Research Article

Study on Carbon Nanocomposite Counterelectrode for Dye-Sensitized Solar Cells

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Carbon nanocomposite electrodes were prepared by adding carbon nanotubes (CNTs) into carbon black as counterelectrodes of dye-sensitized solar cells (DSSCs). The morphology and structure of carbon nanocomposite electrodes were studied by scanning electron microscopy. The influence of CNTs on the electrochemical performance of carbon nanocomposite electrodes is investigated by cyclic voltammetry and electrochemical impedance spectroscopy. Carbon nanocomposite electrodes with CNTs exhibit a highly interconnected network structure with high electrical conductivity and good catalytic activity. The influence of different CNTs content in carbon nanocomposite electrodes on the open-circuit voltage, short-circuit current, and filling factor of DSSCs is also investigated. DSSCs with 10% CNTs content exhibit the best photovoltaic performance in our experiments.

1. Introduction

Since the technological breakthrough of dye-sensitive solar cells (DSSCs) in 1991, a great deal of progress has been made in various aspects ranged from main critical materials constituting DSSCs to the related manufacturing technologies, which covers both fundamental studies on DSSCs with small area and large-scaled industry researches.

The current studies on DSSCs are mainly focused on dye synthesis [1, 2], electron transfer kinetics [3], photoanode [4–7], solid (or quasi-solid) electrolyte [8–10], and so forth, while the specific researches on counterelectrodes (CEs) are relatively rare. As an important part of dye-sensitive solar cell, counterelectrode usually consists of conductive glass loaded with platinum or carbon as catalysts, which can enhance the charge transfer between the CE and electrolyte interface, decrease the recombination possibility of I_3^- and the electrons in the conduction band of TiO_2 , restrain the dark current, and consequently improve the open circuit voltage (V_{oc}) [11, 12]. So far, the platinum (or other precious metals) CEs have superior performance and thoroughly theoretical research, but they cannot be applied in large due to their high cost. Carbon, one low cost but high efficient catalyst [13, 14], can be used in CEs, and after high temperature treatment, the photoelectric properties of carbon CEs approach those

of platinum CEs. Carbon and its mixtures can contact well with the substrate at low temperature, which facilitates the manufacture of large-scaled electrodes, thus having a promising application prospect.

Ramasamy et al. [15] used spray-coated multiwall carbon nanotubes (CNTs) film on fluorine-doped tin oxide glass as CEs, and got a maximum energy conversion efficiency of 7.59% under one sun illumination (100 mW cm^{-2} , AM1.5G). Furthermore, electrochemical impedance spectroscopy analysis indicated a decrease in the charge transfer resistance of multiwall CNT CEs with increase of spraying time. Lee et al. [16, 17] made CEs for DSSCs by nanocarbon powder, which received a 7.56% photoelectric conversion efficiency, after 60 days of aging in dark room, the photoelectric conversion efficiency still remained 6.35% (i.e., 84% of its initial day efficiency (η)), with increases of open-circuit voltage (V_{oc}) and fill-factor (FF) but a decrease of short-circuit current density (J_{sc}). Murakami et al. [18] fabricated carbon CEs by using carbon black, under AM1.5 illumination simulation achieving a photoelectric conversion efficiency (η), short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and fill-factor (FF) up to 9.1%, 16.8 mA/cm², 798 mV, and 68.5%, respectively. As is well known that the fill-factor (FF) depends on the thickness of the carbon layer,

when the thickness is less than 10 μm , the photoelectric conversion efficiency (η) improves as the thickness increases and the impedance decreases as the carbon layer thins. Huang et al. [19] manufactured CEs consisting of hard carbon spherules (HCSs), and the total photoelectric conversion efficiency (η) was 5.7%, while that of platinum CE under the same circumstance was 6.5%. Trancik et al. [20] believe that CNTs can provide accreted locations for reagents due to their microdefects and offer excellent catalytic effect when serving as CEs for DSSCs.

Nevertheless, at present researches on carbon nanocomposite CEs for DSSCs and the corresponding synergistic effect are rarely reported. In this paper, multiwall carbon nanotubes (MWCNTs) were added into nanocarbon black, and the related influence on the catalytic activity of carbon CEs were investigated as well.

2. Experimental Procedure

2.1. Electrode Plate Fabrication

2.1.1. Counterelectrode Fabrication. Carbon nanotubes (99.9%, diameters: 40–60 nm, Shenzhen Nanotechnologies Co. Ltd, China) were added into nanocarbon black (99.9%) with the mass fraction 30%, 15%, 10%, 5%, 0%, and marked as sample A, B, C, D, and E, respectively. To enhance the dispersity of CNTs, a spot of emulsifying agent (Tianjin FuChen Chemistry Ltd., China) was added into above samples, and acetylacetone as pore-forming agent to enlarge the interface between electrode and electrolyte, with ethyl cellulose as adhesive. The mass ratio of CNTs, nanocarbon black, ethyl cellulose, emulsifying agent, and acetylacetone was $x:1:0.125:0.1:0.1$ (x altered from 0.3, 0.15, 0.1, 0.05 to 0), and appropriate amount of butanone was introduced as solvent. The mixture solutions were dispersed by ultrasonic cleaning to obtain homogeneous suspensions. Finally, a specific amount of the suspension was dropped onto the FTO glass, and then dried under room temperature for 1 h. The CE plates for DSSCs were prepared with the dimension 8 mm $\times$ 8 mm. Under the protection of nitrogen, the as-prepared electrode plates were heated at 450°C, 600°C, 800°C for 30 minutes, respectively.

2.1.2. Photoanode Plate Fabrication. The mixture comprising of 3 g nano-TiO₂ powder (Germany Degussa Ltd.), 10 mL ethanol together with 0.5 mL emulsifying agent and acetylacetone was ultrasonically dispersed to homogeneous TiO₂ suspension of proper viscosity. A specific amount of the suspension was dropped onto FTO glass, and then the FTO glass was dried under room temperature for 1 h and then heated at 450°C in atmosphere for 30 minutes. Once the as-obtained TiO₂ plate was cooled, the TiO₂ suspension was once again dropped onto it, and the same drying and heating as mentioned above were sequentially conducted. After 3 or 4 time repetitions of the same procedure, TiO₂ multilayer membrane electrode plates were obtained with the dimension of 8 mm $\times$ 8 mm, the same as that of the CE plate.

2.2. Electrochemical Performance Testing

2.2.1. Carbon Electrodes Catalytic Performance and Interface EIS Testing. The testing system consisted of nanocarbon electrode, platinum (PT) electrode, and electrolytic cell. The testing electrolyte was the mixture of KI and I₂ ($[\text{I}^-]:[\text{I}_2] = 10:1$), 0.1 M KCL as supporting electrolyte. The mixed solution of 25% anhydrous alcohol and 75% deionized water was used to improve iodine solubility. PT electrode served as the cathode.

The electrochemical reaction process of this electrolytic cell is shown in the following equations:

The reaction mechanism is as follows: I₃[−] and I₂ are deoxidized near the cathode and oxidized near the anode. The reduction of I₃[−] and I₂ dominates the whole electrochemical process. The more active the electrode material is, the stronger the reduction of I₃[−] and I₂, and the better catalytic reduction performance for CEs is.

CHI660C electrochemical working station (Shanghai ChenHua instrument Ltd, China) was employed for C-V characteristic curve and EIS testing.

C-V characteristic curve: measuring the reduction performance of CEs for I₃[−], I₂ (such as reduction potential, reduction current density). Testing conditions: initial potential 1.5 V, high potential 1.5 V, low potential 0 V, and scan rate 1–100 mV/s.

EIS testing: 0.6 V initial potential was applied to simulate illumination for DSSCs and then test the interface impedance between the electrolyte and the carbon electrode. Testing conditions: initial potential 0.6 V, high frequency 100000 Hz, low frequency 1 Hz, and amplitude 0.005 V. The test data were fitted by ZView2 software.

2.2.2. DSSCs Photoelectric Properties and EIS Testing. A solar simulator (xenon lamp, AM1.5, 100 mW/cm², calibrated by silicon standard solar cell, facular area 30 cm $\times$ 30 cm, intensity unhomogeneity less than 3%), and Keithley 2400 Source Meter were performed, testing parameters of the cell, such as I-V characteristic curve, open-circuit voltage, short-circuit current density. Testing conditions: initial potential 0 V, high potential 0.8 V, the quantity of measuring points 150.

EIS testing was employed by using CHI660C electrochemical working station, testing the complex impedance to obtain the CT impedance of CEs and electrolyte. Testing conditions: initial potential 0.6 V, high frequency 100000 Hz, low frequency 1 Hz, amplitude 0.005 V. The test data was fitted by ZView2 software.

3. Results and Discussion

3.1. Surface Morphology Analysis of Electrodes. Scanning electron microscope (SEM, S-3400N) was employed to characterize the surface morphology of composite electrodes, and the SEM images of composite electrodes before and after thermal treatment were shown in Figures 1(a) and 1(b). It can be found in Figure 1(a) that, before thermal treatment, CNTs with the diameter 40–60 nm distributes near the carbon black, and the adhesive (ethyl cellulose) remains on the surface of carbon black, which decreases the contacting area between the carbon black and electrolyte, consequently affecting the corresponding catalytic performance. Figure 1(b) is the SEM image of composite electrode after 600°C thermal treatment under nitrogen atmosphere, indicating that the ethyl cellulose distributed between carbon black and CNTs surface decreases greatly. Furthermore, CNTs forms a network, to which carbon black evenly adheres, building a “grape cluster” structure and then getting a synergistic effect. After thermal treatment the outer diameters of CNTs decrease obviously. Due to high conductivity of CNT, electrons can conduct via the CNTs network distributed on the electrode film, which effectively enhances the conductivity of the electrodes. Moreover, the carbon black adhered to CNTs could enlarge the contacting area with the electrolyte, resulting in an increase of catalytic performance.

3.2. Electrochemical Performance Testing Results

3.2.1. Effects of CNTs Addition on the Reduction of I_3^-/I^- . At the scan rate 1–100 mV/s, the current density peak curves of PT CEs and CNTs-nanocarbon black composite CEs are shown in Figure 2. By the comparison of the reduction current peak of I_3^- and I_2 at different scan rates, it is revealed that current densities are all approximately in direct ratio with the square root of scan rates, which indicates that the total reaction rate depends on the ion diffusion in the electrolyte rather than the reduction rate of the ions absorbed onto the electrode surface. Among the reactions taken place on the electrode surface, the required potential of $I_3^- + 2e^- = 3I^-$ is higher than that of $3I_2 + 2e^- = 2I_3^-$, namely I_3^- is much more difficult to deoxidize than I_2 . However, the transmission (or diffusion) rate of electrons and ions within electrodes is less than the reduction rate of ions on the electrode surface, thus the diffusion of I_3^- is the determinant of CEs activity.

We can also find in Figure 2 that, at the same scan rate, composite carbon electrode with CNTs has a bigger reduction current density for I_3^- than that of PT electrode, on the other hand, the reduction current density for I_2 is smaller than that of PT electrode. The above results indicates that composite electrodes have stronger reduction for I_3^- than PT electrodes, but when it comes to the reduction for I_2 , the situation is totally opposite.

Figure 3 reveals the curves of the electrochemical catalytic performance of CEs versus the adding amount of CNTs. CEs with CNTs adding weight of 30%, 15%, 10%, 5%, and 0% enable I_2 with reduction potentials of -0.41 ,

-0.44 , -0.51 , -0.57 , and -0.59 V sequentially, as well as the reduction current density 4.98, 5.37, 4.68, 4.41, and 2.78 mA, respectively. Meanwhile, the corresponding parameters for I_3^- are similarly -0.77 , -0.83 , -0.92 , -0.96 and -0.92 V together with 5.82, 6.04, 5.31, 5.15, 3.44 mA.

It can be concluded that CEs with CNTs have obviously superior catalytic reduction ability to those without. And the catalytic reduction potentials of electrodes decrease after the addition of CNTs.

By adding specific amount of CNTs into counterelectrode, the catalytic performance of CEs is enhanced effectively; however, the enhancement is not direct ratio with the adding amount. We discover that the electrode performance of 15% CNTs adding is better than that of 5% and 10%, nevertheless, when the adding amount reaching 30%, its catalysis declines. Furthermore, once the mass fraction of CNTs in carbon black exceeds 30%, the catalytic reduction potential of electrodes increases and the current density decreases.

3.2.2. Effects of CNTs Addition on Carbon Electrode/Electrolyte Interface Impedance. The electrochemical impedance spectroscopy of nanocarbon electrode at 28°C is displayed in Figure 4, and the electrochemical impedance curves were fitted via the equivalent circuit in Figure 4. When conducting the fit, W , $R(E)$, $CPE(E)$, R_s were set as fixed value in the equivalent circuit model, where $R_{CT}(C)$, $R(E)$, W , R_s stand for the interface impedance between carbon electrode and electrolyte, PT electrode and electrolyte interface, Warburg impedance of electrolyte together with the contact impedance between C, TiO_2 , and FTO. R_{CT} indicates the resistance caused by charge transfer on the electrode surface.

CPE reveals the double-layer capacitance of the interface, with the expression $Z_{CPE} = T(j\omega)^{-P}$ ($0 \leq P \leq 1$). Z_{CPE} has two variables, that is, T and P , to be exactly, T revealing the solid-liquid interface capacitance, and P displaying the surface roughness of the electrode, namely, the deviation from plate condenser, thus indicating the capacitance characteristics of CPE. W characterizes the electrolyte impedance due to diffusion.

Table 1 shows that, the R_{CT} of carbon black-CNTs composite electrodes decreases obviously compared with nanocarbon black electrodes, that is, the resistance caused by charge transfer on the electrode surface decreases, due to the extraordinarily high conductivity and the netted CNTs being the bridges for electron transfer between carbon blacks. Moreover, there are some defects on the surface of CNTs, which can provide attachment position for reagent and accelerate the electron exchange between electrode and reagents. Nevertheless, the CPE-P of composite electrodes is less than that of carbon black, revealing the increase of surface roughness of electrodes after the adding of CNTs into carbon black, which may be caused by the diameter variance between CNTs and carbon black. The CPE-T of composite electrodes increases obviously, manifesting the increase of double-layer capacitance between the solid-liquid interface and the decrease of the interface

FIGURE 1: SEM image of the composite electrode: (a) untreated composite electrode—(b) composite electrode treated at 600°C in nitrogen.

FIGURE 2: Peak current of cyclic voltammograms on composite electrode and Pt electrode.

FIGURE 3: Cyclic voltammograms for composite electrode with different CNTs additions.

FIGURE 4: Electrochemical impedance spectroscopy and its equivalent circuit of nanocarbon electrode.

electric potential difference between the electrode and electrolyte.

3.2.3. Effects of CNTs Addition on the Impedance of DSSCs.

The electrochemical impedance spectroscopy for DSSCs with different CNTs additions at 30°C is shown in Figure 5, and was fitted by the equivalent circuit insetted in Figure 5, where R_{CT} (TiO_2) and CPE (TiO_2) represent the interface impedance between TiO_2 electrode and electrolyte. It is shown in Table 2 that, as the CNTs addition rises, the CPE-P decreases, leading to increases of both the surface roughness and the active catalytic points of the electrode surface; furthermore, the CPE-T decreases, resulting in the rise of the interface capacitance between the carbon electrode and electrolyte and the diminution of the electric potential difference of the two interfaces. Therefore, the catalytic performance of the CE is improved totally, which can be proved, in Figure 6, by all the increases of open-circuit voltage, short-circuit current, and the fill-factor for DSSCs as

TABLE 1: Fitting results for electrochemical impedance spectroscopy of nanocarbon electrode.

Electrode material	$R_{CT}(C)/\Omega$	CPE-T	CPE-P
$\Phi 40-60$ nm CNT	26.70	$3.2462E-5$	0.708
Nanocarbon black	104.3	$9.6948E-5$	0.568
Graphite scale	69.53	$2.0033E-5$	0.411
Composite electrode	43.04	$2.1908E-4$	0.512

TABLE 2: Fitting results for electrochemical impedance spectroscopy for DSSCs with different CNTs addition.

CNTs content	$R_{CT}(C)/\Omega$	CPE-T	CPE-P	R^S
0%	356.4	$2.42E-5$	0.922	65.1
5%	1125.0	$9.09E-5$	0.718	121.4
10%	194.4	$3.39E-4$	0.624	152.3
30%	198.4	$4.78E-4$	0.573	242.3

FIGURE 5: Electrochemical impedance spectroscopy for DSSCs and its equivalent circuit with different CNTs addition.

the rise of CNTs addition. However, as the increase of CNTs addition, R_s has a certain rise, indicating the increasing of the surface resistance between carbon film and FTO glass.

3.2.4. Effects of CNTs Addition on the Photovoltaic Performance of DSSCs. Photocurrent-photovoltage characteristics of DSSCs with different CNTs contents are shown in Figure 6. Combined with Table 2, it can be concluded that adding CNTs can improve the open-circuit voltage and short-circuit current of DSSCs. When the addition is less than 10%, the open-circuit voltage, short-circuit current, and fill-factor increase as the CNTs contents rises, nevertheless, when the adding amount reaches 30%, all the parameters mentioned above begin to reduce. The reason may be that with much CNTs addition, CNTs cannot be perfectly dispersed in carbon black and aggregate, resulting in the reduction of the

FIGURE 6: Photocurrent-photovoltage characteristics of DSSCs with different CNTs additions.

electrode surface area, and the increase of resistance caused by the charge transfer on the electrode surface.

4. Conclusion

CNTs with different content were added into nanocarbon counterelectrodes of DSSCs, and the effects of CNTs addition on the I^- and I_3^- oxidation reduction in the electrolyte as well as the carbon electrode/electrolyte interface were investigated by cyclic voltammetry and electrochemical impedance spectroscopy. DSSCs were assembled to test the parameters of photovoltaic performance. The results indicated that carbon nanocomposite electrodes with CNTs adding exhibit a highly interconnected network structure with high electrical conductivity and good catalytic activity. When the content of CNTs is 15%, the highest catalytic reduction ability of the electrode is obtained. With the CNTs

adding, the interface capacitance between carbon electrode and electrolyte improves but the electric potential difference of the interface decreases.

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