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Quantum dot cosensitized solar cell based on PMOT@CdSe@ZnO core shell nanostructures with dual emission

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ABSTRACT

Quantum dot sensitized solar cell based on poly(3-methoxythiophene) (PMOT)@CdSe@ZnO core shell nanostructure were synthesized where PMOT serves as hole transport material, CdSe acts as a photosensitizer which enhances visible range absorption and also helps in injection of electrons from PMOT to ZnO where ZnO provides channel for efficient electron transport. The properties of the device were assessed with and without CdSe quantum dots and effect of annealing was also observed on the device. After the addition of CdSe QDs, the visible light absorption of PMOT@ZnO was enhanced due to increase in surface area. PMOT@CdSe@ZnO exhibited dual emission, where CdSe and ZnO exhibited visible and UV emission respectively. The interface formed between PMOT and CdSe improves the charge separation. The better photovoltaic measurement of PMOT@CdSe@ZnO over CdSe@ZnO indicates that PMOT efficiently dissociate excitons at interface and suppress the interfacial charge recombination. A power conversion efficiency of 0.989% was attained for the device PMOT@CdSe@ZnO with V_{oc}=0.56 V and J_{sc}=2.5 mA/cm^2. Upon annealing, the efficiency of the device was enhanced to 1.1609% with V_{oc}=0.58, J_{sc}=3.2 mA/cm^2.

1. Introduction

Quantum dot sensitized solar cell (QDSSCs) have attracted considerable attention as an alternative to DSSCs because of quantum dot sensitizers as they can adsorb on the surface of semiconductor with their tunable band gaps and their ability to generate multiple charge carriers with single photon [1–3]. Like dyes, these quantum dot sensitizers generate excitons and transport electrons to the counter electrodes through electrolytes using redox reactions. It also reduces the dark current and increases the open circuit voltage and thus increases the overall efficiency of the cell [4,5]. Cadmium chalcogenide (CdX=Se, Te, and S) attributed to their strong photoluminescence are used as photosensitizers [6,7]. However, these QDSSCs face many challenges because of liquid electrolyte which causes photo corrosion and limits the open circuit voltage. Recently, p-type conjugated polymers, molten salts, are receiving attention of many researchers as an alternative to liquid electrolytes [8,9].

Many papers have been reported about solar cells based on poly (3-hexyl thiophene) (P3HT) and other materials using organic and inorganic modifiers. For instance, Yan Zhang Hao et al. reported an electrochemical route to prepare semiconductor sensitized solar cell based on P3HT@CdSe@ZnO and reported an increase of 104% and 69% in conversion efficiency compared to solar cell based on N719 coated ZnO nanorods. Yan Zhang Hao also reported an enhancement in power conversion efficiency by electrodeposited P3HT layer onto the surfaces of 1D CdS@TiO_2. Jingyang Wang et al. introduced CdSe as an interlayer in P3HT/TiO_2 nanorod arrays hybrid solar cells. The role of CdSe QDs was to enhance light absorption and assisting charge separation at the P3HT/TiO_2 interface. Polymer (P3HT or PMOT) behaves as electron donor and CdSe due to its high mobility and electron affinity acts as an electron acceptor. In addition to CdSe, coating of wide band gap semiconductor oxides such as ZnO, TiO_2 on quantum dots which also accepts and transports electron through its conduction band and avoid the light loss within the polymer layer thus increase the overall efficiency of the device are receiving great deal of attention within scientific community [10–12]. These QDSSCs based on three component core shell structure serve many advantages such as (i) direct charge transport (ii) efficient and controllable charge separation (iii) providing nanometer size hetero-interface at CdSe and ZnO which increase the open circuit voltage and short current density [13–15]. These heterostructures utilize the advantages of good visible light absorbers and their ability to generate multiple charge carriers with single photon.

However, there were many literature reported about the solar cell based in hybrid of poly(3-hexyl thiophene). On the other hand, only a few papers were reported about the solar cell based on poly

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(3-methoxy thiophene). The electronic and optical properties of such polymers can be controlled using monomers that have functional groups present into the structure which contribute to the properties of polymer chain. Poly(3-methoxy thiophene) (PMOT) is receiving enormous attention due to the presence of oxygen in alkoxy group, which acts as an electron donor substituent which decreases the oxidation potential of monomer and polymer [16]. Building from these ideas, we have developed hybrid solar cell based on PMOT@CdSe@ZnO. We have proposed a hybrid system comprising a transport layer of conjugated polymer poly (3-methoxy thiophene) (PMOT), CdSe sensitizer, and wide gap ZnO nanocrystals. Encapsulation of PMOT in the nanocomposites not only seal CdSe quantum dots but also allow the quantum dots to give a better fluorescence by allowing small molecules and ions to contact with these CdSe molecules. CdSe@ZnO nanostructures will exhibit dual emission (UV emission band contributed by ZnO nanocrystals and visible emission is attributed by CdSe quantum dots) which can be tuned by varying the concentration of quantum dots [17]. PMOT@CdSe@ZnO enhanced the visible light absorption and lowers the potential loss. It also facilitates the exciton dissociation which can results in higher fill factor and improved efficiency. This energetic arrangement helps in quick transportation of electrons from PMOT shell to CdSe and then to ZnO core. CdSe quantum dots also serve as photo sensitizers and also help in injection of electrons from PMOT to ZnO. The solar cell based on PMOT@CdSe@ZnO has achieved an energy conversion of 0.989% under 100 mW/cm^2 AM 1.5 radiance. This quantum dot based sensitized solar cell has considerable potential for next generation solar cell.

2. Experimental details

Monomer (3-methoxy thiophene, 99%), tri octyl phosphine oxide (TOPO, 99%), cadmium oxide (CdO, 99.9%), selenium (99.5%), and trioctyl phosphine (TOP, 98%) were purchased from Sigma Aldrich. Thio-di-propionic acid (TDPA, 98%) was purchased from Alfa Aesar. Zinc acetate dihydrate ($Zn(ac)_2 \cdot 2H_2O$, sodium hydroxide, and ferric chloride ($FeCl_3$, 97%) were purchased from CDH Pvt. Ltd. All the reagents were used as received. All the solvents used in synthesis and purification were supplied by Merck and freshly distilled prior to use.

2.1. Synthesis of ZnO nanocrystals

ZnO nanocrystals were synthesized according to literature with little modification [18]. Zinc acetate dihydrate was dissolved in methanol at room temperature. After complete dissolution of zinc acetate dihydrate, NaOH also dissolved in methanol was added to the above reaction mixture with vigorous stirring. White colloids were formed which indicated the formation of ZnO nanoparticles. The obtained nanoparticles were collected by centrifugation and after that it was dispersed in methanol by sonication and subsequent centrifugation was done. The white colloidal gel was dried under vaccum for 6 h at 40 °C.

2.2. Synthesis of CdSe@ZnO nanocomposites

CdSe quantum dots were prepared via chemical route. A mixture of Cadmium oxide, thio dipropionic acid, tri octyl phosphine oxide and zinc oxide synthesized above were heated at 215 °C under inert atmosphere for 20 min. The temperature of the reaction mixture was maintained at 185 °C, after that the mixture of Se powder and tri-octyl phosphine (TOP) was added to the reaction mixture and reaction was allowed to stir overnight under inert atmosphere. To remove the unreacted precursors and other impurities, product was washed thrice with methanol.

2.3. Synthesis of PMOT@CdSe@ZnO core shell nanostructures

PMOT@CdSe@ZnO core shell nanocomposite was prepared through insitu chemical oxidative polymerization by encapsulation of PMOT shell on CdSe@ZnO. In this process, 3-methoxy thiophene in 45 mL chloroform was injected in a 100 mL conical flask and the solution was stirred for 20 min. After that, CdSe@ZnO nanocrystals synthesized above were ultrasonically dispersed in the above reaction. After complete dispersion, suspension of $FeCl_3$ in $CHCl_3$ was added dropwise to the reaction mixture and the reaction mixture was continued to stir for 12 h under N_2 atmosphere at −40 °C [19]. The resulting composite consists of PMOT shell, CdSe quantum dots and ZnO nanoparticles. The product obtained was added to methanol and the precipitates were filtered and subjected to soxhlet extraction with methanol for 10 h. To understand the role of CdSe as photosensitizer and its effect on the optical and photovoltaic properties of the device, we have also synthesized PMOT@ZnO nanocomposites by same procedure as discussed above. The final product was dried under vaccum at room temperature. Films of the PMOT@ZnO, CdSe@ZnO and PMOT@CdSe@ZnO core shell nanostructures were prepared on the conducting substrate by spin coating method at 3000 rpm.

ITO substrate was ultrasonically cleaned with isopropyl alcohol (IPA). PMOT@ZnO, CdSe@ZnO and PMOT@CdSe@ZnO was dissolved in dichlorobenzene and spin coated on the ITO. After that, the film of PMOT@CdSe@ZnO were dried and annealed at 100 °C, 150 °C, 200 °C, 250 °C, and 300 °C under inert atmosphere.

2.4. Characterization

UV–visible absorption spectra were measured using Hitachi U-3010 spectrophotometer. The photoluminescence emission spectra were measured by Hitachi F-7000 spectrophotometer at room temperature. Current voltage measurements were taken in air at room temperature (298 K) using a Keithley 236 high current source power meter under white light illumination from a 500 W Xenon lamp. The light intensity was 100 mW/cm^2 on the surface of sample measured by a photodetector. The short circuit current (J_{sc}) and open circuit current (V_{oc}) were recorded as a function of illumination time to measure decay. Incident monochromatic photoelectron conversion efficiency (IPCE) was recorded by using Keithley 2000 sourcemeter under irradiation of a 150 W tungsten lamp. X-ray powder diffraction studies were performed on a Bruker Model D-8 Advance Diffractometer at CuKα radiation (λ=0.15418 nm, accelerating voltage 40 kV, 100 mA) with a scanning speed of 10°/min was recorded in the 2θ range of 10–100°. The morphology of the composites was observed with Transmission electron microscopy using a JEOL (JEM-200 CX) (LEO-440) using an accelerating voltage of 200 kV. The samples for TEM were prepared by dispersing the product in isopropyl alcohol. Scanning electron microscopy (SEM) images were obtained by using Carl Zeiss EVO-18. Energy dispersive X-ray measurements (EDS) were performed with the spectrometer attached with JEM-200 CX.

3. Result and discussion

Fig. 1 illustrates the UV–vis absorption spectra of ZnO, PMOT@ZnO, CdSe @ZnO and PMOT@CdSe@ZnO core shell. It shows that the ZnO nanocrystals mainly absorb UV light with band edge of approximately 385 nm. After modified with CdSe quantum dots, the optical absorption was enhanced in visible region and its absorption edge was red shifted to 485 nm. This may be attributed to the fact that ZnO absorbs light from CdSe quantum dots and