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Synthesis and characterization of Mn:ZnS quantum dots for photovoltaic applications

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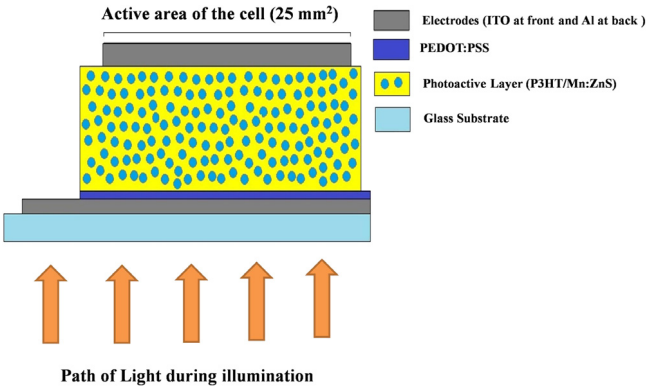
HIGHLIGHTS

- The hydrothermally synthesized QD is optically active with absorption at 269 nm showing optical band gap of 3.86 eV.
- The absorbed radiation was emitted at 587 nm which is visible range showing a red shift.
- This was confirmed by FESEM, TEM, and SEAD. For elemental analysis and active orbital identification in the compound, EDS and XPS were carried out.
- The synthesized material is non-dispersive but showed an excellent photo-activity when combined with P3HT as a solar cell.
- The properties of V_{OC} (310 mV) and I_{SC} (0.002 mA) were clearly identified with a fill factor of 24% and 0.006% efficiency.

GRAPHICAL ABSTRACT



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ABSTRACT

The field of photovoltaics has evolved over the past few decades and introduction of quantum dots (QDs) have further improved their ability to absorb shorter wavelength radiations, which further attracted investigation on quantum dots. Among the QDs, zinc sulfide has shown remarkable results as a semiconductor. It is a low cost and a non-toxic material. Mn:ZnS is synthesized by a hydrothermal process and is characterized by UV–Visible spectroscopy to calculate the optical band gap (3.86 eV) and by X-ray diffractometer (XRD), particle size was calculated (±40 nm) which was confirmed by scanning electron microscopy (SEM). Elemental analysis was carried out by energy dispersion spectroscopy (EDS) and X-ray photoemission spectroscopy (XPS). Here manganese is used as dopant to increase the luminescence property by red shift (587 nm), and thus, making a better candidate for photovoltaic applications. The ability of this material for photovoltaic application is evaluated by constructing a hybrid solar cell with P3HT and calculating the efficiency.

1. Introduction

So for most of the energy demand have been met by fossil fuels all over the globe. In the recent decade the increase in demand and fuel price have lead to explore alternative fuel source such as

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solar energy which is also a clean energy source with abundant availability [1].

Crystalline silicon-based solar cells have dominated the market for the past 5 decades. These required a lot of processing of silicon for construction and production of solar cells which eventually increased the cost. Hence, search for the alternative materials started which lead to the finding of nanomaterials in the field of solar cells.

Nanomaterials have caught attention of many researchers because of their peculiar physical and chemical properties. The increase in surface area to volume ratio and change in electronic structure due to quantum confinement has been significantly utilized by the scientific community [2]. Nano semiconductors in the field of electronics have provided greater scope. These miraculous tiny particles have changed the world by reducing the size of electronic appliances, increasing the storage capacity, and decreasing the processing time of several components.

The nanoscale quantum dots (QDs) have increased the ability to absorb high energy side of the solar spectrum [3,4]. Their ability of quantization show a change in electronic state, which lead them to absorb blue light. These absorptions depend mainly on the size of QDs, hence band gap can be tuned easily [5]. This ability has increased the effective absorption of all wavelengths and in turn improves the efficiency. But these QDs are constructed with transition elements, such as cadmium, lead, mercury and selenium which are heavy metals [6,7]. Thus, focus has shifted towards ZnS which is a non-toxic, easily synthesizable and low-cost luminescent material [8].

Zinc sulfide has demonstrated promising results in the field of semiconductors. It is a II–VI direct gap semiconductor having a better chemical stability than chalcogenides. Accordingly, manganese-doped zinc sulfide is referred to as diluted magnetic semiconductor and has attractive functions [9]. Doping of transition and rare metals like iron, copper, nickel, manganese, yttrium with ZnS have proven to be of greater advantage [10–12]. The presence of manganese is known to change both the optical and physical properties of the ZnS in a recordable scale. Greater research can be carried out by transporting and controlling various spin states by the presence of manganese. Manganese tweaks band gap and other luminance centers by different mixing energy levels of the 3d electrons with the s-p electronic state of the host. The Mn^{2+} ions exhibit a broad change in the crystal field strength with the host. The emission of color may vary accordingly with $^4T_1$-$^6A_1$ transition [13–15]. These properties of the materials find application in optical coatings, electro-optical modulators, photoconductors, sensors, phosphors, reflectors, dielectric filters, and other light emitting materials [16].

In synthesis, hydrothermal method is a promising technique for synthesizing nanoparticles. The process occurs at high temperature and vapor pressure is maintained to get crystallized QDs. This process is less time-consuming and most suitable for zinc sulfide synthesis where a good yield is obtained. The synthesized material can be easily separated by simple filtration.

This paper concentrates on the synthesis and study of various physical and optical properties of manganese-doped zinc sulfide. Application of Mn:ZnS, as a n-type semiconductor against organic semiconductor P3HT in a hybrid solar cell has been discussed. The uniqueness is, synthesis of Mn:ZnS as a non-dispersive material. It is first reported where nondispersive Mn:ZnS has photovoltaic applications [8] (see Fig. 1).

2. Experimentation

2.1. Mn:ZnS quantum dot synthesis and characterization

For the experiment, chemicals such as zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$), manganese acetate ($Mn(CH_3COO)_2 \cdot 4H_2O$) and thiourea ($NH_2CSNH_2$) were procured from Merck India, Mumbai. Double distilled and deionized water was used for the preparing solutions and washing the obtained material.

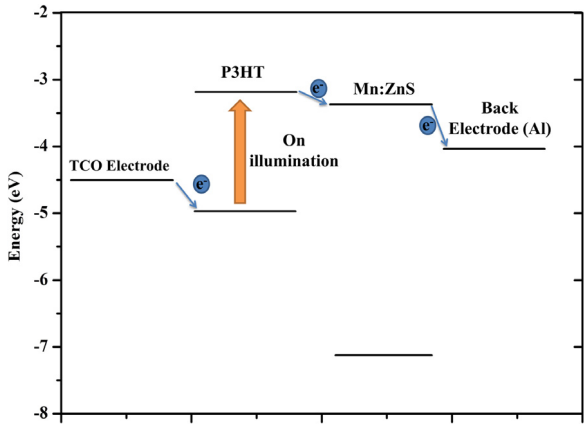

Fig. 1. Energy level diagram of P3HT/Mn:ZnS device in vacuum, showing the work function of electrodes, CB and VB of Mn:ZnS and HOMO, LUMO of polymer P3HT.

In a typical synthesis, 0.25 M zinc acetate and manganese acetate solutions were prepared and kept for 3 h to settle down. A 0.75 M thiourea solution was prepared 30 min prior to the synthesis. Then 12.5 ml of zinc acetate solution was mixed with 12.5 ml of manganese acetate solution with constant stirring, followed by addition of 25 ml of thiourea solution dropwise to seed the reaction. After the addition, the mixture was stirred for 30 min. The mixture was then taken in a sealed Teflon-lined autoclave of 50 ml capacity and placed in a box furnace for 24 h at 200 °C; later the mixture was allowed to cool naturally [17].

The obtained product was a white amorphous material, which was washed copiously with deionized water several times and finally with acetone. The mixture was then dried at 100 °C for 12 h and stored in an airtight container. Synthesized QDs were characterized by UV–visible spectroscopy, photoluminescence, XRD, FESEM-EDS, TEM-SEAD and XPS.

2.2. Construction of cell P3HT/Mn:ZnS

For construction of solar cells, transparent conducting oxide (TCO) glass slides coated with indium tin oxide (ITO) of surface resistance 8–13 Ω/cm^2, poly(3,4-ethylene dioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) and the semiconducting polymer poly(3-hexylthiophene-2,5-diyl) (P3HT) were used along with the synthesized Mn:ZnS. These were procured from Sigma-Aldrich India and used without further processing.

The ITO plates were etched using concentrated HCl and washed with NaOH solution, water and then sonicated in isopropyl alcohol (IPA) for 15 min. These slides were wiped with lint-free tissue papers and stored in vacuum.

The fabrication process started with deposition of PEDOT:PSS on the prepared glass slides. Vacuum spin coating unit was employed for this process. Slide was set up on the stage of the instrument and vacuum was created underneath the slide, this prevented the slide from slipping during deposition. 3–4 drop of PEDOT:PSS was sufficient to cover the complete surface. It was spin coated at 700 RPM for 30 s and deposited slides were annealed at 115 °C for 15 min in vacuum.

Previously equiweight (10 mg/ml) P3HT and Mn:ZnS were dispersed in dichlorobenzene and sonicated for 24 h. This blend was spin coated on pre-deposited slides at 500 rpm for 30 s. These slides were vacuum annealed at 70 °C for 15 min for proper adhesion and were stored in vacuum till further process was carried out [18].