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Buffering agents-assisted synthesis of nitrogen-doped graphene with oxygen-rich functional groups for enhanced electrochemical performance



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HIGHLIGHTS

- Two type of doped graphene can be obtained using different buffering agents.
- The graphene can be doped with controlled nitrogen and oxygenic groups.
- The nitrogen-doped graphene exhibits the capacitance of 383 and 356F/g at 1A/g.
- The capacitance attenuation is 4.8% and 8.81% from 500 to 10000 cycles.
- N- and O- functional groups give different contribution to the capacitance.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, designed growth of two type of N-doped graphene nanosheets has been investigated using $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ as buffering agents, respectively, in a mild hydrothermal process. X-ray photoelectron spectroscopy (XPS) characterization indicates that the graphene nanosheets grown using $\text{NH}_4\text{H}_2\text{PO}_4$ (NGC) have lower nitrogen but higher oxygen content than those using $(\text{NH}_4)_2\text{HPO}_4$ (NGL). Electrochemical measurements in three-electrode systems show that both type of the graphene products exhibit superior electrochemical performance (383 and 356 F g⁻¹ at 1 A g⁻¹). While the specific capacitance of NGC is steadily higher than that of NGL under all investigated current densities, the capacitance attenuation of NGL is 4.80% from 500 to 10000 cycles showing more durable in cyclicality than that of NGC (8.81%). The two-electrode supercapacitor devices for NGC and NGL exhibit high energy density of 12.21 Wh kg⁻¹ and 9.28 Wh kg⁻¹ at 0.25 A g⁻¹. The difference in electrochemical behaviors between NGC and NGL electrodes can be attributed to the different contribution of nitrogen and oxygenic

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groups. The buffer agents assisted synthesis procedure coupled with the reasonable capacitance performance suggests an alternative way in the designed functionalization of graphene for developing high performance supercapacitors.

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1. Introduction

Supercapacitors are a promising energy storage device with desirable properties intermediate to those of common capacitors and batteries, featuring the advantages of high power density, rapid charge and discharge rate and long cycle life [1–3]. According electric energy storage mechanism, supercapacitors are generally classified into electric double layer capacitors (EDLCs) and Faraday pseudo-capacitors (FPCs). The former stores charges in the double layer at the electrode/electrolyte interface, while the later stores charges via the fast Faraday reaction on the electrode surface [4]. Since the charge transfer ability of FPCs is much stronger than that of EDLCs, promising much higher capacity than that of EDLCs, exploration of novel materials for FPCs has arisen steadily increasing research interest.

Carbon materials such as activated carbons [5,6], carbon nanotubes (CNTs) [7], graphene [8], carbon aerogels [9,10], or mesoporous carbons [11] have been widely investigated as electrode materials due to their superior conductivity, different allotropes, accessibility and environmental friendliness. However, chemically inert and hydrophobic surface of carbon makes it weakly interactive with other media and poorly soluble in water and common organic solvents, which limits its application in various electrochemical fields. Fortunately, foreign atom (such as O, N, B, P, etc.) doping has been proven to be an effective way in enhancing comprehensive electrochemical properties of carbon matrix [12–14]. Among these heteroatoms, N element has been most widely investigated benefiting from its high electronegativity, small atomic diameter, and additional free electrons contributing to the conduction band of carbon [15]. In addition, incorporating N atoms in the carbon grid could improve the wettability between the carbon surface and electrolytes, and trigger Faraday reaction [16]. Recently, more efforts have been made on the N-doped graphene due to its high specific capacitance and good cycle ability, in which the pyridine nitrogen (N-6) and pyrrole nitrogen (N-5) can improve the pseudo-capacitance by oxidation-reduction reaction, and the graphitic nitrogen (N-Q) is conducive to the charge and discharge process of electron transport [16]. Apart from nitrogen doping, it has been recently demonstrated that oxygenic functional groups also play an important role in determining capacitance of carbon materials. Apart from N-doping, Xu [17] demonstrated that graphene oxide (GO) is supposed to be suitable for electric electrode materials with higher capacitance, up to 189 F g^{-1} , than that of graphene due to an additional pseudo-capacitance effect of attached oxygen-containing functional groups on its basal planes. From then on, a lot of literature has demonstrated that hydroxyl, carboxyl, carbonyl in the alkaline medium can work in the Faraday reaction to produce pseudo-capacitance, and quinone is proposed to be the largest contribution to the pseudo capacitance in the acid medium [18–21]. Hence, porous carbon [22], carbon fiber [23], carbon nanotube [24,25], carbon sphere [26] decorated with N and O atoms have been successfully synthesized in which good rate capability and excellent cycling stability in varied electrolyte have been well documented. The presence of the N- and O-based functional groups not only improves the wettability between the carbon surface and the electrolyte solution by the formation of polar

functional groups, enhancing the interaction between the carbon electrodes and electrolytes, but also elevate the electrochemical energy storage of the carbon materials by the generation of a pseudo-capacitance.

Although synthesis of N-doped graphene with residual O-groups has been comprehensively reported [27,28], the effect of the functional groups has few been addressed. In addition, N-doped graphene is usually synthesized under alkaline conditions, and the fabrication of N-doped graphene under acidic conditions has rarely been reported [29–31].

In this paper, we prepared two types of nitrogen-doped graphene with oxygen-rich functional groups (NGC and NGL) using amphiprotic phosphates, $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ as buffering agents, respectively. After N-doping and reduction process, oxygen content of NGC is higher than that of NGL, while N content of NGL is higher than that of NGC. While both samples exhibit superior electrochemical properties, how the N- and O- functionalized groups affect the capacitive behaviors of the samples is different. Our research work here may provide a meaningful reference for the future understanding of the synergistic effect of N and O-enriched functionalized groups in carbon materials.

2. Experimental

2.1. Materials

Graphene oxide (GO) was bought from XF nano CO. Ltd. (China). Other chemicals such as diammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), ammonium dihydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$), bought from Tianjing Chemical Reagent CO. Ltd., were all of analytical grade.

2.2. Synthesis of nitrogen-doped graphene

The GO (0.05 g) was dispersed in deionised water (DI) (75 mL) and 0.5 g $\text{NH}_4\text{H}_2\text{PO}_4$ (or the same quality of $(\text{NH}_4)_2\text{HPO}_4$) was added to this GO solution with continuous stirring. After 2 h, the solution was sealed into a 80 mL Teflon autoclave. The autoclave was kept in an oven at 170°C for 12 h. After natural cooling to room temperature, the as-prepared black product was washed several times with DI water to make the $\text{pH} = 7$ and allowed to dry by freeze-drying. The resultant powder was collected and used for the further experiments. The example using $\text{NH}_4\text{H}_2\text{PO}_4$ as the reducing agent was abbreviated as NGC, while that using $(\text{NH}_4)_2\text{HPO}_4$ was abbreviated as NGL.

2.3. Characterization

The surface morphologies of the samples were investigated by scanning electron microscopy (SEM, Hitachi SU8010) and transmission electron microscopy (TEM, JEM 1200EX). The specific surface area was estimated by the Brunauer-Emmett-Teller (BET) method based on nitrogen absorption-desorption (Micromeritics ASAP 2020). The X-ray diffraction (XRD) patterns of the samples were obtained at room temperature on a D8-FOCUS (Bruker, German) using a Cu target ($\lambda = 0.154 \text{ nm}$). The Raman spectra of the samples were obtained using a RENISHAW Raman microscope

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