



Nitrogen and phosphorus co-doped carbon nanosheets as efficient counter electrodes of dye-sensitized solar cells



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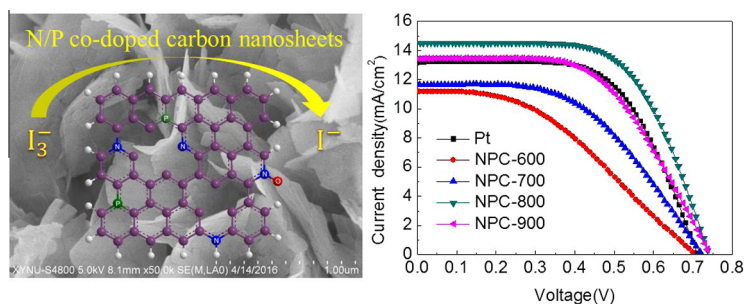
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HIGHLIGHTS

- N/P co-doped carbon nanosheets were synthesized by a simple direct pyrolysis method.
- N/P co-doped carbons showed an enhanced catalytic activity as Pt-free CEs of DSSCs.
- Platelet-like morphology and proper N/P doping level improved catalytic activity of CEs.
- The DSSC with N/P co-doped carbon delivered a higher η (6.74%) than Pt-based one (5.76%).

GRAPHICAL ABSTRACT



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ABSTRACT

N/P co-doped carbon nanosheets (NPC) have been prepared by a simple direct pyrolysis method using amino tris(methylene phosphonic acid) (ATMP) as carbon, nitrogen and phosphorus co-sources, and utilized as Pt-free counter electrodes (CEs) for dye-sensitized solar cells (DSSCs). The prepared N/P co-doped carbons with amorphous structure and platelet-like morphology exhibit rapid electrolyte diffusion. More importantly, the content of N/P dopants and doping states are temperature-dependent, and particularly the N/P dopants are easy to be eliminated at high temperature, accompanied with the introduction of defective sites into the carbon matrix, thus regulating the catalytically active sites and electrical conductivity of N/P co-doped carbon nanosheets. The electrochemical impedance spectroscopy, Tafel, and cyclic voltammetry measurements demonstrate that the NPC carbonized at 800 °C (NPC-800) with appreciable N/P doping content and suitable defective sites displays the best catalytic activity. As a consequence, the DSSC based on NPC-800 CE achieves a power conversion efficiency of 6.74%, which is higher than that of the cell with Pt CE (5.76%).

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1. Introduction

Solar cells are regarded as the most probable alternatives to hazardous and ever depleting fossil fuel, as well as the promising solution for solving the global energy crisis and environmental

pollution of twenty-first century. Solar cell technology has various attractive advantages like sustainability, cleanness, high efficiency and no emission of harmful byproducts. Dye-sensitized solar cell (DSSC) is one of the most promising solar cell technologies because of its lower cost and easier fabrication process than silicon-based solar cell [1–3]. Typically, the DSSC consists of three crucial components: a dye-sensitized TiO₂ photoanode, an electrolyte containing iodide/triiodide redox couples, and a Pt counter electrode (CE). CE is an important part in DSSC for transferring the electrons from

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CE/FTO interface to the electrolyte and catalyzing the reduction of triiodide to iodide, and its electrocatalytic activity strongly affects the final photovoltaic performance [4]. Traditional Pt is a desirable CE electrocatalyst for its extraordinary catalytic property and superior electrical conductivity. However, the high price and low abundance of Pt, and its modest long-term stability in corrosion electrolytes hamper its practical application [5]. In order to substitute Pt catalysts, numerous efforts have been devoted to exploring Pt-free CEs, such as nonprecious metal compounds (carbides [6], nitrides [7] and sulfides [8], etc.), metal alloys [9–12], conducting polymers [13], carbonaceous materials [14–16], and their composite materials [17–21]. Among these new CE materials, carbonaceous materials are the most viable choice in terms of their low cost, remarkable electrical conductivity, high chemical stability and good catalytic activity. A variety of carbonaceous materials [22–24], including carbon black, activated carbon, carbon nanotubes, graphite, mesoporous carbon and graphene have established themselves as robust Pt-free CE alternatives and arouse great attention to the researchers.

In recent years, incorporation of one kind of heteroatom (N, P, B, S) into carbon framework has been widely accepted to be an effective way for modulating the electronic structure and surface properties of carbonaceous materials and improving the electrocatalytic activity of carbon CEs [25–28]. For instance, Yang et al. demonstrated that S dopant in porous carbon could increase the charge density asymmetry of carbon atoms and create lots of catalytically active sites that lowering the charge transfer resistance [28]. Nitrogen-doped hollow core-mesoporous shell carbon (N-HCMSC) capsules were prepared by Kim's group [25]. They concluded that the improvement of the catalytic activity mainly benefits from the positive effects of the pyridinic and quaternary N species. Wang et al. utilized the prepared phosphorus-doped reduced graphene oxide (P-rGO) as a CE electrocatalyst in DSSC [26]. They attributed the enhanced electrocatalytic activity of rGO to the P-doping, which induced charge redistribution, electrons conjugation effect and defect sites. In brief, the single heteroatom doped carbons have been extensively studied and achieved the inspiring scientific progress. However, compared to the single heteroatom of N, P, and S doping, there is only one report about the synthesis and application of binary-heteroatom doped carbon as a CE for DSSC. In Li's work [29], the N/S dual-doped graphene-like carbon films were synthesized by chemical vapor deposition (CVD) and significantly outperformed their single-heteroatom counterparts and the pristine one when utilized as CE catalysts in DSSCs. The introduced defects and additional electrocatalytic active sites in the carbon structure due to the N/S co-doping may be responsible for the enhancement of the charge transfer across the CE/electrolyte interface. Until now, the co-doped carbon with other two kinds of heteroatoms (e.g. N/P, N/B, and B/P) as CE catalyst is rarely reported elsewhere, and the developments of dual-heteroatom doped carbon CEs with high performance become scientifically necessary. Fortunately, various N/P co-doped carbons have been explored in catalyzing the oxygen reduction reaction and exhibited the remarkably synergetic co-doping effect [30,31]. Recent studies proposed that N/P co-doping on carbon induced larger asymmetrical spin and charge density relative to single doping, which are particularly attractive for electrocatalytic application [32–36]. Inspired by these incentives, the co-doped carbon with N and P could be extended to the application of electrocatalytic reduction of the triiodide for CE catalyst in DSSC. To fully demonstrate the potential electrocatalytic activity of N/P co-doped carbons on reducing triiodide, as well as gain mechanistic insight into the roles of heteroatoms played, the manipulation of N/P-heteroatom-containing carbons and the modifying effect of N/P co-doping should also be investigated.

Additionally, the synthetic techniques of N/P-heteroatom doped carbon materials often involve the coprolysis of individual N, P and C, or C/N and P containing precursors, as well as the post-treatment through further carbonization of as-prepared carbon with additional N and P-containing precursors [30,35,37–39]. The main drawbacks of these synthesis routes are relatively complicated, costly and time-consuming. Moreover, the uniform and high-level heteroatom doping in the resultant products is still a big challenge.

Herein, the N/P co-doped carbon nanosheets were synthesized by direct pyrolysis of organophosphorus acid Amino tris(methylene phosphonic acid) (ATMP) in this work, in which the single precursor with the symmetric framework served as carbon, nitrogen and phosphorus co-sources. The N/P co-doped carbons were firstly exploited as Pt-free CE alternatives for DSSCs, and exhibited an excellent electrocatalytic performance for the triiodide reduction, which are comparable and superior to Pt CE. To further gain insight into the synergetic effects of dual-heteroatom doping, the carbons with different nitrogen/phosphorus amount were systematically studied.

2. Experimental section

2.1. Synthesis of N/P co-doped carbon nanosheets (NPC)

In a typical synthesis procedure, a certain amount of solid organophosphorus acid ATMP were placed in a quartz boat and carbonized at 600, 700, 800 and 900 °C for 3 h in a tube furnace with a heating rate of 2 °C min⁻¹ under nitrogen, respectively. The resultant products were collected and correspondingly denoted as NPC-*x*, where *x* represents the pyrolysis temperature.

2.2. Preparation of CEs and fabrication of DSSCs

The NPC-*x* CEs were prepared as follows. 0.13 g of NPC-*x* was firstly dispersed in 3 mL of deionized water and sonicated for 1 h to prepare a dispersion solution. Next, 20 mg of TiO₂ (P25, Degussa) and 15 mg of PEG-2000, as the binder, were successively added to 2 mL of deionized water, stirred continuously for 1 h, and then transferred into the above dispersion solution. After stirring for 2 h, the resulting paste was coated on a FTO (14 Ω □⁻¹, Nippon Sheet Glass) and dried in a vacuum oven at 120 °C for 10 h to obtain NPC-*x* CEs. As references, Pt CEs were also prepared via thermal pyrolysis of 30 mM H₂PtCl₆·6H₂O solution on the FTO substrates at 400 °C for 30 min.

The dye-sensitized TiO₂ photoanodes were fabricated as reported in our previous work [14]. An active area of 0.5 × 0.5 cm² was selected by scrapping the side portions of the composite film off the photoanode. The DSSC device was assembled as sandwich-like structure with a dye-sensitized TiO₂ photoanode (ca. 9 μm in thickness), an electrolyte and a prepared NPC-*x* (ca. 13 μm in thickness) or Pt CE. The photoanode and CE were spaced by using 50 μm scotch tapes between them, and then hot pressed together using thermoplastic surlyn to form a seal. The liquid electrolyte was injected to the space between photoanode and CE by an injector, and the electrolyte consists of 0.05 M I₂, 0.5 M LiI, 0.3 M 1,2-dimethyl-3-propylimidazoliumiodide (DMPII), and 0.5 M 4-tert-butylpyridine with acetonitrile as the solvent.

2.3. Characterization

X-ray diffraction (XRD) measurements were conducted on a Bruker D8 Focus diffractometer, with Cu K_α radiation (λ = 1.5406 Å) operated at 40 mA and 40 kV. Scanning electron microscopy (SEM) measurements were carried out on a Jeol JSM-7500F

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