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Facile and controllable synthesis of N/P co-doped graphene for high-performance supercapacitors

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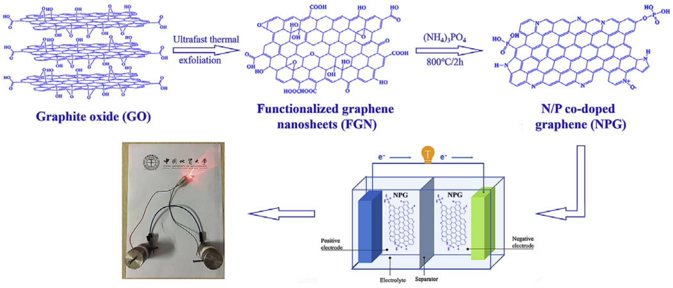
HIGHLIGHTS

- N/P co-doped graphene is controllably prepared by one-step activation.
- Increased oxygen functionalities on the precursor can facilitate N and P doping.
- High volumetric capacitance and excellent rate and cycle performance are observed.
- Enhanced energy density of 8.2 Wh kg^{-1} (4.6 Wh L^{-1}) is obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

Improving the energy density of carbon-based supercapacitors is one of the most urgent demands for developing high-power energy supplies, which in general requires delicate engineering of the carbon composition and textures. By pre-functionalization of graphene nanosheets and successive one-step $(NH_4)_3PO_4$ activation, we prepared a type of nitrogen and phosphorus co-doped graphene (NPG) with high specific surface areas, hierarchical pore structures as well as tunable N and P contents. The as-obtained NPG shows high specific capacitances of 219 F g^{-1} (123 F cm^{-3}) at 0.25 A g^{-1} and 175 F g^{-1} (98 F cm^{-3}) at 10 A g^{-1}, respectively. Accordingly, the NPG-based symmetrical supercapacitor device, working at a potential window of 1.3 V, could deliver an enhanced energy density of 8.2 Wh kg^{-1} (4.6 Wh L^{-1}) at a power density of 162 W kg^{-1} (91 W L^{-1}), which still retains 6.7 Wh kg^{-1} at 6.5 kW kg^{-1}. In particular, under a current density of 5 A g^{-1}, the device endows an 86% capacitance retention of initial after 20,000 cycles, displaying superior cycle stability. Our results imply the feasibility of NPG as a promising candidate for high-performance supercapacitors.

1. Introduction

Supercapacitors have attracted great attention due to their high power density, superior rate capability and long operation life, where the electrical double layer capacitor (EDLC) represents an important branch which electrostatically store charges through reversible ion adsorption/desorption at the electrolyte/electrode

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interfaces [1–4]. EDLCs can be quickly charged and do not lose their storage capabilities over hundreds of thousands cycles [5,6]. However, the energy density of EDLCs is generally low due to the limited surface where ions reside. Improving the energy density without sacrificing the power density and cyclic stability is a great challenge for EDLCs. Given that the energy density of an EDLC is proportional to the specific capacitance (SC) and the square of the operating voltage of the capacitor cell [7,8], it is of essential importance for an EDLC to simultaneously possess high specific capacitance and wide operating voltage in order to achieve satisfactory energy storage ability.

Carbon materials are the most widely used electrode materials for EDLCs. For the carbon electrodes, surface area has been considered to be the key concern that governs their SC. However, in most cases, the SC of carbon-based supercapacitors is less than 250 F g^{-1} even with a very large specific surface area (more than 2500 m^2 g^{-1}) [9,10]. This is because of the fact that most of the micropores in carbon material, which are the major contributor to SC, are inaccessible by the electrolyte or wetting deficiencies of electrolytes [11]. Recently, numerous efforts have been made to improve the SC of carbon-based EDLCs, in which nitrogen doping has been proven to be an efficient method because of the conductivity enhancement and additional pseudocapacitance endowed by N inclusion [12–18]. Significantly, Huang and coworkers recently prepared an N-doped mesoporous carbon which owns a SC of as high as 855 F g^{-1} in aqueous electrolytes, demonstrating the important role of N doping in capacitance increment [10]. On the other aspect, phosphorus doping of carbon materials could markedly increase their SCs because of the highly improved wettability brought by the P-containing groups in aqueous electrolyte [19–26]. In particular, P doping can widen the operating cell voltage due to the enhanced electro-oxidation resistance of carbon electrodes induced by interfacial phosphorus groups [27], which consequently increases the energy density of the carbon-based EDLCs significantly. For example, the P-doped carbons prepared by Hulicova-Jurcakova et al. [19] can operate steadily over a wide cell voltage of 1.3 V and deliver a high energy density of 16.3 Wh kg^{-1} at a power density of 33 W kg^{-1}. Therefore, one can rationally realize that co-doping with N and P would effectively increase the energy storage performance of porous carbon electrodes. In fact, several efforts have demonstrated the potential viability of N and P co-doped (N/P co-doped) porous carbons as high-performance supercapacitors [28–34].

Graphene has been cognized as a promising supercapacitor materials, whose supercapacitive performance can be naturally expected to be enhanced through N/P co-doping. Lei et al. [35] prepared N/P co-doped graphene via a two-step procedure involving the hydrothermally-derived N-containing graphene aerogel followed by phosphoric acid activation. The product exhibited high specific capacitance (204 F g^{-1} at 0.2 A g^{-1}), excellent cycling stability (92% capacitance retention after 10000 cycles), and enhanced energy density (7.1 Wh kg^{-1} at 100 W kg^{-1}). Alternatively, Qiu and co-workers [36,37] synthesized N/P co-doped graphene by a simple thermal annealing of exfoliated graphene oxide in the presence of ammonium phosphate ($(NH_4)_3PO_4$). The electrode shows a specific capacitance of 165 F g^{-1} at 0.1 A g^{-1} and a retention ratio of >80% at 2 A g^{-1}. Unlike the two-step process where N and P doping were carried out in stages [35], the $(NH_4)_3PO_4$ activation provides a simple yet efficient method to simultaneously render N and P sources for N/P co-doping of graphene, which can be easily scaled-up. However, the relatively low specific surface area (152 m^2 g^{-1}) of the co-doped graphene [37] constraints its SC performance, which may originate from the relatively low O contents (C/O ~ 11) of the graphene oxide precursors.

In principle, for doping heteroatoms, specifically N and P in this case, the oxygen-containing groups (carboxyl, carbonyl, and epoxy groups, etc) attached on the surface of graphene are the most critical factor, which determines the porosity and specific surface area of the resultant derivatives [38–40]. However, conventional thermal exfoliation of graphene oxides normally eliminates a high percentage of O-containing groups, which of course will lead to lower co-doping efficiency, resulting in only moderately improved SC performances underneath expectation. Herein, we employed our previously reported ultra-fast thermal exfoliation technique [41] to prepare functionalized graphene nanosheets (FGN) with a high oxygen content (C/O ~ 5.7) to facilitate the N/P co-doping. Using this type of FGN as precursor, $(NH_4)_3PO_4$ activation was sequentially conducted which enables high specific surface areas of up to 320 m^2 g^{-1} in the resultant N/P co-doped graphene (NPG). In particular, by adjusting the $(NH_4)_3PO_4$/FGN mass ratio, the N and P contents can be delicately tuned. Under optimal conditions, the as-prepared NPG promises to show high specific capacitances of 219 F g^{-1} (123 F cm^{-3}) at 0.25 A g^{-1} and 175 F g^{-1} (98 F cm^{-3}) at 10 A g^{-1}, respectively. More importantly, the as-assembled symmetrical supercapacitor delivers an enhanced energy density of 8.2 Wh kg^{-1} (4.6 Wh L^{-1}) and superior cycle stability (86% capacitance retention after 20,000 cycles) within a potential window of 1.3 V.

2. Experimental section

2.1. Sample preparation

The starting materials and chemicals were analytical grade and without any further purification. Graphite oxide (GO) was synthesized by the modified Hummer's method [42]. The detailed synthesis procedures of GO are shown in the Supplementary data. To prepare FGN, the dried GO was firstly ground into fine powder. Then, it was put into a long quartz tube that is sealed at one end and open at the other end. Subsequently, the powder was flushed with nitrogen (N_2) for 30 min, then the quartz tube was quickly inserted into a tube furnace preheated to 800 °C and held in the furnace for 60 s. After that the FGN was obtained.

The NPGs were prepared by thermal annealing of FGN at high temperature in the presence of $(NH_4)_3PO_4$ under an inert atmosphere. Firstly, 0.15 g FGN powder was physically mixed with different amount of $(NH_4)_3PO_4$ (0, 0.15, 0.30, 0.45 g). The mixture was then transferred to a quartz boat and thermally annealed at 800 °C for 2 h under N_2 atmosphere at a temperature ramp rate of 10 °C min^{-1}. The product was collected and washed with hot water to remove any impurities and then dried at 100 °C overnight. According to the amount of $(NH_4)_3PO_4$ introduced during the synthesis, the obtained representative samples in this study are denoted briefly as TRG, 1NPG, 2NPG and 3NPG, respectively. To investigate the roles played by oxygen-containing groups on the surface of FGN, we thermally treated TRG with $(NH_4)_3PO_4$ (mass ratio = 0.5) at the same conditions, and the obtained sample was named NPTG for comparative purpose.

2.2. Materials characterization

The microscopic feature and morphology of the samples were observed by field scanning electron microscopy (FE-SEM, Hitch SU8010) with an energy dispersive spectrum (EDS) analyzing system and transmission electron microscopy (TEM, Philips CM12 TEM/STEM) operated at 120 kV. Powder X-ray diffraction (XRD) patterns of the as-synthesized samples were recorded on a Bruker AXS D8-FOCUS diffractometer using monochromatized Cu-Kα radiation (40 kV, 20 mA; λ = 0.1540598 nm). Surface areas and pore distributions of the samples were carried out by N_2 adsorption-