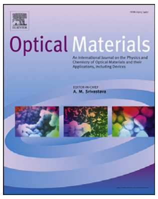
Optical Materials 78 (2018) 132–141

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat



Structural, optical and photovoltaic properties of P3HT and Mn-doped CdS quantum dots based bulk hetrojunction hybrid layers

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ARTICLE INFO

Article history:
Received 22 December 2017
Accepted 6 February 2018

Keywords:
CdS
Band gap tuning
Doping
Mn^{2+}
PL quenching
XPS
Photovoltaic properties

ABSTRACT

Cadmium sulphide (CdS) and Mn-doped CdS nanocrystals were synthesized by co-precipitation method. The nanocrystals were characterized by Fluorescence, Fourier Transformed Infra-red Spectrometer (FTIR), UV–Visible, X-ray diffraction (XRD), X-ray photoelectron spectrometer (XPS), Field Emission Scanning Electron Microscope (FESEM), and High Resolution Transmission Electron Microscope (HRTEM). A considerable blue shift of absorption band with respect to the cadmium sulphide was observed by the Mn concentration (0.5 M) in the doped sample with decreasing the size of nanocrystals. Other reason for this may be Mn doping. Subsequently the band gap was altered from 2.11 to 2.21 eV due to quantum confinement effect. Scanning electron microscope supplemented with EDAX was operated to find grain size and chemical composition of the synthesized nanomaterials. The PL spectrum of Mn-doped CdS nanocrystals displays three PL bands the first one, within the range of 500 nm and the second band at 537 nm, and the third one around 713 nm is labelled red band emission due to attributed to a $^4T_1 \rightarrow {}^6A_1$ transition within the 3d shell of divalent manganese. XRD analysis showed that the material was in cubic crystalline state. A comparative study of surfaces of un-doped and metal doped CdS nanocrystals were investigated using X-ray Photoelectron Spectroscopy (XPS). The synthesized nanomaterial in combination with polymer, poly (3-hexyl thiophene) was operated in the construction of photovoltaic cells. The photovoltaic devices with CdS nanocrystals exhibited power conversion efficiency of 0.34% without annealing and 0.38% with annealing. However, the power conversion efficiency was enhanced by a factor of 0.35 without annealing and 0.42 with annealing with corporation of Mn impurity in CdS lattice. Atomic Force Microscopy was employed for morphology and packing behavior of blend of nanocrystals with organic polymer.

1. Introduction

Nanocrystalline semiconductors have intensified great interest due to their basic scientific research and potential technological applications. In recent years, the optical properties of nanoscale materials have been widely studied [1–4]. Among the nanocrystalline semiconductors, CdS has been studied because of its good photocatalytic activity [5], large non-linear response [6], and optical data storage and optoelectronic devices [7,8]. The synthesis of metal-doped nanomaterials has become a major field of recent studies. Transition metal doped CdS nanoparticles have been considered ideal for use as phosphor material because of its excellent luminescence properties [9]. Mn-doped CdS nanoparticles have been widely investigated because of luminescence of Mn^{2+}ions in CdS lattice. This is due to the fact that good traps have been provided by Mn^{2+} ions for the excited electrons, which have excellent applications in optoelectronic devices, regular and inverted solar cells, and light-emitting diodes [10–13]. It has been investigated that large band gap semiconductors such as ZnS or CdS doped with Mn (<1%) exhibit a bright orange luminescence due to $^4T_1 \rightarrow {}^6A_1$ transition of the Mn^{2+} 3d electron shell configurations.

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https://doi.org/10.1016/j.optmat.2018.02.019
0925-3467/

In contrast, small band gap nanomaterials such as CdTe or HgTe doped with high Mn content (>1%) reveal interesting magnetoptical properties such as giant Faraday rotations [14]. Nag et al. [15] used chemical method for the preparation of Mn^{2+} doped CdS crystals. They used capping agent, 1-thioglycerol and the reaction mixture was stirred at high temperature in the 45–130 °C for 12 h to obtained Mn-doped CdS nanocrystals of average diameter of 1.8 nm.

Recently various efforts has been done to enhance the cell conversion efficiency by changing intrinsic property of nanocrystals by doping [16,17]. By doping of transition metal ions, for example, Mn^{2+} modify the electronic and photophysical properties of nanocrystals [18–22]. The impurity in host generates electronic states in the mid gap hence changing the charge separation and recombination dynamics. In hybrid solar cell, organic polymer acts as electron donor and the inorganic nanocrystals as an electron acceptor. In addition, organic polymer, regioregular poly 3-hexylthiophne (P3HT) is one of the most favorable polymer due to its good electrical conductivity and environmental stability [23,24].

In past years, several groups widely studies high electron affinity inorganic semiconductors including ZnO nanoparticles [25], TiO_2 nanoparticles [26], CdSe nanorods [27] and tetrapods [28] and CdTe nanorods [29] for hybrid bulk heterojunction polymer solar cells. However, there are very few reports on using CdS as an acceptor in nanoparticle-conjugated polymer composite photovoltaic devices due to the large band gap (2.42 eV) that absorbs light in the range from 300 to 512 nm and mismatches with the solar radiation (300–1500 nm) [30]. In addition, Kang et al. [31] constructed a hybrid solar cell with MEH-PPV and vertically aligned CdS nanorods with length of 30 nm and a diameter of 200 nm and achieved an efficiency of 0.60%. Furthermore, the maximum cell conversion efficiency for MEH-PPV/multiarmed CdS hybrid solar cell was investigated by wang et al. [30]. They constructed photovoltaic devices with MEH-PPV and multiarmed CdS nanorods in pyrimidine solvent and achieved an efficiency of 1.17% under AM1.5 illumination (100 mW cm^{-2}).

Though, CdS semiconductor nanoparticles has excellent electron mobility. So we believe there is a much room for further improvement in device efficiency for hybrid CdS/polymer photovoltaic solar cells. So, we investigate the synthesis, characterization and photovoltaic properties of CdS and metal-doped CdS nanocrystals having 0.5 M manganese impurity.

2. Experimental

2.1. Chemicals

Cadmium acetate (Cd $(CH_3COO)_2{\bullet}2H_2O$), sodium sulfide nanohydrate ($Na_2S{\cdot}9H_2O$) and manganese acetate (Mn $(CH_3COO)_2{\bullet}4H_2O$) were purchased from Sigma Aldrich. Deionized water and ethanol (Sigma Aldrich) were used for the synthesis of un-doped and doped nanocrystals. Regio-regular Poly (3-hexylthiophene), P3HT was purchased from Sigma Aldrich too. All the chemicals were used without any purification.

2.2. Synthesis of CdS nanocrystals

Wet chemical method was employed for the synthesis of CdS nanocrystals. The synthesis procedure was performed in deionized water-ethanol matrix. In a typical procedure, 1 M of cadmium acetate was dissolved in 50 ml of deionized water-ethanol matrix. Next, 50 ml of 1 M solution of $Na_2S{\cdot}9H_2O$ was prepared in same solvent and added drop wise to the cadmium acetate solution at 80 °C under constant magnetic stirring in order to obtained a homogenous solution. Then, the homogenous solution was cooled to room temperature. A bright yellow precipitate was appeared after 40 min. The precipitate was washed with deionized water and ethanol several times in order to remove impurities. Lastly, it was dried in oven for 2 h at 120 °C and performed morphological and optical characterization.

2.3. Synthesis of Mn-doped CdS nanoparticles

For the synthesis of Mn-doped CdS nanocrystals, 1 M of Cd $(CH_3COO)_2{\bullet}2H_2O$ was dissolved in 50 ml of deionized water and ethanol matrix. Next, an equimolar solution of sodium sulfide nanohydrate prepared in the same solvent. Afterward, 0.5 M of manganese acetate tetra hydrate was dissolved in 50 ml of deionized water and ethanol matrix. Manganese acetate solution and cadmium acetate solution were mixed with each other and stirred for 15 min. Subsequently, 1 M solution of sodium sulfide nanohydrate was slowly added to the mixture of manganese acetate and cadmium acetate solution. After addition of sodium sulphide solution, the mixture was continuously stirred at 80 °C for 40 min. Finally, the precipitate was washed many times with deionized water and ethanol. Then, the Mn doped CdS nanocrystals were dried in oven 2 h at 120 °C and exposed to different characterization techniques.

2.4. Device fabrication

The patterned ITO substrates were washed repeatedly with detergent powder, distilled water, acetone and isopropyl alcohol in an ultrasonic bath for 15 min each and dried with air. Next, the ITO substrates were baked at approximately 80 °C for 10 min. Furthermore, the dried ITO substrates were undergo the process of plasma cleaning for 20 min. Next, ZnO gel was spin-coated by using spin coater at a rate of 3500 rpm for 20 s. The ITO substrates coated with ZnO gel were heated on hot plate at 120 °C for 4 min under ambient condition. After heating, a uniform layer of ZnO was deposited having thickness of approximately 30 nm. The blend solutions of polymer, P3HT and nanocrystals (CdS and Mn-doped CdS) were made in dichlorobenzene in 1:1 ratio by weight and stirred for 28 h at 60 °C. This solution is called active layer solution. The active layer solution was filtered using poly (tetrafluoroethylene) (PTFE) filter having pore size of 0.45 μm. Then, the active layer was deposited by spin-coating at a rate of 1000 rpm and undergo process of annealing for 15 min at 100 °C. Sloan Dektak II profilometer was used to measure the thickness of active layer which was in the range from 150 to 170 nm. Lastly, physical vapour deposition system (PVD) was used for deposition of 6 nm of MoO_3 and 80 nm of Ag on all the devices under high vacuum at a pressure of 1×10^{-6} mBar. The top and bottom electrodes of the devices were cleaned with chloroform in order to make contacts. It was found that 0.06 cm^2 was the active area of device. The device assembly and energy placement is shown in Fig. 1.

2.5. Characterization

Hewlett-Packard 8453 spectrometer or an Olid® HP8452 Diode Array Spectrometer was used to find absorbance of nanocrystals. Luminescence was determined with a USB2000-Ocean Optics spectrometer. Xpert Pro Philips powder X-ray diffractometer was used to check phase purity and crystalline nature of un-doped and doped nanocrystals. Field emission gun scanning electron microscope (FEI Quanta 650 FEG) supplemented with EDAX (Bruker XFlash detector 1.9) was operated for knowing the size, morphology, composition of nanomaterials. FTIR spectra were achieved with a Nicolet 6700 in the ATR mode. The morphology of