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Letter

Facile solvothermal way to synthesize $CuIn_{0.7}Ga_{0.3}S_2$ nanocrystals and their application in low-cost photovoltaic device

Keywords:
CIGS
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ABSTRACT

Facile solvothermal way to synthesize quaternary $CuIn_{0.7}Ga_{0.3}S_2$ (CIGS) semiconductor nanocrystals has been reported here. X-ray powder diffraction, energy dispersive X-ray spectrometry, transmission electron microscopy, X-Ray photoelectron spectroscopy and UV–Vis spectrometry were used to characterize CIGS nanocrystals. As-synthesized CIGS nanocrystals ink was used to prepare absorber layer. After selenization and device fabrication, the CIGS solar cells exhibited 0.36% power conversion efficiency under 1.5 AM illumination.

1. Introduction

With the increasing demand of energy, renewable energy has attracted considerable attention because they are promising candidates to substitute traditional energy, such as fossil, gas and coal fuels. Solar energy, as a kind of clean energy, has received tremendous attraction in the last decade. Photovoltaic devices are the excellent option in the solar energy field due to their direct conversion of light into electricity without pollution. Thin film solar cells such as: dye-sensitized solar cells [1–5], organic solar cells [6–9], inorganic solar cells [10–12] have gained a large amount of interests of researchers. Because of the advantages of long-term stability and relatively low price, inorganic solar cells are viewed as the best candidate for commercial application.

Among the inorganic solar cells, $CuIn_xGa_{1-x}S_2$ (CIGS) thin film solar cells possess many advantages compared to crystalline silicon and CdTe, such as direct band gap, high absorption coefficient of ~10^4–10^5 cm^{-1}, and non-toxic elements contained. The power conversion efficiency of CIGS has already exceeded 20% [13] and module production with average power conversion efficiency is greater than 10% [14,15], which is an exciting thing for the CIGS solar cells to be industrialized in the future. During process of photovoltaic devices fabrication, the utilization of solution-process semiconductor nanocrystal ink is an effective way, such as: doctor-blade [16], spin-casting [17], which use low-cost manufacturing equipment in order to reduce the fabrication cost of solar cells with high power conversion efficiency.

However, chemical synthesis of colloidal semiconductor nanocrystals is often employed Schlenk line under inert gas atmosphere, which is a complex operated procedure. Another disadvantage of this synthetic approach is that long chain capping agents, such as oleylamine and oleic acid, are often employed to synthesize CIGS nanocrystals. The charge transfer and separation property of as-synthesized semiconductor nanocrystals were greatly affected by these long chain capping agents. Therefore, it is urgent to find an effective way to synthesize high quality CIGS nanocrystals as absorber layer in the solar cells. Herein, a facile solvothermal way was adopted to synthesize CIGS nanocrystals under mild experimental condition. Short chain molecule-hexanamine was used as solvent and capping agent. Carbon disulfide was acted as sulfur source, and the solvothermal reaction was carried out at 180 °C for 2 h. In:Ga ratio of final product is 7:3, which is the optimal ratio for the CIGS thin film solar cells.

2. Experimental procedures

2.1. Materials

Copper monochloride (CuCl, AR), indium trichloride ($InCl_3$, AR), Gallium nitrate hydrate ($Ga(NO_3)_3 \cdot xH_2O$, AR), carbon disulfide (CS_2, AR), hexanamine ($CH_3(CH_2)_5NH_2$, 99%) were purchased from Aladdin.

2.2. Synthesis of $CuIn_{0.7}Ga_{0.3}S_2$ nanocrystals

1 mmol CuCl, 0.7 mmol $InCl_3$, 0.3 mmol $Ga(NO_3)_3 \cdot xH_2O$ were ultrasonic dissolve in 8 mL hexananime in 50 mL conical flask. 12 mL hexanamine was loaded into another 50 mL conical flask, then 1 mL carbon disulfide was slowly added into the conical flask. The former solution was slowly added into the later solution and the color of the solution changed into light yellow finally. Herein, hexanamine was used as capping agent and it took time to cap the metal precursor. Therefore, the precursor solution should be continuously vigorous stirring for one night. Then, the as-prepared solution was transferred into 30 mL Teflon-lined stainless steel autoclave and solvothermal reacted at 180 °C for 2 h. The autoclave was

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naturally cooled to room temperature. The nanocrystals were isolated by precipitation with 40 mL methanol followed by centrifugation at 4000 rpm for 5 min. The purified nanocrystals were re-dispersed in chloroform for TEM and XRD measurement without size selection.

2.3. Characterization

The powder XRD patterns were recorded using a Bruker D8 X-ray diffractometer. Energy Disperse Spectroscopy (EDS) spectra were obtained by using a scanning electron microscope (Hitachi S-4800) equipped with a Bruker AXS XFlash detector 4010. X-ray phototelectron spectra (XPS) were measured with VG ESCALAB MK (VK Company, UK) at room temperature by using a Mg Kα X-ray source ($hV = 1253.6$ eV) at 14 KV and 20 mA. Low resolution and high resolution TEM (LR-TEM and HR-TEM) images and selected area electron diffraction (SAED) were taken on a FEI Tecnai G2 F20 electron microscope with an accelerating voltage of 100 kV and 200 kV. UV–Vis–NIR absorption spectrum was measured by Shimadzu UV-3600.

2.4. Device fabrication

The Mo coated soda lime glass substrates were prepared by DC magnetron sputtering resulting in a 1 μm layer. 1 mmol CIGS nanocrystals were dispersed in 2 mL chloroform and stored in the glovebox. The 200 μL nanocystals ink stored in the glovebox was spin-casted onto the Mo coated substrate at 1000 rpm for 30 s each time, the film was then placed on the 400 °C hot ceramic plate for 5–8 min in order to eliminate volatile solvent and capping agent. The above process repeated 8–10 times. And then the above

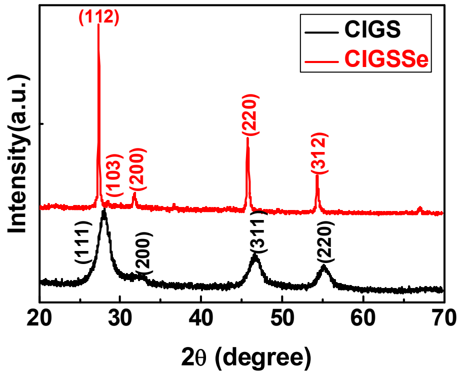

Fig. 1. X-ray diffraction patterns for as-synthesized CIGS nanocrystals (black line) and CIGSSe absorber layer after selenization (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

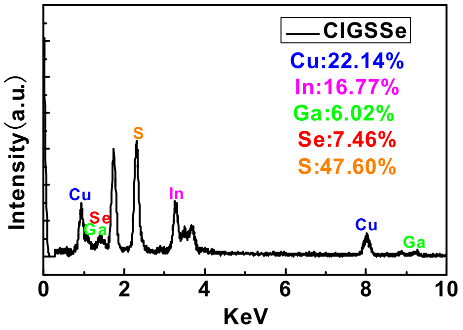

Fig. 2. EDS spectrum and chemical compositions of CIGSSe thin film after selenization.

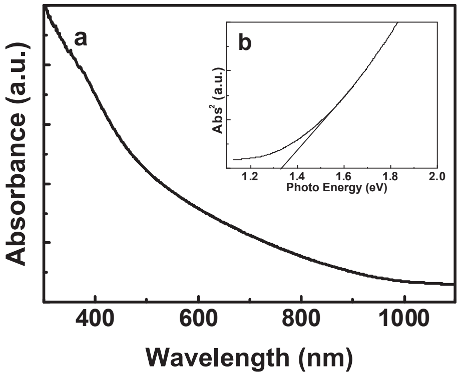

Fig. 3. (a) UV–Vis–NIR absorption spectra of CIGS nanocrystals in chloroform. (b) abs^2 vs ev for the CIGS nanocrystals.

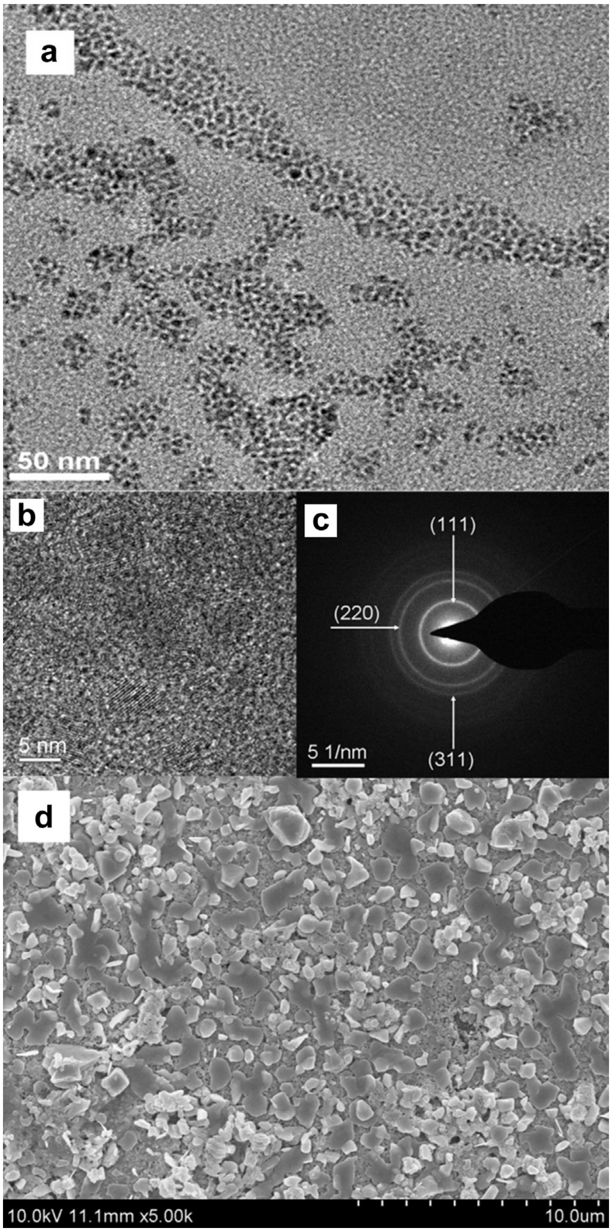

Fig. 4. (a) Low resolution and (b) high resolution TEM image of as-synthesized CIGS nanocryatals, (C) selected area electron diffraction (SAED) of as-synthesized CIGS nanocrystals, (d) SEM image of CIGSSe absorber layer thin film after selenization.