Research Article

Growth of Zinc Oxide Nanorods with the Thickness of Less than or Equal to 1 μm through Zinc Acetate or Zinc Nitrate for Perovskite Solar Cell Applications

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1.Introduction

Studies of zinc oxide (ZnO) material, specifically ZnO nanorod (NR) or nanowire (NW) morphology, are continuously performed because of numerous applications of ZnO NRs in many fields of science, especially in branches of electronics, optoelectronics, electrochemistry, and electromechanics [1–6]. Some examples of these applications are ultraviolet (UV) lasers [7, 8], light-emitting diodes [9], field-emission devices [10–12], high-performance nanosensors [13, 14], solar cells [15–18], piezoelectric nanogenerators [19–21], and nano-piezotronics [22, 23]. ZnO NR is one of the most frequently used forms of nanostructures because of its ease of fabrication by relatively less complicated methods. ZnO material is also nontoxic and environmentally friendly.

Many fabrication methods can be used to synthesize ZnO NRs. In this study, ZnO NRs were synthesized by a two-step...
A method of seed layer deposition, followed by NR growth. Seed layer is an important factor in growing vertically aligned ZnO NRs because the seed affects the growth alignment of ZnO NRs. A report by Ghayour et al. found that the thickness of the seed layer affected the resulting ZnO NRs’ alignment and morphology [24]. Nirmal Peiris et al. also reported how the thickness of the ZnO seed layer affected the output of the ZnO NR-based dye-sensitized solar cell (DSC) [25]. Song and Lim reported how the resulting ZnO NRs' morphology was affected by the ZnO seed layer [26]. Pourshaban et al. reported a development where a higher seed layer's concentration would lead to longer thickness of ZnO NRs [27]. Meanwhile, the types of seed layer that used either monoethanolamine (MEA) or potassium hydroxide (KOH), and their effects on the resulting ZnO NRs, were compared and analyzed by Kashif et al. [28].

Another method to optimize the ZnO NR's properties was by the preheating treatment for the seed layer [29–32]. Dou et al. reported another way to increase photovoltaic performance of ZnO NR-based DSC, i.e., chemical vapor deposition (CVD), involves the use of a heat furnace to produce a flow of vapor that carries the zinc nucleus into the intended substrate. Another method is the vapor-liquid-solid (VLS) method, where the substrate that carries seed droplets is exposed to vapor-carrying zinc particles to form solid NR inside a chamber. The hydrothermal method, where a sealed metal container contains the substrate to be doped while immersed in a growth solution, is also often used. The metal container is heated at a relatively low temperature (less than 100 to 150°C) for some time (a few hours to more than 24 hours). The chemical bath deposition (CBD) method is similar to the hydrothermal method but, instead of using a metal container, a chemical beaker is used as an alternative to carry the substrate immersed in the growth solution. In this study, a CBD method was reported, involving the application of a waterbath machine as a heat source for the beaker container in order to grow ZnO NRs. This method was also used in the previous research to grow 1.0–1.5 μm long ZnO NRs [35]. The same method was used to grow ZnO NRs with a length of less than or equal to 1.0 μm. One suitable application of such short thickness of ZnO NRs is as a metal oxide for perovskite solar cells (PSCs).

2. Experiment

Distilled water, acetone, and ethanol were used consecutively as cleaning solvents for the fluorine-doped tin oxide (FTO) substrates while being sonicated inside an ultrasonic machine before the growth of ZnO NRs. The seed layer’s solution contained 0.1 M of zinc acetate dehydrate while being dissolved in 20 mL of 2-methoxyethanol as solvent and then dripped with 10 drops (about 1 μL) of ethanolamine as stabilizer. The solution was stirred with a magnetic stirrer while being heated at 60°C for 30 minutes. In the next step, the seed layer’s solution was spin coated into the cleaned FTO substrate at a rotational speed of 3000 rpm. Then, the seeded FTO substrates were heated at 100°C for 10 minutes to vaporize the leftover solution. The spin coating and heating process were repeated for three cycles. The seeded FTO substrates were annealed inside a heating furnace at 350°C for 1 hour.

This phase was followed by the development of ZnO NRs using the waterbath method at a designated temperature of 85°C. The growth solutions were made from a solution containing zinc source inside a distilled water solvent and another that contained HMT within a distilled water solvent. In this study, two zinc sources, namely, zinc acetate dihydrate (ZA) or zinc nitrate hexahydrate (ZN), were used for comparison purposes. ZA and ZN were used and combined with the HMT separately and independently to form their own ZnO NRs. The resulting ZnO NR combinations of ZA + HMT and ZN + HMT were used to immerse the seeded FTO substrate using the waterbath method. The time period (t) for the growth process was counted from the moment the waterbath machine reached 85°C. In this study, the time t varied from zero minutes (the waterbath machine was turned off immediately when it reached the temperature of 85°C), 15, 60, 90, to 120 minutes. A schematic diagram showing the waterbath method is shown in Figure 1.

Scanning electron microscopy (SEM) images of the resulting ZnO NRs were generated using a field-emission scanning electron microscope (FE-SEM, JEOL 6335F and SEM JOEL 7001F). The X-ray diffraction (XRD) profiles were characterized using a Rigaku Ultima III machine and Cu Kα radiation (λ = 1.5418 Å). Full width at half maximum (FWHM) analysis was performed to the (002) peak of the ZnO NR, which was based on Scherrer’s equation:

\[
\tau = \frac{K\lambda}{\beta\cos \theta}
\]  

3. Results and Discussion

All ZnO NRs were grown at various growth times with two different zinc sources, namely, ZA and ZN, during the processing phase of the growth solution by the waterbath method. SEM images of the top view of the grown ZnO NRs are presented in Figure 2. According to the top view SEM images, the diameter of the ZnO NRs from both ZA and ZN sources showed little change from t = 0-minute condition to t = 90-minute condition. Figures 2(a)–2(d) show the diameter of the visible ZnO NRs ranging from approximately 10 nm to 20 nm. However, when the growth time t was raised to 120 minutes, the diameter of ZnP NRs from the ZA source ranged from approximately 30 nm to 120 nm. Meanwhile, ZnO NRs from the ZN source with growth time t = 120 minutes did not show any significant change in diameter. Such outcome showed that, from the beginning of the growth process at a room temperature until the designated temperature at 85°C, ZnO NRs' growth had already begun. ZnO NRs from the ZN source showed nearly unchanging diameter at different time t because it was more likely to grow vertically instead of horizontally.

Figure 3 represents an analysis of how growth time t affected the thickness of the resulting ZnO NRs. The growth
Seed layer deposited FTO plate

50mL of 0.050M zinc acetate dihydrate + 50mL of 0.050M HMT solution

Normal water kept at 85°C for \( t \) minutes

For \( t = 0 \) minutes, it meant when the waterbath machine showed temperature of 85°C from starting temperature, growth process was immediately stopped

50mL of 0.050M zinc nitrate hexahydrate + 50mL of 0.050M HMT solution

Figure 1: Growth of ZnO NRs with the waterbath method.

Figure 2: SEM images (top view) of ZnO NRs from both ZA (left column) and ZN (right column) sources processed with the waterbath method for growth time \( t = 0, 90, \) and 120 minutes. (a) \( t = 0 \) minutes, ZA. (b) \( t = 0 \) minutes, ZN. (c) \( t = 90 \) minutes, ZA (d) \( t = 90 \) minutes, ZN. (e) \( t = 120 \) minutes, ZA (f) \( t = 120 \) minutes, ZN.
rate of the ZnO NRs in the vertical axis was affected by how long the time $t$ was counted. At $t=0$ minutes, the thickness of the ZnO NRs from both ZA and ZN sources was estimated at 100 nm. When the time $t$ was increased further, the length of the ZnO NRs also increased in accordance with the processing time $t$. At $t=120$ minutes, the longest ZnO NR was obtained at 2.0–2.1 μm and 0.8–0.9 μm for ZA and ZN sources, respectively. The thickness of ZnO NRs grown from the ZA source had a faster growth rate compared to the ones grown from the ZN source. A report by Akgun et al. mentioned that the presence of acetate ions within the ZA source had an increased capping effect that boosted the

Figure 3: SEM images (cross section view) of ZnO NRs from both zinc sources, i.e., ZA (left column) and ZN (right column), grown using the waterbath method at $t=0$, 15, 60, 90, and 120 minutes. (a) $t=0$ minutes, ZA. (b) $t=0$ minutes, ZN. (c) $t=15$ minutes, ZA. (d) $t=15$ minutes, ZN. (e) $t=60$ minutes, ZA. (f) $t=60$ minutes, ZN. (g) $t=90$ minutes, ZA. (h) $t=90$ minutes, ZN. (i) $t=120$ minutes, ZA. (j) $t=120$ minutes, ZN.
thickneth of the resulting ZnO NRs [36]. Another analysis by Liang et al., who compared the use of ZA and ZN sources for the growth of ZnO NRs, found that both zinc sources had to undergo an intermediate phase of layered basic zinc salts (LBZs) [37]. The LBZ phases of the ZA source produced a higher amount of precipitates compared to the ZN source, which led to boosted growth of ZnO crystals for the ZA source.

Table 1 provides the list of ZnO NR sizes grown from either ZA or ZN sources at various growth times $t$. To grow ZnO NRs with a thickness of less than or equal to $1 \mu m$, the maximum growth time $t$ was 90 minutes for the ZA source, while $t=120$ minutes was still within the acceptable timeframe. According to a finding by Lee et al., shorter lengths of metal oxide in a PSC application resulted in higher efficiency because of smaller series resistance and boosted charge carrier properties [38]. Based on such findings, the ZnO NR with the most suitable thickness for PSC application was found at $t=0$-minute condition for ZnO NRs grown from a ZA source. In the case of the ZN source, Figure 2(b) shows that the grown ZnO NRs had not covered the whole surface of the FTO glass substrate because of a slower growth rate compared to that of the ZA source. Such growing conditions may be suitable for a longer growth time $t$ for ZnO NRs grown from a ZN source; as such, the most suitable ZnO NR thickness was found at $t=15$ minutes.

XRD profiles of ZnO NRs grown from a ZA source are shown in Figure 4. At $t=0$ minutes, there was a noticeable ZnO peak at (002) crystallinity. There were also weak ZnO peaks at (100) and (101) crystallinity and an unidentified peak at point E. The peak E was believed to be detected from leftover zinc acetate, which originated from the seed layer that did not grow into ZnO NRs. With the increase in time $t$, the (002) ZnO peak experienced an increase in intensity in proportion to the time $t$. This was an expected condition as longer time $t$ would result in higher thickness of the ZnO NRs grown from the ZA source, which would make the other ZnO peaks at tilted angles, making it harder to detect. The presence of (100), (002), and (101) ZnO peaks showed that the ZnO crystals possessed wurtzite quality. The growth in a vertical direction ($c$-axis) was represented by the presence of the (002) crystallinity peak for the ZnO NRs.

FWHM analysis for the (002) peak grown from the ZA source at various times $t$ is summarized in Table 2. The (002) peak was chosen because it possessed the highest intensity amongst all the ZnO peaks. Origin software was used to process the XRD data from Figure 4 and give the crystallite size value. Figure 5 illustrates the linear plotting of the crystallite sizes from Table 2 as a function of growth time $t$. The largest FWHM value was obtained at $t=0$ minutes for FWHM = 0.71°. The lowest crystallite size at 10.70 nm was given at zero-minute condition for the ZnO NRs grown from the ZA source. At zero-minute condition, the ZnO NR was still growing and the grains could grow larger. At $t=15$ minutes, the crystallite size of the ZnO NR increased to 20.57 nm and continued to grow to 21.09 nm at $t=60$ minutes. It did not grow larger at $t=90$ minutes. When $t$ was further increased to 120 minutes, the crystallite size increased to 21.62 nm. A linear plotting of the crystallite size as a function of time $t$ is shown in Figure 5. Elakhy et al. reported that a smaller crystallite size leads to lower sheet resistance, which increased the conductivity of metal oxide [39]. Therefore, the most suitable ZnO NR from the ZA source was found to be generated at $t=0$ minutes.

Figure 6 represents the morphology analysis of ZnO NRs grown from the ZN source. The XRD profiles in Figure 6 showed three ZnO peaks at (100), (002), and (101) crystallinity, with (002) having the highest intensity. Some of its differences from the XRD profiles shown in Figure 4 were weaker intensity of (002) peak for the ZN source and modest detection of (100) crystallinity for the ZnO peak. Compared to the ZA source, the ZN source provided little growth in the horizontal direction, which resulted in a smaller diameter for the ZnO NRs. Their growth in the vertical direction was not as fast as the growth of ZnO NRs from the ZA source. This could be seen from the fact that the (002) peak had lower intensity than the FTO peak. In such a situation, the growth of the ZnO NRs from the ZN source became more tilted compared to that of the ZnO NRs from the ZA source, which led to the detection of ZnO NRs (ZN source) at a tilted or horizontal angle.

The crystallite size of the ZnO NRs grown from the ZN source was measured by FWHM analysis. Table 3 lists the FWHM results analysis of the (002) crystallinity peak for the ZnO NRs. Compared with the ZA source, the ZN source produced ZnO NRs with higher crystallite size at zero-minute condition. This outcome showed that at zero-minute

<table>
<thead>
<tr>
<th>$t$</th>
<th>ZA (zinc acetate dihydrate)</th>
<th>ZN (zinc nitrate hexahydrate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 minutes</td>
<td>Diameter = 10–20 nm</td>
<td>Thickness = 0.1 $\mu$m</td>
</tr>
<tr>
<td></td>
<td>Thickness = 0.3–0.4 $\mu$m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diameter = 10–20 nm</td>
<td>Thickness = 0.1 $\mu$m</td>
</tr>
<tr>
<td></td>
<td>Thickness = 0.4–0.5 $\mu$m</td>
<td></td>
</tr>
<tr>
<td>60 minutes</td>
<td>Diameter = 10–20 nm</td>
<td>Thickness = 0.1 $\mu$m</td>
</tr>
<tr>
<td></td>
<td>Thickness = 0.5–0.6 $\mu$m</td>
<td></td>
</tr>
<tr>
<td>90 minutes</td>
<td>Diameter = 10–20 nm</td>
<td>Thickness = 0.1 $\mu$m</td>
</tr>
<tr>
<td></td>
<td>Thickness = 1.0–1.1 $\mu$m</td>
<td></td>
</tr>
<tr>
<td>120 minutes</td>
<td>Diameter = 30–120 nm</td>
<td>Thickness = 0.8–0.9 $\mu$m</td>
</tr>
<tr>
<td></td>
<td>Thickness = 2.0–2.1 $\mu$m</td>
<td></td>
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</table>
condition, starting from room temperature to designated temperature at 85°C, there were hollow spots where the seed layer did not grow into the ZnO NR (Figure 2(b)). Such growth in zero-minute condition might cause fluctuations or noises between the (100) and (002) peaks, causing defects in the (002) peak detection using XRD analysis. When t was increased to 15 minutes, there was a fall in crystallite size. This might be due to the tilted growth of the ZnO NR at t = 15 minutes or flawed (002) detection at t = 0 minutes. The largest FWHM value was found at t = 15 minutes for the ZnO NR from the ZN source at 0.39°. The smallest crystallite size of the ZnO NR from the ZN source was also achieved.

Figure 4: XRD profiles of the grown ZnO NRs from the ZA source with growth time t at 0, 15, 60, 90, and 120 minutes.

### Table 2: FWHM analysis of the (002) XRD peak in ZnO NRs grown from the ZA source.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>ZA 0 minutes</th>
<th>ZA 15 minutes</th>
<th>ZA 60 minutes</th>
<th>ZA 90 minutes</th>
<th>ZA 120 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak position (°)</td>
<td>34.51</td>
<td>34.51</td>
<td>34.50</td>
<td>34.50</td>
<td>34.50</td>
</tr>
<tr>
<td>FWHM (°)</td>
<td>0.71</td>
<td>0.37</td>
<td>0.36</td>
<td>0.36</td>
<td>0.35</td>
</tr>
<tr>
<td>Crystallite size (nm)</td>
<td>10.70</td>
<td>20.57</td>
<td>21.09</td>
<td>21.06</td>
<td>21.62</td>
</tr>
</tbody>
</table>

Figure 5: Linear plotting of crystallite size in a chart as a function of growth time t for ZnO NRs grown from the ZA source.
at $t = 15$ minutes at 19.29 nm. The crystallite size experienced a steady increase from $t = 15$-minute condition to $t = 120$-minute condition. A longer growth time $t$ also leads to a larger ZnO NR (diameter or thickness). The linear plotting of the crystallite size as a function of time $t$ is shown in Figure 7. Based on Table 3, the smallest crystallite size was
found at $t = 15$ minutes, which was the most suitable size for ZnO NRs from the ZN source.

4. Conclusion

ZnO NRs with vertical alignment and wurtzite quality were grown from both ZA and ZN sources. By controlling the growth time $t$, ZnO NRs with thickness of less than or equal to $1 \mu m$ were successfully grown. For PSC application, it was believed that the maximum growth time $t$ was about 90 minutes for a ZA source and 120 minutes for a ZN source. Based on the thickness and coverage of ZnO NRs, the optimum growth time $t$ for PSC application was identified at $t = 0$ minutes for the ZA source and $t = 15$ minutes for the ZN source. ZnO NRs from the ZA source provided faster growth compared to the ones grown from the ZN source. ZnO NRs grown from the ZN source had tilted quality compared to those grown from the ZN source. ZnO NRs from the ZA source (0.71 °) and ZnO NRs from the ZN source (0.39 °). Scherrer’s equation, which were the most suitable sizes for PSC application.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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