The Effect of ZnO Nanorods Morphology on Electrical Properties of Perovskite Solar Cells

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Abstract. Perovskite solar cells have attracted the researchers’ attention because they are one of the most promising candidates that are cheap, easy to fabricate and high-efficiency solar cell. ZnO nanorods (ZnO NRs) can be used as an electron and hole recombination barrier to improve the perovskite solar cell performance. This research aimed to investigate the effect of growing time on the characteristics of ZnO NRs and its application for perovskite solar cell device. The ZnO NRs was synthesized on ITO substrate by hydrothermal method at the different growing times of 4, 6, and 8 hours. The CH3NH3PbI3 perovskite solar cells were deposited on the top of ZnO NRs/ITO thin films by a two-stage spin coating method. The solar cell devices were characterized by using XRD, SEM-EDX, FTIR, UV-vis, and LCR meter. The results showed that ZnO NRs/ITO thin films were formed homogeneously and vertically oriented on all ITO substrates with hexagonal structures of zincite phases. When the growing time of ZnO NRs increased, the degree of homogeneity, density, and length of the rods enhanced as well. All the samples have the bandgap around 3.05 eV. The FTIR results showed the absorbent functional forces at 870 cm\(^{-1}\) and 1250 cm\(^{-1}\) related with H-C-N wavelengths, and ZnO wavelength ranges from 400 to 515 cm\(^{-1}\). The CH3NH3PbI3 perovskite solar cell device still contained PbI2 as impurities phase. The longer the growing time, the rods resulted by ZnO NRs had the wider diameter and the longer length and they were more homogenous. Meanwhile, the effect of the number of PbI2 impurities resulted in the higher dielectric and smaller current.

Keywords: ZnO nanorods, perovskite solar cell, CH3NH3PbI3 and hydrothermal method.

1. Introduction
In some recent decades, many researchers are interested in conducting the research on perovskite solar cells (PSCs) [1–3]. This is because PSCs have the potential to be produced with low cost, relatively easy fabrication and result in high efficiency [3]. The organic-inorganic hybrid compounds (CH3NH3PbX3, X=I, Cl, Br) with the perovskite crystal structure is a material that can absorb the light well [4]. Especially the CH3NH3PbI3 (methyl-ammonium lead halide) perovskite material has resulted in 19% efficiency [5]. The CH3NH3PbI3 has a direct bandgap of 1.55 eV [6]. The organometal perovskite material of halide group has the high absorption coefficient about 10\(^5\) cm\(^{-1}\) with the absorption wavelength above 800 nm and it also has unique electrical characteristic [7].
One of the factors determining the efficiency of perovskite solar cells is the active layer morphology namely CH$_3$NH$_3$PbI$_3$ film. The CH$_3$NH$_3$PbI$_3$ film must have the big crystal size in the range of 500 - 1000 nm and high crystallinity with the cubic and homogeny form to be able to result in perovskite solar cells with the high efficiency [1,2,4]. One of the weaknesses of PCSs is its low stability where the PCs stability decreases to the duration of UV ray radiation. Solving such thing needs certain material that functions as perovskite electron transport with semiconductor materials such as TiO$_2$ [8] or ZnO [9]. ZnO has some benefits since it is cheaper, its band gap is wide so it is easily grown up on the substrate, it is non-toxic and environmentally friendly [9,10].

ZnO synthesis with any kinds of morphology has been conducted by many researchers such as nanorod [11], nanowire [12] nanoflow [13], nano-comblike [14], nanosheet [15], and nanoforest [16]. ZnO with nanorod morphology has the benefit since it is vertically oriented to the substrate so that it can well improve the effectiveness of the electron transport on PSCs [9,17]. ZnO nanorods (NRs) can enhance the electron diffusion on the photo-electrode layer by providing the conduction path directly (direct pathway) so that it reduces the charge recombination level usually occurring in conventional polycrystalline nanoparticles randomly oriented [18].

Synthesis of ZnO NRs that have been carried out were such as chemical bath deposition (CBD) method at the low temperature [19], and the hydrothermal method [20]. Meanwhile, CH$_3$NH$_3$PbI$_3$ perovskite coating is commonly undertaken by one stage and two stages-spin coating method [21]. The perovskite coating with two stages could result in good morphology so that it results in the higher photovoltaic performance [22]. PSCs used ZnO NRs with HTM Spiro-OMeTAD resulted in 8.90 % efficiency on FTO substrate and 2.62% on PET/ITO substrate [19]. PSCs with 11% efficiency based on ZnO NRs were successfully done by Son et al. (2014) using CH$_3$NH$_3$PbI$_3$ perovskite [9]. PSCs efficiency based on ZnO NRs was extremely influenced by the rods morphology besides its perovskite structure and the used HTM. Therefore, this research examined the influence of ZnO NRs morphology resulted from the various growing times to the electrical properties of PSCs.

2. Materials and Methods

This research used Indium Tin Oxide (ITO) substrate coated in the glass. For the synthesis of ZnO seed layer, the main materials of Zinc Acetate Dihydrate, Ethanol, and Monoethanolamine were utilized. Meanwhile, to grow up ZnO NRs, the main materials used were Zinc Nitrate Tetrahydrate, Hexamethylenetetramine (HMT), and Deionized Water.

Making the ZnO seed layer solution was conducted by dissolving Zinc Acetate Dihydrate with ethanol, then stirred using a magnetic stirrer on the hot plate at the temperature of 70 °C for 45 minutes. Subsequently, Monoethanolamine (MEA) was added wisely with the molar ratio between Zinc Acetate Dihydrate and MEA about 1:1. The solution was untreated for 24 hours at the room temperature then sparingly dropped on the ITO substrate, and then the spin coating was done with the velocity of 2500 rpm for 25 seconds. After that, the preheating was done at the temperature of 150 °C for 10 minutes and the annealing was performed at the temperature of 550 °C for two hours so that the ZnO seed layer film was formed.

Growing up ZnO NRs was carried out by the hydrothermal method. The solution for ZnO NRs growing was done by mixing Zn (NO$_3$)$_2$.4H$_2$O 75Mm with HMT with the molar ratio of 1:1. The solution was then stirred using a magnetic stirrer for 45 minutes at the room temperature. Subsequently, ZnO seed layer film was dipped into the prepared solution. The growing process was undertaken at the temperature of 90 °C with the various growing times of 4, 6, and 8 hours. The obtained sample was rinsed with DI-water, dried, and then annealed at the temperature of 550 °C for two hours in the furnace. The sample was then characterized using XRD, SEM, FTIR, and UV-Vis.

The fabrication of PSCs was performed by two-stage spin coating on ZnO NRs substrate. The first step of PbI$_2$ coating was from the mixture of 1 mol/L PbI$_2$ solution and dimethylformamidine (DMF) with the rotational speed of 4500 rpm for 15 minutes. The sample was then dried at the temperature of 100 °C for 30 minutes. The next step was the spin coating of 10 mg/mL CH$_3$NH$_3$I solution dissolved in IPA.
with the rotational speed of 2500 rpm for 10 seconds. The sample was then dried in the oven at the temperature of 100 °C for 30 minutes. The sample was characterized by XRD, LCR meter, and solar cell efficiency test.

3. Results and Discussion
The X-ray diffraction pattern of ZnO NRs/ITO thin film with the precursor concentration of 75 mM in the various growing times of 4, 6, and 8 hours using hydrothermal method is shown in Figure 1. The analysis of ZnO NRs phase informed that the formed diffraction pattern was in accordance with the data of XRD JCPDS standard No.36-1451 with the hexagonal crystal (zincite) system having the space group of P63mc, with the crystal lattice of \(a\), \(b\) = 3.2533 Å and \(c\) = 5.2073 Å. The formed phase was suitable for the report of Rai, et al. (2014), that ZnO NRs were formed in zincite phase [23]. Figure 1 shows the diffraction peak located at (100), (002), and (101). The XRD pattern with the annealing temperature of 550 °C for two hours at the NRs growing temperature of 90 °C had the crystal orientation at the highest intensity peak on (002), while on (100) and (101) the pattern weakened since the ZnO NRs growing was oriented to c direction. This case is in line with the report of Selvan, et al. (2014) [24].

![Figure 1. The diffraction pattern of ZnO NRs/ITO as the function of temperature](image)

Figure 2 shows the cross-section and top-section morphology of ZnO nanorods film with the various growing times of 4, 6, and 8 hours. The results of SEM characterization showed the forming of the structure having rod form with a hexagonal structure on all substrate surfaces.
The results of the SEM characterization were analyzed and tabulated in Table 1. They showed that the longer the growing time of ZnO NRs, the resulted rods were higher and the diameter was bigger. This case showed that the growing time could increase the diameter and length of ZnO as reported by the previous researchers [25,26]. NRs morphology with the higher density can be seen in ZnO NRs synthesized with the growing time of hydrothermal for 8 hours. The longer the growing time with the hydrothermal method, it influenced the increase in the formed NRs density. This case is in line with the statement of Baruah and Dutta (2009) [27]. The more dense structure of ZnO NRs could enhance the orientation degree to a vertical direction. This case was because each rod supported each other so that they minimized the possibility of the rods to be inclined or collapsed.

Table 1. The dimension of ZnO nanorods.

| Samples          | Length (nm) | Diameter (nm) |
|------------------|-------------|---------------|
| ZnO NRs 4 hours  | 835         | 138           |
| ZnO NRs 6 hours  | 934         | 230           |
| ZnO NRs 8 hours  | 1399        | 236           |

The characterization of UV-Vis spectrophotometer in the wavelength range of 350-800 nm has been carried out to identify the transmittance spectrum and optical properties of ZnO NRs. The transmittance spectrum of ZnO NRs is shown in Figure 3. ZnO NRs in the precursor concentration of 75 mM with the various growing times of 4, 6, and 8 hours showed the strongest excitonic absorption at the wavelength of ~376 nm. This result is in line with the research results of Foo et al. (2014) with the strongest excitonic absorption at the wavelength of 378 nm [28]. This case indicated that ZnO NRs had the good optical quality and strong excitonic bonding energy. The strongest peak at the wavelength of ~360 nm was the emission peak of UV from free exciton. The absorption coefficient (α) for the transition direction of the ZnO NRs/ZnO seed layer of ITO is formulated through the Equation 1.

\[
\alpha = \ln \left( \frac{1/T}{d} \right)
\]

where \( T \) is the transmittance of ZnO film and \( d \) is the film thickness [28].
Figure 3. UV-Vis spectra of ZnO NRs as the function of wavelength at the different growing times

Determining the energy of bandgap was based on the Kubelka Munk equation [29] for the semiconductor for the direct type of bandgap described through plot Tauc between \((ahv)^2\) versus \(hv\), as shown in Figure 4. This result is the data interpretation of UV-Vis Spectra in Figure 3. The value of the ZnO NRs bandgap was obtained from the intersection between extrapolation line with \(x\)-axis summarized in Table 2.

Figure 4. Touch graph of ZnO NRs with various growing times
Table 2 presents that the value of the ZnO seed layer bandgap was 3.2 eV. This is in accordance with the range of the bandgap value of ZnO nanoparticles film namely 3.2-3.5 eV [10]. The bandgap values of ZnO NRs at the precursor concentration of 75 mM for the various growing times of 4, 6, and 8 hours were 3.145 eV, 3.120 eV, and 3.049 eV, respectively. By the increase in the growing time, the bandgap decreased. The ZnO NRs bandgap was smaller than the ZnO seed layer. This was because ZnO NRs film has a wider area compared to ZnO seed layer film so that it could increase the high absorption of light and cause the bandgap smaller. This case corresponds to the research conducted by Selvan, et al. (2014) that the longer the growing time, the bandgap value would decrease [24].

| Type of Samples       | Bandgap (eV) |
|-----------------------|--------------|
| ZnO seed layer        | 3.216        |
| ZnO NRs 4 hours       | 3.145        |
| ZnO NRs 6 hours       | 3.120        |
| ZnO NRs 8 hours       | 3.049        |

Figure 5 shows the results of FTIR of ZnO Seed layer and ZnO NRs with the precursor concentration of 75 mM in the various hydrothermal growing times of 4 hours, 6 hours, and 8 hours in the wavelength range of 4000-500 cm⁻¹ at the room temperature. The FTIR results showed three main peaks in the wavelength range of 400-515 cm⁻¹, 870 cm⁻¹, and 1250 cm⁻¹. Generally, ZnO has the absorption at the wavelength range of 400-515 cm⁻¹ in accordance with the report of Gayen, et al. (2010) [30], while in the wavelength of 870 cm⁻¹ and 1250 cm⁻¹ there was H-C-N functional group formed from Hexamethylenetetramine (HMT) material with the chemical formula of C₆H₁₂N₄, in line with the report of Cottin, et al. (2002) [31] and Garcia, et al. (2010) [32].
Figure 6. XRD Pattern of CH$_3$NH$_3$PbI$_3$/ZnO NRs sample with various growing times

Figure 6 shows XRD pattern of PbI$_2$ film, CH$_3$NH$_3$I powder, and CH$_3$NH$_3$PbI$_3$ deposition in ZnO NRs/ITO film with the concentration of 75 mM in 4 hours (sample A), 6 hours (sample B), and 8 hours (sample C) growing times. The XRD pattern of PbI$_2$ film on the ZnO NRs/ITO substrate showed the crystal growth oriented to c-axis indicated by four main peaks namely in the angle of 12.4°, 25.5°, 38.7°, and 52.5° that were respectively the crystal structure of (001), (002), (003), and (004). This case is in accordance with the research conducted by Burschka et al. (2013) showing that the PbI$_2$ peak was located at the crystal structure of (001), (002), (003), and (004) [33]. The diffraction peaks of perovskite appeared at the angle of 14.0°, 28.2°, 31.6°, 40.1°, and 44.9° that were respectively related to the crystal structure of perovskite tetragonal phase of (110), (220), (310), (224), and (134). The similar research was also undertaken by Zheng et al. (2015) showing the perovskite peaks were on (110), (220), (310), (224), and (134) with 2θ at 14.2°, 28.5°, 31.8°, 40.5°, and 44.0° [34]. The percentage of the crystal phase of CH$_3$NH$_3$I and PbI$_2$ in all samples are sorted from the low to the high percentage shown in Table 3 where sample C (sample I$_3$), sample A (sample I$_1$), sample B (sample I$_2$).

Table 3. The percentage of the crystal phase of CH3NH3PbI3/ZnO NRs

| Type of Sample | CH$_3$NH$_3$I (%) | PbI$_2$ (%) |
|---------------|------------------|-------------|
| I$_1$         | 43.01            | 56.99       |
| I$_2$         | 74.67            | 25.33       |
| I$_3$         | 82.32            | 17.68       |

The XRD pattern on sample I$_1$ showed the percentage of the CH$_3$NH$_3$I phase of 43.01% and PbI$_2$ phase of 56.99%. In I$_2$ sample, the percentage of CH$_3$NH$_3$I phase was 74.67% and PbI$_2$ phase was 25.33%, while in I$_3$ sample, the percentage of CH$_3$NH$_3$I phase was 82.32% and PbI$_2$ phase was 17.68%. The percentage of CH$_3$NH$_3$I phase increased as the decrease in PbI$_2$ phase. The percentage of the forming of CH$_3$NH$_3$PbI$_3$ perovskite device was low. This case was because the percentage of PbI$_2$ was still high meaning that the PbI$_2$ phase had not been converted totally became CH$_3$NH$_3$PbI$_3$ perovskite. The conversion of PbI$_2$ to CH$_3$NH$_3$PbI$_3$ occurred quickly when the solution was dropped on the film since the heavy metal halide layered structure tended to interact with a small molecule. Thereby, the dense
perovskite layer was usually formed on the PbI$_2$ surface and blocked the CH$_3$NH$_3$PbI$_3$ diffusion to the basic layer so that it caused imperfect perovskite conversion. Besides, the influence of the oxygen humidity definitely influenced the reaction of perovskite forming directly. CH$_3$NH$_3$PbI$_3$ perovskite has the high sensitivity to the water and will tend to be hydrolyzed due to the humidity. Hence, the fabrication process should be done in the glove box passed by an inert gas.

Figure 7. The influence of frequency on the dielectric constant of CH$_3$NH$_3$PbI$_3$/ZnO NRs with the variation of PbI$_2$ impurities

Figure 7 shows the results of the dielectric constant that tended to decrease as the increase in the given frequency. This case is in line with the research of Hoque et al. (2016) that studied the effect of polarization and perovskite dielectric that the higher the given frequency, the value of dielectric constant tended to decrease [35]. The lowest dielectric constant was resulted by $I_1$ sample with the frequency of 100 Hz. Meanwhile, in the high frequency, the value of dielectric was almost similar to all samples. This case showed that the polarization between the grain groups was more dominant in influencing the dielectric characteristic of the material.

The current resulted by CH$_3$NH$_3$PbI$_3$/ZnO NRs with the variation of $I_1$, $I_2$, and $I_3$ measured by using multimeter used the light through LED 13 Watt lamp with the various spaces between the test sample and the lamp as presented in Table 4.

| Type of Sample | Current (µA) |
|---------------|-------------|
|               | Intensity (400000 lux) | Intensity (173000 lux) | Intensity (120000 lux) | Intensity (8300 lux) |
| $I_1$         | 0.013(7)    | 0.001(1)     | 0.001(1)    | 0.001(1)        |
| $I_2$         | 0.077(6)    | 0.001(1)     | 0.001(4)    | 0.001(1)        |
| $I_3$         | 0.096(8)    | 0.074(3)     | 0.001(1)    | 0.001(1)        |

Table 4 shows that in the CH$_3$NH$_3$PbI$_3$/ZnO NRs film, the resulted current from any light intensities was very small. This case might be because the perovskite as the synthesis result was unwell formed due to the humidity factor where the light absorption by perovskite was not optimal. The highest current was resulted by $I_3$ sample. In general, the smaller the PbI$_2$ impurity of the sample, the resulted current was bigger. This result was consistent enough in any radiation intensity.
4. Conclusion
ZnO NRs synthesis has been successfully conducted using a hydrothermal method. The longer the growing time, the resulted ZnO NRs had the bigger diameter, and their rod length was longer. The created ZnO NRs had the diameter between 138 and 236 nm and the rod length between 835 nm and 1399 nm. Besides, the growing time increased the homogeneity and density of the produced ZnO NRs, while the bandgap was getting smaller. The electrical properties of CH$_3$NH$_3$PbI$_3$/ZnO NRs PSCs were related to the number of PbI$_2$ impurities as well. The smaller the PbI$_2$ impurity, the dielectric value becomes smaller at the low frequency, while it was relatively similar at the high frequency. Moreover, the smaller the PbI$_2$ impurity, the current value was higher in the light source with the high intensity.

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