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Synthesis of wurtzite Cu_2ZnSnS_4 nanocrystals via solvothermal route and their application in photovoltaic devices

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ABSTRACT

Quaternary wurtzite Cu_2ZnSnS_4 nanocrystals have been synthesized via solvothermal way using hexanamine as solvent. The structure, composition, morphology and optical absorption properties of Cu_2ZnSnS_4 were characterized using X-ray powder diffraction, energy dispersive X-ray spectrometry, transmission electron microscopy and UV–vis spectrometry. The short-circuit current and open-circuit voltage of solar cells, fabricated using as-synthesized Cu_2ZnSnS_4 nanocrystal inks, were 7 mA and 0.3 2 v respectively, under AM1.5G illumination.

1. Introduction

Multinary compound semiconductors such as: $CuInS_2$ [1–9], $CuIn_xGa_{1-x}S_2$ [10–17] and Cu_2ZnSnS_4 [18–23], have attracted a large amount of attention due to their excellent optical and electrical properties that can be applied in the field of solar cells and photovoltaic devices. Recently the champion cell efficiency of $CuInGaSe_2$ fabricated by vacuum deposited technique exceeds 20% on the laboratory scale [24], which is exciting and impressive power conversion efficiency. However, the elements of indium and gallium are rare metal elements in the earth's crust and a large capacity of indium is required for transparent conductive coatings to meet the need of growing flat panel display industry, which limited promising utilization on the large scale. Therefore, it is urgent to find appropriate material to substitute $CuIn_xGa_{1-x}S_ySe_{2-y}$. The material of Cu_2ZnSnS_4 (CTZS) composed of naturally abundant and environmentally benign elements, which is a direct band gap of 1.5 eV and absorption coefficient of 10^4 cm^{-1}, has become suitable candidate for low cost solar cells, and theoretical consideration of maximum power conversion efficiency of CZTS is as high as 32.4%. The reported power conversion efficiency (PCE) of CZTS based solar cells were achieved to 8.4%, 12.6% and 7.2%, respectively, based on vacuum deposited technique [25], solution-processed method [26] and nanocrystal inks approach [27]. But vacuum deposited technique makes a large amount of cost and solution-processed method involves hydrazine, which is a kind of highly toxic and easily explosively liquid. Comparatively, nanocrystal inks approach is a low cost, green way to fabricate CZTS solar cells. The ability to control the composition of CZTS nanocrystals plays an important role because the optoelectronic property in the CZTS absorber depends greatly on the composition. Therefore, much research were focused on synthesis of high quality stoichiometry composition CZTS nanocrystals.

In order to synthesize the metastable Cu_2ZnSnS_4 nanocrystals, long chain organic ligand, oleylamine, oleic acid and dodecanethiol were used as capping ligands to synthesized homogeneous wurtzite Cu_2ZnSnS_4 nanocrystals. However, the above capping ligands possess strong coordinated ability, it is difficult to remove from nanocrystals surface, and it will affect the optoelectronic property of as-synthesized semiconductor nanocrystal. Herein, wurtzite, stoichiometry composition and high quality Cu_2ZnSnS_4 nanocrystals were synthesized under low temperature via a solvothermal way using low-boiled hexanamine as solvent, carbon disulfide as sulfur source, 3-mercaptopropionic acid as capping ligands. It is illustrated that short chain 3-mercaptopropionic acid has strong coordinated ability and balance the reactivity of metal cations to form the metastable wurtzite Cu_2ZnSnS_4 nanocrystals. The as-synthesized wurtzite Cu_2ZnSnS_4 nanocrystals have been successfully applied in the thin film solar cells as absorber layer. The as-synthesized wurtzite Cu_2ZnSnS_4 nanocrystals display good optoelectronic property.

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2. Results and discussion

Fig. 1a shows XRD pattern of the as-synthesized wurtzite phase CZTS nanocrystals. As known, sulfur anions occupy the frame of the wurtzite CZTS crystal cell structure and other metal cations randomly occupy a half of interstices of the sulfur anions. The major diffraction peaks exhibit at $2\theta = 26.8°$, 28.32°, 30.37°, 39.43°, 47.35°, 51.31°, 56.16° can be indexed to the (100), (002), (101), (102), (110), (103), (112) of the wurtzite crystal structure, respectively. As shown in the Fig. 1a, the experimental pattern matches well with the simulated one, indicating as-synthesized CZTS nanocrystals have wurtzite structure. During the whole synthesized process, 3-mercaptopropionic acid plays a key role in the formation of wurtzite CZTS nanocrystals. When no or 1 mL 3-mercaptopropionic acid was added, an unknown complicated phase CZTS nanocrystals was obtained. 2 mL 3-merccaptopoionic acid is the optimal volume for the formation of wurtzite CZTS nanocrystals. Another effect of 3-mercaptopropionic acid is to cap with metal cations to eliminate the reactivities of different metal cations. Due to coordinated effect of 3-mercaptopropionic acid, different metal cations form homogeneous CZTS nanocrystals at certain time during the solvothermal process. It is reasonable to speculate that the role of 3-mercaptopropionic acid is to adjust chemical environment preferring the formation of wurtzite CZTS nanocrystals. In order to demonstrate that CZTS nanocrystals are composed of four elements, energy dispersive X-ray spectrometry (EDS) is carried out to analysis elemental composition at the nanoscale. After analysis of EDS data, the result shows that the ratio of Cu/Zn/Sn/S is approximately 2:1:1:4, which corresponds well with stoichiometry of CZTS nanocrystals. It also demonstrates that 3-mercaptopropionic acid can balance the reactivities of metal cations during the solvothermal process. According to the previous literature [29], it is shown from the DFT calculation result that cationic subsystems play a crucial role of the fundamental optical features. Fig. 1c shows the UV–Vis absorption spectra of as-synthesized CZTS nanocrystals. The onset point of the UV–Vis absorption spectra is around 820 nm. Inset of Fig. 1d displays the abs^2 VS eV for the nanocrystals; the band gap energy is approximate 1.51 eV; which is in good accordance with the bulk value 1.45–1.6 eV. The band gap energy shows that CZTS nanocrystals are optimal materials for application in the field of solar cells.

Fig. 2 shows the valence states of Cu, Sn, Zn, S in CZTS nanocrystals were determined by X-ray Photoelectron Spectroscopy (XPS). Two peaks of Cu 2p, Sn 3d and Zn 2p, located at 931.2ev and 951.1 eV, 485.9ev and 494.2 eV, 1020.7 eV and 1043.7 eV, suggest that the valence states of Cu, Sn, Zn in the nanocrystals are +1,+4,+2. The two peaks located at 161.3 eV and 162.5 eV were assigned to S 2p with a valence of –2, which is in good accordance with literature value [28]. Fig. 2e and f shows low TEM image for CZTS nanocrystals. The TEM image shows that the as-synthesized nanocrystals are regularly nanoparticles with an average diameter of 5–6 nm, which is in good accordance with the size calculated from Scherrer equation. The image of selected area electron diffraction (SAED) also confirms that CZTS nanocrystals possess a

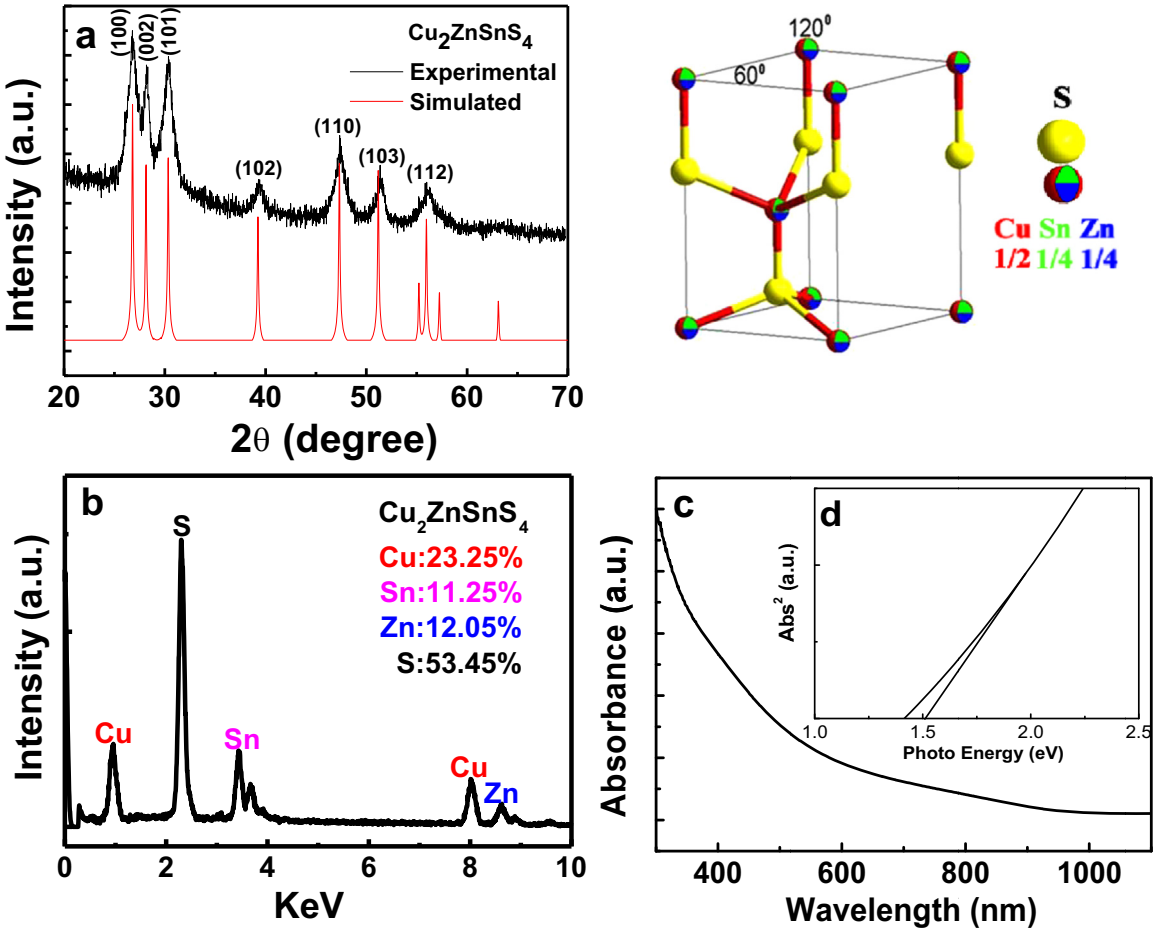

Fig. 1. (a) XRD pattern of as-synthesized (black line) and simulated (red line) Cu_2ZnSnS_4 nanocrystals. (b) EDS spectra of as-synthesized Cu_2ZnSnS_4 nanocrystals. (c) UV–Vis–NIR absorption spectra of Cu_2ZnSnS_4 nanocrystals in chloroform; (d) abs^2 *vs* eV for the Cu_2ZnSnS_4 nanocrystals.

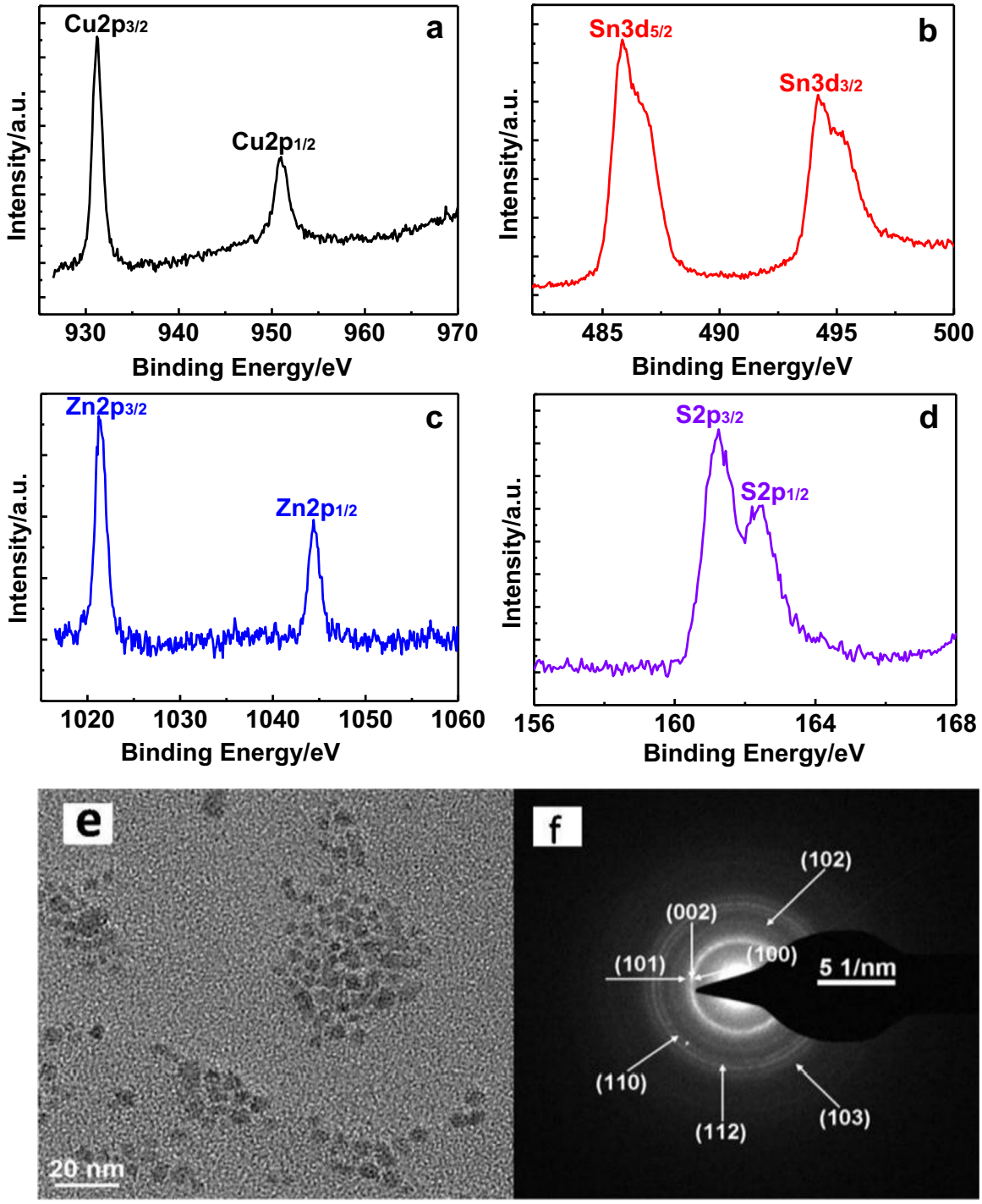

Fig. 2. X-Ray photoelectron spectroscopy of Cu_2ZnSnS_4 nanocrystals; (a) Cu; (b) Sn; (C) Zn; (d) S. (e) TEM image and (f) SAED of as-synthesized Cu_2ZnSnS_4 nanocrystals.

wurtzite structure. That is consistent with the XRD result.

One batch of CZTS thin film solar cells was fabricated by chemical bath deposition of CdS layer on ITO glass first, followed by spin-casting the CZTS nanocrystals as absorber layer, evaporated Al electrode on the absorber layer. The effect area of the final devices is 0.1 cm^2. The corresponding J-V characteristic of the solar cell is shown in the Fig. 3a. The device parameters of CZTS thin film solar cell under AM1.5G illumination are as follows: the open-circuit voltage is 0.32 V, and the short-circuit current is 7 mA/cm^2. The above results have demonstrated that as-synthesized wurtzite CZTS nanocrytals, like wurtzite $CuInS_2$ nanocrytals [5], display photoelectric response property that can be directly used as absorber layer in the thin film solar cells. The optoelectronic property can be greatly affected by the crystal size and residual ligands in the absorber layer, therefore the parameters are lower than the reported ones [18]. The parameters might be improved by increasing the thickness the CZTS absorber layer to absorb more photons and treat the CZTS absorber layer in the selenide vapor atmosphere to enlarge the grain in order to improve chance of the electron-hole pair separation on the film surface.

In summary, we have successfully synthesized quaternary semiconductor CZTS nanocrystals via convenient solvothermal

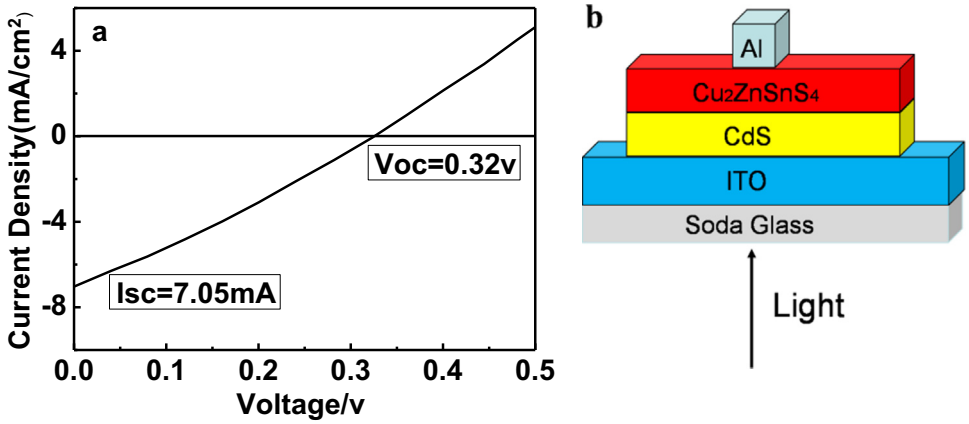

Fig. 3. (a) *J-V* property of the CdS/Cu_2ZnSnS_4 solar cells fabricated with as-synthesized wurtzite Cu_2ZnSnS_4 nanocrystals; (b) the device structure of as-fabricated solar cells.

approach. 3-mercaptopropionic acid plays a vital role in the formation of final products. The photovoltaic devices fabricated by CTZS nanocrystals display 7 mA short-circuit current and 0.32 v open-circuit voltage under 1.5G illumination.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2016.07.090.

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