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Highly defective graphite for scalable synthesis of nitrogen doped holey graphene with high volumetric capacitance

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HIGHLIGHTS

- Holey graphene is prepared by etching abundant and low cost defective graphite.
- Holey graphene with in-plane edges provide more active sites for nitrogen doping.
- Holey graphene shown impressive high capacitance in wide current density range.

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ABSTRACT

Manipulating basal plane structure of graphene for advanced energy conversion materials design has been research frontier in recent years. By extending size of defects in the basal plane of graphene from atomic scale to nanoscale, graphene with in-plane holes can be synthesized by multiple steps oxidation and reduction of defective graphene oxide at low concentration. These complicated and low yield synthetic methods largely limited research and applications of holey graphene based high performance energy conversion materials. Inspired by graphene in-plane holes formation mechanism, an easy and scalable synthetic approach has been proposed in this work. By oxidizing widely available defective graphite mineral under high concentration, holey graphene oxide has been scalable synthesized. Through simple reduction of holey graphene oxide, nitrogen doped holey graphene with high volumetric capacitance of 439 F/cm^3 was obtained. We believe this breakthrough can provide a feasible synthetic approach for further exploring the properties and performance of holey graphene based materials in variety of fields.

1. Introduction

In the latest ten years, extensive work has been devoted to explore potential applications of graphene for its unique electrical, mechanical thermal properties and etc. [1–6] Since chemical method has been setup for scalable and low cost synthesis of reduced graphene oxide (RGO) from natural graphite flake, explosive growth of research on applications of graphene has dramatically promoted its development. Benefited from its high electrical conductivity, high surface area and tunable physical and chemical properties, graphene has been considered as next generation high performance functional materials in sensing, actuation, catalyst and electrochemical energy storage [7–10]. However, widely studied RGO synthesized from nature graphite flake tend to restacked seriously due to strong π-π interaction, resulting in poor solution processability [11,12]. Moreover, restacked graphene in bulk electrode has displayed low electrochemical energy storage performance in both supercapacitors and batteries due to hardness of ionic diffusion and interfacial capacitance formation within neatly stacked graphene electrodes [13–15]. Variety of methods have thus

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been developed to prevent graphene from stacking by introducing artificial pores in bulk graphene electrode and have shown considerable high gravimetric capacitance (C_g) [16–18]. Most of these highly porous materials have very low density (ρ), resulting in low volumetric capacitance ($C_v = \rho C_g$). Though intercalation of mediums between graphene layers can enhance volumetric capacitance at low electrical current density, ion diffusion across dense packed bulk electrode is still need to go through long devious way to make full use of high capacitance, resulting in low capacitance performance at high current density [11,12].

In comparison, holey graphene (HG) based materials have shown great advantage in electrochemical energy storage for the enriched in-plane pores that allow fast ionic diffusion across dense packed bulk electrode in a short pathway and increased electrochemical active interfaces and edges for capacitance enhancement [19]. The in-plane holey structure of HG make it a good component for constructing high performance hybrid materials. Liu and co-authors have designed a HG/polypyrrole nanoparticle hybrid aerogels, which has three-dimensional hierarchical porous structure, with high specific capacitance in a wide current density range by making used of its good ionic diffusion character [20]. Unlimited to the supercapacitor application, HG based materials have recently been found to shown great advantage in varieties of energy conversion applications. Since chemical activity of carbon atoms on the edge area of in-plane holes is different from that of basal plane, Jiang and co-authors have studied role of in-plane holes on nitrogen doped graphene for capacitance and oxygen reduction reaction performance enhancement [21]. Moreover, nitrogen doped HG as metal free electrode has also been found to display better performance than that of Pt based electrode material for dye sensitized solar cells very recently by making use of its interfacial characters [22]. Chen and co-authors have shown that HG with high specific area and active sites are excellent sensor material with tunable polarity for gas sensing [23].

For these reasons, attentions have been paid on synthesis HG based materials through variety of methods in recent five years. These reported methods can be classified into two categories by in-plane hole formation condition. One is solution approach, which requires very low concentration of GO to ensure well dispersion of single layer GO during surface chemical etching process for uniform in-plane holes formation. In this category, reported works include hydrothermal etching GO [23], Au catalyst assisted etching GO [24], etching GO in reflexing nitride acid [25] and also our previously investigated synthetic method by nitride acid etching GO under sonication treatment [26]. Beside low concentration limitation (<0.2 $mgmL^{-1}$) for scalable production of holey graphene, duplicated processes (including single layer GO dispersion, compositing and vigorous reaction condition) and high expense of reactant (including expensive high purity GO and noble metal precursors) make those methods economically unacceptable. Another method is solid state approach, which normally require thermal treatment of GO with reactive gases or substances on GO surface. In this category, reported works include KOH activation of GO at 800 °C[19], thermal annealing of ferrocene/GO composite [27], high temperature etching GO by metal oxide nanoparticles [28] and also thermal treatment of GO in air at 300 °C [29,30]. These methods do can scalable produce holey graphene. However, they still need to prepare GO firstly and then etching it at high temperature not to mention poor solution processing ability of thermal treated sample, which limit their further composition for preparing different functional materials, and extra expense on removing etching agents. A scalable, easy and low cost synthesis method of HG material is still a challenge.

All these reported methods on preparing HG are based on same mechanism: creating sp3-carbon defect sites, which are normally oxygenated groups, on honey-comb lattice of carbon atoms followed by expanding atomic scale defect sites into nanoscale in-plane holes via further chemical etching GO, as has been shown in Scheme 1A. Because the key issue of in-plane pore formation is sufficient sp3-carbon defective sites existence in polycyclic aromatic carbon basal plane, finding a large scale available sp3-carbon defect-rich graphitic carbon material as precursor for HG synthesis is a more promising way, which can avoid complicated steps to create defects sites on graphene basal plane. In the millions years mineralization process of graphite from organic carbon resources, hydrocarbon molecules gradually loss their oxygen and hydrogen atoms along with other elements and were transferred to large basal plane of polycyclic aromatic molecule with gradually reduced defect sites under high temperature and high pressure. Till now, most of naturally available graphite minerals are still insufficiently graphitized and highly defective. These defective graphite (DFG) minerals are abundant and cheap in compared with very limited resources of high quality natural graphite flake which is less than 10% of total graphite resources. The carbon contents of DFG minerals can be very high (>60 wt%) in compared with low carbon contents (<25 wt%) of raw mineral of widely used high quality nature graphite flake. Considerable amount of defective sp3-carbon in the aromatic basal plane of DFG, of which oxygenated groups contents are comparable to that of GO, make them chemically active. Inspired by synthesis mechanism of HG from defective GO and chemical activity of DFG, we proposed a scalable and easy synthesis method of HG based on chemical oxidation of DFG as has been shown in Scheme 1B. Interestingly, we found simple oxidation of this material by widely used modified Hummers method can directly obtain holey graphene oxide (HGO) in oxidation step of DFG. This is very important because HGO is no longer needed to be obtained via duplicated processes and the production of its can be easily achieved at gram scale in a small bottle reactor without low concentration limitation. The scalable synthesized HGO with good solution process ability, which is important for further composition with other substance for different functional applications, can be easily transferred to HG for high capacitance electrode design. In this work, graphite flake, which was widely used as raw material for GO and RGO preparation [11,12,31–34], was compared with DFG under the same experiment condition for proving the role of DFGs' defects on successful synthesis of HG.

2. Experimental

2.1. Materials

As-received defective graphite (DFG) (purity>70%, 325 mesh), which is also called microcrystalline graphite, was obtained from Hunan BinzhouLuyuan graphite Co., Ltd. It was exploited from Lutang graphite mine in 2014. Main impurities of as-received DFG are silicon dioxide along with Chlorite and Muscovite, which are mainly composed of Si, Al and O. In a typical purification process, 10 g as-received DFG was stirred in 50 mL 1 M HCl for 4 h and washed with 200 mL deionized water to remove acid soluble impurities. Then it was stirred in 20 mL HF (40%) overnight at room temperature followed by washing with 200 mL deionized water to remove residual impurities. After purification, the collected sample was dried at 80 °C overnight obtaining ~8 g final product. In the text bellow, DFG refers to purified DFG if there is no special instruction. Graphite (325 mesh, purity 99.8%) was purchased from Alfa Asar and used as received. All other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd.