(IV) (Fig. 3c) [8,16]. The S 2p core level spectrum (Fig. 3d) shows two peaks 2p$_{3/2}$ and 2p$_{1/2}$ at 161.6 and 162.8 eV, respectively, which are consistent with the 160–164 eV range expected for S in sulfide phases [8,16]. The binding energy values for Cu, Fe, Sn and S indicated that the main chemical states of the four elements are +1, +2, +4, and −2, respectively, which correspond with the states in Cu$_2$FeSnS$_4$ chemical formula.

Fig. 4 shows the UV–vis–NIR absorption spectrum of the CFTS powders. The as-prepared CFTS particles exhibited a broad absorption in the whole visible range. As shown in the inset, the band gap of the stannite CFTS particles can be estimated from the plots of $(\text{Absorbance})^2$ versus $h\nu$ ($\lambda$=absorbance, $h$=Planck’s constant and $\nu$=frequency) which were derived from the corresponding UV–vis–NIR absorption spectrum. The band gap was approximately 1.28 eV. This value is in good agreement with the literature value reported for tetragonal CFTS nanocrystals synthesized by the hot-injection method [9], but lower than that for the wurtzite and zinc blende CFTS reported by Zhang et al. [10].

### 4. Conclusion

In summary, a simple solvothermal route was developed for preparing tetragonal CFTS particles using DMF as the solvent.

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**Fig. 3.** XPS spectra of as-synthesized CFTS particles.

**Fig. 4.** UV–vis–NIR absorption spectrum of CFTS particles. The inset image shows the estimated band gap of 1.28 eV.
as-synthesized CFTS particles possessed high crystallinity and large grain size of over 100 nm. The CFTS particles had a broad absorption in the visible range with an optical band gap of 1.28 eV, which are promising for applications in thin film solar cells.

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