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Research Article

Investigation on the Tunable-Length Zinc Oxide Nanowire Arrays for Dye-Sensitized Solar Cells

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We had successfully fabricated ZnO-based nanowires by vapor transport method in the furnace tube. ZnO nanowire arrays grown in 600°C for 30 minutes, 60 minutes, 90 minutes, and 120 minutes had applied to the dye-sensitized solar cells. The dye loading is proportional to the total equivalent surface area of ZnO nanowire arrays in the cells and plays an important role in improving power conversion efficiency. The highest efficiency was observed in DSSC sample with ZnO nanowires grown for 90 minutes, which had the largest equivalent surface area and also the highest dye loading. According to our experimental results, the enhancement in power conversion efficiency is attributed to the higher light harvesting and reduction of carrier recombination. In addition, ZnO nanowires also contribute to the photocurrent in the UV region.

1. Introduction

Due to the low fabrication cost and relatively high efficiency, dye-sensitized solar cells (DSSCs) have been a potential alternative to p-n junction solar cells [1–3]. The porous TiO_2-based DSSCs have overcome the shortcomings of expensive cost related to the construction of photovoltaic modules for solid-state devices. The structure of porous TiO_2 nanoparticles provides a large surface area for anchoring the light-harvesting dye molecules. However, the conversion efficiency of nanoporous TiO_2-based DSSCs had stuck at around 11-12% due to the restricted electron extraction efficiency that resulted from slow electron transport mechanism and charge-carrier recombination by grain boundaries [4]. To significantly improve the electron transport efficiency, it is expected to synthesize promising type of nanomaterial instead of nanoparticle to generate a direct conduction pathway to the collecting electrode.

In addition to the use of TiO_2 structures for the fabrication of DSSCs, heretofore, several other semiconductor materials, such as ZnO, Cd (Se, S), and SnO_2, have also been employed as an electrode material in DSSCs [5]. Among these materials, ZnO is one promising II–VI compound oxide semiconductor material with its wide direct band gap of 3.37 eV at room temperature, strong exciton binding energy of 60 meV, and great physical and chemical stability [6–8]. ZnO-based DSSCs are believed to gain the enhancement of efficiency because of their rapid electron transfer, reduction of charge recombination degree, and collection of carriers through electrical transport pathway. However, overall solar-to-electric energy conversion efficiency (η) of ZnO-based DSSCs is still relatively low [9–11]. Recently, more researchers have been focused on the nanostructured ZnO materials to improve the efficiency of ZnO-based cells using, especially ZnO one-dimensional (1D) structure [12–14].

There are many technologies to grow ZnO 1D structure including vapor-liquid-solid process [15], metalorganic chemical vapor deposition [16], thermal evaporation [17], and chemical solution synthesis [18]. The properties of 1D ZnO are strongly dependent on the fabrication conditions used. Also, it has been shown that photovoltaic response of ZnO nanowires is dependent not only on the rod size but also on their orientation. Typically, the ZnO 1D nanostructures prepared by chemical solution method exhibit inferior material quality compared to vapor deposited samples. In this paper, we put emphasis on the influence of ZnO nanostructures

prepared by vapor transport technique on dye adsorption and carrier transport rather than on efficiency.

2. Experimental Procedure

ZnO nanowires were grown on fluorine doped tin oxide (FTO) substrates. FTO conducting glass with $1 \times 1\,cm^2$ Au buffer layer and pure Zn powder (99.99%) were inserted into the center of quartz tube. The quartz tube was evacuated by using mechanical pump. The high-purity argon gas was infused into the system with a flow rate of 200 sccm. The growth temperature of the furnace was increased to 600°C and maintained for 30, 60, 90, and 120 minutes. After the procedure the as-grown ZnO nanowires substrate was immersed to 0.3 mM N719 dye for 24 hours and used acetonitrile to remove the unnecessary dye, and Pt film was formed on the other FTO substrate. Both substrates were coated on a film of Ag gel and, after that, the cell was assembled with 125 μm surlyn film. The electrolyte (0.5 M 4-tert-butyl-pyridine + 0.05 M I_2 + 0.5 M LiI + 0.6 M tetrabutylammonium iodide) was injected to the cell and then sealed with UV gel.

Surface morphologies of the ZnO nanowires were examined using field-emission scanning electron microscope (FESEM). The conversion efficiency and current density-voltage (*J-V*) curve was characterized by a solar simulator (Yamashita Denso Xenon lamp power supply model YSS-50) with AM 1.5, 100 mW/cm^2 Xe lamp as a photon source. The current-voltage digital meter (Keithley 2410) is attached to the solar simulator. The electrochemical impedance spectroscopy (EIS) was measured under the light illumination of AM 1.5 (100 mW/cm^2) with an impedance analyzer (Autolab PGSTAT 30) when a device was applied with its open-circuit voltage (Voc). An additional alternative sinusoidal voltage amplitude 10 mV was also applied between an anode and a cathode of a device over the frequency range of 0.02~100 kHz.

3. Results and Discussion

Figure 1 shows the XRD results of the ZnO nanowires grown on the FTO conducting glasses. The reflections from FTO glass are present in all patterns. All ZnO nanowires samples have high intensity peak at (002) diffraction plane, indicating that ZnO nanowires are preferential perpendicular to the substrate in the direction of *c*-axis. No other peaks from impurities were found, showing the high purity of ZnO nanowires. SEM images of the high-density ZnO nanowires grown on the substrate are shown in Figure 2. The majority of the nanowires were grown with diameters of 454 nm, 383 nm, 450 nm, and 433 nm and lengths of 2.75 μm, 7.17 μm, 5.17 μm, and 4.33 μm for growth durations of 30 min, 60 min, 90 min, and 120 min, respectively. Moreover, the density of ZnO nanowires samples is 3.8×10^8 cm^{-2}, 2.6×10^8 cm^{-2}, 4.6×10^8 cm^{-2}, and 2.2×10^8 cm^{-2}, respectively. The equivalent surface area of samples is counted and summarized in Table 1. The surface area of samples on 1×1 cm^2 FTO glass grown for 30 min, 60 min, 90 min, and 120 min is 15.6 cm^2, 22.73 cm^2, 34.22 cm^2, and 13.28 cm^2, respectively.

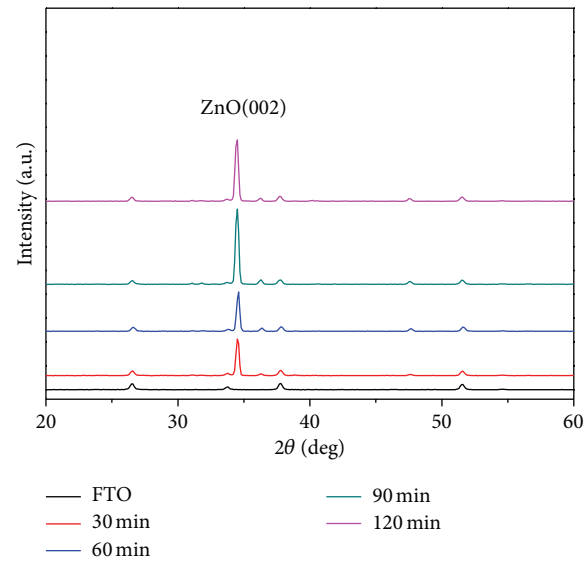

Figure 1: XRD spectra of ZnO nanowires grown on FTO conducting glass.

Table 1: Equivalent surface area of ZnO nanowires on 1×1 cm^2 FTO glass with different growth time.

	30 min	60 min	90 min	120 min
Equivalent surface area	4.97×10^{-4} π m^2/cm^2	7.24×10^{-4} π m^2/cm^2	1.09×10^{-3} π m^2/cm^2	4.23×10^{-4} π m^2/cm^2

Table 2: Dye loading of ZnO nanowires with different growth time.

	30 min	60 min	90 min	120 min
Dye loading	5.95×10^{-6} g	1.12×10^{-5} g	1.32×10^{-4} g	4.07×10^{-6} g

To emphasize the differences in the equivalent surface area of nanowires, dye loading was quantitatively determined by an ultraviolet/visible (UV-VIS) spectrophotometric method, after calibration using a diluted aqueous solution of N719 dye. It is known that the presence of the OH groups can also affect the dye loading, based on the obtained results for ZnO nanowires [16]. Therefore, dye loading was investigated and the obtained results for the absorbance of the desorbed dye are shown in Figure 3. From the results, the dye loading is counted and summarized in Table 2. It seems that the dye loading of the samples is proportional to the total equivalent surface area of ZnO nanowire arrays in the cells. This phenomenon indicates that the more equivalent surface area of the ZnO nanowire arrays provides more opportunities to absorb the dye. The highest dye loading is obtained at samples grown for 90 min, which is consistent with the SEM results mentioned above. The phenomenon can be comprehended as follows. As we increase the growth time from 30 minutes to 90 minutes, the vertical growth mechanism dominates the formation of one-dimensional nanowires. Moreover, two-dimensional growth mechanism will facilitate the two-dimensional growth while growth

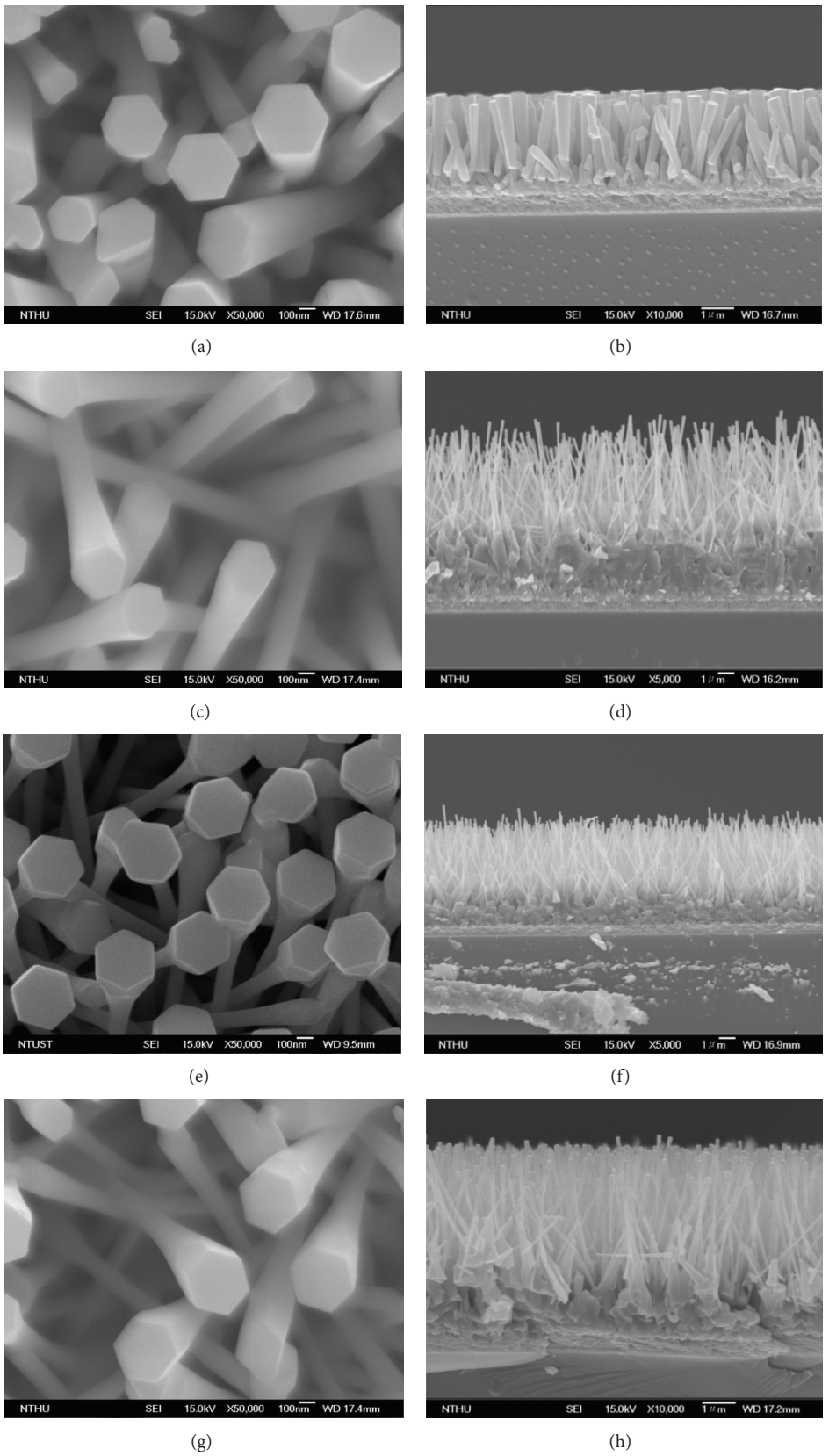

Figure 2: FE-SEM images of ZnO nanowires on the FTO conducting glass with different growth times: (a)-(b) for 30 minutes, (c)-(d) for 60 minutes, (e)-(f) for 90 minutes, and (g)-(h) for 120 minutes.

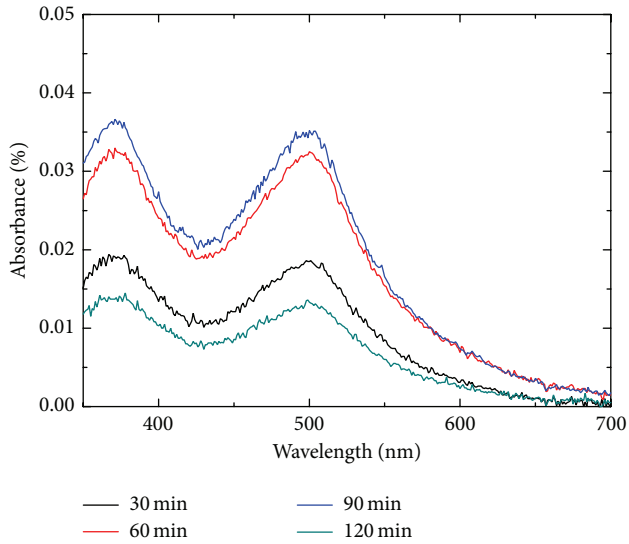

Figure 3: UV-visible spectra of DSSCs with the ZnO nanowires grown for different time.

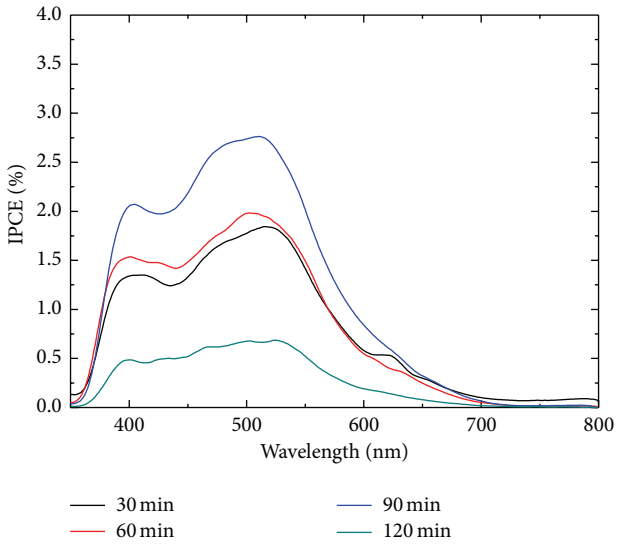

Figure 5: IPCE spectra of DSSCs with the ZnO nanowires with different growth time.

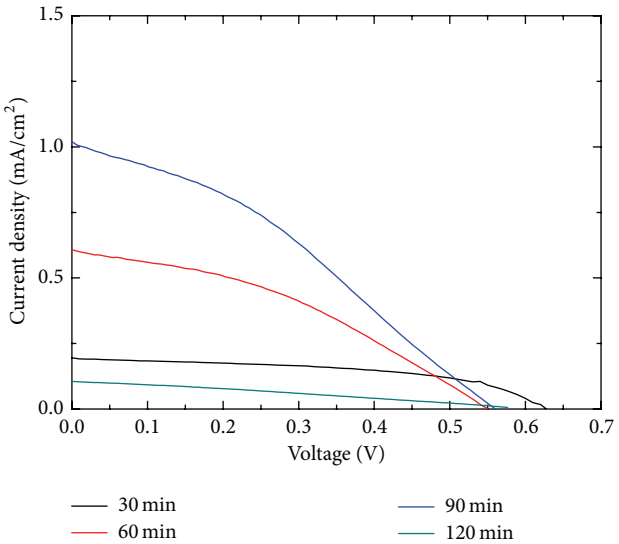

Figure 4: *J-V* characteristic of DSSCs with the ZnO nanowires grown for different time.

duration was increased to 120 minutes. The ZnO bottom layer and the length of ZnO nanowires will become thicker and shorter consequently.

The *J-V* characteristics for a solar cell with 100 mW/cm^2 broadband illumination from a Xe lamp are shown in Figure 4. The short-circuit current density (Jsc) of the DSSCs with ZnO nanowires grown for 30 min, 60 min, 90 min, and 120 min is 0.195 mA/cm^2, 0.607 mA/cm^2, 1.02 mA/cm^2, and 0.105 mA/cm^2, respectively. And the conversion efficiencies are 0.061%, 0.092%, 0.166%, and 0.018% for ZnO nanowires grown for 30 min, 60 min, 90 min, and 120 min. Jsc can be attributed to the dye loading of ZnO nanowires, as the photocurrent increased with the dye loading increasing. The dye loading on the surface of electrode is of much concern for the cell performance. An electrode with larger surface area absorbs more dye molecules. The increased dye loading had played an important role in improving power conversion efficiency. The highest efficiency was observed in DSSC with ZnO nanowires grown for 90 minutes. The enhancement in Jsc might be originated from the largest equivalent surface area and also the highest dye loading.

Incident photon to current efficiency (IPCE) was determined using a Xe lamp and monochromator for the cells with DSSCs with various nanowire arrays equivalent surface area. Shown in Figure 5 are the IPCE spectra, in which the efficiency at the maximum absorption of the dye (at 525 nm) is proportional to the equivalent surface area of ZnO nanowire arrays. Furthermore, from UV-visible spectroscopy in Figure 3, it is found that the more equivalent surface area of nanowire arrays led more dye loading and enhanced the photo-generated current to increase the light harvesting effects. The highest efficiency was observed in DSSC sample with ZnO nanowires grown for 90 minutes, which had the largest equivalent surface area and also the highest dye loading. In addition, another photocurrent peak at 380 nm is clearly observed in Figure 5. The photocurrent peak is attributed to the light harvesting by the ZnO nanowires.

To further elucidate the role of ZnO nanowires in the charge transfer properties of DSSCs, we carried out an alternating current (AC) impedance measurement with a Nyquist plot in an EIS system and the results are plotted in Figure 6. The resistance is extracted from the Nyquist plot in Figure 6, and shown in the inset is the equivalent circuit model where R_h is the resistance of the TCO substrate, R_1 is related to charge transport at the Pt counter electrode, R_2 is related to charge transport at the ZnO nanowires, R_3 is the diffusion effects within the electrolyte, and CPE is the constant phase element. From the extracted values, R_2 have

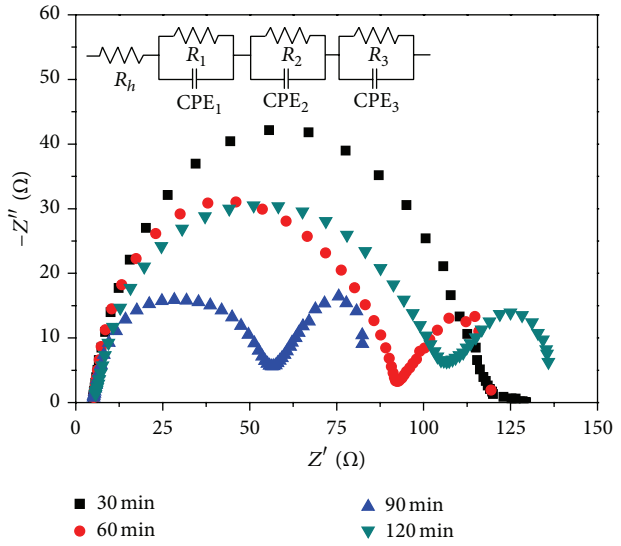

FIGURE 6: EIS spectra of DSSCs with the ZnO nanowires grown at different time, and shown in the inset is the equivalent circuit model.

saliently changed which is related to the ZnO nanowire photoanode. As the equivalent surface area of nanowire arrays increased, the resistance of R_2 had decreased. It is indicated that the resistance (R_2) has direct relation with dye loading. Furthermore, the R_2 value of DSSC with nanowires grown for 120 min was measured under illumination and is smaller than in dark. So R_2 can be considered as the impedance between the dye and the ZnO nanowires photoanode after illumination. From the above impedance analysis, the dye loading has held great importance in the impedance analysis. The more dye loading of the cell had the less resistance and the lower inner resistance of DSSCs, and it effectively reduced the recombination during the electrons transport. From the results, the sample with ZnO nanowires grown for 90 minutes has the highest photoelectric conversion efficiency and the lowest resistance, and the enhancement is attributed to the contribution of the largest equivalent surface area of ZnO nanowire arrays.

4. Conclusion

In summary, ZnO nanowires arrays have been grown on FTO substrate via a simple vapor-phase transport process in a horizontal tube furnace. As the ZnO nanowire arrays applied to the dye-sensitized solar cell, the dye loading is proportional to the total surface area of ZnO nanowire arrays in the cell and has played an important role in improving power conversion efficiency. The more dye loading of the cell had the less resistance, and the lower inner resistance of DSSCs can effectively reduce the recombination during the electrons transport. From the results, DSSC with ZnO nanowires grown for 90 minutes has the highest photoelectric conversion efficiency and the lowest resistance which have the largest equivalent surface area of ZnO nanowire arrays. Though the conversion efficiency (0.166%) is lower than the TiO_2-based cells, further improvement of 1D ZnO-based cell is underway for high illumination without filtering the UV from the visible light.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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