



Preparation of edge-nitrogenated graphene nanoplatelets as an efficient electrode material for supercapacitors



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ABSTRACT

Edge-nitrogenated graphene nanoplatelets (ENGNPs) with high surface area were prepared through a simple and eco-friendly mechanochemical pin-grinding process using the flake graphite as the precursors in the presence of nitrogen and investigated as the electrode materials for supercapacitors. Nitrogen adsorption, SEM, and XPS analysis indicated that the mechanochemical pin-grinding process can effectively delaminates the pristine graphite into graphene nanoplatelets and generates the activated carbon sites that can directly react with nitrogen at the broken edge of graphite framework, leading to ENGNPs with excellent capacitive performance. Electrochemical measurements indicate that the as-prepared ENGNPs exhibits a high specific capacitance of 202.8 F g^{-1} in $1 \text{ M H}_2\text{SO}_4$ aqueous electrolyte at the current density of 0.3 A g^{-1} , meanwhile maintaining a good capacitance retention capability. The excellent capacitive performance of ENGNPs can be attributed to the combined effect of high surface area, edge-nitrogenated structure, and undamaged basal plane.

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1. Introduction

Today, supercapacitors are supposed to be a kind of promising candidate for effective energy storage due to their unique advantage of high power density, long cycle life, good rate capability, and low maintenance cost [1–3]. The charge storage mechanism of supercapacitors is based on the electrostatic attraction to generate charge accumulation in the electric double layer formed at the interface of electrode and electrolyte, and/or based on the pseudocapacitance associated with the fast, reversible redox reactions at the surface of the active materials [4–6]. Therefore, the capacitive performance of supercapacitor is determined, to a large extent, by the physical and chemical properties of their electrode materials. So far, carbonaceous materials such as active carbon [2,7,8], mesoporous carbon [9–12], carbon nanotube [13–15], and graphene [16–18], are still the preferred materials for the electrode of supercapacitors due to their low cost, high specific surface area, good electrical conductivity and chemical stability. To enhance the capacitive performance of supercapacitors based on carbon electrode, much effort has been made to develop advanced carbon materials by

increasing surface area and tuning the pore structure [19,20]. However, the results suggested that increasing surface area and improving pore structure alone might not be as effective as thought to improve the capacitive performance of carbon materials.

Another approach to enhance the electrochemical capacitance of carbon electrode is to introduce pseudocapacitance by doping heteroatoms (such as N, S, P, or B) into carbon framework [21–25]. Recent studies indicate that nitrogen doping seems to be the most promising method for enhancing the capacitive performance of carbon by a mechanism of introducing pseudocapacitive effect [26–29]. In addition, it was found that nitrogen doping can also improve the wettability and enhance the electronic conductivity of carbon material, in favor of high cycle durability and power density of carbon-based supercapacitors. However, nitrogen-doped carbons were generally prepared using complex methods such as post-treatment of carbon with ammonia, amine or urea and pyrolysis of nitrogen-containing precursor including synthetic polymers, biomass, and ionic liquids [30–34]. These methods require multiple steps and high temperature, which are either too expensive for practical applications and/or involving hazardous reagents. Therefore, a simple, low-cost, and eco-friendly process for preparing nitrogen-doped carbon is highly desirable.

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In this paper, edge-nitrogenated graphene nanoplatelets (ENGNPs) with a high surface area were prepared by a facile and eco-friendly mechanochemical process of pin-grinding flake graphite in the presence of nitrogen, through which nitrogen atoms were directly fixed at the edges of graphene nanoplatelets. The plentiful accessible nitrogen-containing species located at the edge of graphene nanoplatelets would provide chemically active sites to greatly improve the capacitive performance of carbon materials by efficiently introducing pseudocapacitance. It is found that the as-prepared ENGNPs manifests a great potential as an efficient electrode material for supercapacitor with relatively high specific capacity and excellent rate performance.

2. Experimental

2.1. Preparation of ENGNPs

ENGNPs were prepared by pin-grinding flake graphite in a magnetic grinding machine in the presence of nitrogen at room temperature. The flake graphite (Qingdao Huatai Corp. Ltd., natural graphite, 200 mesh, 99.9%) was placed into a capsule (750 mL) containing stainless steel pins (500 g, 5 mm in length and 100 μm in diameter). The capsule was sealed and charged with nitrogen, and then fixed on the magnetic grinding machine (schematically shown in Fig. A.1). The magnetic grinding machine uses the magnetic force to drive the steels pin to grind the graphite flake into graphene nanoplatelets. At the same time, nitrogen reacted with graphene nanoplatelets at broken edges of graphite framework to obtain ENGNPs. The yield was about 87%. ENGNPs prepared at the pin-grinding time of 1.5 h, 3 h, 5 h, and 7 h were denoted as ENGNP1.5, ENGNP3, ENGNP5, and ENGNP7, respectively.

2.2. Characterization

The morphology of the ENGNPs was characterized by scanning electron microscopy (SEM, FEI Sirion 200) and transmission electron microscopy (TEM, JEOL 2100). Nitrogen adsorption-desorption measurements were performed with a Micromeritics ASAP 2020 adsorption analyzer at 77 K. X-ray diffraction (XRD) patterns were obtained using Bruker D8 Advance diffractometer with Cu K α radiation. Fourier transform infrared (FTIR) spectra were recorded on Nicolet 5700 spectrometer. Raman spectra were taken with a Renishaw system 200 operating at 514 nm with a CCD detector. X-ray photoelectron spectroscopy (XPS) was performed on an X-ray photoelectron spectrometer (ESCA Lab 220i-XL) with Al K α radiation.

2.3. Electrochemical measurements

All electrochemical measurements were carried out in a three-electrode system using a CHI 660D electrochemical workstation at room temperature. An Ag/AgCl electrode and Pt plate were used as the reference electrode and counter electrode, respectively. 1 M H₂SO₄ aqueous solution was used as the electrolyte. The test electrodes were prepared by pressing a mixture of 90 wt% of ENGNPs, 5 wt% of carbon black, and 5 wt% of PTFE on the Ti foam current collector, followed by drying at 100 °C for 2 h under vacuum condition. The loading mass of active material on the current collector was 2 mg. The area of an electrode was 1 cm². Cyclic voltammetry (CV) measurements were carried out in the potential range of 0–0.9 V by varying the scan rates from 10–500 mV s⁻¹. Galvanostatic charge-discharge curves were obtained at the current density range of 0.3–10 A g⁻¹. Electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 0.01–10⁵ Hz with an amplitude of 5 mV.

3. Results and discussion

As schematically shown in Fig. A.1, ENGNPs were prepared by pin-grinding flake graphite in the presence of nitrogen at room temperature. When magnetic grinding machine work, steel pins in the capsule are driven by the magnetic force to grind graphite flake, resulting in the breakage of large graphite flake into small one. The cleavage of graphite flake by pin-grinding can create numerous active sites at the broken edges of the graphitic framework, which are the reactive sites for nitrogen doping. Therefore, the nitrogen doping at the graphite edges during the mechanochemical cracking is a spontaneous process. As shown in Fig. 1, the mechanochemical cracking results in two kinds of cleavages: armchair (1) and zigzag (2) cleavages. The armchair and zigzag edges are respected to form aromatic pyridazine and pyrazole rings, respectively, from the cyclization between activated carbon sites and nitrogen.

FTIR spectra of ENGNP5 and ENGNP7 (see Fig. 2a) evidently show the aromatic C–N stretching peaks at 1415 cm⁻¹, implying the presence of the nitrogen-containing aromatic rings [35]. XPS characterizations were performed to further analyze the elemental composition and nitrogen bonding configuration in ENGNPs. Fig. 2b shows XPS scan spectrum of pristine graphite, ENGNP5, and ENGNP7. As expected, the pristine graphite shows only a pronounced C 1s peak at the binding energy of 284.1 eV and a weak O 1s peak at the binding energy of 532.1 eV attributed to the presence of a trace amount of physically adsorbed oxygen. In addition to C 1s and O 1s peaks, ENGNP samples show a characteristic N 1s peak at the binding energy of 399.1 eV. XPS is a semi-quantitative technique for surface analysis allowing obtaining an atomic percentage of nitrogen present in the carbon. The content of nitrogen in ENGNP5 and ENGNP7 were calculated from the XPS scan spectrum to be around 1.57% and 2.07%, respectively. The high resolution N 1s spectra of ENGNP5 and ENGNP7 are shown in Fig. 2c and d, and it can be fitted into two peaks located at 398.4 and 399.5 eV, assigning to pyridinic and pyrrolic nitrogen, respectively. Both pyridinic and pyrrolic nitrogen are located at the edges of graphene nanoplatelets, which indicates that nitrogen doping only occur at the broken edges of graphitic framework during the mechanochemical pin-grinding process. It is noteworthy that the pyrrolic nitrogen is the dominant nitrogen component in as-prepared ENGNP samples. The ratios of pyrrolic nitrogen to pyridinic nitrogen are 2.5 for ENGNP5 and 2.4 for ENGNP7, respectively. This implies that zigzag cracking of graphite C–C bonds is major process, promoting the formation of pyrazole ring. The plentiful accessible of pyridinic and pyrrolic nitrogen would provide chemically active sites, and therefore can easily contribute to the total capacitance with the pseudocapacitive effect.

Fig. 3 shows SEM images of pristine graphite and ENGNPs. SEM images clearly show that the pin-grinding process results in the dramatic size reduction of starting graphite; the large graphite flake is grind into loose and porous ENGNP congeries. With the increase of the grinding time, the size of ENGNPs decreases. The BET surface area and pore volume of ENGNPs were measured by Micromeritics ASAP 2020 physisorption analyzer using nitrogen adsorption at 77 K and summarized in Table 1. From Table 1, it can be seen that the BET surface area and pore volume of ENGNPs increase with the increase of grinding time. Pristine graphite displays a low BET surface area of 0.27 m² g⁻¹. For ENGNP1.5, ENGNP3, ENGNP5, and ENGNP7 samples, the BET surface areas increase to 483.8, 625.0, 679.1, and 681.4 m² g⁻¹, respectively. These results further demonstrate that the pin-grinding process driven by magnetic field can effectively grind graphite flake into graphene nanoplatelets. However, the surface area of ENGNP samples is lower than that of individual isolated graphene

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