

A novel counter electrode based on hierarchical porous carbon for dye-sensitized solar cells

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Abstract. Hierarchical porous carbons (HPC) were synthesized by a combination of self-assembly and chemical activation method. A mesoporous carbon with large-size pore was used as raw materials. N₂ sorption measurement indicated that plenty of micropores generated within the mesopore wall in the mesoporous carbon during KOH activation. Electrochemical impedance spectroscopy measurement demonstrated a high electrocatalytic activity of HPC electrode for triiodide reduction. The overall conversion efficiency of dye-sensitized solar cells with HPC counter electrode was 6.48%, which is similar to that of the device with conventional Pt counter electrode.

Introduction

Dye-sensitized solar cells (DSCs) have attracted much attention and have been considered as an alternative to a conventional photovoltaic device due to their low production cost, facile fabrication process and high-energy conversion efficiency [1-3]. Simply, a DSCs consists of a dye-sensitized nanocrystalline TiO₂ photoanode, an electrolyte containing redox couple of iodide/triiodide and a counter electrode. Under illumination, a net direct current would pass from the photoelectrode to the counter electrode within DSCs, and then from the counter electrode to the photoelectrode in the external circuit of this device, finally form a circuit. The counter electrode of DSCs serves to transfer electrons from external circuit to the electrolyte. Up to now, a thin layer of Pt deposited on transparent conducting substrates has been frequently used as the counter electrode in DSCs for its high electrocatalytic activity for triiodide reduction [4,5]. However, Pt is expensive and shows limited stability in corrosive electrolyte containing triiodide [6]. Therefore, it is necessary to seek a low-cost alternative material for the counter electrode with chemical inert, high conductivity and good electrocatalytic activity for triiodide reduction.

In recent years, conducting polymers [7,8] and carbon materials employed as the cost-effective alternatives to Pt in DSCs have been extensively investigated. Among these materials, carbonaceous materials are quite attractive due to their high electronic conductivity, corrosion resistance to iodine, high electrocatalytic activity for triiodide reduction and low cost. Several different carbonaceous materials, such as carbon black [9], carbon nanotube [10], hard carbon sphere [11] and mesoporous carbon [12,13], have been used as the counter electrode in DSCs. According to the reports, the carbon material with high surface area and accessible porous structure is more suitable to be used as the counter electrode materials. Therefore, we synthesized a hierarchical porous carbon (HPC) contained large quantity both of micropores and mesopores, and prepared the HPC counter electrode for DSCs. The overall conversion efficiency of DSCs with HPC counter electrode was 6.48%, which is similar to that of the cell with Pt counter electrode.

Experimental

The preparation of HPC is illustrated in Fig. 1, which comprises of MC preparation by self-assembly and the post activation by KOH.

MC was prepared by the self-assembly of the template agent and carbon precursor, and followed by carbonization [12]. The as-prepared MC was ground into the fine powder by using a planetary ball mill. 3g MC powder and 8 ml acetone was added into a solution of KOH (the mass ratio of KOH to

MC is 4:1). The above mixture was stirred at 100 °C in order to evaporate the acetone and water. When the mixture turned into muddy, it was transferred into a tube furnace for activation in N₂ atmosphere at 800 °C. Obtained product was washed with excess distilled water under vigorous stirring till the pH of the mixture was about 7. After filtrating and drying, HPC was obtained.

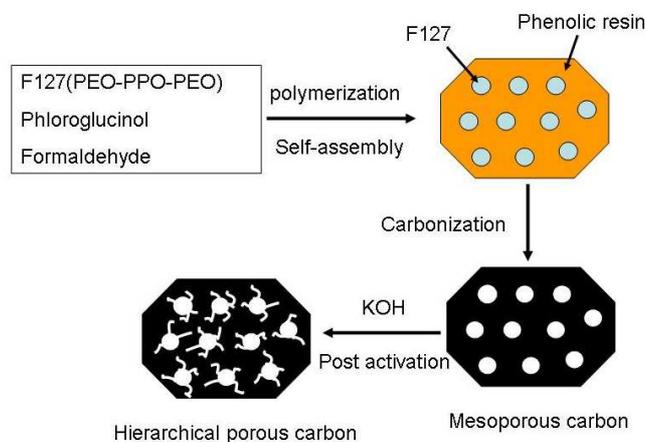


Fig. 1 Preparation strategy of HPC

HPC counter electrodes were fabricated by pasting HPC on fluorine-doped tin oxide (FTO) conducting glass, and then sintered at 400°C for 15 min. HPC paste was obtained by grinding 150 mg the mixture of HPC, 7 ml of n-butanol and 0.1 ml of tetrabutyl titanate in a mortar.

Nanocrystalline TiO₂ electrodes with the thickness of 12 μm were prepared by depositing TiO₂ colloidal paste on FTO glass and then sintered at 450 °C for 30 min in the air. After cooling to 80 °C, the TiO₂ electrodes were immersed into the solution of N3 dye (RuL₂(SCN)₂, L=2,2'-bipyridyl-4,4'-dicarboxylic acid) in ethanol for 12 h at room temperature. A DSC was fabricated by clamping a dye-sensitized TiO₂ electrode, a drop of electrolyte and a counter electrode with two clips. The electrolyte was prepared by dissolving 0.3 M 1-methyl-3-propylimidazolium iodide, 0.05 M iodine, 0.3 M LiI and 0.2 M 4-tert-butylpyridine in 3-methoxypropionitrile.

Micromeritics ASAP 2020 instrument was employed to characterize the surface area and the pore structure of the carbon samples by N₂ sorption at 77 K. Electrochemical impedance spectroscopy was conducted on a SOLARTRON SI 1287 electrochemical interface equipped with a SOLARTRON 1255B frequency response analyzer. The photovoltaic performances of DSCs were measured by a PAR potentiostat (model 273) under irradiation of 500 W Xe lamp at the light density of 100 mW cm⁻².

Results and discussion

The N₂ adsorption-desorption isotherm of MC and HPC are shown in Fig. 2. As shown in Fig. 2, the N₂ adsorption-desorption isotherm of HPC is typical of type IV and displays a pronounced hysteresis loop at medium relative pressure, which indicates that the mesopores were preserved during the KOH activation. On the other hand, in the relative pressure below 0.1, the adsorption amount of HPC is higher than that of pristine MC, which confirms the formation of micropores in large quantities. Accordingly, the as-prepared HPC contain abundant amounts of both the micropores and the mesopores. The pore structural parameters of HPC and pristine MC are summarized in Table 1. The micropore surface area, mesopore surface area and the total pore volume of HPC is higher than that of pristine MC. The increase in the mesopore area may be due to the micropore collapse caused by the over-activation. It is expected that several adjacent micropores collapsed and thus formed the mesopore.

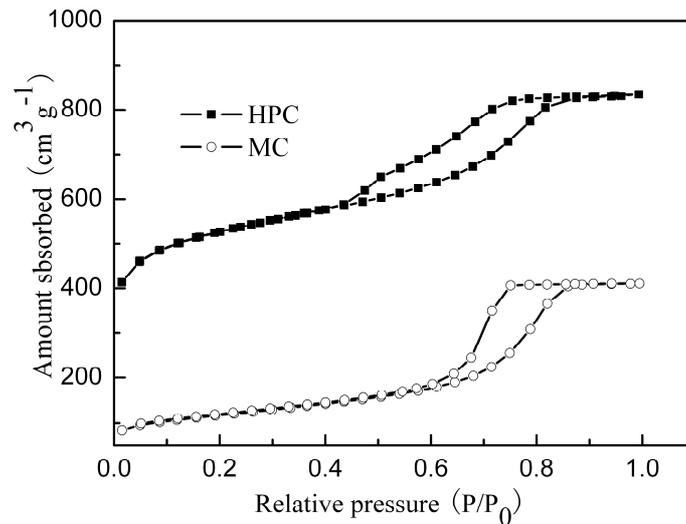


Fig. 2 N₂ adsorption-desorption isotherm of as-prepared MC and HPC sample

Table 1 Pore structural parameters of as-prepared MC and HPC sample

Sample	$S_{\text{BET}}^{\text{a}}$ (m^2g^{-1})	$S_{\text{meso}}^{\text{b}}$ (m^2g^{-1})	$S_{\text{micro}}^{\text{c}}$ (m^2g^{-1})	V_{T}^{d} (cm^3g^{-1})
MC	400	333	108	0.48
HPC	1661	904	1105	1.29

^a BET (Brunauer-Emmett-Teller) surface area; ^b Mesopore surface area; ^c Micropore surface area; ^d Total pore volume;

The electrocatalytic activity of HPC electrode can be studied by using electrochemical impedance spectroscopy. Nyquist plot for HPC electrode measured in a symmetric thin layer cell (shown in Fig. 3a) is displayed in Fig. 3b. In the equivalent circuit for this type of cells described in Fig. 3c, the charge-transfer resistance (R_{ct}), which can characterize the electrocatalytic activity of HPC electrode for triiodide reduction, can be obtained from the diameters of the semicircle in the high frequency region. From Fig. 3b, the R_{ct} $0.3 \Omega \text{ cm}^2$ for HPC electrode is determined. A small value of R_{ct} indicates a high electrocatalytic activity of HPC electrode for triiodide reduction.

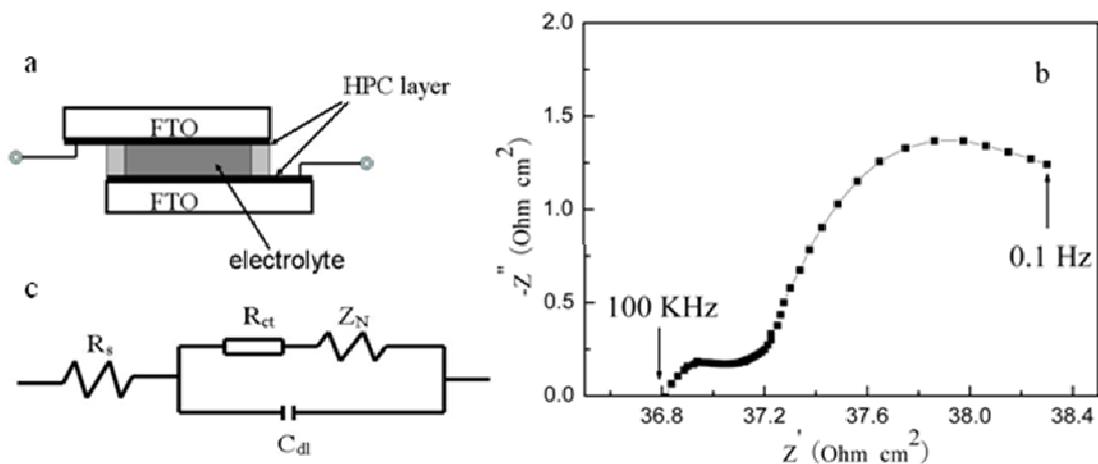


Fig. 3 (a) Electrochemical cell used for the measurement of electrochemical impedance spectroscopy. (b) Nyquist plot for HPC electrode taken at zero bias, ac amplitude 10 mV. (c) The equivalent circuit of the electrochemical cell (R_s : Ohmic serial resistance; R_{ct} : the charge-transfer resistance; C_{dl} : double layer capacitance; Z_N : Nernst diffusion resistance).

The photovoltaic performance of DSCs with HPC counter electrode was obtained under irradiation of 100 mW cm^{-2} . The photocurrent-voltage curve of DSCs with HPC counter electrode was displayed in Fig. 4. For comparison, the photocurrent-voltage curve of DSCs with conventional Pt counter electrode was also shown in Fig. 4. Pt electrode was prepared by thermal decomposition of H_2PtCl_6 on FTO glass (Pt loading is about $10 \mu\text{g cm}^{-2}$). It can be seen that DSCs based on HPC counter electrode exhibits a similar photovoltaic performance to the cell based on Pt counter electrode. The open-circuit voltage, the short-circuit current density, the fill factor and the overall conversion efficiency of DSCs based on HPC counter electrode are 0.626V , 15.44 mA cm^{-2} , 0.67 and 6.48% , respectively. The overall conversion efficiency of the device based on Pt counter electrode is 6.45% .

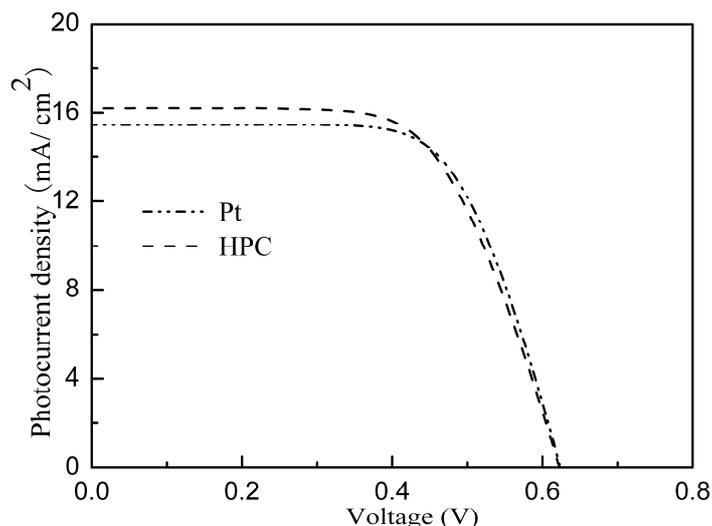


Fig. 4 The photocurrent-voltage curves of DSCs with HPC counter electrode and Pt counter electrode.

Conclusions

HPC containing abundant amounts of both micropores and mesopores were prepared by a combination of self-assembly and post activation. HPC electrode exhibited a high electrocatalytic activity for triiodide reduction. The charge-transfer resistance was $0.3 \Omega \text{ cm}^2$. The overall conversion efficiency of DSCs with HPC counter electrode was 6.48% , which is similar to that of the cell based on Pt counter electrode.

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