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# The effect of metal oxide nanoparticle concentrations in PEDOT:PSS layer on the performance of P3HT:PCBM organic solar cells

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### ABSTRACT

An improved organic solar cell was obtained by focusing on the effects of metal oxide nanoparticles (NPs) concentrations in the buffer layer. The performance was compared by mixing metal oxide nanoparticle into PEDOT:PSS (Poly(3,4 ethylenedioxy-thiophene) Poly(styrene-sulfonate)) based buffer layer. We studied the effect of Fe<sub>2</sub>O<sub>3</sub> NPs by changing its concentration from 0.1 to 1 wt.%. Increasing concentrations of NPs showed good light absorption ability. The solar cells with a bare active layer showed a power conversion efficiency (PCE) of 2.79% while with Fe<sub>2</sub>O<sub>3</sub> NPs at 0.7 wt.% concentration, showed higher performance resulting a PCE of 3.68% under AM 1.5G illumination. A decline in PCE was seen at 1 wt.% of Fe<sub>2</sub>O<sub>3</sub> NPs. This phenomenon was also compared with the use WO<sub>3</sub> NPs in place of Fe<sub>2</sub>O<sub>3</sub> NPs.

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#### 1. Introduction

The bulk heterojunction (BHJ) solar cells have been a very attractive research area of renewable energy sources because of their advantages like light-weight, flexibility, low-cost, and simple fabrication for large processing area. Among the various conducting polymers like polyanilines, polyacetylenes, polypyrroles, etc.; polythiophenes are a promising candidate as electron donor materials for OSCs because of high electron mobility and high light absorption coefficient in the visible region. The most representative high-performance OSCs reported in the literature have been fabricated using the BHJ concept whose PCE has reached as high as 6-8% [1-4]. Commonly in BHJ, a light-absorbing material (donor) and a soluble fullerene (acceptor) forms a three-dimensional structure possessing a large-area phase separated interface for efficient exciton dissociation [5,6]. Owing to these benefits, there is an increased demand to enhance the performance of OSCs. For increased performance, many researchers have optimized processing conditions such as solvent, annealing temperature and time, composition mixture ratio in solvent [7–10]. On the other hand, in the polymer and fullerene blend, the charge carrier mobility is comparatively low with a short exciton diffusion length in the active layer which limits the PCE of the devices [11]. An efficient light trapping in the active layer will enhance the photon absorption without the need for a thick film. The addition of light scattering materials revamps the light intensity in the device, resulting in an increased light absorption. Recently, the use of surface plasmon resonance (SPR) effects, due to scattering of light, has attracted much attention as a means for increasing the photocurrents of OPVs [12-16]. In order to improve the efficiency of organic solar cells, the approach addressed in this paper is the careful use of metallic nanoparticle's properties to induce surface plasmons which enhances the optical absorption and photocurrent generation over a broad range of visible wavelengths [17]. With incident light, the surface charges of metallic nanoparticles interact with the electromagnetic field, leading to an electric field enhancement that can then be coupled to the photoactive absorption region. It has been extensively studied that surface plasmons can be tuned by changing the size, shape, material, and liganding the nanoparticles [18-20]. Also a rough surface increases the light scattering leading to an increased light absorption. As proposed by Paci et al., the use of metallic nanoparticle has a dual advantage on the efficiency of OSCs. Along with the increase of path length of the absorbed light, NPs also enhances the structural stability of the layer leading to a slower device degradation rate during prolonged illumination [21].

In this study, we improved the photovoltaic performance of organic solar cell by mixing  $Fe_2O_3$  NPs into the buffer layer. Similar works reported, used Au NPs in the active layer. Wang et al. compared the effect of 5 wt.% of truncated octahedral Au NPs on solar cells fabricated with different polymer materials and reported an average PCE increase of 0.71% [22]. Likewise, Spyropoulos et al. used surfactant-free Au NPs with a PCE increase of 1.07% at 5% concentration [23]. The artificial buffer layer mixed with metal oxide NPs was used to enhance the scattering effect and to provide a





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mechanical endurance to device without increasing the thickness. The electrical and optical properties of the device were analyzed and the obtained hypotheses were also compared with the use of  $WO_3$  NPs.

#### 2. Experimental

We investigated the effect of Fe<sub>2</sub>O<sub>3</sub> NPs in PEDOT:PSS based buffer layer in the inverted organic solar cells. The fabricated the solar cell devices had a structure of FTO/TiO<sub>2</sub>/P3HT:PCBM/ PEDOT:PSS:Fe<sub>2</sub>O<sub>3</sub>/Ag as shown in Fig. 1(a). In the past we reported that the inverted structure using fluorine-doped tin oxide (FTO) can improve the device performance with higher stability and efficiency [9]. For the fabrication, FTO glass substrates were cleaned in an ultrasonic bath with deionized water, acetone and isopropyl alcohol for 20 min, respectively. TiO<sub>2</sub> was used as a buffer layer for hole-blocking between the active layer and bottom electrode. TiO<sub>2</sub> solution was spin coated onto FTO substrate and then sintered at 500 °C for 1 h in ambient air condition. The active layer (P3HT:PCBM) was deposited on TiO<sub>2</sub> layer by spin coating. The crystallization of P3HT tends to be disturbed when increased amount of PCBM is blended in the active layer [10,11]. The mixture of P3HT:PCBM (40 mg/ml) (P3HT:PCBM = 1:1 weight ratio) was dissolved in chlorobenzene. The thicknesses of active layers were 75 nm in this case (measured by alpha-step). In order to deposit hydrophilic PEDOT:PSS solution onto a hydrophobic active layer, PEDOT:PSS was mixed with 0.5 vol.% of Triton X-100 (C14H22O  $(C_2H_4O)_n$ ) nonionic surfactant. And the prepared PEDOT:PSS solution was mixed with different concentration of  $Fe_2O_3$  NPs (5  $\mu$ m). The concentration of Fe<sub>2</sub>O<sub>3</sub> NPs in PEDOT:PSS ranged from



**Fig. 1.** (a) The schematic of inverted organic solar cell. (b) Energy band diagram with a schematic of hole transportation concept.

0.1 wt.% to 2 wt.%. Then this solution was spin coated on hexamethylene disilazane which was pre-coated on the surface of the active layer. Thermal pre-annealing was conducted at 160 °C for 10 min on a dry oven in ambient air. Then Ag top electrode (100 nm) was deposited on PEDOT:PSS layer by thermal evaporation by defining an active area of 0.1 cm<sup>2</sup>. Fig. 1(b) shows the energy band diagram of buffer layer with Fe<sub>2</sub>O<sub>3</sub> NPs. The UV/visible spectrophotometer (Shimadzu UV-1601) was used to study light absorption and light scattering of the active layer and buffer layer. The short circuit density  $(J_{sc})$ , open circuit voltage  $(V_{oc})$ , J–V characteristics were measured with J-V curve tracer (Eko MP-160) and solar simulator (Yss-E40, Yamashita Denso) under AM 1.5G (100 mW/cm<sup>2</sup>) irradiation intensity. The external guantum efficiency of device was measured using K3100, Mc science. Entire fabrication and measurement processes were conducted in ambient air.

#### 3. Results and discussions

Fig. 2(a) shows the UV/visible absorption spectra of the FTO/ P3HT:PCBM/PEDOT:PSS and FTO/P3HT:PCBM/PEDOT:PSS:Fe<sub>2</sub>O<sub>3</sub> (with different concentration) layer films after annealing at 160 °C for 10 min. Generally the main absorption wavelength region of PCBM and P3HT is around 330 nm and from 400 nm to 600 nm, respectively. As shown in Fig. 2(a), the overall absorption spectra of PEDOT:PSS buffer layer without Fe<sub>2</sub>O<sub>3</sub> NPs is overlapped with Fe<sub>2</sub>O<sub>3</sub> NPs contained buffer layer. The black line represents the bare device without any mixed NPs; in comparison, device with Iron oxide NPs shows more absorbance. The reason for this



Fig. 2. (a) UV-visible absorption spectra of active layer/PEDOT:PSS: $(Fe_2O_3)$  layer. (b) Surface plasmon effect combined with light scattering in the FTO glass substrate by NPs.

observation can be attributed to a phenomenon of formation of localized surface plasmon resonance (LSPR) and increase in scattering of light due to the use of metallic NPs, enhancing the light absorption efficiency (Fig. 2(b)). The light scattering lengthened the optical path in the active layer, thereby trapping it inside [24–26]. Another major reason for the enhancement of the total excitons created in the active layer is that the energy dissipation is proportional to the intensity of the electromagnetic field [27]. This result corresponds to a 6.5% increase of the total optical absorption of the device in the spectral range of 500 nm. As the amount of  $Fe_2O_3$  NPs increased in buffer layer, the absorbance of device increased.

The measured J-V characteristics of organic solar cells with PEDOT:PSS and PEDOT:PSS:Fe<sub>2</sub>O<sub>3</sub> (different concentration) using a solar simulator is shown in Fig. 3. All the devices have similar open circuit voltage ( $V_{oc}$ ) and fill factor (F.F). The thin film resistivity remained unchanged but the performance of device improved due to light scattering. The bare device showed a short circuit density  $(J_{sc})$  of 8.93 mA/cm<sup>2</sup>. The addition of 0.1% Iron oxide elevated the  $J_{sc}$  to 9.31 mA/cm<sup>2</sup>. Increasing concentration of Fe<sub>2</sub>O<sub>3</sub> NPs showed higher short circuit density. Finally, a threshold was seen at 0.7% where the device gave a  $J_{sc}$  of 11.12 mA/cm<sup>2</sup> while the device with 1% showed a lower  $I_{sc}$  of 10.28 mA/cm<sup>2</sup>. The exciton generation was proportionate to light absorption in the active layer. The performance of all the organic solar cells is summarized in Table 1. Use of 0.7% Fe<sub>2</sub>O<sub>3</sub> NPs increased the short circuit current density by 25%. It can be observed that the highest performance of organic solar cells was shown by 0.7 wt.%. The energy band diagram in Fig. 1(b) explains the reason why  $Fe_2O_3$  NPs the  $J_{sc}$  is reduced above 0.7%.

Fig. 1(b) shows the energy band diagram of our device. Many studies have shown the energy level of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) for Fe<sub>2</sub>O<sub>3</sub> NPs at 4.78 eV and 6.98 eV, respectively. This higher concentration of Fe<sub>2</sub>O<sub>3</sub> NPs increases the exciton generation. But it appears that at a very high concentration of 1%, the energy levels of PEDOT mixture changes. Also a higher concentration of the NPs interferes with the binding of PEDOT and PSS domains which reduces the carrier mobility. A blockage in hole transfer is seen even though a high number of excitons are generated leading to a decreased current density. This change in energy level in Fe<sub>2</sub>O<sub>3</sub> NPs devices prevents the transport of holes from P3HT:PCBM to silver electrode.

For comparison we also used WO<sub>3</sub> (100 nm) instead  $Fe_2O_3$  in the buffer layer. The energy level of WO<sub>3</sub> NPs at LUMO is 5.24 eV

#### Table 1

Summary of organic solar cell performances with different concentrations of Fe<sub>2</sub>O<sub>3</sub> NPs in PEDOT:PSS buffer layer.

Fe <sub>2</sub> O <sub>3</sub>	J <sub>sc</sub> [mA/cm <sup>2</sup> ]	$V_{\rm oc}$ [V]	F.F	PCE [%]
Ref.	8.93	0.62	0.5	2.79
0.1 wt.%	9.31	0.62	0.51	3.0
0.3 wt.%	9.61	0.63	0.51	3.12
0.5 wt.%	9.94	0.63	0.51	3.23
0.7 wt.%	11.12	0.63	0.52	3.68
1 wt.%	10.28	0.62	0.51	3.28

and at HOMO is 7.94 eV. Though a direct comparison of both the nanoparticles is not possible due to the difference in their size, WO<sub>3</sub> NPs were used just to compare the mechanism of light scattering and SPR generation. All the devices were fabricated with the similar conditions. The concentration of WO<sub>3</sub> in PEDOT:PSS ranged from 0.1% to 2%. The I-V curve of devices with WO<sub>3</sub> is shown in Fig. 3 (b) while *I*<sub>sc</sub> and PCE are plotted in the inset. The bare device showed a  $I_{sc}$  of 9 mA/cm<sup>2</sup> whereas the device with optimized concentration of 1.5% WO<sub>3</sub> NPs showed a  $J_{sc}$  of 11.1 mA/cm<sup>2</sup>. Increasing concentration of WO<sub>3</sub> NPs showed higher  $J_{sc}$ , but, the device with 2% showed a decreased current density of 10.2 mA/cm<sup>2</sup>, a phenomenon similar to that of 1% Fe<sub>2</sub>O<sub>3</sub>. Formation of a hole blocking layer is a habitual feature of metallic nanoparticles which has been proved by these NPs also. A stoppage in holes migration reduced the current density directing to a lower PCE. The theory of an artificial hole blockage layer is stated, keeping in mind, only the energy level of bulk layer along with the metal NPs. The energy level of bulk layer is extensively reported but the energy level of only NPs is seldom reported, which limits the study of the actual reason for the hole blockage layer formation at high nanoparticle concentration.

Fig. 4 shows the external quantum efficiency (EQE) of OSCs measurement. We compared the curve of the increase in EQE between PEDOT:PSS and PEDOT:PSS:Fe<sub>2</sub>O<sub>3</sub> (different concentration) device. The photocurrent within the wavelength range from 400 to 700 nm increased significantly after addition of the Fe<sub>2</sub>O<sub>3</sub> NPs. The EQE data supports the UV/visible data corresponding to Figs. 2 and 3. An increase in EQE was seen, with the increase in the concentration of Fe<sub>2</sub>O<sub>3</sub> NPs, up to 0.7%. The device also showed enhanced quantum efficiency in the broad wavelength range due to adequate scattering of light. Spyropoulos et al. in his work discussed that metallic nanoparticle can act as an antenna or a scattering element for different wavelength of light, which



**Fig. 3.** (a) *J*–V characteristics of inverted organic solar cells using PEDOT:PSS buffer layer with different concentrations of Fe<sub>2</sub>O<sub>3</sub> NPs. (Inset: Fe<sub>2</sub>O<sub>3</sub> NPs wt.% versus current density, PCE) (b) *J*–V characteristics of inverted organic solar cells using PEDOT:PSS buffer layer with different concentrations of WO<sub>3</sub> NPs. (Inset: WO<sub>3</sub> NPs wt.% versus current density, PCE).



**Fig. 4.** The external quantum efficiency of organic solar cells using PEDOT:PSS buffer layer with different concentrations of Fe<sub>2</sub>O<sub>3</sub> NPs.

collectively increases the efficiency of OSCs. The enhanced quantum efficiency of the device is the outcome of such properties of NPs [23].

#### 4. Conclusion

We investigated the effect of Fe<sub>2</sub>O<sub>3</sub> NPs in PEDOT:PSS light harvesting system for OSCs. Light absorption of device differs with different concentration Fe<sub>2</sub>O<sub>3</sub> NPs and showed different  $J_{sc}$  due to much exciton generation. Fe<sub>2</sub>O<sub>3</sub> NPs contributed in increased light harvesting. On the other side, the high concentration of Fe<sub>2</sub>O<sub>3</sub> NPs reduced  $J_{sc}$ . The high concentration Fe<sub>2</sub>O<sub>3</sub> NPs also prevents the transport of holes. A 32% increase in power conversion efficiency was obtained between the bare device and optimized device due to the addition of Fe<sub>2</sub>O<sub>3</sub> NPs.

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