



Application of carbon materials as counter electrodes of dye-sensitized solar cells

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Abstract

Hard carbon spherule (HCS) has been investigated as a counter electrode for dye-sensitized solar cells. The overall conversion efficiency of the cell reached 5.7%, which is comparable to 6.5% of the counter electrode of platinum-sputtered fluorine-doped tin oxide used in Grätzel-type solar cells under the same experimental condition. It is found that the photovoltaic performance was strongly affected by the specific surface areas of the carbon materials.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention due to its moderate light-to-electricity conversion efficiency (10.4%), easy fabrication and low cost [1,2]. Counter electrode serves to transfer electrons from external circuit to triiodide and iodine in the redox electrolyte. Currently, a layer of platinum coated on transparent conducting oxide (TCO) substrate is widely used as counter electrode in DSSCs. This is not economy way for mass production. Carbonaceous materials are quite attractive to replace platinum due to their high electronic conductivity, corrosion resistance towards I₂, high reactivity for triiodide reduction and low cost [3–5]. Under simulated sunlight (AM 1.5 at 100 mW cm⁻²), graphite, carbon nanotubes and activated carbon showed conversion efficiency of 6.67% (active area 0.40 cm²), 4.5% (0.25 cm²) and 3.9% (0.05 cm²), respectively

[6–10]. It seems that high crystallinity of carbon is favorable. In this letter, a disordered carbon material (named hard carbon spherule, HCS) with different specific surface area was tested as counter electrodes for DSSCs [11–13]. It shows a conversion efficiency of 5.7%. In this case, the efficiency is depending on the surface area.

2. Experimental

2.1. Carbon counter electrode preparation

HCS was prepared following the method reported in the literature [13]. In brief, aqueous sugar solution of 1.5 M was filled in a stainless steel autoclave with a filling ratio of 90%. After 5 h hydrothermal treatment at 190 °C, the obtained black powder was further carbonized at 1000 °C in a tube furnace in argon atmosphere, the obtained sample is named as HCS-1. HCS-1 was activated by heating at 900 °C under water vapor flow for 5 h to give HCS-2 with higher the surface area. Both HCS-1 and HCS-2 were mechanically milled for 2 h to decrease the particle size before next step. A kind of natural graphite powder

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(1 μm average particle size) was also used for comparison. Carbon counter electrode was prepared by screen-printing a slurry of carbon powder, conductive carbon black (30 nm average size) and polyvinylidene fluoride (PVDF) in *N*-methyl-2-pyrrolidone (NMP) onto the F-doped tin oxide conducting glass substrate (FTO, 10 Ω/\square). Then the counter electrode was dried in vacuum oven at 100 $^{\circ}\text{C}$ overnight. Dried electrode is composed of 75 wt% carbon powder, 20 wt% carbon black and 5 wt% PVDF. Fig. 1 shows a cross-section of the electrode. The average thickness of the four kinds of carbon films was about 1.0 μm .

2.2. Cell fabrication

The TiO_2 (P25, Degussa AG, Germany, average particle size 21 nm) porous film was deposited on FTO by a screen-printing technique, followed by sintering at 450 $^{\circ}\text{C}$ for 30 min [14]. The thickness of the TiO_2 film was about 10 μm . The mesoporous TiO_2 film was preheated at 120 $^{\circ}\text{C}$ for 30 min before it was immersed into a solution of the dye ($\text{RuL}_2(\text{NCS})_2 \cdot 2\text{H}_2\text{O}$, $\text{L} = 2,2'$ -bipyridyl-4,4'-dicarboxylic acid, Solaronix) with a concentration of 3×10^{-4} mol/L in dry ethanol overnight [2]. The composition of the organic solvent-based liquid electrolyte is 0.6 M dimethylpropylimidazolium iodide, 0.1 M of iodine, 0.5 M *tert*-butylpyridine, and 0.1 M of lithium iodide in 3-methoxyacetonitrile [14]. Electrolytes were dropped on the dye-anchored TiO_2 films and then counter electrode was clipped firmly with the TiO_2 /dye/electrolyte/glass plate. A mask with a window of 0.15 cm^2 was also clipped on the TiO_2 side to define the active area of the cell.

2.3. Measurements

The cells were illuminated by an Oriol solar simulator (91192) under AM 1.5 (100 mW cm^{-2}) irradiation. The incident light intensity was measured by a radiant power/energy meter (Oriol 70260). The I - V characteristics of the cells were recorded by a potentiostat/galvanostat (Princeton Applied Research, Model 263 A). Cyclic voltammetry

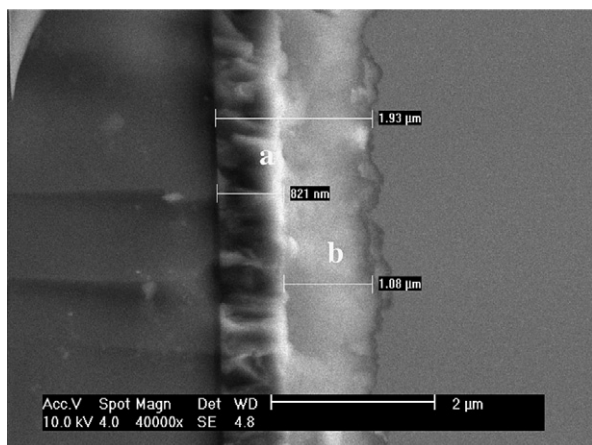


Fig. 1. SEM image of the cross-section of the carbon electrode, (a) fluorine-doped tin oxide conductive layer, (b) carbon film.

was conducted in a conventional three-electrode system in acetonitrile solution containing 0.1 M LiClO_4 as supporting electrolyte, a self-made carbon electrode or Pt plate was used as the working electrode, Pt as a counter electrode and Ag^+/Ag as a reference electrode.

3. Results and discussion

3.1. Redox behaviors

Fig. 2 compares cyclic voltammograms of I_2/I^- system for the HCS-1, HCS-2, graphite and Pt plate electrodes at $[\text{I}^-]/[\text{I}_2] = 9/1$, the same electrolyte of the DSSCs. Two pairs of redox peaks were observed in all cases. The relative negative pair is assigned to the redox reaction (1) and the positive one is assigned to redox reaction (2) [15].



It can be observed that HCS-2 shows high redox reactivity towards I_3^- and I_2 , even higher than Pt. Fig. 3 illustrates the dependence of the current density of the I_3^-/I_2 reduction peaks on the scanning rate. The current density is roughly proportional to $\nu^{1/2}$, suggesting the diffusion process of I_3^- ions is a decisive step to the activity of the counter electrode. The transfer rate of both electrons and ions are fast enough for the reduction rate of I_3^- on the HCS-2 electrode.

3.2. Current–voltage characterization

Fig. 4 gives photocurrent–voltage characteristics of DSSCs using the HCS-1, HCS-2 carbon electrodes (thickness: about 1.0 μm) and the sputtered Pt electrode as the counter electrode. The conversion efficiencies (η) of several carbon materials are summarized in Table 1. As we can see

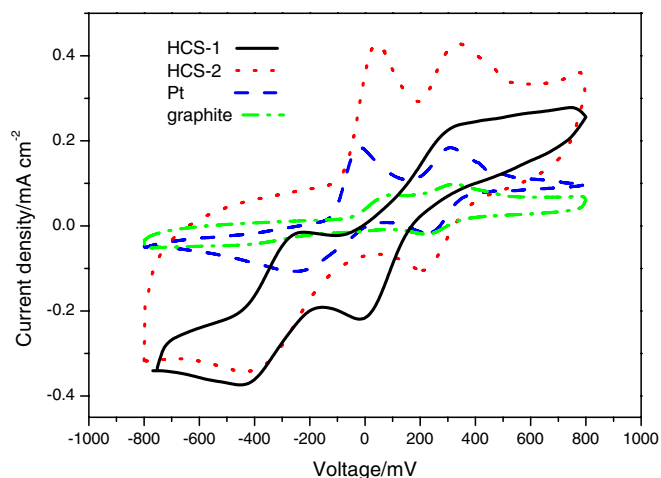


Fig. 2. Cyclic voltammograms for the HCS-1 electrode (solid line), HCS-2 (dot line), Pt plate electrode (dash line) and graphite electrode (dash dot line) in 5 mM $\text{LiI} + \text{I}_2$ acetonitrile solution containing 0.1 M LiClO_4 as the supporting electrolyte. $[\text{I}^-]/[\text{I}_2] = 9/1$, reference electrode: Ag/Ag^+ reference electrode in acetonitrile.

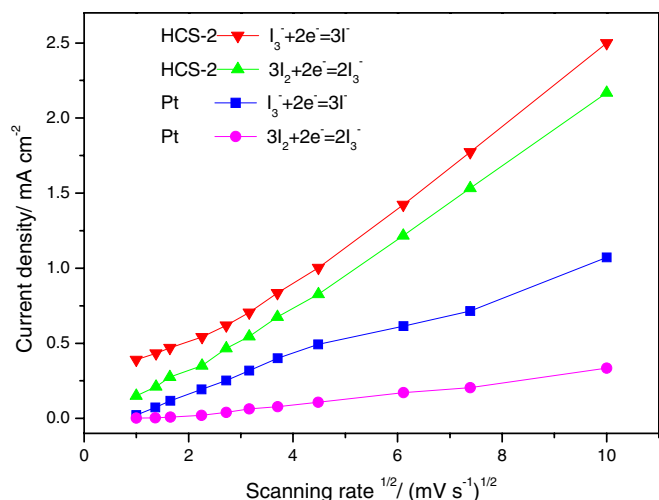


Fig. 3. Peak current of cyclic voltammograms on the HCS-2 carbon electrode and Pt electrode in 5 mM LiI + I₂ acetonitrile solution containing 0.1 M LiClO₄ at different scanning rate. [I⁻]/[I₂] = 9/1, reference electrode: non-aqueous Ag/Ag⁺ reference electrode.

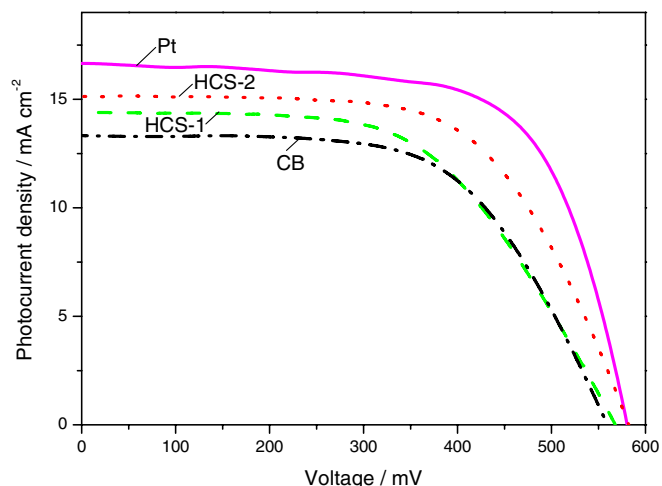


Fig. 4. Photocurrent–voltage characteristics of DSSCs with different counter electrode (thickness: about 1.0 μm) under AM 1.5–100 mW cm⁻² light irradiation. Pt electrode (solid line), HCS-2 (dot line), HCS-1 (dash line), CB (dash dot line).

Table 1
Conversion efficiency (η) of the cells and specific surface area (S) of carbon materials

Catalyst	η %	S^a (m ² g ⁻¹)
Graphite (+20 wt% CB)	3.8	13
Carbon black (CB)	4.5	77
HCS-1	4.7	161
HCS-2	5.7	833
Pt	6.5	–

^a The specific surface area of the samples was determined by nitrogen gas adsorption.

in Table 1, the carbon materials all show lower conversion efficiencies than Pt plate although they show higher redox reactivity. It is known that the Pt plate itself at the same time acts as a light reflector, thus can remarkably improve the efficiency of the solar cell [2]. The results in Figs. 3 and 4 seem support this suggestion.

The electrochemical activity of the carbon film was strongly influenced by surface area of carbon materials (see Table 1). HCS-2 has larger specific surface area (800 m² g⁻¹) than HCS-1, thus gives much higher conversion efficiency. This indicates that electrochemical activity of the cell is enhanced by the large surface of the carbon materials. The graphite (containing 20 wt% carbon black) counter electrode is prepared by the method in the literature [3], and its conversion efficiency (3.8%) is lower than the HCS-2 electrode under the same experimental condition. This indicates that electrochemical activity of HCS-2 is higher than graphite (containing 20 wt% carbon black).

4. Conclusion

In summary, the disordered microporous hard carbon spherules showed high electrocatalytic activity in iodide/triiodide redox reaction, and thus is suitable for fabrication of counter electrode on dye-sensitized solar cells.

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References

- [1] B. O'Regan, M. Grätzel, *Nature* 353 (1991) 737.
- [2] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.* 115 (1993) 6382.
- [3] A. Kay, M. Grätzel, *Sol. Energ. Mat. Sol. C.* 44 (1996) 99.
- [4] H.S. Wroblowa, A. Saunders, *Electroanal. Chem. Int. Electrochem.* 42 (1973) 329.
- [5] M.R. Tarasevich, E.I. Khrushcheva, in: B.E. Conway, J.O'M. Bockris, R.E. White (Eds.), *Modern Aspects of Electrochemistry*, vol. 19, Plenum Press, New York, 1989, p. 295.
- [6] K. Suzuki, M. Yamaguchi, M. Kumagai, S. Yanagida, *Chem. Lett.* 32 (2003) 28.
- [7] N. Koprinarov, R. Stefanov, G. Pchelarov, M. Konstantinova, I. Stambolova, *Synth. Met.* 77 (1996) 47.
- [8] H. Ago, K. Petritsch, M.S.P. Shaffer, A.H. Windle, R.H. Friend, *Adv. Mater.* 11 (1999) 1281.
- [9] D.B. Romero, M. Carrard, W.D. Heer, L. Zuppiroli, *Adv. Mater.* 11 (1996) 899.
- [10] K. Imoto, K. Takahashi, T. Yamaguchi, T. Komura, J. Nakamura, K. Murata, *Sol. Energ. Mat. Sol. C.* 79 (2003) 459.
- [11] Q. Wang, H. Li, L. Chen, X. Huang, *Solid State Ionics* 152 (2002) 43.
- [12] J. Hu, H. Li, X. Huang, *Solid State Ionics* 176 (2005) 997.
- [13] Q. Wang, H. Li, L. Chen, X. Huang, *Carbon* 39 (2001) 2211.
- [14] M.K. Nazeeruddin, P. Péchy, T. Renouard, S.M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, C.A. Bignozzi, M. Grätzel, *J. Am. Chem. Soc.* 123 (2001) 1613.
- [15] A.I. Popov, D.H. Geske, *J. Am. Chem. Soc.* 80 (1958) 1340.