Sulfur-doped porous carbon as metal-free counter electrode for high-efficiency dye-sensitized solar cells

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HIGHLIGHTS

- DSSCs based on low-cost sulfur-doped porous carbon (S-PC) counter electrodes are fabricated.
- S doping can significantly enhance the charge-transfer ability toward iodide reduction.
- S-PC electrode shows a comparable photovoltaic performance with Pt electrode.
- Our work provides a new way in making high-efficient but low-cost DSSCs.

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ABSTRACT

In this study, we demonstrate a high performance of sulfur-doped porous carbon (S-PC) as metal-free low-cost counter electrodes (CEs) for dye-sensitized solar cells (DSSCs). The S-PC material is synthesized by using pitch as carbon source and basic magnesium sulfate (BMS) whiskers as both template and S source. The doped sulfur is mainly present in the C–S–C configuration. The enhanced electrocatalytic performance can be attributed to the S atoms doped into the carbon framework which has large effective surface areas due to their porous or rough morphology. Therefore, it enhances the asymmetry of the atomic charge density in C atoms, leading to a large number of reduction sites and low charge transfer resistance. The S-PC significantly enhances the performance compared to the pure porous carbon (PC) due to the lower charge-transfer resistance. The DSSC with S-PC as the CE exhibits a high conversion efficiency of 6.97% which is comparable to that of the traditional Pt CE (7.28%).

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1. Introduction

Since the pioneering work reported by M. Grätzel and B. O'Regan in 1991 [1], dye-sensitized solar cells (DSSCs) have aroused considerable attention as potential candidates to replace traditional silicon-based solar cells [2,3]. DSSCs as a representative of the third generation photovoltaic devices have many virtues, such as the use of cheap materials, the ease of device fabrication, the eco-friendly nature, and the relatively high energy conversion efficiency [4–6]. A typical DSSC is composed of a transparent conducting oxide on glass, a dye-sensitized nanocrystalline TiO_2 film as the photoanode, an electrolyte with the redox couple such as iodide/

triiodide (I^-/I_3^-) and a counter electrode. Among these, the counter electrode (CE) is an indispensable component which collects electrons from the external circuit and then injects electrons into the redox electrolyte to catalyze triiodide reduction [7,8]. For a superior alternative CE, it should possess high reduction electrocatalytic activity for the redox couples, low resistance to transport charges, good chemical stability and a low cost [9]. In most cases, the noble metal platinum (Pt) is the most commonly used cathode material for the CE of DSSC [10]. Although it has been confirmed that Pt is a superior CE material with excellent catalytic activity and high electrical conductivity, the major drawbacks such as the high cost, the limited reserves in nature and the susceptibility to corrosion by iodide stimulate the search for new counter electrodes. Therefore, it is highly desirable to exploit a competent substitute for reducing the overall fabrication cost, without compromising in photovoltaic performances of DSSCs.

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To overcome the above-mentioned limitations associated with Pt-based counter electrode, until now several kinds of materials have been applied to replace or reduce Pt-based electrodes in DSSCs, such as conductive organic polymers [11–13], metal compounds (carbides, nitrides, etc.) [14–16], alloy materials [17–20] and carbonaceous materials [8,21–32]. In particular, carbonaceous materials like graphite [21,22], carbon black [23], carbon nanofibers [24,25], activated carbon [26], carbon nanotube [8,27,28], and graphene [29–31] have been used as CEs in DSSCs. In contrast to Pt, carbon-based materials can be produced in scalable quantity at low cost, and they have remarkable electrical conductivity and better corrosion stability in DSSCs. So the carbonaceous materials have been widely studied in hopes of finding promising alternatives to Pt-based materials. However, the carbon-based counter electrode can hardly achieve a high performance due to the comparatively low reduction activity. In order to resolve the road block, enormous efforts have been focused on the doping heteroatoms (*e.g.* N, B, P and S) into carbon lattice to break the electroneutrality of carbon with minimum structural damage to improve the electrocatalytic performance. To date, numbers of researchers have demonstrated that doping nitrogen (N) or boron (B) into a graphitic framework used as counter electrode in DSSCs exhibited notably higher electrocatalytic activity [32–38]. Meanwhile, sulfur (S) doped carbon materials have been widely used as electrode materials in oxidation reduction reaction (ORR) [39,40] and Li-ions batteries [41,42] which exhibit high performance. However, the synthesis and application of S-doped carbon material as a CE in a DSSC is quite sparse up to date. So far only N−S dual-doped graphene nanosheet based on an I^-/I_3^- redox couple and N−S dual-doped graphene reduced graphene oxide based on an disulfide/thiolate redox couple have been reported by G. Kannan et al. [43] and Luo et al. [44] respectively. Nevertheless, to the best of our knowledge, the application of the single sulfur-doped porous carbon (S-PC) as a counter electrode for DSSC has never been investigated.

Here, according to our previous work, we employed a cost-effective strategy to massively synthesized S-PC by using pitch as carbon source and basic magnesium sulfate (BMS) whiskers as both template and S source, and then the as-synthesized S-PC was used as Pt-free CE which achieved a high performance in I^-/I_3^- redox shuttle mediated DSSCs [45,46]. The structural, morphological properties, chemical compositions of the synthesized materials and electrocatalytic activities were systematically investigated. Our studies reveal that S doping can effectively enhance the catalytic activity of PC. The DSSC with S-PC CE shows a conversion efficiency of 6.97% which is comparable to that of Pt CE under the same conditions.

2. Experimental

2.1. Material and chemicals

All chemicals were purchased from Sigma−Aldrich Corporation (Shanghai, China) in analytical purity and directly used without any further purification.

2.2. Synthesis of S-PC and PC

BMS whiskers were prepared by a previously reported hydrothermal procedure [47]. A typical synthesis route for S-doped porous carbon (S-PC) according to our previous reports was as follows [45,46]. Firstly, the BMS whiskers were added into the pitch toluene solution with violent agitation, followed by filtering and drying in an oven at 80 °C. Secondly, the obtained pitch/BMS whisker mixture was put in an alumina combustion boat, then the

boat in a quartz tube furnace was heated to 900 °C in flowing Ar for 30 min. Finally, the obtained black power was taken out after cooled to room temperature and purified by a hydrochloric acid and deionized water washing, respectively. The as-produced S-PC was dried overnight at 80 °C. For comparison, the porous carbon (PC) sample was prepared under the same conditions using MgO porous whiskers as templates without any addition.

2.3. Fabrication of the counter electrodes

The counter electrodes were prepared according to the following procedure. The as-synthesized S-PC was homogeneously dispersed in 2-propanol solution (1 mg/mL) by ultrasonication for 60 min. The resultant solution was sprayed directly onto cleaned fluorine-doped tin oxide (FTO) glass [48]. Briefly, the dispersion solution was loaded into a plastic syringe equipped with a 10-gauge stainless steel hypodermic needle. The needle was connected to a high voltage power supply. Then a high voltage of 9.0 kV was applied between a metal orifice of the needle and the conducting copper plate substrate at a distance of 5 cm. The feed rate was controlled by the syringe pump at a constant flow rate of 120 μL min^{-1}. The electric field overcomes the surface tension of the droplets, resulting in the minimization of numerous charged mists. The obtained film was finally annealed in Ar atmosphere at 250 °C for 1 h prior to device fabrication. The fabrication process of the PC CEs was prepared in similar way as that of the S-PC CEs. For comparison, platinized FTO electrode was prepared by drop-casting 10 mM H_2PtCl_6 in 2-propanol and calcination at 400 °C for 15 min.

2.4. Preparation of photo anodes and assembling the DSSCs

The FTO conducting glass (8 Ω/square, Yingkou OPV Tech New Energy Co., Ltd., China) was cut into 10×15 mm^2 and sonicated in a successive series of baths of deionized water, ethanol and acetone for 15 min each to clean the surface. The working electrode was composed of a layer of 10-μm-thick nanocrystalline TiO$_2$ with average diameter of 20 nm (Kunshan Sunlaite New Energy Technology Co., Ltd., China) and a light-scattering layer of 2-μm-thick TiO$_2$ with 300 nm particle size prepared by screen printing technology. The surface area of the TiO$_2$ electrodes was 0.16 cm^2. The FTO glass with the TiO$_2$ film was gradually heated to 450 °C (rate = 10 °C/min) in air, and subsequently sintered at that temperature for 30 min. After sintering at 450 °C and cooling to 80 °C, it was immersed into an N719 (Dalian Hepta Chroma Solar Tech Co., Ltd., China) dye solution (0.3 mM) in absolute ethyl alcohol at the room temperature for 14 h. Then the N719-incorporated electrode was carefully rinsed with absolute ethyl alcohol. The working electrode and counter electrodes were sandwiched together with a 30 μm Surlyn (Yingkou OPV Tech New Energy Co., Ltd., China) and then hot pressed to form a seal. The electrolyte which consists of 0.05 M I$_2$, 0.1 M LiI, 0.1 M guanidinium thiocyanate, 0.6 M 1-butyl-3-methylimidazolium iodide, and 0.5 M 4-tert-butyl pyridine in acetonitrile was injected through a hole from the back side of the counter electrode via vacuum backfilling. The hole was sealed with cover glass using a glass cement.

2.5. Characterization

The morphology of the synthesized samples was characterized transmission electron microscopy (TEM; FEI F20). The pore texture was characterized by nitrogen adsorption at 77 K using Micromeritics ASAP 2020 instrument. X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advance X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo Fisher K-Alpha spectrometer. Current-