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# Effect of Seed Layer on the Morphology of Zinc Oxide Nanorods as an Electron Transport Layer in Polymer Solar Cells

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***Abstract***

*Zinc oxide has been considered as a promising semiconductor material for fabrication of transparent conductive oxides (TCOs), electronic devices, optoelectronics, and solar cells. Among the various morphologies of zinc oxide, nanorods are more widely used because of the ease of synthesis and providing a direct path for the transport of charge carriers. The electrochemical deposition method (ECD), due to its simplicity, low cost, and production of nanostructures with fewer defects is a more suitable method for producing zinc oxide nanorods. Heretofore, the effect of different parameters such as the temperature of growth solution, the concentration of precursors and pH on the morphology of the final product were studied. In this paper, the effect of the seed layer number on morphology, absorption, and electrical conductivity of zinc oxide nanorods was investigated using SEM images, UV-Vis spectroscopy, and four-point probe. The results showed that increasing the number of seed layers from 0 to 5 lead to the production of vertical, uniform, regular, and high-density nanorods. Also, the use of high-density zinc oxide nanorods, in the structure of polymer solar cells increased the performance of polymer solar cells by 68%. The polymer solar cell with zinc oxide nanorods as the electron transport layer showed short-circuit current, open-circuit voltage, and the power conversion efficiency of equal to 9.04* mA/cm$^2$*, 0.53V, and 2.51%, respectively.*

***Keywords:*** *Zinc oxide, Seed layer, Zinc oxide nanorods, Polymer solar cells.*

## 1. INTRODUCTION

Zinc oxide (ZnO) is a semiconducting material with a direct band gap of 3.37 eV at room temperature and high light transmittance (80%) in the visible region. ZnO is an important semiconductor that used because of its high electrical conductivity as a promising material in conductive transparent oxides, emitting diodes, piezoelectric devices, and solar cells [1]. Zinc oxide has various nanostructures with various morphologies such as nanorods [2], nanowire [3], nanotubes [4], nanoflowers [5], and nanoparticle. Among the various morphologies of zinc oxide, nanorods are more widely used because of the ease of synthesis and providing a direct path for the transport of charge carriers. There are several methods for synthesis zinc oxide nanorods, such as a hydrothermal [6], vapor-liquid-solid [7], sol-gel [8, 9], and electrochemical deposition [10]. The electrochemical deposition method, due to its simplicity, low cost, and production of nanostructures with fewer defects, is a more suitable method for producing zinc oxide nanorods. In this method, the formation of zinc oxide nanorods, occurs in two stages, including nucleation and growth. The nucleation process performed by coating a zinc oxide seed layer on suitable substrates. The growth of zinc oxide nanorods is also carried out using a potentiostat-galvanostat device in a three-electrode system. Heretofore, the effect of different parameters such as the temperature of growth solution, the concentration of precursors, growth time and pH on the morphology of the final product has been studied [11, 12]. Another

critical parameter affecting the growth of zinc oxide nanorods is the seed layer [13]. The seed layer acts as the primary nucleus for nanorods growth. The high density of the nucleus leads to the formation of uniform zinc oxide nanorods with proper orientation, which plays an important role in the mobility and conductivity of transparent conductive oxides and solar cells. In the present paper, the appropriate number of seed layers for reaching uniform and high-density nanorods, and its effect on the electrical conductivity of zinc oxide nanorods was investigated. The effect of the seed layer on the final morphology of zinc oxide nanorods was investigated using a scanning electron microscope (SEM) and UV-Vis spectroscopy. Also, the electrical conductivity of the synthesized samples was determined using a four-point probe. The results showed that increasing the number of seed layers from 0 to 5 leads to the production of vertical, uniform, regular, and high-density nanorods. As an inorganic semiconductor, ZnO has been widely used in polymer solar cells due to its unique characteristics such as low cost, ease of synthesis, non-toxicity, high stability, and good optoelectronic properties[14-16]. In this article, uniformly synthesized ZnO nanorods were used as the electron transport layer in the structure of the polymer solar cells.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Zinc acetate dihydrate, zinc nitrate hexahydrate, and hexamethylenetetramine (HMTA) were purchased from Alfa Aesar and Merck Company, respectively. The materials needed for the manufacture of polymer solar cells, including poly (3–hexylthiophene)[a], [6, 6] poly phenyl $C_{61}$ Butyric acid methyl ester)[b], poly (3, 4–ethylene dioxythiophene): poly (styrene sulfonate)[c] and indium tin oxide[d] was purchased from Sigma Aldrich Company. All solvents used include ethanol, acetone, and chlorobenzene related to Merck Company.

### 2.2. ZnO Nanorods Preparation

Indium-tin-oxide-coated glass substrates (ITO) were washed using appropriate detergent, deionized water, and ethanol by an ultrasonic bath and then dried. A solution of zinc acetate (0.15M) was prepared with ethanol and coated by spin coating (1500rpm, 60s) on cleaned substrates, and after each coating, the substrate was exposed to a temperature of 150 °C for 2 min. This step was repeated from 0 to 5 times to evaluate the effect of the seed layer number on the morphology of the final nanorods. After completion of the coating, the samples were exposed under a temperature of 350 °C for 20 min. The synthesized samples were named as $ZnO_0$, $ZnO_1$, $ZnO_3$, and $ZnO_5$, where 0-5 shows the number of the seed layer coating. A solution of zinc nitrate (0.02M) and hexamethylenetetramine (0.02 M) in ultrapure water (18MΩ) was used as a growth solution. The electrochemical synthesis of zinc oxide nanorods was carried out by the potential-galvanostat device at a constant potential of -1V for 30 min at 80 °C. Finally, the synthesized ZnO nanorods were rinsed with water and ethanol and dried under nitrogen gas flow. To investigate the morphology changes and absorption properties of the synthesized samples, SEM images and absorption spectra were analyzed by using the Philips XL30 device and Lambda 45 Perkin Elmer spectroscopy, respectively. For the preparation of a polymer solar cell, 100 µl of P3HT: PCBM (10 mg/ml solution of with a 1:1 ratio) as the active layer was coated on the zinc oxide nanorods. Then a layer of PEDOT: PSS (0.05g in 5 ml DI water) was coated as a hole transfer layer. Finally, a layer with a thickness of 100 nm of Au was deposited on the sample by physical vapor deposition. The power conversion

[a] P3HT
[b] PCBM
[c] PEDOT:PSS
[d] ITO

efficiency (PCE) of polymer solar cells was investigated using I-V curves.

## 3. RESULTS AND DISCUSSION

To study the effects of the seed layer number on the morphology of zinc oxide nanorods, four samples were synthesized and were named $ZnO_0$, $ZnO_1$, $ZnO_3$, and $ZnO_5$ where 0-5 shows the number of the layer coating. All conditions, including the temperature of the growth solution and the growth time were considered to be the same for all sample. Figure 1 shows the current-time curves for the synthesis of the samples.

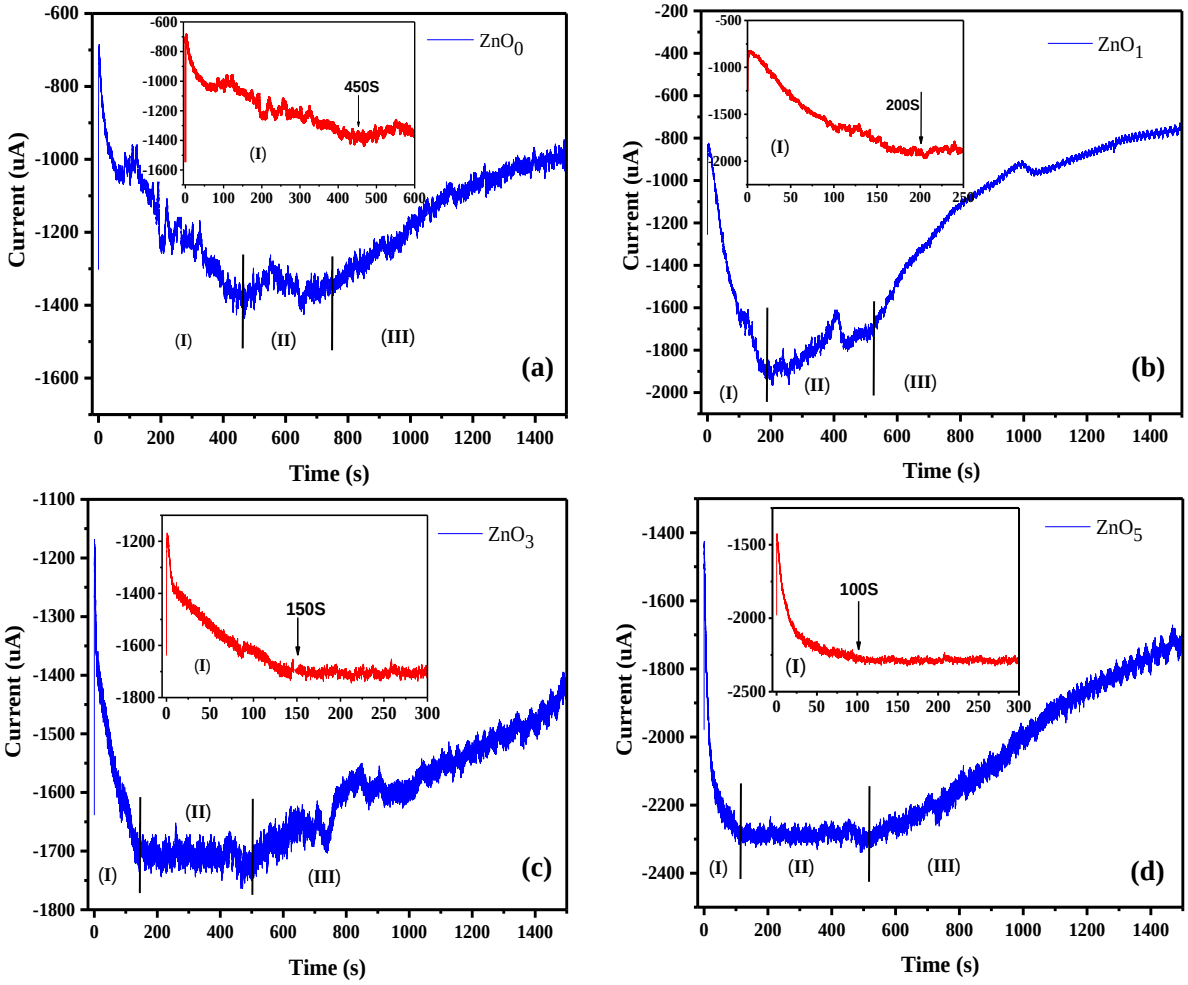


***Figure 1.*** *The current-time curves of synthesized nanorods (a) $ZnO_0$ (b) $ZnO_1$ (c) $ZnO_3$ (d) $ZnO$.*

The mechanism for the formation of zinc oxide nanorods described as the following reactions[17]:

$$(NO_3)_2Zn \rightarrow Zn^{2+} + 2NO_3^- \quad (1)$$

$$(CH_2)_6N_4 + H_2O \rightarrow 4NH_3 + 6HCHO \quad (2)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (3)$$

$$NO_3^- + 2e^- + H_2O \rightarrow NO_2^- + 2OH^- \quad (4)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \xrightarrow{\Delta} ZnO \quad (5)$$

In current-time curves, the cathodic current according to reaction (4) is due to the reduction of $NO_3^-$ ions to produce $OH^-$ on the surface of the ITO. The produced $OH^-$ ions react according to reaction (5) with $Zn^{2+}$ at the ITO surface. This reaction results in the production deposition of $Zn(OH)_2$ and disappears due to instability, and the ZnO nucleation begins on the ITO surface. As seen in the current-time curves shown in Figure 1, these curves consist of three regions [18]. The region (I) indicates the duration of nucleation on the ITO substrate. The high

duration of region (I) indicates that the density of the initial nucleus on the ITO is low[19]. In the region (II), growth occurs on the primary nucleus, and the deposition reaches stable conditions, which remains current at a constant value. In the region (III), the production of $OH^-$decreases due to the decrease of the $NO_3^-$ transfer rate to the electrode surface. In the current-time curve of the $ZnO_0$ sample (Figure 1(a)), since no layer of zinc acetate has been coated on the ITO, the region (I) appeared during 400 seconds, indicating the formation of a very low density of the primary ZnO nuclei. The $ZnO_1$ sample (Figure 1(b)) with a zinc acetate layer coated on the ITO shows a nucleation duration of 200 seconds, which is lower than that observed for the $ZnO_0$ sample. The $ZnO_3$ sample with three layers of zinc acetate on the ITO substrate, according to the current-time curve Figure (1c), was spent 150 seconds on the nucleation process. The $ZnO_5$ sample current-time curve (Figure (1d)) shows a period of fewer than 100 seconds for the nucleation process. This means that during the synthesis of $ZnO_5$ nanorods due to the presence of the initial nucleus on ITO, a lower time span is required to create the ZnO nucleus. SEM images of $ZnO_0$, $ZnO_1$, $ZnO_3$, and $ZnO_5$ are shown in Figure 2.

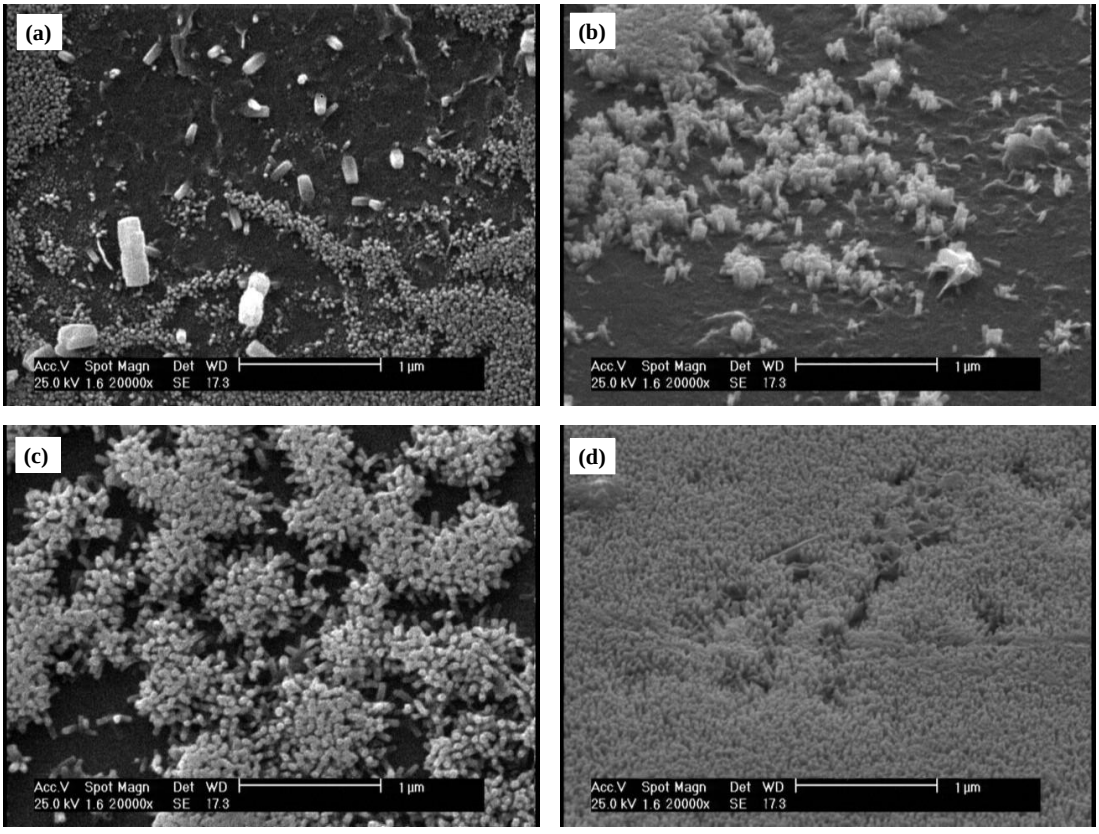


***Figure 2.*** *SEM images of $ZnO_0$ (a), $ZnO_1$ (b), $ZnO_3$ (c), and (d) $ZnO_5$.*

In Figure 2 (a), the SEM image of the $ZnO_0$ sample is shown. For the $ZnO_0$ sample, which was not coated the ZnO seed layer, ZnO nanorods were not formed. This can be expected by depositing a high percentage of the pre-materials used to grow in the bottom of the container. With the addition of the first ZnO seed layer in the $ZnO_1$ sample (Figure. (2b)), ZnO nanorods have grown sporadically, but their density and height were not suitable. $ZnO_3$ sample (Figure (2c)) with three seed layers, due to the increase in the number of initial ZnO nucleus, a large surface of the ITO was covered by zinc oxide nanorods. In the $ZnO_5$ sample with five seed layers, a

uniform and regular coating of ZnO nanorods formed on ITO (Figure 1(d)). Therefore, five seed layers were used as the best choice for the synthesis of zinc oxide nanorods.

The absorption spectra of $ZnO_0$, $ZnO_1$, $ZnO_3$, and $ZnO_5$ samples are shown in Figure 3. The absorption spectrum of the sample, $ZnO_0$, shows a poor absorption peak at 353 nm. The absorption peak of the ZnO nanorods is related to electron transport from the valance band to the conduction band [20]. This weak absorption confirms the very low density of ZnO nanorods formed on the ITO substrate. By coating the first seed layer on ITO, $ZnO_1$ shows its peak absorption spectrum at 361 nm. With the addition of the first seed layer, the absorbance of the $ZnO_1$ sample increased compared to the $ZnO_0$ sample, and a redshift was also observed. The $ZnO_3$ sample shows a higher absorption than $ZnO_1$ at 365 nm, due to the formation of higher concentration of ZnO nanorods on ITO. With five seed layers on ITO, the absorption spectrum shows an absorption peak at 370 nm. The absorption rate of the $ZnO_5$ sample is higher than that of other samples, due to more and uniform growth over the entire ITO surface. Also, the largest redshift in the absorption spectrum is related to the $ZnO_5$ sample. The redshift in the absorption spectrum of the samples is due to changes in particle size and quantum constraints. These quantum confinement can be easily explained by the particle energy relation in the three-dimensional box:

$$E = A\,(n_x^2/x^2 + n_y^2/y^2 + n_z^2/z^2) \quad (6)$$

In this relation, A is a constant, $n_x$, $n_y$ and $n_z$ are quantum numbers and x, y and z are the coordinate directions. Since the ZnO nanorods are restricted to x and y and only operate freely along the z-axis and also assuming the nanorods are in the base level ($n_z = n_y = n_x = 1$), the energy relationship is simplified as follows:

$$E = A\,(1/x^2 + 1/y^2) \quad (7)$$

So the larger the nanorod dimensions, the bandgap is smaller and the energy needed to excite the electrons is reduced. So by increasing the size of the nanorods, a redshift in the absorption spectrum will occur [21-23].

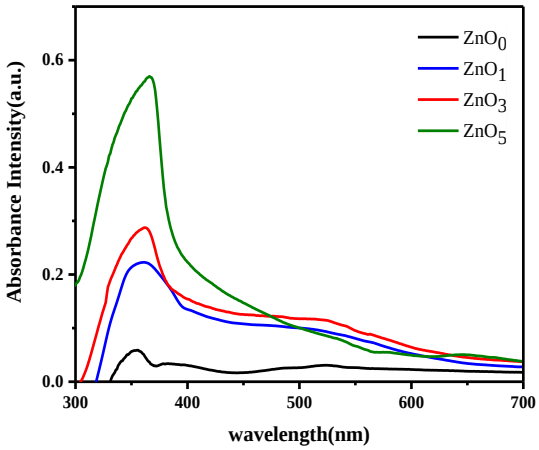


***Figure 3.*** *Absorption spectra of $ZnO_0$, $ZnO_1$, $ZnO_3$, and $ZnO_5$.*

The values obtained from measuring the surface resistance of the synthesized samples are shown in Table 1.

***Table 1.*** *Sheet resistance values of $ZnO_0$, $ZnO_1$, $ZnO_3$, and $ZnO_5$ samples.*

| $ZnO_5$ | $ZnO_3$ | $ZnO_1$ | $ZnO_0$ | sample |
|---|---|---|---|---|
| 90 | 150 | 800 | 1400 | *Sheet resistance (Ohm/sq.)* |

According to the values of Table 1, increasing the number of seed layers for the synthesis of zinc oxide nanorods has led to an increase in the electrical conductivity of the samples. Since higher electrical conductivity of zinc oxide nanorods is essential for the application of transparent conductive oxides and solar cells, increasing the number of seed layers during the synthesis of zinc oxide nanorods will be essential. Polymer solar cell has been considered due to advantages such as flexibility, low weight, and proper absorption coefficient [24]. The problem of polymer solar cells is low efficiency. One of the factors affecting the low efficiency

of polymer solar cells is the inefficient collection of electrons and holes as well as their recombination. Therefore, the design of solar cell systems requires a layer for the effective acceptance of electrons from the active layer and their transfer to the corresponding electrode [25]. This layer is known as the electron transfer layer (ETL). The role of this layer is to increase the electron transfer rate from the active layer to the corresponding electrode and reduce the recombination of the electrons and holes generated in the active layer, thereby increasing the efficiency of the polymer solar cell [26]. ZnO nanorods provide a direct pathway for electrons passing from the electron receiving point (active layer) to the collector electrode. This direct path increases the electron transfer rate to the collector electrode several times over than random electron transfer mechanism. As a result, the possibility of recombining the electrons with the holes decreases and ultimately leads to an increase in the efficiency and performance of the polymer solar cell. In Figure 4, the schematic structure of a polymer solar cell with zinc oxide nanorods as an electron transport layer is shown.

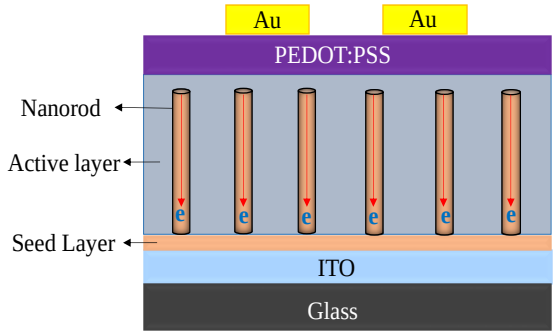


***Figure 4.*** *Schematic structure of polymer solar cell with zinc oxide nanorods as an electron transport layer.*

Electrochemical impedance spectroscopy (EIS) was used to investigate the effect of seed layer number on zinc oxide nanorods as an electron transfer layer in polymer solar cell. Figure 5 shows the Nyquist curve for polymer solar cells with $ZnO_0$ and $ZnO_5$. The Nyquist curve contains one semicircle at high frequencies (smaller semicircle) and the other semicircle at low frequencies, which corresponds to the interface between zinc oxide nanorods/ active layer and the interface between P3HT and PCBM, respectively. The equivalent circuit shown as an inset in Figure 5 was used to fit the EIS data. *Rs* represents the solution and metal contact resistances. *R1* is related to the charge transfer resistance at the interface between zinc oxide nanorods and the active layer, while *R2* is attributed to the recombination resistance at the P3HT and PCBM interfaces. As can be seen from the Nyquist curve, the use of $ZnO_5$ compared to $ZnO_0$ reduces the charge transfer resistance ($R_1$) and increases the recombination resistance ($R_2$). The reason for this improvement is the uniformity of the nanorods at $ZnO_5$, which increases the charge transfer between the active polymer and the collecting electrode and reduces the recombination between electrons and holes.

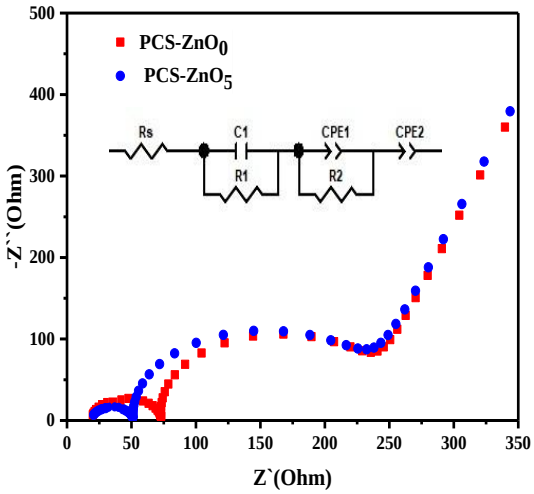


***Figure 5.*** *The Nyquist curve for polymer solar cells with $ZnO_0$ and $ZnO_5$.*

In the present work, reference polymer solar cells (without zinc oxide nanorods) and polymer solar cells with zinc oxide nanorods were named PSC-Ref and PSC-$ZnO_5$, respectively. Figure 6 shows the current-voltage curve (I-V) of the prepared polymer solar cells.

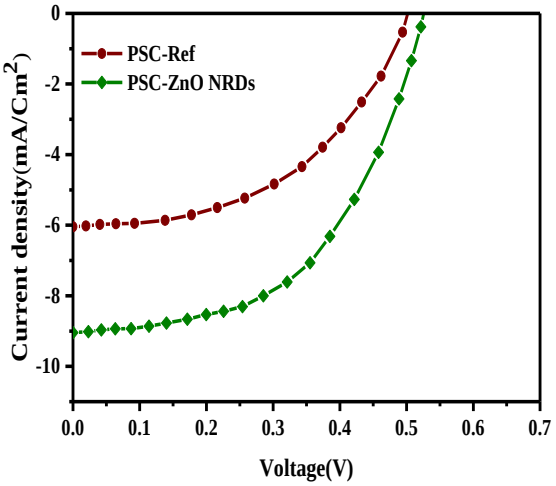


***Figure 6.*** *Current-voltage of the prepared polymer solar cells.*

The efficiency and performance of polymer solar cells are calculated from the following equations:

$\eta = Pm / Pin = (Voc \times Jsc \times FF) / Pin$

$FF = Pm / (Voc \times Jsc)$

In this equation, Pm, Pin, Voc, Jsc, and FF, respectively, are the maximum output power, input power, open circuit voltage, short circuit current, and Fill Factor. As the current-voltage curves are observed, the application of high-density zinc oxide nanorods ($ZnO_5$) as an electron transport layer in a polymer solar cell increases open circuit potential, short circuit current and generally causes increases the efficiency of polymer solar cell. The numerical values of the photovoltaic parameters of polymer solar cells are shown in Table 2.

***Table 2.*** *Numerical Values of Photovoltaic Parameters of Polymer Solar Cells.*

| Photovoltaic parameters | PSC-Ref | PSC-$ZnO_5$ |
|---|---|---|
| *Jsc (mA/cm$^2$)* | 6.05 | 9.04 |
| *Voc (V)* | 0.5 | 0.53 |
| *FF (%)* | 49.1 | 52.7 |
| *PCE (%)* | 1.49 | 2.51 |

As the numerical values of Table 2 indicate, the addition of zinc oxide nanorods to the structure of the solar cell has increased the 49% short circuit current, increased the open circuit voltage by 6%, increased the fill factor by 7%, and increased the performance of the polymer solar cell by 68%. So, the power conversion efficiency of the polymer solar cell increased from 1.49 to 2.51%.

## 4. CONCLUSION

In summary, using SEM images, UV-Vis absorption spectra, and four-point probe, we showed that increasing the number of seed layers leads to the formation of regular-structure ZnO nanorods with high-density, and high electrical conductivity. The use of the electrochemically-grown ZnO nanorods grown on five layers of zinc acetate (as the seed layer) as ETL in fabrication of polymer solar cells resulted in 49% increase in short-circuit current, 6% increase in open circuit voltage, 7% increase in Fill Factor, and consequently a 68% increase in the power conversion efficiency of the polymer solar cells compared to the reference cell.

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