



Controlled synthesis, characterization, and optical properties of ZnIn_2S_4 and CdIn_2S_4 nanostructures with enhanced performance for solar cell applications



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ABSTRACT

In this paper, we present the design, synthesis and characterization of ZnIn_2S_4 (ZIS), CdIn_2S_4 (CIS) nanostructures and their nanocomposites to enhance the solar cell high light harvesting efficiency via the simple chemical Polyol method. Results show that pure ZIS and CIS nanostructures could significantly enhance the separation of photo excited electron-hole pairs, thereby increasing the photo current density. The CIS/ZIS and ZIS/CIS composites exhibit superior photovoltaic performance under light illumination compared to the unalloyed ZIS and CIS. The improvement of performance is ascribed to the uniform distribution of ZIS nanoparticles around CIS and vice versa.

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1. Introduction

Semiconductor nanostructures play important roles in the fields of solar energy conversion and storage. ZnIn_2S_4 and CdIn_2S_4 are a chalcogenide semiconductor that belongs to the AB_2X_4 family of ternary compounds [1–4]. In this present work, we report the synthesis and characterization of ZnIn_2S_4 , CdIn_2S_4 , $\text{ZnIn}_2\text{S}_4/\text{CdIn}_2\text{S}_4$ and $\text{CdIn}_2\text{S}_4/\text{ZnIn}_2\text{S}_4$ nanostructures by a facile Polyol method. Final products were investigated by the facility of XRD, SEM and TEM. Furthermore, Doctor's blade method was used for fabrication of ZnIn_2S_4 , CdIn_2S_4 , $\text{ZnIn}_2\text{S}_4/\text{CdIn}_2\text{S}_4$ and $\text{CdIn}_2\text{S}_4/\text{ZnIn}_2\text{S}_4$ layer on the fluorine doped tin Oxide (FTO) glass substrate in order to measure photovoltaic properties.

2. Experimental

2.1. Characterization

X-ray diffraction (XRD) patterns were recorded by a Philips X'PertPro, X-ray diffraction using Ni-filtered $\text{Cu K}\alpha$ radiation at scan range of $10 < 2\theta < 80$. Scanning (Transmission) electron microscopy (SEM&TEM) images were obtained on LEO-1455VP

and Philips EM208S, respectively. Photocurrent density-voltage (J-V) curve was measured by using computerized digital multimeter under a 300 W metal xenon lamp as an assimilated sun lights source.

2.2. Synthesis ZnIn_2S_4 , CdIn_2S_4 , $\text{ZnIn}_2\text{S}_4/\text{CdIn}_2\text{S}_4$ and $\text{CdIn}_2\text{S}_4/\text{ZnIn}_2\text{S}_4$ nanostructures

The CdIn_2S_4 (or ZnIn_2S_4) nanoparticles were synthesized via the thermal reaction between $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (600 mg) and thioacetamide (300 mg), also reduction of $\text{Cd}(\text{acac})_2$ (310 mg) (or $\text{Zn}(\text{acac})_2$ (263 mg)) in 1,2 hexadecanediol (365 g) in the presence of oleic acid (800 μl) and oleylamine (850 μl) at temperature of 300 °C under N_2 atmosphere and kept at this temperature for 120 min before cooling down to room temperature. The precipitate obtained was separated by centrifuging, washed with methanol and dispersed in hexane several times.

The synthesis of $\text{ZnIn}_2\text{S}_4/\text{CdIn}_2\text{S}_4$ (or $\text{CdIn}_2\text{S}_4/\text{ZnIn}_2\text{S}_4$) nanostructures, were prepared by the following procedure: $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (300 mg), thioacetamide (150 mg), $\text{Cd}(\text{acac})_2$ (155 mg) (or $\text{Zn}(\text{acac})_2$ (131 mg)), 1,2 hexadecanediol (365 g), oleic acid (400 μl) and oleyl amine (425 μl) are mixed together in 10 mL benzyl ether at room temperature under a flow of N_2 atmosphere. 10 mL hexane solution of as-synthesized ZnIn_2S_4 (or CdIn_2S_4) nanoparticles was added and then the mixture was heated to the boiling point of benzyl ether (300 °C).

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3. Results and discussion

3.1. Morphology and structure characterization

In order to understanding the growth process and morphology of the CIS and ZIS nanostructure, SEM images were prepared, which are shown in Fig. 1. It can easily observe that the individual CIS particles have a spherical-like shape (Fig. 1(a)). Carefully, sounding into the low magnification of CIS nanostructure shows self assembled particles with quite uniform size distribution (Fig. 1(b)). The average diameters of spherical-like CIS nanoparticles are estimated ranging from 15 nm to 20 nm. It's found that the solvent used in the synthetic process has an important role in the morphology and trapping state of electron for solar cell application. The ZIS nanostructures show the similar morphology as obtained in CIS nanostructures, but with smaller particles size. The mean diameters of ZIS nanoparticles are estimated ranging from 10 nm to 15 nm (Fig. 1(d) and (e)). Energy Dispersive Spectroscopy (EDS) analyses were hired to navigate the chemical composition of as-synthesized CIS and ZIS nanostructures. Peaks of the element's Cd, In, Zn and S are disclosed in the EDS profile (Fig. 1(c) and (f)). Atomic ratio of element's Cd:In:S and Zn:In:S is very close to 1:2:4 for both CIS and ZIS, which is supporting the purity of the nanostructures.

To further characterize, the size and morphology of ZIS/CIS and CIS/ZIS have been evaluated throughout TEM images. The images demonstrate that the yield structures are on the whole composed of a large amount of sphere core/shells like-shape with average size of 7–8 nm. In addition, narrow size distribution with some aggregation particles has been monitored (Fig. 2(a)–(b)). The phase compositions of as-synthesized ZIS/CIS and CIS/ZIS nanocomposites were investigated by the X-ray diffraction. For comparison, pure ZIS and CIS nanostructures were also prepared. By attaching the Zn component in the reaction process, a hexagonal phase emerges in the XRD pattern, which is corresponding to the profile of Hexagonal ZIS (JCPDS 65-2023) (Fig. 2(c)). XRD pattern in Fig. 2(cII) indicates a cubic spinel CIS structure with characteristic (311) and (440) peaks (JCPDS 27-0060). As it clearly can be understood,

the pattern of CIS/ZIS and ZIS/CIS denoting the existence of both ZIS and CIS component (Fig. 2(cIII) and (cIV)). In addition, there is no sign of the other structure such as CdS, In₂S₃ or ZnS in the XRD patterns, displaying the high purity and good crystalline of the final product.

3.2. Optical and photovoltaic properties

The absorption spectra of ZIS and CIS and their composites have been attained through the chemical Polyol process (Fig. 3(a–d)). In a wide wavelength from UV to Visible light, the products present a strong with steep shape on the visible edge. Even so, their absorption edges are located at different wavelength, as 460 nm for ZIS, 500 nm for CIS (Fig. 3(a–b)). The extreme absorption edges announce single phase of product, which is in good agreement with the XRD result. The effects of ZIS on the optical properties of CIS and vice versa are demonstrated in Fig. 3(c) and (d). Compared with pure ZIS, it can be found that CIS/ZIS presented the large absorption edge ($\lambda = 490$ nm). It is quite possible that the CIS nanoparticles are covered completely with ZIS nanoparticles and this large amount of ZIS contributes to increase the absorption edge. This implies that the size of CIS/ZIS nanocomposites is increased, leading to a corresponding decrease in the band gap. This is in consistent with our observation from TEM and reveals that the nanocomposites have a large size than the pure nanoparticles. The band gaps calculated from the absorption edges are about 2.68 eV and 2.53 eV for pure ZIS and CIS/ZIS nanocomposite, respectively. The similar results were achieved for CIS and ZIS/CIS product. It can be perceived that the ZIS/CIS nanocomposite reveal a slight shift toward high wavelength, which are located at 540 nm, corresponding well with the band gap of about 2.30 eV (Fig. 3(b) and (d)). The results exhibit that the CIS/ZIS and ZIS/CIS nanocomposites, could have a better light harvesting application than the pure ZIS and CIS nanoparticles.

The FTO/ZIS/CIS/CdS/Pt-FTO structure was arranged as reported in the literature. The CIS (or ZIS) solar cell consists of four layers such as: an absorber p-type layer (CIS, ZIS), buffer n-type layer (CdS thin film), transparent conductive oxide (ITO as a front con-

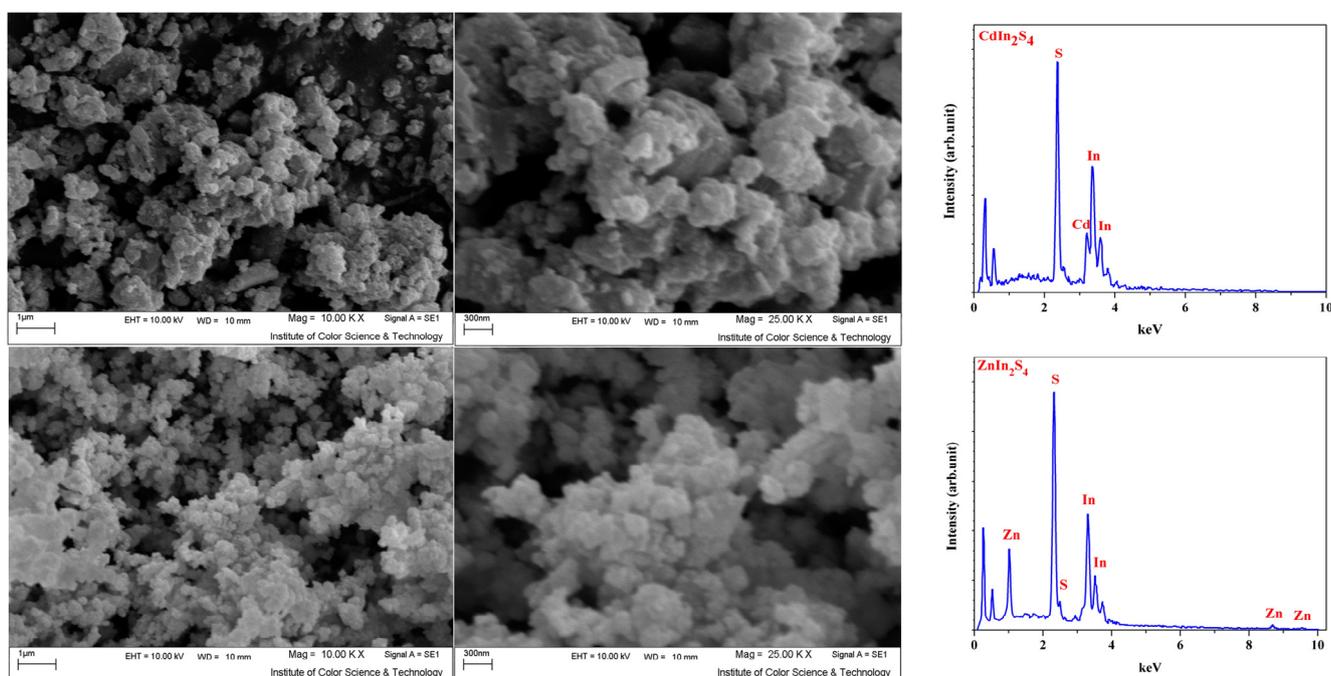


Fig. 1. SEM images with different magnification (a&b) CdIn₂S₄ (d&e) ZnIn₂S₄ EDS profile of nanostructure (c) CdIn₂S₄ (f) ZnIn₂S₄.

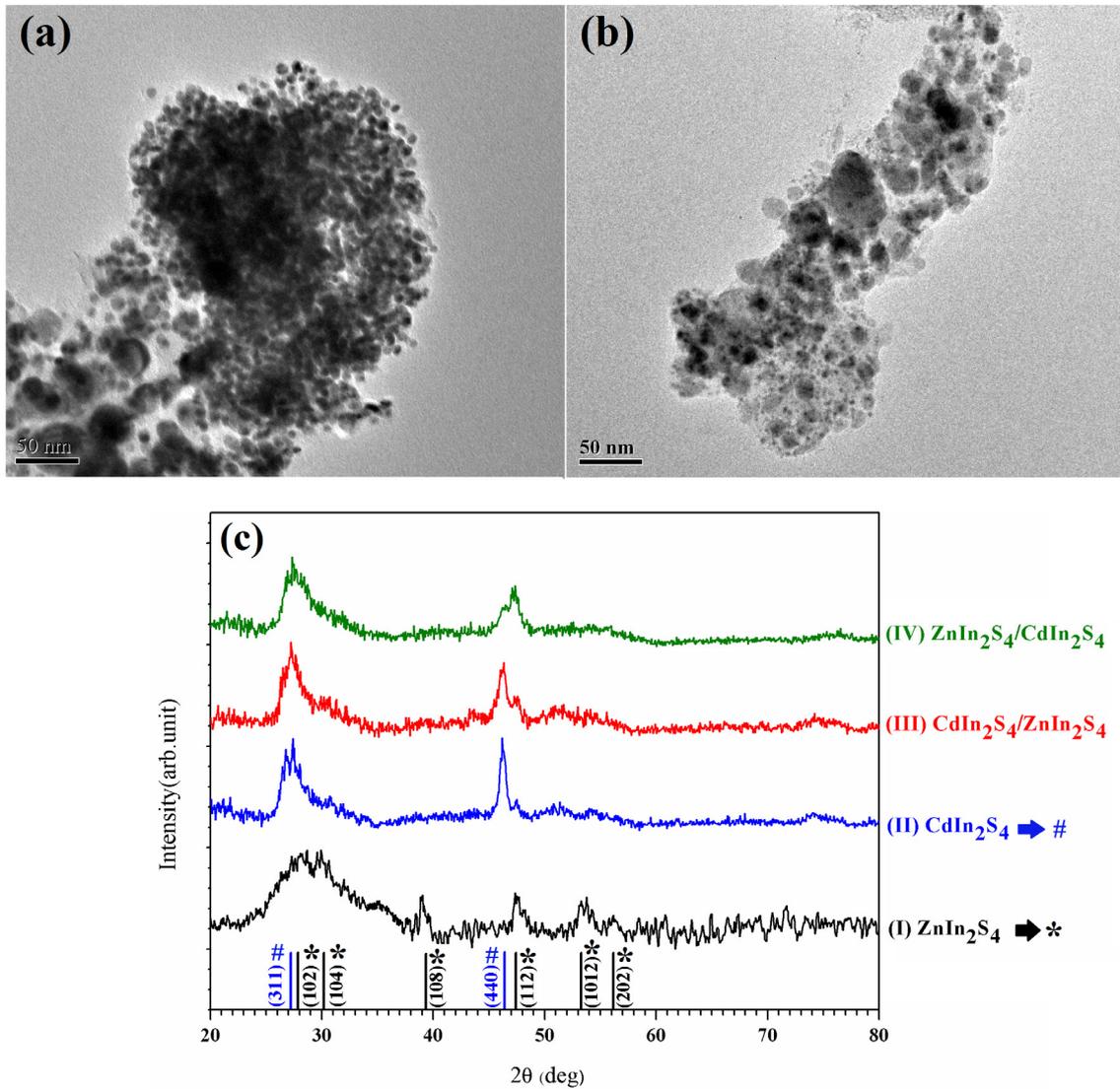


Fig. 2. (a&b) TEM images with different magnification $\text{CdIn}_2\text{S}_4/\text{ZnIn}_2\text{S}_4$ and $\text{ZnIn}_2\text{S}_4/\text{CdIn}_2\text{S}_4$, respectively. (c) XRD patterns of as-synthesized nanostructures.

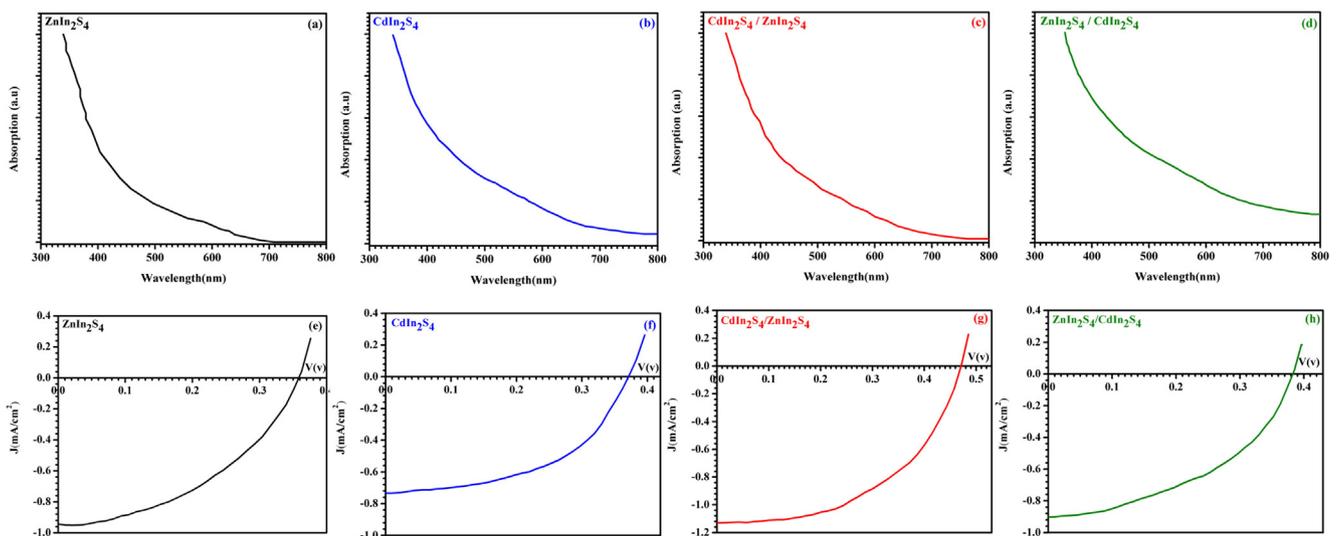


Fig. 3. UV-vis absorption spectra and J-V characterization of solar cell nanostructures (a&e) ZnIn_2S_4 (b&f) CdIn_2S_4 (c&g) $\text{CdIn}_2\text{S}_4/\text{ZnIn}_2\text{S}_4$ (d&h) $\text{ZnIn}_2\text{S}_4/\text{CdIn}_2\text{S}_4$.

Table 1Photovoltaic parameters of the solar cells based on ZIS, CIS and their nanocomposites under AM1.5 illumination of 100 mW/cm².

Sample	V_{oc} (V)	J_{sc} (mA/cm ²)	FF%	$\eta\%$	E_g (eV)
ZIS	0.35	0.94	46	15	2.68
CIS	0.37	0.74	38	10.5	2.48
CIS/ZIS	0.47	1.12	30	15.8	2.53
ZIS/CIS	0.38	0.90	36	12.5	2.30

tact) and glass substrate (electrolyte (I3₋/I₋) for transition of electron between p-type and n-type semiconductors and Pt-ITO as counter electrode are required). In this work, The CIS (or ZIS) films were prepared by doctor's blade method using slurry of 0.05 g of CIS (or ZIS) powders dispersed in 5 mL of ethanol, 0.05 g of ethyl cellulose and 0.05 mL of Triton X-100 on ITO-coated glass substrate. The substrate was kept at 200 °C to eliminate the organic compounds. CdS thin film has been coated on CIS (or ZIS) electrode by CBD method. The bath was heated at 80 °C and then, the sample was submerged. A Pt coated ITO electrode was placed over the CdS/CIS (or ZIS) electrode. The redox electrolyte was consisted of LiI (0.05 M), I₂ (0.05 M), and 4-tert-butylpyridine (0.5 M) in acetonitrile as solvent [3–4]. The current density–voltage (J–V) curve was used to estimate short-circuit current, open-circuit voltage, and fill factor (FF) of this cell (Fig 3(e)–(h)).

J–V characterization was carried out under the illumination of AM1.5 (100 mW/cm²). The photovoltaic parameters of the solar cells were summarized in Table 1. It shows that solar cells based on CIS/ZIS nanocomposite indicate power conversion efficiency (η) of 15.8%, which is higher than cells based on pure ZIS nanoparticle ($\eta = 15\%$). Similar results were obtained for solar cell based on ZIS/CIS nanocomposites that have higher power conversion efficiency than cells based on pure CIS nanoparticles. The relative high efficiency is ascribed to the uniformly surrounding of ZIS around CIS and vice versa nanoparticles, which effectively controlled the surface for the photo generated electrons. The results are in good agreement with the band gap measurements.

4. Conclusion

In Summary, we have synthesized a novel ZIS, CIS and their nanocomposites via a simple chemical Polyol method for enhanced solar cell applications. Results show that pure CIS and ZIS reach a maximum photoconversion efficiency of 10.5% and 15%, respectively. After incorporation of Zn and Cd to the reaction process to prepare the nanocomposites features, the photovoltaic properties of ZIS/CIS and CIS/ZIS nanocomposites enhance in comparison to the pure ZIS and CIS nanoparticles.

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