Evolution in Electrical and Electronic Engineering Vol. 1 No. 1 (2020) 136 - 144


**EEEE**

Homepage: http://penerbit.uthm.edu.my/proceeding/index.php/eeee
e-ISSN : 2756-8458

# Nanostructure Zinc Oxide Film Based Dye-Sensitized Solar Cell

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DOI: https://doi.org/10.30880/eeee.2020.01.01.016
Received 02 August 2020; Accepted 06 September 2020; Available online 30 October 2020

**Abstract**: Solar energy is the most abundant renewable source and a continuous source of clean energy. Dye sensitized solar cell (DSSC) is the third generation of solar cells and as a new trend in the photovoltaic technology. DSSC had been widely studied due to it is low cost and high conversion efficiency. Zinc Oxide (ZnO) become potential candidates as the photovoltaic material in DSSC due to its unique properties. Fluorine doped thin oxide (FTO) had been used to fabricate ZnO thin film. Preparation of ZnO thin film were using hydrothermal method in this research. The recipe for prepare the Zinc Oxide (ZnO) solution that used consists of zinc nitrate hexahydrate [(Zn(NO3)2.6H2O], hexamethylenetetramine (HMTA) [C6H12N4] and deionized (DI) water in this research. The ratio of 1:1 for zinc nitrate hexahydrate and hexamethylenetetramine. The growth of ZnO were implemented with various concentration of ZnO solution, which carried out as deposited, 40mM, 60mM, 80mM and 100mM. The dye D149 had been used because of its well absorbance properties for sensitization process. X-ray Diffraction (XRD) is used to determine the crystal substances Moreover, the surface morphology of ZnO nanostructure is characterized by using field emission scanning electron microscope (FE-SEM). Besides, solar simulator acts as an artificial sun to test the behavior of solar cell in this research. Lastly, the sheet resistance and resistivity of ZnO thin film is determined by using two-point probe. The 100mM of ZnO solution concentration is a suitable concentration to grow the nanorods with larger surface area to obtain a higher efficiency.

**Keywords**: Dye Sensitized Solar Cell (DSSC), Zinc Oxide (ZnO), Fluorine doped thin oxide (FTO), Hydrothermal method.

## 1. Introduction

In recent years, there has been a rise in the world's attention to the international energy crisis and concern regarding the green technology trend. Researches have acknowledged that there is an increase in demand of renewable energy to substitute fossil fuel. Fossil fuel can generate a million watts of power and it is an effective source formed by natural processes. In addition, coal, oil and natural gas also known as non-renewable energy that consumed in our daily life which lead to significant environmental concern such as pollutions and high level of carbon dioxide in the air [1].

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Dye sensitized solar cells (DSSCs) are the new trends in the photovoltaic technology and proposed as a low-cost fabrication. The category of third generation photovoltaics was placed as the DSSCs [2]. DSSC has a unique working mechanism in its p-n junction solar cell and become a practical alternative in technology of solar cell [1]. In DSSC, sunlight is absorbed by sensitizer which is dye for transforming solar energy into electrical energy [3]. There were a large number of experiments had been subjected to DSSC photo electrochemical cells since 1991. The optical absorption and charge separation process had been separated in DSSC by associating a sensitizer with a wide band gap semiconductor [4].

In the past few years, there is much attention has been given to Zinc Oxide (ZnO) which as a potential photovoltaic material in DSSCs. It is due to properties of ZnO such as a wide and direct band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature. It has high chemical and physical stability, low cost price, non-toxicity and high electrical conductivity which are the advantages of the use of ZnO as layers in DSSC. ZnO thin film can be fabricated by various techniques to produce various nanostructure [5].

## 2. Experiment

ZnO thin film had been fabricated by fluorine doped thin oxide (FTO) via hydrothermal method. The steps of this method are seeding process deposited by zinc acetate dehydrate and methanol and then prepare ZnO solution by zinc nitrate hexahydrate and hexamethylenetetramine (HMTA) to form various concentration. Hydrothermal method is carried out after the ZnO solution had been prepared. Before seed layer process, the cleaning process for FTO substrate was needed by using acetone, ethanol and deionized water for 15 minutes in ultrasonic cleaner machine. The FTO substrates were ready to be used for growth process..

### 2.1 Seeding process

The Zinc Oxide (ZnO) seed layers were prepare by using 10mM of zinc acetate dehydrate [$Zn(CH_3COOH)_2$.2H2O] and 20ml of methanol [CH3OH]. The size of FTO glass substrate is 2.5cm x 1cm, however the size used for this experiment is fixed to 1cm x 1cm. So, the glass with 1.5cm x 1cm is user to cover the unused place of FTO substrate. Then, the glass is placed on the FTO substrate and wrapped with white tape. After stirring for 10 minutes, the FTO substrate is placed on the hot plate at 100℃. Five drops of solution is dropped on the selected surface of FTO substrate by using plastic pipettes dropper. After that, the FTO substrates was annealed at 100℃ for 1 hour.

### 2.2 Preparation of ZnO solution

The recipe for prepare the ZnO solution that used consists of zinc nitrate hexahydrate [(Zn(NO3)2.6H2O], hexamethylenetetramine (HMTA) [C6H12N4] and deionized (DI) water. The ratio of zinc nitrate hexahydrate and hexamethylenetetramine is 1:1. Firstly, 40mM of zinc nitrate hexahydrate is stirred with 100ml of deionized (DI) water for 10 minutes using the stirrer. Then, by using different beaker, 40mM of hexamethylenetetramine is stirred with 100ml of deionized (DI) water for 10 minutes using the stirrer. Then, both solution are mixed and then stirred again for another 10 minutes. Next, stirred differences concentration of zinc nitrate hexahydrate and hexamethylenetetramine which are 60mM, 80mM and 100mM..

### 2.3 Hydrothermal method

For hydrothermal process, The FTO substrate was placed upward into bottle made liner and the solution will be put into the bottle carefully. Next, the bottle will be placed into the oven with a constant temperature of 90℃ for 3 hours. Noted that the FTO surface need to be check by using multimeter and if there is resistance on that surface, then it is an FTO layer. Since that the FTO glass substrate only have one FTO surface that allow the growth of the nanorods.

After the process ended, the bottle will be takeout from the oven and let it cool in the room temperature for at least two hours. After that, the substrate will be rinsed by using DI water and dried them. The surface morphology and the structural property of the nanostructure growth on top of FTO surface will be observed by using FESEM and XRD respectively.

2.4 Study the DSSC performance

The indoline dye D149 has a better performance for an efficient sensitization process with good absorbing properties [6]. The ZnO thin film placed in a small container and then the dye solution dripped into the small container until the solution cover the thin film. After that, the ZnO thin film was immersed in the D149 dye solution for 24 hours to make sure that dye attached on the surface.

The photocurrent density-photovoltage (J-V) parameters had been assessed by solar simulator with the range less than 1 sun (100 $mWcm^{-2}$). The fill factor (FF) and conversion efficiency (η) of the solar cell were can be calculated by equation (1) and (2) respectively.

$$FF = \frac{V_{max} \cdot I_{max}}{V_{oc} \cdot I_{sc}} \quad (1)$$

$$\eta\ (\%) = \frac{I_{sc} . V_{oc} \cdot FF}{P \cdot M \cdot S} \quad (2)$$

Where, $V_{max}$ = maximum voltage generated, $I_{max}$ = maximum current generated, $V_{oc}$ = open circuit voltage, $I_{sc}$ = short circuit current, η = efficiency, P = power of incident light, M = mismatch factor, and S = surface area of film.

## 3. Results and Discussion

The results and discussion will focus on the analysis data which collected by the equipment for characterization of ZnO thin film. There are four different characterization methods which are X-Ray Diffraction (XRD) Analysis, Field Emission Scanning Electron Microscopy (FE-SEM), Two-Point probe I-V analysis and Solar Simulator.

3.1 X-Ray diffraction (XRD)

Figure 1 shows the XRD profiles of the thin film with different concentrations of ZnO solution of 40mM, 60mM, 80mM and 100mM. The rutile [010], [002] and [011] crystal planes which corresponded to the diffraction peaks at 31.777, 34.433 and 36.264, respectively are presented by the XRD pattern from the thin film. The rutile [002] crystal plane is assigned as the preferential growth for the hexagonal wurtzite structure of ZnO due to the direction with high crystallinity [7].

3.2 Field emission scanning electron microscopy (FE-SEM)

The surface morphology of ZnO thin films are observed by using the Field Emission Scanning Electron Microscopy (FE-SEM). Figure 2, 3, 4 and 5 (a) to (d) are shown the FE-SEM images of top view at 10,000, 25,000, 50,000 and 100,000 magnifications with various concentration of ZnO solution. It is obtained from Figure 2 that sample of 40mM ZnO solution, the width of diameter shows in the range between 28.1 nm to 41.3 nm. Based on Figure 3 shows that the width of diameter in the range between 31.7nm to 67.2 nm which is the sample of 60mM ZnO solution. The width of diameter in the range between 63.8 nm to 94.3 nm from Figure 4 which the sample of 80mM ZnO solution. For Figure 5 which the sample of 100mM ZnO solution, it shows the width of the diameter in the range of 46.6 nm to 104 nm.

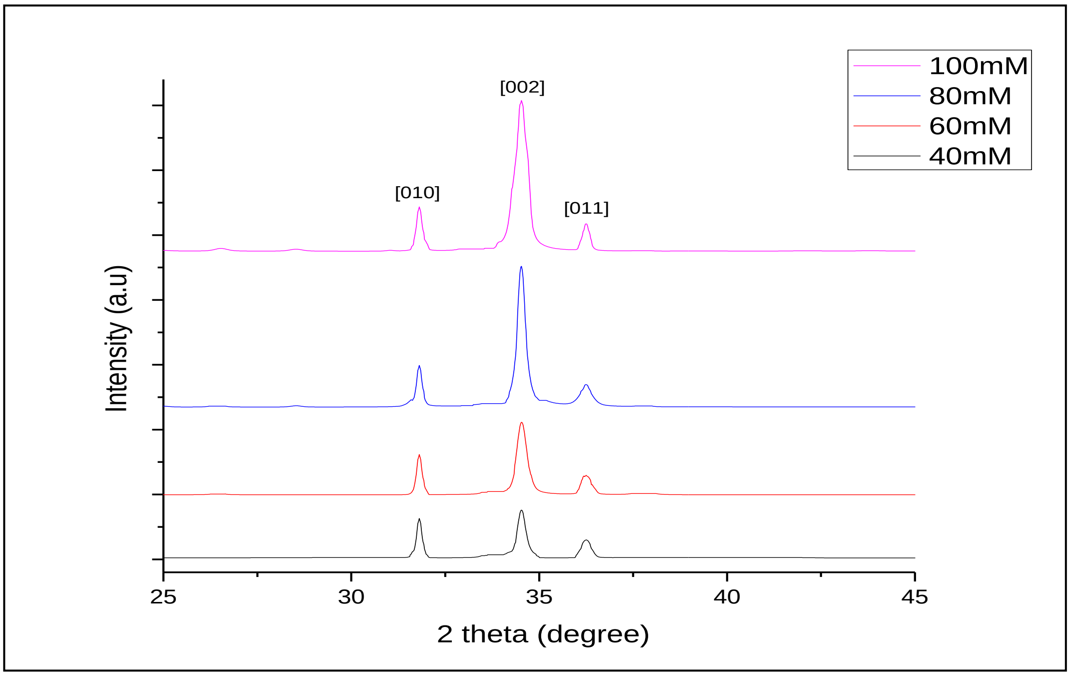


**Figure 1: XRD profiles of the thin film with various concentration of ZnO solution**

The highest thickness of the diameter for ZnO nanorod is obtained as 104nm which shown in Figure 5 which is the sample of 100mM ZnO solution. The Figure 2 which is the sample of 40nm ZnO solution shows the lowest the thickness of the diameter for ZnO nanorod is observed as 28.1nm. The study shows that the top end of ZnO nanorods of the FESEM image, the diameter of ZnO nanorods was observed slightly increase while the concentration of the ZnO solution increase [7]. Furthermore, the study [1] reported that the increment in the length of nanorods as the efficiency of dye-sensitized solar cells increases.

3.3 Two-Point probe I-V analysis

The Figure 6 shows different concentrations of the ZnO solution for annealing the sample. For the sample of 40mM ZnO solution, the peak value for the current is 1.85 mA. The peak current value of 60mM ZnO solution is 1.92 mA. For the sample of 80mM ZnO solution, the peak value for the current is 3.3 mA. The last sample that anneals is 100mM of ZnO solution with its peak current value is 4.5 mA. The graph shows the highest concentration of ZnO solution that is used to anneal the sample gives the lowest value of resistivity. In contrast, the lowest concentration of ZnO solution which is used to anneal the sample gives the highest value of resistivity. The study shows that the reduction of the ZnO nanorods diameter will increase the resistance [8]. Table 1 shows resistance, resistivity and conductivity with different concentration of ZnO solution.

3.4 Solar simulator

Figure 7 shows the J-V curve for samples with different concentration of ZnO solution. For the sample of 100mM ZnO solution, it has the highest J-V curve with the highest voltage value of 0.64 V. The lowest J-V curve corresponds to 40mM ZnO solution with the lowest voltage value of 0.48 V. It is presented that the sample with the concentration of ZnO solution increased, the value of voltage, $V_{oc}$ and current density, $J_{sc}$ also increased.

The photovoltaic parameters of each sample with different concentration of the ZnO solution are analyzed in Table 2. As the concentration of ZnO solution increases, it leads to an improved efficiency. The sample of 100mM ZnO solution resulted in the highest cell efficiency DSSC of 1.73% whereas the sample of 40mM ZnO solution has the lowest efficiency of 0.64%. The study [1] presented that as the concentration of the ZnO solution increases, the current density, Jsc, will also increase . The current density is determined by the amount of dye (D149) absorbed on the nanorods of ZnO. The study shows that the highest value of current density was expected for the nanorods had the largest surface area [9].

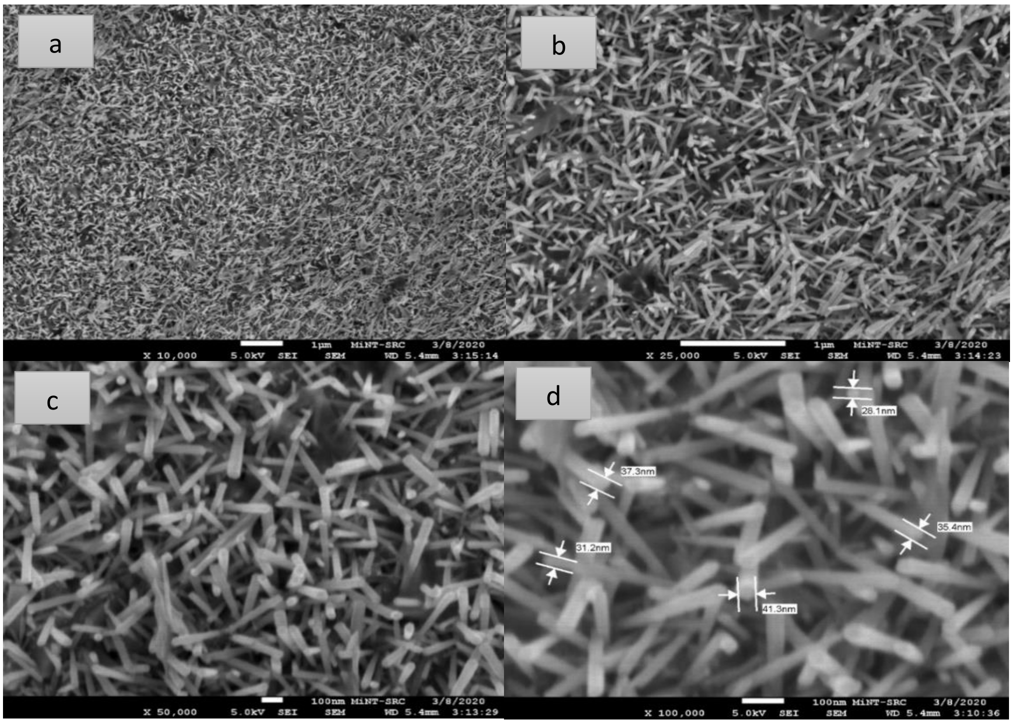


**Figure 2: FE-SEM image of nanorods of ZnO grown on FTO substrate in concentration of 40mM of ZnO solution. (a) top view at 10,000 magnification, (b) top view at 25,000 magnification, (c) top view at 50,000 magnification, (d) top view at 100,000 magnification**

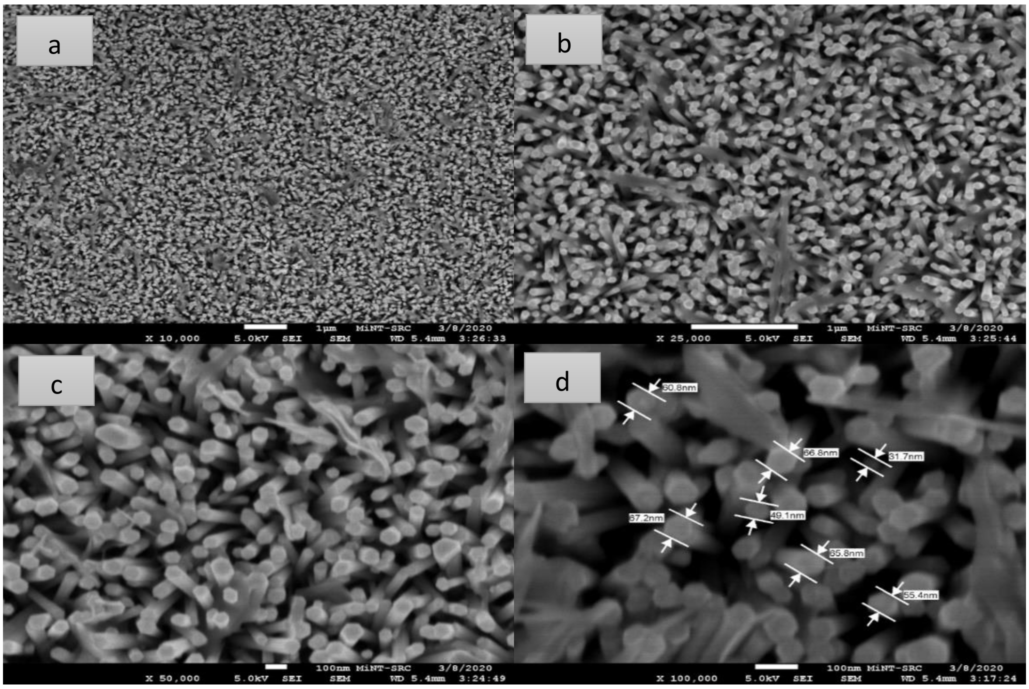


**Figure 3: FE-SEM image of nanorods of ZnO grown on FTO substrate in concentration of 60mM of ZnO solution. (a) top view at 10,000 magnification, (b) top view at 25,000 magnification, (c) top view at 50,000 magnification, (d) top view at 100,000 magnification**

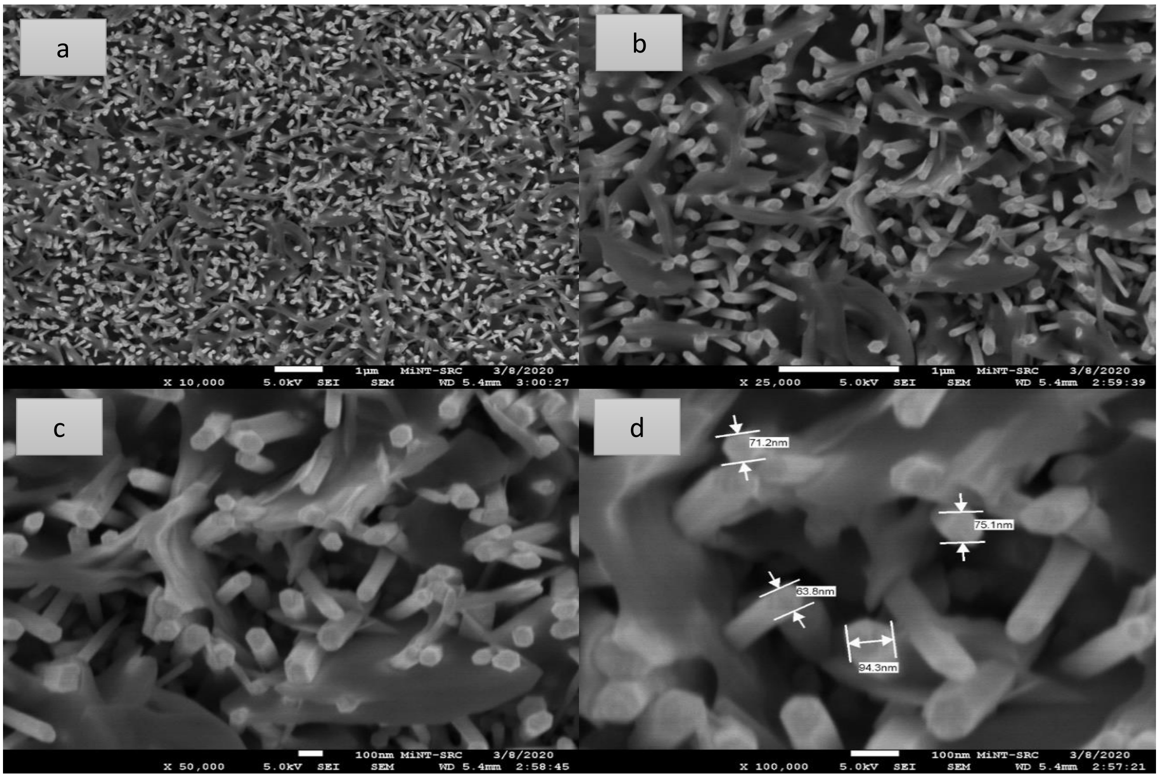


**Figure 4: FE-SEM image of nanorods of ZnO grown on FTO substrate in concentration of 80mM of ZnO solution. (a) top view at 10,000 magnification, (b) top view at 25,000 magnification, (c) top view at 50,000 magnification, (d) top view at 100,000 magnification**

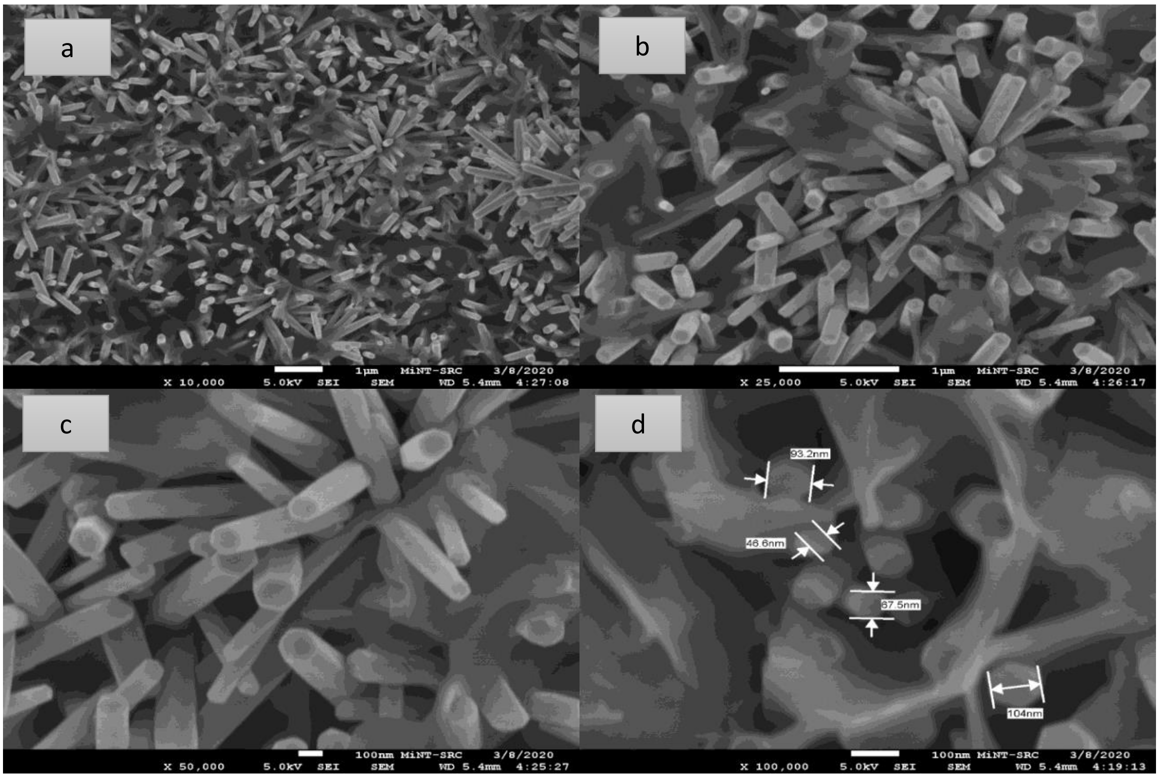


**Figure 5: FE-SEM image of nanorods of ZnO grown on FTO substrate in concentration of 100mM of ZnO solution. (a) top view at 10,000 magnification, (b) top view at 25,000 magnification, (c) top view at 50,000 magnification, (d) top view at 100,000 magnification**

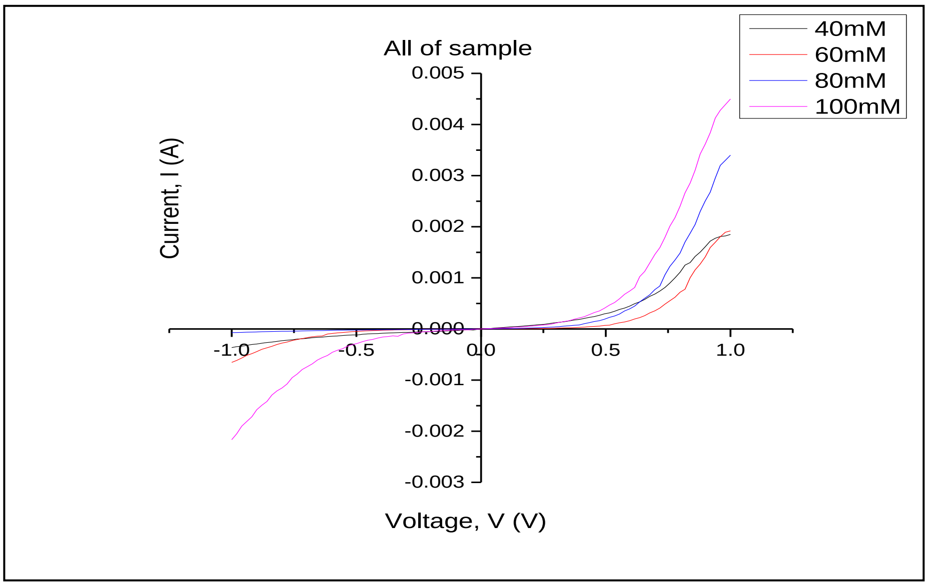


**Figure 6: I-V graph of ZnO with various concentration of the ZnO solution**

**Table 1: Resistance, resistivity and conductivity with different concentration of ZnO solution**

| Concentration of ZnO solution | Resistance, R (Ω) | Resistivity, $\rho$ (Ωcm) | Conductiv3ity, $\sigma$ (S/cm) |
|---|---|---|---|
| 40mM | 531.07 | 531.07 | $1.88\times 10^{-3}$ |
| 60mM | 552.94 | 552.94 | $1.80\times 10^{-3}$ |
| 80mM | 318.64 | 318.64 | $3.14\times 10^{-3}$ |
| 100mM | 227.60 | 227.60 | $4.39\times 10^{-3}$ |

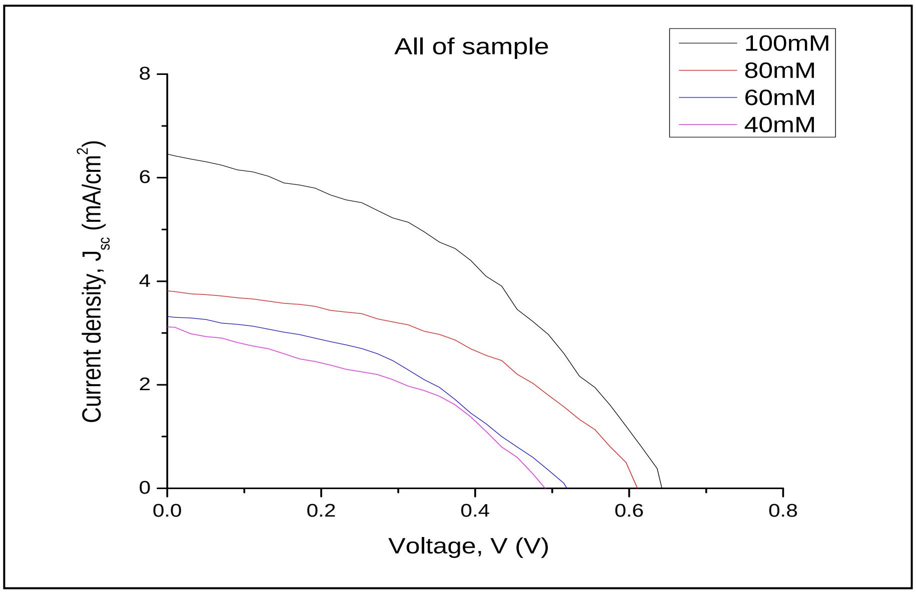


**Figure 7: J-V curve of the DSSC of sample with various concentration of ZnO solution**

**Table 2: Photovoltaic properties of DSSC with different concentration of ZnO solution**

| Concentration of ZnO solution | $V_{oc}$, (V) | $I_{sc}$, (A) | $J_{sc}$, ($mA/cm^2$) | Fill Factor | Efficiency (%) |
|---|---|---|---|---|---|
| 40mM | 0.48 | 0.00078 | 3.12 | 42.63 | 0.64 |
| 60mM | 0.51 | 0.00083 | 3.32 | 42.56 | 0.72 |
| 80mM | 0.59 | 0.00083 | 3.31 | 44.59 | 0.88 |
| 100mM | 0.64 | 0.00161 | 6.46 | 42.21 | 1.73 |

## 4. Conclusion

In a nutshell, this research is concluded that Zinc Oxide (ZnO) thin film had deposited on the fluorine doped tin oxide (FTO) with various concentration of ZnO solution. The hydrothermal method is used to deposit the ZnO thin film. From result part of XRD, the profiles of ZnO thin film are shown in the rutile which corresponded to the diffraction peaks. From the observation of nanorods, when the concentration of ZnO solution increased the diameter of nanorods ZnO are increased. The efficiency of dye-sensitized solar cells will increase while the thickness of nanorods increased.

Furthermore, the characterization of ZnO thin film through two-point probe had shown its resistivity increasing the concentration of ZnO solution decreased. However, its conductivity of ZnO increases when the concentration of ZnO solution is increased. Results from solar simulator found that 100mM of ZnO solution is the most suitable concentration to grow the nanorods with larger surface area to obtain the higher efficiency.

**Acknowledgement**

The authors would like to sincerely appreciate the facility used in this study Faculty of Electrical and Electronic Engineering, Universiti Tun Hussein Onn Malaysia.

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