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Research Article

Electrodeposition Combination with Hydrothermal Preparation of ZnO Films and Their Application in Dye-Sensitized Solar Cell

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A suitable method is necessary for the high performance of dyes-sensitized solar cells (DSSCs). In this paper, photoanodes of DSSCs have been fabricated through electrodeposition and combination with hydrothermal method. The results of mix method showed better performance than the single one. After the second step electrodeposition, the ZnO films formed flack finally. With the increase of hydrothermal time, ZnO films become thicker and bigger, which can offer large surface area to absorb much more dyes. The short-circuit current (2.4 mA/cm^2) and open-circuit voltage (0.67 V) were greater than the single one, alternating current impedance indicating that electrodeposition and hydrothermal mix are a more suitable method for high performance DSSCs. We expected to obtain higher conversion efficiency of DSSCs by this method.

1. Introduction

As a promising solar-to-electric energy converter, DSSCs have attracted much attention due to their high efficiency and low cost [1–3]. With regard to photovoltaic devices, the conventional silicon-based solar cells are usually too bulky and heavy for flexible applications. Fortunately, new generation photovoltaic devices, such as dye-sensitized solar cells (DSSCs) and organic solar cells [4–6], make it possible to utilize solar energy more efficiently. As a result, invented new methods have recently attracted much attention to mesoporous film in the photoanodes of dye-sensitized solar cells (DSSCs) and quantum dots-sensitized solar cells (QDSCs). However, insufficient internal surface area limits conversion efficiency at a relatively low level owing to deficient dyes loading and light harvesting [3].

ZnO is one of the most important semiconductor materials as the photoanodes of DSSCs and QDSCs due to its suitable energy-band structure and excellent physical properties. ZnO has a potential in the applications ranging from catalysis and sensors to dye-sensitized solar cells (DSSCs) and quantum dots-sensitized solar cells (QDSCs) [7–12]. Up to now, to get high performance, many methods have been explored to prepare ZnO porous films to offer large specific surface area for high device performance, such as doctor-blade (DB) method, chemical bath deposition, and electrodeposition (ED). In this paper, we expected to fabricate high performance photoanodes for dyes-sensitized solar cells (DSSCs). TiCl4 pretreatment was used on FTO before fabricating ZnO films by electrochemical method. The morphology of ZnO films was changed after TiCl4 pretreatment, which can offer large surface area to absorb much more dyes. We try to differentiate electrodeposition time. When the time of electrodeposition was 3 min, the quantum dyes-sensitized solar cells (DSSCs) based on TiCl4 pretreatment ZnO films showed more superior photoelectrochemical performance.

2. Experimental

2.1. Preparation of ZnO Photoanodes. The first step is hydrothermal method. Preparing the molar concentration of 0.005 M $Zn(NO_3)_2$ and hexamethylenetetramine solution, then ultrasonically processing for 10 min so it is completely dissolved and then mixed. Put the prepared FTO into the beaker, pour into the prepared reaction solution, and seal,

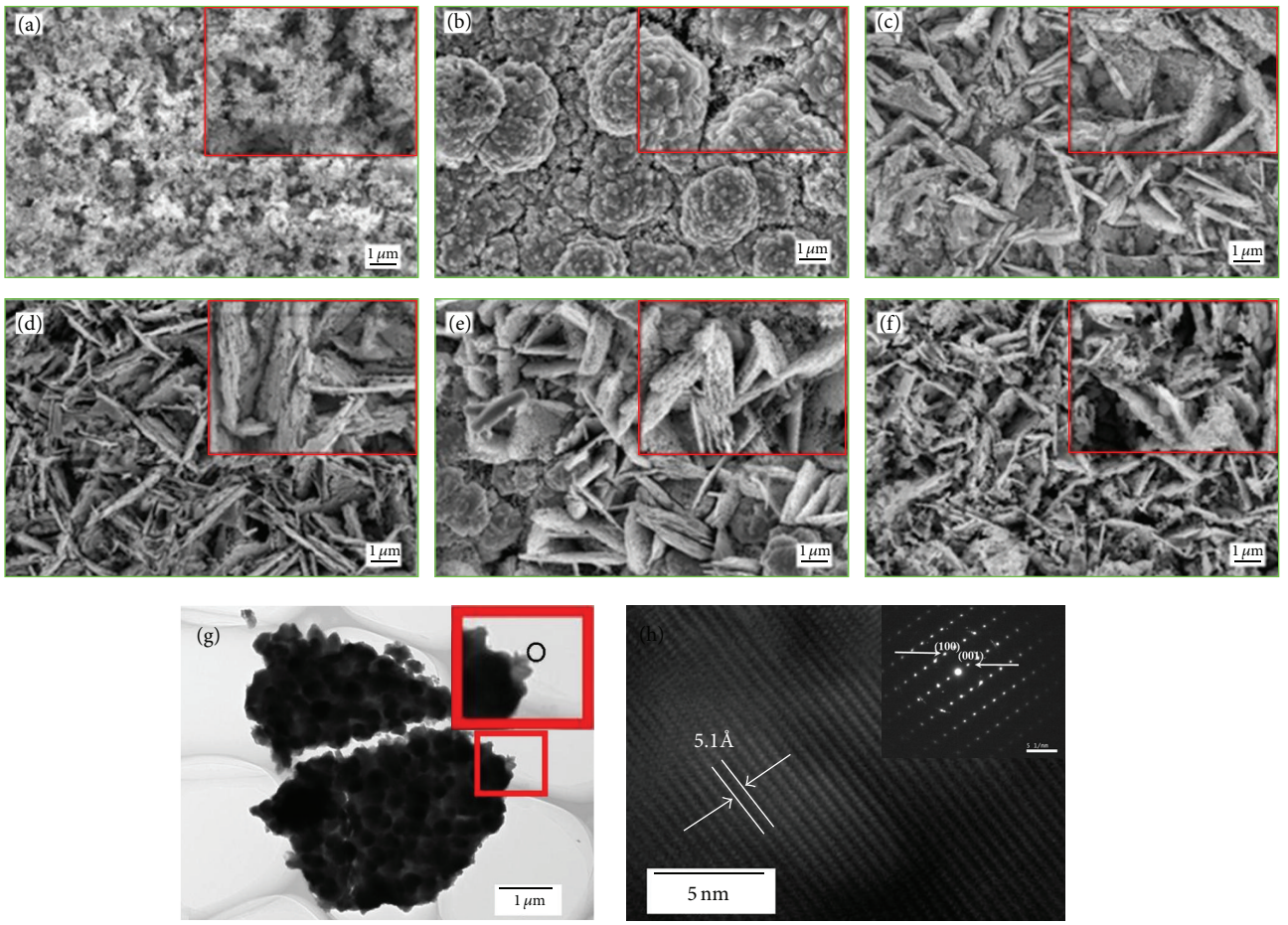

FIGURE 1: SEM images of the samples D2, E2, and F2, and G2, H2, and I1 after annealing, corresponds to (a), (b), (c), (d), (e), and (f), respectively. (g) Typical TEM and (h) HRTEM image of the sample, inset is the SAED of (g).

then put the beaker in the oven to maintain constant temperature at 95°C; reaction time was 0.5 h, 1 h, 2 h, 3 h, and 4 h, respectively. After the reaction, remove and wash with deionized water, and then it is calcined at 450°C for 30 min, the samples D1, E1, F1, G1, and H1 were obtained, respectively.

The second step is electrochemical method. Electrodeposition time is 8 min, while electrodeposition current is 10 mA. When the reaction stopped, remove and wash with deionized water, dry reserve, obtaining the samples D2, E2, F2, G2, and H2, respectively. Intended as a comparison, only carry out the second step electrochemical preparation of ZnO films as sample I1.

The above prepared samples F1, D2, E2, F2, G2, and H2 were calcined at 450°C for 30 min, to be naturally cooled to 80°C and removed. Then they were immersed in the prepared N719 dye for 12 h and removed out, consequently washed with ethanol and air dried. Finally ZnO photoanode samples F1′, D3, E3, F3, G3, H3, and I2 were obtained.

2.2. Characterizations. In order to be able to observe the characterization of ZnO films, we used scanning electron microscope (SEM) to observe and XRD to analyze. The samples D2, E2, F2, G2, H2, and I1 calcined at 450°C for 30 min, SEM, as shown in Figure 1. It can be seen from the SEM images from (a) to (c), as the first step in the growth of the hydrothermal time, after the second step of the electrochemical preparation of ZnO gradually reunite and ultimately the formation of flakes of ZnO films are obtained. With the continued growth of the hydrothermal time, flake structure of ZnO begins to become thicker and larger, as shown in the SEM (d) and (e). (f) is the SEM of only by step electrochemical preparation of sample I2. It can be seen by the SEM, ZnO structure is also flake, too. Although samples prepared both by using electrodeposition combination with hydrothermal method and only by step electrochemical method are all porous flakes, two-step prepared sample porousity were higher than that in the sample prepared by one-step. Soaked in the dye will be absorbed more dyes, so it can improve the DSSC short circuit current density, thereby enhancing the performance of the DSSC.

Typical TEM, HRTEM image and SAED of the sample are shown in Figures 1(g) and 1(h).

The XRD pattern of sample F1, F2, I1 in Figure 2. Because the sample F1 growth time is too short, only 2 h, so few ZnO products are obtained. It can be seen from the XRD

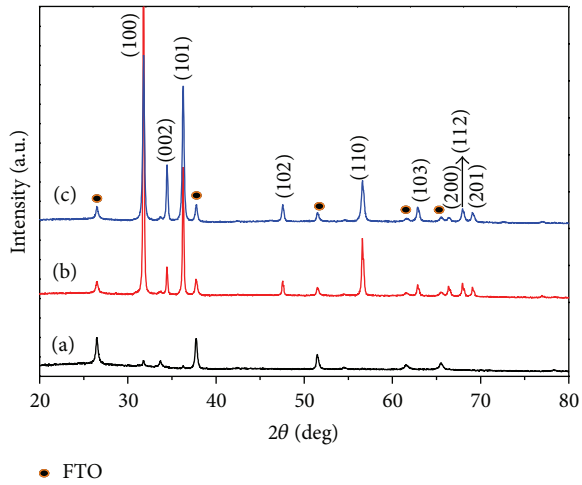

Figure 2: XRD pattern of the samples F1, F2, and I1, corresponds to the curves (a), (b), and (c), respectively.

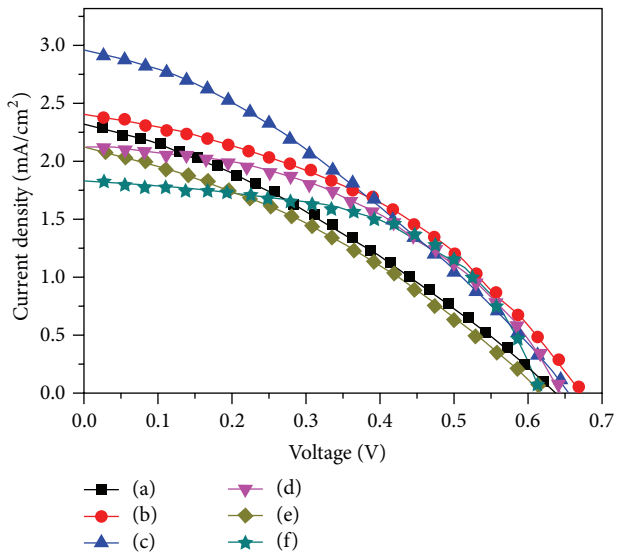

Figure 3: J-V curves obtained from the samples D3, E3, F3, G3, H3, and I2 of DSSC, corresponds to the curves (a), (b), (c), (d), (e), and (f), respectively.

patterns that, for one step hydrothermally prepared samples of F1, peak is less and the intensity of each peak is not high, indicating the crystallization is not very good. But electrodeposition combination with hydrothermal method preparation of the samples F2 and only by step electrochemical method preparation of sample I1 the main peak position and peak intensity are almost the same. Compared with I1, F2 is slightly higher than only the peak intensity of (100) direction in the crystal. This is similar to the morphology of the F2 and I1.

3. Results and Discussion

The above prepared samples D2, E2, F2, G2, H2, and I1 were immersed into dyes (N719) 12 h, obtaining the ZnO photoanodes D3, E3, F3, G3, H3, and I2, then with Pt counter electrodes they were assembled into dye-sensitized solar cells (DSSCs) and performance testing, respectively.

Based on samples D3, E3, F3, G3, H3, and I2, J-V curves obtained from DSSCs are presented in Figure 3; Table 1 presents the parameters of DSSCs. Because of only by step hydrothermal method preparation, ZnO films assembled into DSSCs performance are very low, so they are not listed in this table. It can be seen by the J-V curve, as with increasing in the time of the hydrothermal growth in the first step, the DSSCs short-circuit current density and photoelectric conversion efficiency decreased. The main reason is that with the growth of hydrothermal time, after the second step electrochemical method by the ZnO surface reunion, flakes of ZnO gradually formed, resulting in the increase in the surface area, as well as the increase in the load of the dye adsorption. So the short circuit current density and photoelectric conversion efficiency of DSSCs are also increased. But with the growth of the hydrothermal time, flake structure of ZnO begins to become thicker and larger, the surface area and dyes adsorption decrease, so the short-circuit current density and photoelectric conversion efficiency of DSSC decrease. When the hydrothermal time was 2 h, the performance of

Table 1: The performance parameters of DSSC based on samples D3, E3, F3, G3, H3,and I2.

Samples	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
D3	0.63	2.32	0.33	0.49
E3	0.55	2.95	0.39	0.65
F3	0.67	2.40	0.40	0.66
G3	0.59	2.13	0.49	0.62
H3	0.61	2.11	0.34	0.45
I2	0.61	1.82	0.54	0.62

electrodeposition combination with hydrothermal method preparation of samples F3 assembled into DSSC is better than only by step electrochemical method preparation of samples I2 assembly of the DSSC. The main reason is that, compared with only by step electrochemical method, electrodeposition combination with hydrothermal method preparation of ZnO films have a lot of holes; it is conducive to adsorption of more dyes, resulting in higher short-circuit current density and photoelectric conversion efficiency.

ZnO photoanodes I2, F1′, and F3 prepared by electrochemical method, hydrothermal method, and electrodeposition combination with hydrothermal method were assembled into DSSC, respectively. Then we do IPCE test and get the test curve shown in Figure 3. It can be seen from IPCE spectra, the wavelength range of photo-electron conversion in the DSSC is between 380–700 nm. The response spectrum by electrodeposition combination with hydrothermal method preparation of samples F3 assembly of DSSC is broader than only by one step method preparation of samples I2 and F1′ assembly of DSSC. Demonstrate that the capture efficiency based on electrodeposition combination with hydrothermal method preparation of samples F3 assembly of DSSC is higher than the assembly of the DSSC based on only by

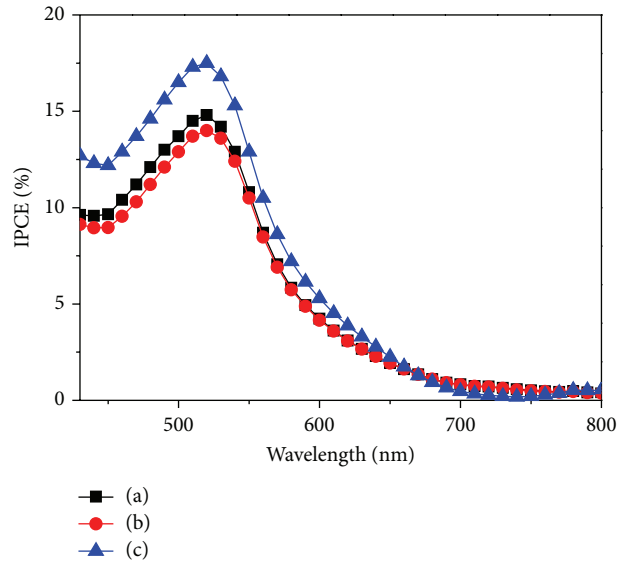

Figure 4: The IPCE of samples I2, F1′, and F3, corresponds to the curves (a), (b), and (c), respectively.

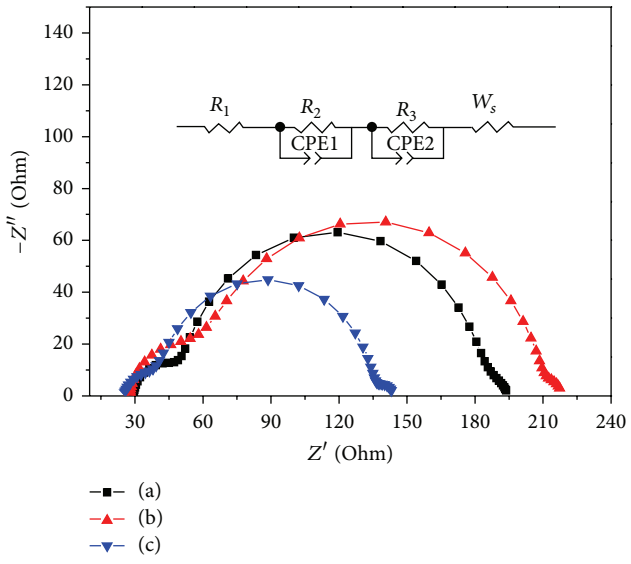

Figure 5: The EIS of samples F1′, I2, and F3, corresponds to the curves (a), (b), and (c), respectively.

step hydrothermal method and only by step electrochemical preparation of samples. At 520 nm, the photoelectric conversion efficiency of samples I2, F1′, and F3 attains 14.5%, 14%, and 17.5%, respectively (Figure 4).

Figure 5 shows the alternating current impedance spectra of DSSC based on samples F1′, I2, and F3, the inset in Figure 5 is the equivalent circuit fitting impedance curve by using the Z-View software. Fitting results are shown in Table 2. As shown in Figure 5, samples F1′, I2, and F3 of the EIS appear three semi-circulars; the semicircle of intermediate frequency corresponds to ZnO and electrolyte interface electronic composite process, and at the same time corresponds to the R_3 equivalent circuit. The low

Table 2: The fitting results of DSSC electrochemical impedance spectroscopy based on samples F1′, I2, and F3.

Samples	R_1 (Ω)	R_3 (Ω)	CPE2 (μF)	W_s (Ω)
F1′	29.25	130.6	38.56	14.41
I2	27.16	120.8	57.42	5.67
F3	25.22	94.22	41.13	9.28

frequency semicircle corresponds to the electrolyte diffusion impedance, the equivalent circuit of the W_s. CPE2 represents ZnO and electrolyte electric double layer of capacitance. It can be seen from the fitting data in Table 2, compared to DSSC assembled with the sample F1 only by one step of hydrothermal method, DSSC assembled with the sample I2 only by one step of electrochemical method has the smaller electronic composite impedance (R_3), demonstrating that the electron recombination rate of anode of the sample I2 is relatively low and has longer electron lifetime, while CPE2 is larger. Meanwhile, the Warburg impedance (W_s) of the electrolyte is smaller, so the electrochemical method preparation of ZnO structure is more conducive to the electrolyte ion diffusion. Compared with one-step preparation of samples F1′ and I2, electrodeposition combination with hydrothermal method preparation of the sample F3 assembled into DSSC, the external circuit impedance R_1 minimum. Warburg impedance of the electrolyte W_s is slightly larger than only by step electrochemical method preparation of sample I2, but smaller than only by step hydrothermal method preparation of sample F1′, CPE2 is less than I2, but greater than F1′. In the three types of DSSC, the F1′ electronic complex impedance R_3 is maximum, demonstrating the F1′ light electrons on the anode composite probability minimum. On the whole, electrodeposition combination with hydrothermal method preparation of the samples was assembled into DSSC, its performance is superior to only one step method preparation of samples assembled into DSSC. In only one step method preparation of samples, the DSSC performance of electrochemical method preparation is better than the hydrothermal method preparation; it is consistent with the IPCE test results of the previous.

4. Conclusions

We have demonstrated an efficient method for preparation of high performance ZnO photoanodes. After all steps, the ZnO films formed flack finally. The holes of sample prepared by the electrodeposition combination with hydrothermal method are more than one-step preparation method. It is conducive to absorb more dye; the DSSC short circuit current density is greater than before, thereby enhancing the performance of the DSSC. With the increase of hydrothermal time, the change of ZnO films surface can offer large surface area to absorb much more dyes. Our results clearly demonstrate that ZnO photoanodes prepared by electrodeposition combination with hydrothermal method have more functions and show a high performance in solar cells. In addition, we expected to, through deep research, obtain higher conversion efficiency of DSSCs by this method.

Conflict of Interests

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

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