A general approach for fabrication of nitrogen-doped graphene sheets and its application in supercapacitors

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ABSTRACT

In this paper, a general and efficient strategy has been developed to produce nitrogen-doped graphene sheets (NGs) based on *hard and soft acids and bases* (HSAB) theory. Under hydrothermal conditions, any salt with amphiprotic character have a strong tendency to hydrolysis, it is possible to provide reducing agent and nitrogen source simultaneously. It is worth noting that, NGs can be prepared under hydrothermal conditions by using some common ammonium salts with hard acid-soft base pairs as nitrogen-doping agents. The morphology, structure and composition of the as-prepared NGs were studied in detail. The results demonstrated that large amount of nitrogen was incorporated into the nanocarbon frameworks at the same time as the graphene oxide (GO) sheets were reduced. The electrochemical behavior of the synthesized NGs as supercapacitor electrodes was evaluated in a symmetric two-electrode cell configuration with 1 M H_2SO_4 as the electrolytes. It was found that the nitrogen groups making the as-prepared NGs exhibited remarkably enhanced electrochemical performance when used as electrode materials in supercapacitors. The supercapacitor based on the NGs exhibited a high specific capacitance of 242 F g^{-1} at a current density of 1 A g^{-1}, and remains a relatively high capacitance even at a high current density. This work will put forward to understand and optimize heteroatom-doped graphene in energy storage systems.

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1. Introduction

With the fast-growing energy demand in electrically powered vehicles and mobile electronics, great efforts have been made to exploit various energy-related devices and to improve the efficiency of conversion and storage [1,2]. Supercapacitors, also known as electrochemical capacitors, are the most promising candidates for various portable systems and automotive applications owing to their high power density, wide operating temperature and longer lifetime even in harsh conditions [3–6]. Since it was demonstrated and patented by General Electric in 1957, supercapacitors can be found a wide range of applications including, but not limited to, back-up power supply, portable electronics, and braking system [7–10]. Consequently, supercapacitors have attracted tremendous attention in recent years and became one of the most intense research focuses in the electrical energy storage field. As a unique two-dimensional carbon nanostructure, graphene has attracted intense interest for its promising applications in supercapacitor electrodes, mainly due to its superior electrical conductivity, exceptional large specific surface area, and excellent structural stability [11–14]. Ruoff and coworkers first demonstrated that graphene based supercapacitors has a specific values of 135 F g^{-1} and 99 F g^{-1} in aqueous and organic electrolytes, respectively [15]. However, the specific energy and capacitance of graphene based supercapacitors is several orders of magnitude lower than that of batteries and fuel cells, which limits its adoption for numerous possible applications. Generally, the capacitive behavior of graphene electrode materials can be improved largely by introducing faradic redox reactions involved components (*e.g.* transition metal oxides, conducting polymers). Nonetheless, these multi-component graphene materials suffer from poor intrinsic conductivity of these oxide materials and less satisfactory cyclability. Moreover, elaborate procedures to fabricate electrode materials with metal oxide and/or polymer and graphene are complex and expensive to scale up for widespread commercialization. Alternatively, chemical doping with electron-donating or electron-withdrawing elements, such as N, B, and O, is a promising route to improve the electrochemical properties of the graphene-based materials [16–18]. The specific capacitance of the graphene electrode in aqueous electrolytes can be enhanced by incorporating heteroatoms such as N, B and O in the carbon framework because of the redox reactions between the electrolyte ions and the heteroatom-containing functional groups as well as the surface wettability, and electronic conductivity has been improved [19–21]. These unique features endow heteroatoms-doped

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graphene as a promising electrode for supercapacitors with high capacity, excellent rate capability, and long-term stability. It has been demonstrated that the heteroatoms in graphene derivatives, such as N and O, played a critical role in redox reactions to increase their charge-storage capacity because the oxygen functional groups such as quinone/hydroquinone and nitrogen functional groups such as pyridinic N and pyrrolic N groups can result in a pseudocapacitive response in aqueous electrolytes, and as a result, the electrochemical performances of graphene-based electrode materials have been improved significantly [22–24].

Recent studies have shown that the nitrogen-doped graphene electrode exhibit comparable capacitances to those of pseudocapacitors but still utilize the robust electrical double layers near the electrode surfaces [25]. Hence the nitrogen-doped graphene exhibited superior electrochemical performances to its non-incorporated counterparts when used as supercapacitor electrodes. For example, Jeong et al. reported the synthesis of nitrogen-doped graphene sheets (NGs) by using nitrogen plasma treatment of graphene and found that it exhibited excellent cycle life and high power capability for supercapacitors [25]. Feng and coworkers develop an efficient and facile strategy to fabricate highly crumpled NGs and the as-prepared NGs exhibit significant improvement in terms of various performance parameters of supercapacitors (*e.g.* capacity, rate, cycling) [26]. Very recently, Rao and coworkers carried out the first preparation of heavily nitrogenated graphene oxide by microwave synthesis [27]. The specific capacitance of the as-prepared NGs reached a value of 320 F g^{-1} at 0.3 A g^{-1} in a two-electrode system. Thereupon, nitrogen-doped graphene is a promising electrode material for supercapacitors because of its excellent capacitive behavior. Up to now, several strategies, including chemical-vapor deposition in the presence of N-containing precursors, arc discharge in N-containing atmosphere, nitrogen plasma treatment, and postsynthesis treatment have been proposed to introduce nitrogen into the graphene framework for high performance supercapacitors [20,28–31]. Of course, these processes suffered from either toxic precursors or sophisticated equipment, accompanied by high cost and labor-intensive preparations. Therefore, it will be of great significance to develop effective and facile methods to fabricate N-doped graphene materials for high-energy density supercapacitors.

Recently, hydrothermal and solvothermal reactions have been used as effective approaches to fabricate NGs with a high nitrogen level for supercapacitors. For example, urea, hexamethylenetetramine and ammonia as well as organic amine have been studied for use as nitrogen-doping agents for graphene [32–36]. Even though the capacitance of NGs has been enhanced to some extent by these nitrogen-doping agents, there is still a great of interest to further improvement the capacitive of NGs by introducing new doping agents. Moreover, nitrogen-doping agents will react with oxygen functional groups first before introduce nitrogen into the graphene framework. In this process, nitrogen-doping agents also play a role as reducing agents, the nitrogen groups introduced in at the cost of oxygen groups. Inspired by those ideas, a general method has been developed to produce nitrogen-doped graphene sheets (NGs) based on HSAB theory. Different from the previous report process, there exists an additional reducing agent after hydrolysis. For example, ammonium oxalate is a typical amphoteric salt with hard acid–soft base pairs, which has a strong tendency to hydrolysis to produce ammonia and oxalic acid, where ammonia is an effective nitrogen doping agent and oxalic acid is a well-know reducing agent. Therefore, it is reasonable to produce high quality NGs in the presence of in situ produced reducing agent. Moreover, we found other ammonium salt with amphoteric character can also be used as an effective doping agent for the synthesis of NGs, which provide a new and general concept for the preparation of NGs.

In this work, we report nitrogen-doped graphene synthesized by a facile hydrothermal reaction with the assistance of amphoteric salt. During the hydrothermal reaction, amphoteric salt can gradually release NH_3 that continually reacts with the oxygen functional groups of GO, which is favorable for doping of high-level nitrogen into graphene skeleton. Moreover, the in situ produced reducing agent can further remove the oxygen functional groups of GO. The high nitrogen content in this approach could be achieved under lower mass ratio of the salt and GO. Significantly, such NGs contained abundant of nitrogen component exhibited outstanding pseudocapacitive behavior in terms of highly specific capacitance, good rate capability, and excellent cyclability when used as electrode materials for supercapacitors. The purpose of this work is not only provide a simple and versatile approach to obtain NGs for high-performance supercapacitors but also put forward the presence of heteroatoms functional groups is an effective approach to maximum the performance of the NGs materials.

2. Experimental

2.1. GO preparation

GO sheets were attained by oxidation and exfoliation of graphite powder using a well-known modified Hummers method as described previously [37]. GO (20 mg) and water (20 mL) was ultrasonicated in a beaker for 90 min, and then centrifuged at 4000 rpm for 10 min to remove any unexfoliated aggregations. In this way, a homogeneous GO aqueous dispersion ($\sim$1 mg mL^{-1}) was obtained (see Fig. S1).

2.2. Synthesis of NGs

For preparation of the NGs, 18 mL of GO suspensions and 150 mg of $(NH_4)_2C_2O_4 \cdot H_2O$ were mixed in a breaker first. After being vigorously stirred for 5 min, the mixture was sealed into a 25 mL Teflon autoclave and maintained at 180 °C for 8 h. Then the autoclave was naturally cooled to room temperature and the as-prepared black product was washed with deionized water to remove residual inorganic compounds and freeze drying for further characterization. The same procedures are applied to synthesize other NGs samples when $(NH_4)_2SO_3 \cdot H_2O$ or $NH_4H_2PO_2 \cdot H_2O$ was used as nitrogen doping agent, respectively. For comparison, reduced GO (RGO) was also prepared under the same experimental parameters but without adding the nitrogen doping agents into the GO aqueous dispersion.

2.3. Characterization

The phase structure of the products was measured by powder X-ray diffraction (XRD) experiments on a RigaKu D/max-RB diffractometer with Ni-filtered graphite–monochromatized Cu Kα radiation (λ = 1.54056 Å). Transmission electron microscopy (TEM) studies were characterized using a transmission electron microscope (TEM, FEI) with an accelerating voltage of 100 kV. Samples were prepared by first dispersing the final powder in ethanol through ultrasonic treatment, and the dispersion was dropped on a carbon-coated copper grid, drying the samples in air for observation. Scanning electron microcopy (SEM) studies were carried on FEI, Quanta 200. The specific surface area was estimated by the Brunauer–Emmet–Teller (BET) method based on nitrogen absorption–desorption (Micromeritics ASAP 2020). X-Ray photoelectron spectrometer (XPS, X-Ray monochromatisation, Thermon Scientific) was carried out with Al Kα as the excitation source; the binding energies obtained in the XPS analysis were calibrated against the C 1s peak at 285.0 eV. All chemicals were of analytical grade