Synthesis and characterization of Cu_2ZnSnS_4 from Cu_2SnS_3 and ZnS compounds

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The Cu_2ZnSnS_4 (CZTS) powders are successfully synthesized by using ZnS and Cu_2SnS_3 as raw materials directly without any intermediate phase at 450 °C for 3 h in Ar atmosphere. The crystalline structure, morphology and optical properties of the CZTS powders are characterized by X-ray diffraction (XRD), Raman spectrum, field emission scanning electron microscopy (FESEM) and ultraviolet-visible (UV-vis) spectrophotometer, respectively. The results show that the band gap of the obtained CZTS is 1.53 eV. The CZTS film is fabricated by spin coating a mixture of CZTS powders and novolac resin with a weight percentage of 30%. The photoelectrical properties of such CZTS films are measured, and the results show an incident light density of 100 mW·cm^{-2} with the bias voltage of 0.40 V, and the photocurrent density can approach 9.80×10^{-5} A·cm^2 within 50 s, giving an on/off switching ratio of 1.64.

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Chalcopyrite semiconductor compounds, such as $Cu(In,Ga)Se_2$ (CIGS), are the promising absorber materials for thin film solar cell with demonstrated power conversion efficiency (PCE) of 20.8%[1,2]. However, CIGS requires rare scattering elements of In and Ga, which could limit the low-cost and large-scale application of CIGS. Therefore, seeking and synthesizing an abundant and environmental absorber material candidate with suitable photovoltaic properties has been becoming urgent. The quaternary Cu_2ZnSnS_4 (CZTS) has received remarkable attention as a promising candidate for absorber materials due to its abundance, low toxicity, and suitable optical and electrical properties[3-5]. CZTS is a p-type semiconductor with a band gap of 1.45–1.6 eV which approaches the optimum value for solar photoelectric conversion[6]. CZTS has been fabricated by various methods, including solvothermal method[7,8], hot injection method[9,10], microwave-assisted solution method[11,12], and so on[13-15]. Among these methods, the use of organic solvent is the common shortcoming. Considering environmental and energy conservation issues, a more environmental method with a low annealing temperature is constantly being pursued. Wen Li et al[16] reported a two-step hydrothermal method to synthesize Cu_2SnS_3@ZnS nanoparticles with core-shell structure. This method reduced the production cost, but the procedure was complex. In this paper, we report a low-cost, simple and environmental method for the fabrication of CZTS, and in the production process, Cu_2SnS_3 and ZnS directly react to synthesize CZTS for 3 h at 450 °C in Ar atmosphere without using toxic materials. In addition, this method is advantageous to the large-scale application of CZTS solar cell.

In a typical synthesis process of ZnS, 0.1 mol zinc (II) chloride ($ZnCl_2$, 98%) and 0.1 mol sodium sulfide ($Na_2S·9H_2O$, 98%) were dissolved in deionized water, respectively, and then the Na_2S solution was slowly dripped into $ZnCl_2$ solution. The resulting ZnS precipitates were centrifuged and washed several times with distilled water, and then dried at 70 °C for 6 h in vacuum.

The synthesis of Cu_2SnS_3 powders was carried out by chemical precipitation. 0.2 mol copper monochloride (CuCl, 97%) and 0.1 mol tin (IV) chloride ($SnCl_4·5H_2O$) were first dissolved in 100 mL deionized water, and the pH value was adjusted to be 1.0–2.0 under Ar gas atmosphere at room temperature. Then 0.3 mol $Na_2S·9H_2O$ solution was slowly dripped into the CuCl and $SnCl_4·5H_2O$ solution under Ar gas atmosphere at room temperature. The Cu_2SnS_3 precipitates were then centrifuged and washed with ethanol and deionized water several times to remove the solvent and by-products, and then dried in an oven at 70 °C for 6 h in vacuum.

The CZTS powders were synthesized by using ZnS_2 and Cu_2SnS_3 with equal molar ratio for heating process of 3 h at 450 °C in Ar atmosphere.

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The obtained products were characterized with X-ray diffraction (XRD) with Cu Kα radiation (λ=0.154 178 nm). Scanning electron microscopy (SEM) images were taken with a field emission scanning electron microscopy (FESEM, JEOL, JSM-6340F) operated at an accelerating voltage of 200 kV. Room temperature Raman spectra were recorded using a Horiba's LabRam HR high resolution spectrometer equipped with a multichannel charge coupled device (CCD) detection system in backscattering configuration. Then, the adsorption ultraviolet-visible (UV-vis) spectrum of the centrifuged solution was recorded using a UV-vis spectrophotometer (UV-2550, Shimadzu).

Fig.1(a) shows the XRD pattern of ZnS powders and the standard card of ZnS (JCPDS No.65-1691). The FESEM image of ZnS is shown in Fig.1(b). It can be seen that the ZnS powders are severely agglomerated, and the smallest particle size is less than 100 nm.
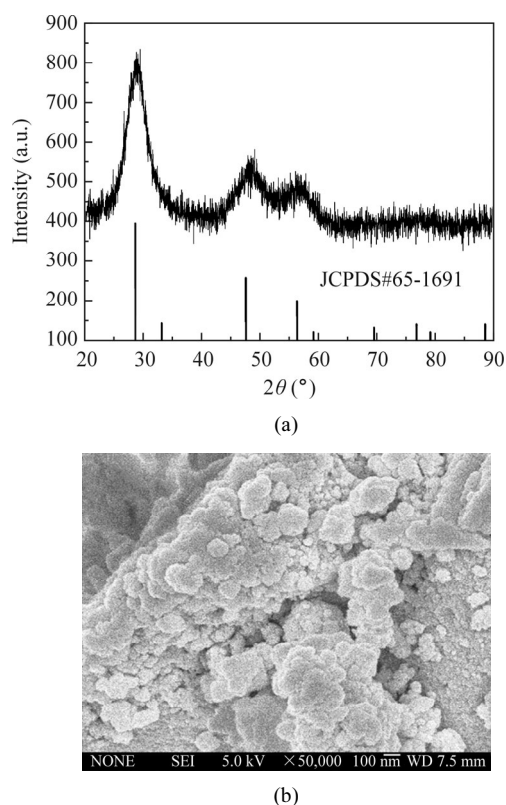

(a)

(b)

Fig.1 (a) XRD pattern of ZnS powders and the standard card of ZnS (JCPDS No.65-1691) and (b) FESEM image of ZnS powders

The XRD pattern of Cu_2SnS_3 obtained by chemical precipitation and the standard card of Cu_2SnS_3 (JCPDS No.27-198) are shown in Fig.2(a). The FESEM image of Cu_2SnS_3 is shown in Fig.2(b). It can be seen that the Cu_2SnS_3 powders have better dispersivity than ZnS powders, but the powders with particle size of 100–300 nm are also agglomerated.
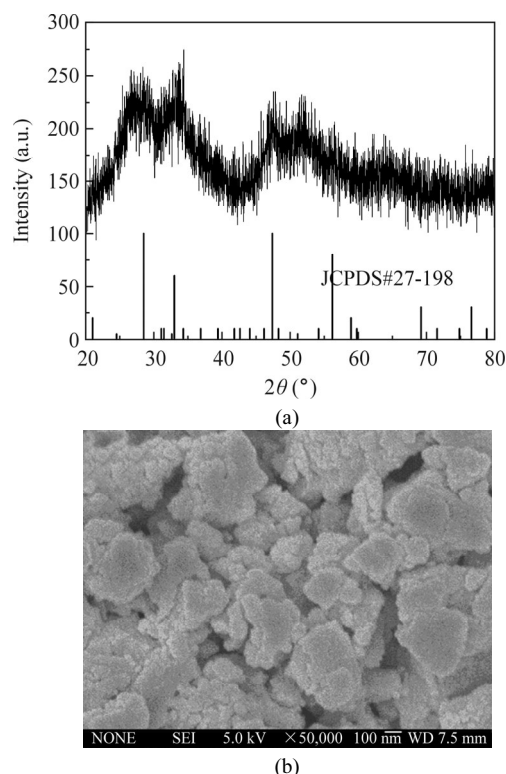

(a)

(b)

Fig.2 (a) XRD pattern of Cu_2SnS_3 powders and the standard card of Cu_2SnS_3 (JCPDS No.27-198) and (b) FESEM image of Cu_2SnS_3 powders

Fig.3(a) shows the XRD pattern of obtained mixtures after being calcined at 450 °C for 3 h and the standard card of CZTS (JCPDS No.26-0575). It demonstrates that ZnS and Cu_2SnS_3 phases react and directly transform into CZTS without any intermediate phase at 450 °C for 3 h. It can be seen clearly that the major XRD diffraction peaks appear at 2θ of 28.52°, 33.08°, 47.64°, 56.60° and 76.44° which are attributed to (112), (200), (220), (312) and (332) planes, respectively. The phase composition of CZTS is further examined with Raman analysis as shown in Fig.3(b). A peak located at 335 cm^{-1} and the weak peak at 287 cm^{-1} are observed, which is consistent with the reported value (333–338 cm^{-1}) of the characteristic peak of kesterite CZTS[17]. No other characteristic peaks of impurities[18] are observed, such as Cu_2S (475 cm^{-1}), ZnS (351 cm^{-1} and 274 cm^{-1}) and Cu_3SnS_4 (318 cm^{-1}, 348 cm^{-1} and 295 cm^{-1}). This result excludes the presence of other binary or ternary impurity phases, and confirms that the composition of products is only CZTS.

Fig.4 shows the SEM image of the as-obtained CZTS powders. It can be seen that the shape of CZTS powders is close to that of the raw material Cu_2SnS_3. But the particle size of CZTS powders is about 100 nm, which is smaller than that of Cu_2SnS_3 powders, and the CZTS powders are also a little more dispersed.

Fig.5(a) shows the room temperature UV-vis absorption spectrum for the as-prepared CZTS powders. In Fig.5(a), the spectrum exhibits a broad absorption in visible region with a tail in the long wavelength direction, which indicates a potential application for solar cells. $(ahv)^2$ as a function of the photon energy hv is plotted as shown in Fig.5(b), where a repre-

sents the absorption coefficient, h is the Plank's constant and v means the frequency, and the optical band gaps for CZTS nanoparticles can be estimated from Fig.5(b) as 1.53 eV, which is consistent with the reported value of 1.45–1.60 eV[19]. It further evidences that this phase is CZTS. This value is close to the optimum for photovoltaic solar conversion in a single-band-gap device.
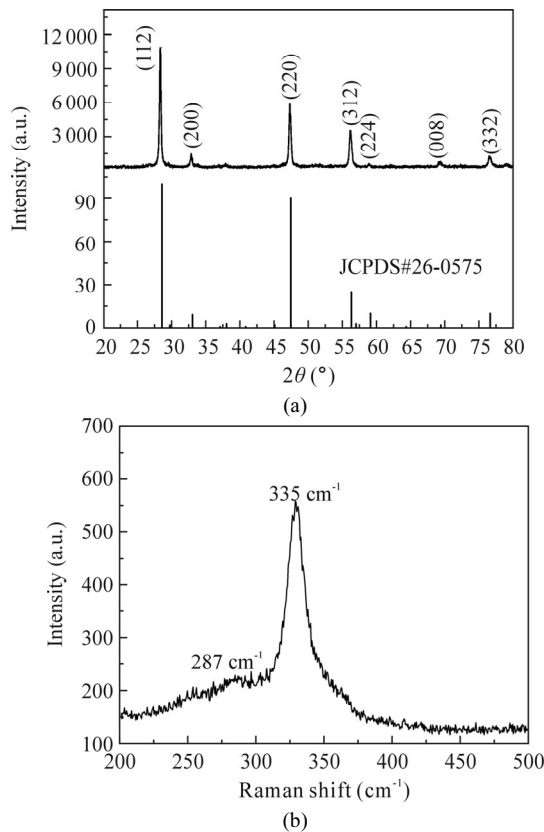

(a)

(b)

Fig.3 (a) XRD pattern of CZTS powders obtained after being calcined for 3 h at 450 °C and the standard card of CZTS (JCPDS No.26-0575) and (b) Raman spectrum of the CZTS powders
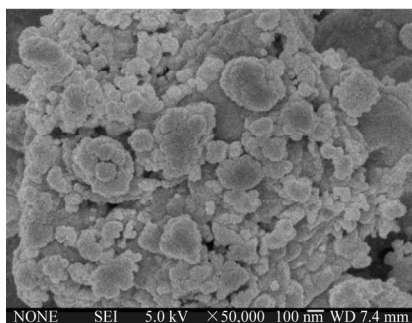

Fig.4 SEM image of the CZTS powders

The film of CZTS was fabricated by mixing CZTS nanoparticles and novolac resin with a weight percentage of 30%, spin coating the mixture onto molybdenum substrate and drying in air. The CZTS hybrid film exhibits excellent photoresponse characteristics under AM 1.5 G irradiation (100 mW·cm^{-2}) as shown in Fig.6. With the light irradiation on and off, the current in the film shows two distinct states,

which are a low current in the dark and a high current under illumination. The switching between these two states is very fast and reversible, allowing the film to act as a high-quality photosensitive switch. In the dark, the current density is only 1.52×10^{-4} A·cm^{-2}. However, at an incident light density of 100 mW·cm^{-2} and a bias voltage of 0.40 V, the current density can approach 2.50×10^{-4} A·cm^{-2}, giving an on/ off switching ratio of 1.64. The photocurrent density of CZTS thin film is 9.80×10^{-5} A·cm^{-2} within 50 s. It should be noted that the CZTS film shows outstanding stability, and no obvious degradation is observed during the test cycles.
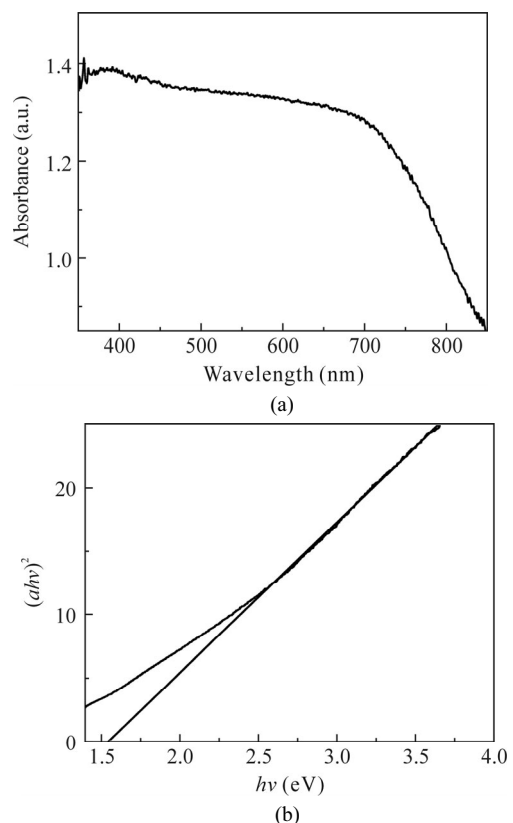

(a)

(b)

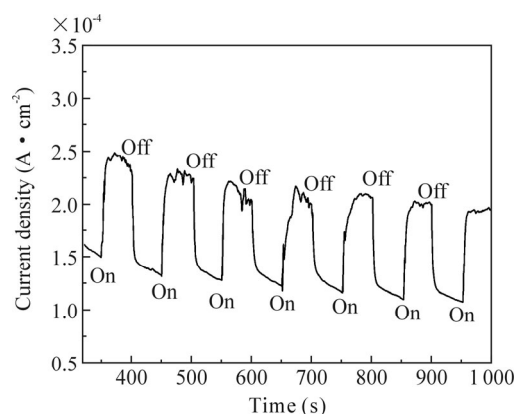**Fig.5 (a) UV-vis absorption spectrum of CZTS nanocrystals; (b) The plot of (ahv)^2 against hv for the absorption spectrum**

Fig.6 On/off switching of the device fabricated from a CZTS hybrid film at an incident light density of 100 mW·cm^{-2} and a bias voltage of 0.40 V

CZTS powders are successfully prepared by using ZnS and Cu_2SnS_3 as raw materials at 450 °C for 3 h in Ar atmosphere. This method is relatively simple and environmental. The FESEM image shows that the particle size of CZTS powders is about 100 nm. The absorption spectra show that the band gap of the obtained CZTS is 1.53 eV, which is optimal for photovoltaic applications. In our system, at an incident light density of 100 mW·cm^{-2} and a bias voltage of 0.40 V, the photocurrent density can approach 9.80×10^{-5} A·cm^{-2} within 50 s, giving an on/off switching ratio of 1.64.

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