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Colloidal $CuZnSnSe_{4-x}S_x$ nanocrystals for hybrid solar cells

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ABSTRACT

We report the synthesis of different colloidal $CZTSe_{4-x}S_x$ nanocrystals and their performance in [6,6]-phenyl C61 butyric acid methyl ester (PCBM) based organic/inorganic hybrid bulk heterojunction solar cells. Synthesis of colloidal $CuZnSnSe_{4-x}S_x$ were performed and characterized by XRD, TEM, SEM, UV–Visible absorption techniques. Electrochemical and photovoltaic properties were investigated. The best device concept, ITO/PEDOT:PSS/CZTS:PCBM blend (1:10)/Al, showed 280 μA/cm^2 short circuit current, I_{sc} with 300 mV open circuit voltage V_{oc}, and fill factor FF of 0.38.

1. Introduction

In the last decade, $CuZnSnSe_{4-x}S_x$ (Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe)) nanocrystals (NCs) have gained significant attention due to their advantages such as low band gap (1.0–1.5 eV), remarkable consistency of earth abundant elements, high absorption coefficient, extremely low toxicity, and high radiation stability [1,2]. These features make them good candidates for low-cost and highly efficient solar cell fabrication. $CuZnSnSe_{4-x}S_x$ nanocrystals have two types of tetragonal crystal structures, known as stannite and kesterite, due to the different arrangement of Cu and Zn atoms [3,4]. However, thermodynamically stable kesterite structure is dominant and considered to be an alternative material for $Cu(In_{1-x}Ga_x)S_2$ [5]. $CuZnSnSe_{4-x}S_x$, as a p-type semiconductor, have been generally used in electrochemically deposited pn-junction solar cells with an n-type semiconductor such as CdS [6–9]. The dye sensitized solar cells consisting of CZTS films as counter electrode was reported by Xin et al. [10]. Hybrid solar cells (HSC) have a heterojunction consisting of organic and inorganic materials that gives advantages of both [11,12]. Thus, HSCs have a promising potential for thin, flexible, light-weight, and easily producible devices [13]. Saha et al. reported on hybrid pn-junction solar cell based on CZTS/[6,6]-phenyl C61 butyric acid methyl ester (PCBM) fabricated layer by layer deposition and also including ligand exchange process [14].

Since, we could not have been found any report on $CZTSe_{4-x}S_x$:PCBM bulk heterojunction solar cells in the literature. Therefore, the aim of this paper was to investigate the bulk heterojunction solar cell performance of CZTS, CZTSe and $CZTSe_{4-x}S_x$ nanocrystals with PCBM. For this purpose, we synthesized colloidal CZTS, CZTSe and $CZTSe_{4-x}S_x$ nanocrystals to compare their solar cell performance with PCBM.

2. Material and methods

2.1. Materials

Zinc acetate dihydrate ($C_4H_6O_4Zn{\cdot}2H_2O$), Se powder, oleylamine – 70% (OLA), trioctylphospineoxide (90%), ethanol, were supplied from Sigma–Aldrich. Copper (II) acetate monohydrate $(CH_3COO)_2Cu{\cdot}H_2O$ and toluene were purchased from Merck. 2-Prophanol was supplied from VWR. Tin (II) acetate $Sn(OOCCH_3)_2$ and Sulfur powder (99.5%) were purchased from Alfa Aesar. PCBM ([6,6]-phenyl C61 butyric acid methyl ester) was purchased from Sigma–Aldrich. PEDOT:PSS (Clevios PVP AI4083) was supplied from H.C.STARK. ITO substrates were purchased from KINTEC Co.

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2.2. Synthesis of colloidal $CZTSe_{4-x}S_x$ nanoparticles

Synthesis of nanocrystals was carried out according to previously published procedure [15,16] 0.5 mmol Copper (II)acetate, 0.25 mmol Zinc(II)acetate, 0.25 mmol Tin(II)acetate dihydrate, 1 gr TOPO and 20 ml OLA (>70%) are mixed in a 25 ml three-neck flask and heated to 200 °C under N_2 flow. When a reddish-brown solution is observed, 1 ml OLA including 1 mmol sulfur powder is added to reaction flask. Then, the temperature is increased to 280 °C and kept for 30 min by stirring. The reaction mixture is cooled to room temperature. Finally, CZTS nanocrystals are precipitated by adding toluene – 2-propanol (4:1) mixtures and then filtered. CZTS nanocrystals are washed several times with ethanol and left to dry at 70 °C for 2 h.

Selenium and selenium:sulfur mixture (1:1) are used in OLA to synthesize CZTSe and $CZTSe_{4-x}S_x$ nanocrystals, respectively.

2.3. Device fabrication

Indium-tin-oxide (ITO) coated glasses are patterned by a conventional wet-etching process using the mixture of HCl and H_2SO_4. Patterned ITO coated glass substrates are cleaned with water, acetone and iso-propanol in ultrasonic bath for 15 min. Finally ITO glasses are kept in UV/O_3 chamber for 30 min.

ITO glasses are spin casted with PEDOT-PSS (~40 nm) at 2000 rpm. PEDOT:PSS coated glasses are dried at 120 °C for 30 min. Then, CZT(S, Se or SeS):PCBM blends in chlorobenzene are spin casted onto PEDOT:PSS layer at 1500 rpm. 20 mg/ml CZT(S, Se or $Se_{4-x}S_x$) and 20 mg/ml PCBM solutions are prepared in chlorobenzene and used as stock solutions. Mg/Al cathode (30/100 nm) is deposited by thermal evaporation through a shadow mask giving an active area of 0.12 cm^2. All device fabrication and characterization procedures are carried out in glove box under nitrogen atmosphere.

2.4. Instrumentation

X-ray diffraction (XRD) pattern of colloidal nanoparticles was recorded with a Bruker Advance D8 XRD (Cu ∝ source with 1.5406 wavelength), in powder mode. ZeissEvo model scanning electron microscope and JEOL JEM-2100F 200 kV model transmission electron microscope were used to collect microscopic images. Biochrom Libra S22 UV–Vis spectrometer was used to measure absorption spectra of nanocrystal solutions. Cyclic voltammetry measurements were carried out with BAS Epsilone model potentiostat. The electrochemical measurements of NCs were performed in an electrolyte solution consisting of 0.1 M [TBA][PF 6] in MeCN/CHCl 3: 5/1 solvent mixture. Glassy carbon electrode (GCE), platinum wire, and Ag/AgCl were used as working, counter, and reference electrodes, respectively. CZT(S, Se or SeS) nanocrystals are not soluble in electrolyte solution. Therefore, NCs were drop casted onto glassy carbon working electrode to prevent the precipitation in electrolyte solution. Current–voltage (I–V) characteristics of devices were measured with Keithley model 2400 sourcemeter. MBRAUN glove box systems equipped with Leybold PVD, Laurell spin coater and Atlas AM1.5 solar simulator were used for fabrication and characterization of solar cells.

3. Results and discussions

3.1. Structural characterization

XRD patterns of the CZTS, CZTSe and $CZTSe_{4-x}S_x$ nanocrystals are given in Fig. 1a–c. Characteristic peaks for nanocrystals are clearly observed on XRD patterns. Due to their same crystal structure, nanocrystals show similar patterns indicating kesterite crystals. The diffraction peaks are slightly shifted to lower values of 2θ by replacing smaller S (1.84 Å) atoms with larger Se (1.98 Å) atoms. Therefore, the diffraction values of 2θ for $CZTSe_{4-x}S_x$ nanocrystals appear between CZTSe (JCPDS 70-8930) and CZTS (JCPDS 26-0575) values. Scherrer equation is used to calculate the particles size of nanocrystals. The average particle size distribution of nanocrystals are found to be around 14–20 ±1 nm, which is also confirmed by SAXS (see Fig. 2).

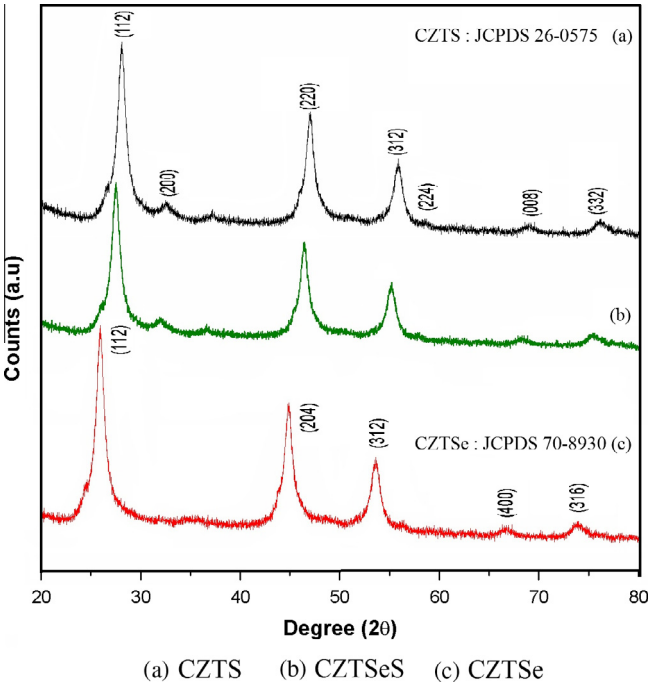

Fig. 1. XRD patterns of CZTS (a) $CZTSe_{4-x}S_x$ (b) CZTSe (c) nanocrystals.

Fig. 3 shows TEM images of CZTS NCs. We have to indicate that we show only TEM image and SAED pattern of CZTS NCs, since similar feature is observed for CZTSe and $CZTSe_{4-x}S_x$ NCs. It is clear from Fig. 3, CZTS nanocrystals are spherical and slightly polydispersed; however, the size of nanocrystals mostly distributed between 15 and 20 nm. The selected area diffraction pattern (SAED) is in agreement with the structure of CZTS (see Fig. 3).

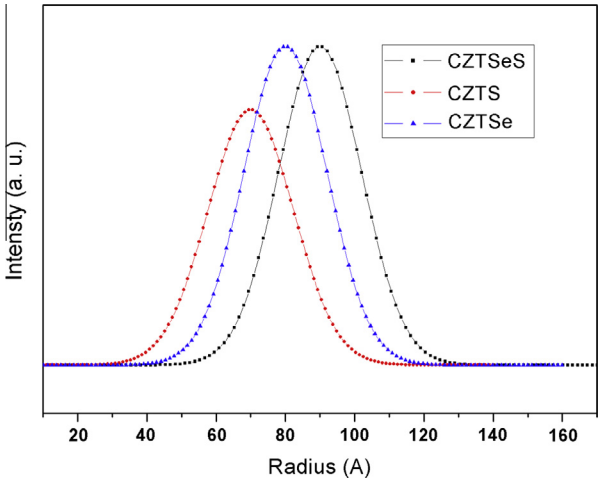

Fig. 2. SAXS results for $CZTSe_{4-x}S_x$ NCs.