Manganese Doped Zinc Sulphide Nanoparticles for Enhanced Performance of Organic Solar Cells

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Abstract

Manganese doped zinc sulphide (ZnS:Mn) nanoparticles (NPs) were employed in the functional layer of thin film organic solar cells whose photoactive layer is composed of a polymer blend poly(3-hexylthiophene-2,5-diyl):phenyl-C_{61}-butyric-acid methyl-ester (P3HT:PCBM). The incorporation of the nanoparticles in the solar absorber layer of the solar cells brought significant improvement on device performances. Such improved performances, however, are dependent on the doping concentration of NPs, and the best power conversion efficiency (PCE) recorded was 4.53% at the optimum concentration of 3 wt%. However, increasing the concentration to 5 wt% turned out to be unfavourable for the device performance resulting in a slight reduction in PCE of 4.25 %. This performance enhancement was attributed to occurrence of near-field enhancement and light scattering effects of the nanoparticles in the organic solar cells.

Keywords: Organic solar cells, metallic nanoparticles, plasmon resonance, zinc sulphide, P3HT, PCBM

1. Introduction

Organic solar cells (OSCs) have attracted tremendous attention from researchers because of several advantages over other solar cell technologies. OSCs offer flexible solar panels, lightweight, roll-to-roll large scale device fabrication, cheap and fast production processes (Riede et al., 2021, Yuan et al., 2022). Furthermore, organic molecules based solar cells (SCs) possess tunable energy band gaps allowing absorption of near-infrared light (Hu et al., 2020). These organic materials also have higher absorption coefficients compared to their inorganic counterparts (Hu at al., 2020). Due to intensive research and development, OSCs power conversion efficiencies (PCEs) increased well over 19 % as reported (Ike et al., 2023).

However, OSCs suffer from low carrier mortality and short diffusion lengths. In most polymers, the exciton diffusion lengths are in the region of 3 – 10 nm (Dang et al., 2011). Diffusion length is the average distance an exciton travels before recombination if it is not dissociated. The short exciton diffusion length limits the photoactive layer thickness to roughly 100 - 200 nm for an effective charge carrier generation (Oseni et al., 2025, Sandzhieva et al., 2022). Such limitation of the photoactive layer thickness leads to poor optical absorption and lowers the generation of photocurrents. There is a need to keep the photoactive layer thin due to short diffusion length, while also improving the optical absorption. Researchers have investigated several mechanisms to enhance the performance of organic solar cells while keeping the photoactive layer thickness thin. These include ternary or tandem solar cell structures, solvent additives, reflective back surfaces, development of new donor and acceptor materials, and incorporation of metallic nanoparticles within the solar cells.

Metallic nanoparticles embedded within OSCs have been utilized to improve light trapping and exciton dissociation leading to enhanced PCEs. These NPs offer local surface plasmon resonance effect (LSPR) and light scattering (Kaçuş et al., 2021) which aid in light trapping, enhanced optical absorption (Sandzhieva et al., 2022) and exciton dissociation for improved collection of photocurrents. The LSPR effect is due to the collective oscillation of loosely bound electrons in the metallic nanoparticles in response to an incident electromagnetic field. The LSPR and scattering effect are closely related to the size of the nanoparticles compared to the wavelength of the incident electromagnetic field. Nanoparticles have been incorporated into different solar cell technologies like bulk heterojunction organic solar cells (Mkawi et al., 2021), inorganic (silicon) solar cells, dye-sensitized solar cells (Li et al., 2023), and perovskite solar cells (Kazici et al., 2025). Furthermore, NPs have been incorporated at different locations within solar cells, such as in the charge transport layer (Seimela et al., 2025), photoactive layer (Mkawi et

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al., 2021), and in the interfaces between two layers. The most studied NPs are the noble metal NPs gold (Au) and silver (Ag). Both possess superior chemical stability and are the best for plasmonic nanoparticles applications (Cathcart et al., 2018). However, due to their high cost, alternative metal nanoparticles (MNPs) such as copper (Cu) have been widely explored. Furthermore, several alternative MNPs that are cheaper and easier to synthesize have been studied either as mono- or bimetallic NPs. We report here PCE enhancement of P3HT:PCBM based OSCs incorporated with manganese doped zinc sulphide (ZnS:Mn) incorporated within the photoactive layer.

2. Materials and methods

2.1. Materials

Chemical materials for the fabrication of OSCs were purchased from chemical suppliers and used as received without any further processing except the synthesis of ZnS:Mn NPs. Poly(3-hexylthiophene-2,5-diyl) (P3HT), phenyl-C_{71}-butyric acid methyl ester (PCBM) and PEDOT:PSS were purchased from Ossila Co. Ltd. Zinc nitrate hexahydrate and sodium sulphide nonahydrate were purchased from Sigma-Aldrich and Merck, respectively. Manganous chloride tetrahydrate was purchased from Associated Chemical Enterprises, Johannesburg. Polyvinylpyrrolidone (PVP, $(C_6H_9NO)_n$, MW of 25 000 - 30 000) LAB.

2.2. Synthesis and characterization of ZnS nanoparticles

The ZnS:Mn NPs were synthesized using a simple solution method in laboratory environment as explained in (Murugadoss, 2012) with some modifications. In this study, 2.5 g of sodium sulphide ($Na_2S{\cdot}9H_2O$) was dissolved in 12.5 mL deionized water and stirred for 60 minutes at room temperature. On separate beakers, 2 g of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and 0.5 g of manganous chloride tetrahydrate ($MnCl_2{\cdot}4H_2O$) were each dissolved in 12.5 mL deionized water and stirred. The zinc nitrate and manganous chloride solutions were then mixed and poured into the sodium sulphide solution and stirred for 4 hours at room temperature. The resulting precipitate was centrifuged and separated from the solution. It was then washed with methanol repeatedly to remove impurities. The precipitate was then dried overnight at 150 °C in a convection oven.

2.3 Device fabrication

P3HT:PCBM blend based organic solar cells doped with ZnS:Mn plasmonic nanoparticles were fabricated on unpatterned ITO coated glass substrates. The substrates were first partially etched with acid solution ($HCL:H_2O:HNO_3$ at 48%:48%:4%) to remove part of the ITO. They were then successively cleaned in ultrasonic bath with detergent, distilled water, acetone and isopropanol, respectively, for 10 min waiting time. The samples were then dried in an oven at 120 °C for 30 min. A thin layer of PEDOT:PSS was spin coated onto the samples at 3 500 rpm. The samples were dried again in the oven under ambient atmosphere. Three P3HT:PCBM (1:1) blend solutions with 0 wt%, 3 wt% or 5 wt% of ZnS:Mn NPs were prepared in chloroform and sonicated for 3 hours at 40 °C to ensure good dispersion of the NPs and miscibility of the polymer-fullerene blend. The P3HT:PCBM solutions incorporated with ZnS:Mn NPs were then spin coated onto the PEDOT:PSS film at 1 300 rpm for 40 sec. The samples were then dried in oven under nitrogen atmosphere for 10 min before being transferred into a vacuum deposition chamber (Edwards Auto 306) for deposition of lithium fluoride (LiF) and aluminium (Al). Thin layers of LiF (0.5 nm) and Al (80 nm) were deposited onto the samples at a base pressure of 10^{-6} mBar resulting in devices with the following structure; ITO/PEDOT:PSS/P3HT:PCBM:NPs/LiF/Al.

3. Results and discussion

3.1. Optical properties

The optical properties of OSC films were studied using UV-vis absorption and the results are shown in Fig. 1. The spectra exhibit the typical broad absorption spectra of P3HT:PCBM blend in the range 300 – 650 nm. The spectra show the three P3HT related absorption peaks at about 515 nm, 560 nm and 610 nm. Kadem et al. (2018) observed absorption bands at 520 nm, 560 nm and 600 nm. These absorption peaks, 520 nm, 560 nm and 600 nm were ascribed to the $\pi - \pi^*$ transition in the P3HT conjugated backbone, the extended conjugated P3HT and the inter-chain stacking of P3HT, respectively (Kadem et al., 2018). Similarly in this study, an absorption peak at 515 nm was observed, see Fig. 1, and is attributed to the $\pi - \pi^*$ transition in the P3HT. Furthermore, the two vibronic shoulders at around 560 nm and 610 nm can be attributed to extended conjugated P3HT and inter-chain stacking of P3HT,

respectively. The spectra exhibit slight blue shift of the central peak which could be due to the interaction of the polymer with NPs.

Pristine ZnS nanoparticles have an excitonic peak at 273 nm and an absorption edge at 330 nm (Dhupar et al., 2021). The PCBM also has an absorption peak at about 334 nm (Zhuo et al., 2011). It is concluded in this report that the absorption shoulder around 330 – 335 nm in Fig. 1 is due to PCBM. The addition of ZnS:Mn enhanced the optical absorption intensity of the P3HT:PCBM films in the region of 325 nm – 650 nm. Incorporating 3 wt% ZnS:Mn in P3HT:PCBM increased absorption in the wavelength range of 325 nm – 650 nm. Increasing the concentration of ZnS:Mn to 5 wt% further enhanced absorption in the range 325 nm – 700 nm. This enhanced absorption can be attributed to NP LSPR and increased light scattering in the medium by the NP (Sandzhieva et al., 2022). NPs embedded in thin film solar cells can cause light scattering and enhanced electro-magnetic field localization near the NPs confining the incident light by increasing the optical pathlength (Shim et al., 2016). The increased optical pathlength results in increased photon harvesting and improved device performance. This optical pathlength increase is very important as it enables the active layer thickness to remain thin (100 nm – 250 nm) favouring the short exciton diffusion lengths.

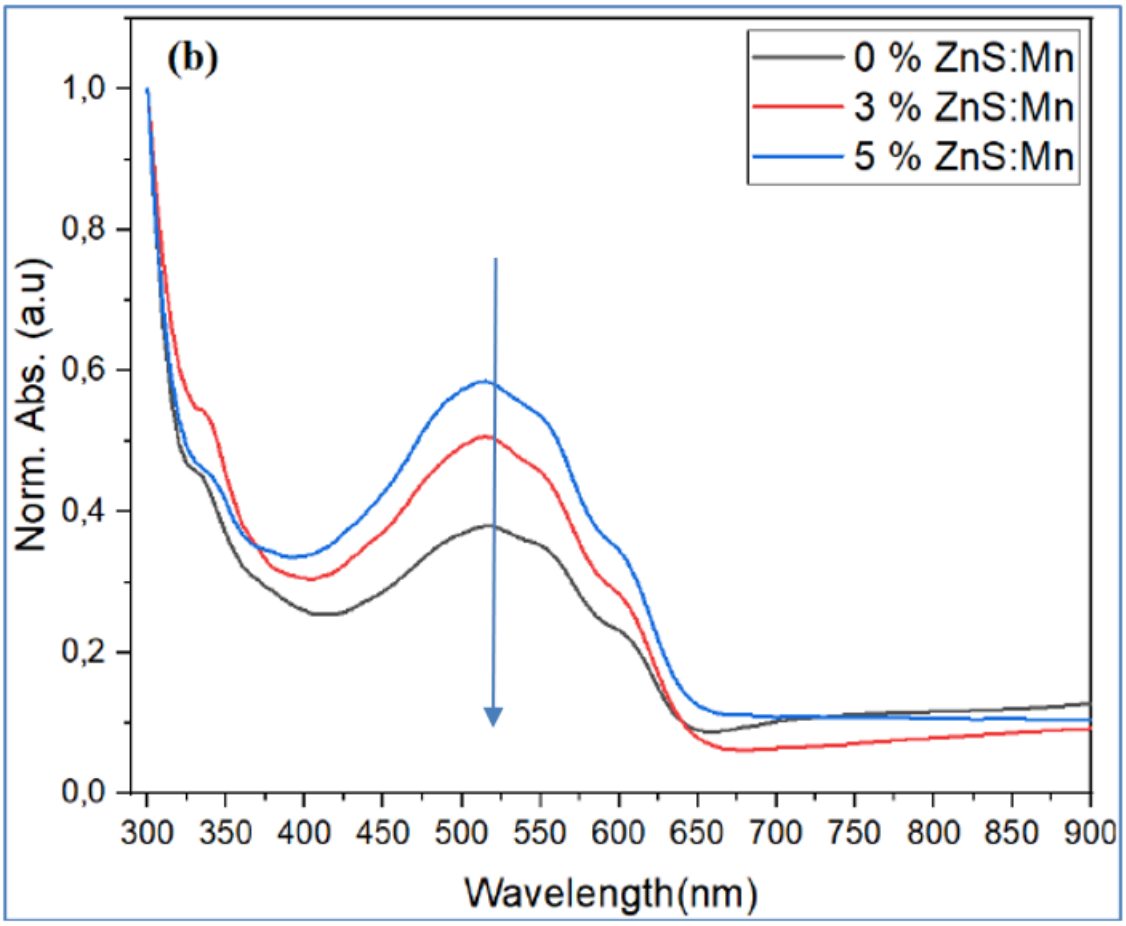

Figure 1: Optical absorption of P3HT:PCBM based solar cells w/o ZnS:Mn NPs.

3.2. Electrical properties

The solar cell performances were determined from the measured current density-voltage (J-V) data. Fig. 2 shows the electrical properties of the fabricated OSCs measured under AM 1.5G illumination and the results are summarized in Table 1.

The open-circuit voltage of the devices showed no significant changes which may be as a result of well-established ohmic contact between the anode and the photoactive layer. Additionally, it also suggests that there is low recombination rate and enhanced electron collection efficiency. There are several factors that affect the open-circuit voltage such as donor-acceptor interface, morphology, electrodes' work function, defects of states, crystallinity, carrier density, charge transfer states, density of states and ideality factor (Elumalai et al., 2016). The incorporation of the ZnS:Mn NPs may results in changes on the device morphology. Correlation between the V_{oc} and device morphology is still not fully understood and is still a topic under study.

Tab. 1: The electrical properties of P3HT:PCBM OSCs doped with ZnS:Mn NPs.

ZnS:Mn (wt%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
0	0.51	11.64	54.35	3.23
3	0.55	14.79	55.37	4.53
5	0.55	14.00	55.05	4.25

Nanoparticles incorporated within solar cells may increase its surface roughness. Li et al. (2013) reported surface roughness increase of a P3HT:PCBM layer from 11.707 nm to 14.257 nm upon addition of Ag nanomaterials. Such an increase in surface roughness may be beneficial for the J_{sc} it increases the effective contact area between the photoactive layer and hole/electron transport layer. However, this interface surface roughness increase which is beneficial for J_{sc} may be compensated by corresponding increase in charge recombination. Incorporation of the ZnS:Mn NPs in the active layer increased the short-circuit current density of the devices from 11.64 mA/cm for pristine devices to a highest J_{sc} of 14.79 mA/cm for a NP concentration of 3 wt%. This is a significant increase in J_{sc} of at least 20 % when compared to that of the pristine devices.

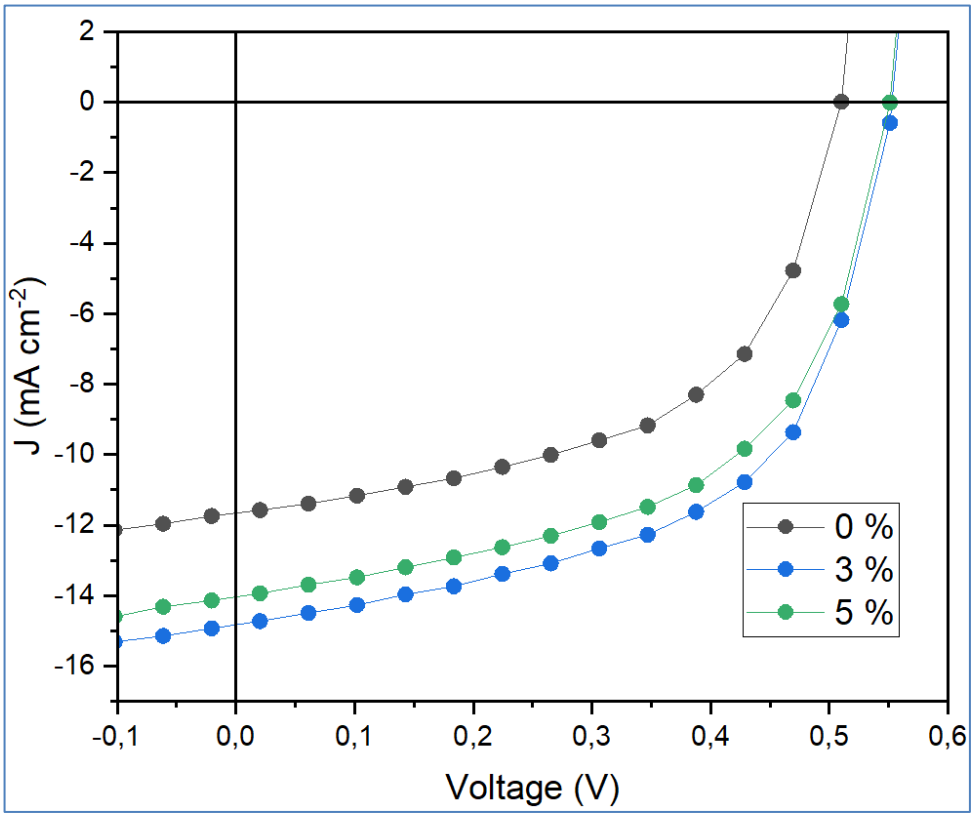

Figure 2: The current-voltage characteristic of P3HT:PCBM based solar cells prepared w/o ZnS:Mn NPs.

The significant enhancement of the J_{sc} by incorporation of the ZnS:Mn in the photoactive layer improved the power conversion efficiency of the devices. The PCE of the devices increased from 3.23 % for pristine devices to a maximum of 4.53 % for devices with 3 wt% ZnS:Mn NPs. Similar enhancements of device performances due to the incorporation of NPs in OSCs has been reported in literature. Shim et al. (2016) reported an increase of PCE in P3HT:PCBM from 2.11 % to 2.55 % for devices doped with gold NPs. Additionally, the PCE was increased from 2.11 % to 2.23 % when the devices were doped with Ag NPs (Shim et al., 2016). This was attributed to increased optical pathlength in active layer resulting in enhanced solar cell efficiency (Shim et al., 2016, Yu and Chan, 2013). The performance enhancement observed upon incorporation of the NPs is attributed to their LSPR and light scattering effects. Light scattering by the NPs incorporated into the photoactive layer confines incident photons within the photoactive layer increasing its effective optical thickness and hence absorption. This leads to more excitons in the photoactive layer being produced and create more charge flow. High NP concentration in the photoactive layer may become impurities and cause defects which lead to high recombination rate and leakage currents. Increasing the NP concentration beyond 3 wt% to 5 wt% resulted in a reduced J_{sc} and PCE. As the NP concentration increases, the NPs may become recombination centres quenching excitons. Even though devices with 5 wt% ZnS:Mn possessed the highest optical absorption, the high concentration of NPs in the photoactive layer started to degrade the electrical

properties of the devices and hence their PCE started dropping.

The device fill-factors (FF) remained relatively unchanged within the range 54 - 56 %. The PCE also depends on this important parameter, FF, which is more sensitive and is determined by comprehensive and complicated courses, including charge generation, transport, recombination and extraction (Guo et al., 2021). Furthermore, the FF is affected by device morphology, thickness and regioregularity of the conjugated polymer and morphology of the active/transport layers interface. P3HT forms crystalline domains due to its regioregularity. The crystallinity of the P3HT can be tuned by thermal annealing. For this study, the devices were all annealed at a same temperature and equal annealing times. Therefore, the regioregulality of the device films is expected to be comparable and hence has no significant effect on the device fill-factors. The FF can be determined from the series resistance (R_s) and shunt resistance (R_{sh}) of a device. The series and resistances are determined from the inverse of the slope of the J-V curve shown in Fig 2. The J-V curves in Fig 2 show relatively similar slopes in the first quadrant hence the comparable fill-factors. Therefore, the PCE enhancement is attributed to the increased J_{sc} due to enhanced optical absorption by the incorporation of the ZnS:Mn NPs.

4. Conclusion

ZnS:Mn NPs were successfully incorporated into the photoactive layer of P3HT:PCBM based OSCs at a concentration of 0 wt%, 3 wt% and 5 wt%. Enhanced optical and electrical properties were observed from the analysis of the measured data taken from the fabricated solar cells. The results showed significant enhancement in the PCEs recorded increasing from 3.23 % (pristine device) to 4.53 % for NP concentration of 3 wt% ZnS:Mn NPs. These enhancements were attributed to the LSPR and light scattering caused by the ZnS:Mn NPs in the photoactive layer. This an important progress on the use of NPs for the realization of cheap and affordable solar panel.

5. References

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