



# Electrochemical Exfoliation of Graphite into Nitrogen-doped Graphene in Glycine Solution and its Energy Storage Properties



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## ABSTRACT

Electrochemically anodic exfoliation of graphite has been developed for nitrogen-doped few-layer graphene sheets (N-FLGS), demonstrating high N-doping levels of 6.05 atom%. The process for the preparation of N-FLGS is involved with the intercalation of glycine anions  $\text{H}_2\text{NCH}_2\text{COO}^-$  into the graphite layers, electro-polymerization of large electro-oxidation products  $\text{H}_2\text{NCH}_2\text{CONHCH}_2^-$ , and *in situ* N-doping in the graphite layer. Transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and Raman spectroscopy were employed to characterize the structure and properties of the N-FLGS. The as-fabricated N-FLGS utilized as electrode materials for supercapacitor exhibit enhanced electrochemical performance, including excellent cycling stability (the capacitance ratios after 10 000 cycles is 96.1%) and a remarkable rate capability ( $184.5 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$ ,  $132.7 \text{ F g}^{-1}$  at  $50 \text{ A g}^{-1}$ ).

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## 1. Introduction

Graphene, a two dimensional single-atom-thick sheet of honeycomb carbon lattice, has been recently received significant attention as electrode materials for energy storage devices like lithium ion battery (LIB), sodium ion battery (SIB) and supercapacitor due to its superior electrical conductivity ( $64 \text{ mS cm}^{-1}$ ), extremely high theoretical surface area ( $2675 \text{ m}^2 \text{ g}^{-1}$ ) and mechanical robustness [1–7]. However, pristine graphene is easy to restack during the electrode preparation because of the strong van der Waals interactions between graphene sheets, which seriously reduce its real surface area and thereby worse its energy density and rate capability [8,9].

Recent studies reveal that substitutional doping of graphene with heteroatoms atom N, can tailor its electrical conductivity, wettability and electro-active surface area to facilitate charge-transfer and electrolyte–electrode interactions, and may give rise to its electrochemical performance [10,11]. For example, Ajayan et al. demonstrated that a N-doping of graphene film grown directly on Cu current collectors through chemical vapor deposition (CVD) technique showed enhanced lithium storage performance [4]. Choi et al. developed an ultracapacitor using nitrogen doped graphene produced by a plasma process whose capacitance is about 4 times higher than that of pristine graphene without sacrificing cycle life and power capability [3]. 3D nitrogen-doped graphene foams, designed by Dai et al. by annealing the freeze-dried graphene oxide foams in ammonia, could deliver a charge capacity of  $594 \text{ mAh g}^{-1}$  at  $500 \text{ mA g}^{-1}$  when used as the anode for SIBs [5].

Until now, many *in situ* doping approaches such as CVD [12], solvothermal [13], segregation growth [14], and arc-discharge methods [15] have been utilized to prepare nitrogen-doped graphene [10]. It has been shown that the *in situ* doping methods can create a homogeneous doping throughout the bulk material.

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Nevertheless, these direct synthesis approaches often require sophisticated equipment, rigorous reaction conditions such as high vacuum and high temperature, and use of extremely toxic chemicals [10]. The post-treatment approaches such as heat treatment of graphene (graphene oxide) in nitrogen medium [16], plasma treatment [3,17] and chemical reduction by hydrazine [18] can also produce nitrogen-doped graphene, but the as-resulted products are always surface doping only [10].

Due to simplicity, low cost, high efficiency, and environmentally friendly nature, electrochemically anodic and cathodic exfoliation of graphite for the fabrication of graphene have been reported and attracted increasing attention [19–21]. Electrochemically cathodic exfoliation of graphite always involves the intercalation of guest cations such as  $\text{Li}^+$ ,  $\text{TBA}^+$  and  $[\text{BMP}]^+$  under highly negatively charge followed by graphite expansion [22–24]. The as-prepared graphene demonstrated low density of structural defects, low oxygen functional groups and high electrical conductivity [22,25]. In contrast, anodic exfoliation of graphite starts with oxidation and hydroxylation of graphite edge planes and then intercalation by anions which lead to the expansion of the graphite anode [19,20]. In this way, functional graphene with rich oxygenic functional groups can be obtained [19,20]. Recent works from Zhao and co-workers [26,27] develop a anodic exfoliation strategy to synthesis nitrogen-doped graphene in nitrate-based protic ionic liquid ethylammonium nitrate and ammonium nitrate. This material with 2.4at% nitrogen doping level demonstrated improved electrocatalytic activity but still not well enough for applications in the area of energy storage and conversion.

In this work, an electrochemically anodic exfoliation method is developed to fabricate nitrogen-doped few layer graphene sheets (N-FLGS) with high nitrogen-doping level (6.05 atom%) in natural biocompatible glycine ( $\text{H}_2\text{NCH}_2\text{COOH}$ ) and ammonia aqueous solution. Unlike other electrochemical exfoliation of graphite, the anodic exfoliation here involves the intercalation of glycine anions  $\text{H}_2\text{NCH}_2\text{COO}^-$  into the graphite layers, electro-polymerization of large electro-oxidation products  $\text{H}_2\text{NCH}_2\text{CONHCH}_2^-$ , and *in situ* N-doping in the graphite layers, which destroy the van der Waals interactions between graphite interlayers, and then lead to graphite exfoliation and nitrogen-doping. The as-resulted N-FLGS are tested as electrode materials for energy storage devices, and they show enhanced electrochemical behavior for supercapacitor.

## 2. Experimental Section

### 2.1. Chemicals and materials

Highly ordered pyrolytic graphite (HOPG SPI-3,  $10 \times 10 \times 1$  mm) was bought from SPI Supplies. High-purity graphite rods (6 mm in diameter) were supplied from Qingdao Xinlei Graphite Produce Co., Ltd., China. Glycine (99.5%) was purchased from Alfa Aesar. Aqueous ammonia (25–28%) was bought from Sigma-Aldrich. All other chemicals (purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) used in this experiment were analytical grade and were used without further purification.

### 2.2. Synthesis of N-doping few-layer graphene sheets

In a typical synthesis, HOPG or graphite rod was used as the anode, a Pt sheet (12 mm in length, 10 mm in width) was employed as the counter electrode and an electrolyte of 3 M glycine ammonia aqueous solution was used as electrolyte solution. Static potentials of 10 V were applied to the two electrodes using a DC power supply (LW10J2, Shanghai LiYou Electric Co., Ltd.). After electrolysis for 12 h, the exfoliated products were sonicated for 1 h and were then collected by filtration and thoroughly washed with water and

ethanol. This washing cycle was repeated six times and the final sediment was dispersed in 100 mL deionized water. After one-day sedimentation, the large/thick graphitic flakes completely precipitated on the bottom of the bottle. The supernatant was filtrated through glass fiber filtering membrane (Waterson, GF/C) under vacuum and then dried at 50 °C under vacuum overnight to get the N-FLGS samples.

### 2.3. Materials characterization

Transmission electron microscopy (TEM) analysis was conducted using a JEM-2100F instrument with an accelerating voltage of 200 kV. Raman spectra were obtained on a Renishaw RM1000 confocal Raman spectrometer (Renishaw Inc., New Mills, UK) with 633 nm excitation operating at 25% power (ca. 3.5 mW). Surface compositions were analyzed with an ESCALab250 X-ray photoelectron spectroscopy (XPS). X-ray diffraction (XRD) patterns were obtained with a Rigaku D/max 2550 VB+ 18 kW X-ray diffractometer with  $\text{Cu K}\alpha$  radiation (0.1542 nm).

### 2.4. Evaluation of Li/Na storage properties

Dried N-FLGS were mixed with a binder poly(vinylidene fluoride) (PVdF) at weight ratios of 90:10 in N-methyl-2-pyrrolidone (NMP) solvent to form a slurry. Then, the resultant slurries were uniformly pasted on Cu foil with a blade. The average mass of the active material in the prepared electrode sheets is  $0.8 \text{ mg cm}^{-2}$ . The prepared electrode sheets were dried at 100 °C in a vacuum oven for 12 h and pressed under a pressure of approximately 20 MPa. CR2016-type coin cells were assembled inside an mBraun glovebox ( $\text{H}_2\text{O} < 0.5 \text{ ppm}$ ,  $\text{O}_2 < 0.5 \text{ ppm}$ ) using the metallic lithium or sodium counter/reference electrode and a polypropylene separator (Celgard 2400). The electrolyte solutions for LIBs and SIBs are 1 M  $\text{LiPF}_6$  in ethylene carbonate and dimethyl carbonate (EC/DMC, 1:1 vol) and 1 M  $\text{NaClO}_4$  in propylene carbonate (PC), respectively. Galvanostatic charge/discharge cycles were carried out with an Arbin battery cycler (BT2000) between 3.0–0.01 vs  $\text{Li}^+/\text{Li}$  and 2.5–0.01 V vs  $\text{Na}^+/\text{Na}$  at 100 mA  $\text{g}^{-1}$ .

### 2.5. Evaluation of supercapacitor properties

The electrodes for supercapacitor were prepared by mixing N-FLGS, acetylene black, and PVdF with a ratio of 80:10:10, the N-methyl-2-pyrrolidone (NMP) was dropped into the above mixture and ground to form the coating slurry. This slurry was pressed onto nickel foam ( $1.76 \text{ cm}^2$ ) current collector, and then dried in a vacuum oven at 50 °C overnight. The loading mass of N-FLGS material was ca.  $2.5 \text{ mg cm}^{-2}$ . A typical three-electrode experimental cell equipped with the prepared electrodes, a platinum foil counter electrode, and a Hg/HgO reference electrode was used to measure the electrochemical properties. All electrochemical measurements were carried out in 6 M KOH solution at room temperature. Cyclic voltammetry (CV) tests were also conducted on Solartron Analytical between –1 and 0 V vs Hg/HgO at scan rates of 10, 20, 50 and  $100 \text{ mVs}^{-1}$ . Galvanostatic charge/discharge cycles were carried out with an Arbin battery cycler (BT2000) between –1 and 0 V vs Hg/HgO. The electrochemical impedance spectroscopy (EIS) measurements were performed on Solartron Analytical at an AC voltage of 10 mV amplitude in the frequency range of  $10^5 \sim 10^{-2} \text{ Hz}$ . The specific capacitance of the electrode at different current densities can be calculated by using  $C_s = It/m\Delta V$ , where,  $C_s$  ( $\text{Fg}^{-1}$ ) is the specific capacitance,  $I$  (A) is the discharge current,  $t$  (s) is the total discharge time,  $m$  (g) represents the mass of active materials within the composite electrodes and  $\Delta V$  (V) is the potential drop during discharge.

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