



# Colloidal synthesis of wurtzite CuInS<sub>2</sub> nanocrystals and their photovoltaic application



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## ABSTRACT

Ternary wurtzite CuInS<sub>2</sub> nanocrystals were successfully synthesized and characterized by X-ray powder diffraction, energy dispersive X-ray spectrometry, transmission electron microscopy and UV–vis spectrometry. In this paper, the solar cell is fabricated by as-synthesized wurtzite CuInS<sub>2</sub> nanocrystals as absorber layer. The *J*–*V* property of the CdS/CuInS<sub>2</sub> solar cell shows that the open-circuit voltage is 0.409 V and the short-circuit current is 0.5 mA/cm<sup>2</sup> under 1.5 G illumination. All of *J*–*V* result displays that as-synthesized CuInS<sub>2</sub> nanocrystals can be directly applied in thin film solar cells.

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## 1. Introduction

The group I–III–VI<sub>2</sub> (CuInS<sub>2</sub>, CuInSe<sub>2</sub>, CuIn<sub>x</sub>Ga<sub>1-x</sub>(S,Se)<sub>2</sub>, (CIGSSe)) semiconductor materials which possess excellent optical properties with direct band gap in the range of 1–1.5 eV and high absorption coefficient of 10<sup>4</sup>–10<sup>5</sup> cm<sup>-1</sup> have attracted a lot of attention because of their wide range of applications, such as, electronic devices-solar cells [1–4], light emitting diode [5–9], photocatalysis [10–12], and bio-label [13,14]. Recently, with the increasingly environmental pollution and intensified energy crisis, solar cells based on I–III–VI<sub>2</sub> semiconductor materials have received more and more attention [15–21]. The best power conversion efficiency of CIGS solar cells by vacuum deposited approach has exceeded 20% [22]. However, high-cost of vacuum deposited approach has greatly limited the commercial utilization of CIGS solar cells, it is urgent to seek a low-cost method to fabricate solar cells. Recently, the solution process to fabricate thin film solar cells has become an active research area due to its scalable utilization and low-cost. CuInS<sub>2</sub> semiconductor nanocrystals, which are one of the promising candidates in chalcopyrite family, have been investigated a lot as absorber layer material for thin film solar cells and quantum-dot sensitized solar cells. As-synthesized CuInS<sub>2</sub> chalcopyrite colloidal nanocrystals have been directly applied to fabricate Mo/CISSe/CdS/i-ZnO/ITO/Al thin film solar cells, and the power conversion efficiency is achieved 5.1% [23].

Meanwhile, CuInS<sub>2</sub> quantum dots have been successfully synthesized and applied to sensitize mesoscopic TiO<sub>2</sub> film and 3.91% power conversion efficiency have been achieved [24]. In recent years, 1.14% power conversion efficiency of solar cells fabricated by aqueous CuInS<sub>2</sub> quantum dots have also been reported [25].

The first report about synthesis of wurtzite structure CuInS<sub>2</sub> nanoparticles was published by Pan et al., who used copper and indium diethyl dithiocarbamate in octadecene (ODE), with oleylamine (OLAM) as activated agent and 1-dodecanethiol (1-DDT) as capping ligand, to obtain CuInS<sub>2</sub> wurtzite structure nanoparticles [26]. Brutchey's group [27], Omata's group [28], Vittal's group [29], Huang's group [30] and Waclawik's group [31] have also synthesized CuInS<sub>2</sub> particles with wurtzite structure via various raw materials and under different experimental conditions. Herein, a hot-injection route was presented to synthesize wurtzite CuInS<sub>2</sub> nanocrystals by using oleylamine as capping agents. In the synthesis of CuInS<sub>2</sub> nanoparticles with wurtzite structure, our work is similar with previously reported work. The most important point of our work is that the first experimental evidence of the solar cells with wurtzite structure CuInS<sub>2</sub> nanocrystals as absorber layer was presented. In the wurtzite structure, CuInS<sub>2</sub> have a random distribution in the unit cells, which is very different from the chalcopyrite and kesterite structure CuInS<sub>2</sub>. The photovoltaic performance of wurtzite structure CuInS<sub>2</sub> nanocrystals is still not studied so far. After post treatment in the mixed solution of hexylamine, 3-mercaptopropionic and chloroform, solar cells based on CIS nanocrystals as absorber layer were fabricated and *J*–*V* curve was tested. The performance of solar cell fabricated via as-synthesized wurtzite CuInS<sub>2</sub> nanocrystals displays that wurtzite CuInS<sub>2</sub> nanocrystals could be directly applied in the thin film solar cells.

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## 2. Results and discussion

Fig. 1 shows the XRD patterns of as-synthesized CIS nanocrystals. As shown in the patterns, the experimental pattern matches well with the simulated one, and the major diffraction peaks exhibited at  $2\theta=26.6^\circ$ ,  $27.66^\circ$ ,  $29.81^\circ$ ,  $38.66^\circ$ ,  $46.45^\circ$ ,  $50.27^\circ$ ,  $54.85^\circ$  can be indexed to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) planes of the wurtzite crystal structure. In the wurtzite CIS crystal structure, sulfur anions occupy the frame of crystal cell;  $\text{Cu}^+$ ,  $\text{In}^{3+}$  cations are randomly occupied a half of interstices of the sulfur anions and each occupation is 50%. During the reaction, oleylamine, as capping agents and solvent, can play a significant role to balance the reactivity of metal cations, therefore  $\text{Cu}^+$  and  $\text{In}^{3+}$  are statistically distributed and the whole symmetry is still the same in the wurtzite CIS crystal cell. Sulfur source is also very important to synthesize wurtzite structure nanocrystals. The sulfur source with different reactivity can form different structure semiconductor nanocrystals. Herein carbon disulfide with high reactivity is inclined to synthesize metastable wurtzite CIS semiconductor nanocrystals at relatively low temperature.

It is well known that the chemical composition can improve optical property and further influence the overall performance of optoelectronic device, therefore energy dispersive X-ray spectrometry (EDS) is used to analyze elemental composition of CIS. The random ten points were chosen to analyze elemental composition. The result discloses that stoichiometry of CIS is 22.94%:25.17%:51.89% (Fig. S1), generally corresponding to the ratio of 0.9:1:2 of the CIS nanocrystals, which is an ideal stoichiometry composition for CIS nanocrystals that can be applied in the field of thin film solar cells.

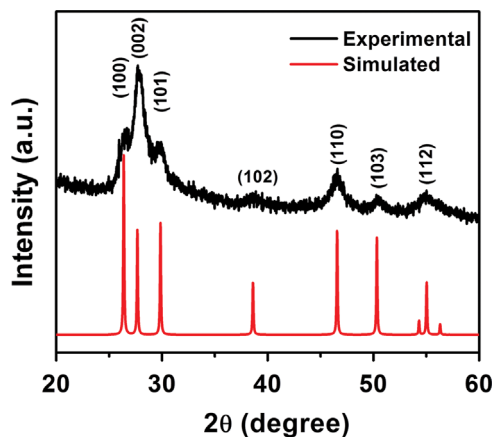


Fig. 1. XRD patterns of CIS nanocrystals with wurtzite structure.

In order to evaluate optical property of CIS nanocrystals, UV–vis spectra, as one of the most effective methods, is employed. Fig. 2(a) shows the UV–vis spectra of CIS nanocrystals. The onset absorption of the spectra is approximately 833 nm, corresponding to the calculated bandgap of 1.49 eV, which is closed to 1.5 eV of bulk CIS, matching well with the AM 1.5 G solar spectrum.

Fig. 3 displays the electronic valence of oleylamine capped CIS nanocrystals was probed by the X-ray photoelectron spectroscopy (XPS). The Cu 2p splits into two peaks, 2p<sub>3/2</sub> (932 eV) and 2p<sub>1/2</sub> (951.9 eV). The observed peak separation (19.9 eV) agrees well with the reported literature of CIS nanocrystals [26], indicating that valence state of Cu in the CIS nanocrystals is +1. Two peaks located at 444.5 eV and 452.1 eV suggest the valence state of In is consistent with +3. Two peaks located at 161.8 eV and 163 eV, respectively, are assigned to S 2p with a valence of –2.

Fig. 4 shows transmission electron microscopy (TEM) images for CIS nanocrystals. As can be seen in the image, the average size of the CIS nanocrystals is about 7 nm. CIS nanocrystals display good solubility in common solvents, such as: toluene, hexane, chloroform, which paves the way for nanocrystals to fabricate photovoltaic devices through spin-casting or printing method.

The  $J$ – $V$  curve of the CIS solar cells is shown in Fig. 5(a). The as-fabricated solar cell has 0.409 V open-circuit voltage ( $V_{oc}$ ) and 0.5 mA/cm<sup>2</sup> short-circuit current ( $J_{sc}$ ). The  $V_{oc}$  can be compared to previously reported CIS solar cells [26]; however, the  $J_{sc}$  and overall performance of the solar cell are relatively poor. The reason for low short current can be attributed to the process of annealed CIS nanocrystals to remove ligands, and carbon residues were generated and became the recombination center of the electron–hole pair, therefore electron–hole pair cannot be effectively separated on the interface between absorber layer (CIS layer) and buffer layer (CdS). Small size of CIS nanocrystals is another reason for the poor performance of solar cell because the charge separation property depends greatly on the size in the absorber layer. The power conversion efficiency can be greatly improved by using molybdenum as substrate and selenization or sulfurization of absorber layer in order to enlarge the particle size of CIS to reduce the recombination center of electron–hole pair, and then improve the property of charge separation.

## 3. Conclusions

Ternary wurtzite structure  $\text{CuInS}_2$  nanocrystals have been successfully synthesized via a hot injection way by selecting appropriate capping ligands and sulfur source. Photovoltaic devices are fabricated by using as-synthesized  $\text{CuInS}_2$  nanocrystals as absorber layer, and  $J$ – $V$  curve shows that the  $J_{sc}$  is 0.5 mA/cm<sup>2</sup>

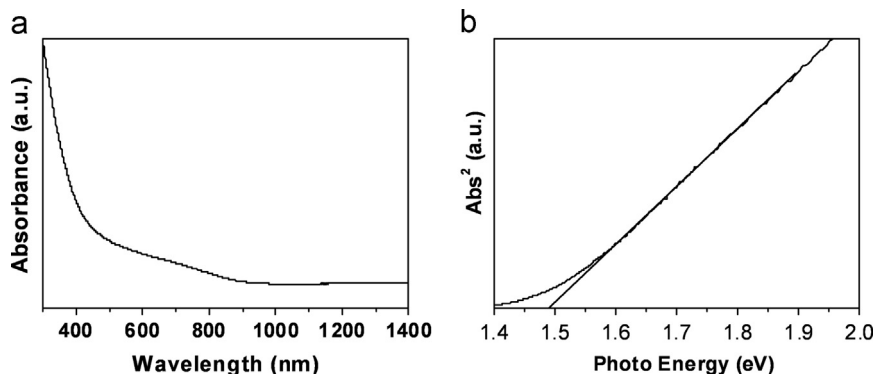


Fig. 2. (a) UV–vis–NIR absorption spectra of CIS nanocrystals in toluene; (b)  $\text{abs}^2$  vs eV for the CIS nanocrystals.

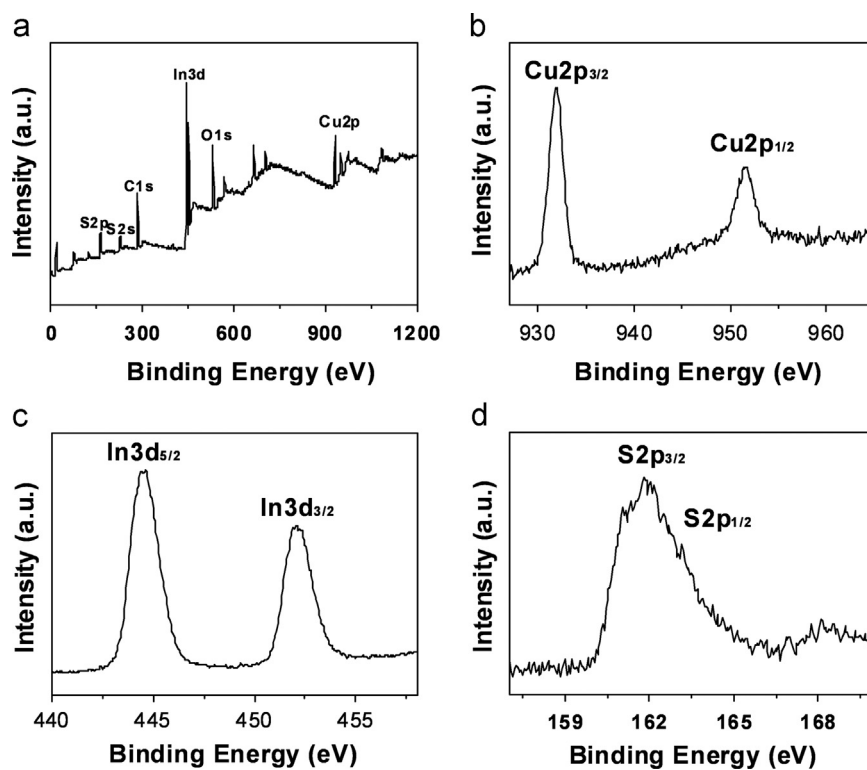


Fig. 3. (a) X-ray photoelectron spectroscopy of CIS nanocrystals; (b) Cu2p; (c) In3d; (d) S2p.

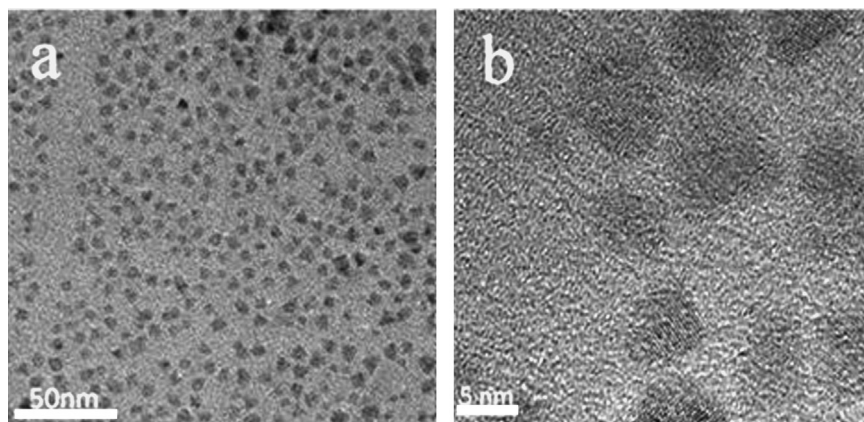


Fig. 4. TEM image of as-synthesized CIS nanocrystals, (a) low resolution; (b) high resolution.

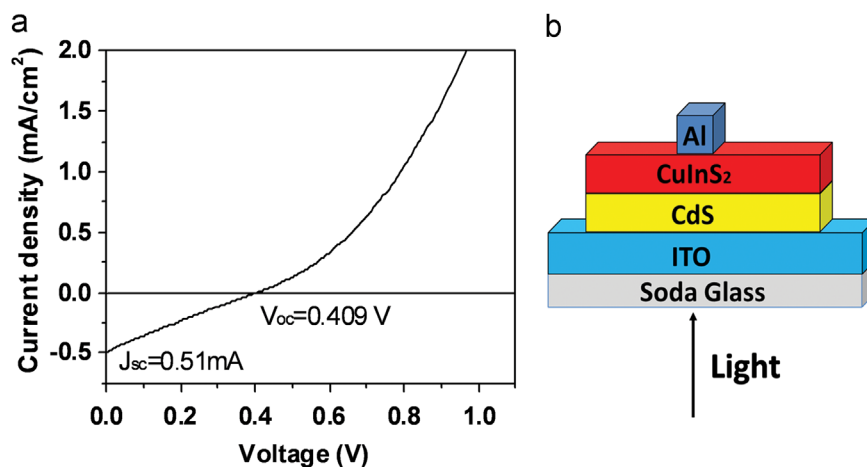


Fig. 5. (a)  $J$ - $V$  property of the CdS/CuInS<sub>2</sub> solar cells with as-synthesized wurtzite CuInS<sub>2</sub> nanocrystals; (b) the device structure of as-fabricated solar cells.

and the  $V_{oc}$  is 0.409 V, respectively. The as-synthesized wurtzite structure  $CuInS_2$  nanocrystals offer a new material to fabricate solar cells.

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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.2015.02.015>.

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