Preparation and application of porous nitrogen-doped graphene obtained by co-pyrolysis of lignosulfonate and graphene oxide

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HIGHLIGHTS

- Nitrogen-doped porous graphene was fabricated by co-pyrolysis of LS, GO and urea.
- Lignosulfonate performed as both dispersant and porogen in the co-pyrolysis process.
- The porous structure of graphene resulted from the pyrolysis of lignosulfonate.

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ABSTRACT

Nitrogen-doped graphene with in-plane porous structure was fabricated by simple co-pyrolysis of ligno-sulfonate and graphene oxide in the presence of urea. Lignosulfonate first performs as a dispersant adsorbed on the surface of graphene oxide to prevent the aggregation of graphene oxide sheets for preparing homogeneous nitrogen-containing precursor, and then acts as a porogen to render graphene sheets with nanopores in the pyrolysis process of the nitrogen-containing precursor. Urea was used as a nitrogen source to incorporate nitrogen atoms into graphene basal plane. The special nanoporous structure combined with nitrogen content of 7.41 at.% endows the nitrogen-doped graphene electrode material with super capacitance up to 170 F g^{-1}, high rate performance, and excellent cycling stability.

1. Introduction

With the increasing shortages of fossil energy and worsening environmental pollution, people are in an intensive research of some energy storage/conversion devices such as supercapacitors, Li-ion batteries and fuel cells instead of traditional energy in the past few decades (Simon and Gogotsi, 2008). Supercapacitors have caused special attention due to their potential applications in hybrid electric vehicles and portable electronic devices. On the basis of charge storage mechanism, supercapacitors can be divided into electrical double layer capacitors and pseudocapacitors (Zhang and Zhao, 2009). The types and structures of electrode materials are of great importance for the performances of supercapacitors, which affect the charge transfer in the electrode and electrolyte ion diffusion during the electrochemical process. Pseudocapacitive materials, such as metal oxides and conducting polymers, through fast and reversible redox surface process, could achieve high pseudocapacitance. However, metal oxides generally suffer from poor electrical conductivity, poor ion transport kinetics and pronounced volume variation during charge–discharge process, leading to poor rate and cycling performance. Conducting polymers are almost confronted with the same problem of swelling and shrinking in the redox process. Carbon-based materials as supercapacitor electrode can overcome this issue and show an excellent cycling stability, due to the electrical double layer charge storage mechanism quite different from that of pseudocapacitive materials (Yan et al., 2014).

Various kinds of carbon-based materials with high surface area and special structure, such as activated carbon (Farma et al., 2013), porous graphene (Jiang and Fan, 2014), carbonaceous hydrogels and aerogels (Wu and Xu, 2014) have wide applications in the fields of biosensors (Zan et al., 2013), electrode materials (Liu et al., 2012; Pham et al., 2014), and catalyst supports (Wang et al., 2014). Among them, graphene, an emerging two-dimensional nanomaterial, due to its excellent physical and chemical

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properties, has been gradually given special attention in the last decade. However, single layer graphene tends to agglomerate and restack into graphite structure via strong π–π stacking and van der Waals interaction (Li et al., 2008), which greatly reduces the specific surface area, thus limiting its application as electrode material. Therefore, it has been a hot research area to endow graphene with unique structures ranging from porous graphene (Jiang and Fan, 2014), graphene foams (Huang et al., 2012), graphene sponges (Bi et al., 2012) to graphene based gels (Wu et al., 2012). When used as electrode materials of supercapacitors, these unique porous structures not only inherit the excellent properties of graphene, but facilitate ion diffusion into the inside of electrode materials as well, leading to improved supercapacitive performances (Wu and Xu, 2014). Recently, doping heteroatoms (such as N, B, P and S) (Liang et al., 2012; Wang et al., 2014, 2013) into graphene lattice can cause defects, tailor its electronic property and finally improve its electrochemical property, which is attributed to the improved wettability and the redox actions between the heteroatoms and electrolyte ions contributing pseudocapacitance (Guo et al., 2013). Nitrogen-doped graphene could reach up to a high capacitance nearly paralleling to pseudocapacitive materials, because of the presence of pyridinic N, pyrrolic N and graphitic N (Wen et al., 2012). Many X-ray photoelectron spectra (XPS) measurements have demonstrated that pyridinic N and pyrrolic N play major roles in improving the capacitance of graphene due to faradic reactions (Sun et al., 2012), while graphitic N improves the conductivity, facilitating the transportation of electrons and ions (Sun et al., 2012). However, fabrication of nitrogen-doped porous graphene usually need a hard template such as sulfonated polystyrene (s-PS) (Wang et al., 2013), poly(methyl methacrylate) (PMMA) (Pham et al., 2014), and SiO$_2$ (Yang et al., 2012) via certain heat treatment processes in the presence of a nitrogen source. For instance, nitrogen-doped mesoporous reduced graphene oxide (rGO) was prepared via the pyrolysis of PMMA-rGO composites in a mixed nitrogen and ammonia atmosphere, which exhibited an excellent specific capacitance up to 290 F g^{-1} (Pham et al., 2014). The supercapacitive behaviors of nitrogen-doped porous graphene have been greatly improved by means of faradic reactions of nitrogen heteroatoms and short diffusion distances of ions and electrons (Pham et al., 2014). Hence, it is of great importance to fabricate nitrogen-doped porous graphene without a hard template.

Ligin is the second most abundant natural renewable bioresource on earth. Due to the abundant oxygen-containing groups on its surface, its wide applications have ranged from natural adsorbent to precursor of activated carbon (Suhas et al., 2007). As a derivative of ligin and byproduct of pulping industry, lignosulfonate (LS) is also an amphiphilic biopolymer, which has been widely used as a surfactant (Lou et al., 2013) to fabricate stable aqueous suspensions of graphene nanosheets (Yang et al., 2010), and nitrogen-containing carbon spheres (He et al., 2013). Furthermore, LS was also used as a carbon source to synthesize graphene by thermal treatment process in the presence of Fe nanoparticles as a catalyst (Mun et al., 2013). In our recent work, LS was used as a dopant to prepare the lignosulfonate-graphene oxide-polyaniline ternary nanocomposites (Yang et al., 2014), which performs as an effective adsorbent to remove Pb^{2+} from industrial wastewater.

In this work, LS was used as a porogent to prepare porous graphene in order to further explore its application in the graphene fields. Nitrogen-doped graphene with in-plane nanoporous structure was fabricated by co-pyrolysis of LS and graphene oxide with urea as a nitrogen source. LS not only performs as a dispersant adsorbed on the graphene oxide (GO) sheets to prevent the aggregation of GO when the homogeneous nitrogen-containing precursor was prepared, but also acts as a porogen to render graphene

sheets with nanopores during the pyrolysis process of the as-prepared nitrogen-containing precursor. During the co-pyrolysis process, GO was thermally reduced (Acik et al., 2010), and nitrogen atoms were introduced into the graphene lattice (Lin et al., 2012), thus fabricating in-plane nanoporous nitrogen-doped graphene (PNG). When investigated as an electrode material for supercapacitor, the nanoporous nitrogen-doped graphene exhibits excellent supercapacitive performance in terms of specific capacitance, rate performance and cycling stability.

2. Methods

2.1. Materials

Expansible graphite (100 meshes), sulfuric acid (H$_2$SO$_4$), phosphoric acid (H$_3$PO$_4$), potassium permanganate (KMnO$_4$), hydrogen peroxide (H$_2$O$_2$), Sodium lignosulfonate (LS), urea and other experimental drugs were all purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used without further treatment.

2.2. Preparation of graphene oxide

Graphene oxide (GO) was prepared from expansible graphite by using a modified Hummers' method (Wakeland et al., 2010). Typically, expansible graphite, KMnO$_4$, concentrated H$_2$SO$_4$, and concentrated H$_3$PO$_4$ were precooled in the refrigerator. Firstly, 1.0 g expansible graphite was added into a 250 mL flask, and then 133 mL mixture of concentrated H$_2$SO$_4$ and H$_3$PO$_4$ with a volume ratio of 9:1 was slowly poured into the reactor. Finally, 6.0 g KMnO$_4$ was slowly added into the above mixture. The flask was then transferred to oil bath (50 °C) and stirred for 12 h. The flask was cooled to room temperature and the mixture after reaction was poured into 250 mL ice water and then added a certain amount of 30% H$_2$O$_2$ drop by drop until the mixture turned into golden yellow. The obtained slurry was washed with 5% HCl to remove metal ions and purified by dialysis for one week to further remove the metal ions residue. The purified GO was then diluted with deionized water to get GO suspension of 9.36 mg mL^{-1} for further use.

2.3. Preparation of nitrogen-containing precursor

To prepare nitrogen-doped in-plane porous graphene, 21.5 mL GO suspension (about 200 mg) was first diluted with 80 mL deionized water, and then 20 mg LS and 20 g urea were added into the above solution in regular sequence. The mixture was under ultrasonic wave for 2 h. After that, the resulting suspension was transferred into an evaporating dish and dried at 60 °C for 2 days, thus forming a homogeneous nitrogen-containing precursor. Then the precursor was ground into powder. The precursor without adding LS was also prepared in the same way.

2.4. Pyrolysis of the nitrogen-containing precursor

Nitrogen-doped graphene was fabricated by high temperature co-pyrolysis method without air under atmospheric pressure. The typical pyrolytic procedure was as follows: a certain amount (5–10 g) of precursor was put into a closed corundum crucible, and then transferred into a temperature-controlled furnace. The furnace was then heated to 800 °C with a heating rate of 3 °C min^{-1} under nitrogen flow and maintained at the temperature for 2 h, followed by naturally cooling to room temperature. Finally, the product was washed with an excessive amount of deionic water to remove Na$^+$ and dried at 60 °C for a night. The black power was