

M. AHMADI*[#], S. RASHIDI DAFEH*, S. GHAZANFARPOUR*, M. KHANZADEH***FIRST OBSERVATION OF VERTICALLY ALIGNED CESIUM DOPED ZnO NANORODS AS AN EFFICIENT ELECTRON TRANSPORTER IN POLYMER SOLAR CELL**

Single crystalline cesium doped ZnO nanorods with homogeneous size and shape were grown hydrothermally on ITO substrates that are presented in our previous work. According to the previous work, XRD analysis showed that cesium doped ZnO nanorods are wurtzite single crystals and are grown preferentially along the c-axis. Also, the electrical conductivity of doped ZnO showed higher values for the 1% cesium, which confirmed incorporation of the cesium dopant. Cesium doped ZnO nanorods are suitable candidates for applications in solar cells. So, in this research, we employed cesium doped ZnO nanorods with the different dopant concentration in inverted polymer solar cell. By comparing the effect of doped ZnO nanorods with diverse dopant concentration (0, 0.5, 1.0, 1.5 and 2%) on the performance of devices, 1.0% cesium doped ZnO was found as the most effective doping level among the selected doping concentrations. Also, using 1.0% cesium doped ZnO nanorods, J_{sc} of 8.21 mA/cm², V_{oc} of 0.541V and Fill Factor of 63.01% were achieved, which led to power conversion efficiency of 2.80%.

Keywords: Inverted polymer solar cell, Cs doped ZnO nanorod, electron transporter.

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1. Introduction

Recently, bulk heterojunction Polymer solar cells (PSCs) had attracted great concentration, owing to their numerous profits such as flexibility, low-temperature processing, and low-cost preparation on large area [1-4]. Rapid progress in the efficiency of PSCs has been gained by continuous efforts such as optimizing preparation conditions [5]. We should know that polymer solar cell with regular structure suffers from the degradation of active layer and ITO for the reason that acidic nature of PEDOT: PSS and oxidation of low-work-function top metal layer in air [6-8]. One approach to solve this problem is to apply an inverted structure and using modified buffer layer between the cathode and the active layers. Utilizing a suitable buffer layer between the active layer and the bottom electrode is a serious strategy for yielding high-performance polymer solar cells. N-type metal oxides such as titanium oxide [9-11], ZnO [12-14] have been shown to be effective, selective electron and hole blocking layer. Among these, ZnO nanostructures on account of their solution process ability, better electron transportation, high transparency, nontoxicity and more, are preferable over other materials [15,16]. ZnO is intrinsically an n-type semiconductor has been the subject of a huge number of scientific and technological studies due to its direct wide band gap of 3.37 eV at room temperature (RT) with the large exciton binding energy (60 meV)

[17,18]. Some properties of ZnO thin film can be improved by doping with impurities such as Al [19], Ga[20] and so on that the properties of ZnO thin film can be improved with a small amount of impurities. However, pure ZnO thin films have poor properties, usually presents a low conductivity due to a low carrier concentration and doping with various dopants are usually necessary to improve these properties. Some elements such as Ga have been commonly pragmatic in this regard. because of its properties such as resistance to oxidation and cheaper than other materials. Furthermore, the covalent bond length of Cs-O is similar to that of Zn-O. There are some reports that describe the doping of ZnO with alkali metals such as cesium. Recently, inverted polymer solar cells using a cesium doped ZnO electron transport layer has been also reported [21]. Although the role of cesium as an effective interfacial material has been proven [22], ZnO thin films doped with elements such as Cs have been rarely used as ETL in polymer solar cells. In previous work [22], we synthesized Cs doped ZnO NRs via hydrothermal method under optimum conditions. But, in the present work to make the high efficiency inverted polymer solar cell based on P3HT: PCBM we used and examined the Cs doped ZnO nanorods (NRs) with dopant concentration from 0.0 to 2.0% to make of high efficiency inverted polymer solar cell based on P3HT: PCBM.

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2. Experimental details

Pure ZnO and Cs doped ZnO thin film NRs were prepared via hydrothermal method were presented in our previous report [22]. In order to study the effect of doping on the photovoltaic performance, inverted organic solar cells were fabricated using Cs doped ZnO NRs with dopant concentrations from 0.0 to 2.0%. For fabrication of them, an active layer of P3HT:PCBM (1:0.9 wt.%) prepared from chlorobenzene and was doctor-bladed on top of the pure and Cs doped ZnO NRs. Afterward, around 30 nm thick layer of poly (3,4-ethylenedioxythiophene) polycation doped with poly(styrene sulfonate) (PEDOT: PSS) diluted in isopropyl was bladed on top of the active layer. The whole stack was annealed in an inert atmosphere at 140°C for 5 min. Finally, ~85 nm an Ag layer was thermally evaporated on the PEDOT: PSS surface at through a shadow mask to define an active area of 10.4 mm². Fig. 1 represents a schematic of the 3D nano-structured inverted device based on pure or Cs doped ZnO NRs.

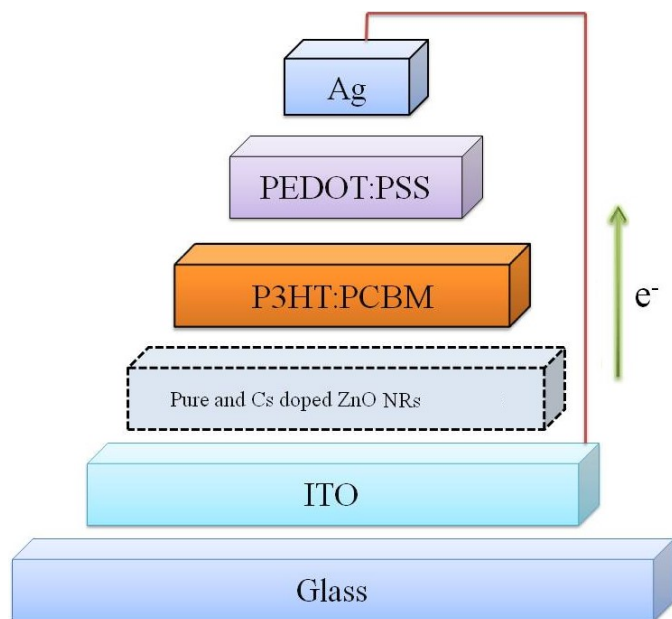


Fig. 1. Schematic representation of the 3D nano-structured inverted device based on pure or Cs doped ZnO NRs

3. Results and discussion

According to the previous work [22] and after choosing the best condition for the growth of pure and Cs doped ZnO NRs, we fabricated our inverted polymer solar cell with the configuration of (ITO/pure and Cs doped ZnO NRs/P3HT: PCBM/PEDOT: PSS/Ag). The cross-sectional FESEM image of our solar cell employed with ZnO thin film is shown in Fig. 2. The thickness of the ZnO thin film is 30 nm.

The J-V curves of the samples under illumination are shown in Fig. 3. The device performance key-parameters are summarized in Table 1. The sample that was employed based on the ZnO seed layer (ITO/ZnO seed layer/P3HT: PCBM/PEDOT:PSS/Ag)

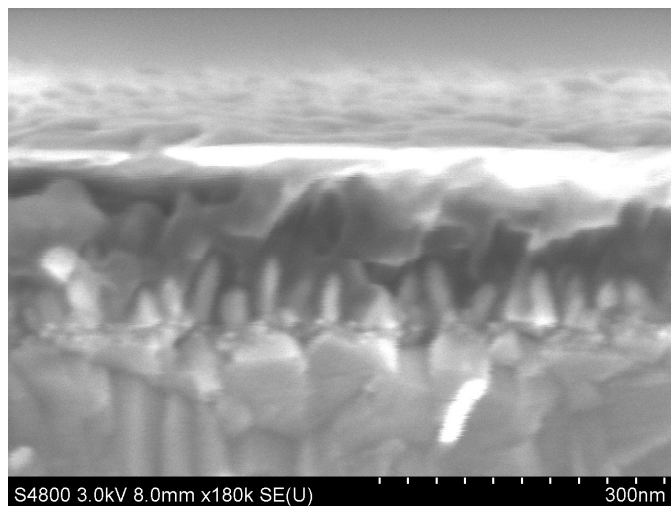


Fig. 2. Cross-sectional FESEM image of the inverted solar cell employed with Cs doped ZnO NRs thin film

yields power conversion efficiencies (PCE) of 2.40% with a short circuit current density (J_{sc}), open circuit voltage (V_{oc}), and fill factor (FF) of 7.81 mA/cm², 0.548 V, and 56.7%, respectively. Also, PCE of the device with employing of ZnO NRs (ITO/ZnO NRs/P3HT: PCBM/PEDOT:PSS/Ag) was obtained about 2.7%. As can be seen, the difference in PCE is sufficient to prove the enhancement, but the comparison between the samples with ZnO seed layer and nanorods indicates that Cs doped ZnO NRs can effectively serve as an electrode for inverted polymer solar cells. This performance agrees well with the values reported in the literature based on the P3HT: PCBM inverted device of the same structure [23-25]. Several work reported that the inverted PSCs with ZnO NRs and P3HT: PCBM/PEDOT:PSS blend exhibited average PCEs ~3% [25,26]. It could be an indication of the high conductivity of the ZnO NRs prepared in this condition. Also, the light J-V curve shows the FF improvement of the device with ZnO NRs compared to the ZnO seed layers. According to Table 1, using the sample with 1.0% Cs doped ZnO NRs (ITO/Cs doped ZnO NRs/P3HT: PCBM/PEDOT:PSS/Ag), maximum PCE of 2.80% is achieved. Also, this sample showed J_{sc} of 8.21 mA/cm², V_{oc} of 0.541 V and FF of 63.01%. Maximum J_{sc} was noticed for 1.5% Cs doped ZnO NRs whereas for 2% doped samples the J_{sc} and PCE of the device was found much lower. The reason may be that as increasing the concentration of cesium, the crystalline structure disrupted or probably by increasing the concentration, new phases appear. Also, the insignificant increase in PCE of the samples could be related to the removal of defect emission from the NRs. It is worth noting the short circuit current density of doped ZnO is superior to the J_{sc} of pure ZnO for all doping contents. Finally, high PCE solar cell on the Cs doped ZnO NRs with a FF ~63.01% for the active layer as thick as ~180 nm could be an indication of the larger interfacial area for the charge separation and more efficient charge extraction. The larger interfacial area between active area and electron transporter layer minimized the distance charge carriers need to travel in the active area to reach the electrodes [25]. Our 2.80% PCE, was more than the efficiency of recently reported P3HT:

PCBM based on inverted PSCs that employed Ga doped ZnO NRs [20]. One of the contribution for better performance of the device employing 1.0% Cs doped ZnO can be better fill factor. FF depended on series resistance that is the inverse slope of J-V curve. Loss in efficiency, despite high J_{sc} , was probably explainable by drop in FF coming from increased series resistance (R_s) at polymer/cathode interface. Series resistance was a particular problem at high current densities. Nevertheless, achieving both high V_{oc} and J_{sc} is a challenging issue in polymer solar cells technology. Enhanced efficiency of hybridized polymer solar cells could be obtained by further improving in synthesizing condition, morphology control and doping concentration of ZnO NRs and so on [26].

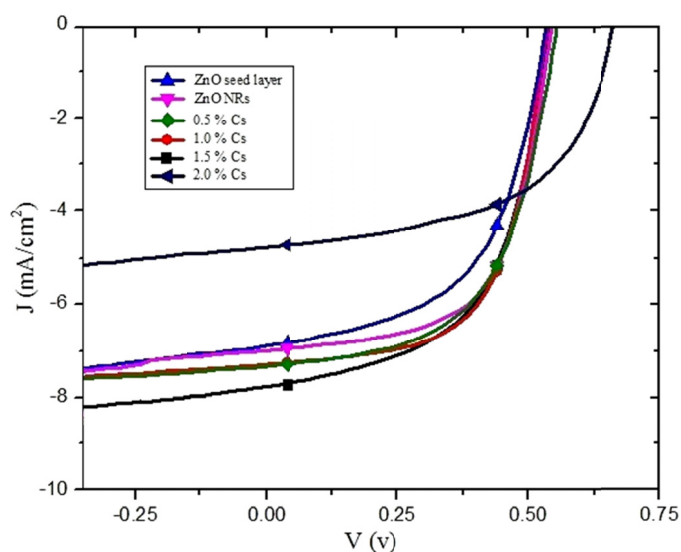


Fig. 3. J-V Curves of devices using pure and Cs: ZnO NRs thin films

TABLE 1

Brief key parameters of inverted polymer solar cells

Sample	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	Eff. [%]
ZnO seed layer	0.548	7.81	56.74	2.40
ZnO NRs	0.552	7.92	61.04	2.71
Cs doped ZnO NRs (0.5%)	0.562	8.26	58.68	2.72
Cs doped ZnO NRs (1.0%)	0.541	8.21	63.01	2.80
Cs doped ZnO NRs (1.5%)	0.550	8.70	58.44	2.75
Cs doped ZnO NRs (2.0%)	0.685	5.70	57.35	2.22

The structure of ZnO thin film was examined using X-ray diffraction (XRD) (Fig. 4). The XRD peaks of ZnO thin film can be indexed to (100), (002), (101), (102), (110), (103), (112) orientation plane. All of them are attributed to the hexagonal wurtzite structure of ZnO crystal ascribed according to card number 36-1451 from JCPDS. It is well-known that ZnO are highly textured with the c-axis perpendicular to the substrate surface, especially in the (002) orientation. To study the effect of

cesium doping on the electrical properties of ZnO NRs, electrical conductivities of pure ZnO and Cs doped ZnO NRs were measured and summarized in Table 2. The electrical conductivities were measured by a two point layout with a KEITHLEY 236 Source Measure Unit. As can be seen, the conductivity of Cs: ZnO is superior to the conductivity of pure ZnO for all doping contents. From 0 to 1% doping concentration, the conductivity is improved. From 1 to 2%, it is decreased again. This is a well-known effect previously described by Alam et al. [27]. Low concentrations of the doping element lead to an increased number of charge carriers. When the concentration is increased further, the crystal structure of the host material is disrupted by the added impurities.

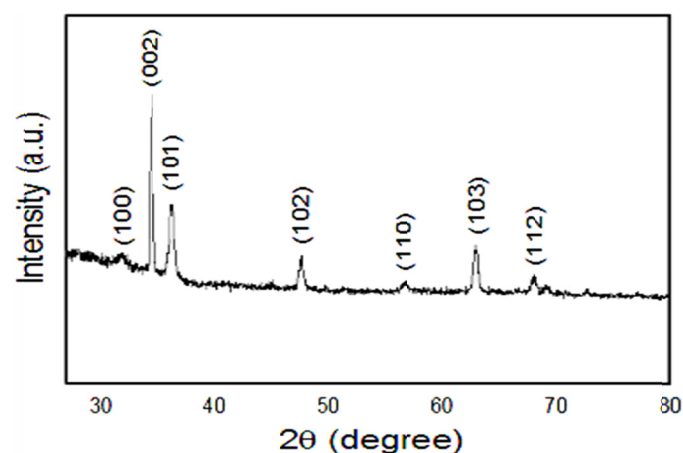


Fig. 4. XRD pattern of synthesized ZnO thin film

TABLE 2

Electrical conductivity of pure and Cs doped ZnO NRs

Sample	Dopant ratio (%)	Conductivity (S/Cm)
ZnO NRs	0.0	2.96×10^{-5}
Cs doped ZnO NRs (0.5%)	0.5	9.82×10^{-5}
Cs doped ZnO NRs (1.0%)	1.0	4.12×10^{-4}
Cs doped ZnO NRs (1.5%)	1.5	2.24×10^{-4}
Cs doped ZnO NRs (2.0%)	2.0	1.89×10^{-4}

4. Conclusions

In this research, we synthesized and fabricated undoped and Cs doped ZnO NRs thin film with diverse dopant concentration using simple and efficient hydrothermal method and employed them to the fabrication of polymer solar cell. From the results, it was found that 1.0% Cs doped ZnO NR thin films showed the best performance in the investigated ratios. Using 1.0% Cs doped ZnO NRs, J_{sc} of 8.21 mA/cm², V_{oc} of 0.541V and Fill Factor of 63.01% were achieved, which led to power conversion efficiency of 2.80%.

REFERENCES

- [1] S.H. Park et al., *Nat. Photonics* **3**, 297-302 (2009).
- [2] L. Gang et al., *Nat. Mater.* **4**, 864-868 (2005).
- [3] S. Günes, H. Neugebauer, N.S. Sariciftci, *Chem. Rev.* **107**, 1324-1338 (2007).
- [4] C.J. Brabec, S. Gowrisanker, J.J.M. Halls, D. Laird, S. Jia, S.P. Williams, *Adv. Mater.* **22**, 3839-3858 (2010).
- [5] L.M. Chen, Z. Hong, L. Gang, Y. Yang, *Adv. Mater.* **21**, 1434-1449 (2009).
- [6] K. Norrman, S.A. Gevorgyan, F.C. Krebs, *ACS Appl. Mater. Interfaces* **1**, 102-112 (2009).
- [7] M.P.D. Jong, L.J.V. IJzendoorn, M.J.D. Voigt, *Appl. Phys. Lett.* **77**, 2255-2257 (2000).
- [8] B. Paci et al., *Appl. Phys. Lett.* **87**, 194110-194110-3 (2005).
- [9] G.K. Mor, *Appl. Phys. Lett.* **91**, 152111-152111-3 (2007).
- [10] K. Lee, J.Y. Kim, S.H. Park, S.H. Kim, S. Cho, A.J. Heeger, *Adv. Mater.* **19**, 2445-2449 (2007).
- [11] C. Waldauf, *Appl. Phys. Lett.* **89**, 233517(1-3) (2006).
- [12] A.K.K. Kyaw, X.W. Sun, C.Y. Jiang, D.L. Kwong, *Appl. Phys. Lett.* **93**, 221107 (1-3) (2008).
- [13] T. Kuwabara, T. Nakashima, T. Yamaguchi, K. Takahashi, *Org. Electron.* **13**, 1136-1140 (2012).
- [14] P.D. Bruyn, D.J.D. Moet, P.W.M. Blom, *Org. Electron.* **11**, 1419-1422 (2010).
- [15] K. Ellmer, *J. Phys. D: Appl. Phys.* **34**, 3097-3108 (2001).
- [16] S. Yanming, H.S. Jung, J.T. Christopher, S. Jason, J.H. Alan, *Adv. Mater.* **23**, 1679-1683 (2011).
- [17] J. Wan, L. Hui, K. Chen, *Mater. Chem. Phys.* **114**, 30-32 (2009).
- [18] S. Salari, M. Ahmadi, K. Mirabbaszadeh, *Electron. Mater. Lett.* **10** (1), 13-20 (2014).
- [19] T. Stubhan, H. Oh, L. Pinna, J. Krantz, I. Litzov, C.J. Brabec, *Org. Electron.* **12**, 1539-1543 (2011).
- [20] M. Ahmadi, S. Rashidi Dafeh, *Indian. J. Phys.* **90**, 895-901 (2016).
- [21] M. Ahmadi, K. Mirabbaszadeh, S. Salari, H. Fatehy, *Electron. Mater. Lett.* **10** (5), 951-956 (2014).
- [22] K. Mirabbaszadeh, M. Ahmadi, M. Khosravi, R. Mokhtari, S. Salari, *J. Inorg. Organomet. Polym.* **23** (6), 1219-1225 (2013).
- [23] S. Nobuyuki, C.C. Hsuan, K.W. Lek, Y. Yang, *Org. Electron.* **10**, 1473-1477 (2009).
- [24] J.S. Huang, C.Y. Chou, M.Y. Liu, K.H. Tsai, W.H. Lin, C.F. Lin, *Org. Electron.* **10**, 1060-1065 (2009).
- [25] M. Ahmadi, S. Rashidi Dafeh, *Chin. Phys. B* **24** (11), 11723-(1-6) (2015).
- [26] M. Ahmadi, K. Mirabbaszadeh, M. Ketabchi, *Electron. Mater. Lett.* **9** (6), 729-734 (2013).
- [27] M.J. Alam, D.C. Cameron, *J. Vac. Sci. Technol.* **19**, 1642-1646 (2001).