



Interconnected nitrogen and sulfur dual-doped porous carbon as efficient electrocatalyst for triiodide reduction in dye-sensitized solar cells



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HIGHLIGHTS

- An interconnected N/S-PC has been used as counter electrode in DSSC.
- N/S dual-doping can significantly enhance the activity toward I_3^- reduction.
- N/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

Exploiting cost-effective and efficient counter electrodes (CEs) for the reduction of triiodide (I_3^-) has been a persistent objective for the development of dye-sensitized solar cells (DSSCs). Here, we propose a strategy for the synthesis of nitrogen and sulfur dual-doped porous carbon (N/S-PC) via a thermal annealing approach by using melamine as N source, and basic magnesium sulfate (BMS) whiskers as S source and templates. Benefiting from the high surface area, unique interconnected structural feature and synergistic effects of N/S dual-doping, the N/S-PC shows excellent electrocatalytic activity toward I_3^- reduction, which has simultaneously been confirmed by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements. The DSSC devices with N/S-PC CE exhibit a PCE up to 7.41%, which is higher than that of DSSC devices with single heteroatom (N or S) doped CEs and even Pt CEs (7.14%).

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1. Introduction

Harvesting energy directly from sunlight using photovoltaic technology is being increasingly recognized as an essential component of future global energy production. Over the past two decades, dye-sensitized solar cells (DSSCs) have attracted great attention because of their facile assembly, low manufacture cost, as well as recent high power conversion efficiency [1–3]. A typical design of DSSCs consists of a mesoporous TiO_2 photoanode sensitized by dye molecules, an electrolyte with iodide-triiodide (I^-/I_3^-)

as redox couple, and a counter electrode (CE) as the cathode. The key roles of CEs in DSSCs are to transfer electrons from the external circuit to the electrolyte and catalyze the reduction of the redox couples used as mediators to regenerate the sensitizer after electron injection [4,5]. Platinum (Pt) has been widely employed as the standard CE in DSSC owing to its excellent electrocatalytic activity and electrical conductivity [6]. However, Pt is an expensive and scarce noble metal, and it is unstable against corrosion. These drawbacks prevent Pt from being used for large-scale manufacturing of DSSCs, which also have stimulated great efforts to exploit substitutes for Pt in order to reduce the overall cost and without sacrificing the cell performance. In recent years, a range of materials have been proposed as substitutes for Pt CEs in DSSCs, including carbonaceous materials [7–9], inorganic compounds [10,11], and conductive polymers [12–14]. In particular,

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carbonaceous materials, such as carbon black [15], mesoporous carbon [16,17], carbon nanotubes [18,19] and graphene nanosheets [20–22], have been under remarkable investigations because of their excellent electrical conductivity, low cost, as well as high specific surface areas and good chemical stability, enabling them to serve as potential candidates to replace Pt-based CEs. Nevertheless, the progress is far from satisfactory considering that the resultant DSSCs exhibit comparatively poor performance compared with those using Pt-based CEs, owing to the relative low electrocatalytic activity of pure carbon-based CEs. Therefore, rational design of carbonaceous material with high electrocatalytic activity being comparable to or outperforming Pt still remains highly desirable. And it is closely related to the defective sites and its electronic structures within carbon matrix.

Recently, both theoretical calculation and experimental studies have proved that the introduction of heteroatoms (e.g., N, B, S and P) into carbon frameworks is an effective way in improving its electrical properties and electrocatalytic activity, which are originated from the changes in charge and spin densities of carbon atoms adjacent to the doped heteroatoms [23–28]. Lately, researchers have focused their attention on exploiting dual-doped carbon nanomaterial to further enhance the electrocatalytic activity due to the increased number of dopant heteroatoms and the synergetic effect arising from nitrogen and non-nitrogen element [29–33]. However, the application of dual-doped carbon materials as CEs in DSSCs is quite sparse up to date. Kannan et al. [34] first reported that the DSSCs based on I^-/I_3^- redox shuttle with N and S dual-doped graphene nanosheets CEs obtained a conversion efficiency of 7.42%, similar to that of the Pt CEs (7.56%). Xu et al. [35] revealed that N and S dual-doped could enhance the catalytic activity of graphene-like carbon films for I_3^- reduction. However, the obtained efficiency was relatively low (4.22%) due to the limited active sites of thin films. Additionally, Yu et al. [36] recently proposed to dope graphene with both B and N atoms to further improve the catalytic activity of I_3^- reduction for DSSCs. It was found that the commonly used nanostructured carbon material was graphene nanomaterials. However, the strong π - π interaction between graphene sheets would cause inevitable aggregation and restacking, which significantly reduced the surface area and active sites [37,38]. Due to the relatively high surface area and interconnected pore structure, porous carbon possesses a vast range of application prospect [39,40]. As is well known, the large surface area of porous carbon materials will affect the density of the catalytically active sites, which is closely related to the catalytic activity. Furthermore, the porous structure with high surface area provides favorable paths for mass transport, in which more active sites are exposed to the redox couple in the electrolyte, thus facilitating the ingress of I_3^- , the reduction of I_3^- and the diffusion of I^- . Hence, it is anticipated that dual-doped porous carbon materials with high surface area, interconnected porous structure and good conductivity will exhibit high activity for I_3^- reduction.

Herein, we report an approach to synthesize N and S dual-doped porous carbon (N/S-PC) through pyrolyzing the basic magnesium sulfate (BMS) whiskers/PVA nanofibers containing melamine dopant. The obtained N/S-PC shows an interconnected network structure with enriched nanopores, high surface area ($814 \text{ m}^2 \text{ g}^{-1}$) and good conductivity. Owing to the unique structural features and synergistic effects of N and S dual-doped, the N/S-PC offers great advantage as CE material for DSSC. The N/S-PC-based DSSCs exhibit a PCE as high as 7.41%, which is much better than that of porous carbon catalysts doped solely with S or N atoms due to the synergistic effect of the dual-doped heteroatoms. Considering the efficiency obtained by Pt-based DSSCs (7.14%), it is evident that the proposed N/S-PC exhibits great potential in replacing Pt as CEs in DSSCs.

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 N/S-PC, S-PC, N-PC and PC

A typical synthesis route for N/S-PC was as follows, similar to our previous works [27,41]. Firstly, the basic magnesium sulfate (BMS) whiskers as templates and S source were prepared by a previously reported hydrothermal procedure. Secondly, 2 g polyvinyl alcohol (PVA) was dispersed in 80 ml H_2O under vigorous stirring at 60°C to form a transparent solution. Then 2 g melamine as N source and 2 g BMS whiskers were added into the PVA solution and stirred for 8 h. The mixture was dried at 80°C in an oven overnight and then further carbonized at 900°C under Ar for 2 h in the tube furnace with a heating rate of $3^\circ\text{C}/\text{min}$. Finally, after being cooled to room temperature, the resultant black powder was taken out and immediately purified by hydrochloric acid and deionized water washing, respectively. The as-produced N/S-PC was dried at 80°C for 12 h. S-PC sample was prepared without melamine, and the other procedures were the same with the case of N/S-PC. For the synthesis of N-PC and PC, the MgO whiskers were employed as the templates, and the following procedure is similar to the synthesis of N/S-PC and S-PC, respectively.

2.3. Fabrication of the counter electrodes

A homogeneous solution was prepared by dispersing the N/S-PC powder into 2-propanol solution (2 mg/mL) under ultrasonication for 1 h. Then the resultant solution was deposited directly onto a cleaned fluorine-doped tin oxide (FTO) glass using an e-spray technique according to our previous work [27]. The obtained film was immediately annealed in Ar atmosphere at 250°C for 1 h prior to device fabrication. The fabrication processes of the S-PC, N-PC and PC CEs were in the same way compared with N/S-PC CEs. For comparison, Pt CE was prepared by deposition of 10 mM H_2PtCl_6 in 2-propanol and calcination at 400°C for 20 min in furnace.

2.4. Fabrication of the DSSCs

In the fabrication of DSSC device, a $12 \mu\text{m}$ thick film consisting of 20 nm-sized TiO_2 particles (Kunshan Sunlaite New Energy Technology Co., Ltd, China) was first screen-printed on the FTO electrode and further screen-printed by a $2 \mu\text{m}$ thick second layer of 300 nm light-scattering TiO_2 particles. The active area of TiO_2 electrodes was 0.16 cm^2 . Then the TiO_2 electrodes were gradually heated to 450°C with a heating rate of $10^\circ\text{C}/\text{min}$ in air, and subsequently sintered at that temperature for 30 min. After sintering and cooling to room temperature, the obtained photo anodes were dye-coated by immersing them into an N719 (Dalian HeptaChroma SolarTech Co., Ltd, China) dye (0.3 mM) ethanol solution at the room temperature for 16 h. The working electrode and counter electrode were sandwiched together with a $30 \mu\text{m}$ Surlyn (Yingkou OPV Tech New Energy Co., Ltd, China) and then sealed through hot-pressing using a heat sealing machine at 115°C for 25 s. 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. Finally, the hole was sealed with a Surlyn film and a thin glass cover by heating.

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