Synthesis and Characterization of ZnO Nanorods by Hydrothermal Methods and Its Application on Perovskite Solar Cells

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Abstract. The aim of this research is to investigate the effect of ZnO Nanorods (ZnO NRs) morphology synthesized by the hydrothermal method to electrical properties of CH$_3$NH$_3$PbI$_3$/ZnO NRs perovskite solar cell (PSCs). ZnO nanorods were synthesized on the ITO substrate by a hydrothermal method. ZnO NRs were synthesized using hexamethylenetetramine (HMT) and zinc nitrate with a 1:1 molar ratio for 6 h. The growth temperature varied at 90°C and 100°C. The zinc nitrate concentration also varied at 25mM and 50 mM. The perovskite was made through a two-step deposition by spin coating with PbI$_2$ and CH$_3$NH$_3$I as the main ingredients. The effects of the synthesis conditions on ZnO NRs and Perovskite films were systematically investigated by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), LCR AC meters and multimeters. The SEM results showed that as the temperature and concentration of zinc nitrate increase the size of the diameter and length of the rods are increasing. ZnO NRs synthesized with 50 mM concentrations of zinc nitrate at a growth temperature of 90°C temperature showed the best results in terms of ZnO NRs morphology. The XRD characterization results showed that the formed CH$_3$NH$_3$PbI$_3$ film contained PbI$_2$ impurities. The existence of PbI$_2$ was suspected in opening the gap of recombination causing in low current and high dielectric constant.

Keywords: ZnO nanorods, perovskite solar cell, CH$_3$NH$_3$PbI$_3$ and hydrothermal method.

1. Introduction
The increasing energy demand, environmental issues, and limited availability of fossil fuels are demanding the research on sustainable and renewable energy resources [1]. The sunlight is an ultimate source to accomplish clean energy demand. Solar cell technology provides an eco-friendly and renewable energy route to convert photon energy into electricity directly [2,3]. The organometallic halide of CH$_3$NH$_3$PbI$_3$ has attracted interest due to high efficiency, transparent and easy to synthesis. CH$_3$NH$_3$PbI$_3$ has a direct band gap of 1.55 eV determining an offset absorption of up to 800 nm [4]. CH$_3$NH$_3$PbI$_3$ has met 19 % efficiency in numerous studies, and it is expected to achieve the target of 20% efficiency [3]. However, the research on CH$_3$NH$_3$PbI$_3$ PSCs stability to UV lighting and efficiency...
is still developed. The efficiency and stability of PCSs can be improved by using an electron transport material (ETM) and hole transported material (HTM) to prevent the electron-hole pair recombination [3].

The ZnO is one of ETM that widely for PSCs [6]. ZnO in nanoscale have better electronic and optical properties compared to bulk materials [7]. It has been considered that vertical 1D structures with high crystallinity are important keys in the manufacture of good solar cells [8,9]. One of the advantages of the 1D structure is that it can provide a ballistic transport effect, in which electrons can move in a medium regardless of the electrical resistance caused by scattering. Thus, the possibility of energy loss in the electron transport process can be minimized. Moreover, scattering in the transport process can occur due to impurities, defects in the crystal and structures that allow the oscillation of electron motion in the transport process [10]. Among the various forms of the structure modifications, the formation of ZnO with rods has been studied intensively [11].

ZnO is a compound that does not need a high temperature to show a better performance; therefore, it could function as ETM instead of other metal oxides which are processed at high temperatures. In a low-temperature PSCs, ZnO has been coated on both rigid and flexible substrates, by different techniques such as Electrodeposition [12], chemical bath deposition [13], sonochemical [14], sol-gel [15], hydrothermal [16] and solvothermal [17]. Meanwhile, the steam phase methods such as chemical vapor deposition [18] and vapor-liquid-solid (VLS) [19] have been successfully employed for the growth of ZnO NRs on a glass substrate. However, the steam phase methods have some weaknesses that include the need for a high temperature, high operational cost, and a relatively long time.

The ZnO NRs can be improved by optimizing the length and diameter of the rods formed. The size of the diameter and length of the rods formed will have an effect on the surface area [20]. Therefore, it is important to investigate growth parameters like growth temperature and concentration of zinc nitrate to optimize diameter and length of the ZnO NRs. Moreover, it is also important to study the effect of perovskite impurities to output current and dielectric of PSCs

2. Materials and Methods

2.1. ITO Preparation
The ITO substrate with 2.5 cm x 2.5 cm dimension was washed for 10 minutes in an ultrasonic cleaner with acetone and then continued washed by Deionized Water for 10 minutes. The clean ITO was dried at room temperature. The ITO surface was checked by a multimeter to identify the conductive surface.

2.2. Preparation of ZnO seed layer
The ZnO seed layer was synthesized by employing Zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, Aldrich, 98 %) as a precursor, ethanol as a solvent, and monoethanolamine (MEA) as a stabilizer. The concentration ratio (Zn(CH₃COO)₂·2H₂O): MEA was maintained at 1:1 molar. The ZnO seed layer deposition coated by a spin coating method at the rate of 3000 rpm for 20 seconds. A preheating process at 150 °C was performed for 10 minutes, and then continued by an annealing process at 550 °C for 2 hours in order to eliminate the organic and solvent components.

2.3. The Growth of ZnO NRs
The ZnO NRs were grown by using a hydrothermal method on ZnO seed layer substrate. The concentration of precursors used was 25 mM and 50mM and the molar ratio between Zn (NO₃)₂·4H₂O and HMT was 1:1. During the growing process, the solution was heated in a variety of growth temperatures of 90 °C and 100 °C for 6 hours. The sample was cleaned by DI-Water to remove the remaining salt from the sample surface and dried at room temperature. Lastly, the ZnO nanorods on the ITO substrate were annealed for 2 hours at 550 °C. When the hexamethylenetetramine (HMT) and Zn(NH₃)₄²⁺ was used as a precursor, the chemical reaction could be stated in the following mechanism [14]:

\[
Zn(CH₃COO)₂·2H₂O + 6H₂O \rightarrow ZnO + 4CH₃COOH + 4H₂
\]
\[(\text{CH}_3\text{NH})_3\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 6\text{HCHO} + \text{NH}_3\]  
\[\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-\]  
\[\text{Zn}^{2+} + \text{NH}_3 \rightarrow \text{Zn} (\text{NH}_3)_2^{2+}\]  
\[\text{Zn}^{2+} + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-}\]  
\[\text{Zn(NH}_3)_2^{2+} + 2\text{OH}^- \rightarrow \text{ZnO} + 4\text{NH}_3 + \text{H}_2\text{O}\]  
\[\text{Zn(OH)}_4^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^-\]  

On the initial growth of the ZnO nanorods, the HMT started to decompose into ammonia (Equation (1)) and produce hydroxide ion, namely OH\(^-\) (Equation (2)). The \text{Zn}^{2+} cation further reacted to \text{NH}_3 and \text{OH}^- anion forming ZnO core (Equation (3) and Equation (4)). The crystal core would develop, and further degraded into the ZnO core nanorods under the influence of more OH\(^-\) ion at a specific temperature, according to Equation (5) and (6) [30]. Hence, as the time passed by, the ZnO core would keep growing. Subsequently, the Zn on the surface of the Zn substrate would oxidize to form ZnO nanorods on the substrate. In the meantime, the oxidation process resulted in the lateral growth of the ZnO core during the attachment of Zn atom on the ZnO nuclei core [20].

2.4. \text{CH}_3\text{NH}_3\text{PbI}_3 Synthesis

The next deposition following the ZnO nanorod formation was the fabrication of the CH\(_3\)NH\(_3\)PbI\(_3\) perovskite device by a two-step deposition. First, a Methyl-ammonium iodide (MAI) solution was generated from a mixture of 30 ml hydroiodic acid of 0.227 mol (57 wt\% in water) and 27.8 ml methylamine of 0.273 mol (40 wt\% in methanol). Second, a solution was made from 2.3-gram PbI\(_2\) powder and dissolved in 5 ml dimethylformamide (DMF) stirred for 30 minutes. The two solutions fabricated in the first and second methods were prepared for the deposition process via a spin coating method on the substrate of ITO/ ZnO NRs. The first deposition layer was the PbI\(_2\) solution followed by the CH\(_3\)NH\(_3\)I solution. Then, a preheating step was carried at 100 °C for 30 minutes on each stage of deposition. Next, the layered substrate was kept in a tightly sealed and put in a dry place.

2.5. Material Characterization

The ZnO NRs surface morphology analyzed by Scanning Electron Microscopy (SEM, FEI INSEPCT-S50 type). The crystallization and structural properties of ZnO NRs characterized by X-Ray Diffraction (XRD, Philips X'Pert PRO) with a Cu K\(\alpha\) radiation (\(\lambda = 1.54\) Å). Fourier-Transform Infrared Spectroscopy (FTIR) was used to investigate the optical property of the ZnO NRs. The dielectric constant and current of the CH\(_3\)NH\(_3\)PbI\(_3\)/ZnO NRs PSCs were measures by LCR meter and multimeter.

3. Results and Discussion

3.1. XRD Diffraction

The structural properties of ZnO NRs characterized by XRD in 2\(\theta\) range between 10 – 90 degrees with a Cu K\(\alpha\) wavelength (\(\lambda\)) of 1.54 Å. Figure 1 shows the diffraction patterns of ZnO NRs at different concentration and growth temperature. The diffraction peak at the 2\(\theta\) of 31.08° (d\(_{100}\)); 34.56° (d\(_{002}\); and 35.54° (d\(_{101}\)) is identified as hexagonal crystal system (wurtzite). The x-ray diffraction pattern of this ZnO NRs is in agreement with JCPDS standard (No.36-1451). The three main observed peaks observed related with Bragg plane of (100), (002) and (101).
Figure 1. XRD patterns of the ZnO Nanorods at different zinc nitrate concentration and growth temperatures

The indication of a tetragonal CH$_3$NH$_3$PbI$_3$ crystal structure formation could be seen from the XRD peaks indicated at 2θ angles, namely 14.05°, 24.9°, 28.45°, 31.87°, 40.45°, and 43.13° that were generated at XRD fields of (001), (202), (220), (310), (224), and (314), respectively [21]. Meanwhile, the highest peak of the perovskite crystal structure was found at (001) crystal field, and the PbI$_2$ peak was at 12.4° (001), 25.5° (002), 38.7° (003), and 52.5° (004). It is in excellent agreement with the research conducted by Li showing PbI$_2$ peaks at the (001), (002), (003), (004) fields [22]. Figure 2 shows the diffraction patterns of perovskite films synthesized by a two-step solution deposition. The perovskite CH$_3$NH$_3$PbI$_3$ diffraction peaks were observed at the (001), (202), and (220) planes. The PbI$_2$ diffraction peaks observed as impurities.

Figure 2. Diffraction patterns of CH$_3$NH$_3$PbI$_3$/ZnO NRs/ITO perovskite crystal with a variation of growth temperature and zinc nitrate concentration.
3.2 SEM Characterization

The surface morphologies of ZnO NRs were analyzed by using a scanning electron microscope (SEM) and presented in Figure 3. While, the cross-section of ZnO NRs shows in the insert to measure the length of the rods. Figure 3 shows that all ZnO NRs that have been synthesized have a hexagonal form, growth vertically and well-distributed. The diameter and length of ZnO NRs increase by increasing growth temperature and zinc nitrate concentration. The diameter and length of ZnO NRs summarize in Table 1.

![Figure 3](image)

**Figure 3.** ZnO NRs morphology growth at (a) 25 mM 90 °C (b) 25 mM 100 °C (c) 50 mM 90 °C (d) 50 mM 100 °C for 6 hours. The insert is the cross section of ZnO NRs.

The increasing diameter and length of ZnO NRs by increasing precursor concentration and growth temperature is in good agreement with a study performed by Rani et al. (2018) [23]. Table 1 shows that growth temperature from 90 °C to 100 °C can improve the nanorods diameter from 81 nm to 365 nm and improve the length from 1.2 µm to 5.1 µm. This improvement due to a temperature growth slows down ZnO nucleation rate and increases the development of Zn(OH)₂ that acts as the intermediate compound of the ZnO NRs [19].

**Table 1.** The average diameter and length of ZnO NRs with variation of growth temperature and zinc nitrate concentration.

| Diameter of rods (nm) | Lengths of rods (µm) |
|------------------------|-----------------------|
| ZnO NRs 25 mM 90 °C    | 81                    |
| ZnO NRs 25 mM 100 °C   | 92                    |
| ZnO NRs 50 mM 90 °C    | 148                   |
| ZnO NRs 50 mM 100 °C   | 365                   |


3.3 FTIR Characterization

Figure 4 illustrates the FTIR spectra of CH$_3$NH$_3$PbI$_3$ perovskite film with a 25 and 50 mM zinc nitrate concentration and some variation of the growth temperature of 90 °C and 100 °C. It could be seen that the absorption area of the material ranged from 500 to 4000 cm$^{-1}$. In general, the references present that the FTIR spectra of ZnO NRs are approximately 406 cm$^{-1}$ and around 540 cm$^{-1}$–560 cm$^{-1}$ in the blue shift range [34]. In this study, the FTIR spectra of ZnO NRs are between 485 cm$^{-1}$ and 562 cm$^{-1}$.

![Figure 4. FTIR spectra of CH$_3$NH$_3$PbI$_3$/ZnO NRs/ITO perovskite film with variation of growth temperature and zinc nitrate concentration.](image)

3.4 Current Measurement

The output current and resistivity of PCs device are summarized in Table 2. Even though the perovskite solar cell film has a small size, it also produced a current. The higher the lux and the light distance, the smaller the current production. The results showed that sample 50 mM 100 °C had the most significant current among the others, namely of 2.35 x 10$^{-7}$ µA. The relatively high current is also supported by the nanorod morphology that is relatively uniform and homogeneous. Such homogeneity would result in higher light absorption. Generally, a high current shows a declining resistivity value. The output current is lower compared to perovskite PCSs that reported previously [21,21] due to the CH$_3$NH$_3$PbI$_3$ perovskite phase is not well synthesized as shown in XRD results. The PSCs device still contains impurities of PbI$_2$ phase.
Table 2. Currents and resistivity of the Perovskite solar cells with variation of growth temperature and zinc nitrate concentration.

| Type of Film | 25 mM 90 °C | 25 mM 100 °C | 50 mM 90 °C | 50 mM 100 °C |
|--------------|------------|-------------|-------------|-------------|
| Output Current (µA) | 6.42 | 17.7 | 2.35 | 235 |
| Resistivity (Ohm.cm) | 2.94 x 10^4 | 1.48 x 10^4 | 1.81 x 10^4 | 5.66 x 10^2 |

3.5 Dielectric Constant Measurement

The measurement of dielectric constant of the ITO/ZnONRs/CH$_3$NH$_3$PbI$_3$ perovskite solar cell device was performed by using an LCR meter AC. The measurement was done via a two-probe method under the influence of the variation of frequencies towards the dielectric constant. Some variation of frequencies includes 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 200 kHz. The measurement would result in the values of capacity that could be directly observed from the LCR monitor screen. The dielectric constant could be measured by using the following equation:

$$\varepsilon_r = \frac{C}{\varepsilon_0 A} d$$

Where $\varepsilon_r$ is dielectric constant, $\varepsilon_0$ is vacuum permittivity (8.854 x 10$^{-12}$ F/m), C is capacitance (F), $d$ is the thickness of the perovskite film (m), and $A$ is the surface of the perovskite film active area (m$^2$). The measurement results of the impact of frequency on the dielectric constant of ITO/ZnONRs/CH$_3$NH$_3$PbI$_3$ solar cells are illustrated in Figure 5.

![Figure 5](image)

**Figure 5.** Dielectric constant of perovskite solar cell as a function of frequency with a variation of growth temperature and zinc nitrate concentration.

A high frequency had a low dielectric constant since the dipoles could not maintain its delivery on the alternating current. A steep decrease of dielectric constant was found at low frequencies, namely from 100 Hz – 1 kHz. It could be observed at the sample 25 mM, 50 mM 90 °C and 25 mM, 50 mM 100 °C film showing a steeply decreasing trend with a frequency of 200 kHz and dielectric constant 6.4x10$^{-5}$, 1.8x10$^{-4}$ and 3.2x10$^{-4}$, 1.2x10$^{-4}$, respectively. A small dielectric constant of material would result in high conductivity.
4. Conclusion
In this study, ZnO NRs were synthesized by hydrothermal method with variation of growth temperature and zinc nitrate concentration. The SEM showed that the ZnO NRs have diameters from 81 nm to 365 nm with the average rod length between 1.2 µm and 5.1 µm. The XRD diffraction showed that the ZnO NRs have a good crystal quality and orientations at (101) field. The ZnO NRs that had been synthesized by using 50 mM PbI₂ in CH₃NH₃PbI₃ PSCs might cause low output current with the maximum current of 235 µA. The structure and synthesis condition of CH₃NH₃PbI₃ Perovskite is very important for PCSs efficiency.

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