

HYBRID ORGANIC SOLAR CELLS BASED ON POLYMER/METAL OXIDE NANOCRYSTALS

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In this paper, we investigated the effects of ZnO nanoparticles in the active layer of organic solar cells with different hole transport layers (PEDOT:PSS and TiO₂ nanoparticles). The active layer consists of conjugated polymer poly (3-hexylthiophene) (P3HT), phenyl C₆₁-butyric acid methyl ester (PCBM) and ZnO nanoparticles. The power conversion efficiency (PCE) of the devices was improved by incorporating ZnO nanoparticles in the active layer of the devices. The mixing increased the absorbance in the visible region of the absorption spectra. The conjugation of ZnO nanoparticles enhanced the surface roughness of the films. The mixing improved the percolation path for charge carriers in the active layer of the devices.

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1. Introduction

During the last decade, new photovoltaic technologies have gained a lot of interest besides the established silicon based solar cells. Among them organic solar cells (OSCs) based on conjugated polymers have drawn a lot of attention for the manufacturing of flexible, lightweight and environment friendly photovoltaic devices. Hence, due to remarkable combination prospective of inexpensive photovoltaic devices, this can be utilized in many low cost applications. Hybrid polymer/nanoparticle solar cells are solar cells that have a light harvesting layer composed of semiconducting inorganic nanoparticles and a semiconducting conjugated polymer [1–3].

Bulk hetero-junction (BHJ) solar cells based on intimate blends of polymer donor and acceptor materials are of particular interest. Recently, the BHJ solar cells have achieved PCE of about 8.5% where P3HT with an optical band gap of 1.9 eV, acts as a photon absorber and a donor and a fullerene derivative PCBM acts as an acceptor [4-5]. However, there are some limitations in the P3HT and PCBM blend solar cells: low charge mobility, weak absorption in the visible spectrum, and low open-circuit voltage (V_{oc}) (about 0.6 V) due to extremely deep-lying “lowest unoccupied molecular orbital” (LUMO) levels of PCBM. One of the common approaches to increase the spectral breadth of absorbed photons is the use of so-called low-band-gap (less than 1.5 eV) polymers [6]. Unfortunately, low-band-gap polymer-based BHJ solar cells have achieved efficiency not more than 3.5% so far.

As an alternative polymer-based photovoltaic cell, the organic-inorganic hybrid solar cell is promising because of the advantages resulting from two types of materials with low cost and easy preparation from organic material, high electron mobility, excellent chemical and physical stability, size tunability, and complementary light absorption from the inorganic semiconductors. Various hybrid solar cells have been reported, including devices that utilize polymer in conjunction with CdSe [7], ZnO [8], TiO₂ [9], PbSe [10], CuInS₂ [11] and Si [12] spherical nanocrystals. Air-stable polymer photovoltaics were demonstrated by replacing fullerenes with ZnO nanoparticles [13].

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In our devices ZnO nanoparticles are blended with the polymers to fabricate hybrid solar cells. ZnO is a II-VI compound semiconductor with a wide band gap of 3.4 eV and a stable wurtzite structure. It has attracted intensive research owing to its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters and spin electronics [14-17]. ZnO is a potential candidate to be used as an acceptor material to increase light absorption in the active layer of P3HT:PCBM solar cells. Moreover, ZnO has an advantage of being a stable, inert and environment friendly material. Our works aim to study not only the effect of the mixing of ZnO nanoparticles but also the effect of replacing the buffer layer of PEDOT:PSS by the TiO₂ on the electrical and optical properties of the blend and hence, on the power conversion efficiency of the P3HT:PCBM solar cells.

2. Experimental Details

Indium tin oxide (ITO) coated glass substrates with sheet resistance of 5Ω/□ were purchased from Delta Technologies USA. Conducting polymer PEDOT:PSS (poly (3,4-ethylene dioxythiophene)- polystyrenesulfonate) was obtained from Heraeus Material Technology USA. Highly regioregular P3HT was purchased from Rieke Metals USA. PCBM was received from Nano-C while ZnO nanoparticles and bulk form of TiO₂ were purchased from Sigma Aldrich.

ITO were cleaned in an ultrasonic bath using detergent, acetone, 2-propanol and deionized water for 15 minutes each and dried under N₂ environment. The PEDOT:PSS was passed through 0.45 μm PVDF filter membrane. A layer of PEDOT:PSS was spin coated on cleaned ITO at 5000 rpm for 60 seconds. The PEDOT:PSS coated films were annealed at 130°C for 10 minutes in N₂ filled glove box. While, TiO₂ layer was deposited on the ITO using electron beam chamber. After annealing, the blends of P3HT:PCBM and P3HT:PCBM:ZnO in 3ml chlorobenzene solvent was stirred for 18 hours at 40°C and then spin coated on the PEDOT:PSS and TiO₂ coated ITO. These coated films were annealed at 150°C for 15 minutes in a N₂ filled glove box. Finally, for top contacts, aluminium Al (100nm) was thermally evaporated on the active layer with a contact area of 0.4cm². In further study, we denote the devices as ITO/PEDOT:PSS/P3HT:PCBM/Al (A), ITO/PEDOT:PSS/P3HT:PCBM:ZnO/Al (B), ITO/TiO₂/P3HT:PCBM/Al (C) and ITO/TiO₂/P3HT:PCBM:ZnO/Al (D)

3. Results and Discussion

Energy level diagram (a) and Schematic diagram of hybrid organic solar cells (b) are shown in Fig. 1. When light falls on the device, excitons (a combination of electron-hole pair) are generated at the interface of P3HT and PCBM. The energy of the excitons is based upon the energy level diagram. The electrons move towards top contact (Al) and holes transfer toward ITO after passing through hole transport layers.

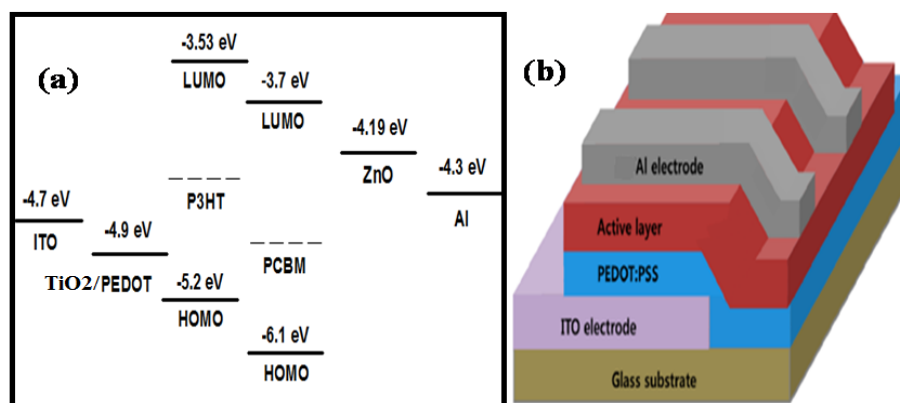


Fig. 1: Energy level diagram (a) and Schematic diagram of hybrid organic solar cells (b).

The electrical properties of the hybrid organic solar cells were measured using Keithley 2400 source meter connected with a solar simulator CT100 AAA. The current density versus voltage (J-V) graphs were recorded under AM 1.5 G and intensity of $100\text{mW}/\text{cm}^2$ as shown in Figure 2. The increase in short circuit density (J_{sc}) can be seen in Figure 2. It is observed that the PCE has been increased with the incorporation of ZnO nanoparticle in the active layer of P3HT:PCBM solar cell. It may be due to the reason that incorporation of ZnO improved the percolation path for charge carriers and enhanced the conductivity of the devices.

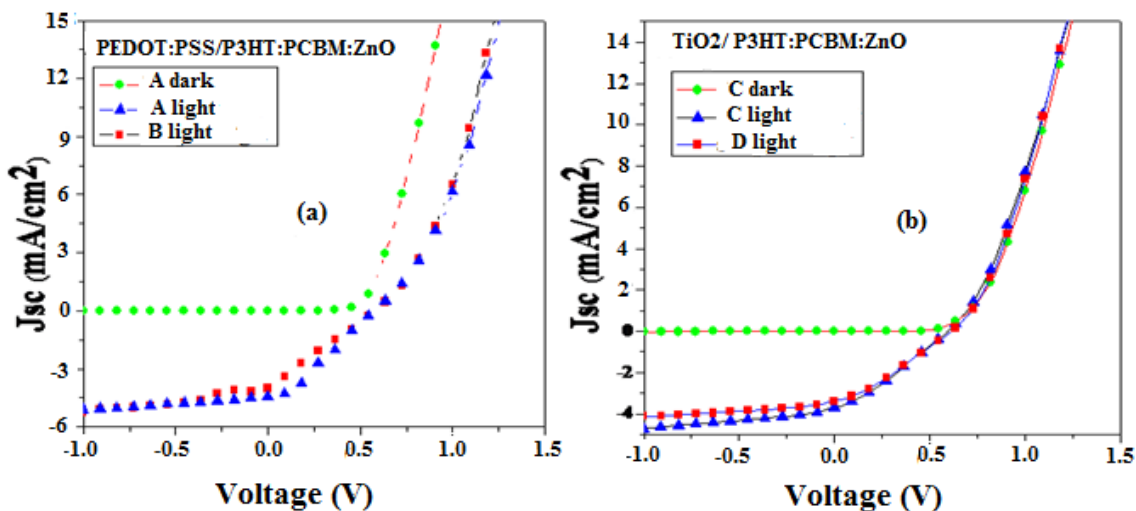


Fig. 2: J-V characteristics of the hybrid organic solar cells using different hole transport layer (HTL) as PEDOT:PSS (a) and TiO₂ (b).

The increase in efficiency is mostly due to decrease in R_s with the addition of ZnO nanoparticles in the active layer of P3HT and PCBM solar cells. This decrease in R_s improved the fill factor FF and hence PCE as shown in Table 1. The PCE increased from 0.65 to 0.77% of the active layer grown on PEDOT:PSS layer and increased from 0.61 to 0.63% using TiO₂ as a hole transport layer. The increase in J_{sc} is attributed to an increase in absorption from the ZnO and a decrease in recombination of charges owing to supportive rearrangements of energy levels of the active layer, with the addition of ZnO nanoparticles. The parameters obtained from these curves are listed in Table 1.

Table 1: photovoltaic parameters obtained from J-V curves of Figure 2.

Devices	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	R_{sh} ($\Omega\text{-cm}^2$)	R_s ($\Omega\text{-cm}^2$)	PCE (%)
A	0.59	3.70	30.0	367	20	0.65
B	0.58	4.44	30.0	560	18	0.77
C	0.59	4.11	27.0	216	25	0.61
D	0.61	3.38	30.0	464	20	0.63

The scanning electron microscope (SEM) images of all the active layers are shown in Figure 3 a-d (Refer to Table 1 for device name). It can be clearly seen from control devices A and C (Figure a and c) that P3HT and PCBM are nicely distributed throughout the film. While the

addition of ZnO nanoparticles in the active layer of P3HT:PCBM is forming percolation networks. ZnO nanoparticles agglomerated with P3HT:PCBM can be seen from samples B and D in Figures b and d.

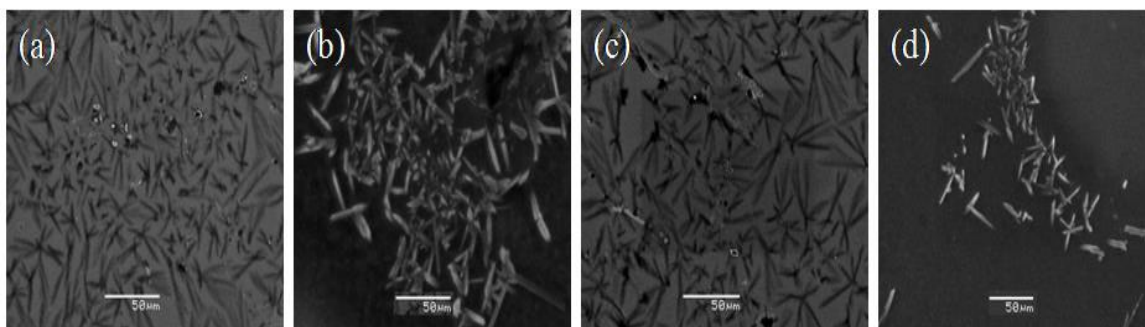


Fig. 3. SEM images of the various active layers on different HTL.

In order to correlate the relation between the roughnesses of the surfaces with the performance of the devices, atomic force microscopy (AFM) was performed as shown in figure 4. AFM images show the topography of the active layers. It shows that the films are smooth, but not uniform. The films of control device P3HT:PCBM on different hole transport layer materials have RMS roughness 3 nm with PEDOT:PSS and 4 nm on TiO_2 as shown in figure 4a and 4c. However, the films with ZnO nanoparticles in the active layer blends shows cluster feature and rough surfaces. The value of RMS roughness on PEDOT:PSS was 11 nm and on TiO_2 was 10 nm as shown in figure 4b and 4d respectively. It is reported that rough surface is a signature of polymer self-organization and ordering. The ordered structure decreases the internal resistance of the devices, increasing the photocurrent.

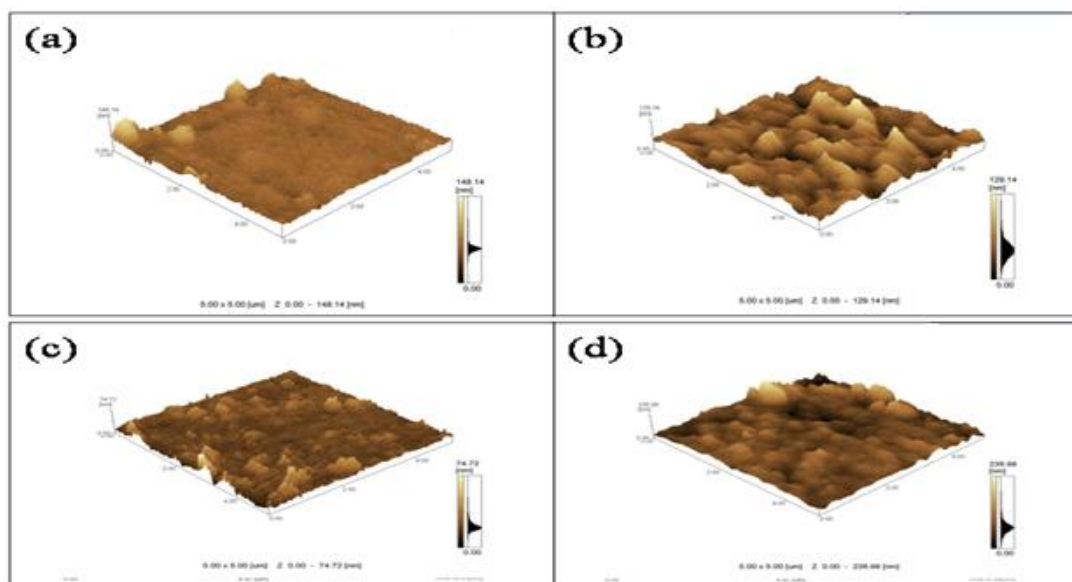


Fig. 4: AFM images of the various active layers of hybrid organic solar cells.

Figure 5 shows the absorption spectra of different active layers of the samples. It shows that the addition of ZnO nanoparticles in the active layer blends increased the absorption in the visible region and absorbed a wide range of wavelengths as is clear from Figure 5. The incorporation of ZnO improved the crystallinity of P3HT as confirmed by most pronounced shoulder at 600 nm in absorption spectra for samples 'B' and 'D'. As discussed earlier, the mixing increased the film roughness, the rough surface can absorb more sunlight due to scattering [18].

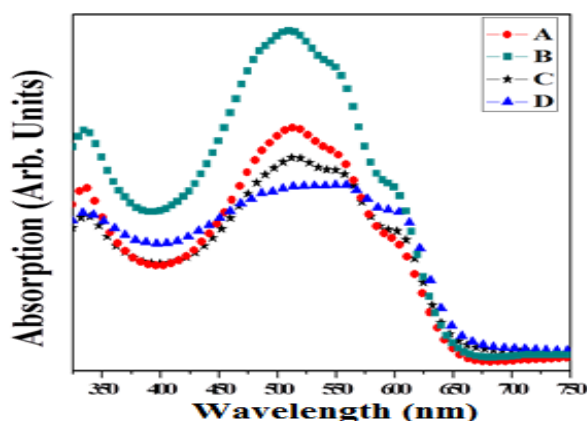


Fig. 5. Absorption spectra of various active layers on different HTL.

4. Conclusion

Hybrid organic solar cells were fabricated by incorporating ZnO nanoparticles in the active layer of P3HT:PCBM with various buffer layers were studied. The mixing of ZnO nanoparticles in the active layer of P3HT:PCBM devices enhanced the PCE of the devices from $\sim 0.6\%$ - 0.8% with PEDOT:PSS and 0.61 to 0.63 with TiO_2 buffer layer. It is found that introduction of TiO_2 as a HTL results in the rearrangement of energy levels. The increase in PCE is due to decrease in R_s and hence increase in FF with the mixing of ZnO nanoparticles in the active layer. The aggregation of ZnO nanoparticles in the active layer and formed percolation network. The film roughness and absorption in the visible region increased with addition of ZnO nanoparticles in the active layer of P3HT and PCBM.

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