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Performance Enhancement of P3HT: ZnO Solar Cells by Incorporating Metal Oxide Fe₂O₃ Nanoparticles

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Abstract

The ferric oxide nanoparticles (Fe₂O₃) which are deposited at interface which is related to hole collecting buffer layer [poly(3,4-ethyl-enedioxythiophene): poly(styrene-sulfonate) (PEDOT: PSS)] as well as regioregular poly(3-hexyl-thiophene): Zinc oxide nanoparticles (P3HT): (ZnO) active layer have been considerable increasing the performance of solar cell. Also, the solar cell devices have been fabricated with a weight ratio of 1:0.7, 1:0.8, 1:0.9 and 1:1 of P3HT and ZnO, respectively. In addition, photo physical characteristics regarding such devices with different value of the weight ratio were examined. This work is indicating that the absorption spectrum related to blend will be broad with varying ratios that was extremely required for the devices of the organic solar cells. Furthermore, the film morphology was estimated via atomic force microscope (AFM). EQE (i.e. External quantum efficiency) and XRD patterns measures were achieved for the optimal device, while the improvement in the efficiency with regard to a device with 1:1 was more considerable compared to 1:0.90, 1:0.80 as well as 1:0.70 values of weight ratio of P3HT and ZnO. With different weight ratio values, a solar cell upon (1:1) provides PCE (i.e. Power Conversion Efficiency) of 4.1%, dissimilar to 3.92% for (1:0.9), 3.9% for (1:0.8) and 3.6% devices.

Keywords: Iron(III) oxide nanoparticle, P3HT:Fe₂O₃ NPs, PEDOT:PSS, ZnO NPs, Buffer layer, active layer.

تحسين اداء الخلية الشمسية (P3HT: ZnO) باضافة جزيئات اوكسيد الحديد الثلاثي النانوي

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الخلاصة

تم في هذا البحث دراسة تأثير اضافة الجسيمات النانوية لأوكسيد الحديد الثلاثي الى بوليمر (بولي (3،4-إيثيل-إنديوكسي ثيوفين): بولي (ستايرين-سلفونات) عند الطبقة الوسطى وكذلك اضافة اوكسيد الزنك النانوي الى البوليمر هكسانثيوفين المنتظم عند الطبقة الفعالة. ادت هذه الاضافة الى زيادة كبيرة في اداء الخلايا الشمسية المحضرة. تم تصنيع أجهزة الخلايا الشمسية بنسبة وزن 1: 0.7 ، 1: 0.8 ، 1: 0.9 و 1: 1 من البوليمر هكسانثيوفين و اوكسيد الزنك النانوي. تم دراسة و فحص الخصائص الفيزيائية للصورة لهذه الأجهزة للنسب الوزنية المختلفة. حيث وجد إلى أن طيف الامتصاص للمواد المتراكبة اعطى مدى واسعاً لكل النسب

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المتختلفة ولكل اجهزة الخلايا الشمسية العضوية المحضرة. علاوة على ذلك ، تم تقدير مورفولوجيا النمذج المحضرة عبر جهاز المجهر القوة الذرية. تم دراسة كفاءة الكم الخارجية ومقاييس أنماط XRD لجميع النماذج. حيث وجد ان اعلى قيمة للكفاءة وجدت عند النسبة الوزنية 1 : 1 مقارنة بـ 1:0.9 و 1:0.8 بالإضافة إلى 1:0.7 وزن . تم حساب قسمة كفاءة الخلية الشمسية عند (1 : 1) فكانت 4.1% و 3.92% لـ (0.9 : 1) و 3.9% لـ (0.8 : 1) و 3.6% لـ (0.7 : 1)

1. Introduction

Lately, The organic-inorganic semiconductors have been of high importance in many studies because of their significance in the applications of optoelectronic devices (various photo-physical potentials) [1, 2]. The major characteristics regarding P3HT conjugated polymer have been intentionally tailored via many designs as well as structural modifications for achieving optimal efficiencies [3, 4]. In addition, P3HT is majorly utilized in fabrication of bulk heterojunction organic PV devices because of its low band gap and particularly its elevated absorption coefficient (order of 10^5 cm^{-1}) in visible [3, 5–10]. The main limitation of organic semiconductors is its low charge mobility. For the purpose of overcoming this issue, this study suggested hybrid heterostructure on the basis of P3HT that include inorganic ZnO NPs, with the aim of improving the optoelectronic characteristics due to the benefits from elevated electron mobility regarding ZnO in P3HT [11]. There are many studies in literature associated with the hybrid based polymer heterostructures consisting of inorganic nanostructures [3,12–17]. Many researches concentrated on P3HT ZnO heterostructures and focused on different aspects including the power conversion efficiency (PCE) enhancements [7, 18], charge dynamic, thermal properties, structural properties, morphology, exciton generation, and photoexcitation [19–21]. Also, many researchers examined the impact of processing parameters on the blended photo-active nanophase [22–26]. The molecular weight and regioregularity [27, 28] related to P3HT affects the performance of P3HT: ZnO NP devices, while the electric power which is obtained from PV device is on a basis of photovoltage and photocurrent of diode within illumination of certain intensity. For the purpose of increasing the PCE of a PV device, a significant method is to elevate the photocurrent to maximum , due to the fact that solar cell was limited through built in potential, also it was the differences between lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of acceptor materials and electron donor [29]. Various interface morphologies and device geometries were estimated to tap extra light, dissociate excitons more effectively, transport charges with few impediments for extracting more photocurrent [30]. Actually, solvents utilized to prepare active layer are significantly impacting its morphology, which affect the photocurrent generation in devices [31, 32]. Until this date, there are no conclusive results made for nanophase's optimal processing.

2. Experimentation

2.1. Fabrication of the Photo-voltaic device

Pre-patterned ITO coated glass slides (thickness of 80 nm, sheet resistance $10\Omega/\text{sq}$). Initially, the ITO substrates were cleaned by ultrasonication in isopropyl alcohol and acetone for a period of 10 min, then heat dried in an oven at a temperature of 120°C and lastly treated via ozone ultraviolet cleaner for a period of 10 min. A film of poly (ethylene dioxy-thiophene) (PEDOT: PSS: Fe_2O_3 NPs) is spin cast on ITO substrate's tip with 1,000 r/min speed for a period of 30 seconds to create hole transport layer, then dried at 140°C for 15 mins . the mixed solutions includes ZnO NP (10 mg/mL, Sol-Gel) and P3HT (10mg/mL, Sigma Aldrich) in co solvent through the mixing of the solvent of chlorobenzene as well as chloroform (CB:CF) in a 1:1 weight ratio have been spin cast, after that spin-coated at 800 rpm on PEDOT: PSS film for creating the active layer. The thickness of the active layer was ~150 nm, while the thickness regarding PEDOT: PSS layer was (30nm) by using by M2000V (J.A.Woollam Co., Inc.) spectroscopic ellipsometer is operating

in the wavelength range 350-850 nm. . Lastly, bi-layer cathode includes 100 nm. Aluminum is thermally-evaporated within elevated vacuum of approximately 2×10^{-5} Pa with a 0.20 nm.s^{-1} rate on the layer of the polymer as a cathode for creating a device that has a 9 mm^2 active area specified via shadow mask on active layer for the creation of the cells with a 1 cm^2 active region. Figure 1 shows a schematic diagram related to device structure.

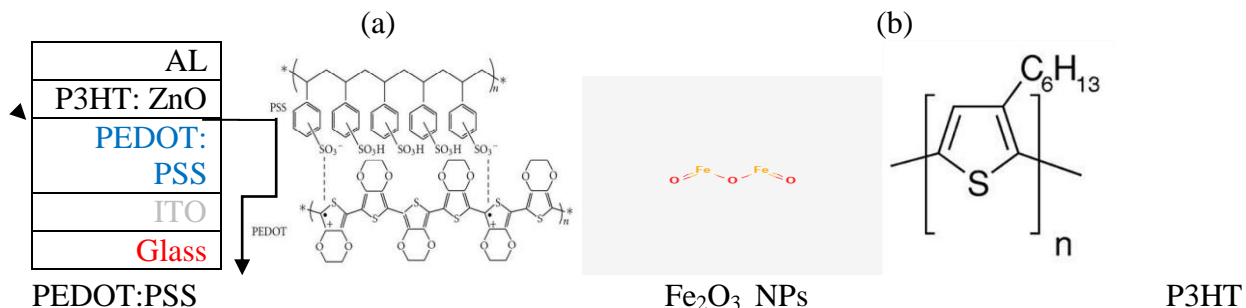


Figure 1-(a) PV device structure (b) Molecular structures of PEDOT: PSS: Fe₂O₃NPs /P3HT: ZnO NPs

2.2 The Characterization of the Device

The present density- voltage (J–V) properties of the device was evaluated through the use of a computer programmed Keithley2400 Digital Source Meter; also photo-current was created under AM 1.5G 100 mW/cm^2 irradiation. P3HT: ZnO NPs films were produced via spin coating of P3HT: ZnO NPs solution on glass substrates for AFM and UV-Vis spectroscopy with . Varian Cary 5000 UV-VIS NIR spectro-meter as well as Raman spectroscopy utilizing Horiba JobinYvon HR-800 micro Raman spectro-meter.

In addition, the intensity of the light which is related to solar simulator was standardized with the PV reference cell, while . incident photon to electron conversion efficiency (IPCE)curves were evaluated by the Stanford lock in an amplifier 8,300unit. Furthermore, AFM images of the polymer films were obtained with BRUKER Nano Scope 4 Multimode Adapter AFM with a tapping mode. The thickness of the film was evaluated with TencorP-10 Alpha Step profiler, whereas PCE (g) was defined by the relation $g = FF \times (V_{oc} \times J_{sc}) / P_{light}$, in which FF was specified as $FF = (I_{max} \times V_{max}) / (I_{sc} \times V_{oc})$ and P_{light} was the power of the incident light. PCE of pristine and hybrid OSC are evaluated for Fe₂O₃NPs.

3. Result and Discussions

The UV-Vis absorption spectra in the range of (400-900 nm) of PEDO: PSS: Fe₂O₃ NP/P3HT: ZnO NPs films with various ratio weights of ZnO NP: P3-HT of 1:0.70, 1:0.80, 1:0.90 as well as 1.0:1.0 are displayed in Figure 2. It is noticed that the absorption spectra of the blend are broad, which is extremely required for the devices of the solar cell. Also, the variation of the ZnO NPs: P3HT active layer ratio films is signified by the different locations and intensities of the absorption peaks due to the fact that P3HT and ZnO NPs have various absorption positions, also they have been mixed in various ratios. The increase in the absorption intensity values with an increase in ZnO NPs: P3HT active layer ratios between 1: 0.70 and 1:1.0 is due to the fact that P3HT have strong absorption in the spectra of the visible light via π - π^* interactions of the P3HT molecules [30]. At low ZnO NP: P3HT ratio of 1:0.7, in the absorption intensity is the lowest which is due to the uneven distributions regarding P3HT in the blend. The film with the ZnO NP: P3HT ratio of the active layer at 1.0:1.0 had maximum intensity of the absorption, which is a considerable factor to enhance photo-electric performance which is related to solar cell as can be seen in the Figure 2.

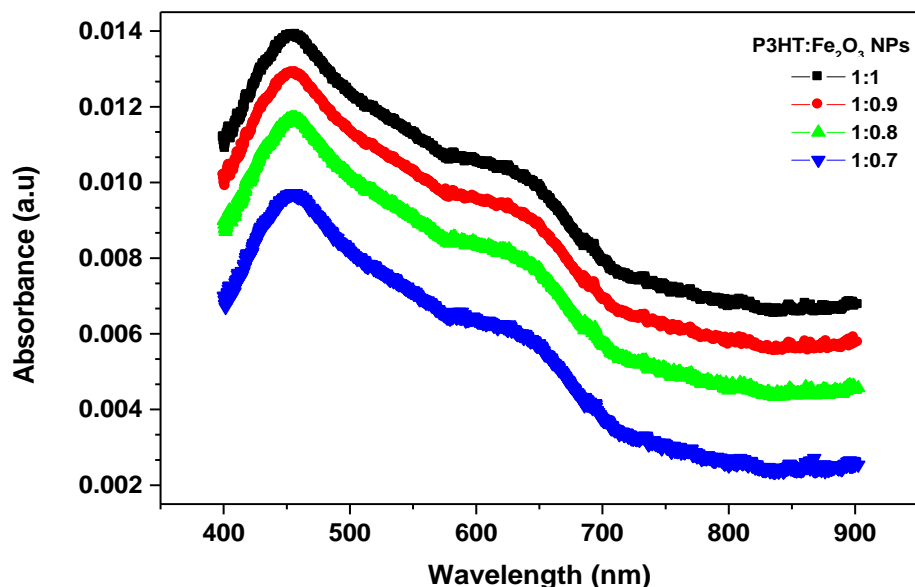


Figure 2-UV-VIS spectra of absorption of the PEDOT: PSS: Fe₂O₃ NPs /P3HT: ZnO NPs films with various values of ratio of weight 1:0.7, 1:0.8, 1:0.9 and 1.0:1.0.

The patterns of the X-ray Diffraction, which are related to PEDOT: PSS: Fe₂O₃NP /P3HT: ZnO NP films with various weights: ZnO NP: P3HT active layer ratio values 1:0.70, 1:0.80, 1:0.90 and 1.0:1.0, are displayed in the Figure 3. With regarding all the prepared of P3HT: ZnO NP active layers, a property, (which is corresponding to 1st order peak of reflection \rightarrow 100) peak about $2\theta=5.4^\circ$ which represent oriented edge on the P3HT crystallites with the lamella structure that is related to the rings of the thiophene in the P3HT [33] was significantly grown up with 1:0.70, 1:0.80, 1:0.90, and 1.0:1.0, while there was a decrease in its half width, indicating an increase in crystallization degree or/and the size of the grain regarding the domains of the P3HT via 1.0:1.0 ratio. In addition, ratio values of 1:0.80 as well as 1:0.90 films showing decreased intensity (100) peak in comparison to the intensity of 1.0:1.0 ratio film, whereas minimum crystallinity is identified for as deposited 1.0:0.70 film. It must be assumed that the existence of ZnO NP molecules will impact the structures regarding P3HT crystallites at 25 Celsius. Also, upon a ratio 1:1, there was a considerable increase in the P3HT crystallinity due to full self-assembly regarding conjugated chain resulting in orderly-formed and elevated conjugated bond's length. This is because of the increase in the homogeneous diffusion that is related to the ZnO NP molecules at increased temperatures for creating large ZnO NP aggregates [34]. Thus, the regions with reduced ZnO NP concentration will happen. With regard to such regions with reduced ZnO NP concentrations (phase separated nets), P3HT aggregates create large crystallites and therefore facilitating charge transport to the electrodes [35].

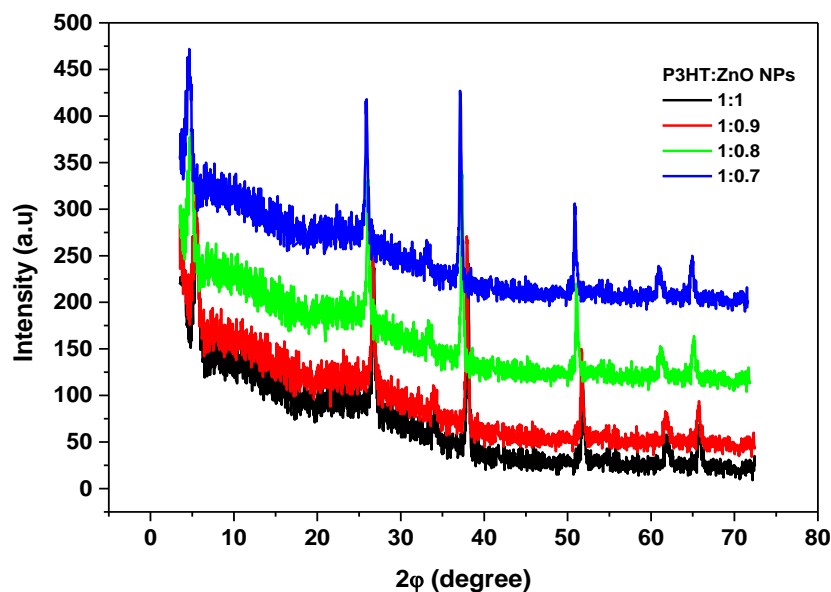


Figure 3-XRD curves of the PEDOT: PSS: Fe₂O₃NPs /P3-HT: ZnO NPs films with various values of the weight ratio 1.0:0.70, 1.0:0.80, 1.0:0.90 and 1.0:1.0.

Raman spectroscopy, which is related to the PEDOT: PSS: Fe₂O₃NP /P3HT: ZnO NP films with various weights ZnO NP: P3HT active layer ratio values 1.0:1.0, 1:0.90, 1:0.80 and 1.0:0.70, which have been deposited on the Aluminum substrate, have been displayed in Figure 4. It has been specified via Raman spectroscopy between 1300 and 1700 cm⁻¹. There were many Raman modes between 1350 and 1550 cm⁻¹ [36, 37]. Also, the spectrum regarding the blend which is deposited on the characteristics of the Aluminum, all of the vibrational frequency values, which are anticipated for the organic conjugated polymer [38], while the major in plane modes of the ring skeleton between 1,452 and 1,468cm⁻¹ (symmetrical stretching mode of C=C), also between 1,381 and 1,391cm⁻¹ (C-C intra-ring mode of stretching). This study is focusing on 2 major in plane modes of the ring skeleton at approximately 1,450 as well as ~1,380cm⁻¹, since they were anticipated for having high sensitivity to π -electron delocalization (conjugation length) that is related to the P3HT molecules [39] and the crystallinity extent [40, 41]. It has been indicated that the downward shift in wavenumber typically indicated that there will be an increase in crystallinity related to P3HT polymer as well as the extension of effective conjugation length along the backbone of polymer [42]. In addition, the intensity as well as FWHM regarding P3HT, also its blends of C=C stretching deformation have been sometimes utilized for indicating the material's ordering, while P3HT polymer film that is prepared with ZnO NP has desired molecular morphology for transport regarding the carriers of the charge and it is accountable for improvements in the efficiencies of the cell. There aren't any Raman mode characteristics which are a result of ZnO NP, like A_{1g}1469cm⁻¹ mode related to fullerenes might be resolved. A study conducted by Huang YC [42] specified that Raman modes regarding the P3HT polymer in blends aren't impacted via contributions of ZnO NP fluorescence, while the results are acquired from Raman spectra, via indicating that increasing P3HT: ZnO NP blend ratio will cause reduction in length of the effective conjugated polymer which is related to the polymer back-bone and therefore the order in polymer. Which is why, the polymer film that is prepared with the P3HT: ZnO NP 1.0:1.0 ratio of weight has desired molecular morphology types for transporting charge carriers and thus enhanced efficiencies of the cells.

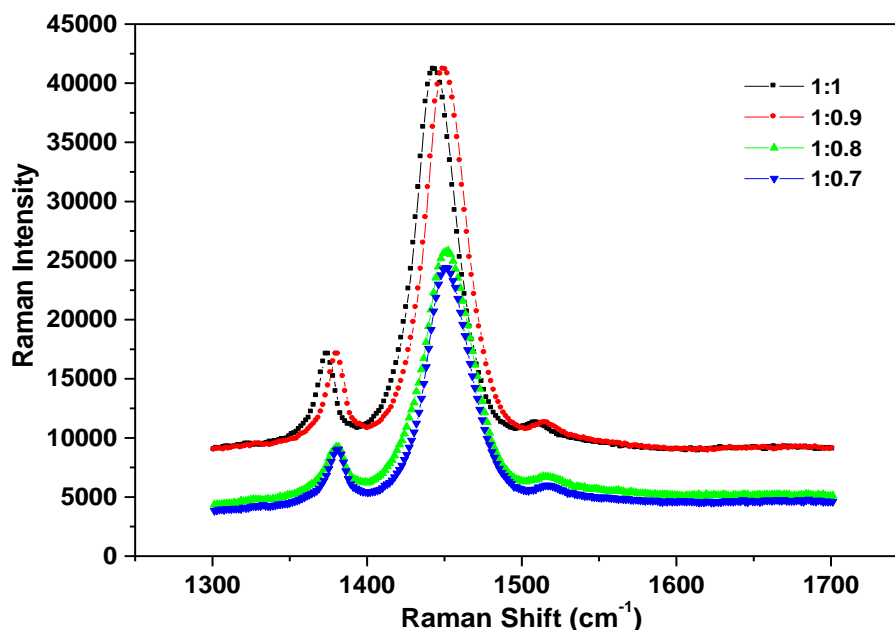


Figure 4-Raman spectroscopy for the PEDOT: PSS: Fe₂O₃ NPs /P3HT: ZnO NPs films with various values of ZnO NP: P3HT weight ratio 1.0:0.70, 1.0:0.80, 1.0:0.90 and 1.0:1.0.

AFM of PEDOT: PSS: Fe₂O₃ NP/P3HT: ZnO NP films with various weight ZnO NP: P3HT active layer ratio values 1.0:1.0, 1.0:0.90, 1.0:0.80 as well as 1.0:0.70, which were deposited on the Silicon substrate, as can be seen in the Figure 5 (a, b, c and d). In addition, 1.0: 0.70 film ratio in Figure. 5a, showing smooth surface and more even in the thickness with existence of the separation of the phase, where it isn't identified and film's R.M.S roughness was 3.21 nm. Figure 5 (b, c & d) is showing pictures regarding P3HT: ZnO NP surface morphologies in a ratio of 1.0:0.90, 1.0:0.80 and 1.0:0.70. Also, it has been indicated that the increase in the concentration of ZnO NP, will cause an increase in film surface roughness, like in the ratios 1:0.8 and 1:0.9, as can be seen in the Figure 5. In addition, there is an increase in the concentrations of ZnO NP (1:1) large aggregates (domains) regarding ZnO NP identified and it is because of the percolation related to ZnO NP molecules. At the same time, with regard to the concentrations of ZnO NP for 1.0:1.0 ratios, the film includes homogeneous mix, which is related to P3HT chains as well as separate ZnO NP molecules, while the RMS roughness, which has been estimated for 1.0:0.80, 1.0:0.90 and 1.0:1.0 films, has been subjected to an increase from 3.14, 4.15 and 6.22. Table 1 is showing the parameters of the film as acquired from the analysis of the AFM image; Ra was the average roughness of the film, R_{max} representing the film's maximum height and R.M.S representing its R.M.S roughness.

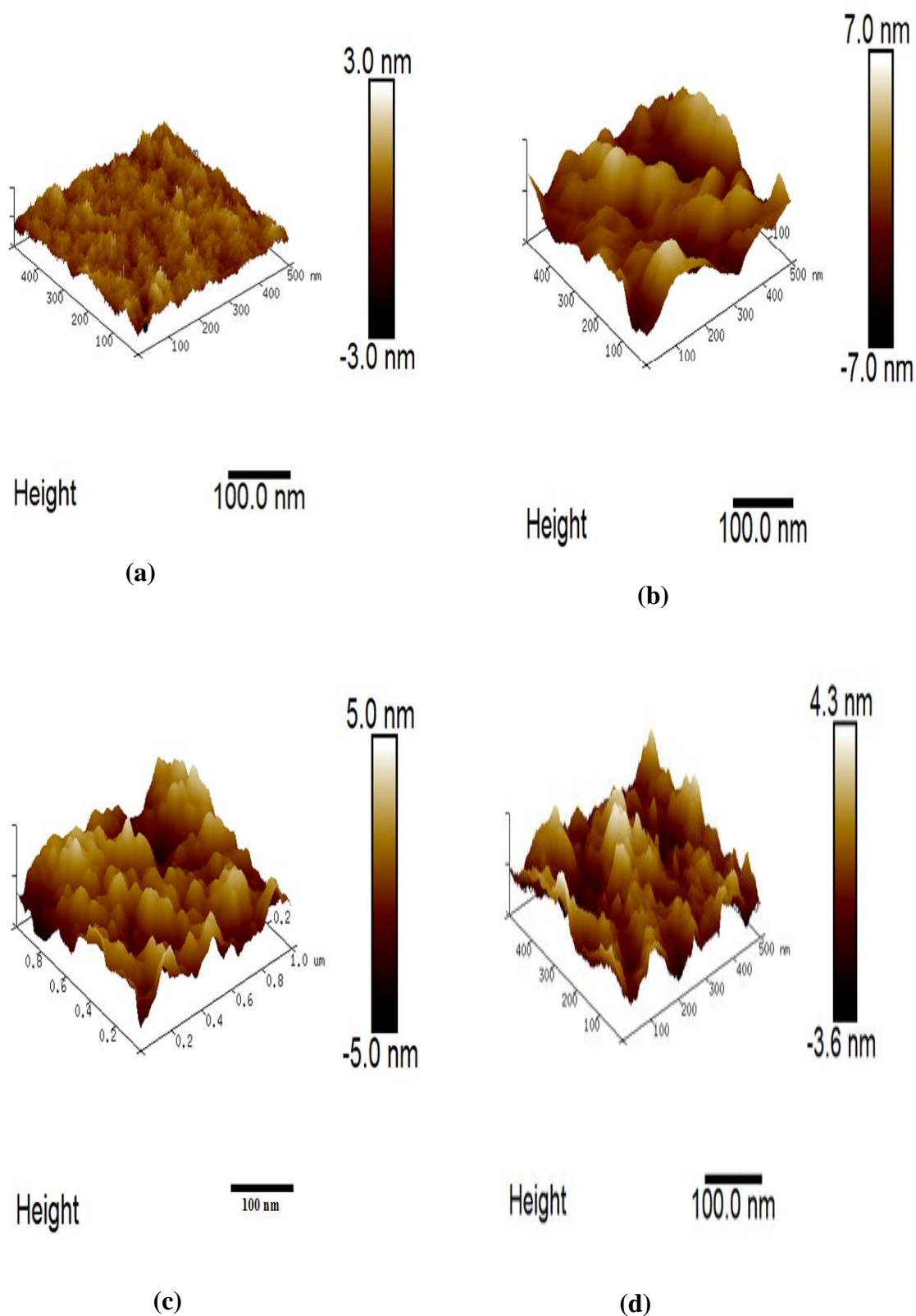
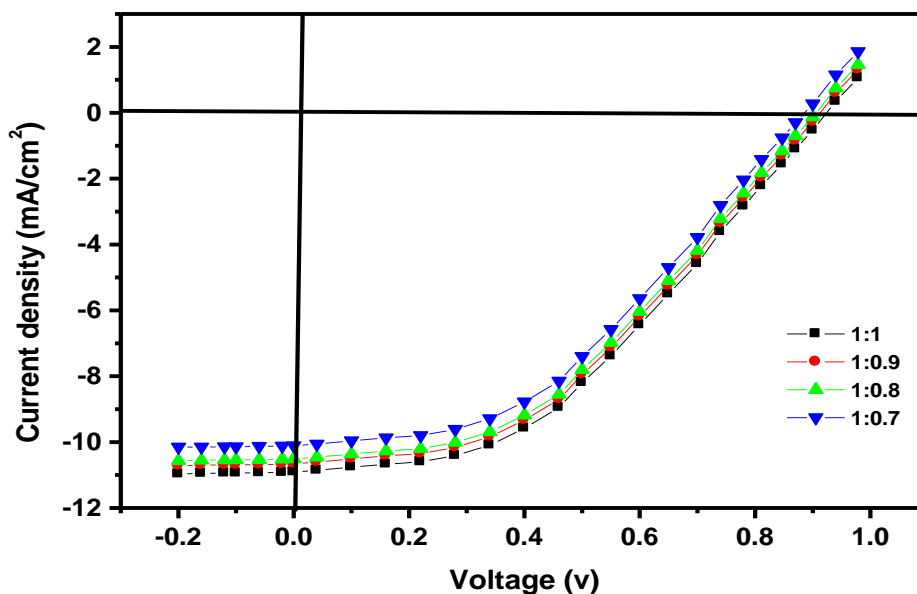


Figure 5-PEDOT: PSS: Fe₂O₃ NPs /P3-HT: ZnO NPs films' AFM images, with weight ratio values of (a) 1.0:0.70, (b) 1.0:0.80, (c) 1.0:0.90 & (d) 1.0:1.0

Table 1-AFM for the Photo-voltaic characteristics of the PEDOT: PSS: Fe₂O₃NPs/ P3HT: ZnO NPs active layer ratio values of (a) 1.0:0.70, (b) 1.0:0.80, (c) 1.0:0.90 & (d) 1.0:1.0.

Weight Ratios %	R.M.S (nm)	R _a (nm)	R _{max} (nm)
1:1	6.51	5.81	46.3
1:0.9	4.84	4.31	30.4
1:0.8	3.94	3.37	25.8
1:0.7	2.34	2.05	14.6

**Figure 6**-J-V curves of the ITO/PEDOT: PSS: Fe₂O₃ NPs /P3HT: ZnO NPs /Al active layer ratio values of 1:0.70, 1.0:0.80, 1.0:0.90 and 1.0:1.0.

The current Voltage (*J-V*) characterizations regarding PEDO: PSS: Fe₂O₃ NP /P3HT: ZnO NP films have been displayed in the Figure 6. Considerable enhancements showed in results of *J-V* characterizations, which are related to the solar cells, particularly on *I*_{SC}, *V*_{OC} as well as *FF*, whereas the weight ratio regarding P3HT: ZnO NP films change from 1:0.7, 1:0.8 1:0.9 and 1:1. In addition, the value of *I*_{SC} different from 10.11, 10.50, 10.53 and 10.91 mA/cm². Yet, more increase in ZnO NPs content result in a decrease in *I*_{SC}, while the *V*_{OC} values with regard to the weight ratios 1:0.7, 1:0.8,1:0.9 and 1:1 slightly varying because of the developed ohmic contacts between active layer and anode. Also, the values related to *V*_{OC} were comparable to the former of 0.87, 0.90, 0.91 and 0.92 V. In the case when the two electrodes are establishing ohmic contact with active layer, the *V*_{OC} in such bulk Hetero-junction cells was directly associated with the energy differences between the HOMO levels regarding donor (P3HT) as well as LUMO levels of acceptor (ZnO NP) components. Whereas there will be an increase in *FF* with the increase in the ratio of the weight of 1.0:0.70, 1.0:0.80, 1.0:0.90 and 1.0:1.0 from 0.41, 0.41, 0.42, & 0.42. Thus, 1.0:1.0 weigh ratio composition with regard to blend film providing maximum *I*_{SC}, *V*_{OC} and *FF*, blend ratio decreases the two. Therefore, maximum values related to *PCE* as high as 4.1 were acquired for structure organic solar cells, utilizing enhanced blend weight ratio of 1.0:1.0. In addition, the rest of the values, which are related to the *PCE* for the weight ratios 1:0.7, 1:0.8, and 1:0.9 regard P3HT: ZnO NP films change from 3.6, 3.90 and 3.92. Increasing the PEC related to PEDOT: PSS: Fe₂O₃ NP /P3HT: ZnO NP film might be due to the increase in the interfacial contact area between P3HT: ZnO NP active layer as well as PEDOT:PSS: Fe₂O₃ NP intermediate layer, that allow

more effective hole collection at anode, and thus increasing J_{sc} and FF . With regard to blend material system, it was verified that homogenous blend was acquired for ZnO NP contents about 50% (1:1) by weight and that at high ZnO NP content, ZnO NP rich domains will segregate. Because of the elevated electron mobility in the ZnO NP, the ZnO NP rich domains assisting charge collection in the blends, that is inducing enhancements on the performance of device. Yet, more increase in ZnO NP content induces a decrease on charge carrier collection due to re-combination in over enlarged ZnO NP rich domains.

Table 2-The Photo-voltaic parameters for the solar cell device with various values of ZnO NP: P3-HT weight ratio 1.0:0.70, 1.0:0.80, 1.0:0.90 and 1.0:1.0.

Weight Ratios %	V_{oc} (v)	J_{sc} (mA/cm ²)	FF	PCE (%)	R_s (Ω)	R_{sh} (Ω)
1:0.7	0.87	10.11	0.41	3.60	15.3	724
1:0.8	0.9	10.5	0.41	3.90	14.1	835
1:0.9	0.91	10.53	0.42	3.92	9.5	901
1:1	0.92	10.91	0.42	4.1	10.6	731

4 Conclusions

We have investigated the organic solar cells with different weight ratios by comparing the optical properties, morphological, and power conversion efficiency of devices. Best device performance for organic solar cell was observed with 1:1 as compared to 1:0.9, 1:0.8, and 1:0.7 concentration weight ratios of P3HT and ZnONPs. An optimized cell with a intermediate layer (PEDOT:PSS:Fe₂O₃) nanoparticles and P3HT: ZnONPs ratio of 1:1 had a short circuit current of 10.91 mAcm⁻², an open circuit voltage of 0.92 V, a fill factor of 0.42 and a power conversion efficiency of 4.1%.

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