

## Polythiopene sodium poly [2-(3-thienyl)-ethoxy-4-buthylsulfonate] Inkjet Printed Film-Sensitized ZnO Nanorods Solar Cells

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This paper reports the study of the sensitizing effect and the structure of the water soluble polymeric dye of polythiopene sodium poly [2-(3-thienyl)-ethoxy-4-buthylsulfonate] (PTEBS) ink-jet thin film on the performance of the dye sensitized solar cells (DSSC) based-ZnO nanorods (ZNRs). DSSC device with sandwich structure of FTO/ZNRs/PTEBS/electrolyte/ Pt was prepared in this study with the electrolyte used was  $I/I^3$  redox couple. The PTEBS thin film was deposited onto the ZNRs-coated FTO substrate via an inkjet printing technique from the aqueous solution. To obtain a variation in the thin film structure, the PTEBS was grown via a multiple-step printing approach, namely from three to up to seven times. It was found that the PTEBS ink-jet printed film exhibit effective sensitizing effect on the DSSC by giving enhanced photovoltaic performance of multiple higher order (approximately 3 times) compared to a controlled device, the device without PTEBS and its structure was found to influence the charge transfer process in the device. A high performance DSSC device can be obtained from the PTEBS film with highly compact and even structure that prepared by three time printing process, which gives performance of  $J_{sc}$ ,  $V_{oc}$  and  $FF$  as high as  $0.96 \text{ mA/cm}^2$ ,  $0.42 \text{ V}$  and  $34\%$ , respectively, which is corresponding to power conversion efficiency ( $PCE$ ) as high as  $0.14\%$ .

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**Keywords:** Poly [2-(3-thienyl)-ethoxy-4-buthylsulfonate]; Water soluble polymer; ZnO nanorods; Inkjet printing; Dye-sensitized solar cell.

## 1. INTRODUCTION

Dye-sensitized solar cell (DSSC) has been considered as one of the promising potential photovoltaic devices due to its simple, easy and cost-effective preparation process [1, 2] [2, 3]. In the DSSC device, dye material is an important component that absorbs the light, which then excites its electrons to the lowest unoccupied molecular orbital (LUMO) and injects them to the conducting band of the high band-gap semiconducting material photo anode [3, 4].

To obtain effective sensitizing effect of the dye in the DSSC, the dye should be in a perfect contact with the semiconducting material, so that facile charge transfer process can be attained [5]. In many case, the effective attachment of the dye onto the semiconducting materials surface strongly depend on the solvent used [6-9]. Special solvent, particularly, those with specific polarity, miscibility, viscosity, vapor pressure, and etc., are commonly used to obtain high-quality thin films [9]. A special treatment, such as overnight stirring, heat treatment, and etc., [10, 11] should also be applied to produce high quality thin film structure, inferring the process is intricate and expensive. The use of dye that can be prepared in common solvent or water is highly demanded for producing practicable DSSC.

Water soluble polymer is receiving an increasing attention as the dye in DSSC [12-15]. It is due to the nature of water that is environmental friendly, which then leads to a green device fabrication process. Polythiophene sodium poly [2-(3-thienyl)-ethoxy-4-buthylsulfonate] (PTEBS) is among the water soluble polymer that attracts active attention in DSSC fabrication [13]. This material is chemically stable in ambient condition. Thin film of PTEBS has been found to form good contact with most metallic surface, makes it potential for photovoltaic device fabrication. For example, Miller and his coworkers reported that the PCE of solar cell significantly improved when spin-coated PTEBS thin film was applied in the solar cell composed of carbon nanotubes [16]. Since the structure of the dye strongly influence the nature of charge transport properties in the device [10], to study the effect of structure of PTEBS on the performance of DSSC should be continuously demonstrated. Here, we report the study of the effect of thin film structure on the dye sensitizing process of water soluble PTEBS thin film that prepared by ink-jet printing technique in a DSSC solar cell utilizing ZnO nanorods. By controlling the structure of the thin film via multiple deposition method, power conversion efficiency as high as 0.14% was obtained. This efficiency is relatively higher than that recently reported utilizing this material as active materials in solar cell presumably due to the highly compact and uniform structure of the PTEBS. Owing to its unique water soluble property and its thin film property can be finely adjusted via ink-jet printing process; the ink-jet printed film of PTEBS should find extensive use in DSSC.

## 2. EXPERIMENTAL

### 2.1. Preparation of ZnONRs

Zinc nanorods were firstly prepared by a two step growth process, namely seeding and growth process. Seeding process, namely growth of nanoparticles of ZnO of size ca. 5 to 10 nm, was carried

out by simply immersing the FTO substrate into an ethanolic solution that contains 0.1 M zinc acetate ( $\text{Zn}(\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ) (98%, Sigma Aldrich) and 0.1 M DEA ( $\text{C}_4\text{H}_{11}\text{NO}_2$ ) (99%, Sigma Aldrich) in ethanol. The substrate was then annealed at 350°C in air for an hour. Using this process, high density ZnO nanoseed can be obtained on the surface. Meanwhile, the growth process was carried out by using a hydrothermal growth approach [17], by immersing the ZnO nanoseed coated FTO into aqueous solution that contains equimolar (0.04 M) of zinc nitrate hexahydrate and hexamethyl-tetramine (99%, Sigma Aldrich). The reaction was then isolated in a stainless steel autoclave and transferred into an electrical oven and heated at 90°C. The growth time was 45 min.

## 2.2. Preparation of PTEBS thin films on ZnO nanorods (ZNRs)

Water-soluble PTEBS was purchased from American Dye Source Inc. and used as received. Prior to preparing ink-jet printed film, aqueous PTEBS ink was prepared by dissolving the chemical in 2 mL deionized water (DI) at concentration of 30 mg/mL. The solution was then stirred overnight to obtain a homogeneous solution. 0.1 mL of 0.1 M NaOH was then added into the solution to maintain the pH at 9.0. The solution was then transferred into a pneumatic plastic cartridge. Ink-jet printed film of PTEBS on ZNRs was prepared using a Dimatic Ink-jet Printer (USA) at acceleration voltage of 5 V and substrate temperature of 25 °C. The as prepared thin film was then annealed at 100 °C for 10 min in air. This procedure was repeated to obtain multiple growth of PTEBS thin film.

## 2.3. Fabrication of DSSC cell

The DSSC of FTO/ZNRs/PTEBS/electrolyte/ Pt was fabricated to study the effect of dye sensitizing of PTEBS films and the relationship of thin film structure of the solar cell performance. The platinum film counter electrode on FTO substrate was prepared by using magnetron sputtering technique at an acceleration voltage of 2.5 kV for 2 min. Meanwhile, an electrolyte containing 0.5 M LiI, 0.05 M iodine and 0.5 M tertbutylpyridine in acetonitrile was used as the redox couple [18]. The electrolyte was sandwiched between the PTEBS-coated ZnONRs structure and the counter electrode, which was clamped each other using paper clipper. The active area of the DSSC was 0.23 cm<sup>2</sup>. The schematic structure of the device is shown in Figure 1.

## 2.4 Characterizations

The surface morphology of the ZNRs sample was obtained using Carl Zeiss Supra 55VP field emission scanning electron microscopy (FESEM). Meanwhile, the crystallinity was characterized using the X-ray Diffractometer (XRD, Bruker D8) with  $\text{CuK}\alpha$  irradiation. The scanning rate of as low as 0.002°/s was used throughout the experiment. The optical properties of the ZNRs and the PTEBS coated ZNRs were collected using Halo DB-20 UV-Vis spectrometer.

The performance of the DSSC was studied using a Keithley high voltage source-measure unit (SMU) model 237 under AM 1.5 simulated irradiation (100 mW/cm<sup>2</sup>) provided by the Newport low-

cost solar simulator 150W.

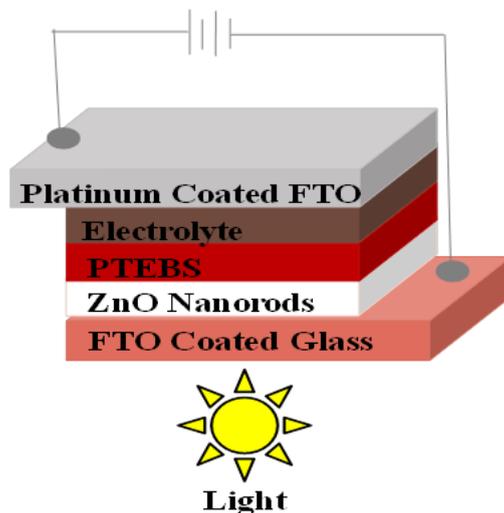


Figure 1. The DSSC with FTO/PTEBS coated PTEBS/Electrolyte/Platinum structure

### 3. RESULTS AND DISCUSSION

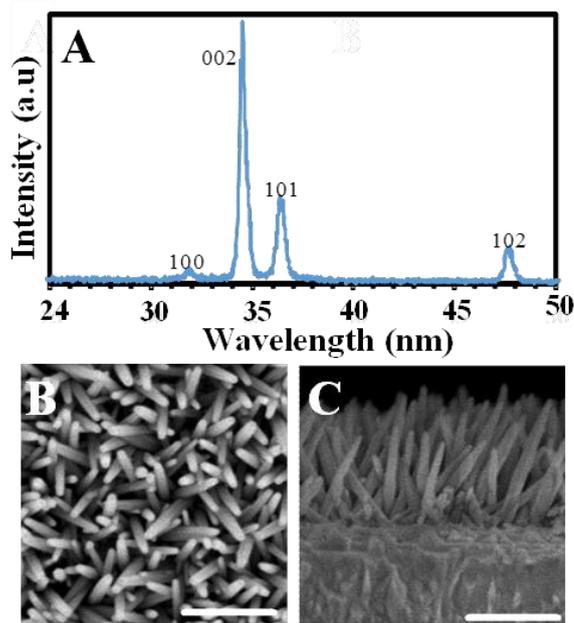
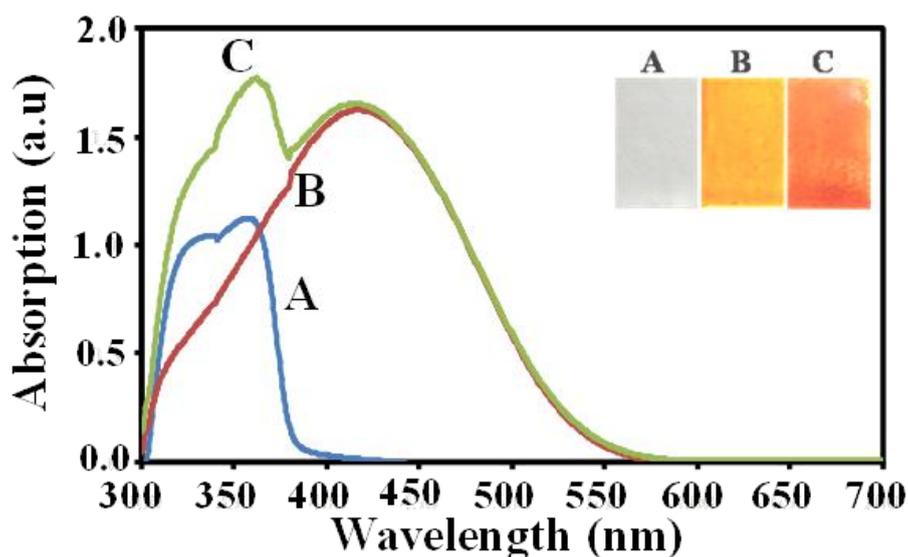


Figure 2. (A) Typical XRD spectra of Zinc oxide Nanorods (ZNRs), (B) FESEM images of ZNRs and its cross-sectional view (C). Scale bar are 1 $\mu$ m

The ZnO nanorod (ZNRs) has been successfully grown on the FTO substrate. Their XRD analysis has confirmed the formation of them of which their result presented in Figure 2A. As Figure 2A shows, 5 diffraction peaks, namely at  $2\theta=32.01^\circ$ ,  $34.5^\circ$ ,  $36.5^\circ$ , and  $47.8^\circ$  are obtained in the spectrum. This spectrum profile is in good agreement with the JCPDS file: No. 84-1286 for ZnO with

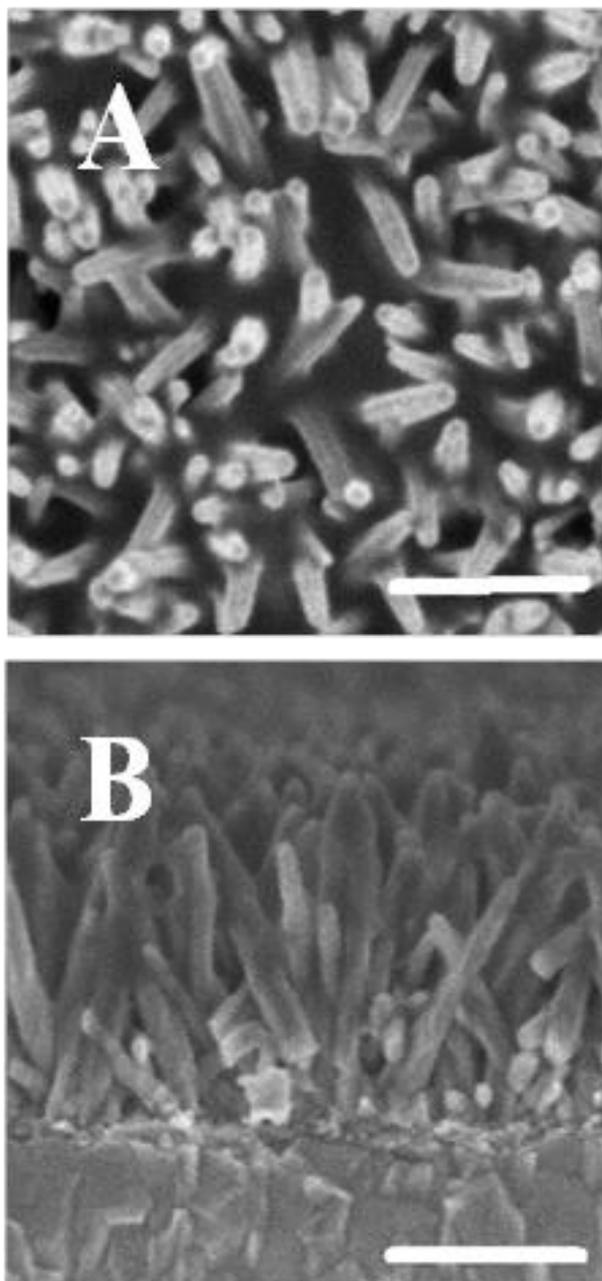
peaks corresponding to the diffraction from (100), (002), (101), and (110) Bragg planes, respectively. Figure 2B shows the typical FESEM images of the ZnO nanorods (ZNRs) on the FTO substrate. As can be seen from the figure, ZNRs with diameter and length of approximately 80 and 400 nm were homogeneously grown on the FTO substrate. As also revealed in the image, the ZNRs oriented randomly on the surface. This may produce high-surface area, which is advantageous for solar cell device fabrication. Cross-sectional analysis (Figure 2B) further confirms such random nature of the ZNRs orientation on the surface. It was also confirmed that the FTO substrate has been effectively covered by the ZNRs, enabling the fabrication of a solar cell device.



**Figure 3.** UV-Vis absorption spectra of (A) ZNRs, (B) PTEBS and (C) PTEBS-coated ZNRs. Insets are their corresponding digital image

Next, the PTEBS thin film was ink-jet printed on the ZNRs. Figure 3 and its inset's pictures shows their absorption spectra and typical digital image of the samples, namely ZNRs, PTEBS film and PTEBS-coated ZNRs on the ITO substrate. As can be seen from the inset picture, actually original color of the ZNRs film on the surface is whitish-transparent, resulting presumably from the small structure of ZNRs grown on the surface. Greyish color shown in this image is due to the background effect. In the inset, the original color of the ink-jet printed PTEBS thin film is also presented (inset B). The film exhibits yellowish color. When the PTEBS thin film ink-jet printed on the ZNRs, the color our changed to brownish (inset C). As can be seen from the figure, the PTEBS film was compactly, evenly and homogeneously grown on the surface of ZNRs structure. This condition should be suitable for solar cell device fabrication as these characteristic may feature low structural defect, facilitating a facile carrier transport in the device. Figure 3B shows the optical absorption spectra of the sample, namely ZNRs, PTEBS thin film and PTEBS-coated ZNRs. As can be seen from the spectra, the original ZNRs exhibits well-shaped absorption band that consists of two excitonic characters in the region of 300 to 400 nm. This infers the ZNRs structure used in this work is high crystallinity in nature. The growth of PTEBS on the ZNRs effectively broadens the absorption windows up to 570 nm.

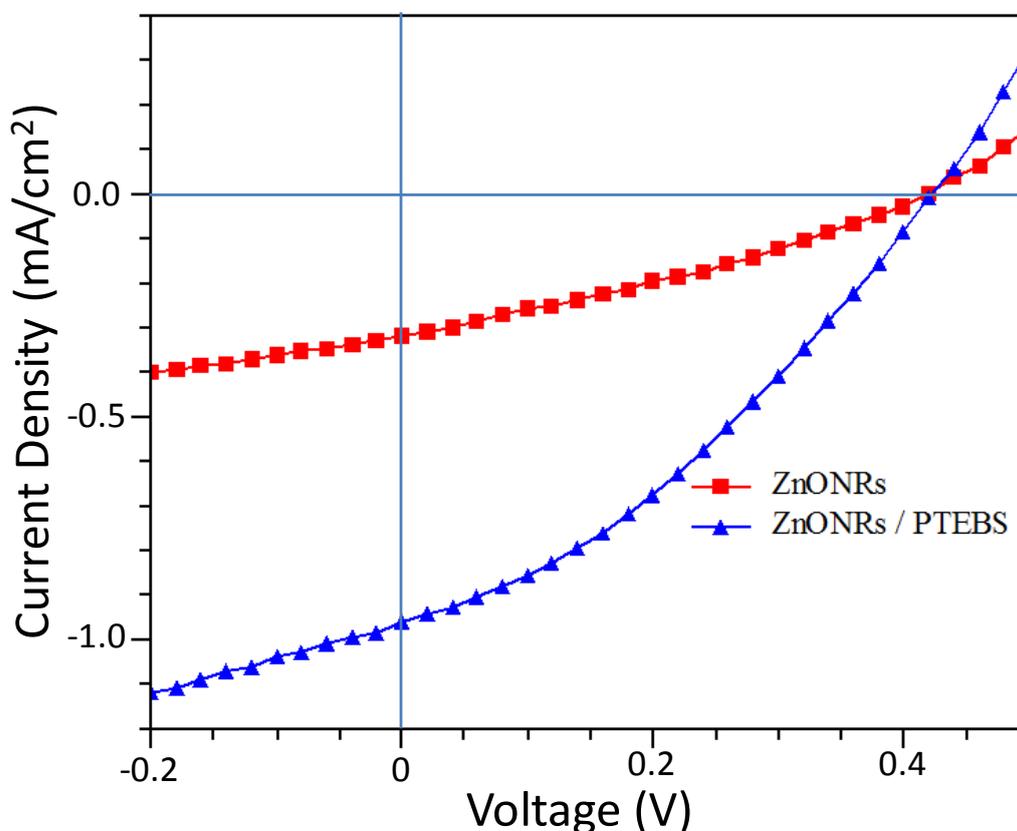
Interestingly, the original absorption profile of ZNRs is still observed and even enhanced. This could be an indication of the effective synthesizing effect of the PTEBS thin film.



**Figure 4.** Typical FESEM image of ink-jet printed film of PTEBS-coated ZNRs (A) and its cross-sectional image (B). Scale bar are 1  $\mu\text{m}$

While the UV-vis analysis confirmed the successfulness of the PTEBS growth on and “sensitizing” the ZNRs by broadening the absorption window of the PTEBS-coated ZNRs system, the FESEM images analysis on the PTEBS-coated ZNRs as shown in Figure 4 further confirms the successful attachment of PTEBS on the ZNRs surface. As the Figure 4 shows, the PTEBS (shown by

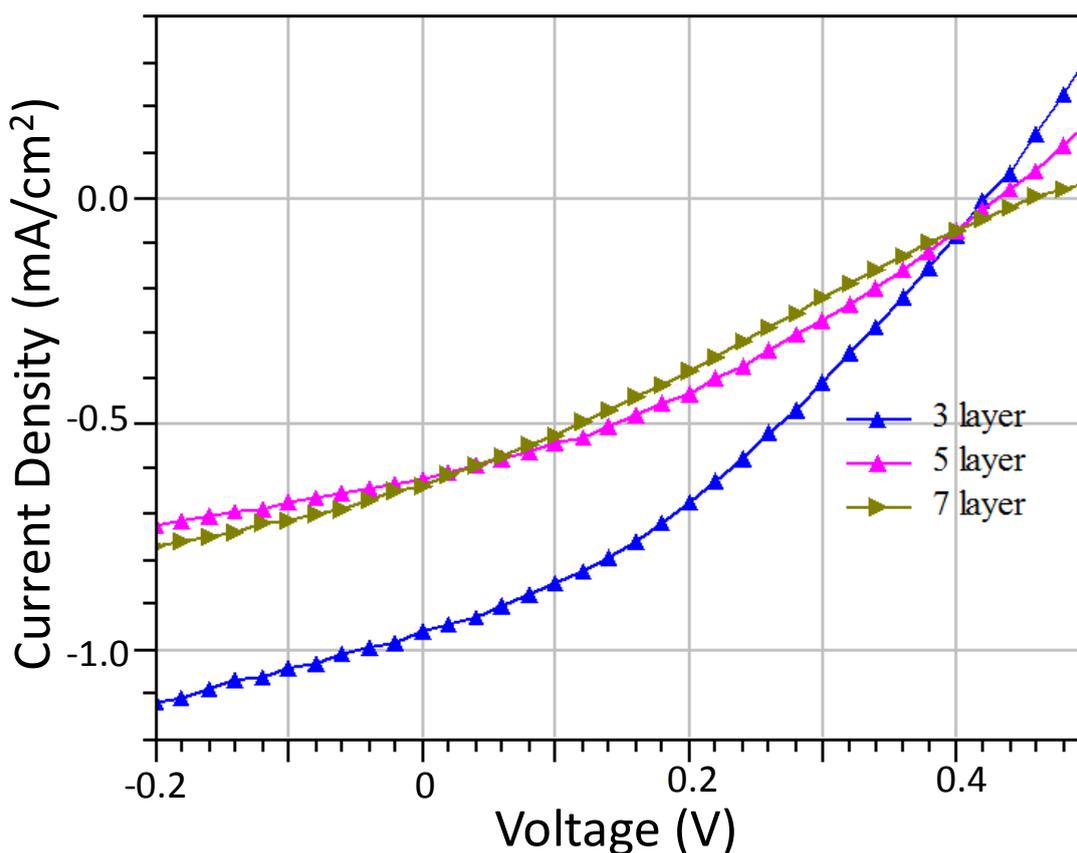
the darker contrast on the ZNRs surface) have efficiently covered the entire surface of the ZNRs. This could be the reason of the effectiveness of sensitizing effect of PTEBS as previously shown in Figure 3B. Cross-sectional analysis shown in Figure 4 further indicated that the ink-jet printed film of PTEBS not only covers the surface but also well infiltrates into the deeper part of the ZNRs. This condition may promote effective charge transfer between PTEBS and ZNRs or provide efficient electron pathway, thus improve the cell performance [18].



**Figure 5.** Current-voltage ( $J$ - $V$ ) characteristics of DSSC with ZNRs and PTEBS-coated ZNRs

After assembling a DSSC, as shown in Figure 1, utilizing the PTEBS-coated ZNRs, their photovoltaic response under simulated AM. 1.5G ( $100 \text{ mW/cm}^2$ ) light irradiation was analysed. The result of  $J$ - $V$  curves for device utilizing ZNRs and PTEBS-coated ZNRs is shown in Figure 5. As can be seen from the figure, the device with PTEBS-coated ZNRs yields  $J_{sc}$  and  $V_{oc}$  as high as  $0.96 \text{ mA/cm}^2$  and  $0.42 \text{ V}$ , respectively. This is corresponding to the field factor ( $FF$ ) and power conversion efficiency ( $PCE$ ) as high as  $34\%$  and  $0.14\%$ , respectively. This result is much higher (ca.~ 3 times) compared to that of without PTEBS films, which only yields  $PCE$  as high as  $0.04\%$ . On the basis of this result, it can be worth mentioning that the PTEBS ink-jet printed film has excellent sensitizing effect on the ZNRs. As the structure of the dye film is understood to determine the performance of the DSSC, we then modified the structure of the PTEBS thin film by preparing the thin film via multiple printing processes of PTEBS on the ZNRs and evaluated the photovoltaic performance. The results are

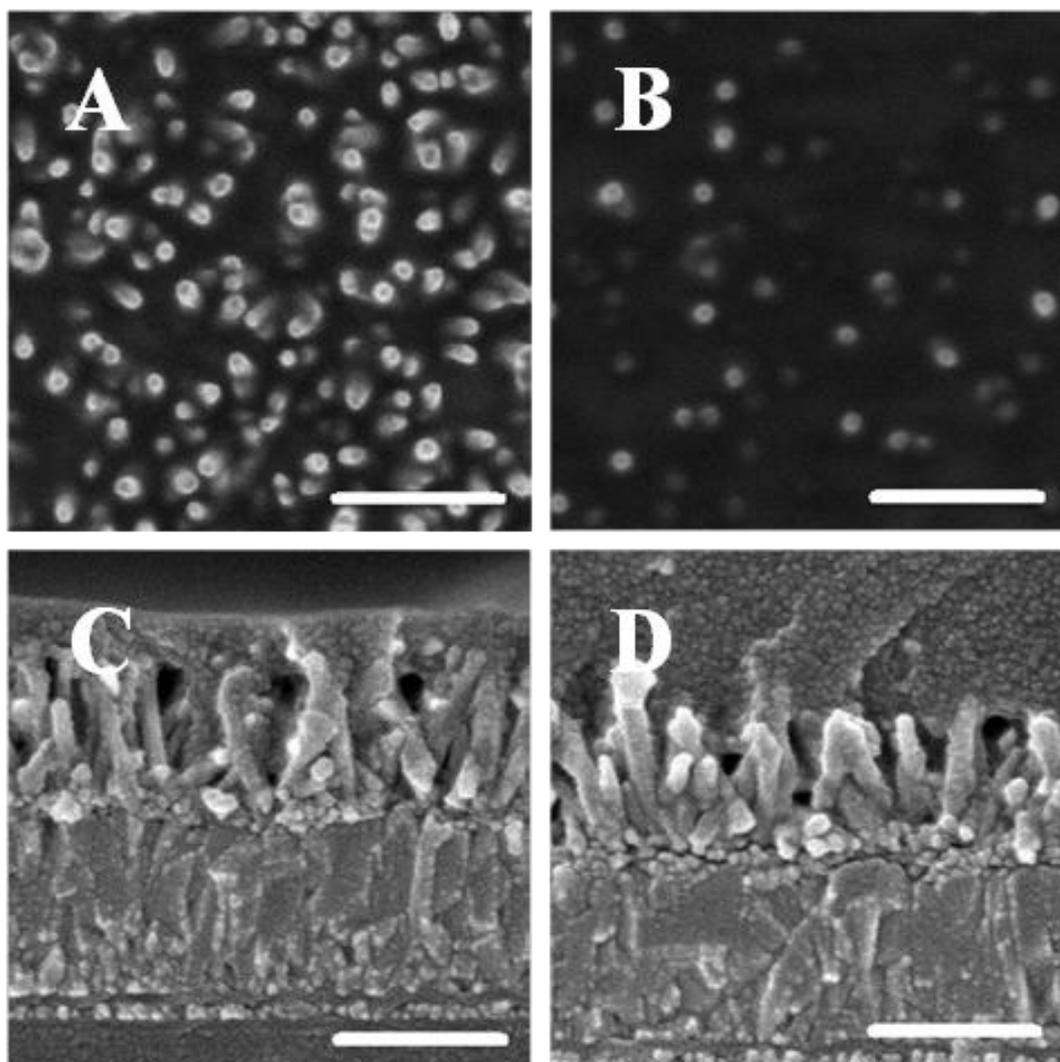
shown in Figure 6. As can be seen from the Figure 6, the performance of the DSSC was found to decrease with the increasing of the printing repetition. Typical *PCE* for the device utilizing 5 and 7 times PTEBS print are 0.09% and 0.08%, respectively, which are much lower compared to the optimum device (utilizing 3 times printing of PTEBS film). This could be due to the increasing in the series and shunt resistance of the device as the PTEBS printing repetition increase, leading to active exciton recombination process. FESEM analysis on the samples as shown in Figure 7 further confirmed that the increasing of the printing repetition has increased the un-evenness of the PTEBS film. This condition may cause the increasing in the trapping site as well as increasing the series resistance of the device, thus degrades the charge transport to the electrode. The photovoltaic parameter of the DSSC prepared using different number of ink-jet printing repetition is presented in Table 1.



**Figure 6.** The current-voltage (J-V) characteristics of DSSC cell with different number PTEBS film printing repetition.

It is true that the present efficiency is relatively low compared to the recently reported result on the DSSCs [19, 20], however, it is little bit higher or comparable with the result reported by Baeten et al.[21] and Qiao et. al [22] on the water soluble polymer film for solar cell application. For example, Qiao achieved efficiency as low as 0.015% when using PTEBS in  $\text{TiO}_2$  base solar cell. Meanwhile, Baeten, by using water soluble P3HT, obtained the efficiency as high as 0.2%, which is more or less

similar with the present study. There are several factors, including the nature of the dye-adsorption on the ZNRs, the nature of the charge transfer at the interface between the electrolyte and photocathode and the electrolyte and dye, that influence the photovoltaic performance of the DSSC [23-25]. We realized that at this stage all of the influencing factors in the current device are still yet to control. Further study is necessary to obtain a high-performance DSSC. However, as the quality of PTEBS film on the ZNRs structure is relatively good with excellent infiltration to the deeper part of the ZNRs (see Figure 3), we hypothesized that the loss might be contributed by the nature of the charge transport in the ZNRs structure, the interface between ZNRs and the FTO or the interface between electrolyte and photocathode. High performance PTEBS-coated ZNRs DSSC may be achieved when optimum parameters, such as contact between PTEBS and ZNRs as well as homogeneity in its film structures including film distribution on the ZNRs surface, are obtained. The effort towards this goal is being pursued.



**Figure 7.** FESEM micrographs for PTEBS-coated ZNRs at different printing repetition, namely 5 (A) and 7 times (B). C and D are their cross-sectional image, respectively. Scale bars are 1  $\mu\text{m}$

**Table 1.** The photovoltaic parameter of PTEBS-coated ZNRs DSSC solar cell

Number of layer	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
Control device	0.40	0.32	33	0.04
3	0.42	0.96	34	0.14
5	0.42	0.62	34	0.09
7	0.44	0.64	28	0.08

#### 4. CONCLUSIONS

The sensitizing and the structural effects of ink-jet printed film of PTEBS on ZNRs DSSC device performance have been demonstrated. It was found that the ink-jet printed film of PTEBS exhibits relatively good sensitizing effect to ZNRs that yields power conversion efficiency as high as 0.14% with  $J_{sc}$  and  $V_{oc}$  as high as 0.96 mA/cm<sup>2</sup> and 0.42 V, respectively, which is approximately 3 times higher than the control device. It was also found that the structures of the ink-jet printed film determined the sensitizing effect of which the film with high homogeneity produced the highest in the performance of the DSSC. Owing to the simplicity of the film preparation and aqueous base solution processing makes the PTEBS thin film as the prospective polymeric dye materials for high performance DSSC.

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