



A facile preparation of edge etching, porous and highly reactive graphene nanosheets via ozone treatment at a moderate temperature



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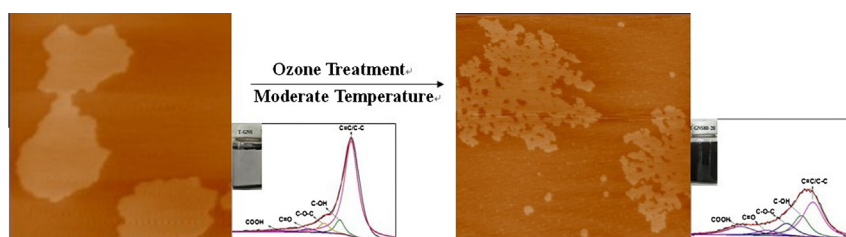
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HIGHLIGHTS

- A facile method to modify graphene nanosheets by ozone treatment.
- The edge etching, porous and highly reactive graphene nanosheets were prepared.
- The ozone treatment time and temperature jointly affect the final results.
- The dispersion of modified graphene nanosheets was significantly improved.
- The modified graphene nanosheets can be conveniently used for further application.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple method to modify thermal-exfoliated graphene nanosheets (T-GNS) by using streaming ozone under different time and temperature is described in this paper. The results indicated that a wide variety of oxygen-containing groups such as C–OH, C–O–C, C=O and COOH could be introduced on the surface of T-GNS by ozone treatment. Especially when ozone modification was taken under 80 °C for 20 min, the atomic ratio of O/C was increased to 0.503, and the percentage of carboxyl groups was up to 14.37%, which was more than 10 times compared with the original T-GNS. In addition, it is worth mentioning that ozone treatment under a moderate temperature could cause etching on the edge of T-GNS and form porous structure in basal plane. As a result, the dispersion of ozone-treated T-GNS in aqueous solution was greatly improved, and the enhanced oxygen-containing groups and dispersion would facilitate its further functionalization and application.

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1. Introduction

Graphene nanosheets (GNS), two-dimensional layers of sp²-bonded carbon atoms [1,2], have outstanding performance and excellent thermal, mechanical and electrical properties. Moreover, its nanostructure is fascinating [3–6]. Since been found, GNS have been fully demonstrated the infinite charm in the theoretical

study and practical application [7,8]. Several methods have been developed to produce these two-dimensional carbon materials. Compared with other preparation strategies such as exfoliation of graphite and epitaxial growth on silicon carbide [9], oxidation-reduction method appears to be much more feasible in that it enables mass production of GNS at low cost. First, graphite oxide (GO) was prepared by oxidation from graphite, and then GO was exfoliated into GNS by ultrasonic exfoliation or thermal exfoliation method. However, GNS prepared by ultrasonic method usually tended to aggregate during the drying process because the reaction

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was taken under the liquid phase. In contrast, thermal exfoliation method could get relatively fluffy GNS, but the functional groups on its surface are fewer. As a result, it is difficult for GNS to disperse into aqueous solution and organic media, which will greatly limit their further functionalization for various specific purposes [9,10]. In order to improve their solubility, a variety of modifications on GNS have been reported [11–15]. The easiest way to covalently attach chemical groups is oxidation, such as liquid oxidation, oxygen plasma treatment and ozone treatment, resulting in the formation of carboxyl and hydroxyl groups on the surfaces of GNS (typical oxidation results were listed in Table 1).

Among all these oxidation methods, liquid oxidation using chemical reagents is the most common method for surface modification in the past, which enables the formation of oxygen-containing functional groups on the surface of GNS. However, liquid oxidation methods need complicated processing steps and take rather long time [9,10]. Moreover, the liquid wastes generated from these solution-phase oxidation methodologies together with the tedious purification procedures would greatly limit their further development for industrial application. Plasma treatment is a new and efficient method in the field of surface modifications in recent years [12,16–21]. The excited species, radicals, electrons and ions within plasma strongly interact with the surfaces of GNS, breaking the C=C and creating active sites for binding of functional groups [22], which causes several chemical and physical modifications occurring on the surfaces. Compared to liquid oxidation methods, plasma oxidation method has the advantages of shorter reaction time, nonpolluting process, and providing a wide range of different functional groups depending on plasma parameters such as power, gas species, treatment time, and pressure [19,23]. Although plasma treatment has a number of advantages, this method also have several problems, such as the unfavorable oxidation degree and difficulties on producing large quantities necessary.

Ozone treatment is a relatively new and facile method. In recent years, ozone treatment has been used to modify carbon materials such as active carbons, carbon black, carbon fibers and graphite materials [24–30]. In addition, carbon exposure to ozone may lead to the formation of carboxylic, hydroxyl, ether and carbonyl groups. Compared with the previous two oxidation methods, the characteristics of ozone oxidation are simple experimental apparatus, easy operation, low cost, and efficient. In addition, this method can realize the mass production, which makes up for the defects of plasma treatment. Moreover, it is worth mentioning that, ozone oxidation can realize the simultaneous processing by adjusting the reaction temperature or adding water vapor or ultraviolet as auxiliary conditions [13,14,31,32], which could realize multifactor synergetic enhancement effect and significantly improve the degree of oxidation. Therefore, several researches on ozone treatment for surface modification on GNS have been carried out in recent years. Krawczyk [13] reported that results of expanded graphite modification strongly depend on the temperature of ozone treatment and demonstrated that ozone treatment increases the specific surface area and creates additional oxygen functionalities. In his study, expanded graphite was placed under room temperature and 140 °C for ozone oxidation, and the O/C was increased to 0.199 and 0.052 after ozone treatment, respectively. Then he pointed out that ozone is trapped within the porous structure of graphene at 140 °C, with subsequent reactions taking place at the surface and altering the distribution of oxygen-containing functional groups. What is more, he found that ozone treatment at elevated temperatures would cause partial decomposition of the graphite skeleton and yielding CO and CO₂. Tao et al. [32] presented a study of single-layer and few-layer graphene sheets exposed to chemical species inside an ozone generator and demonstrated a crossover from a

nano-crystalline phase to an amorphous carbon phase in single-layer graphene as the exposure time is increased.

Although the research work mentioned above has made considerable progress, studies on the influence factors of ozone treatment were not comprehensive enough. The amount of oxygen-containing groups introduced on their surface is far enough for the further functionalization and application of GNS partly due to the unsatisfactory temperature conditions in ozone treatment. In the present work, a series of suited ambient temperature were designed for the ozone treatment of thermal-exfoliated graphene nanosheets (T-GNS) and the surface chemical contents and morphology changes of T-GNS were investigated as a function of treatment time and temperature. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were used to estimate the influence of treatment time and temperature on the generation of oxygen-containing groups onto the surfaces of T-GNS. For further study, the surface morphology and structural changes of T-GNS before and after ozone modification were observed by atomic force microscopy (AFM) and Raman spectra, and the mechanisms of T-GNS oxidation were proposed based on the analysis of all these results mentioned above.

2. Experimental

2.1. Preparation of T-GNS

T-GNS were prepared by a two-step synthesis. First GO was prepared by the modified Hummers method [33] and then T-GNS were obtained by thermal exfoliation from GO. For the modified Hummers method, a 9:1 mixture of concentrated sulfuric acid (H₂SO₄) and phosphoric acid (H₃PO₄) was added to a mixture of natural graphite flakes and KMnO₄, and the reaction was heated to 50 °C and stirred for 12 h. Then the mixture was washed with deionized water until the pH value was up to 6, and then vacuum-dried at 60 °C for 48 h. For exfoliation process, the prepared GO was thermally exfoliated in a vacuum tube furnace at the temperature of 1050 °C for 30 s, yielding the final product – the T-GNS.

2.2. Ozone modification of T-GNS

The ozone method treatment device was shown in Fig. 1. The modification of T-GNS was performed under a continuous flow of ozone through T-GNS beforehand placed into a three-neck flask. Ozone was produced in an ozone generator supplied by oxygen and then passed through the T-GNS at a constant flow rate of 2 L/min [13]. Ozone treatment temperature was 25 °C, 50 °C and 80 °C, monitored by a constant temperature water bath apparatus which was placed below the three-neck flask, and the treatment time was set for 5 min, 10 min and 20 min, respectively (listed in Table 2). It was found that the T-GNS samples get burned in flask when the treatment time exceeded 20 min while the reaction temperature was 80 °C. As a result, only little modified

Table 1
Typical results of different oxidation methods of GNS.

	Oxidation methods	Experimental conditions	O/C	Reference
1	Liquid oxidation	In nitric acid solution 60 °C 2 h	0.390	[11]
2	O ₂ plasma	50 min	0.194	[12]
3	Ozone	Room temperature 1 h	0.199	[13]
4	Ozone	140 °C 1 h	0.052	[13]
5	Ozone	80 °C 20 min	0.504	This work

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