EFFECT OF MIXING ZNO:TIO$_2$ NANOPARTICLES IN P3HT:PCBM SOLAR CELLS

S.Ali
A. Zareen
Dept. of NREM, University of Kurdistan, Erbil, Iraq
M. Ikram
Solar Application Lab, Department of Physics, G. C . University Lahore Pakistan
R. Murray
Department of Physics and Astronomy, University of Delaware, USA
A. Hussain
Pakistan Council of Renewable Energy Technologies Islamabad, Pakistan
S. Ismat Shah
Department of Materials Science and Engineering, University of Delaware, USA

Abstract

In this study, we examine the effect of various ratios of TiO$_2$ and ZnO nanoparticles in the active layer of organic solar cells (OSC). The organic polymers used in active layer are poly (3-hexylthiophene) (P3HT) and acceptor phenyl-C61-butyric acid methyl ester (PCBM). The active layer blend was prepared in chlorobenzene using various amount of metal oxides and PCBM, while keeping the constant ratio of P3HT. The power conversion efficiency (PCE) of the devices is found to decrease in presence of metal oxides in the blend of active layer of the devices. The PCE dropped from 1.43% to 1.29 %. The PCE decreased due to poor distribution of inorganic metal oxides in the active layer of the device, due to significant difference size of nano particles of the metal oxides. The mixing in active layer is found to decrease series resistance (Rs) of the devices and increasing fill factor (FF), but the Jsc is found to decrease probably due to increase in recombination current origionating from poor mixing of metal oxides in the active layer. The absorption and surface roughness increased with addition of the metal oxides in the active layer of the devices. The performances of the devices depend upon the optimun ratios of metal oxides with P3HT and PCBM.

Keywords: P3HT, PCBM, TiO$_2$, ZnO

Introduction

A technology that has become a cheap renewable energy source is solar cells based on polymers. Many recent studies and detailed studies have documented so far most promising results [1-6]. Copper phthalocyanine was used as electron donor (p-type) material, in the first solar cell which was designed by Tang while for electron donor (n-type) material perylene derivative has been used [7].

In organic semiconductors the efficiency of planar heterojunction devices is limited due to low exciton diffusion lengths which is usually below 20nm [8]. So the exciton generated at a distance of more than 20 nm form the interface (between p and n type materials) will not contribute to charge generation [9]. Because of this downside, the power conversion efficiency of planar heterojunction devices lie in the range of 1.0 to 1.5% [10].

With the advent of bulk heterojunction concept revolutionary breakthrough occurred [11]. According to bulk heterojunction concept, p and n type materials are thoroughly mixed and organized on Nano scale to form three-dimensional interpenetrating networks which have ability to generate charge and transport them efficiently. By amalgamation of inorganic semiconductor materials the performance of these devices can be increased to form hybrid organic-inorganic solar cells (HSC) [12]. Till now various n-type semiconductor oxides have been applied such as TiO_2, ZnO [13], SnO_2, and Nb_2O_5 [14]. These oxides gives high stability to photo corrosion can absorb the UV [15] and have a large band gap. In HSC the light harvesting conjugated polymer acts as the hole transporter while the semiconductor oxides can be used as an electron acceptor to increase the electron mobility [16]. The blends of polymer and metal oxide can be formed by the interaction of semiconductor oxide and conjugated polymer [17]. Solar cells prepared from hybrids of polymers and inorganic nanoparticles of metal oxide have fascinated extensive importance due to their light weight and without vacuum processing by spray deposition on flexible substrates.

Our work focus to explore the effect of metal oxide nanoparticles which has been added in the active layer with P3HT & PCBM due to excellent carrier mobility. Many metals oxide nanoparticles available for this purpose but the mostly used are ZnO & TiO_2. However, the PCE of devices was improved by mixing the different ratios of ZnO& TiO_2 nanoparticles with size (<100nm) in the blend of active layer. We used different proportions of PCBM: ZnO: TiO_2 while keeping the constant ratio of P3HT in the solvent of chlorobenzene. PCBM and TiO_2: ZnO nanoparticles were used as an acceptor material with P3HT as donor.

Experimental details

Hybrid solar cells devices were fabricated by spin coating poly (3,4 polyethylene dioxythiophene polystyrenesulfonate) PEDOT:PSS polymer at 3000 rpm on ultrasonically cleaned Indium tin oxide (ITO) glass substrates with sheet resistance of 8-10 Ω/square). The samples were baked in N_2 enviroment inside glovebox at 130^0C for 10 minutes. The blend of P3HT:PCBM:ZnO:TiO_2 of different weight ratios (1:0.7:0, 1:0.55:0.075:0.075, 1:0.35:0.175:0.175, 1:0.15:0.275:0.275 and 1:0:0.35:0.35) in 1.0 ml chlorobenzene (CB) solvent after stirring 12 hours at 40 ^{0}C was spuned on the top of PEDOT:PSS layer. The spuned film were sintered on the hotplate at 150 ^{0}C for 15 minutes in nitrogen environment. Finally, the Aluminium (Al) contact 100 nm film thickness were deposited using thermal evaporator. The aluminium contact area of 0.4 cm^2 was maintained for all devices. The devices structure was ITO/PEDOT:PSS/(P3HT:PCBM:ZnO:TiO_2)/LiF/Al.

Results and discussion

The Fig. 1 shows absorption spectra with the different ratios of the devices. The addition of metal oxides enhanced the absorption of the active layer of the devices and introduce red shift in the absorption spectra. The maximum absorption is achieved in the case of the ratio of 1:0.55:0.075:0.075. The absorption increased due to modification in band gaps of the donor material due to mixing of metal oxides. As we increased the amount of both metal oxides the absorption spectra shows decrease in absorption for ratios above the optimum value.

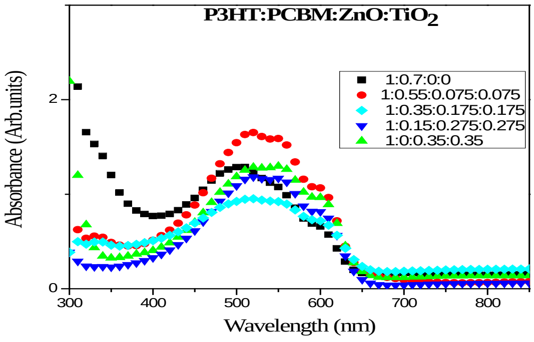

Fig 1. Optical properties of different ratios of P3HT: PCBM: ZnO: TiO_2 devices.

Fig. 2 shows the current density curves of the devices under dark and illumination condition. The addition of the metal oxides in the active layer of the devices shows decrease in the PCE with respect to pure P3HT:PCBM devices. The decrease in PCE is attributed different particle size of both metal oxide nanoparticles ZnO(<100 nm) and TiO_2 (10 nm) nanoparticles in the blend of P3HT and PCBM. The Table-1 shows improvement in FF and decrease in Jsc. The devices with active layer ratios of 1:0:0.35:0.35 showed low efficiency due to agglomeration of both TiO_2 & ZnO nanoparticles probably due to lack of PCBM, the acceptor material also acting as surfactant for the metal oxides. This may result in damaging the interpenetrating network of charge carriers.

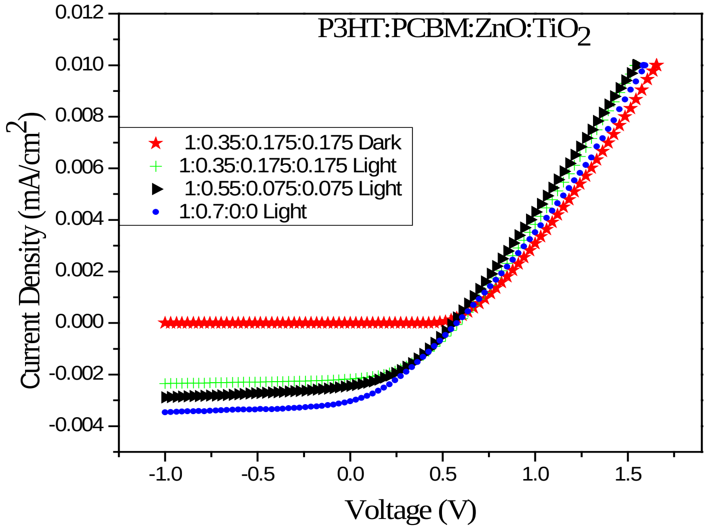

Fig. 2. J-V characteristics of P3HT: PCBM: ZnO:TiO_2 devices with different ratios.

External quantum efficiency (EQE) curves are shown in Fig. 3. Both the metal oxides are an absorber of UV (200-400 nm). The presence of ZnO& TiO_2 in P3HT: PCBM blend can be seen in the figure in the form of hump. The value of EQE of P3HT:PCBM device of 39 % in visible region at 480 while in the presence of both metal oxides in active layer of the device, its value is 26.8%. EQE decreased with increasing amount of metal oxides in the blend of active layer of the devices. The fact is attributed to increase in recombination current with mixing of metal oxides.

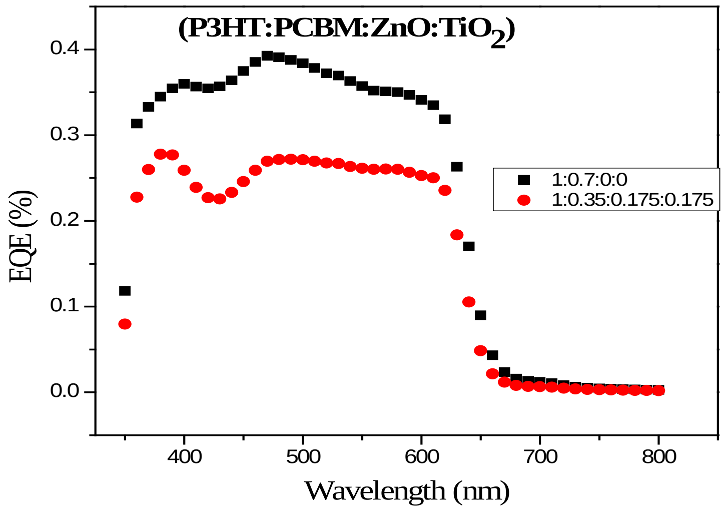

Fig. 3. EQE curves of P3HT: PCBM: ZnO: TiO_2 with different ratios (1:0.7:0:0, 25:9:4.50:4.50)

Fig. 4 shows the field emission scanning electron microscope (FESEM) images of different blend composition of P3HT: PCBM: ZnO:TiO_2. Fig. 4a shows that the ZnO & TiO_2 particles have poorly mixed in the blend of 1:0.35:0.075:0.075 and form chunks of metal oxides probably due to lack of PCBM in the blend. Whereas the ratio without PCBM 1:0.55:0.175:0.175 shows the rice grain trend type surface, also suggesting poor distribution of metal oxides as shown in Fig. 4b.

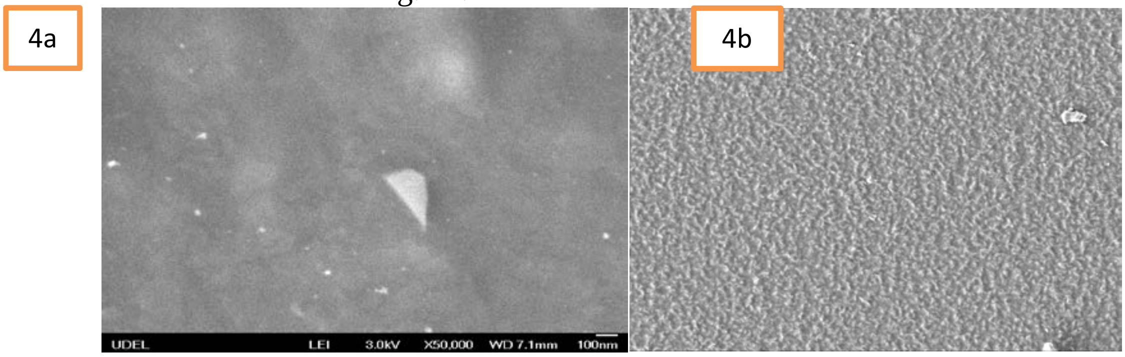

Fig. 4. FESEM images of devices with different ratios of P3HT: PCBM: ZnO: TiO_2 1:0.35:0.175:0.175 a, 1:0.55:0.075:0.075 b.

The surface topography of the blend with different ratios 1:0.35:0.175:0.175 and 1:0.55:0.075:0.075 measured by atomic force microscopy (AFM) are shown in Fig. 5. Both Figures (5a& b) show surfaces are smooth and uniform with roughness values of 18.6 nm and 23 nm respectivly. The rough surface suggests a higher degree of agglomeration of metal oxides.

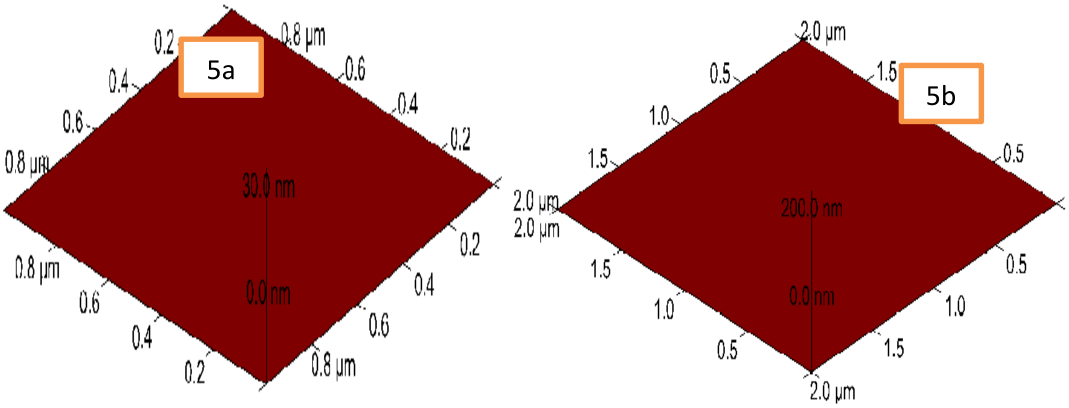

Fig. 5.

AFM images of devices with different ratios of P3HT:PCBM:ZnO:TiO_2 (1:0.35:0.175:0.175 a), 1:0.55:0.075:0.075 b)

S:No	**P3HT:PCBM:TiO_2:ZnO**	**V_{oc}(V)**	**J_{sc}(mA)**	**FF (%)**	**R_{sh}(ohm)**	**R_s(ohm)**	**PCE%**
1	1:0.7:0	0.57	7.61	32.56	553	101	1.43
2	1:0.55:0.075:0.075	0.55	6.11	38.43	888	92	1.29
3	1:0.35:0.175:0.175	0.58	5.42	40.64	1780	82	1.28
4	1:0.15:0.275:0.275	0.52	3.08	36.09	794	103	0.57
5	1:0:0.35:0.35	0.24	0.02	37.11	75600	116	0.0013

Table 1. PV parameters obtained from J-V curves in Fig. 2

Conclusion

In summary, We prepared hybrid solar cells with different ratios of PCBM, ZnO and TiO_2 keeping constant ratio of P3HT in CB solvent. The results show that the mixing of various ratios of metal oxides in P3HT & PCBM blend introduce red shift in absorption spectra and improves the absorption in the visible region. The presence of metal oxides in the blend of devices decreases Rs and increases FF but decreases Jsc and EQE. This result in low PCE of the devices. The irregular distributions of metal oxides in chlorobenzene with different particle size increases recombination current. The recombination current dominates Rs and decrease the PCE of the devices. The EQE results exhibited the presence of ZnO& TiO_2 in UV region of the curve in the blend of P3HT: PCBM. The replacement of PCBM with suitable quantity of metal oxides enhanced the Voc and FF of the device. But the extra amount of both metal oxides in the blend damaged the performance of the device due to agglomeration of ZnO and TiO_2. The FESEM images show formation of chunks with small amount of PCBM in the blend and rice grain trend in excess of PCBM. The AFM images show that films are smooth and uniform. The film roughness increase with increasing amount of metal oxides in the blend of active layer.

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