Characterization of Dye-Sensitized Solar Cell with ZnO Nanorod Multilayer Electrode

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Abstract

In this study, zinc oxide (ZnO) nanorods were synthesized on indium-tin-oxide (ITO) glass substrates by a hydrothermal process. The growth process was carried out one to five times to obtain ZnO nanorods of different generations (1st to 5th generation). Scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), and x-ray diffraction (XRD) were used to obtain the surface morphology, chemical composition, and crystallographic structure of the synthesized ZnO nanorods. These ZnO nanorods were submerged in the dye solution and were used as the working electrode (anode) of dye-sensitized solar cell (DSSC). I-V and optoelectronic characteristics of the DSSCs using ZnO nanorods of different generations as the electrodes were measured to obtain their fill factors and conversion efficiency. Experimental results reveal that the ZnO film of the 4th generation exhibits a uniform distribution of dense nanorods whose shape and microstructure are beneficial to dye adsorption and carrier transport. Therefore, the DSSC fabricated with the ZnO nanorods of the 4th generation has an improved short-circuit current, fill factor, and conversion efficiency.

Keywords: –Zinc oxide (ZnO) nanorods, Dye-sensitized solar cell (DSSC)

1. Introduction

Zinc oxide (ZnO) is a wide-bandgap II-VI compound semiconductor with a direct bandgap of 3.37 eV at room temperature. With an electron binding energy of 60 meV [1] and the superior properties such as anti-oxidation and chemical stability, ZnO is a promising optoelectronic material with great potential in the applications for optical detector [2], gas sensor [3], solar cell [4], short-wavelength UV laser, and blue or green optoelectronic devices [5]. In the present time, the synthesis of ZnO with novel shapes (e.g. wire, rod, lamina, and tube) has attracted widespread attention.

Many processes have been used to prepare ZnO including thermal evaporation [6-7], pulsed laser deposition (PLD) [8], magnetic enhanced sputter [9], metal-organic chemical vapor deposition (MOCVD) [10], and chemical vapor deposition [11]. However, the processes stated above not only require expensive equipment but also are not suitable for batch-type production. In comparison, using chemical solution to prepare ZnO has several advantages over the growth processes stated above. Not only it is an inexpensive process requiring only low-cost equipment, but also ZnO with excellent crystallinity, chemical stability, and thermal stability can be attained with this process.

ZnO was used to fabricate electrode much earlier than TiO₂. Early in 1969, Gerischer [12] studied the feasibility of using crystalline ZnO electrode in dye-sensitized solar cell (DSSC). Matsumura [13] presented a report on the research of the optoelectronic characteristics of DSSC with ZnO electrode in 1976. Matsumura [14] used porous ZnO as the electrode to achieve a conversion efficiency of 2.5% at the wavelength of 562 nm in 1980.
In 1994, Fitzmaurize [15] used ruthenium complex as the dye to obtain a monochromatic conversion efficiency of 13% at the wavelength of 520 nm and a conversion efficiency of 0.4% under sunlight. In 1997, Hagfeldt [16] reported a monochromatic conversion efficiency as high as 58% and a conversion efficiency of 2% under sunlight. These results clearly demonstrated the plausibility of using ZnO in the high efficiency DSSC. In the study by Hagfeldt [17] in 2002, the conversion efficiency of ZnO solar cell was 5%. At present, the highest conversion efficiency of ZnO solar cell under full sunlight (AM-1.5, 100 mW/cm²) is 4.1% achieved by Fujihara [18].

The incorporation of crystalline semiconductor nanowires can effectively lower the potential barrier at the grain boundary and reduce the loss of electron transport. Therefore, the transport property of carrier is improved and the conversion efficiency of solar cell is increased [19]. Hence, they have become the material selection for electrode in DSSC device application. In this study, ZnO nanorods were synthesized with an inexpensive hydrothermal process. The purpose of using ZnO nanorods as the working electrode was to increase its carrier transport capability. ZnO multilayer was used with the intention to increase the adsorption of dye thereby increasing the optical absorption and rendering a higher conversion efficiency for the DSSC. The ZnO multilayer was achieved through multiple growths of ZnO nanorods (called multiple generations in this paper). The I-V characteristics of DSSCs using ZnO nanorods of different generations as the working electrode were measured and investigated to study their effects on the conversion efficiency of solar cell.

### 2. Experimental Details

In this work, ZnO nanorods prepared by a simple hydrothermal process were used to fabricate the working electrodes for DSSC applications. First, indium-tin-oxide (ITO) glass substrate was cut into 2 cm × 2 cm pieces, and then rinsed with acetone, methanol and deionized water. After cleaning, the ITO glass substrates were blown with nitrogen to dry. Transparent tapes were adhered along the peripheral of ITO glass substrate. Only the central area of 1 cm × 1 cm was reserved for the growth for ZnO nanorods. In addition to ITO substrates, ZnO nanorods were also synthesized on silicon substrates since they are more suitable for SEM and EDS measurements. Second, deionized water was added to zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and methenamine (C₆H₁₂N₄, HMT) to obtain the reagents used for the growth of ZnO nanorods. These two solutions were mixed at the ratio of 1:1 to obtain a mixture of 0.1M molar concentration. The mixed solution was vigorously stirred for 20 min at room temperature to ensure full and uniform mixing. The mixture was heated indirectly through water at 85°C. After the temperature of mixture was stabilized, ITO glass substrates were submerged in the mixture with ITO facing upwards. After 1 hr of high temperature process, samples were removed from the beaker and were rinsed with deionized water for 20 min to halt the growth process of ZnO nanorods. Finally, the synthesized ZnO samples were placed into a box for 5 hours so that they can dry by themselves. This completed the growth process of ZnO, and the ZnO nanorods of the 1st generation were achieved. The 2nd, 3rd, 4th, and 5th growth processes were then carried out sequentially to obtain the ZnO nanorods of 2nd, 3rd, 4th, and 5th generations. The ZnO nanorods synthesized in the previous growth process were used as the starting point of the next growth process and were covered by the ZnO nanorods synthesized in the next growth process. The processing parameters (e.g. molar concentration of mixture, growth temperature, and growth time) in all subsequent growth processes of ZnO were the same as those used in the 1st growth process. After the working electrodes using ZnO nanorods of different generations were fabricated, they were submerged in the dye solution for 8 hours so that the dye can be fully adsorbed by ZnO nanorods. Subsequently, the working electrodes were assembled with the counter electrode of Pt film/ITO glass and electrolyte was injected to form
DSSC.

The purpose of this work is to study the surface morphology, chemical composition, and microstructure of the ZnO nanorods of different generations. Scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), and x-ray diffraction (XRD) were used to obtain the surface morphology, chemical composition, and crystallographic structure of ZnO nanorods. Afterwards, $I-V$ characteristics of the DSSCs using ZnO nanorods of different generations were measured, and open-circuit voltage, short-circuit current, fill factor, and conversion efficiency were determined.

### 3. Results and Discussions

In this study, zinc nitrate hexahydrate ($\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}$) and hexamethylene tetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, HMT) were mixed at the ratio of 1:1 in water. The molar concentration ratio of $\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}$ and $\text{C}_6\text{H}_{12}\text{N}_4$ was 1:1 which was the optimum value determined from our previous experimental results. HMT is non-toxic and its water-soluble polymer ring dissolves in acidic solution into functional groups to form NH$_3$. $\text{Zn(NO}_3\text{)}_2$ can react with HMT in water to synthesize ZnO nanorods. The chemical reactions involved in the growth of ZnO nanorods are: [20-22]

\[
\begin{align*}
\text{C}_6\text{H}_{12}\text{N}_4 + 6\text{H}_2\text{O} &\rightarrow 6\text{HCHO} + 4\text{NH}_3 \\
\text{NH}_3 + \text{H}_2\text{O} &\rightarrow \text{NH}_4^+ + \text{OH}^- \\
2\text{OH}^- + \text{Zn}^{2+} &\rightarrow \text{ZnO} + \text{H}_2\text{O}
\end{align*}
\]

First, $\text{C}_6\text{H}_{12}\text{N}_4$ is disintegrated into formaldehyde (HCHO) and ammonia (NH$_3$) as shown in equation (1). Ammonia tends to disintegrate water to produce OH$^-$ anions (equation 2). Finally, OH$^-$ anions react with Zn$^{2+}$

![Figure 1. The top-view SEM images of ZnO nanorods of the: (a) 1st, (b) 2nd, (c) 3rd, (d) 4th, and (e) 5th generations. The magnification factor is $1\times10^3$.](image)

[Image 373x268 to 515x381] [Image 227x267 to 369x381] [Image 81x267 to 223x381] [Image 156x151 to 298x264] [Image 301x151 to 443x264]
cations to form ZnO (equation 3). In the growth process of ZnO nanorods, the concentration of OH\textsuperscript{−} anions is the dominant factor. Therefore, C\textsubscript{6}H\textsubscript{12}N\textsubscript{4} that supplies OH\textsuperscript{−} anions play a key role in the growth of ZnO nanorods. The hydrolysis rate of C\textsubscript{6}H\textsubscript{12}N\textsubscript{4} is low and thus can provide OH\textsuperscript{−} anions at a steady rate rendering a solution with a constant concentration of OH\textsuperscript{−} anions. At low concentrations of C\textsubscript{6}H\textsubscript{12}N\textsubscript{4} + Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, the reaction rate of OH\textsuperscript{−} anions is low; on the other hand, the reaction rate and the growth rate of ZnO nanorods is high at high concentrations of C\textsubscript{6}H\textsubscript{12}N\textsubscript{4} + Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O. In this study, the molar concentration of mixture used in the growth process was 0.1M. Since our previous study has demonstrated that DSSC using ZnO nanorods electrode prepared with 0.1M mixture, same concentration of mixture was used in this work to study the effect of ZnO multilayer electrode on the operating characteristics of DSSC.

![Figure 1](image1)

Figure 1. The top-view SEM images of ZnO nanorods of different generations.

![Figure 2](image2)

Figure 2. The enlarged SEM images of ZnO nanorods of the: (a) 1\textsuperscript{st}, (b) 2\textsuperscript{nd}, (c) 3\textsuperscript{rd}, (d) 4\textsuperscript{th}, and (e) 5\textsuperscript{th} generations. The magnification factor is 3×10\textsuperscript{4}.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>1\textsuperscript{st}</th>
<th>2\textsuperscript{nd}</th>
<th>3\textsuperscript{rd}</th>
<th>4\textsuperscript{th}</th>
<th>5\textsuperscript{th}</th>
</tr>
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<tbody>
<tr>
<td>O</td>
<td>77.82</td>
<td>60.18</td>
<td>53.49</td>
<td>52.85</td>
<td>50.60</td>
</tr>
<tr>
<td>Si</td>
<td>2.80</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Zn</td>
<td>19.37</td>
<td>39.82</td>
<td>46.51</td>
<td>47.15</td>
<td>49.40</td>
</tr>
<tr>
<td>Zn:O</td>
<td>1:4.02</td>
<td>1:1.51</td>
<td>1:1.15</td>
<td>1:1.12</td>
<td>1:1.02</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition for the ZnO nanorods of different generations.

Figure 1 shows the top-view SEM images of ZnO nanorods of different generations, while the enlarged images are shown in the Figure 2. The magnification factor is 1×10\textsuperscript{5} for Figure 1, and is 3×10\textsuperscript{4} for Figure 2. The growth parameters are listed as follows: the growth temperature was 85\textdegree C, growth time was 1 hr, the molar concentrations of
Zn(NO$_3$)$_2$$\cdot$6H$_2$O and C$_6$H$_{12}$N$_4$ were 0.1M (the molar ratio was 1:1), and the growth process was repeated 1 to 5 times. From Figure 1(a), (b), (c), (d), and (e), it is clearly seen that no obvious change in the surface morphology of ZnO nanorods of different generations can be observed. Figure 2(a) shows the ZnO nanorods of the 1st generation which is obtained with a mixture solution of 0.1M. The average diameter of ZnO nanorods is ~420 nm. The average diameter of nanorods increases logarithmically from ~693 nm for the ZnO of the 1st generation to ~858 nm for the ZnO of the 5th generation. As shown in Figures 2(d) and (e), the shape of nanorods tends to become short and wide. Since fresh mixture solution was added before every growth process in order to maintain a constant ion concentration of 0.1M in the solution, the ZnO nanorods that have been adhered to the substrate already will have the opportunity to replenish newly added anions. Since the growth rate on the six side walls is higher than that on the tip surface, it is reasonable for the shape of ZnO nanorods to become short and wide after multiple growth processes.

![XRD spectra for ZnO nanorods of different generations.](image)

**Table 2.** Intensities of characteristic peaks in XRD spectra for the ZnO nanorods of different generations.

<table>
<thead>
<tr>
<th>Generation of ZnO</th>
<th>Ia</th>
<th>Ic</th>
<th>Ib</th>
<th>Ia/Ic</th>
<th>Ib/Ic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^{st}$</td>
<td>602</td>
<td>511</td>
<td>893</td>
<td>1.18</td>
<td>1.74</td>
</tr>
<tr>
<td>2$^{nd}$</td>
<td>829</td>
<td>653</td>
<td>1169</td>
<td>1.27</td>
<td>1.79</td>
</tr>
<tr>
<td>3$^{rd}$</td>
<td>959</td>
<td>710</td>
<td>1292</td>
<td>1.35</td>
<td>1.82</td>
</tr>
<tr>
<td>4$^{th}$</td>
<td>1502</td>
<td>1058</td>
<td>2000</td>
<td>1.42</td>
<td>1.89</td>
</tr>
<tr>
<td>5$^{th}$</td>
<td>1669</td>
<td>1135</td>
<td>2290</td>
<td>1.47</td>
<td>2.02</td>
</tr>
</tbody>
</table>

In this study, EDS was used to measure the chemical composition of ZnO nanorods of different generations and is listed in Table 1. As observed in the EDS analysis, the atomic content of silicon in the ZnO nanorods of the 1st generation is 2.8%. Since no silicon-containing reagent was used in the growth process, the detected silicon content is caused by silicon atoms on the substrate. Obviously, the ZnO nanorods were not dense enough to completely
cover the entire substrate. As the ZnO nanorods evolve into the 2nd generation, the atomic percentage of silicon drops to 0% indicating that the distribution of ZnO nanorods is uniform and dense. The silicon substrate is completely covered by ZnO nanorods. This is beneficial to the uniform adsorption of dye molecules. The chemical composition for ZnO nanorods of different generations can be clearly seen in Table 1. It seems that the atomic ratio of zinc to oxygen decreases as the ZnO nanorods evolve. The atomic ratio of zinc to oxygen on the surfaces of nanorods is 1:4.02 for the ZnO nanorods of the 1st generation, whereas this atomic ratio decreased to 1:1.02 for the ZnO nanorods of the 5th generation which is close to the theoretical value of 1 as is expected for ZnO.

Figure 3 shows the XRD spectra for the ZnO nanorods of different generations. In Figure 3, all spectra exhibit five characteristic peaks. Of these five peaks, the diffraction peaks located at diffraction angles of \(2\theta = 31.77^\circ, 34.42^\circ, \) and \(36.25^\circ\) are most pronounced. These 3 peaks correspond to \((100), (002), \) and \((101)\) directions of crystallization of wurtzite ZnO nanorods, i.e., the growth along the directions of \(a, b,\) and \(c\)-axis of nanorod hexagonal structure, respectively. These intensities of characteristic peaks in XRD spectra for the ZnO nanorods of different generations are summarized in Table 2. In the diffraction spectra, the intensity ratio in the direction of a axis and c axis \((I_a/I_c)\) and the intensity ratio in the direction of a axis and c axis \((I_b/I_c)\) are useful. As ZnO nanorods evolve from the 1st generation to the 5th generation, the values of \(I_a/I_c\) and \(I_b/I_c\) increase. The value of \(I_a/I_c\) increases from 1.18 to 1.47, and \(I_b/I_c\) increases from 1.74 to 2.02. The aspect ratio of nanorod also increases with the evolution of ZnO nanorods. This is because the increases in the growth rate on the \((100)\ and \((101)\ surfaces of ZnO nanorods are higher than that on the \((002)\ surface. Hence, nanorods become short and wide. This assertion is verified by the SEM image shown in Figure 1(e).

Figure 4 shows the \(I-V\) characteristics of the DSSCs fabricated with ZnO nanorods of different generations. The corresponding open-circuit voltage \((V_{oc})\), short-circuit current \((I_{sc})\), and fill-factor \((FF)\) are tabulated in Table 3. For the DSSCs prepared with ZnO nanorods of the 1st and 2nd generations, their short-circuit current and fill factor are very low. In sharp contrast, the DSSC prepared with ZnO nanorods of the 4th generation exhibits much improved short-circuit current and fill factor, and hence a much higher conversion efficiency. However, it is found that the DSSC prepared with ZnO nanorods of the 5th generation has a lower short-circuit current, open-circuit
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voltage, fill factor, and hence a lower conversion efficiency. Possible explanations are given as follows. For the ZnO nanorods of the 1st generation, the distribution of nanorods on the ITO glass substrate is not uniform. Lots of voids and vacancies are found in the ZnO film so that dyes can not uniformly adsorbed in the film. Therefore, the DSSC prepared with the 1st generation ZnO nanorods exhibit poor I-V characteristics. The distribution of ZnO nanorods of the 2nd generation is still non-uniform indicating that there are some voids and vacancies in the ZnO film. This can affect the adsorption of dye molecules so that only slight improvement in the I-V characteristics of DSSC can be achieved. For the DSSCs using ZnO nanorods of the 3rd and 4th generation, substantial improvement in their I-V characteristics is evident. Compared with the DSSC prepared with ZnO nanorods of the 1st generation, short-circuit current increases by a factor of 7 for the DSSC using ZnO nanorods of the 4th generation, and a large increase in the conversion efficiency of DSSC is achieved. From the atomic ratio of zinc to oxygen in EDS analysis, the structure of the ZnO nanorods of the 3rd and 4th generations is considerably better than that of the ZnO nanorods of the 1st and 2nd generations. Much fewer bonding vacancies are present in the nanorods. Therefore, electrons are easier to travel in these films and the conversion efficiency of DSSC is increased.

The reason for the degradation in the I-V characteristics as found in the DSSC prepared with ZnO nanorods of the 5th generation is presumably caused by the larger thickness of ZnO film. The distance which electrons have to travel through the ZnO film is increased, thus electron-hole recombination is more likely to take place and photocurrent is decreased accordingly. Furthermore, the average diameter of ZnO nanorods becomes larger for the ZnO nanorods of the 5th generation so that the aspect ratio of nanorods increases and nanorods become short and wide. The voids and vacancies lying between nanorods become larger, and intimate contact between nanorods is unlikely now. This results in an increase in the internal resistance of working electrode. Fill factor and conversion efficiency are decreased drastically and the operating characteristics of DSSC are severely degraded.

Table 3. Open-circuit voltage (Voc), short-circuit current (Isc), and fill factor (FF) for the DSSCs using ZnO nanorods of different generations as the working electrode.

<table>
<thead>
<tr>
<th>Generation of ZnO</th>
<th>Voc (V)</th>
<th>Isc (A)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>0.44</td>
<td>9.812×10^{-5}</td>
<td>53.101</td>
</tr>
<tr>
<td>2nd</td>
<td>0.43</td>
<td>1.694×10^{-4}</td>
<td>44.287</td>
</tr>
<tr>
<td>3rd</td>
<td>0.43</td>
<td>4.477×10^{-4}</td>
<td>44.050</td>
</tr>
<tr>
<td>4th</td>
<td>0.42</td>
<td>7.074×10^{-4}</td>
<td>41.979</td>
</tr>
<tr>
<td>5th</td>
<td>0.37</td>
<td>2.348×10^{-4}</td>
<td>40.745</td>
</tr>
</tbody>
</table>

4. Conclusions

In this study, ZnO nanorods of different generations were used as the working electrodes for DSSCs. Experimental results reveal that the average diameter of ZnO nanorods increases with the evolution of ZnO nanorods. As the ZnO nanorods evolve, the shape of ZnO nanorods varies from long, slender hexagonal column to short, wide rods after multiple growth processes. As the ZnO nanorods evolve into the 4th generation, substantial improvement in the open-circuit voltage, short-circuit current, and conversion efficiency of DSSC are achieved. As the ZnO nanorods evolve into the 5th generation, the average diameter of nanorods increases to lower the specific surface area.
Less dye molecules are adsorbed which makes the photocurrent decrease. Another possible reason is the increase of internal resistance in the ZnO nanorods working electrode which can also lower fill factor and conversion efficiency.

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References


