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ZnO NANORODS FORMATION FOR DYE-SENSITIZED SOLAR CELLS APPLICATIONS

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ABSTRACT

Different morphologies of zinc oxide (ZnO) can be obtained through various synthesizing methods, such as that of the water bath. By synthesizing under various conditions, different ZnO morphologies can be seen as the result of the water bath method. Replacing ZnO nanoparticles with vertically aligned ZnO nanorods results in a much higher energy conversion efficiency. Yet vertically aligned nanorods can only be grown through difficult and expensive methods. Several researchers have studied the growth of one-dimensional (1D) nanorods on homogeneous film with various growth conditions. However, there has been little in the way of research on ZnO nanorods grown on ZnO seed layers using the water bath method. In this research, vertically aligned nanorods with an optimum size ratio were formed through a simple water bath method. This method reveals that the ZnO nanorods are well aligned and grown with a high density and uniformity on the substrate. Their X-ray diffraction patterns reveal that the nanorods are grow in the [001] direction. The density, diameter, and length of the ZnO nanorods can be altered by changing the growing condition. All of the samples were characterized using a scanning electron microscope, X-ray diffraction, and micro Raman spectroscopy. To investigate crystal growth, zinc nitrate and zinc acetate were used when preparing the solution. The results demonstrate that the morphology and alignment of ZnO nanorods are determined by the precursor's type and deposition time.

Keywords: DSSC; Nanorods; Nanostructure; One-dimensional; Thin film; Water bath; ZnO

1. INTRODUCTION

Previously, in 1991, Grätzel and Brian introduced a solar cell that used a combination of organic semiconductor materials with inorganic semiconductors known as dye-sensitized solar cells (DSSC). The most obvious advantage of DSSC application is the potential it offers for a simple fabrication process that does not require the use of a sophisticated and expensive device, thus permitting more affordable manufacturing costs.

There are many ways to increase the performance of DSSCs. One such method is by increasing the electron transport rate, with one-dimensional nanorods being one of the solutions by which this can be achieved (Unalan et al., 2008). Growing vertically aligned nanorods presents the possibility of increasing the electron transport rate. One important element of growing vertically

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aligned nanorods is the seed layer (Huang et al., 2008). Furthermore, an investigation was carried out to determine the effect of the seed layer on the morphology and behavior growth of ZnO nanorods, the results of which are discussed in this paper.

There are many methods that can be used for synthesizing ZnO nanorods, such as the vapor and solution-phase approaches. However, this research focuses primarily on the solution-phase approach. The solution-phase approach is based on zinc nitrate and hexamethlytetra amine using the water bath and hydrothermal methods and can be carried out under relatively low temperature and pressure (Lee et al., 2003; Law et al., 2005; Baxter et al., 2005). Synthesizing ZnO through the vapor phase requires a high temperature (>450^{o}C), with this method being capable of producing high-quality single crystals with a high aspect ratio (Ridhuan et al., 2012). Some of the disadvantages of using this method are its limitations in terms of sample uniformity and low product yield. By contrast, the solution method is preferable since it can be carried out at a low temperature (<200^{o}C). This method also allows the choice of many kinds of substrates, including organic and inorganic substrates (Wu et al., 2007).

Zinc acetate is commonly used as a precursor solution for seed layer deposition. In this experiment, we also tried using zinc acetate as the precursor solution for growing ZnO nanostructure.

2. EXPERIMENTAL METHOD

2.1. Seed Layer

2.1.1. Seed layer preparation

The ZnO seed layer was deposited using the following method. The fluorine-doped tin oxide (FTO) substrate was cleaned with acetone and ethanol for 15 minutes with an ultrasonic cleaner to remove any organic and inorganic contamination. The seed layer solution was made by mixing 0.7 grams of zinc acetate $(CH_3COO)2Zn.2H_2O$ and 10 drops of methoxyethanol in 20 mL ethanol under vigorous stirring for 20–30 minutes. First, we mixed zinc acetate with ethanol and stirred it for 10 minutes. After the solution had become milky in color, methoxyethanol was added drop by drop as a stabilizer. During the stirring process, the seed solution was heated to 60°C to increase its solubility.

2.1.2. Seed layer deposition

Rotation speed, solution viscosity, and spinning duration are parameters that affect the morphology of the thin film. In this experiment, we used 500 RPM for 10 seconds during the spin-up step and 2500 RPM for 1 minute during the spin-off step. Applying a rotation speed of less than 2500 RPM or a spinning duration of less than 1 minute generates a recoil effect because the solution does not completely evaporate.

The seed layer was then annealed at 100°C for 10 minutes. These processes form a seed layer with a 15–20 nm thickness. We were able to repeat this process to form multiple layers or to increase the seed layer thickness. Once satisfied with the thickness of the seed layer, the final step was to anneal the substrate at 350°C for 1 hour.

During the experimental process, a 0.03M concentration and an annealing temperature of 300°C were used to see the effect on the morphology of seed layer.

2.2. ZnO Thin Film

Two different precursor solutions were made; one by mixing 0.03M zinc acetate and 0.03M hexamethylenetetramine in 30ml deionized water, and the other by replacing the zinc acetate with zinc nitrate. The solution was stirred at room temperature for 10 minutes until the color become transparent. A solution that was milky in color had a solution concentration that was too high. By using these precursor solutions, ZnO nanorods were grown using the following

methods.

2.2.1. Hydrothermal

The ZnO nanostructure thin film was grown by immersing the FTO substrate, which was already coated in a seed layer, into the precursor solution inside an autoclave. The substrate was arranged inside the autoclave in a vertical position. The hydrothermal process was carried out by putting the autoclave inside a ceramic oven and heating it at 150^{o}C for 12 hours. The resulting white thin film on the FTO surface was cleaned to remove excess materials by dipping it into deionized water. The substrate was then kept dry at room temperature for 20 minutes.

2.2.2. Water bath

The FTO substrate, which was already coated in a seed layer, was immersed in the precursor solution and kept in a vertical position. The temperature of the water bath was maintained at 85^{o}C. After keeping the substrate for 2 hours, it was then cleaned with deionized water and dried at room temperature.

3. RESULTS AND DISCUSSION

The morphology of thin film image was taken using a Scanning Electron Microscope (JSM-6320F FE-SEM) at an accelerating voltage of 20 kV. The molecular structure of ZnO crystal was investigated using a RIGAKU RINT Ultima III X-ray diffractometer through Cu Kα radiation (λ=1.5418Å) in the 2θ range from 20°to 50° at a 2°/min scanning speed.

3.1. Hydrothermal

After 12 hours' growth, the morphology of ZnO thin film on FTO substrate was observed. Both types of zinc (zinc acetate and zinc nitrate) grew into a nanoflower form. No vertically aligned nanorods can be seen on the surface of the FTO substrate. The nanoflower structures from both types of ZnO can be seen in Figure 1.

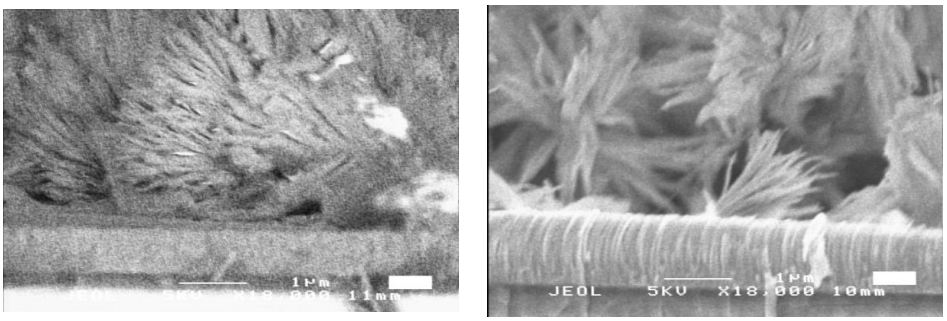

Figure 1 Nanostructures formed through hydrothermal; zinc acetate (left) and zinc nitrate (right)

There was the potential for the ZnO seed layer to fail during the hydrothermal process due to the high temperature, longer duration process, and high pressure (Sholehah et al., 2017).

3.2. Water Bath

In order to provide a comparison with the result obtained from the hydrothermal process, we then sought to produce a seed layer using the water bath method. This method employed a shorter process duration, lower temperature, and no high pressure (Peterson et al., 2004; Liu et al., 2006). The results can be seen in the SEM images below.

Figure 2 contains images of the ZnO nanorod arrays obtained using the water bath method. The synthesized ZnO nanorods were well aligned. A significant difference between both ZnO types was the length of the nanorods. Using zinc acetate, we were able to synthesize vertically aligned nanorods of length for five times longer than nanorods synthesized through zinc nitrate.

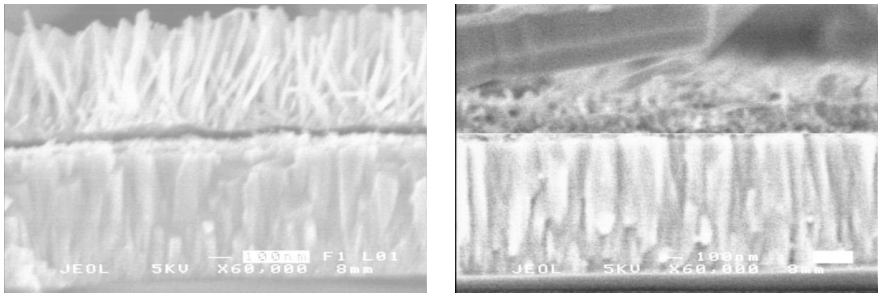

Figure 2 Nanostructures formed through water bath; zinc acetate (left) and zinc nitrate (right)

This could mean that the reaction time of zinc nitrate is less than that of zinc acetate (Penn et al., 2001; Oskam et al., 2003; Yamabi et al., 2005). There is the possibility of synthesizing longer nanorods from zinc nitrate through the application of a longer duration process (Ridhuan et al., 2012).

3.3. Structural and Photovoltaic Properties

The XRD patterns of each ZnO thin layer from the different ZnO types and different synthesizing methods are shown in Figure 3. From these results, we can see three peaks at 31.8^{o}, 34.6 ^{o}, and 36.9 ^{o} that correspond to the [100], [002], and [101] planes of wurtzite structure of ZnO (Weißenrieder et al., 1997; Srikant et al., 1998; Yubuta et al., 2007). It has been observed that [100] reflection is on the maximum intensity, which indicates that ZnO films have a preferred orientation in the [100] plane.

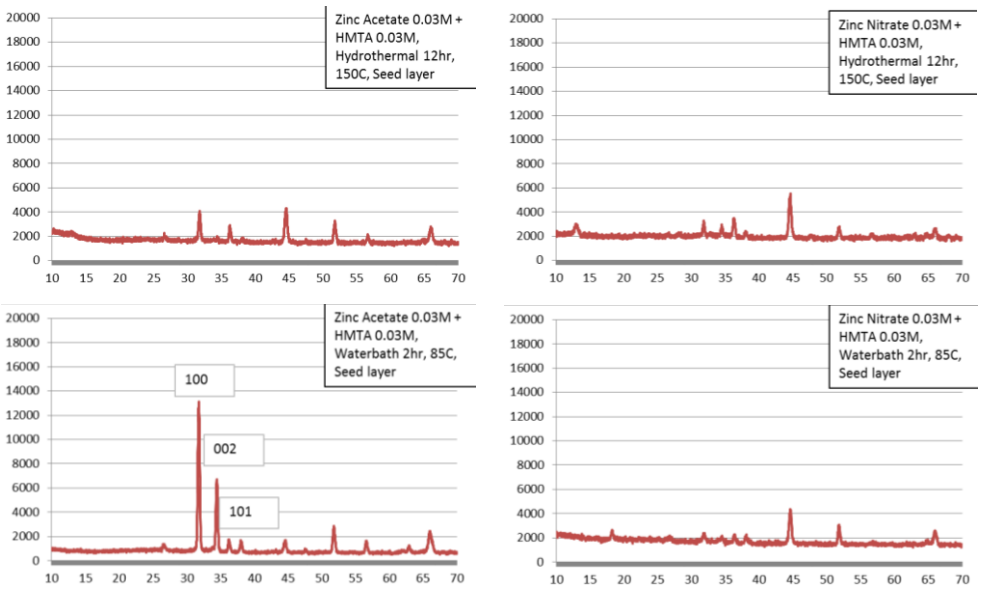

Figure 3 ZnO thin film from different zinc types and synthesizing methods

The highest [100] peaks were obtained from ZnO thin film synthesized from zinc acetate through the water bath method. This result corresponds to the SEM image in the previous section that shows well-aligned nanorods. Based on the experiment that resulted in the highest peak, a further experiment was carried out to observe the effect of synthesizing duration on the morphology of the seed layer. The durations were varied between 1, 2, and 3 hours. The XRD pattern from this experiment can be seen in Figure 4.

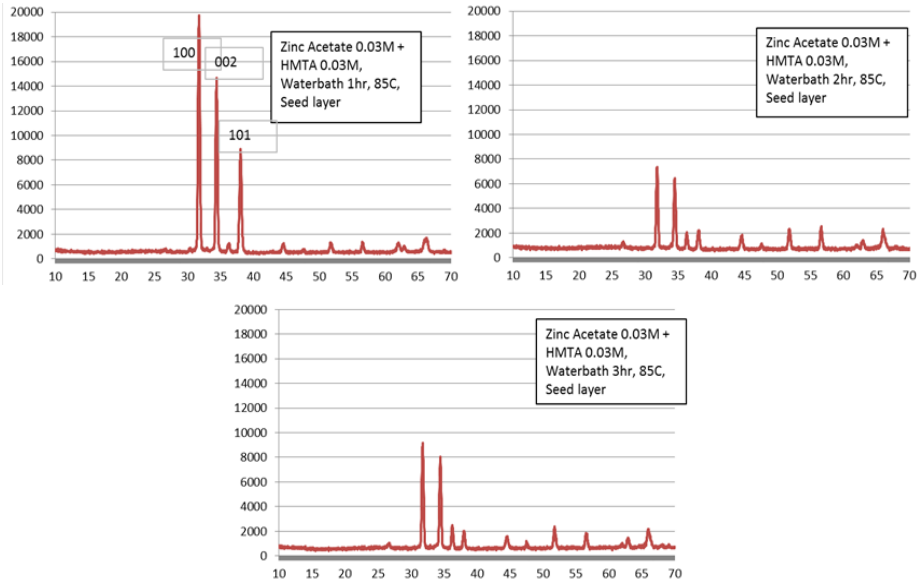

Figure 4 Zinc film XRD patterns from different synthesizing durations

Observing the crystal growth, it can be seen in Figure 5 that the growing process ends after 120 minutes because of insufficient Zn ion.

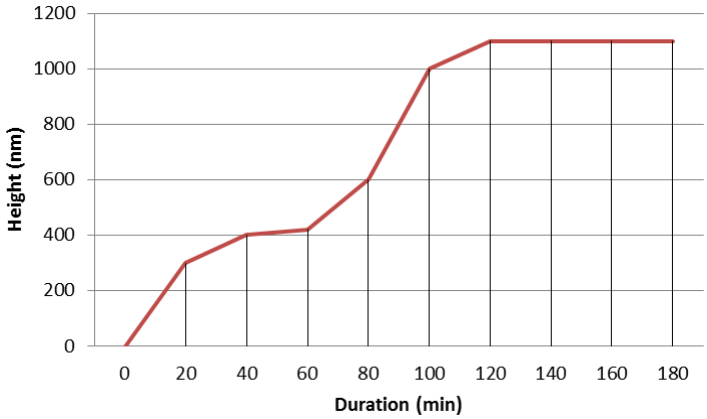

Figure 5 ZnO nanorods growth rate

Both ZnO films were synthesized with the same parameters, except for the seed layer. Depositing the seed layer on the FTO surface allowed the ZnO nanorods to grow on the FTO surface, as shown in Figure 6.

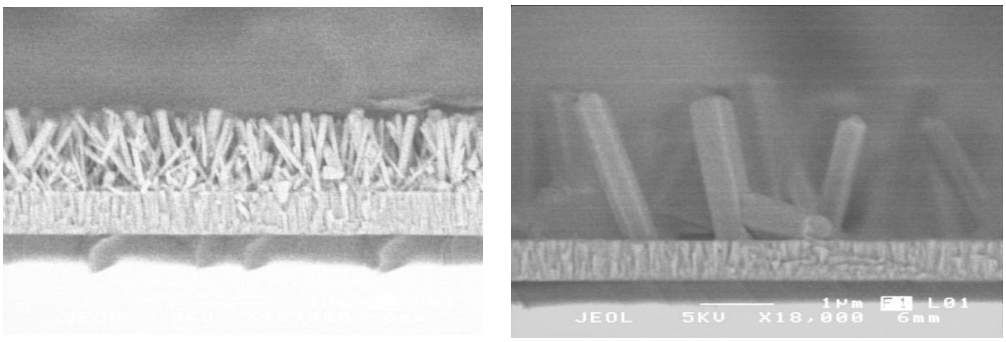

Figure 6 ZnO nanorod arrays with (top) and without (bottom) a seed layer

From the Transmission Electron Microscope (TEM) image in Figure 7, it can be concluded that the average diameter is in the range 35–55 nm. Fourier transform reveals a symmetrical pattern, which indicates that the nanorods are well crystallized. The spacing between the adjacent lattice planes stacks, as taken from the tips of the nanorods along the growth direction, is around 0.26 nm. This spacing corresponds to the d-spacing of the [0001] planes. This confirms that ZnO grows with a c-axis orientation.

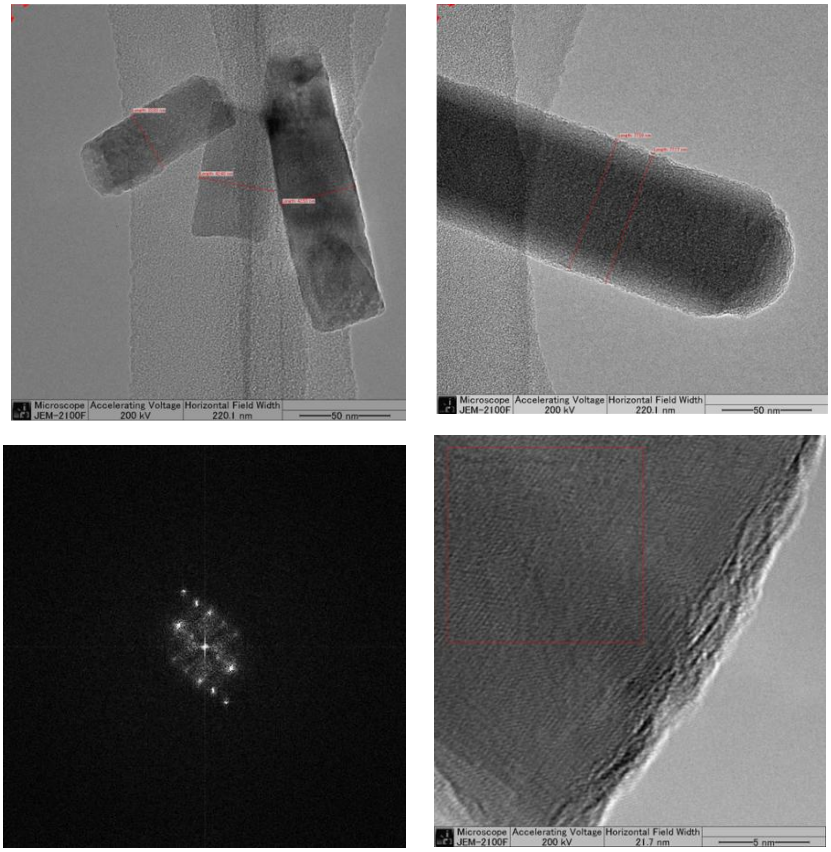

Figure 7 TEM image of ZnO nanorods

To see the advantages of well-aligned nanorod arrays on photovoltaic application, the I-V characteristic needs to be measured. By comparing 2 different samples (with and without a seed layer) that are synthesized through the same nanorod growing conditions, the effect of aligning the nanorods can be observed. The I-V characteristic curve in Figure 8 shows the effect of a seed layer that gives better alignment of the nanorod arrays.

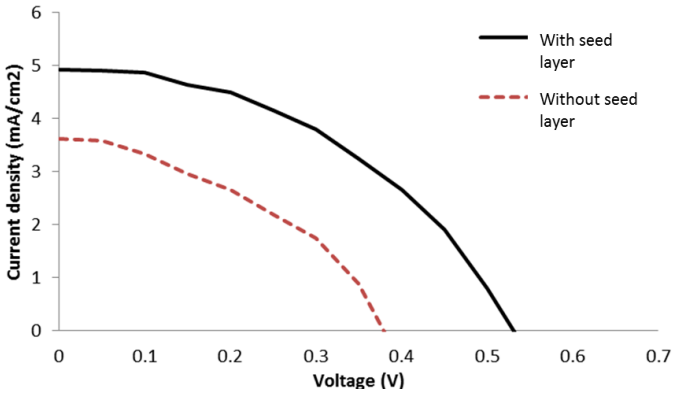

Figure 8 I-V characteristic curve on vertically aligned nanorods

The V_{oc} was improved by altering the alignment of the nanorods. This may indicate that vertically aligned nanorods can potentially improve the charge transfer rate, thus resulting in an improvement in efficiency from 1.0% to 1.60%.

4. CONCLUSION

Seed layer was confirmed to be successful in growing vertically aligned nanorod arrays. Through I-V characteristic measurement, it has been proved that well-aligned nanorods provide better photovoltaic efficiency. There is a need for better alignment through longer synthesizing duration. This could be done by increasing the density and length of the nanorods. In this case, the optimum concentration of seed layer solution needs to be found. Combinations of zinc acetate dehydrate as a precursor solution and the water bath process have been proved to be an optimum method for synthesizing vertically aligned ZnO nanorods. Using this combination, ZnO nanorods can be grown in 2 hours.

5. ACKNOWLEDGEMENT

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