Growth control of ZnO nano-rod with various seeds and photovoltaic application

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Abstract. ZnO has attracted much interesting as one of unique materials. Especially, it is suitable for the easy fabrication of nano-structures such as rod, wire and tube as well as particles. ZnO nano-rod is one of good sensitized electrodes because it has good electron transfer and is easily fabricated. In the chemical bath deposition process, seed layer plays an important role in the growth of nano-rod. This work investigated and analyzed the effect of seed layer on the growth of ZnO nano-rod. Fabricated nano-rods were applied to dye-sensitized solar cell. For better performance, ZnO was surface-modified by TiO2. Surface-modified ZnO had improved electron transfer and wider surface area. Consequently, the current and fill factor were much improved and overall performance was also enhanced with them.

1. Introduction
ZnO has attracted in a wide range of research fields with its multiple properties such as non-toxicity, good electrical conductivity, stability in a hydrogen plasma atmosphere, and low cost. It has been widely studied in the photovoltaics with its band-gap between 3.1 and 3.4 eV. Especially, ZnO has been expected to be comparable to TiO2 because of its higher electronic mobility and similar energy level of the conduction band [1,2]. However, overall conversion efficiency of ZnO-based solar cell has been lower than that of TiO2-based solar cell, hence the enhancement on its performance is still a challenging study [3-7]. ZnO is more advantageous than TiO2 in the structural aspect because it is suitable for the easy fabrication of nano-structures such as rod, wire, and tube. ZnO nano-rods (NRs) were used for the photovoltaic application in this work [8-12]. Among a range of various fabrication methods for ZnO NRs, the chemical bath deposition (CBD) is widely used [13-17]. In the CBD, the seed layer plays an important role in the formation and growth of NR. However, most of related researches have mainly focused on only growth materials as ZnO source and the growth methods. The seed layer was often not specified although the seed layer affects the growth characteristics of NRs. In this work, the effect of the seed layer on the growth of ZnO NR was investigated. The characteristics of ZnO NR such as the growth speed, NR density, and the crystallinity were analyzed according to materials and fabrication of seed layer. After that, fabricated NRs were applied to the photochemical cell as the sensitized electrode. For better performance, ZnO NRs were surface-modified by TiO2. In order to verify the influence of seed layer and surface modification, the photovoltaic performance, the electrochemical impedance, and structural properties were examined.
2. Experimental

4 kinds of seed layers including a reference were applied for the fabrication of ZnO NR. One ZnO seed was deposited on Fluorine-doped tin oxide (FTO) substrates (15 Ω per sq., Nippon Sheet Glass Co., Ltd.) by RF magnetron sputtering with ZnO target. Working pressure was 0.3 Pa of Ar and 100 W RF power with 13.56 MHz was applied. Substrate temperature was fixed at 500 °C during the deposition and deposition time was 270 s. Other ZnO seeds were deposited on FTO substrates by spin-coating with 50 mM zinc acetate dihydrate (Zn(CH$_2$COO)$_2$·H$_2$O) and zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) aqueous solutions [18-23]. For uniform layer, they were spin-coated at 3000 rpm for 60 s and at 4000 rpm for 60 s again. Spin-coated layers were sintered at 200 °C for 10 min finally. Their reactions were showed in equation 1 and 2. As a reference, bare FTO substrate was also used without any seed layer.

\[
\text{Zn(CH}_2\text{COO)}_2\text{H}_2\text{O} \rightarrow \text{ZnO} + 2\text{CH}_2\text{COOH} \tag{1}
\]

\[
\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{Zn}^{2+} + 2\text{NO}_3^- + 7\text{H}_2\text{O}, \tag{2}
\]

For the growth of ZnO NRs, FTO substrates with and without seed layers were dipped in 50mM Zn(NO$_3$)$_2$·6H$_2$O aqueous solution. Hexamethylenetetramine (HMT) was added to solution because it is difficult to grow NR based on only Zn(NO$_3$)$_2$·6H$_2$O. For the vertical growth, the substrates were reversely dipped and NRs were grown from top to down. In this case, the growth speed was relatively slower than that of normal growth but it was possible to make more uniform and vertical NRs. Temperature was fixed at 90 °C during the growth. Grown NRs were sintered at 500 °C for 30 min. They were characterized by their morphological and compositional properties. The scanning electron microscopy (SEM, S-4200, Hitachi) operated at 15 kV was used to characterize their nano-structure. And their formation was ascertained by measuring X-ray diffraction (XRD, X’pert PRO MRD, Philips) under optimized operating conditions of 30 mA and 40 kV. TiO$_2$ solution was prepared for the surface modification of ZnO NRs. 2 ml titanium isopropoxide was slowly added in 20 ml ethanol. After adding 1 ml distilled water and 1ml hydrochloric acid as a catalyst, the solution was turned to be milky under stirring and aged for 24 h. And then, ZnO NR electrodes were dipped in TiO$_2$ solution for 1 min. Taken electrodes out of solution were dried and sintered at 450 °C for 30 min.

Fabricated ZnO NRs were applied to dye-sensitized solar cell (DSC). DSCs were fabricated as follows. FTO/ZnO NR electrodes were soaked in a 0.2 mM N719 dye (cis-bis (isothiocyanato) bis (2, 2’-bipyridyl-4, 4’-discarboxylyato)-ruthenium(II)-bis-tertbutylammonium, RuC$_{8}$H$_{8}$N$_{4}$O$_{8}$S$_{4}$) solution for 24 h. Dye-sensitized NR electrodes were rinsed with ethanol and dried using a stream of nitrogen. The platinized counter electrode with a thickness of about 0.1 μm was sputtered at a power of 150 W. After that, both electrodes were sealed using a thermoplastic hot-melt sealant (SX 1170-25, Solaronix) for 24 h. Dye-sensitized NR electrodes were rinsed with ethanol and dried using a stream of nitrogen. The platinized counter electrode with a thickness of about 0.1 μm was sputtered at a power of 150 W. After that, both electrodes were sealed using a thermoplastic hot-melt sealant (SX 1170-25, Solaronix) for 24 h. Dye-sensitized NR electrodes were rinsed with ethanol and dried using a stream of nitrogen. The platinized counter electrode with a thickness of about 0.1 μm was sputtered at a power of 150 W. After that, both electrodes were sealed using a thermoplastic hot-melt sealant (SX 1170-25, Solaronix) for 24 h. Dye-sensitized NR electrodes were rinsed with ethanol and dried using a stream of nitrogen. The platinized counter electrode with a thickness of about 0.1 μm was sputtered at a power of 150 W. After that, both electrodes were sealed using a thermoplastic hot-melt sealant (SX 1170-25, Solaronix) for 24 h. Dye-sensitized NR electrodes were rinsed with ethanol and dried using a stream of nitrogen. The platinized counter electrode with a thickness of about 0.1 μm was sputtered at a power of 150 W. After that, both electrodes were sealed using a thermoplastic hot-melt sealant (SX 1170-25, Solaronix) for 24 h. Dye-sensitized NR electrodes were rinsed with ethanol and dried using a stream of nitrogen.

Before their characterization, the completed cells were stored in the dark under open-circuit conditions for 24 h to allow the electrolyte to penetrate into nano-rods. The photovoltaic performance was measured under 1 sun (air mass 1.5, 100 mW/cm$^2$) by a source meter (Model 2400, Keithley Instrument, Inc.). During their irradiance and characterization, the cells were covered with a black mask fitting the active area of the cell. The irradiated cell area was 0.20 cm$^2$. The I-V characteristic curve and equations 3 were used to calculate the short-circuit current ($I_{sc}$) and density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF) and the overall efficiency ($\eta$). The internal impedance of DSCs was measured by electrochemical impedance spectroscopy (EIS, SP-150, Biologic SAS). The EIS spectra were measured over the frequency range from 10 mHz to 1 MHz at room temperature. The
applied bias voltage and AC amplitude were set at $V_{OC}$ of the DSC and 10 mV, respectively. The electrical impedances were characterized using the Nyquist diagram.

\[ \eta = \frac{P_{\text{max}}}{P_{\text{in}}} \times 100 = \frac{FF \cdot V_{OC} \cdot J_{sc}}{P_{\text{in}}} \times 100(\%) \]  

(3)

3. Results and discussion

Figure 1 shows SEM images of ZnO NRs on (a) bare FTO substrate, (b) sputtered ZnO seed, (c) Zn(CH$_3$COO)$_2$·H$_2$O seed, and (d) Zn(NO$_3$)$_2$·6H$_2$O seed. ZnO NRs were not grown well. NRs were randomly grown and re-grown based on the generated rods because there is no seed as the basis of growth. Sputtered seeds were formed as rod type from the first and they were so uniform and vertical. However, they were different from rods grown by the CBD. ZnO NRs were grown independently of sputtered seed layer and they were not grown uniformly and vertically. In case of Zn(CH$_3$COO)$_2$·H$_2$O seed, NRs were well grown but some rods were partially changed to film by the aggregation. Aggregated rods made the surface area reduced and many pores were blocked. On the other hand, ZnO NRs were well grown on Zn(NO$_3$)$_2$·6H$_2$O seed. The growth was also uniform and vertical without the aggregation.

![Figure 1. SEM images of ZnO nano-rods on (a) bare FTO substrate, (b) sputtered ZnO seed, (c) Zn(CH$_3$COO)$_2$·H$_2$O seed, and (d) Zn(NO$_3$)$_2$·6H$_2$O seed.](image)

These results were confirmed by XRD measurement. XRD patterns show their composition in figure 2. ZnO NRs were mainly grown to (100) and (101) by the CBD. The growth was the best with Zn(NO$_3$)$_2$·6H$_2$O seed like SEM results. The growth was the worst without seed and CBD growth was different from sputtered seed. Therefore, it was concluded that Zn(NO$_3$)$_2$·6H$_2$O was used for the seed layer.

![Figure 2. XRD patterns ZnO nano-rods on according to seed layers.](image)
Figure 3 shows (a) rod diameter and (b) normalized efficiency according to HMT ratio. HMT concentration was varied from 10 to 50 mM. Zn(NO$_3$)$_2$·6H$_2$O and aqueous solution provided Zn$^{2+}$ and O$_2^-$ ions as the source of growth. HMT was hydrolyzed in the solution and produced OH$^-$ during the growth. Heterogeneous nucleation of ZnO crystals was formed on the surface with Zn$^{2+}$ and OH$^-$. After that, the crystals grew as NR. The increase of HMT ratio led to increase the diameter. The performance was not matched with the increase of diameter. It was increased up to 40 mM HMT but decreased since then. Therefore, next step was conducted with fixed concentration of HMT as 40 mM.

![Figure 3](image)

**Figure 3.** (a) Rod diameter and (b) normalized efficiency of DSCs according to HMT ratio.

Figure 4 shows (a) the NR length and (b) performance change according to the growing time from 1 to 8 h. NRs were reasonably grown. It was almost proportional to the growing time although they were not grown within 1 h. Longer rods led to increase of the photocurrent because more dye molecules were adsorbed on wider surface of longer rod. However, the performance was not proportional to the length of rod although the current was continuously increased. It came from the worse electron transfer. Figure 5 shows I-V characteristic curves of ZnO NR DSCs according to the growing time. As mentioned above, the current was the largest with the longest growing time but FF was decreased. It meant that longer rod had much charge recombination from the contact with redox electrolyte. Then, overall performance was deteriorated with bad electron transfer.

![Figure 4](image)

**Figure 4.** (a) Rod length and (b) performance change according to growing time.
For better performance, ZnO NRs were surface-modified by TiO$_2$ because overall performance including current and FF was still low in spite of the optimization of growth condition. Figure 6 shows (a) I-V characteristic curves and (b) EIS diagram of ZnO NR DSCs with and without the surface modification. After the surface modification, FF and the photocurrent were much increased while $V_{OC}$ was slightly decreased. The conduction band of TiO$_2$ was more positive than that of ZnO. Then, the difference between the conduction band and redox potential was reduced, hence $V_{OC}$ was decreased. On the other hand, the surface area was increased and charge recombination was much decreased by the surface modification. More dye molecules were adsorbed and more electrons were photo-generated. Also, the dark current was reduced and it confirmed the reduction of charge recombination. Accordingly, $J_{SC}$ was increased. Improved electron transfer made FF much enhanced from 0.28 to 0.43. In the EIS analysis, internal impedance was much deceased. Decreased impedance proved the improvement of electron transfer at the interfaces of ZnO NR/dye/electrolyte. Consequently, improved current and FF led to enhance the overall performance after the surface modification.

**Figure 5.** I-V characteristic curves of ZnO nano-rod DSCs according to growing time.

**Figure 6.** (a) I-V characteristic curves and (b) EIS diagram of ZnO nano-rod DSCs with and without the surface modification.

### 4. Conclusions

In this work, ZnO NRs were fabricated from various seed layers. Zn(NO$_3$)$_2$·6H$_2$O was suitable as the seed and NRs were also grown uniformly and vertically. In the growth process, HMT ratio affected the diameter of NR and the length of NR was longer with the increase of growing time. ZnO NRs fabricated under the optimized condition were applied to DSC but its performance was bad because of
low FF, especially. For better performance, ZnO surface was modified by TiO$_2$. The surface modification improved electron transfer and reduced the charge recombination and increased the surface area. Consequently, the current and FF were much improved, resulting in the enhancement of overall performance.

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6. References
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