Research Article

Atmospheric Environment Fabrication of Composite Films by Ethanol Catalytic Combustion and Its Use as Counter Electrodes for Dye-Sensitized Solar Cells

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The composite films which consist of amorphous carbon, carbon nanotube, and iron nanoparticles were prepared by ethanol catalytic combustion in atmospheric environment. The as-prepared composite films have good electrocatalytic activity and high conductivity which is due to their particular structure. The efficiency of the composite films based dye-sensitized solar cells (DSSCs) is closed to that of the Pt based one. Most importantly, the DSSC employing the composite films presents a higher FF than those of Pt based solar cell. In addition, it is a simple method for mass production of composite films counter electrode (CE) which is expected to reduce the cost of fabricating DSSCs.

1. Introduction

Since the report by O'Regan and Grätzel in 1991 [1], DSSCs have been regarded as promising devices for energy applications because of their advantages of low cost, ease of manufacture, and a relatively high photo-to-current conversion efficiency [2]. Moreover, the solar energy conversion efficiency of DSSCs with a ruthenium sensitizer and Pt counter electrode reaches 13.1% [3].

Counter electrode serves to transfer electrons from external circuit to triiodide and iodine in the redox electrolyte. Pt has been widely used as the counter electrode in DSSCs. Although Pt exhibits excellent catalytic activity for triiodide reduction and good electric conductivity, it is extremely expensive. Therefore, some nanosized carbon materials, such as hard carbon spherule [4], carbon nanotubes [5], mesoporous carbon [6], and ordered multimodal porous carbon [7], have been investigated extensively as counter electrode to replace the FTO/Pt electrode. However, the application of composite films which consist of amorphous carbon, carbon nanotube, and iron nanoparticles as counter electrode in

DSSCs has not been reported yet. Herein, the composite films were prepared by ethanol catalytic combustion in atmospheric environment. The as-prepared composite films as the counter electrode exhibit a good photovoltaic performance of DSSCs.

2. Experimental

2.1. Fabrication of Composite Film CEs. The preparation of composite electrode was conducted in the ethanol catalytic combustion (ECC) process. A small amount of thiophene was added to 100 mL anhydrous alcohol and then we added right amount of ferrocene to the solution which poured into the alcohol lamp at last. In this experiment, FTOs were employed as substrate which were fixed on the small lift then placed in the flame. The distance between the FTOs and the alcohol lamp wick was 6 cm. After several seconds, the composite films were obtained on FTOs.

2.2. Assembly of DSSCs. The clean FTO was treated with 40 mM TiCl_4 aqueous solution at 70°C for 30 min. Then the

FIGURE 1: The typical SEM images of the film grown on the FTO; (a) and (b) are the low magnification image and high magnification image of the composite film, respectively.

TiO₂ was coated on the FTO substrates by screen printing technique, followed by sintering at 450°C for 30 min. The thickness of the TiO₂ film was about 6.6 μm which was controlled by the times of the screen printing technique. The TiO₂ film was annealed at 450°C for 30 min and then was soaked into the TiCl₄ aqueous solution with the concentration of 0.2 M at 70°C for 30 min. Following annealing for 30 min at 450°C, the TiO₂ film was cooled to 80°C and then immersed into a solution of the dye of cis-di(thiocyanato)-N-N'-bis(2,2'-bipyridyl-4-carboxylic acid-4'-tetrabutylammonium carboxylate) ruthenium (II) (N-719) overnight. To prepare FTO/Pt electrode, the Pt catalyst was deposited on the FTO glass by coating with a drop of H₂PtCl₆ solution with repetition of the heat treatment at 450°C for 30 min. The electrolyte was LiI (0.5 M), I₂ (0.05 M), 1-propyl-2,3-dimethylimidazolium iodide (DMP, 0.3 M), and 4-terbutylpyridine (4-TBP, 0.3 M) in an acetonitrile solution which was introduced into the cell gap between the anode and counter electrode. The active area of the cell was 0.25 cm².

2.3. Characterization and Measurements. The morphologies of the composite films were characterized using the scanning electron microscopy (SEM, Zeiss ULTRA 55) and transmission electron microscopy (TEM, JEOL 2100). The composition of the as-prepared films was analyzed by the energy dispersive X-ray spectra (EDX, Zeiss ULTRA 55), Raman spectroscopy (Renishaw 2000), and thermogravimetric analysis (TGA, SDIA8H).

Electrochemical impedance spectroscopy (EIS) measurements were recorded using electrochemical workstation with bias DC voltage of -0.6 V over the frequency range of 0.1 Hz to 100 kHz. The incident photo-to-current conversion efficiency (IPCE) was measured by using a lab-made IPCE setup in institute of plasma physics. The photocurrent-voltage (I-V) curves were measured by the electrochemical workstation under an illumination of xenon lamp. The irradiance is 100 mW/cm² which is measured by a radiometer

(FZ-A, Photoelectric Instrument Factory of Beijing Normal University).

3. Results and Discussion

Figures 1 and 2 show the typical SEM and TEM images of the composite films, respectively. The SEM shows that the composite film is made up of nanoparticles and nanotube. From the TEM, we can see clearly the structure of the carbon nanotube, metal nanoparticles, and amorphous carbon. Moreover, we can see that the metal nanoparticles are wrapped in the surface of nanotube and the amorphous carbon.

For further analysis, we have characterized the composite films by Raman spectroscopy. Figure 3 shows that the G-band (1586.4 cm⁻¹) is much higher than its D-band (1339 cm⁻¹) which reveals that the composite films have a high graphitization degree. Moreover, there are some peaks in 0 to 400 cm⁻¹ named radial breathing vibration mode (RBM) which shows that the composite films contain single-walled carbon nanotubes. Figure 3(b) is the enlarged of RBM in Figure 3(a). From Figure 3(b), we can see that the frequency of the peaks is 209 cm⁻¹, 222 cm⁻¹, 230 cm⁻¹, and 268 cm⁻¹ which correspond to the diameter of single-walled carbon nanotubes at 1.12 nm, 1.05 nm, 1.02 nm, and 0.87 nm, respectively.

Figure 4 shows the EDX spectrum of the composite films. From the EDX spectrum, we can see that the sample consists of C, O, Fe, and a very small amount of Sn. The existence of Sn is probably from the FTO.

In order to determine the content of carbon nanotube, iron nanoparticles, and amorphous carbon, we have analyzed the composite films by TGA (Figure 5). The TGA curve declines slowly from 20°C to 191.7°C which corresponds to the reduction of water of the composite films. In this process, the weight of the sample is loss of 5%. When the temperature

FIGURE 2: The typical TEM images of the film grown on the FTO; (a) and (b) are the low magnification image and high magnification image of the composite film, respectively.

FIGURE 3: (a) is Raman spectrum of the composite films in Figure 1; (b) is the enlarged of RBM in (a).

is more than 254.68°C, the slope of TGA curve increases which shows that the amorphous carbon reduces. When the temperature is from 330°C to 509.2°C, the slope of the TGA curve continues to increase and the weight loss of the sample is sped up; the mass loss is about 34.4%. When the temperature is more than 509.2°C, the slope of the TGA curve reduces till 758.3°C which corresponds to the reduction of carbon nanotube. In this process, the mass loss is about 5.5%. The rest of the sample is iron and iron oxide which is about 54.16%.

IPCE characteristics of the DSSCs with composites films counter electrode and Pt are shown in Figure 6. The maximum IPCE value at 540 nm of the DSSCs with composite films counter electrode is approximately 72%, and those of the DSSC with the Pt are 76.3%. Adsorbed spectra of the DSSCs with composite films counter electrode are lower than those

of the DSSC with the Pt in the range 380–650 nm and both the adsorbed spectra change almost unanimously at longer wavelengths above 650 nm. In general, the IPCE of the DSSCs with composite films counter electrode is comparable to that of the DSSC with FTO/Pt counter electrode.

To investigate the electrochemical activity of the as-prepared composite films, electrochemical impedance spectra (EIS) were measured. Figure 7 shows the equivalent circuit for the DSSCs, where R_1 is the ohmic serial resistance mainly related to the FTO glass, CPE_1 and CPE_2 are the capacitance of electrical double layer, respectively, R_2 is the charge-transfer resistance of the counter electrode and electrolyte, R_3 is the recombination resistance of the anode electrode and the electrolyte, and W_s is the Warburg impedance of the electrolyte. As shown in Figure 7, R_1 can be determined by the

FIGURE 4: The EDX spectrum of the composite film corresponding to the Figure 1.

FIGURE 5: The TGA curve of the composite films at 20°C to 800°C.

impedance at high frequency of around 100 kHz, while R2 and R3 are derived from the semicircles in the high and middle frequency ranges, respectively, through fitting the plots with Z-VIEW software. The resistance elements R1, R2, CPE1, and Ws values are summarized in Table 1. Obviously, the charge-transfer resistance of the composite films is much lower than Pt. It means that the composite films have an excellent electrocatalytic activity and high conductivity which is likely attributed to the big effective contact area of the composite films and the electrolyte and the high conductivity of the carbon nanotube. The composite electrodes exhibit larger CPE1 values than that of the Pt, which means that the composite electrodes have longer electronic life [8]. However, the Ws values of the composite electrode is larger which is likely due to the thicker layer along the composite electrode, as compared with the Ws in a thin layer of the smooth FTO/Pt electrode [9, 10].

Figure 8 shows photocurrent-voltage characteristics of DSSCs using the composite electrodes and the Pt electrode as the counter electrode and the corresponding parameters are listed in Table 2.

As we can see in Table 2, as reference, the DSSCs with a typical FTO/Pt as counter electrode has an open-circuit

FIGURE 6: IPCE characteristics of the DSSCs with composite films counter electrode (a) and Pt (b).

FIGURE 7: EIS spectra of the DSSCs with the composite films counter electrode and Pt electrode. The cells were measured with the frequency range of 100 mHz to 100 kHz.

voltage (V_{OC}) of 0.8072 V, short-circuit current density (J_{SC}) of 12.91 mA cm⁻², fill factor (FF) of 0.5316, and conversion efficiency (η) of 5.54%. When composite electrode is used as the counter electrode, the V_{OC} , J_{SC} , FF, and η of DSSC can reach as high as 0.7940 V, 10.70, 0.5603, and 4.76%, respectively. Compared with Pt electrode, the V_{OC} , J_{SC} , and η are lower, but the FF is larger, which should be attributed to the effective contract area of the electrolyte and the composite films counter electrode.

4. Conclusions

In summary, the composite films were obtained by ethanol catalytic combustion in atmospheric environment and were

FIGURE 8: I-V characteristic curves of DSSCs with the composite films and Pt, respectively.

TABLE 1: R_1 , R_2 , and CPE1 values of DSSCs with the composite films and Pt.

Counter electrode	R_1 (Ω)	R_2 (Ω)	CPE1 (μ F)	Ws (Ω)
Composite films	24.17	6.27	27.36	16.68
Pt	32.57	12.97	26.41	14.3

TABLE 2: I-V parameters of these cells in Figure 8.

Counter electrode	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	η (%)
Composite electrode	0.7940	10.70	0.5603	4.76
Pt	0.8072	12.91	0.5316	5.54

used directly as the counter electrode for DSSCs. It is demonstrated that the photovoltaic performance of the DSSCs with the composite films as the counter electrode is excellent and compared to that of the DSSCs with FTO/Pt counter electrode, which is attributed to their good electrocatalytic activity and high conductivity. A detailed understanding of the relationship between the electron transfer and electrolyte diffusion needs further investigation.

Conflict of Interests

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

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