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Dissimilar mechanism of executing hole transfer by WO_3 and MoO_3 nanoparticles in organic solar cells

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ABSTRACT

We investigated the effect of metal oxide nanoparticles (NPs) in poly (3,4 ethylenedioxythiophence):poly (styrene-sulfonate) layer for the light harvestation in poly (3-hexylthiophene):[6,6]-pheny-C_{61}-butyric acid methyl ester organic solar cells. The role of tungsten trioxide nanoparticles (WO_3) and molybdenum trioxide nanoparticles (MoO_3) in enhancing the efficiency of solar cells was compared. Due to the difference in the energy band structure of the two nanoparticles, the WO_3 NPs acted as a hole blocking layer, whereas MoO_3 NPs helped in the hole transfer. The solar cell with WO_3 NPs at 1.5 wt% concentration showed a power conversion efficiency of 4.22% under AM 1.5G illumination and the device blended with 2 wt% of MoO_3 NPs showed a power conversion efficiency of 4.40%. We measured various electrical properties including, electrochemical impedance spectroscopy and recombination mechanisms using the light intensity dependent current–voltage measurement of organic solar cell.

1. Introduction

The organic solar cells (OSCs) have an infinite potential of becoming a renewable energy source because of the advantages like low-cost, simple fabrication, light-weight, and flexibility [1–3]. However, 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 power conversion efficiency (PCE) of the devices [4]. The short-circuit current density (J_{sc}) and PCE of solar cells depend on the efficient harvesting of light and efficient charge separation.

The scattering of light due to the surface plasmon resonance effect is the most sought-after technique to enhance the J_{sc} of organic solar cells [5]. The addition of light scattering materials revamps the intensity of light in the device, resulting in an increased light absorption. The metallic NPs can be used as an optical spacer in the buffer layer (Au, MoO_3, $CsCO_3$, V_2O_5, ZnO, Ca) [6–11]. A number of reports focus on the thermal evaporation, chemical vapor deposition, or sputtering of the metallic nanoparticle (NPs). Other hole-injecting polymers with larger work functions have also been synthesized to enhance the hole injection [12,13]. Inorganic layers of transition metal oxides have been discussed as an alternative to poly (3,4 ethylenedioxythiophence):Poly (styrene-sulfonate) (PEDOT:PSS), such as vanadium (III) oxide (V_2O_3) and molybdenum trioxide (MoO_3) vacuum deposited onto the indium tin oxide (ITO) in OSCs [10]. Although these techniques proved to be effective; commercial or bulk production of these devices will take longer fabrication time and are much expensive.

However, the approach addressed in this paper is the careful use of metallic nanoparticle's properties to induce surface plasmons, which increases the optical absorption and photocurrent generation over a broad range of visible wavelengths [14]. The use of NPs also roughens the surface, thereby increasing the active surface area and the scattering of light. As proposed by Paci et al., metallic nanoparticles have a dual advantage on the efficiency of OSCs. Along with the increase of path length of the absorbed light, nanoparticles also enhances the structural stability of the layer leading to a slower device degradation rate during prolonged illumination [5].

In this study, the artificial buffer layer mixed with metal oxide NPs (WO_3, MoO_3) was used to enhance the scattering effect and to provide a mechanical endurance to the device without increasing the thickness. For metallic NPs, Shockley–Read–Hall (SRH) recombination at interfacial traps [15] is proposed as the dominant mechanism at monomolecular and bimolecular recombination. Moreover, the electrochemical impedance spectroscopy (EIS) was used to study the interface charge transport process, resistance and constant phase element. The electrical and optical properties of the devices were analyzed.

2. Experiment details

We investigated the effect of metal oxide nanoparticle mixed in PEDOT:PSS-based buffer layer on the inverted organic solar cells. The size of both the particle used in this work was 100 nm. Poly (3-hexylthiophene):[6,6]-pheny-C_{61}-butyric acid methyl ester (P3HT: PCBM) was used as an active layer. As shown in Fig. 1(a), the fabricated

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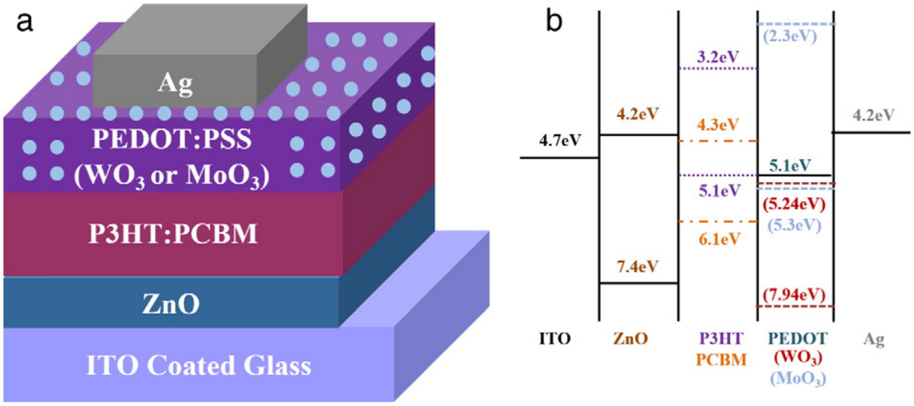

Fig. 1. (a) Schematic of the inverted organic solar cell showing ITO/ZnO/P3HT:PCBM/PEDOT:PSS(WO_3 or MoO_3)/Ag layers. (b) The energy band diagram with WO_3 and MoO_3 in PEDOT:PSS layer.

solar cells had a structure of ITO/ZnO/P3HT:PCBM/PEDOT:PSS (WO_3 or MoO_3)/Ag. For the fabrication, ITO glass substrates were cleaned in an ultrasonic bath with acetone, isopropyl alcohol, and deionized water for 20 min, respectively. ZnO was used as a buffer layer for hole blocking between the active layer and bottom electrode. At first, ZnO solution was spin coated on ITO substrate and then annealed at 200 °C for 20 min in a dry oven in ambient air. The active layer (P3HT:PCBM) was deposited on a ZnO layer by spin coating. The P3HT:PCBM mixture (P3HT:PCBM = 1:1 weight ratio) was dissolved in chlorobenzene at a concentration of 40 mg/ml. The thickness of the active layer was 200 nm in all the devices. In order to deposit hydrophilic PEDOT:PSS mixed with or without NPs on hydrophobic active layer, PEDOT:PSS was also mixed with 0.5 vol% of Triton X-100 ($C_{14}H_{22}O(C_2H_4O)n$) non-ionic surfactant. This solution was then spin coated on hexamethylene disilazane, which was pre-coated on the active layer. Thermal pre-annealing was conducted at 160 °C for 10 min in a dry oven in ambient air. Ag top electrode (100 nm) was deposited on PEDOT:PSS layer through a shadow mask by thermal evaporation, defining an active area of 0.1 cm^2. The UV-visible spectrophotometer (Shimadzu UV-1601) was used to study light absorption of the active/buffer layers. Current density–voltage (*J*–*V*) characteristics were measured with *J*–*V* curve tracer (Eko MP-160) and a solar simulator (Yss-E40, Yamashita Denso) under AM 1.5G (100 mW/cm^2) irradiation intensity. The impedance was measured using EIS. External quantum efficiency (EQE) spectra was measured under calibrated, monochromatic light illumination obtained from a xenon light source operating in the wavelength range of 300–700 nm (K3100, Mc Science). The light intensity was calibrated with a standard silicon cell (PV Measurements, Inc.). The output voltage of solar cells depends on the intensity of light. To study the light dependency, we altered the illumination intensity of solar simulator, by varying the power of the lamp power supply. The intensity of the illumination was checked every time before the measurement with a calibrated silicon cell and meter. Entire fabrication and measurement processes were conducted in ambient air.

3. Results and discussion

Fig. 1(a) and (b) shows the structure and energy band diagram of different of OSCs. The measured *J*–*V* characteristics of OSCs with PEDOT:PSS and PEDOT:PSS:WO_3 (different concentration) using a solar simulator is shown in Fig. 2(a). The control device showed a J_{sc} of 12.80 mA/cm^2. The addition of 0.1 wt% tungsten trioxide elevated the J_{sc} to 13.69 mA/cm^2. Increasing concentration of WO_3 NPs resulted in higher J_{sc}, but a threshold was seen at 1.5 wt%. At this concentration, the device gave a J_{sc} of 14.61 mA/cm^2 while the device with 5 wt% showed a lower J_{sc} of 13.22 mA/cm^2. The performance of devices improved due to light scattering. The performance of all the organic solar cells is summarized in Table 1. Use of 1.5 wt% WO_3 NPs increased the J_{sc} by 14%. 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 WO_3 NPs at 5.24 eV and 7.94 eV, respectively. The higher concentration of WO_3 NPs increased the exciton generation. However, a very high concentration of the NPs interfered with the binding of PEDOT and PSS domains which reduced the carrier mobility. A blockage in holes migration reduced the current density directing to a lower PCE. The

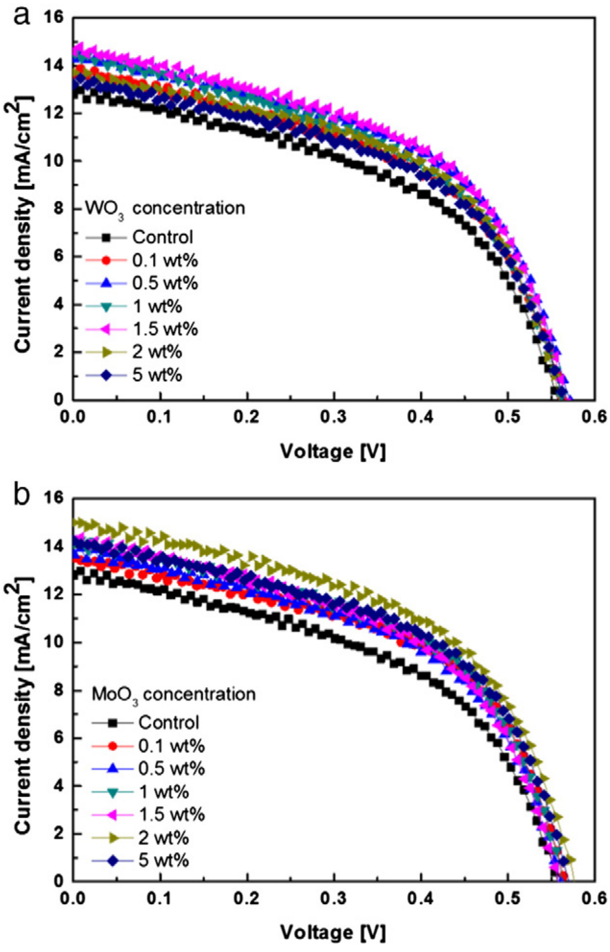

Fig. 2. (a) *J*–*V* characteristics of inverted organic solar cells using PEDOT:PSS buffer layer with different concentration of WO_3 NPs; (b) *J*–*V* characteristics of inverted organic solar cells using PEDOT:PSS buffer layer with different concentration of MoO_3 NPs; Under AM 1.5G irradiation at 100 mW/cm^2.