

The Photovoltaic Performance of Nano Plate ZnO as Solar Cells

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ABSTRACT

A new novel approach for synthesizing ZnO nano plate (ZNONPLs), ZnO nanowire, ZnO doped by Al, ZnO thin film by ALD on Indium Titanium Oxide (ITO) coated glass substrates for photovoltaic applications. The fabricated ZnO NPLs, ZnO, nanowire have been used to build bulk heterojunction solar cells with blends of P3HT (poly(3-hexylthiophene)) and PCBM ((6,6)-phenyl C61 butyric acid methyl ester). Scanning electron microscopy, X-ray diffraction, photoluminescence, UV-vis absorption spectroscopy, and photovoltaic measurements for studying morphology and device solar cells performance which prepared. The microstructure of the ZnO nanoplate ZNONPLs arrays plays two roles one for increase junction surface area and collecting the photo-generated electrons where has conducting paths to ITO glass. The Fill factor, and power conversion efficiency increased when using ZnO NW Modified by porphyrin.

فعالية الفولتية الضوئية لاوكسيد الزنك النانوي كخلية شمسية

الخلاصة:

تهيج جديد لتوليفة (ZnO) ذات اللوح النانوي (ZNONPLs), الاسلاك النانوية (ZnO), المطعم بـ (Al), غشاء (ZnO) على (ITO) المرسيه على الزجاج لاستخدامها في تطبيقات (photovoltage). تصنيع ZnO NPLs والاسلاك النانوية لـ (ZnO) حيث استخدمت لبناء خلية شمسية ذات الوصلة المباشرة ممتزج بـ P3HT (poly(3-hexylthiophene)) و PCBM ((6,6)-phenyl C61 butyric acid methyl ester).

قياسات UV-Vis, SEM, XRD بالإضافة الى قياسات photovoltaic قد استخدمت لدراسة تشكيل العينات المستخدمة وفعاليتها ضمن الخلية الشمسية. ان التركيب المايكروي لـ (ZnO) و (ZNONPLs) ادى لزيادة مساحة الوصلة السطحية وكذلك زيادة تجميع الالكترونات المتولدة باتجاه (ITO). ان عامل الشغل والكفاءة قد ازدادت عند استخدام الاسلاك النانوية لـ (ZnO NW) المعدلة.

INTRODUCTION

The photovoltaic Organic /inorganic of conjugated polymer and inorganic semiconductor nanostructure have attracted attraction due to a great and very wide application for photovoltaic cells^{1,2} and light emitting diodes,^{3,4} The hyper solar cells using p-type poly(3-hexylthiophene)(P3HT) and ZnO nanowire as an n-type has very good performance where the efficiency around 0.4 %⁵, Hyper solar cells ZnO thin film as n-type and P3HT as a p-type the photovoltaic performance for this bi layer design is low. In general mixing an electron accepting materials and an electron donor materials in a bulk heterojunction (BHJ) in a blend of conjugated polymers and inorganic materials in the molecular scale⁷⁻¹⁰. There are large number of donor/acceptor created when making donor/acceptor conjugated polymer and there are big surface area as interfaces junction solar cells, the photo-generated excitations within limitation of diffusion length where the charges will move to two electrodes. The main two problems are the poorly formed donor-acceptor interfaces and discontinuous for electron transport paths in the active layers. To solve this problem are growth of inorganic nano crystalline structure in the shape of rigid thin film three dimension mesoporous structure,¹¹ tetrapods¹², or vertically aligned nanorods,¹³ and we used ZnO nanoplate which is unique device has revealed the interfacial donor-acceptor contact area. Zinc oxide (ZnO) nanostructure is promising material as an n-type for hybrid photovoltaic devices because it has suitable optical and electronic properties¹⁴⁻¹⁶. The ZnO nanostructure wide band gap energy of 3.37 eV and exciton binding energy is 60 meV¹⁵⁻¹⁶. The ZnO nanostructure has electron mobility several times higher than organic conductive polymer where reach to 100 cm²/Vs at 300 K. Many researcher using ZnO in different form like Nano particles, nanoridges, nanorods in the solar cells devices^{7-10,14} and we successfully use ZnO nanoplate, ZnO NW in photovoltaic devices.

There are several methods to growth ZnO but most common, among them Solution based methods (CVD) is best method due to their cost, easy prepare and low temperature. The control of topography of the film of ZnO depends on optimum condition of the concentration of materials, percentage volume between DI-water/methanol where the nanotopography of Thin film has relationship with performance of solar cells¹⁷. we report growth ZnO nanoplates by using aqueous based synthesis method of ZnO on ITO glass at low temperature 65 C.

EXPERIMENTAL

Zinc nitrate hydrate [Zn (NO₃)₂.6H₂O, 99.9%] where purchased from Alfa Aesar, poly(ethylenedioxythiophene)/poly(styrenesulfonic acid)(PEDOT:PASS), Tetrahydrofuran (THF), poly(3-hexylthiophene), and (6,6)-phenyl C₆₁ butyric acid methyl ester (PCBM) were purchased from Sigma Aldrich C₄H₈O, ITO coated glass substrates (14 Ohm/cm²) were purchased from SPI supplies.

The ITO glass cleaned by path sonic in acetone, isopropanol, and distilled water prior to use.

ZnO nanoplates were synthesized by a one step process, using Zinc nitrate hydrate [Zn (NO₃)₂.6H₂O, 99.9%] 2.99 gram in 40 ml water until dissolve totally in DI water then add it to 160 ml methanol which corresponding to the volume percentage (20% : 80%) (DI Water : Methanol) put in the electrochemical cells where both counter electrode

and working electrode from gold wire on hot plate when reach the solution temperature to 65 °C then applied -1.5 Voltage by connect working electrode with 1.5 cm² of ITO glass for 30 min finally take the ITO glass out then carefully rinsed with distilled water to remove any residual salts to be ready as electrode in solar cells .

The organic thin film prepare by using spin coater for P3HT or P3HT: PCBM (1:1) for 2000 rpm on the top of ZnO nanoplates with 15 mg for each ml of chlorobenzene. After drying at 120 °C in N₂ atmosphere

Then deposit thin layer of PEDOT: PSS where spin coat on organic thin film 4000 rpm to get thickness between 20 -35 nm, then annealing the sample another time for 100 °C for 10 min and dried under vacuum for 10 min .We use in this paper 4 type of ZnO such as ZnO thin film seed layer ,Seed layer ZnO NW ,and ZnO NW modified by porphyrin fabricate and study ZnO nanorod/P3HT: PCBM/PEDOT: PASS/Ag electrode for many reasons. First of all, polymer photovoltaic have become attractive for potential large area, low cost, and mechanically flexible solar cells ¹². Secondly, bulk heterojunction (BHJ) structures usually have a large number of donor/acceptor interfaces for exciton dissociation within their diffusion length of 20 nm ¹³. Third, inorganic semiconductors incorporated into the BHJ structures will improve carrier mobility as compared to most of the organic materials. Fourth, ZnO is an inexpensive material with good stability. It is highly processible using low temperature solution phase growth ¹⁴, ZnO shows good hole blocking capability and provides a low resistive pathway for efficient electron extraction ¹⁵. Specially, the nanorod arrays also reduce largely the electron transport distance in BHJ to the cathode ¹⁶. Based on these reasons, devices of ITO/ZnO nanorod/P3HT: PCBM/PEDOT: PASS/Ag electrode will be investigated. The detailed experimental procedures to make the devices is described as below. Electrolyte containing 0.35 M zinc acetate dihydrate in 2-methoxyethanol as a solvent with a solution volume of 50 ml. The solution needs to be heated to 60 °C on a hot plate with stirrer at around 200 rpm for 2 hours. This heating/stirring should produce a clear and homogeneous solution then allow it to cool to room temperature and sit for 2 days prior to use. Once the ZnO solution is ready, it can be applied to the substrate of choice (ITO glass) with spin coater rotating at 3000 rpm for 30 sec, take the substrate out of spin coater and dry on hot plate at 500-600 °C for 1 hour. This process produces around 50-70 nm of film thickness. The vertically aligned ZnO NW arrays will be fabricated on ITO glass substrates (SPI Supplies) by a low-temperature electrochemical method ¹⁶. ZnO NW arrays will be grown on top of the ZnO thin film using an electrolyte containing 0.01 M zinc nitrate and 0.01 M hexamethylenetetramine in deionized water. The growth will be performed at 95 °C with an applied potential of -2.6 V between working and counter electrodes.

Photovoltaic devices were fabricated using the oriented ZnO nanorod arrays and the mixture of P3HT: PCBM (1:0.8 by weight in chlorobenzene) which will be spin-coated on top of ZnO nanorod arrays at 1200 rpm for 45 sec. The polymer mixture can be continuously infiltrated into the gaps between nanorods before the solvent dries. The resulting photoactive layer is approximately 150-200 nm. Finally, it will be sandwiched by Ag/glass deposited by thermal evaporation.

The devices will be packed inside a glove box under a Nitrogen atmosphere. The current-voltage (J-V) characteristics of the devices will be evaluated by using a Keithley Model 2400 source meter under illumination intensity of a 100 mW/cm² from solar simulator with AM 1.5 G filter.

CHARACTERIZATION TECHNIQUES

The structure and the morphology of the as-prepared ZnO nanoplate and the Nanoplate/P3HT structures were characterized by scanning electron microscopy (SEM, JSM 7000F). Optical absorption spectra were measured by LAMBDA 750 UV-vis spectrophotometer. Raman scattering was collected at room temperature using a Horiba JobinYvonLabRam HR800 spectrometer equipped with a grating of 600 lines/mm and a charge-coupled detector. A He-Ne laser (633 nm) were used as excitation sources. Photoluminescence (PL) spectra were measured using a He-Cd laser (325 nm) as excitation source. The emission light was focused onto the entrance slit of a monochromatic and detected by a CCD (coupled charge device) camera. The Fourier transform infrared (FTIR) spectra were collected on a Nicolet MAGNA-IR 550 Series 2 Spectrometer with a resolution of 8 cm^{-1} . The photovoltaic properties were measured by monitoring current density-voltage (J-V) characteristics of solar cell devices under dark and illumination. A Keithley 2400 Source measure unit collected the data.

RESULTS AND DISCUSSION

Figure (1 a) show The SEM of top view Image of ZnO nanoplate as-grown. As seen from the image has large number of Walls or vertically alignment array of nanoplate almost normal to the surface and the average dimension of nanoplate, the width of the plate around $1\ \mu\text{m}$ and the length around $5\text{-}6\ \mu\text{m}$.

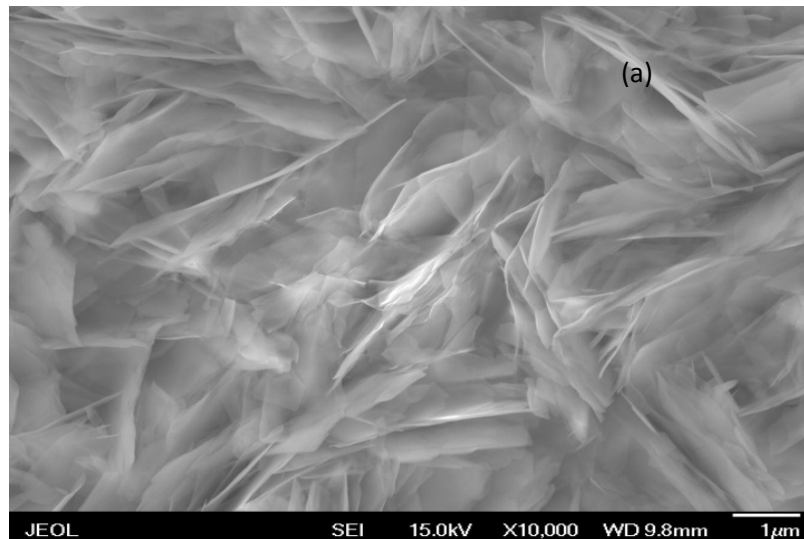


Figure (1a) SEM Image of ZnO nanoplate top view, (b) ZnO NW on seed layer, cross section P3HT:PCBM/ ZnO NW.

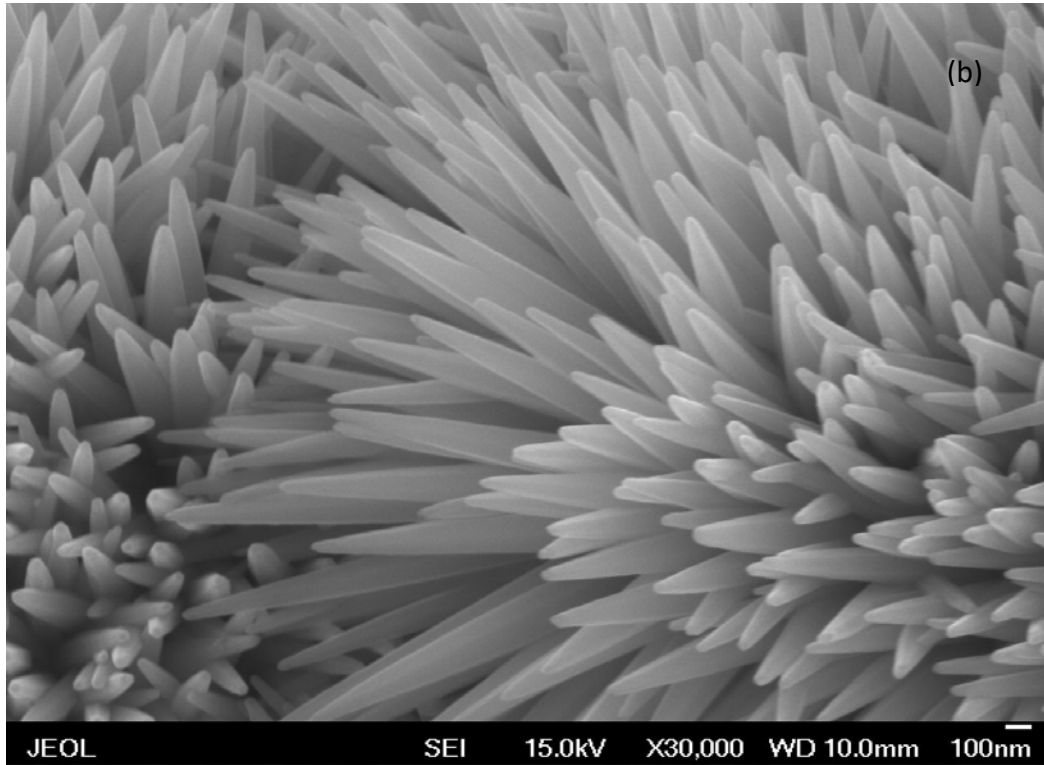


Figure (2) Explains the XRD for ZnO nanoplate patterns, the peaks observed between 20-70^o These peaks explained in the Figure (2).

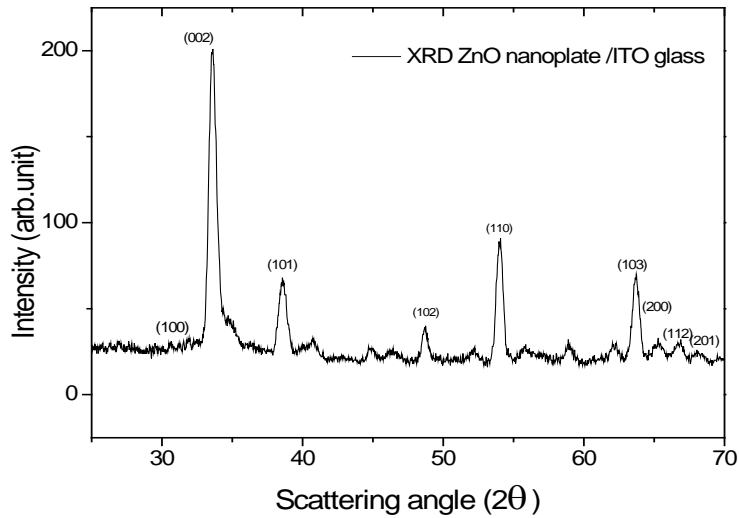


Figure (2) shows XRD for ZnO nanoplate array.

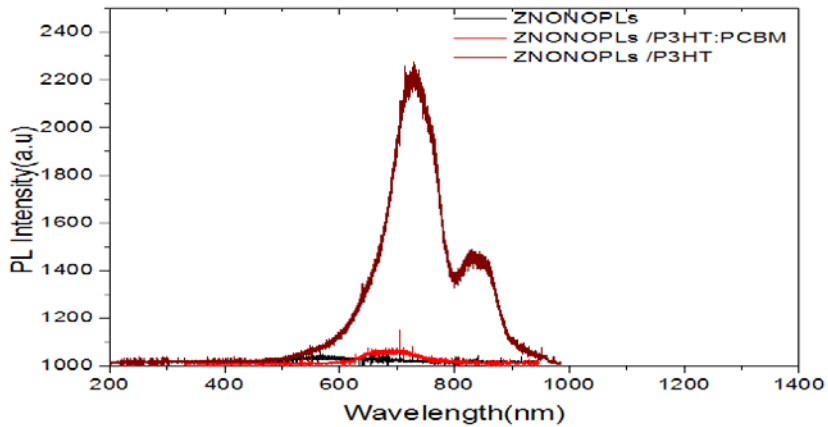


Figure (3) Photoluminescence Spectra of P3HT and P3HT: PCBM (1:1) on ZnO nanoplates.

As seen from the Figure (3) most of the P3HT quenched when mixing it with PCBM. The PL for P3HT and nanocomposite P3HT / PCBM (1:1 wt %) The peak at 837 nm for ZNONOPLs/P3HT represent as direct evidence for the optical transition of type 2 band alignment which is describe the recombination of electrons in conduction band of ZnO and holes in highest occupied molecular orbital(HOMO) band of P3HT^{14,15,18}

Figure (4) shows the UV-vis absorption spectra of P3HT, ZNONOPLs, P3HT/ZNONOPLs, and P3HT: PCBM/ZNONOPLs thin films. The ZNONANOPLs absorb light in the wavelength shorter than 400 nm. The UV vis for P3HT/ZNONOPLs composite where overlap between ZnO nanopl (300-400) and P3HT (400-650) nm, while ZnONOPLs/P3HT: PCBM explained much more interested and much strong deep overlap visible light in addition the band (300-400) nm which leads to improve performance solar cells.

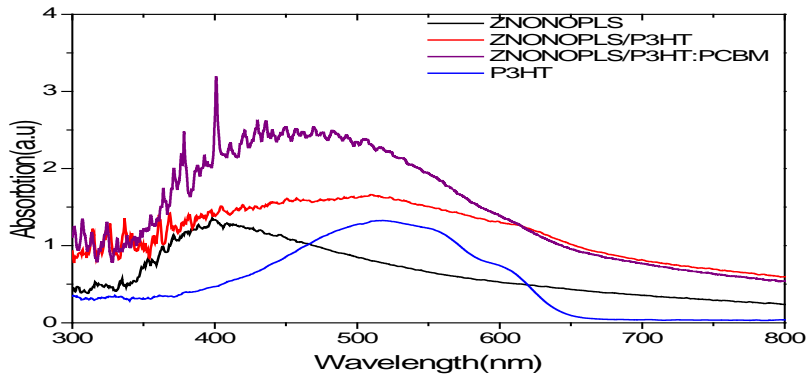


Figure (4) UV-visible absorption spectra of ZNONOPLs, P3HT, ZNONOPLs/P3HT and ZNONOPLs/P3HT: PCBM.

The Figure (5) shows diagram of energy for the materials where the excitons form when the light absorb by P3HT .The PCBM and ZNONOPLS both acceptor materials the excitons will be disassociated at the interfaces of P3HT with ZNONOPLs and interfaces between P3HT /PCBM .The transport processes and the charge-carrier collection both those parameters control by the electron mobility and the typical microstructure of ZNONOPLS .It has been demonstrated that ZnO improve performance of solar cells ¹⁸.as seen from the figure 5 that the electrons at LUMO of PCBM (-3.7eV) will be easily transfer to the conduction band of ZnO(-4.2) and further to ITO glass(-4.8 ev).

Figure (6) shows the I-V characteristic dark and under 1.5 AM Illumination, the photovoltaic of the hybrid solar cells For both designs are ITO glass/ZNONOPLS /P3HT/PEDOT: Pss/Ag and ITO glass/ZNONOPLS/P3HT:PCBM/PEDOT: Pss/Ag where the Table (1) explain Current short circuit, Open circuit Voltage, Fullfactor, Efficiency for both designs.

Table (1) Explains short circuit current, open circuit Voltage, Fullfactor, Efficiency for both designs.

devices	V _{oc}	I _{sc}	FF	Efficiency %
ITO/ZNOPLs/P3HT	0.102	0.4	0.22	0.009
ITO/ZNONOPLs/P3HT:PCBM	0.366	4.87	0.359	0.64
ITO/ZNONOPLs/P3HT:PCBM Porphyrin	0.46	8.4		1.39

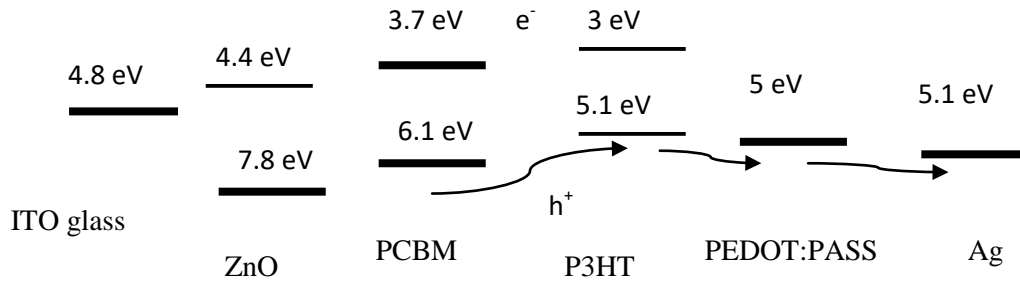


Figure (5) schematic representation of the energy levels of the components in the ITO glass/ZNONOPLS/P3HT: PCBM/PEDOT:Pss/Ag .

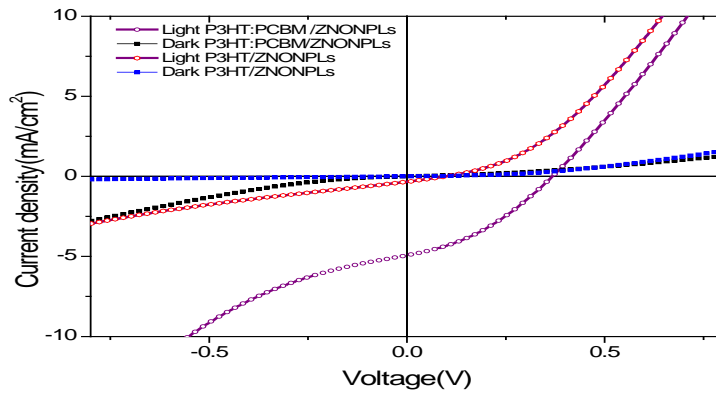


Figure (6) Current-Voltage Characteristic of devices for P3HT/ZNONOPLs and P3HT:PCBM/ZNONOPLs.

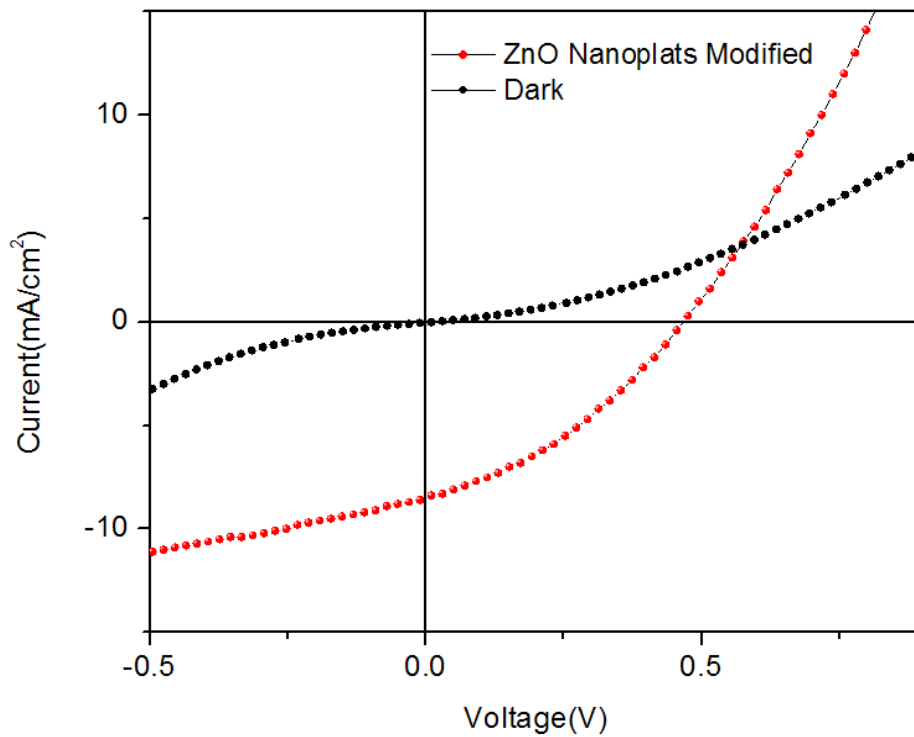


Figure (7) Current-Voltage Characteristic of devices for P3HT/ZNONOPLs and P3HT:PCBM/ZNONOPLs modified by porphyrin .

From the Table (1) the low value of V_{oc} is due to high electron mobility for ZnO nanoplate, leading to enhanced carrier recombination at the ZNONOPLs interfaces. On the other hand, the large spacing between the walls or plates could have effects on the exciton diffusion and limit the current short circuit. While the device with PCBM improve performance of solar cells due to the aligned nanowalls or nanoplates, which ZnO this time working as effective electron collectors by shortening the average electron diffusion distance in the PCBM network and work as direct carrier transport pathways to the ITO electrode, which reducing the charge recombination.

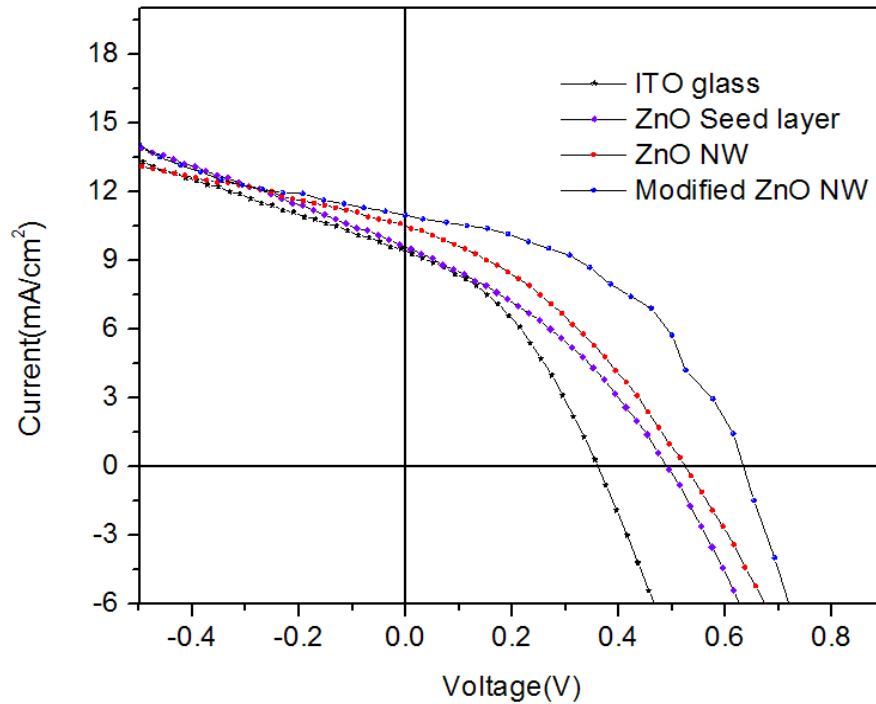


Figure (8) Current-Voltage Characteristic of devices for P3HT: PCBM /ZnO Seed layer, without ZnO, ZnO NW, and P3HT: PCBM /ZnO NW Modified by porphyrin.

Table (2)

Devices	V_{oc}	I_{sc}	FF	PCE
ITO glass	0.34	9.467	0.44	1.3
ZnO Seed layer	0.49	9.57	0.45	1.63
ZnO NW	0.51	10.61	0.47	1.93
Modified ZnO NW	0.63	10.97	0.56	3.18

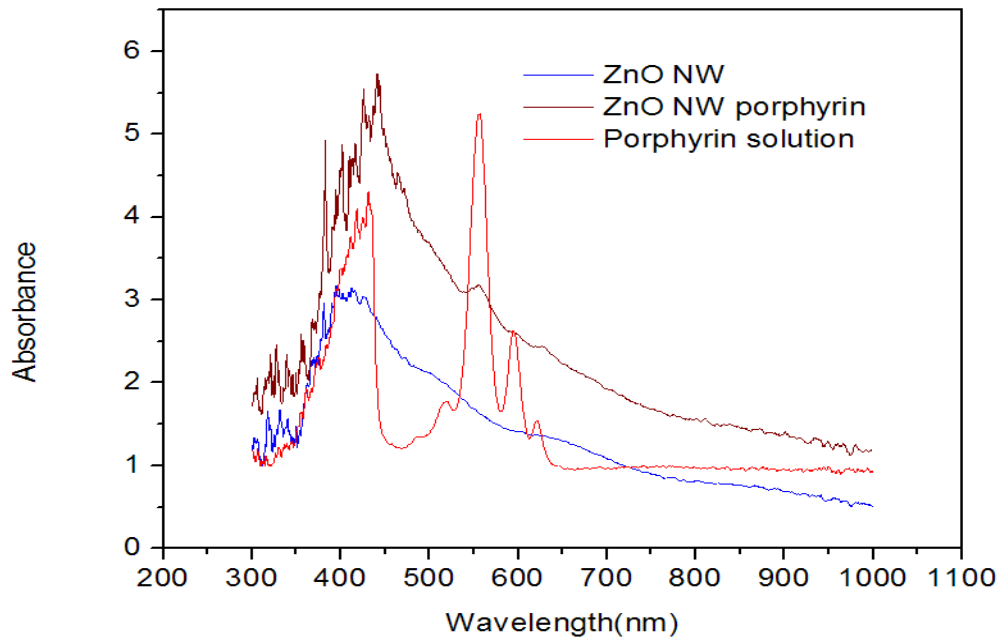


Figure (9) UV-Vis absorption spectra of ZnO thin film, porphyrin, and ZnO thin film coated with porphyrin.

CONCLUSIONS

ZNONOPLs arrays were successfully synthesized on ITO-coated glass substrates at the low temperature of 65 C in one step. The structure and morphology of ZNONOPLs arrays were investigated using XRD and SEM. The ZNONOPLs arrays have been used to fabricate photovoltaic devices with pristine P3HT and P3HT:PCBM blends. The power conversion efficiency improved up to 71 % in the presence of PCBM. Further improving performance by changing the nanostructure of ZnO like ZnO nanorods, ZnO nanotrees

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