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Research Article

Photoanode of Dye-Sensitized Solar Cells Based on a ZnO/TiO_2 Composite Film

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A photoanode of dye-sensitized solar cells based on a ZnO/TiO_2 composite film was fabricated on a transparent conductive glass substrate using different techniques including electrophoretic deposition, screen printing, and colloidal spray coating. The ZnOs used in the composite film were ZnO tetrapods prepared via thermal evaporation and ZnO nanorods obtained via hydrothermal growth. The structural and morphological characterizations of the thin composite films were carried out using scanning electron microscope (SEM). The best power conversion was 1.87%, which corresponds to the laminated $TiO_2/ZnO/TiO_2$ structure prepared via screen printing.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted increasing attention due to their high efficiency for energy conversion and low production cost compared with silicon solar cells [1, 2]. Photoanodes are important components of DSSC because of their functions in supporting dye molecules and transferring electrons. A high electron transport rate is required to reduce electron-hole recombination rate and enhance conversion efficiency. ZnO is one of the semiconductor materials containing abundant nanostructure morphologies and having high electron mobility (about 10^{-1}–10^{-3} $cm^2\,V^{-1}\,s^{-1}$ in ZnO nano-particle film and $>100\,cm^2\,V^{-1}\,s^{-1}$ in bulk ZnO). Recently, significant efforts have been given to the ZnO photoanode in place of the porous TiO_2 photoanode, in the hope of further enhancing the performance of solar cells by improving electron gathering and transporting efficiency and inhibiting charge recombination at the same time [3–6]. However, the instability of ZnO in acid dyes and its low electron injection efficiency from Ru-based dyes resulted in a low conversion efficiency of DSSC based on a pure ZnO photoanode [7]. Therefore, photoanodes built by two or more materials have attracted new attention due to the obvious advantages of combining different materials, that is, the high electron transport rate of ZnO and the high electron injection efficiency of TiO_2 from Ru-based dyes.

In this paper, a hybrid photoanode composed of ZnO and TiO_2 was fabricated on a SnO_2: F (FTO) transparent conductive glass substrate using different techniques including electrophoretic deposition, screen printing, and colloidal spray coating. Two kinds of ZnO, namely, ZnO tetrapods and ZnO nanorods, were adopted in this study. The structural and morphological characterizations of the composite thin films were carried out using scanning electron microscope (SEM). The current density-voltage (I-V) curve, under AM 1.5 illumination with a $100\,mW/cm^2$ light intensity, was measured and analyzed.

2. Experimental

2.1. ZnO Tetrapods and Nanorods Synthesis. ZnO tetrapods were prepared via the thermal evaporation method from our previous report [8]. ZnO nanorods were synthesized on the FTO glass substrates, with predeposited ZnO seed particles via the hydrothermal growth route. The ZnO seed layer was

prepared through combining a sol-gel process and a spin-coating technique, following the steps reported in [9].

2.2. Screen Printing. Approximately, 2.0 g of TiO_2 and 2.0 g of ZnO tetrapods were dispersed into two mixtures, each containing 0.4 g PEG-20000, 10 mL terpineol, 0.4 g ethyl cellulose, and 0.4 mL acetylacetone, and ground for 2 h, respectively.

A TiO_2 layer was screen printed on the faced-up conductive surface and then annealed at 450°C for 0.5 h. The procedure was repeated for the ZnO mixture. Lastly, another TiO_2 layer was screen printed and annealed under the same conditions. An alternative method for this process would be to spin coat one layer of TiO_2 sol first, and then screen printing the ZnO/TiO_2 layers to get the composite thin films.

2.3. Colloidal Spray Coating. The slurry used in colloidal spray coating is same with that used in screen printing. FTO glasses were vertically fixed on the walls with paper tape, and the spray gun is 30 cm away from the glasses. A ZnO layer was first spray coated on the FTO glasses followed by another TiO_2 layer. Afterward, the composite ZnO/TiO_2 layers were annealed at 450°C for 0.5 h.

2.4. Electrophoretic Deposition. The preparation of ZnO tetrapods/TiO_2 thin films through electrophoresis involves the following steps: (1) the mixture of 0.1000 g ZnO tetrapods and 0.0010 g TiO_2 were dispersed into the mixed solvent composed of 75 mL of ethanol and 25 mL of water under ultrasonic dispersion for 10 min; (2) two clean FTO glass substrates were used as positive and negative electrodes with a 1.5 cm space between the two electrode surfaces; (3) the electrophoresis voltage was set to 60 V; (4) the sample was annealed at 150°C for 20 min after electrophoresis; (5) steps 1–4 were repeated to obtain three ZnO tetrapods/TiO_2 layers; (6) finally, the composite films were annealed at 450°C for 0.5 h.

2.5. ZnO Nanorods/TiO_2 Composite Film. TiO_2 sol was first prepared using 16 mL of tetrabutyltitanate, 10 mL of ethylene glycol monomethylether, 40 mL of ethanol, and 0.0240 g of PEG, which were mixed and stirred at 60°C.

Subsequently, the FTO glass with ZnO nanorods was soaked in the solution for about 0.5 h and then annealed at 450°C for 0.5 h.

2.6. DSSC Assembly. The prepared ZnO/TiO_2 hybrid photoanodes were immersed in a N3 ethanol solution for 5 h to absorb the dye and then washed with ethanol several times. A Pt-coated FTO glass was used as a counterelectrode. The electrolyte was then dropped into it, and a sandwich type of solar cell was fabricated and employed to measure the photo-to-electric conversion efficiency.

2.7. Characterizations. The morphology of the ZnO/TiO_2 composite photoanodes was measured using SEM (Hitachi S-4800). The *I-V* characteristics of the solar cells were measured using a Keithley 2410 source meter under 1-sun illumination (AM 1.5, 100 mW/cm^2) from a solar simulator.

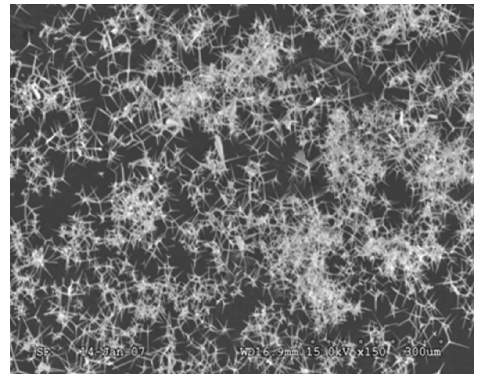


Figure 1: SEM image of the ZnO tetrapods.

3. Results and Discussion

3.1. Morphology of ZnO and ZnO/TiO_2 Composite Film. Figure 1 shows the SEM image of the ZnO tetrapods obtained via the thermal evaporation method, which is the easiest way to prepare ZnO tetrapods. Zinc powder was placed directly into the reactor for thermal evaporation and oxidation. No catalyst is needed in this process, and the reaction atmosphere needs not be controlled in the reactor as well. In addition, the ZnO tetrapods prepared using thermal evaporation exhibited perfect morphology with high crystal quality.

Figure 2 shows the SEM image of ZnO nanorods obtained via hydrothermal growth. The ZnO nanorods showed perfect hexagonal shapes with good orientations.

Figure 3 shows the cross-sectional and top-view images of the ZnO tetrapods/TiO_2 photo-anode fabricated via screen printing. The image shows that the ZnO tetrapods/TiO_2 composite film exhibits a uniform porous structure, which can greatly increase the surface area and improve dye absorption.

Figure 4 shows the SEM image of the composite film fabricated through colloidal spray coating. The film also has a porous structure. However, this porous structure is not uniform compared with the film prepared via screen printing. Figure 5 presents the morphology of the electrophoretic deposited ZnO tetrapods/TiO_2 composite film, which also shows a porous structure.

Figure 6 shows the morphology of ZnO nanorods/TiO_2 composite film, and the TiO_2 nanoparticles show a dense packing that is unfavorable to dye absorption.

3.2. DSSC Performance. Figure 7 shows the *I-V* characteristics of DSSC under AM 1.5 illumination with a 100 mW/cm^2 light density. The short-circuit current density (JSC), open-circuit voltage (VOC), fill factor (FF), and energy conversion (η) derived from the *I-V* curve are listed in Table 1. The DSSC based on the screen printing laminated TiO_2/ZnO tetrapods/TiO_2 photoanode has the highest efficiency of

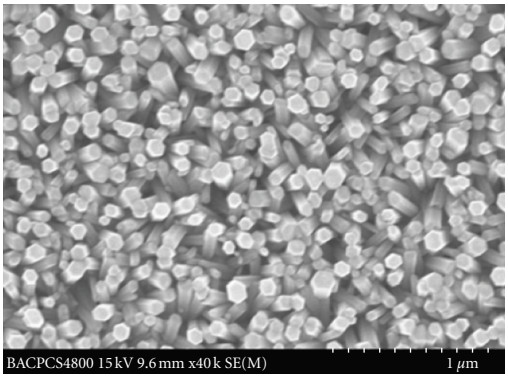
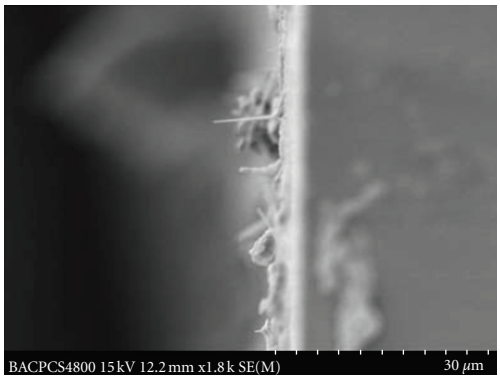
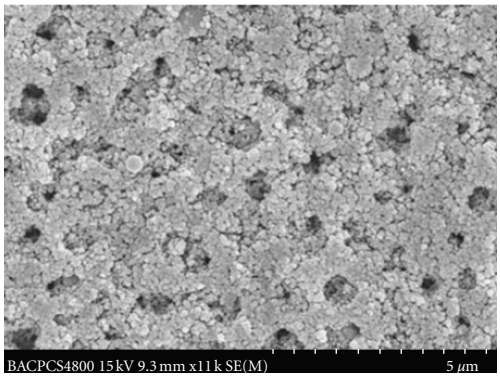


Figure 2: SEM top-view image of the ZnO nanorods.

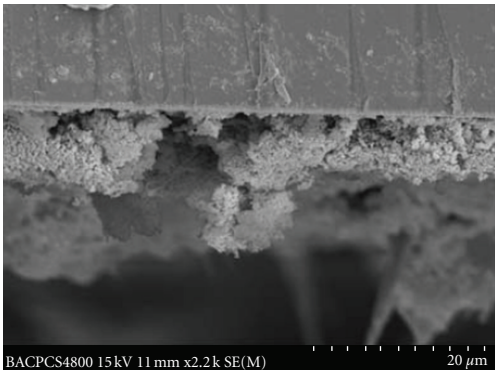


(a)

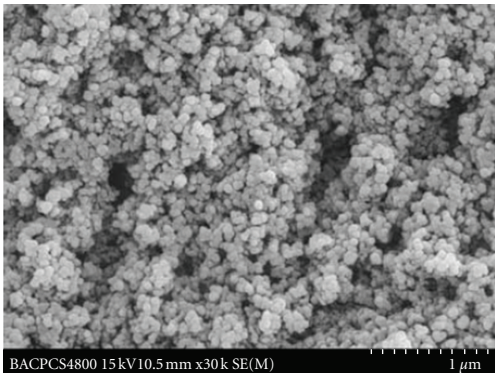


(b)

Figure 3: SEM cross-sectional (a) and top-view image (b) of ZnO tetrapods/TiO_2 photoanode fabricated via screen printing.



(a)



(b)

Figure 4: SEM cross-sectional (a) and top-view image (b) of ZnO tetrapods/TiO_2 photoanode fabricated through colloidal spray coating.

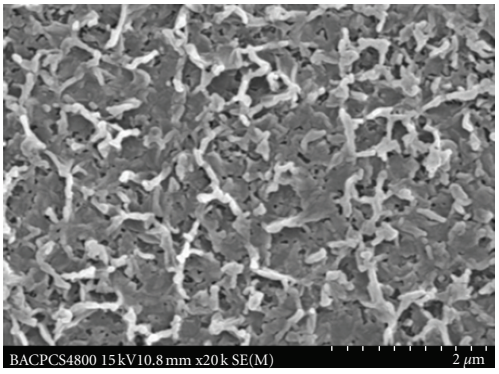


Figure 5: SEM image of ZnO tetrapods/TiO_2 photoanode fabricated via electrophoretic deposition.

1.87%, which is attributed to its uniform porous structure. On the other hand, the colloidal spray coated ZnO tetrapods/TiO_2 composite film has a nonuniform porous structure; thus, the efficiency of DSSC based on it decreased to 0.34%. The ZnO nanorod/TiO_2 has a densely packed structure and is unfavorable for dye absorption, causing its efficiency to decrease to 0.24%. The DSSC based on the electrophoretic deposited ZnO tetrapods/TiO_2 composite photoanode has the lowest efficiency of 0.1%, which may be due to the microlevel size of the ZnO tetrapods. This condition is unfavorable to electrophoretic deposition, resulting in a poor quality composite film. Another reason may be that the best ratio of ZnO to TiO_2 and the optimal electrophoresis parameters remain unknown. On account of the high electron transport efficiency and a variety of morphology structures of ZnO, ZnO/TiO_2 composite photoanodes still prove to be very good prospects in improving the photoelectric conversion efficiency of DSSCs.

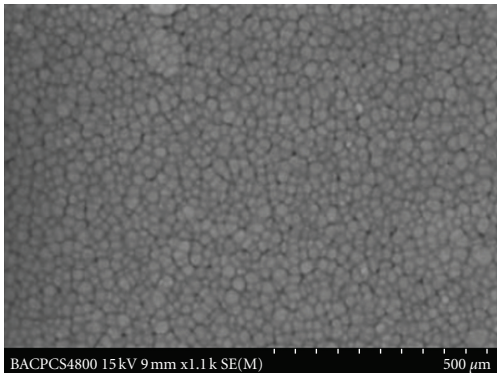


Figure 6: SEM image of ZnO nanorods/TiO_2 photoanode.

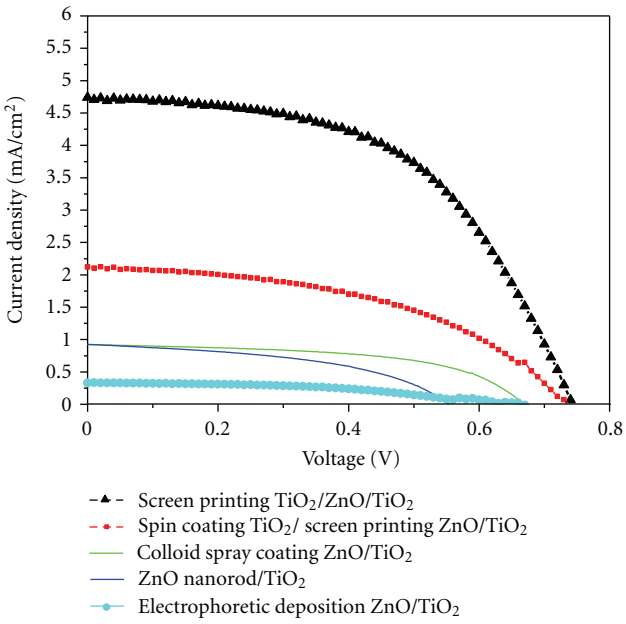


Figure 7: IV curve of DSSC based on ZnO/TiO_2 composite film.

4. Conclusions

Hybrid ZnO/TiO_2 photoanodes were prepared using electrophoresis deposition, screen printing, and colloidal spray coating to utilize the high electron transport rate of ZnO and the high electron injection efficiency and stability of TiO_2 materials. DSSCs based on these hybrid photoanodes were assembled. DSSC based on screen printing has the highest power conversion of 1.87%, whereas DSSC based on electrophoresis deposition has the lowest power conversion of 0.10%. Meanwhile, the large-sized ZnO tetrapods from thermal evaporation are not suitable for electrophoresis deposition and yielded a poor quality electrophoresis film. Thus, smaller-sized ZnO tetrapods from microemulsion and organic pyrolysis methods will be used for future electrophoresis deposition processes.

Table 1: Photovoltaic performance of DSSC based on ZnO/TiO_2 composite film.

Samples	Jsc (mA/cm^2)	Voc (V)	FF	Eff (%)
1	4.74	0.74	0.53	1.87
2	2.12	0.74	0.47	0.73
3	0.92	0.67	0.55	0.34
4	0.93	0.55	0.46	0.24
5	0.34	0.67	0.43	0.10

Acknowledgments

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