Linkage modification of a zinc oxide photoelectrode prepared with polyethylene glycol for electron transport improvement in dye-sensitized solar cells

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Abstract. The purpose of this study is to synthesize ZnO aggregate films using simple precipitation with polymer modification for linkage improvement of the ZnO photoelectrode. The starting materials of zinc acetate solution and ammonia solution were mixed under violent stirring conditions. A portion of the polymer (polyethylene glycol) was slowly added into the mixed solution to obtain the viscous ZnO precursor. The precursor was then coated onto a fluorine-doped tin oxide substrate and annealed to form ZnO films. The scanning electron microscopy results revealed the formation of ZnO aggregates with flower-like microstructures. The appearance of Zn and O elements indicated a fair ZnO formation. The X-ray diffraction patterns and Raman shift confirmed the hexagonal wurtzite crystal structure of the ZnO aggregates. For dye-sensitized solar cell (DSSC) application, power conversion efficiency was enhanced because of the improved photovoltaic characteristics including the open-circuit voltage, fill factor, series resistance, shunt resistances and recombination resistance, perhaps, due to the large particle size of the ZnO aggregates and their flower-like microstructures. The flower-like microstructure likely acts as a bridge to link each ZnO particle. The flower-like microstructure plays the role of an express pathway in electron transport in the DSSC. Therefore, the ZnO aggregation with a flower-like microstructure has the potential to improve the electron transport for efficiency enhancement of a DSSC.

Keywords. ZnO; flower-like; microstructure; electron transport; dye-sensitized solar cell.

1. Introduction

ZnO nanoparticles (NPs) have been used as photoelectrodes in dye-sensitized solar cells (DSSCs) due to their advantages such as high electron mobility, a wide band gap semiconductor, low cost and environmentally friendly [1–3]. ZnO photoelectrodes play major roles in the functioning of DSSCs including dye adsorption, electron separation and electron transport [4]. Among these, electron transport could be considered as a volatile factor that is decreased due to the electron scattering effect. The effect is due to the presence of many grain boundaries of NP structures [5]. The effect occurs when the electrons transport between the particle–particle connections. After hitting the grain boundary, some electrons may be reflected and the electron transporting direction is deviated from the original direction causing the loss of electron transport. This effect can significantly decrease the DSSC performance. To solve this problem, the structure and connection of ZnO should be investigated. For example, Wan *et al* [6]

introduced Bi₂Te₃ nanosheets (NSs) as a composite photoelectrode to achieve an enhanced DSSC performance. The composite photoelectrode was prepared by mixing Bi₂Te₃ NSs and ZnO NPs. The Bi₂Te₃ NSs played an important role in improving the charge transport, suppressing charge recombination and also acting as a heat sink to reduce the temperature of the DSSC device. DSSCs fabricated with the composite photoelectrode showed a significant enhancement in the power conversion efficiency (PCE), even though the dye adsorption decreased. Xu *et al* [1] demonstrated an enhancement of PCE using a double-layered photoelectrode of ZnO NPs/ZnO micro-flowers. The PCE was enhanced due to the improvement in electron transport and light harvesting efficiency. Nevertheless, a reduction of electron recombination was found simultaneously. Song *et al* [7] showed that a modified double-layered photoelectrode can be used to enhance the DSSC performance. They initially prepared the double-layered photoelectrode of ZnO NPs/ZnO nanowires, modified with multi-walled carbon nanotubes and TiCl₄. A DSSC

Figure 1. Diagram of ZnO film preparation.

fabricated with the modified photoelectrode exhibited an excellent enhancement in the PCE achieving 3.8% compared to that with bar ZnO NPs (1.5%). The successful enhancement was due to the co-functions of faster electron transport, less electron recombination and increased dye adsorption. These photoelectrodes modified in multi-steps such as composite materials, or post-treatments produced a successful DSSC application. However, multi-step modification could make the fabrication process difficult and costly. In the current work, ZnO aggregates with flower-like microstructures synthesized using a simple precipitation process with polymer modification is proposed to reduce the fabrication process. The addition of polyethylene glycol (PEG) is expected to improve the linkage between ZnO particles during the reaction to obtain ZnO aggregates with a flower-like microstructure. The structure is believed to provide an express pathway for electron transport in a DSSC. Due to the pathway improvement, the performance of a DSSC fabricated with the ZnO aggregate photoelectrode could be enhanced.

2. Experimental

2.1 ZnO photoelectrode preparation

Starting materials of zinc acetate solution and ammonia solution were separately prepared. The zinc acetate solution was prepared by dissolving 1.76 g zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O; RCI Labscan) in 20 ml distilled water. The ammonia solution was prepared by dissolving 1.27 g of ammonium hydrogen carbonate (NH₄HCO₃; RCI Labscan) in 20 ml distilled water/ethanol mixture (1/1, v/v). Both solutions were violently stirred for 1 h to form clear solutions. Before mixing, the zinc acetate solution was heated at 70°C for 15 min. Next, the ammonia solution was added into the zinc acetate solution drop by drop. After mixing,

the polymer modification was carried out by adding 8 g PEG-4000 into the mixed solution under continuous violent stirring and heating. After 1 h, the solution was cooled down to room temperature and the solution was dropwise added into filter paper for 12 h to obtain the viscous ZnO precursor. For ZnO film preparation, the ZnO precursor was coated onto fluorine-doped tin oxide (FTO; Sigma-Aldrich) substrate using a screen printing method with an active area of 1 cm². The thickness was controlled by the template of the screen printing system to around 18 μm. Next, the precursor films were annealed at 400°C for 1 h to obtain the ZnO films used as the ZnO photoelectrode. The steps involved in the preparation of the ZnO photoelectrode are diagrammatically described in figure 1. For comparison, commercial ZnO NPs (Nano Materials Technology Co. Ltd., particle size ~ 20–40 nm) were used to prepare referent films with a similar active area and thickness. The preparation details of the ZnO NP films were described in previous reports [8,9].

2.2 DSSC fabrication

Before the DSSC fabrication process, the ZnO photoelectrode was immersed into N719 solution in the dark for 1 h to adsorb dye molecules, then rinsed with ethanol and dried in air to form a dye-sensitized photoelectrode. The N719 solution was prepared by dissolving 0.3 mM N719 (Dyesol) into an ethanol/acetone mixture (1/1, v/v) and stirring for 1 h in the dark. At the same time, the counterelectrode was prepared by dropwise adding Pt solution onto the FTO substrate, spin-coating for 30 s and annealing at 550°C for 1 h. The Pt solution was prepared by dissolving 12 mg Cl₆H₂Pt (Merck) in 1 ml acetone under sonication for 1 h. For DSSC fabrication, the photoelectrode and counterelectrode were sandwich-fabricated and sealed with polymer films. Finally, the liquid electrolyte was injected into the gap between the

photoelectrode and the counterelectrode. The electrolyte was prepared by dissolving 0.03 I₂, 0.3 M LiI and 0.03 M DMPII in acetone-nitride under stirring.

2.3 Characterization and measurement

Characterization of the ZnO photoelectrode was investigated using various techniques. The morphology was observed using scanning electron microscopy (SEM). The chemical composition was detected using energy dispersive spectroscopy (EDS). The crystal structure was investigated using X-ray diffraction pattern (XRD). Raman shift analysis was performed using Raman spectroscopy. Dye adsorption was measured using ultraviolet–visible–near infrared (UV–Vis–NIR) spectroscopy. The dye-sensitized ZnO photoelectrode was immersed into 0.1 M NaOH solution (dissolved in an equal volumetric ratio of distilled water and ethanol) to extract dye molecules. Next, the solution carrying the dye molecules was measured. Photovoltaic characteristics were evaluated using current–voltage (*J*–*V*) measurements and electron recombination was investigated using electrochemical impedance spectroscopy (EIS).

3. Results and discussion

3.1 Morphology

Figure 2 shows the morphology of the ZnO films prepared from commercial ZnO NPs (ZnO NP films) and synthesized from zinc nitrate with PEG assistance (ZnO aggregate films). The ZnO NP films (figure 2a and b) and the ZnO aggregate films (figure 2c and d) showed an apparent difference in their surface morphology. The ZnO NP films had a non-smooth film formation as could be seen from numerous pore positions. The pores at the surface may have formed because of the evaporation of PEG during the annealing process. Note that the high magnification image (figure 2b) shows that the ZnO NP films were formed with a combination of small ZnO NPs. For the ZnO aggregate films (figure 2c), the morphology showed a comparatively larger particle size with sticking-out parts which were the same as a flower-like microstructure. The flower-like microstructure was elongated from one particle reaching the other particle like a bridge for particle–particle linkage. It is believed that the linkage in the ZnO aggregate films may be modified for better electron transport. Moreover, the high magnification SEM image of ZnO aggregate films (figure 2d) revealed that the surface of the

Figure 2. Morphology of ZnO films prepared from commercial ZnO NPs (a, b) compared with ZnO aggregate films (c, d).

flower-like microstructure consisted of small NP attachments. These attached particles may be formed after flower-like microstructure formation and accumulated over the surface of the flower-like microstructure. To estimate the particle size, the diameters of the ZnO NP films and the ZnO aggregate films were measured using Image-J software as shown in figure 3. The diameters of the ZnO NP films and the ZnO aggregate films were in the range of 36–230 nm and 0.65–2.10 μm , respectively. The average diameters were 82.57 nm and 1.16 μm , respectively. Generally, chemical processes for ZnO formation can be described [6,10–12] according to the following equations [13,14]:

ZnO is commonly obtained after the addition of ammonia solution into zinc acetate solution. When the Zn^{2+} ions reacts with OH^- , precipitation of the $\text{Zn}(\text{OH})_2$ complexes is obtained *via* equation (3). These complexes are finally decomposed as ZnO as shown in equation (4) under the reaction conditions. From the growth mechanism, ZnO NPs can be obtained under appropriate control of the ammonia concentration. In this work, ZnO aggregates with flower-like microstructures were obtained in the presence of PEG. The growth mechanism of the ZnO aggregates prepared with PEG modification can be described according to the schematic diagram in figure 4. After the addition of PEG into the mixture of zinc acetate solution and ammonia solution, the $\text{Zn}(\text{OH})_2$ complexes can easily adsorb PEG because the available OH^- groups have the potential to directly bond with PEG. This effect leads to carrying the $\text{Zn}(\text{OH})_2$ complexes with polymer chains, and Zn^{2+} ions may be collected at the same time due to ionic interactions. Under saturation conditions, the $\text{Zn}(\text{OH})_2$ complexes and Zn^{2+} ions are transformed into ZnO aggregates. After the formation of the ZnO aggregates, some surface ZnO may adsorb PEG molecules at the O-site. The effect may cause anisotropic reduction of ZnO and surface activity reduction. The growth rate of ZnO at the PEG adsorbed surface will be slowed down which results in a non-homogeneous growth of ZnO. The non-homogeneous growth results in the flower-like microstructure formation which agrees with previous reports [15–17]. Thus, it can be stated that the ZnO aggregates with flower-like microstructures can be successfully synthesized using a simple precipitation process with PEG modification.

3.2 Chemical composition

The chemical composition of the ZnO films was detected using EDS as shown in figure 5. The ZnO formation was

Figure 3. Particle size distributions of ZnO films prepared from commercial ZnO NPs (a) compared with ZnO aggregation (b).

clear based on the Zn and O peaks. The Zn/O atomic ratio was 0.86, indicating a fair ZnO formation. However, a Zn/O ratio less than 1.0 may indicate non-purity in the ZnO formation. It should be noted that the unlabelled peak around 2.2 keV is ignored because it is the Au peak from the Au coating to assist with better SEM operation [18,19].

3.3 XRD analysis

The crystal structure of the ZnO aggregate films was investigated using XRD analysis and the diffraction peaks are shown in figure 6. The detected peaks correspond to the hexagonal wurtzite structure of ZnO (JCPDS no. 36-1451) [20]. This result indicates that the chemical reaction can transform the mixed solution phase to ZnO [21]. To estimate the crystalline

Figure 4. Growing mechanisms of ZnO aggregate films with PEG modification.

Figure 5. Chemical compositions of ZnO aggregate films.

size (D) of the ZnO aggregate films, a calculation was carried out based on the Scherrer's formula [20,22]:

$$D = K\lambda/(\beta \cos \theta) \quad (5)$$

where K is a constant (0.89), λ is the wavelength of the X-ray source (1.5406 Å), β is the full width at half-maximum intensity of the peak and θ is the Bragg angle for the measured peak. For better calculation, the crystalline size was calculated from the three high-intensity peaks of (100), (002) and (101) [23], and the average size was 20.21 ± 1.35 nm. The result indicated that the crystal structure of the ZnO aggregate films was a nanostructure.

3.4 Raman measurement

Raman spectroscopy was performed to investigate molecular vibration and chemical structure. It was performed using interactive light to observe the disorder states or defects in ZnO, which cannot be detected using XRD. The ZnO formation can be analysed from the group theory of vibration modes according to the Raman shift shown in figure 7. The dominant peak at 438 cm^{-1} represents the ZnO nonpolar optical phonon E_2 mode, which corresponds to the characteristic peak of the

Figure 6. XRD patterns of ZnO aggregate films.

Raman active mode of the wurtzite hexagonal ZnO structure [24]. The weak peak at 381 cm^{-1} represents the transverse optical modes of A_{1T} . The detected peak at 333 cm^{-1} represents the boundary phonon $E_{2H}-E_{2L}$ mode. The broad peak around 580 cm^{-1} represents the quasi-LO mode, because the peak location is found between A_{1LO} (574 cm^{-1}) and E_{1LO} (591 cm^{-1}). The quasi-LO mode attributes the disorder state or defect in the ZnO [25]. Thus, it can be interpreted that impurity of the ZnO aggregate films occurred which was in agreement with the Zn/O atomic ratio.

3.5 Photovoltaic characteristics

To evaluate the performance of the ZnO aggregate films for DSSC application, commercial ZnO NP films were used as the reference cell. For each condition, solar cell devices were repeatedly fabricated with five samples. The current density (J) vs. voltage (V) curve of the measured photovoltaic characteristics at standard measurement is shown in figure 8 and

Figure 7. Raman shift of ZnO aggregate films prepared on the FTO substrate.

Figure 8. Current density vs. voltage of DSSCs fabricated with different ZnO photoelectrodes.

the corresponding photovoltaic parameters are summarized in table 1. The short-circuit current density (J_{sc}) of the DSSC fabricated using the ZnO aggregate films was lower than that of the ZnO NP-based DSSC. This result was caused by lower dye adsorption for the ZnO aggregate films as can be seen from the lower dye adsorption spectra in figure 9a. Quantitative comparison of dye adsorption was evaluated from the

UV-Vis-NIR result and calculated using the Beer-Lambert law [26]:

$$A = c\epsilon L \quad (6)$$

where A is the absorbance, c is the dye concentration, ϵ is the molar extinction coefficient of N719 dye ($\epsilon = 14,100 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 515 \text{ nm}$) and L is the path length of the measured dye. The calculated dye adsorption values were 3.56×10^{-8} and $4.22 \times 10^{-8} \text{ mol cm}^{-2}$ for the ZnO aggregate films and ZnO NP films, respectively. The dye adsorption of the ZnO aggregate films was quite lower than that of the ZnO NP films. It is well-known that the reason for this low dye adsorption is due to the low surface-to-volume ratio of the larger particle, which reduces the effective area for the dye molecules to adhere to the ZnO surface. By assuming a spherical shape for both films, the surface-to-volume ratio of the ZnO aggregate films was 10^{-1} times lower than that of the ZnO NP films but there was not much difference in the dye adsorption. It was noted that the dye adsorption of ZnO aggregate films was not directly correlated with the surface-to-volume ratio. The dye adsorption of the ZnO aggregate films was higher than that for a comparatively calculated surface-to-volume ratio. This effect can be explained by the small amount of ZnO NPs attached over the surface of the flower-like microstructure perhaps improving the surface area of the ZnO aggregate films as seen from the high magnification image in figure 2d. These small ZnO NPs have potential to gain dye adsorption in this case. Even though the ZnO aggregate film-based DSSCs had a lower J_{sc} , the open-circuit voltage (V_{oc}) and fill factor (FF) were higher in values. The results indicated an improvement in V_{oc} and FF. This improvement led to a PCE enhancement of 2.24%, which was higher than that for the ZnO NP film-based DSSCs (2.12%).

To understand the improvement in V_{oc} , dark current was measured as shown in figure 9b. It could be clearly seen that the ZnO onset voltage of the aggregate film-based DSSCs was higher than that of the ZnO NP film-based DSSCs which corresponded to an improvement in the V_{oc} . The increase in the V_{oc} could be attributed to maintaining a high electron concentration in the conduction band (CB) of the ZnO aggregate films. On the other hand, the lower V_{oc} of the ZnO NP film-based DSSCs was due to the electron loss during the transport process. In brief, electrons in the ground state of the dye molecules will increase the energy level to the excited state after absorbing energy from incident sunlight. These excited electrons are transferred from dye molecules to the

Table 1. Photovoltaic parameters of DSSCs.

Films	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)	R_s (Ω)	R_{sh} (Ω)
NPs	7.24 ± 0.11	0.61 ± 0.01	0.48 ± 0.01	2.12 ± 0.03	40.57 ± 0.34	580.44 ± 77.63
Aggregates	6.51 ± 0.09	0.66 ± 0.01	0.52 ± 0.01	2.24 ± 0.02	36.66 ± 0.39	904.38 ± 103.08

Figure 9. Dye adsorption of N719 extracted from different ZnO photoelectrodes (a) and photovoltaic characteristics under dark conditions (b).

CB of ZnO, extending the voltage. Next, the electrons are continuously transported from one particle to another particle until reaching an external load. However, some electrons may be lost during the transport process due to the electron scattering effect. The electron scattering effect occurs when an electron hits a grain boundary of ZnO and it cannot pass to another particle. The scattered electrons will immediately recombine with an electrolyte on the surface of ZnO [27]. For ZnO NP films with small particles, there are many grain boundaries that can scatter electrons when moving from one particle to another particle. Moreover, the connection of ZnO NPs may be an inconvenient transport pathway because the surface contact of spherical particles is not appropriate. Thus, the electron scattering effect may occur due to the small particle size of ZnO NPs. It is believed that the scattering effect could be solved by a large particle size (the ZnO aggregate films with flower-like microstructures). The large particle size can reduce the grain boundary and the flower-like microstructure can perform as an electron transport pathway. Therefore, it is believed that ZnO

Figure 10. EIS of the DSSCs fabricated with different ZnO photoelectrodes.

aggregate films have the potential to maintain electrons in the CB of ZnO which can increase the V_{oc} . In addition, the improved dark current not only increases the V_{oc} but also increases the FF simultaneously. The increase in the FF is believed to be due to a change in the internal resistances including the decreased series resistance (R_s) and increased shunt resistance (R_{sh}) as seen in table 1. These results confirm that the large particle size of ZnO aggregate films with flower-like microstructures can provide better electron transport, which is reflected in the decreased R_s . Moreover, the increased R_{sh} can be assumed to indicate that the electron scattering effect or the electron recombination effect is reduced.

To deeply investigate the internal dynamic exchange behaviour, EIS was performed under dark conditions with a forward bias of $-V_{oc}$ to observe any electron recombination resistance (R_{rec}) as a means to investigate the electron recombination effect. The measurement results are shown in figure 10. The resistance can be estimated from the diameter of the semicircle of the real part (Z' -axis). Generally, the small and large semicircles refer to the total resistance (R_t) and R_{rec} of DSSCs, respectively. Note that R_t cannot be clearly observed because it has a very small value compared with the large semicircle. However, it is enough to focus only on the large semicircle for the evaluation of R_{rec} . A large R_{rec} value means that most electrons can be transported through the external load with low recombination, while a small R_{rec} means the opposite. The EIS results showed that the R_{rec} of the DSSC fabricated with the ZnO aggregate films was greater than that of the ZnO NP films, which can be interpreted as most electrons are transported through the external load. The result may be due to the reduction in the electron recombination effect [28], which can be explained by a reduction in the transfer coefficient (B) from the following relationship [29]:

$$R_{rec} = R_0 \exp(-eBV/k_B T) \quad (7)$$

where R_0 is a constant, e is the electron charge, V is the applied voltage, k_B is the Boltzmann constant and T is the absolute temperature. The increase in R_{rec} may be a result of the reduced transfer coefficient, when the other parameters are not changed. In this case, the reduced transfer coefficient for electron recombination can be assumed due to better forward electron transport provided by the linkage of the flower-like microstructure. The improved electron transport efficiency is normally believed to reduce the probability density of electron recombination. Moreover, a reduction in the transfer coefficient can decrease the recombination rate (k_r) which results in an increase in V_{oc} , according to the following relationship [7,30]:

$$V_{\text{oc}} = (k_B T / e) \ln(I_{\text{inj}} / n_{\text{cb}} k_r c) \quad (8)$$

where I_{inj} is the injected electron current, n_{cb} is the electron density in the CB of the photoelectrode and c is the concentration of triiodide species in the electrolyte. Thus, the increased R_{rec} can keep most of the injected electrons in the CB of the ZnO which results in an increased V_{oc} . Nevertheless, it can support the electron transport effectively due to the high electron density and reduced electron recombination which is reflected in the decreased R_s and increased R_{sh} . The increase in R_{rec} not only increases V_{oc} , but also improves internal resistances (decreased R_s and increased R_{sh}) concurrently. From the results, it is believed that the aggregate formation with a flower-like microstructure can improve the linkage within the ZnO aggregate photoelectrode. The improved linkage has the ability to provide better electron transport and to prevent electron scattering as illustrated in figure 11. The large particle size of ZnO aggregates is believed to reduce the scattering boundaries, compared with the small particle size of ZnO NPs [31]. Moreover, the flower-like microstructure is believed to improve the electron transport efficiency at the same time. Therefore, most electrons have better potential to transport through an external load for a large particle size of ZnO aggregates with flower-like microstructures compared with the small size of the NPs. For overall photovoltaic performance comparison, there were small differences in the photovoltaic parameters between ZnO NP- and ZnO aggregate-based DSSCs. However, the ZnO aggregates with flower-like microstructures synthesized using a simple precipitation with polymer modification shows an interesting development method for DSSC application due to its low cost and being a simple process. For ZnO NP-based DSSCs, high purity ZnO NPs must be purchased at a high cost or synthesized using effective technology. Then, the addition of ZnO NPs into a polymer solution, binder solution or several solvents is carried out to transform the viscous ZnO NP precursors before the coating process. Next, the viscous precursors are coated onto a substrate to form precursor films and finally annealed to form ZnO NP films. All these steps make the synthesis of ZnO NP films a complicated process. On the other hand, the ZnO aggregates with flower-like

Figure 11. An illustration of electron transport pathway for different ZnO structures.

microstructures is an interesting simpler method at low cost. After the synthesis of the ZnO aggregates, the synthesized ZnO aggregates can be immediately coated onto the substrate and annealed to obtain ZnO aggregate films. Therefore, the ZnO aggregates with flower-like microstructures synthesized using simple precipitation with polymer modification can be considered as an alternative method for DSSC fabrication which is a low cost and a simple process to obtain photovoltaic parameters similar to those for ZnO NP-based DSSCs. Furthermore, the enhanced photovoltaic performance of ZnO aggregate-based DSSCs may be achieved by reducing from microstructure to nanostructure for increasing dye molecule adsorption which should be further investigated.

4. Conclusion

The ZnO aggregates with flower-like microstructures was successfully synthesized using a simple precipitation with polymer modification. The viscous ZnO precursor was coated onto the substrate and annealed. Large size ZnO aggregate films with flower-like microstructures were finally obtained. The chemical composition ratio of Zn/O revealed a fair ZnO formation. The hexagonal wurtzite structure of ZnO was confirmed using the XRD and Raman results. For DSSC application, the DSSC fabricated with the ZnO aggregate films as a base exhibited a lower current density compared with the ZnO NP-based one due to lower dye adsorption. However, the improved linkage of ZnO aggregate films with flower-like microstructures play an important role of an express pathway

to provide better electron transport and reduce electron scattering in the DSSCs. This improvement finally results in an enhanced photovoltaic performance. Therefore, the synthesis of the ZnO photoelectrode using polymer modification has the potential to modify the linkage of ZnO aggregates with flower-like microstructures, and the modified structure can provide an express pathway for electron transport improvement in DSSCs.

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