



Polymeric Solar Cells Efficiency Increase Using Doped Conjugated Polymer Nanoparticles

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Authors' contributions

This work was carried out in collaboration between all authors. Authors NM designed the study, carried out the experimental work and analyses and discussed the results and wrote the first draft of the manuscript. Authors AH and ZF reviewed the existing literature, managed the literature searches and placed the research objectives of the paper in perspective. All authors managed the analyses of the study, read, edit, and approved the final manuscript.

Original Research Article

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ABSTRACT

Organic photovoltaic cells are made by sandwiching a composite active layer of organic electronic materials conjugated copolymer (BEHP-co-MEH-PPV) mixed with ZnO nanoparticles, between two metallic conductors, typically a layer of indium tin oxide (ITO) with high work function(4.8 eV) and a layer of low work function metal(3.7eV) such as Aluminum. In this work, the spin coated conjugated copolymer blends (BEHP-co-MEH-PPV): ZnO thin films, deposited on both Silicon and glass substrates have been studied for morphology using atomic force microscopy (AFM). All films examined by AFM, showed a dense structure with average roughness of 20 -40 nm. Optical properties were explored for films coated onto glass substrates at a spin speed of 1200 rpm, using a spectrophotometer for optical absorption in the visible region. The photo luminescence (PL) spectra of the pure and blended BEHP-co-MEH-PPV films were recorded. Ellipsometry were used for refractive index, extinction coefficient and thickness. The current-voltage characteristics (I-V's) of the solar cell showed that incorporation of the ZnO nanoparticles in the copolymer resulted into further increase in the power conversion efficiency compared to that in their absence. All deposited films showed good adhesion to substrates, and good optical properties. The conductivity of the active layer increases with the increment of the ZnO nanoparticles into

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the nanocomposite thin films. Such characteristics make the polymer: nanoparticle blended layer (BEHP-co-MEHPPV: ZnO) very favourable to charge injection and conduction for photovoltaic device.

Keywords: Polymer; BEHP-co-MEH-PPV; thin films; solar cells; injecting electrode; ZnO nanoparticles.

1. INTRODUCTION

Organic Conjugated polymers are of wide interest for applications in electronics and optoelectronics, including light emitting diodes [1–4], thin film transistors [5–7], photovoltaic cells [8,9], and electrochromic cells [9]. The organic polymers have the advantages that they can be easily processed by spin coating so that the manufacturing cost of organic solar cells can be significantly reduced. However, these solar cells have low efficiency which limits their uses in practical applications. Spin coating is the primary process for the deposition of uniform thin and ultrathin films of conjugated polymers for these device applications. Fundamental studies of the morphology and physical properties of conjugated polymers, such as photo physics, charge transport, electrical conductivity, photoconductivity, optical nonlinearity, are also commonly done on spin coated thin (0.2–1.0 μm) and ultrathin (<0.2 nm) films [7-11].

The UV-Vis absorption and photo luminescence (PL) characteristics of poly [2-methoxy-5-(2'-ethyl hexy loxy)-1,4-phenylene vinylene (MEH-PPV) films were studied [1-10].

According to Cai et al , by using solar cells fabricated from low bandgap polymers, it is possible to capture more of the solar radiation and thereby increase their efficiency [12]. The performance of organic photovoltaics is severely limited by low efficiencies, short lifetimes and low charge mobilities in polymers. This challenge can be met through the use of blended and layered heterojunctions such morphologies offer thicker and more absorbing polymer films [13].

Chang et al reported on the use of the MEH-PPV film as the emitting layer of OLED structure. The layer of MEH-PPV was spin coated from a toluene solution at a concentration of 4 mg/mL with three different spin speeds. The UV-Vis absorption and photo luminescence (PL) spectra of these MEH-PPV films were recorded [8].

Although there have been many studies of the spin coating process for many other materials including photo resists [13] and sol-gel materials [8]. There is no much experimental analysis reported on the processing of BEHP-co-MEH-PPV conjugated copolymers by spin coating for solar cell applications.

Spin coated conjugated polymers for electronic or optoelectronic devices typically have a thickness in the sub-micron range. For example, the film thickness of conjugated polymers in light emitting diodes or photovoltaic cells is generally in the range of 50 -200 nm [1,4,14-16]. For such ultrathin films spin coated from diluted polymer solutions, there are just few prior studies of the spin coating process of the BEHP-co-MEH-PPV polymer for solar cell applications. Sanchez et al reported on the use of pure BEHP-co-MEH-PPV thin films as an active layer in Light emitting diodes [17].

Organic and polymer based solar cells are currently of much research interest due to its low cost, simple processing at room temperature and promising efficient solar energy conversion. Conjugated polymers often participate as electron donors and hole conductors in the active layer of organic solar cells. Doping the conjugated polymer with semiconducting nanoparticles becomes an area of current interest, such integration of both organic polymers and nano-scale materials would allow the manufacturing of efficient electronic and optical devices. The BEHP-co-MEH-PPV is an attractive conjugated polymer for EL/PL emission in the green region because of its high PL efficiency. The oxide semiconductor ZnO is a promising material for EL/PL emission in the blue-UV region. The composite made of these two materials has not yet been investigated thoroughly that makes an analysis of the dominant mechanism of charge capture and radiative recombination in the BEHP-co-MEH-PPV:ZnO structure important.

In this paper, we represent a study of the morphology, optical and electrical properties of BEHP-co-MEH-PPV films doped with Zinc Oxide nanoparticles to support its use in organic solar cells, since less work has been carried out on this conjugated copolymer in such research field. The composite films made of these two materials have not yet been investigated thoroughly for organic cell applications.

2. EXPERIMENTAL

Conjugated copolymer powder (BEHP-co-MEH-PPV) were purchased from (Sigma-Aldrich) and used as received. The chemical structure of (BEHP-PPV)-co- MEH- synthesized is shown in Fig. 1.

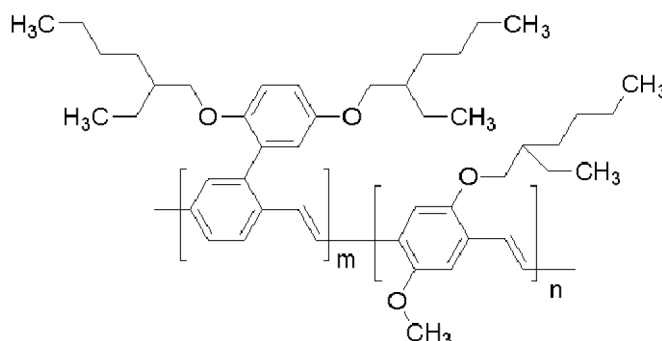


Fig. 1. Chemical structure of (BEHP-PPV)-co MEH-PPV polymer

The solution of (BEHP-co-MEH-PPV) (0.1 mg/ml) was first prepared using benzene as the solvent, stirred on magnetic stirrer and filtered thoroughly prior to casting onto the indium doped tin oxide (ITO) glass substrates with a spin speed (1200 rpm). The ITO films have thickness of 150 nm, low resistivity of $2.25 \times 10^{-4} \Omega \cdot \text{cm}$, and transmittance around 90% in the visible range. Prior to spin coating, the ITO glass substrates were cleaned using ultrasonic bath with detergent (acetone) then rinsed with de-ionized water and dried by nitrogen blow. The spin coated polymer films were dried at room temperature, and protected from light to avoid photo degradation process.

In order to investigate the changes in properties if any two sets of solar cells were made. One with pure conjugated copolymer before Zinc Oxide nanoparticles were added into the

solutions, and another set using variable concentration of Zinc oxide nanoparticles (diameter 20-30 nm) dispersed in the semiconducting polymer which forms the active layer of the solar cell.

The solar cell structures are: Glass/silicon substrate/ ITO/ZnO: BEHP-co-MEH-PPV/ Al and Substrate/ ITO/BEHP-co-MEH-PPV/ Al. The Aluminium cathodes were deposited through a mask by thermal evaporation at a base pressure of 10^{-6} Torr. The device active area was around 0.15 cm^2 . Fig. 2 shows a cross-sectional view of the fabricated silicon-based solar cell.

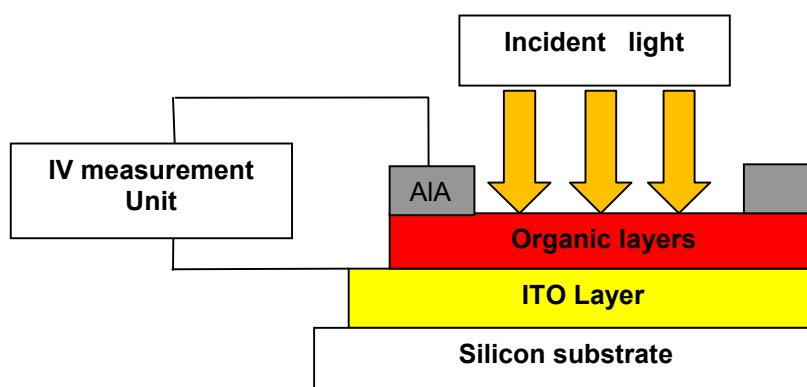


Fig. 2. A cross-sectional view of the silicon-based solar cell.

The absorption spectra of the polymer films were measured using a spectrophotometer over the range from 280 to 750 nm and the photoluminescence (PL) measurements were recorded using a monochromator equipped with a CCD detector, in the range from 500 to 750 nm, at room temperature.

Atomic force microscopic (AFM) was used to evaluate the morphology and surface roughness of the coated polymer films.

Electrical measurements have been performed at room temperature and atmosphere using a Keithley source-meter model 2400 interfaced to a personal computer. The solar cells were characterized in the dark and under illumination of 10 mW/cm^2 provided by a halogen tungsten lamp.

A spectrophotometer was used to obtain optical absorption curves in the visible region (340 – 700 nm) for thin films deposited on glass substrates.

All experiments were then repeated by mixing of BEHP-co-MEH-PPV with ZnO Nanoparticles (diameter 20-30 nm) that were deposited on Silicon/glass substrates resulting in thin films with even distribution of nanoparticles on the substrates.

3. RESULTS AND DISCUSSION

3.1 Absorption

Absorption spectra of pure BEHP-co-MEH-PPV diluted in benzene at different concentrations from $1\mu\text{M}$ to $500\mu\text{M}$, with optical density in arbitrary unit over the spectral range 280 – 650 nm are shown in Fig. 3. Films were deposited onto pre-cleaned glass substrates.

The absorption peak shifts towards its maximum at a wavelength region of 450 nm with increasing concentration to $500\mu\text{M}$, i.e. increasing the number of photons absorbed in the visible range.

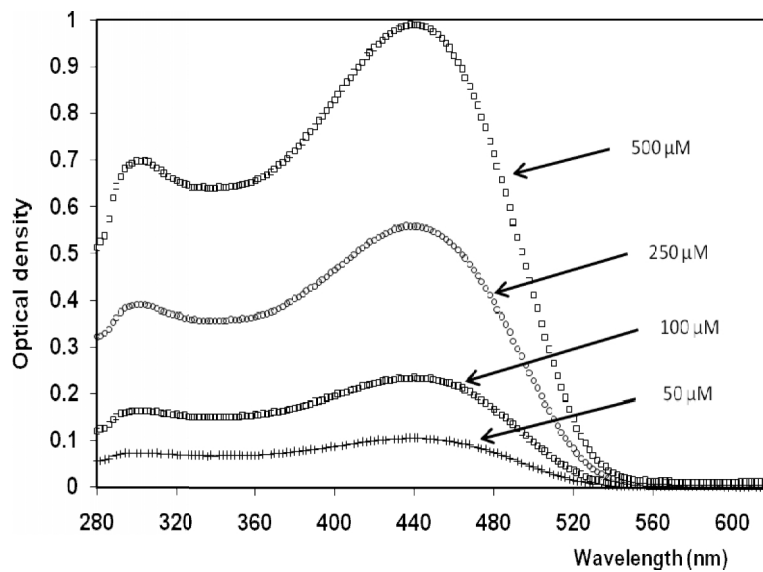


Fig. 3. Absorption spectra of the BEHP-co-MEH-PPV at different concentrations (50 μM to 500 μM)

From Fig. 4 It is clear that there is no changing in the polarity of the medium at $0.1\mu\text{M}$. Strong peak in the visible region at 450 nm and a weak peak at 300 nm in the UV region. The absorption spectra of BEHP-co-MEH-PPV have similar shape for same concentration in different solvents.

For the conjugated copolymer blended with Zinc oxide nanoparticles, the spectra of the blended composites peak around $\lambda = 475\text{nm}$. Increasing the ZnO content into the copolymer [BEHP-co-MEH-PPV (0.5Mm): ZnO (0.1g)] resulted in increase of the optical density of the blend over the spectral range 300-750 nm. The absorption spectra of the copolymer blended with Zinc oxide nanoparticles at different concentration (0.02 mg, 0.06 mg and 0.1mg) are represented in Fig. 5.

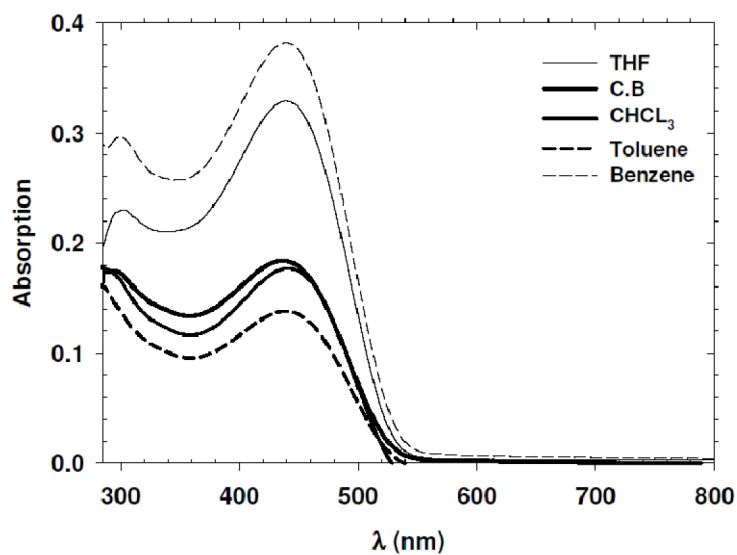


Fig. 4. Absorption spectra of BEHP-co-MEH-PPV at 0.1μM in different solvents.

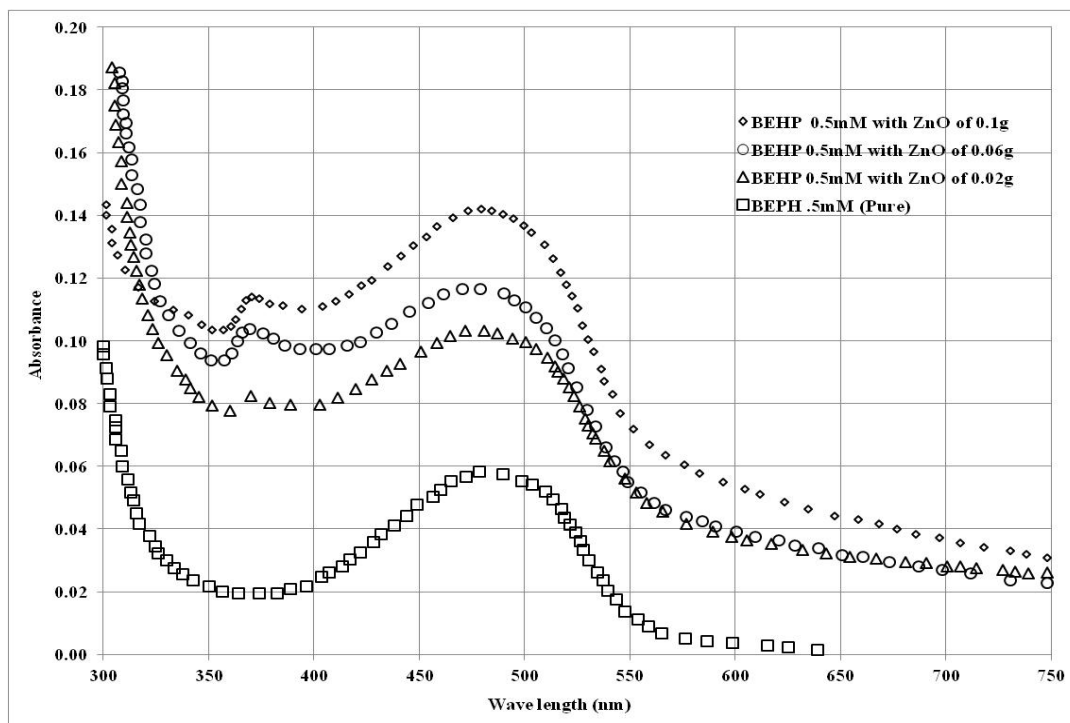


Fig. 5. The absorption spectra of the BEHP-co-MEH-PPV (0.5mM) and ZnO nanoparticles with different concentration ratios, where Absorption is in arbitrary units (a.u.)

3.2 Photoluminescence

The comparison of the Photoluminescence (PL) spectra of pure spin coated BEHP-co-MEH-PPV thin films, with various copolymer/ ZnO nanoparticle concentration ratios, represents a well resolved peak at 576 nm for the films with high concentration of ZnO (0.1g), deposited at (1200rpm) and measured at room temperature. Fig. 6 shows the PL spectra of spin coated BEHP-co-MEH-PPV films with various ZnO nanoparticle concentrations.

As can be seen from Fig. 6, the resulting spectra include the PL from both materials involved. The increase in the ZnO nanoparticles concentration in the composite film leads to an efficient quenching of the green-yellow PL peak at 570 nm attributed to the BEHP-co-MEH-PPV copolymer. At the same time the intensity of the PL line at 570 nm increases significantly.

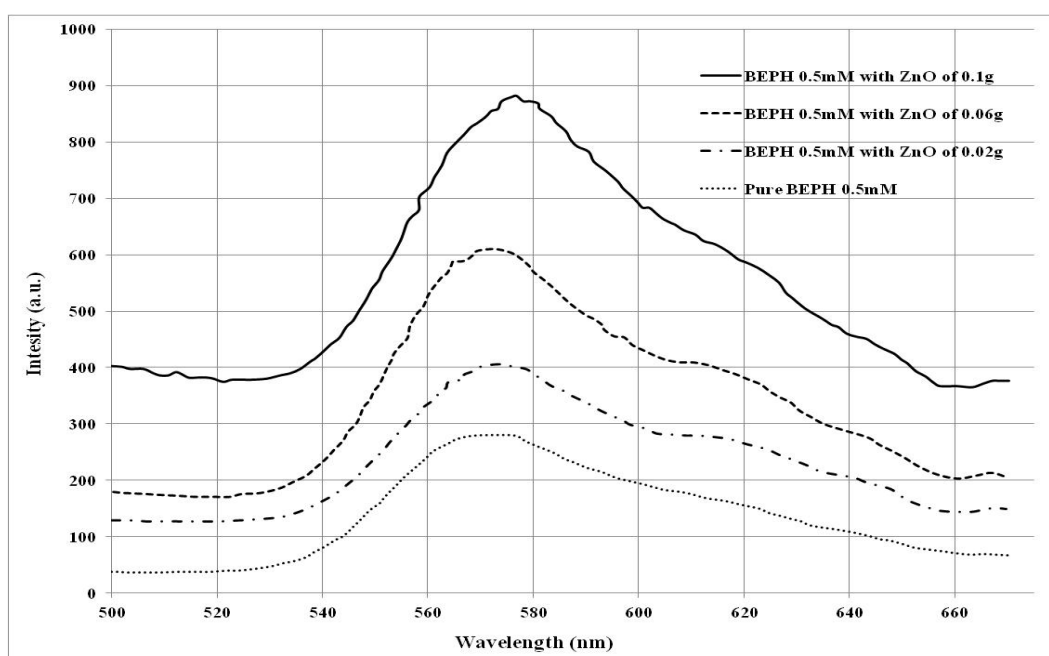


Fig. 6. shows The Photoluminescence spectra of pure and blended BEHP-co-MEH-PPV with various ZnO concentration ratios, span at (1200 rpm).

The incorporation of metal oxides as blocking layers improves device performance by imposing charge selectivity at the collecting electrode as well as by preventing shorting in the devices. Other benefits include improving stability of the polymers due to the absorption of UV light. ZnO has attracted particular interest for hole blocking layers due to its intrinsic high carrier mobility and ease of processing in nanostructured form [18].

It is well known that the defect chemistry of ZnO is complex, with a range of oxygen or zinc defects of varying charges and with concentrations that are interdependent on each other. With particular relevance to their use in solar cells, it is important to understand the influence of the defects on photovoltaic performance. However, despite the wide impact of use of metal oxides in organic solar cells [18-19],

Zinc oxide (ZnO) is a wide band gap semiconductor with potential applications in optoelectronics, transparent electronics, and spintronics. The high efficiency of UV emission in this material could be harnessed in solid-state white lighting devices. The problem of defects, in particular, acceptor dopants, remains a key challenge. As grown, ZnO is usually *n*-type, a property that was historically ascribed to native defects. However, experiments and theory have shown that O vacancies are deep donors, while Zn interstitials are too mobile to be stable at room temperature [19].

For the conjugated polymer/ZnO nanoparticles based solar cell, the morphology of the polymer blend and photovoltaic effect were directly related to the concentration of electron acceptor ZnO in the solar cell structure.

The improvement of solar cells performance has been suggested by optimizing processing parameters such as solvent, solvent drying conditions, and electron donor to acceptor ratio. The oxide semiconductor ZnO which has an energy gap $E_g = 3.35$ eV and electron affinity of 2.7 eV, is a promising material for EL/ PL emission in the blue-UV region. While the BEHP-co-MEH-PPV is an attractive conjugated polymer which has a high PL efficiency and an energy gap $E_g = 2.4$ eV. As result an integration of both materials may have resulted into a significant improvement of the fabricated solar cells.

Finally, the film thickness plays an important role in the morphology and properties of BEHP-co-MEH-PPV film, thereby varying optical properties of the polymer films. Table 1 shows the typical properties for the BEHP-co-MEH-PPV films.

Table 1. Typical PL properties and results obtained for the BEHP-co-MEH-PPV: ZnO films. (λ represents the wavelength)

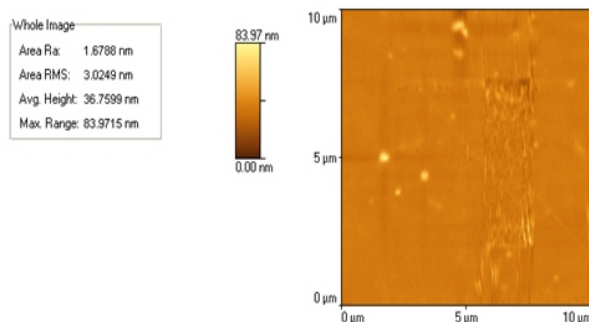
ZnO's weight (g)	Thickness (nm)	PL (a.u)
0 g	35	280 at $\lambda=570$ nm
0.02g	45	400 at $\lambda=575$ nm
0.06g	49	600 at $\lambda=575$ nm
0.1g	52	880 at $\lambda=580$ nm

3.3 Atomic Force Microscopy

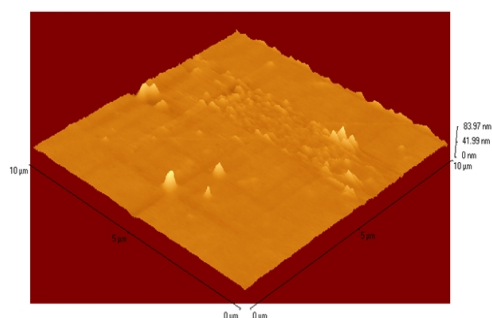
Atomic Force Microscopy (AFM) was used to find surface roughness and morphology of the deposited organic films. Fig. 7 shows the AFM micrographs of pure BEHP-co-MEH-PPV films. Average roughness R_a of the deposited films was 7 - 14.3 nm for film (35 nm thick).

3.4 Ellipsometric Measurements

Film thickness of the deposited BEHP-co-MEH-PPV layers span off at (1200 rpm) was (35 nm). While the refractive index, n , and the extinction coefficient, k , obtained were $n = 1.46$ and $k = 0.06$.



(a) The Surface of BEHP-co-MEH-PPV Film with dense structure.



(b) The Roughness of the film. (1200 rpm).

Fig. 7. AFM morphology of BEHP-co MEH-PPV films spin coated at (1200 rpm)

3.5 Current-voltage Measurements

The used light intensity for the I-V measurements is standardized at 10 mW/cm^2 with a spectral intensity distribution matching that of the sun on the earth's surface at an incident angle of 48° .

The effect of the ZnO concentration on the photovoltaic properties of the devices has been investigated. ZnO nanoparticle material was selected as the n-type material for its advantageous properties in carrier/electron mobility, ease of being processed at relatively low temperatures, transparency and controllability of electrical conductivity. The PV characteristics of the devices for different ZnO nanoparticle concentration are shown in Fig. 8. Increasing the concentration of ZnO nanoparticles resulted in improvement of the photovoltaic performance. Ahn et al reported that BEHP-co-MEH-PPV is a p-type semiconductor having lowest unoccupied molecular orbital (LUMO) value of 2.82 eV and highest occupied molecular orbital (HOMO) value of 4.94 eV [20].

With the copolymer as a p-type material, this has resulted into further increase in the power conversion efficiency compared to that in their absence. This improvement may be explained by more electron mobility induced by the ZnO nanoparticles into the conjugated copolymer.

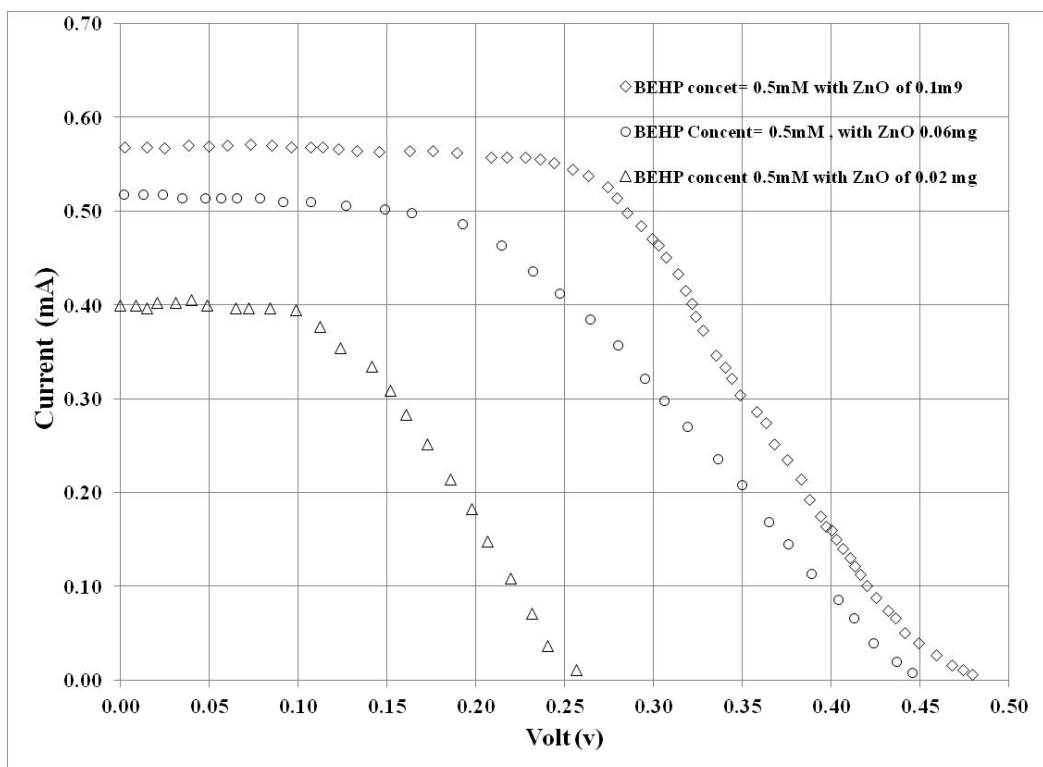


Fig. 8. The PV characteristics of the devices for different ZnO nanoparticle concentration.

The open-circuit voltages (V_{oc}) of the devices increase by increasing the ZnO concentration, also an increase in the short-circuit current was observed. A higher fill factor (FF) were observed for the solar cell with the high concentration of ZnO (0.1mg) compared to lower concentration at (0.02mg) as shown in Table 2. This indicates a higher mobility of charges due to the n-type ZnO nanoparticles induced into the p-type conjugated copolymer layer.

Table 2. Photovoltaic characteristics of the BEHP-co-MEH-PPV polymer

Active layer	Thickness (nm)	V_{oc} (V)	I_{sc} (mA/cm ²)	η (%)	F.F. (%)
BEHP: (0.5mM) ZnO (0.1mg)	52	0.47	3.8	10.6	52
BEHP: (0.5mM) ZnO (0.06mg)	49	0.45	3.53	6.4	40
BEHP: (0.5mM) ZnO (0.02mg)	45	0.27	2.66	3	38

Table 2 represents the Photovoltaic characteristics of the BEHP-co-MEH-PPV polymer, where V_{oc} is the open circuit voltage, I_{sc} the short circuit current, .F.F the ratio between the product of the maximum current and voltage and the V_{oc} and I_{sc} , and η is the efficiency of the solar cell. The active area of the solar cell devices was $0.5\text{cm} \times 0.3\text{cm} = 0.15\text{cm}^2$.

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Power conversion efficiency: $\eta = (V_{oc} \times I_{sc}) \times F.F. / P_{in}$

P_{in} is the power of incident radiation per cm^2 .

Fill Factor = F.F. = $(V_{max} \times I_{max}) / (V_{oc} \times I_{sc})$

As far as the solar cell fabricated with pure BEHP-co-MEH-PPV is concerned, pure conjugated polymer have less an efficiency between 2% and less than 3% [21].

4. CONCLUSION

We have demonstrated that the power conversion efficiency of organic solar cell can be improved by manipulating the composition of the active layer spin coated onto ITO coated substrates. Our results showed an enhancement in the short circuit current I_{sc} from (2.26mA to 3.8mA/cm²) due to the improvement in charge carrier mobility as a result of adding of ZnO nanoparticles to the active layer. The BEHP-co- MEH-PPV and ZnO nanoparticles used in this work, are promising materials for optoelectronic application and especially as active layers for organic solar cells due to their interesting optical, structural and optical properties.

The Photoluminescence (PL) spectra of the copolymer/Zinc oxide blend (120nm thick) thin films presents two maxima: one weak at $\lambda = 390$ nm for the nanoparticles and another sharp resolved peak at $\lambda=490$ nm for the copolymer films deposited at (1200rpm) and at room temperature.

Al/ Silicon/ITO/ BEHP-co-MEH-PPV: ZnO Blend/Al solar cell has shown a photovoltaic performance with open circuit voltage of the cells $V_{oc} = 0.27$ to 0.47 V. The cells fabricated in this study with an active layer made by solution-processed polymer blended with semiconducting nanoparticles can play an important role in the current research area of organic nanoelectronics.

Further research work is required to optimize blend composition, processing conditions and device structure to achieve more improved photovoltaic properties.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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