



Performance enhancement of inverted type organic solar cells by using Eu doped TiO₂ thin film

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ABSTRACT

In the present work, europium (Eu) has been used as a dopant element in titanium dioxide (TiO₂) crystal structure to enhance the photovoltaic performance of the inverted type organic solar cells fabricated with TiO₂ thin film as an electron transport layer. Poly(3-hexylthiophene):phenylC61-butyric acid methyl ester (P3HT:PCBM) blend has been used as an active layer and Eu:TiO₂ thin films have been fabricated with different Eu concentrations as 0, 1, 5, 7 and 10% (w/w) by sol-gel method. Effect of Eu doping concentration on the photovoltaic performance of the inverted type solar cells has been investigated. Inverted type organic solar cells using Eu doped TiO₂ thin films as electron transport layer has been fabricated as a structure of ITO/Eu:TiO₂/P3HT:PCBM/Ag. Power conversion efficiency of the fabricated solar cells increased from 1.16% to 2.47% at 5% Eu doping concentration. Electron transport and hole blocking properties of the TiO₂ inter layer has been improved by Eu doping.

1. Introduction

Nowadays, bulk-heterojunction (BHJ) type organic solar cells formed by conductive polymers and fullerene derivatives have attracted much attention because of their some advantages such as low fabrication cost, enabling flexible and large area device manufacturing, light weight [1–3]. Although many studies have focused on improvement the power conversion efficiency and life time of organic solar cells with new device structures and new donor-acceptor materials it has not yet been sufficient progress. [4–6]. Generally, conventional organic solar cells are fabricated to replace the active layer between the low work function metal cathode and hole transport layer (PEDOT:PSS). The major problem in such devices is degradation of low work function metal cathode due to oxygen diffusion and corrosion of ITO surface because of acidic nature of PEDOT:PSS [7–10]. In order to overcome such problems, inverted type organic solar cells having excellent device stability and low production cost have been developed in recent years [11–13]. The direction of the charges in inverted type solar cells is reversed, and thus, air stable high work function metals such as Au, Ag etc. can be used as anode layer. Also, the use of acidic PEDOT:PSS on

ITO surface as buffer layer is prevented, all of which opens the way for the commercialization of organic solar cells [14–16]. Extensively, metal oxide materials such as SnO₂, Cs₂CO₃, ZnO and TiO₂ etc. are used as buffer layer to collect electrons by ITO electrode [17–19]. Among these metal oxides TiO₂ is a very famous oxide material for using in inverted type solar cells as electron collective and hole blocking layer. TiO₂ is a non-toxic material and has high charge carrier mobility, low manufacturing cost and high optical transparency in the visible region [20–22]. Besides, TiO₂ is a candidate material for inverted solar cells because of the conduction band (–4.4 eV) of TiO₂, and LUMO (–4.3 eV) level of PCBM are very suitable for each other to charge transfer, and valance band (–7.5 eV) of TiO₂ is low enough to block hole transport [23,24]. Physical properties of metal oxide semiconductors such as electrical, optical and structural can be enhanced by doping them with various elements. It is well-known that the physical characteristics of TiO₂ thin films such as charge carrier recombination, electron transfer, structural, photo activates and magnetic properties are changed easily by doping process. Because of this, various metal ion doped TiO₂ thin films are used and investigated very extensively as interlayer to use in the inverted type organic solar cell structures.

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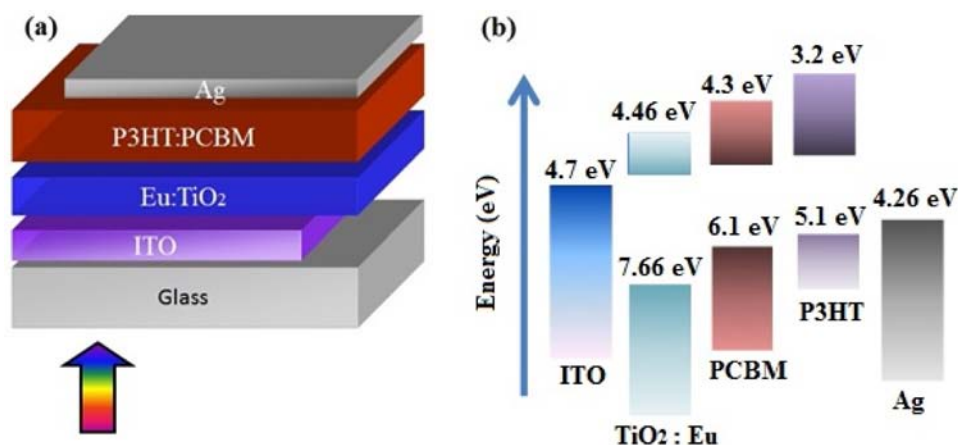


Fig. 1. (a) Schematic illustration of inverted type organic solar cell. (b) energy level diagram of the fabricated devices.

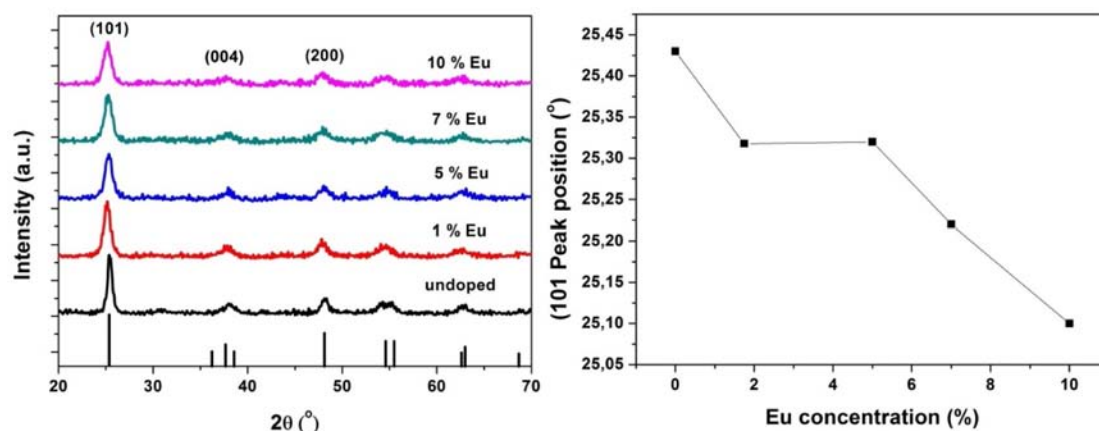


Fig. 2. (a) X-ray diffraction spectra of the Eu-doped TiO_2 thin films with the standard differential peaks of anatase TiO_2 (JCPDS No. 21–1272). (b) the (101) peak position according to Eu concentrations.

Doping process of TiO_2 can be significant effect on its electrical and optical properties. Metal ion doping process especially rare earth ion doping is a common used way to modify the mobility and surface roughness, optical and electrical properties of electron transport layer in the inverted type organic solar cells [25–28].

Many studies were performed in the literature about effect of dopant ions on the properties of the TiO_2 thin films. Cd, Sn, Zn, Mn and Fe elements was used as dopant materials in TiO_2 to improve power conversion efficiency of inverted type solar cells [29–31]. Lanthanides are very suitable dopants for modifying the electronic, crystal and optical properties of TiO_2 due to their 4f electronic configuration. Among the lanthanides, especially Eu was used as dopant for TiO_2 extensively in the literature for various application areas. Hoda Hafez and coworkers used Eu as doping element in TiO_2 nanorods for dye sensitized solar cell application. They have obtained the positive effect of Eu doping in TiO_2 on power conversion efficiency of dye sensitized solar cell [32].

In the present paper, Eu doped TiO_2 thin films were fabricated and characterized for used as an electron transport layer in inverted type organic solar cell structure. Device structures were constructed as ITO/Eu:TiO₂/P3HT:PCBM/Ag. The effect of Eu doping concentration (0, 1, 5, 7, 10%) on structural properties of TiO_2 thin films and efficiency of inverted type organic solar cells manufactured by using TiO_2 interlayer were investigated. Short circuit current density of the fabricated inverted type organic solar cells was increased up to 5% Eu doping concentration. Fabricated inverted solar cell efficiency was enhanced by using Eu doped TiO_2 thin films as an interlayer. This can be attributed to that charge injection and selection in the TiO_2 interlayer is affected by Eu doping.

2. Experimental

TiO_2 thin films were synthesized using the sol-gel method. Titanium n-butoxide, ethyl alcohol, 2-propanol, and acetic acid were mixed with (1:20:20:0.15) molar ratio, respectively, for 5 nights at RT. Eu doped TiO_2 thin films were prepared with $\text{Eu}(\text{CH}_3\text{CO}_2)_3$ (Europium acetate) adding into the solution containing a mixture of ethyl alcohol, 2-propanol, and acetic acid and stirring for five hours at room temperature. Next titanium n-butoxide was added drop wise to this sol-gel mixture. The Eu amounts in samples were arranged as 1, 5, 7 and 10% according to Ti amount (weight) in the solution. To fabricate the inverted type devices, ITO substrates were firstly ultrasonicated with propanol, acetone, and distilled water respectively, for 15 minutes. In order to obtain the Eu doped and undoped TiO_2 thin films spin coating method was used and then TiO_2 thin films was annealed at 500 °C for 60 min. with a heating rate of 10°C/min. In order to prepare the active layer P3HT and PCBM (1:1 wt/wt) were solved in dichlorobenzene and stirred with a magnetic stirrer at 50 °C for 24 h and coated on TiO_2 layers with spin coater at 1000 rpm for 60 s. Then, Ag (100 nm) was coated with thermal evaporation as hole collecting and contact layers by using a shadow mask to define an active area of 0.04 cm². The inverted type organic solar cells with structure of ITO/ TiO_2 /P3HT:PCBM/Ag and ITO/Eu: TiO_2 /P3HT:PCBM/Ag were manufactured as shown in Fig. 1(a) and (b) present the energy level diagram of the assembled device structure [33,34]. Current density-Voltage measurements were carried out with Keithley 4200 semiconductor characterization system and 100 mW/cm² solar simulator (Thermo Oriol) (AM 1.5G) was used as a light source. A reference photodiode was used to calibration of solar simulator. The surface properties of the Eu doped and undoped

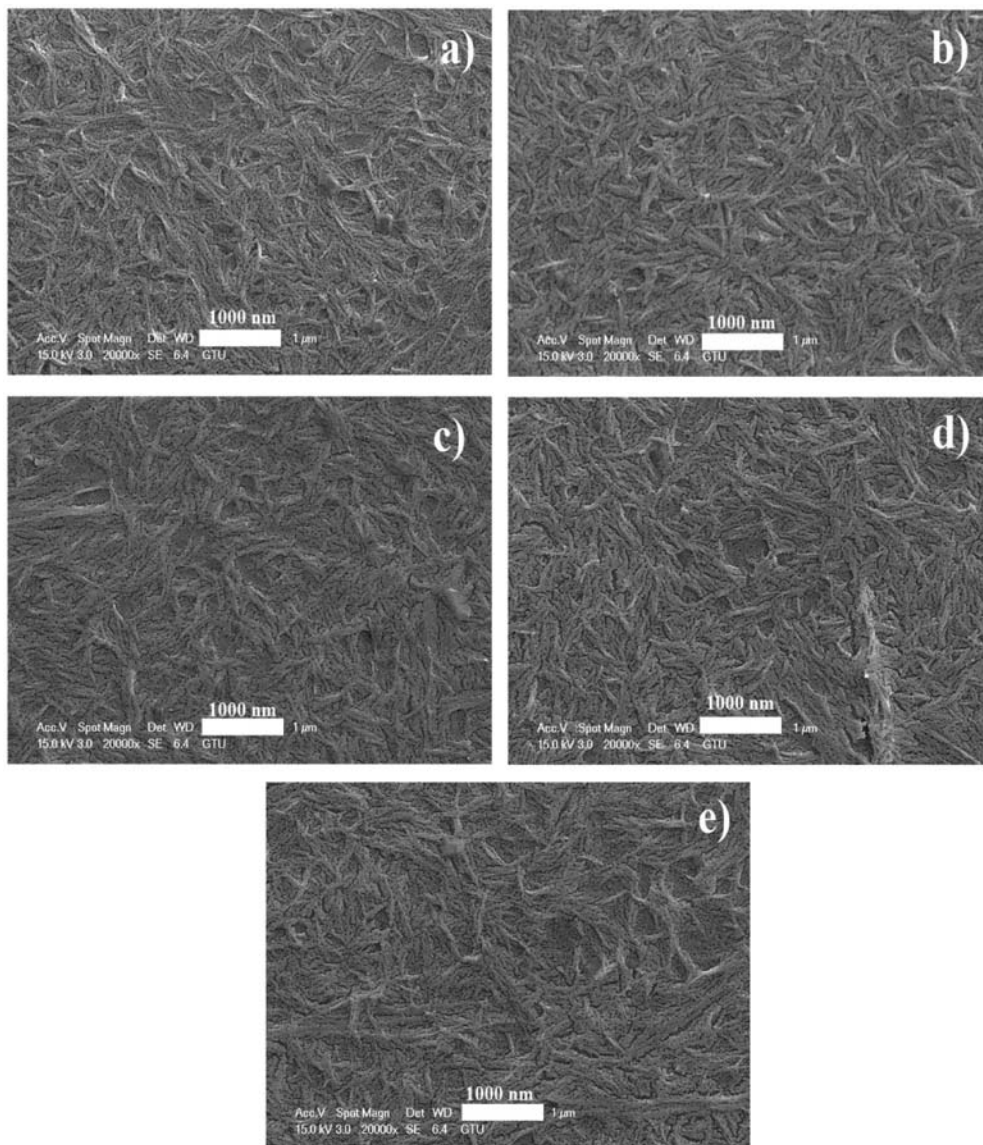


Fig. 3. SEM image of TiO₂ thin films with Eu doping concentration of 0 (a), 1 (b), 5 (c), 7 (d), 10 (e) at %. Scale bar given in the figures is 1 μ m.

TiO₂ thin films were investigated by using scanning electron microscopy (SEM, SEM-Jeol JSM 6335). XRD measurements of the TiO₂ thin films were carried out by using Rigaku smart lab. X-Ray diffractometer (XRD, CuK α , λ = 0.154 nm). XPS analyses of pure and Eu doped TiO₂ thin films were performed by using a Thermo 10 Scientific K-Alpha X-ray photoelectron spectrometer with monochromatic Al K α radiation (1486.3 eV) as a X-ray source.

3. Results and discussion

X-Ray diffraction (XRD) was used to characterize the crystal properties of Eu doped and undoped TiO₂ thin films. XRD spectra of the thin films on the Y axis offset were given in Fig. 2(a). It is clearly seen from Fig. 2 that diffraction peaks of the fabricated TiO₂ thin films point out anatase phase and no other phase were obtained by Eu doping. Moreover, it can be noticed from Fig. 2(a) that while increases Eu doping concentration intensity of diffraction peaks decreases. Fig. 2(b) displays the (101) peak position as a function of Eu concentration in the TiO₂ crystal structure. The XRD peaks of the (101) plane shift to lower diffraction angle by increasing Eu doping concentration. It can be attributed that doped Eu ions cause to deterioration the crystal structure of the TiO₂ thin films due to the charge imbalance and unconformity of

the atomic radii between the Eu and Ti ions (Eu^{3+} = 0.95 Å and Ti^{4+} = 0.68 Å) in the crystal structure. The expansion of the volume of Eu-doped TiO₂ crystal cell occurs because the Ti–O bonds are shorter than the Eu–O bonds. The change in cell volume, bond length and charge balance may cause the shift (101) peak position to lower angles. [28,35,36].

The scanning electron microscope (SEM) images of Eu doped TiO₂ thin films and pure TiO₂ thin film are given in the Fig. 3. SEM images of the manufactured Eu doped and undoped TiO₂ thin films are given in Fig. 3. It is clearly seen from Fig. 3 that fiber like structures were formed in the surface of the all samples. Moreover surface properties almost unchanged by Eu doping.

The chemical components of the Eu doped and pure TiO₂ thin films were investigated by X-Ray Photoelectron Spectroscopy (XPS). Fig. 4(a) shows the XPS survey spectra of Eu doped and undoped TiO₂ thin films that give Ti3p, Ti3s, Ti2p, O1s, C1s and Eu4d peaks. The XPS survey spectra show that the Eu doped and undoped TiO₂ films contain Ti, O, C, and Eu elements. High resolution XPS spectra's of O1s, Ti2p and Eu4d of doped and undoped TiO₂ thin films are given in Fig. 4(b), (c) and (d), respectively. The O1s spectra contain only one peak at 530.65 eV for undoped TiO₂ thin films, and no hydroxyl peaks were observed in the spectra (Fig. 4(b)). Peak position of the O1s slightly

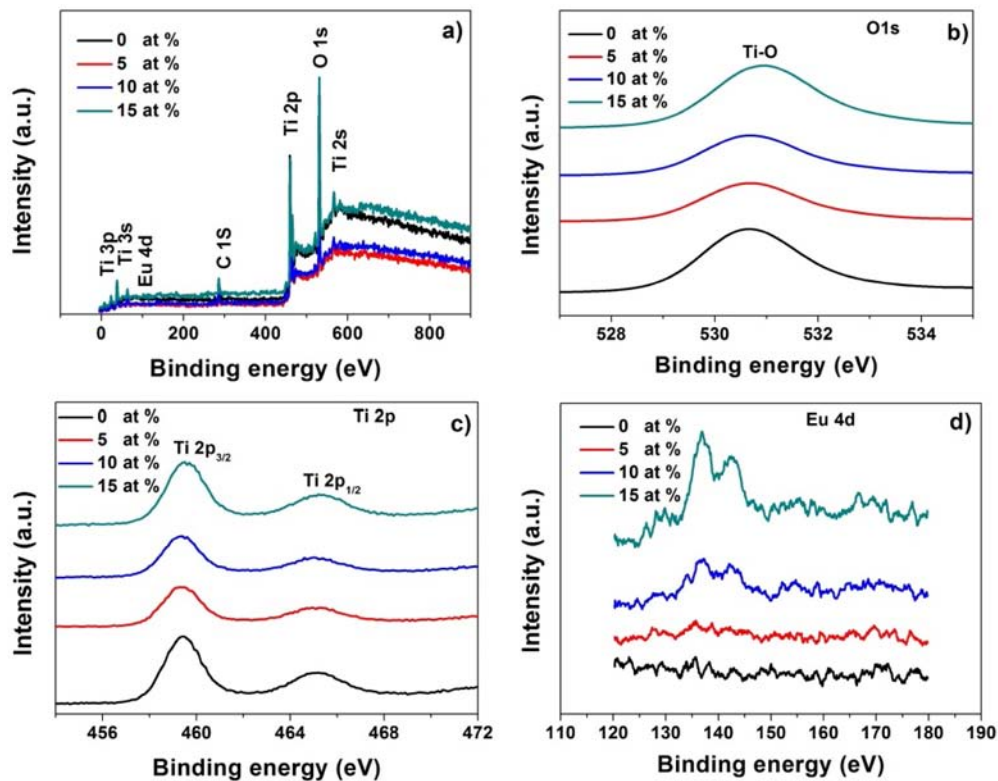


Fig. 4. Core level XPS spectra for the Eu doped and undoped TiO_2 thin films, (a) The XPS survey spectra of Eu doped and undoped TiO_2 thin films that gives Ti3p, Ti3s, Ti2p, O1s, C1s and Eu4d peaks, (b) XPS spectra's of O1s, (c) Ti2p and (d) Eu4d of doped and undoped TiO_2 thin films.

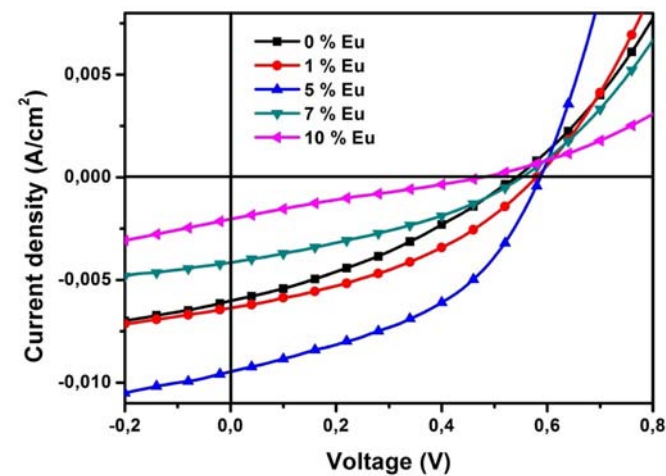


Fig. 5. J-V characteristics of inverted type organic solar cells fabricated with Eu doped and pure TiO_2 thin films.

Table 1
Photovoltaic parameters of the fabricated devices with Eu doped and pure TiO_2 thin films.

Eu concentration	FF	V_{oc} (volt)	J_{sc} (mA/cm ²)	η (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)
0%	0,36	0,54	6,01	1,16	62	238
1%	0,40	0,56	6,37	1,42	47	268
5%	0,44	0,58	9,47	2,47	25	241
7%	0,35	0,54	4,16	0,78	71	277
10%	0,24	0,46	2,01	0,22	250	212

shifts for 15% doped sample at 530.97. There are two peaks positions for Ti2p spectrum as $\text{Ti}2p_{1/2}$ and $\text{Ti}2p_{3/2}$ at 465.38 eV and 459.40 eV, respectively (Fig. 4(c)). This indicates that Ti^{4+} is placed in tetragonal crystal structure. Fig. 4(d) shows that the energy level of Eu 4d stays at

136.7 eV and 142.3 eV. These peaks can be attributed to Eu^{3+} ions configurations, and here, the existence of Eu in the $\text{TiO}_2:\text{Eu}$ thin film can be proved with this spectra [37]. Both of the O1s and Ti2p peaks shifts demonstrate that Eu^{3+} is placed in TiO_2 and the $\text{Eu}-\text{O}-\text{Ti}$ bonds are formed in the crystal lattice [38,39]. According to literature values of pure europium, the Eu 4d region shows two peaks in the range of 128.5–128.7 eV. [40]. The XPS spectrum of Eu_2O_3 is given by both the shifting of Eu 4d peaks and O1s. Fig 4(b) and (d) depict that Eu 4d peaks shift from low binding energy to higher binding energy as O1s peak. Our XPS results are agreement with literature values for Eu_2O_3 [41]. In addition, the binding energy values of Ti 2p get higher and higher values with increasing Eu doping, this behavior is compatible with TiO_3 format [40].

Current density- voltage (J-V) curves of the solar cells fabricated with different Eu doping concentrations ranging from 0% to 10% under illumination conditions are shown in Fig. 5. Shunt resistance (R_{sh}) and series resistance (R_s) were obtained from the invers slope at V_{oc} and J_{sc} in the J-V graph, respectively. The open circuit voltage (V_{oc}), short circuit current, filling factor (FF), power conversion efficiency (η), shunt resistance (R_{sh}) and series resistance (R_s) were estimated from the J-V curve and summarized in Table 1. Inverted type organic solar cell fabricated with undoped TiO_2 electron selective layer exhibited power conversion efficiency of 1.16%, short circuit current of 6.01 mA/cm², filling factor of 0.36 and open circuit voltage of 0.54 V. The V_{oc} , FF and J_{sc} increased with increasing Eu dopant concentration in TiO_2 layer from 0% to 5% concentration value. On the other hand, photovoltaic performance of the device decreased with lower FF, V_{oc} and J_{sc} when concentrations continued to increase. Besides, R_s increase and R_{sh} decrease with increasing Eu concentration up to 5%, and after that concentration level, R_s begun to increase and R_{sh} begun to decrease again.

Fig. 6 shows the photovoltaic performance of the fabricated inverted type solar cells depend on Eu concentrations. FF, V_{oc} , J_{sc} and η were investigated and dependence of Eu concentration clearly demonstrated. It is clearly seen that J_{sc} , V_{oc} and FF are enhanced by increasing

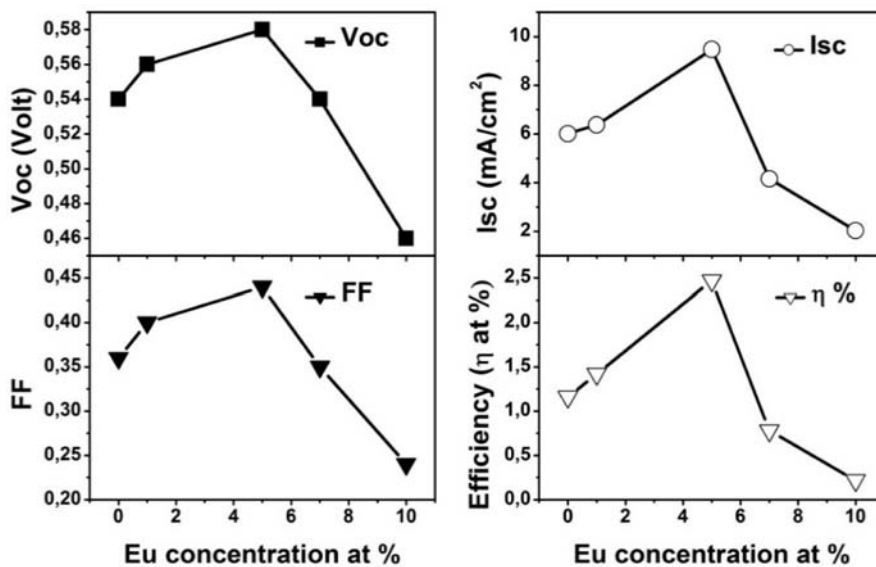


Fig. 6. Solar cell parameters of the solar cell fabricated with Eu doped and undoped TiO₂ electron transport layer (a) Voc; (b) Jsc; (c) FF; and (d) η (%).

Eu concentration up to 5%. For higher concentration of Eu than 5% all photovoltaic parameters decreased. Similarly, the power conversion efficiency of the devices increased from 1.16% to 2.47% with 5% Eu concentration, and it suddenly decreased to 0.78%, and then, to 0.22% at 7% and 10% doping concentration, respectively.

In order to enhance the transport properties of the TiO₂ layer doping with metal ions frequently used method. Eu was used as a dopant material in this study and power conversion efficiency enhanced by 2 times with 5% Eu doping concentration according to undoped sample (Table 1). It can be attributed to that electron transport properties of the TiO₂ layer improved with Eu doping. Eu doped TiO₂ can behave luminescence conversion material and it is considered one of the best red luminescence material (at 580–640 nm) [42]. Eu doped TiO₂ absorb UV light and convert it to red light because of that active layer can absorb more photon and this phenomena can cause the increase the Jsc [32]. Doping of Eu in TiO₂ can increase Fermi level [REF] due to fact that injection of electrons can increase from active layer to TiO₂ conduction band and also this behavior can reduce electron – hole recombination's at the interface. Deep trapping levels can be occur when Eu doped in TiO₂ because of that lowering the Fermi level close to conduction band edge which enhance the electron transport and current density. [25,43,44]

Eu doped TiO₂ has been used to improve efficiency of the dye sensitized solar cells and it has been obtained doping of Eu effectively increase current density and power conversion efficiency. In this study we show that for the first time Eu doping process works effectively for the inverted type organic solar cells and increase current density almost by 2 times. The improved FF and Jsc values of the fabricated solar cells with Eu doped TiO₂ electron transport layer are because of smaller R_s of Eu doped sample than undoped sample, and larger R_{sh} of Eu doped sample than pure TiO₂ sample (Table 1). It was obtained from the resistivity measurements of the fabricated solar cells that the resistivity of the Eu doped TiO₂ electron selective layer is smaller than the undoped sample. This low resistivity enhances the electron transport from the active layer to charge collecting electrode. For this reason, Jsc of the solar cell increased from 6.01 mA/cm² to 9.47 mA/cm² for inverted organic solar cell with 5% Eu doping concentration. The decrease of the device performance for higher doping concentrations can be attributed to the saturated electron barrier height and more electron trapping centers that decrease the photo current transport from the active layer to electrode [45].

4. Conclusion

Eu doped and undoped TiO₂ thin films were successfully produced on ITO substrates and effect of Eu doping on structural and morphological properties of the TiO₂ thin films were investigated. Fiber-like structures was observed on the all samples. The existence of Eu in the TiO₂:Eu thin film can be proved with XPS spectra. P3HT:PCBM active layer based inverted type organic solar cells were produced by using Eu doped TiO₂ thin films as an electron transport interlayer in the present work. The most significant output of this study is to exhibit a quantitative and valuable optimization for fabrication of inverted type organic solar cells with Eu doped TiO₂ thin films. J_{sc} of the fabricated inverted type organic solar cells was increased from 6.01 mA/cm² to 9.47 mA/cm² with the 5% Eu doped TiO₂ thin film, and solar cell efficiency (2.47%) was enhanced by using Eu doped TiO₂ as electron selective layer compared to solar cell fabricated with undoped TiO₂ thin film (1.16%). This can be attributed that electron transport and hole blocking in the TiO₂ interlayer is affected by Eu doping.

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