Fabrication and photovoltaic properties of dye-sensitized ZnO thick films by a facile doctor-blade printing method using nanocrystalline pastes

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ZnO films used as photoanodes for dye-sensitized solar cells were fabricated by a facile doctor-blade printing method. Pastes containing nanocrystalline ZnO powders and polyethylene glycol (PEG) were coated on conducting glass sheets and heated at 450°C for 10 min in air. It was shown that the microstructure of the resultant films was largely dependent on the amount of PEG in the pastes. The film without PEG had large interconnected voids, which were decreased by increasing the PEG amount. The films were dyed with a ruthenium complex dye (N-719) and their photoelectrochemical performance was investigated in terms of film properties such as thickness, specific surface area, density, and roughness factor. By optimizing the film thickness and introducing the light scattering layer, a light-to-electricity conversion efficiency of a cell using our ZnO/N-719 photoanode reached 4.3% under the AM 1.5 illumination at 100 mW/cm² (1 sun).

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1. Introduction

Since the first use of nanoparticulate porous titanium dioxide (TiO₂) films for dye-sensitized solar cells (DSCs),¹⁾ considerable efforts have been made to improve their performance by elaborating photoanodes from the viewpoint of materials chemistry. Zinc oxide (ZnO) has been expected to be comparable to TiO₂ because of its higher electronic mobility and similar energy level of the conduction band.^{2)–4)} In fact, when using eosin Y as a sensitizer, an overall light-to-electricity conversion efficiency (η) of ZnO-based DSCs was reportedly higher than that of TiO₂-based DSCs.^{4),5)} Adversely the use of Ru-complex dyes such as N-3 (RuL₂(NCS)₂; L = 2,2'-bipyridyl-4,4'-dicarboxylic acid) and N-719 (RuL₂(NCS)₂:2TBA; TBA = tetrabutylammonium) was believed to be ineffective for ZnO photoanodes. Keis et al.⁶⁾ attempted to clarify a problem arising from interaction between ZnO and Ru-dyes. They concluded that protons derived from Ru-dyes made dye loading solutions relatively acidic and dissolved the surface of ZnO, generating other Zn²⁺/dye aggregates. Such aggregates consume the incident light without injecting excited electrons to the conduction band of ZnO. Furthermore, they tend to fill mesopores of electrodes and interrupt the electrolyte diffusion in DSCs.

Recently, we have fabricated ZnO films having novel nanostructures for the use in DSCs, overcoming the above-mentioned problem.^{7)–10)} Nanosheet-like particles composed of ZnO nanograins were deposited on substrates using precursor templates based on zinc hydroxide salts. The cell using the resultant nano/macroporous ZnO/N-719 photoanodes yielded the highest η value of 4.1% in full sunlight (AM 1.5, 100 mW/cm²). These results imply that we can possibly take advantage of ZnO elec-

trodes, so long as their microstructure is designed suitably for DSCs. We have then paid renewed attention to more feasible fabrication processes for ZnO electrodes.

In the present study, ZnO films have been fabricated using a simplified doctor-blade printing method, which is one of the facile printing methods available for modern electronics. This method is suitable for mass production of electroceramic thick films and is comparable with tape casting. Therefore it has been commonly employed for preparing TiO₂ photoanodes showing conversion efficiencies over 10% in DSCs.^{11)–15)} We examined experimental conditions for fabricating ZnO thick films thoroughly, and finally found an appropriate condition to make ZnO/N-719 photoanodes exhibiting η = 4.3% under the AM 1.5 illumination at 100 mW/cm² (1 sun) with good reproducibility.

2. Experimental procedure

2.1 Thick film fabrication

The commercial ZnO nanoparticles (Sakai Chemical Industry, Co., Ltd.), 20 nm in average diameter, were used in this study to fabricate thick films. Polyethylene glycol (PEG; average molecular weight: 10,000) was employed as a binder because it has often been used to prepare TiO₂ pastes. PEG was dissolved in an ethanol-water mixed solvent (ethanol : water = 2 : 1 in volume ratio). The ZnO nanoparticles were then dispersed in the resultant PEG solution, which was stirred for 1 h. The ZnO pastes thus obtained were coated on SnO₂ : F-coated (FTO) conducting glass sheets (Nippon Sheet Glass Co., Ltd.) by a doctor-blade method. The film thickness was controlled by using plastic tapes 58 or 182 μ m in thickness as a spacer. The coated films were initially dried at 90°C for 30 min, and then heated at 450°C for 10 min in air to burn out organic components and make interconnections between ZnO nanoparticles. To investigate the effect of PEG on the film fabrication process, the amount of PEG was varied according to solvent : ZnO : PEG = 80 : 20 : x (x = 0, 5, 10,

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20, 30, and 50) in weight ratio. Hereafter, the ZnO pastes are designated “Px” (for instance, P20 represents the paste of $x = 20$). The film thickness was also changed by repeating the coating process. In an additional set of experiments, pastes containing larger ZnO particles (Sakai Chemical Industry Co., Ltd.) 600 nm in diameter were also prepared and coated on the already obtained ZnO films in the same manner.

2.2 Film characterization

Thermogravimetry-differential thermal analysis (TG-DTA; Mac Science 2020S) and Fourier transform infrared spectroscopy (FT-IR; Digilab FTS-60A) were used to examine organic residues in the heat-treated ZnO films. The film morphology was observed by field emission scanning electron microscopy (FESEM; FEI Sirion). The specific surface area of the films was determined by the Brunauer-Emmett-Teller (BET) method based on the nitrogen adsorption isotherm (77 K) with a micro-metric analyzer (Shimadzu Trister 3000). The samples for the measurement were collected by scratching the films.

2.3 Assembly of dye-sensitized solar cells

Dye-loading of the ZnO films was performed by immersing in a 0.3 mM ethanolic solution of N-719 (Solaronix S. A., Switzerland) at 60°C for 90 min. The amount of adsorbed dye was determined as follows. The dye was desorbed from the film by immersing in a 0.5 M NaOH_{aq}-ethanol (1 : 1 in volume ratio) solution. The solution was then analyzed with a uv-vis spectrophotometer (Hitachi, Ltd., U-3300). An absorption spectrum measured was calibrated with standard solutions of N-719.

The ZnO/N-719 electrode thus fabricated was then assembled into a sandwich-type open cell using flat platinum plate as a counter electrode. Both the electrodes were spaced by Parafilms™ 120 μm in thickness and pressed by clamps. An electrolyte solution, which was composed of 0.1 M LiI, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.05 M I₂, 1.0 M 4-tert-butylpyridine, and 3-methoxypropionitrile, was introduced into the clamped electrodes by the capillary action. Photocurrent (I) and photovoltage (V) of the cell were measured with an active area of 0.25 cm² under the AM 1.5 illumination at 100 mW/cm² (1 sun).

3. Results

3.1 The effect of PEG on the ZnO film fabrication

Thermal behavior of the dried pastes was examined first because it would influence the microstructural evolution of the thick films. **Figure 1** shows TG-DTA curves of the P50 paste, which contained the largest amount of PEG (solvent : ZnO : PEG = 80 : 20 : 50 in weight ratio), after drying at 90°C for 30 min. The first great weight loss occurring at temperatures between 130 and 240°C comes from the evaporation of the solvents and the combustion of PEG. The latter is accompanied by a sharp exothermic peak at 208°C. The second slight weight loss at temperatures between 240 and 310°C is probably ascribed to the evaporation of physically adsorbed species and the further combustion of the remaining PEG. The total weight loss was observed to be 71%, which corresponded to the calculated value (71.4%) from the composition of the P50 paste.

The presence of PEG in the pastes was further examined by FT-IR spectroscopy. **Figure 2** shows FT-IR spectra of the P50 paste before and after the heat treatment at 450°C for 10 min. A spectrum for PEG is also shown for comparison. At a higher wavenumber range between 3700 and 3200 cm⁻¹, a broad absorption band is observed due to stretching vibration modes of

Fig. 1. TG-DTA curves of the dried P50 paste.

Fig. 2. FT-IR spectra of the P50 paste before and after the heat treatment at 450°C for 10 min. A spectrum for PEG is also shown for comparison.

the hydroxyl group (–O–H) for all the samples. The paste before the heat treatment shows almost the same spectrum as PEG, except the presence of absorption bands due to Zn–O stretching modes¹⁶⁾ at wavelengths around 500 cm⁻¹. On the other hand, the paste after the heat treatment has no characteristic absorption bands of PEG. Minor absorption peaks observed at 1400, 1640, and 2350 cm⁻¹ are attributed to adsorbed CO₂. These results indicate that PEG in the P50 paste is burned out. The resultant ZnO does not contain detectable organic residues which would influence the dye adsorption and the cell performance.

A series of the Px pastes were coated on the FTO substrates with plastic tapes 182 μm in thickness. **Figure 3** shows FESEM images of the ZnO films obtained by heating the coated pastes at 450°C for 10 min. The film from the P0 paste (without PEG) shows large islands 50–100 μm in size, separated by interconnected voids approximately 20 μm in width. Probably this kind of microstructure comes from a large shrinkage of the paste, having relatively low viscosity, on the substrate. Such voids would work effectively as channels in quasi-solid-state DSCs, which will be our future concern. A comparison between the images in Fig. 3 clearly shows the effect of PEG on the film microstructure. That is, the width of voids is considerably reduced with increasing the amount of PEG, especially from $x = 10$ to 50. As listed in **Table 1**, the film thickness was approximately 26–30 μm . The

Fig. 3. FESEM images of the ZnO films fabricated using Px ($x = 0, 5, 10, 20, 30$, and 50) pastes.

Table 1. Film Properties (Thickness, BET Surface Area, Film Density, and Roughness Factor), the Amount of the Adsorbed Dye (A_{dye}), and the I - V Characteristics of the Cells Using the ZnO Films from the Px Pastes

Sample	Thickness (μm)	BET surface area (m^2/g)	Film density (g/m^3)	Roughness factor	A_{dye} ($\times 10^{-7} \text{ mol}/\text{cm}^2$)	J_{sc} (mA/cm^2)	V_{oc} (V)	ff	η (%)
P0	28.6	28.5	30.3	864	1.24	8.63	0.582	0.644	3.23
P5	28.4	28.9	28.7	829	1.20	9.71	0.570	0.637	3.53
P10	25.8	27.9	26.6	741	1.36	10.81	0.578	0.602	3.76
P20	28.2	29.5	24.6	726	1.18	10.27	0.591	0.643	3.90
P30	37.0	28.7	23.1	663	1.25	10.33	0.590	0.641	3.91
P50	29.5	27.5	19.3	530	1.37	9.92	0.601	0.639	3.81

BET surface area was almost constant (approximately $29 \text{ m}^2/\text{g}$) among the samples in spite of the different microstructures. However, this result is reasonable because the samples for the BET measurement were collected by scratching the films and the measured value was not affected by the presence of the voids.

Figure 4 shows a magnified FESEM image of the film from the P20 paste, exhibiting some aggregation of the ZnO nanoparticles after the heat treatment. This can explain the lower specific surface area of our films, as compared with that of the typical TiO_2 films.¹⁵⁾ The Barret-Joyner-Halenda method¹⁷⁾ was applied to the adsorption branch of the N_2 adsorption-desorption isotherm to obtain a pore size distribution. The result showed that pores were present in the films in the 2–5 nm size distribution with a peak at 2.8 nm, indicative of the mesoporous structure.

Fig. 4. An FESEM image of the ZnO film fabricated using the P20 paste.

3.2 Photoelectrochemical performance of the ZnO/N-719 electrodes

The ZnO films from the Px pastes were dyed with N-719 and assembled into the sandwich-type open cell using flat platinum plate as a counter electrode. **Figure 5** shows I - V curves of the representative cells, and Table 1 summarizes the ZnO film properties and I - V characteristics of all the cells. The film density (g/m^2) was determined by dividing mass of the films by their area on the substrate. The roughness factor was obtained by multiplying the film density by the BET surface area (m^2/g). It is seen from the table that the film density is monotonically decreased with increasing the amount of PEG. This is because the number of ZnO nanoparticles per unit volume in the pastes was decreased by the addition of PEG. The roughness factor of the P50 film is then only about 60% of that of the P0 film. Nonetheless, the amount of adsorbed dye shows almost no appreciable change among the samples. From Fig. 5 and Table 1, it is noticed that an open-circuit voltage (V_{oc}) and a fill factor (ff) are not largely dependent on the film microstructure. In contrast, a short-circuit photocurrent density (J_{sc}) is influenced by the film properties. That is, the J_{sc} value initially increases from 8.63 (P0) to 10.81 mA/cm^2 (P10) and then decreases to 9.92 mA/cm^2 (P50). The conversion efficiency basically reflects this trend but the highest η value of 3.9% is obtained for the P20 and P30 samples. These results, together with the microstructural data shown in Fig. 3, indicate that the addition of an appropriate amount of PEG in the pastes can lead to the enhancement of the DSC performance with the ZnO/N-719 electrodes.

3.3 Optimization of the ZnO/N-719 electrodes

We have shown above that the ZnO/N-719 electrodes obtained by the doctor-blade method can work efficiently in the DSCs. Attempts were then made to optimize the cell performance. First, the film thickness was changed by repeating the coating/drying process of the P20 paste on the FTO substrate, using thinner plastic tapes 58 μm in thickness. The coating time was varied between one, two, and three, resulting in the thickness of the heat-treated ZnO films of 11.6, 19.0, and 29.0 μm , respectively. **Figure 6** shows I - V curves of the cells using each ZnO film dyed with N-719, and **Table 2** summarizes their I - V characteristics. Both the amount of dye and the J_{sc} value increase, which can be well explained by the increase in the film thickness. However, the second increment of the J_{sc} value (between the films with 19.0 and 29.0 μm in thickness) is smaller than the first increment (between the films with 11.6 and 19.0 μm in thickness). This means that most of the incident light is absorbed by the film in the distance from the FTO substrate to 30 μm , which is thought to be an optimized thickness of our ZnO film in terms of the light harvesting. Contrarily, the V_{oc} value slightly decreases with increasing the thickness. Such the reduction of V_{oc} is explained by the extended electron diffusion length (L), following the relation

$$L = (D\tau)^{1/2} \quad (1)$$

where D and τ are the diffusion coefficient and the lifetime of electron, respectively.¹⁸⁾ When the electron diffusion length is extended over L , recaptures of electrons by the oxidized form of the redox couple in the electrolyte and the oxidized sensitizer occur more easily before reaching the FTO layer.

Finally, we introduced a light scattering layer, consisting of the ZnO particles 600 nm in diameter, on the 19.0 μm thick ZnO film mentioned above. Physicochemical properties of this multilayered ZnO film were as follows; 26.3 μm in film thickness,

Fig. 5. I - V curves of the cells using the ZnO/N-719 photoanodes, fabricated using the P0, P10, P20, and P50 pastes.

Fig. 6. I - V curves of the cells using the ZnO/N-719 photoanodes, fabricated using the P20 paste by changing the number of the coating with 1, 2, and 3 times.

Table 2. Film Thickness, the Amount of the Adsorbed Dye (A_{dye}), and the I - V Characteristics of the Cells Using the ZnO Films from the P20 Paste. The Number of the Coating was Varied between 1, 2, and 3

The number of the coating	Thickness (μm)	A_{dye} ($\times 10^{-7}$ mol/ cm^2)	J_{sc} (mA/cm^2)	V_{oc} (V)	ff -	η (%)
1	11.6	0.83	9.27	0.614	0.524	2.98
2	19.0	1.16	11.03	0.600	0.620	4.11
3	29.0	1.54	11.66	0.583	0.613	4.16

30.2 g/m^2 in film density, 17.2 m^2/g of BET specific surface area, 521 of roughness factor, and 1.18×10^{-7} mol/ cm^2 of the amount of adsorbed dye. The cell using the resultant ZnO multilayered film exhibits an excellent performance as shown in **Fig. 7**. It shows the J_{sc} value of 11.32 mA/cm^2 , the V_{oc} value of 0.622 V, and the fill factor of 0.614. As a result, the overall conversion efficiency reaches 4.32%.

Fig. 7. I - V curve of the cell using the ZnO/N-719 photoanodes having the light scattering layer.

4. Discussion

The preceding papers reporting the ZnO-based DSCs have not discussed the relationship between the cell performance and the film properties such as the film thickness, the specific surface area, and the roughness factor. Keis et al. fabricated a ZnO film, using larger particles approximately 150 nm in diameter, with less than 14 μm in film thickness and 17.7 m^2/g of specific surface area.^{3),6),19)} Unfortunately, the roughness factor of their film might be much lower than that of the TiO_2 films commonly used in DSCs. We believe that the major reason for the lower photoelectrochemical performance of the ZnO/N-719 electrodes lies not in the compatibility with the Ru dye but in the film properties.

In this study, we could easily fabricate the DSCs exhibiting over 4% of the conversion efficiency using the ZnO films, using the smaller (20 nm in size) particles, with 20–30 μm in thickness and 500–800 of roughness factor. This result indicates that designing the film properties such as the film thickness and roughness factor is essential to fabricate DSCs of high performance. Moreover, when comparing the I - V characteristics of the cells using the P0 and the P20 paste, the cell performance of P20 was found to be improved in spite of the decrement of the roughness factor. This may be due to smaller voids observed in the P20 film than in the P0 film, as shown in Fig. 3. Therefore it can be said that not only roughness factor but also the overall film microstructure largely influences the cell performance. Anyway, our results demonstrate that even the facile doctor-blade method is applicable to fabricate efficient ZnO electrodes. We believe that this fact opens a new possibility for the practical use of ZnO in DSCs in the future.

5. Summary

We fabricated the ZnO films as photoanodes for DSCs by coating the ZnO pastes containing PEG as the binder. It was found that PEG worked effectively to decrease the large interconnected voids in the films, improving their photoelectrochemical performance. The ZnO/N-719 photoanodes were shown to be efficient when the film properties were controlled suitably for the DSC. Consequently, our cell using the ZnO/N-719 photoanode exhibited the overall conversion efficiency as high as 4.3%. Because the present achievement is based on the facile doctor-blade method used for fabricating the films, ZnO should be reconsidered as the most promising alternative to TiO_2 with further optimization of the factors other than the fabrication process.

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