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Merocyanine-540 grafted on ZnS and CdS nanocrystals- an approach for enhancing the efficiency of inorganic- organic hybrid solar cell

Uzma Jabeen[a,b,c], Tham Adhikari[c], Syed Mujtaba Shah[a,**], Sajid Ullah Khan[d], Dinesh Pathak[c,*], J.M. Nunzi[c]

[a] Department of Chemistry, Quaid-i-Azam University, Islamabad, 45320, Pakistan
[b] Faculty of Basic Sciences, Sardar Bahadur Khan Women's University Quetta, 87300, Pakistan
[c] Department of Chemistry, Department of Engineering Physics and Astronomy, Queen's University, Kingston, Ontario, Canada
[d] Department of Materials Science Institute of Space Technology Islamabad Highway Islamabad, 44000, Pakistan

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ABSTRACT

Highly photoactive merocyanine 540 is revealed to form charge transfer complex with zinc sulphide and cadmium sulphide nanocrystals confirmed by FT-IR Spectroscopy, Fluorescence emission and UV-Visible spectrophotometer. The semiconducting nanocrystals were synthesized by co-precipitation method and characterized by Fluorescence emission spectroscopy, UV-Visible spectroscopy, Scanning electron microscopy (SEM), X-ray spectroscopy and Energy dispersive X-ray spectroscopy (EDAX). Merocyanine, in different concentrations was chemisorbed on the surface of ZnS and CdS nanomaterial. ZnS and CdS nanoparticles were used in hybrid solar cells in combination with organic polymer. These cells performed good efficiency at (6×10^{-6} M) dye concentration. The decreased power conversion efficiency with short circuit current density below and above the optimal merocyanine concentration (6×10^{-6} M) may be due to aggregation of merocyanine dye on CdS nanocrystals and subsequent self-quenching phenomena among dye molecules. The power conversion efficiency of the devices fabricated from P3HT-CdS-MC540 was higher than devices fabricated from P3HT-ZnS-MC540 because of particle size effect.

1. Introduction

Photovoltaic technology offers a clean and renewable energy that can reduce the world's dependence on fossil fuels. Dye sensitized solar cell (DSSC) is one of the best choices because of its application for flexible devices and low fabrication cost. [1], these cells work on principles similar to the processes in natural photosynthesis. They use an organic dye to absorb the light and produce excited electrons which will produce electrical current. The absorption band of the dye has to be as large as possible from 350 nm to 900 nm in the visible and near-infrared region of the solar spectrum.

Semiconductor nanoparticles (II-VI) attract lot of interest because of their electro luminescence and size dependent photo properties and bright applications in optoelectronics. Among the family of II–VI semiconductors, ZnS [2,3], CdS [4], ZnO [5], CdTe [6], etc. are the primary candidates because of their propitious optical and electronic properties for optoelectronic applications. ZnS is an excellent semiconductor nanoparticles having band gap energy of 3.8 eV [7]. ZnS exists in two different crystal structures; hexagonal wurtzite and cubic zinc blende structure. In the cubic crystal structure of ZnS, there are x, y and z axes identical, and their optical properties are isotropic [8,9]. Zinc sulphide (ZnS) is an important semiconductor and extensively used in thin film transistors, solar cells, electroluminescent displays and strong electric fields [10]. Similarly CdS is an important semiconductor with outstanding physical and chemical properties having band gap energy of 2.4 eV. Cadmium sulfide is fascinating materials for optoelectronic device applications and has been widely studied in light emitting diodes, solar cells, photocatalysis, biological sensors and photodegradation of water pollutants [11–14].

Donor-acceptor dyes of the merocyanine type have great attraction because they show an important solvatochromic shift or multiple absorption bands in the visible region of the spectrum [15]. Merocyanine dyes are classified as meropolymethine dyes. Meropolymethine dyes are characterized by a chain of methine groups (-CH =) which are normally in the Trans configuration. The extension of methine chain length caused a significant red-shift of the spectra of cyanine dyes [16,17]. The length of the conjugated system may affect absorption spectra as well as the redox potentials of the excited and ground states of the dyes. The

* Corresponding author.
** Corresponding author.
E-mail addresses: smschem69@yahoo.com (S.M. Shah), dineshpathak80@gmail.com (D. Pathak).

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absorption is shifted by the formation of dye aggregation. Some cyanine dyes formed J- and H-aggregates on the surface of silver halide [18,19]. The J-aggregates show the shift of the absorption to the higher wavelength region and the H-aggregates show the shift to the shorter wavelength region. MC540, an anionic cyanine dye, is a heterocyclic chromophore that is commonly used as a sensor of transmembrane potential [20–22], lipid packing [23], a sensitizer in chemotherapy and in photoelectrochemical cells for solar energy conversion [24–26], sensor in quantifying lipid domains in tumor cells [27] and in leukemia cell studies [28].

Solvent polarity effects on absorption spectrum shifts in merocyanine [29,30]. Morley et al. [29] proposed that there are dimer states and as well as a lot of stable non-planar conformations in Brooker's merocyanines and they were expected to absorb at higher and shorter wavelength respectively as compared with the other planar conformer. Solvatochromic behavior in polar solvents can be positive or negative persuading the blue or red shift of the absorption and fluorescence band respectively as compared to the band in nonpolar solvents depending on the dye molecular structure. Large shifts were seen in merocyanine spectra and also source to the both dielectric effect of the solvent and its ability to form a hydrogen bond with merocyanine molecules, leading to greater stabilization of a more polar ground state over the first excited state in solvents of high polarity [30,31]. The fluorescence yield of MC540 is dependent on the polarity of the solvent, and increases with decreasing solvent polarity [32,33].

Here we report a detailed study of the interaction of MC540 with ZnS and CdS nanoparticles, a strategy for the synthesis of novel photoactive nanohybrids for potential applications in photovoltaic devices. The experimental results that elucidate photosensitization aspects of the MC540 adsorbed on ZnS and CdS nanoparticles are presented here.

2. Experimental section

2.1. Chemicals

Analytical grade cadmium acetate (Cd $(CH_3COO)_2 \cdot 2H_2O$), zinc acetate (Zn $(CH_3COO)_2 \cdot 2H_2O$) and sodium sulfide nanohydrate were obtained from Sigma Aldrich. Absolute alcohol and deionized water were used for synthesis as medium. Regio-regular Poly (3- exylthiophene) was purchased from Solaris Chem Inc. All the chemicals were used as purchased. No further purification was done.

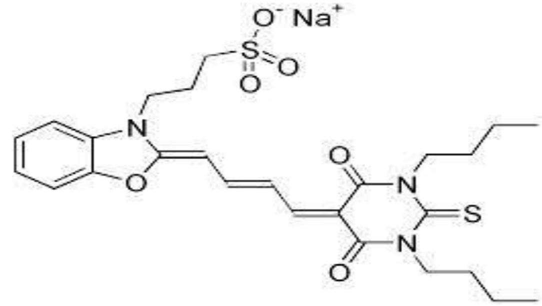
2.2. Synthesis of ZnS and CdS nanocrystals

ZnS and CdS nanocrystals were synthesized by co-precipitation method [34]. In a typical experiment 0.1 M of Zinc acetate was dissolved in 50 ml of deionized water and then 0.1 M of sodium sulphide nanohydrate was dissolved by ultrasonification in the same solvent separately. Then, sodium sulphide solution was added drop wise to the above solution of zinc accetate under constant magnetic stirring at 70 °C. A white precipitates of ZnS nanocrystals were appeared after the addition of sodium sulphide solution.

CdS nanoparticles were synthesized in aqueous medium at an air atmosphere. In this procedure, 0.1 M solution of cadmium acetate and sodium sulphide were prepared in deionized water separately. Next, solution of Na_2S was added drop wise to the zinc acetate solution under constant magnetic stirring at 70 °C. A yellow precipitates of CdS nanocrystals were appeared after adding sodium sulphide solution. The precipitates were washed with deionized water and ethanol several times to remove impurities. Finally, the nanocrystals were dried in oven for 2 h at 120 °C and properly characterized.

2.3. Functionalization of ZnS and CdS nanocrystals with MC540

An organic dye merocyanine 540 was used as photo sensitizer. The structure of MC540 is shown in Scheme 1. Solutions of five different



Scheme 1. Chemical structures of Merocyanine 540 used as a photo-sensitizer.

concentrations of MC540 were prepared from dilution of mother solution by changing the solution from 2 μM to 10 μM and next by taking 2 ml from each concentration of merocyanine solution and 2 ml of ZnS nanocrystals solution having concentration of (0.1 mg/ml) and then they were blend with each other in 1-butanol, after that the mixture was stirred for 16–18 h at room temperature to confirm contact of merocyanine molecules with the ZnS nanocrystals. The stirring was stopped and 1 ml of each of the blend solutions were centrifuged in the micro centrifuge at 5000 rpm for 3 min. The solvent was discarded and the centrifuged sample was re dissolved in 1-butanol. This was done to wash away the fraction of the non-chemisorbed dye molecules from the surface of nanoparticles. The samples were diluted before the optical analysis. Similar grafting procedure was employed for CdS nanoparticles.

2.4. Fabrication of photovoltaic cell

For fabrication, the merocynine 540 was adsorbed on to the surface of ZnS and CdS nanoparticles in different concentrations by the same procedure as already examined. The resulting hybrid sample was labeled as solution 1. The polymer, P3HT solution (20 mg/ml) was prepared when 80 mg of the polymer was dissolved in 4 ml of methanol by heating at 60C for 20 min under argon atmosphere. This solution was labeled as solution 2. Next, equal volume of solution 1 and 2 were mixed and stirred for 10 min. Then the patterned ITO substrates were washed with detergent powder and then washed with tap water. Next, ITO substrates were washed with distilled water, acetone isopropyl alcohol and finally with chloroform for 20 min each in an ultrasonic bath and dried under ambient conditions. Now the substrates were heated at 90 °C for 20 min. After the baking process, the ITO substrates were subjected to plasma cleaning for 20 min. Now the substrates were ready for spin coating with PEDOT: PSS layer. A p-type polymer, PEDOT: PSS, was deposited on patterned ITO glass by spin coating at 5000 rpm for 1 min and with acceleration of 7000 rpm/min, at the same time small portion about 0.3 cm of the p-type polymer was thoroughly cleaned with distilled water. After that, the devices were baked in oven at 1400C for 10 min. The function of PEDOT: PSS is to remove the roughness of the ITO surface. Next, an active layer which is a mixture of dye sensitized semiconductor nanocrystals and P3HT polymer in a ratio 70:30. The active layer was deposited on thin film of PEDOT: PSS in two steps. Firstly, the process of spin coating took place at the rate of 1500 rpm for 20 s and acceleration of 2000 rpm/min. Secondly, another spin place at 500 rpm for 20 s and 100 rpm/min in order to vaporize the solvent. A deposition of Al took place by thermal evaporation under high vacuum. Finally, the devices were annealed at 85 °C for 20 min to attain good morphological distribution of active blend.

2.5. Characterization

UV-Visible spectrophotometer (Shimadzu 1601) was used to study the optical properties of ZnS and CdS nanocrystals and the nanohybrid material. Fluorescence Emission spectra were attained using