



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



Zhiwei Xu^{a,*}, Mengyao Yue^a, Lei Chen^a, Baoming Zhou^b, Mingjing Shan^b, Jiarong Niu^b, Baodong Li^b, Xiaoming Qian^{b,*}

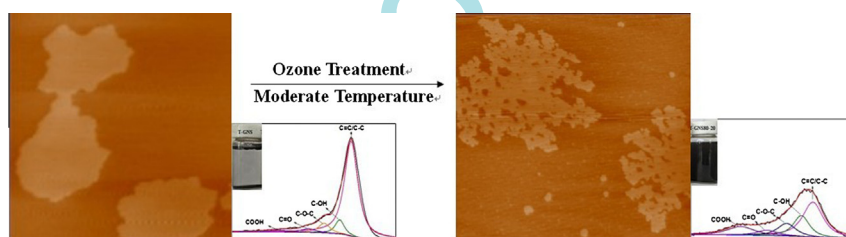
^a Key Laboratory of Advanced Braided Composites, Ministry of Education, Tianjin Polytechnic University, Tianjin 300387, People's Republic of China

^b School of Textiles, Tianjin Polytechnic University, Tianjin 300387, People's Republic of China

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



ARTICLE INFO

Article history:

Received 11 August 2013
Received in revised form 10 November 2013
Accepted 22 November 2013
Available online 1 December 2013

Keywords:

Graphene nanosheets
Ozone treatment
Edge etching
Oxygen-containing groups
Porous structure

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

* Corresponding authors. Tel.: +86 022 83955231 (Z. Xu).

E-mail address: Chinaxuzhiwei@tjpu.edu.cn (Z. Xu).

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

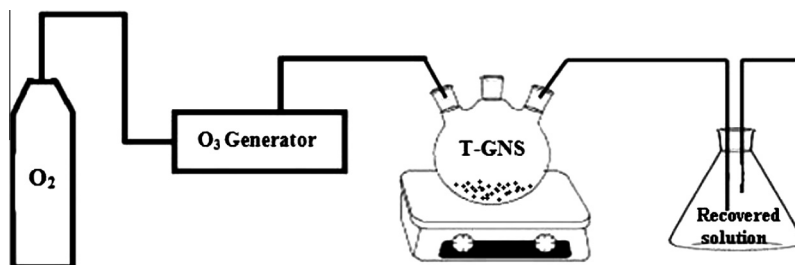


Fig. 1. The structure chart of ozone treatment apparatus.

Table 2
Experimental conditions of T-GNS.

Sample	Temperature (°C)	Treatment time (min)
T-GNS 25-5	25	5
T-GNS 25-10	25	10
T-GNS 25-20	25	20
T-GNS 50-5	50	5
T-GNS 50-10	50	10
T-GNS 50-20	50	20
T-GNS 80-5	80	5
T-GNS 80-10	80	10
T-GNS 80-20	80	20

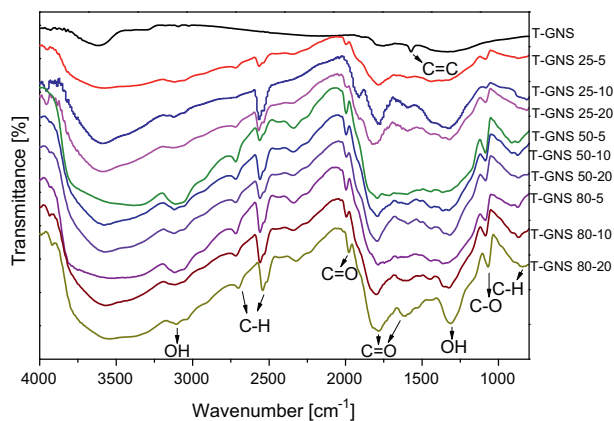


Fig. 2. FTIR spectra of T-GNS before and after ozone treatment.

T-GNS products could be obtained, and the yield was sharply reduced.

2.3. Characterization

FTIR was acquired using a Bruker Tensor 27 system in the 4000–800 cm^{-1} wave-number range to analyze the functional groups grafted onto the surface of T-GNS before and after ozone modification. All the samples were pressed into a pellet with potassium bromide (KBr) before measurement. The spectra were collected by cumulating 32 scans at a resolution of 2 cm^{-1} . XPS investigations were carried out with a PHI 5700 ESCA System with Al $K\alpha$ (1486.6 eV) radiation to characterize changes of the chemical components of all T-GNS samples and the pressure in the XPS analyzing vacuum chamber was less than 3×10^{-9} mbar. AFM measurements with the typical contact-mode were performed using Digital Instrument CPM5500, and all samples were dispersed by sonication in a mixture of ethanol, then dried and tested under the contact mode. The Raman spectra were measured by a Renishaw RM2000 Microscopic Confocal Raman Spectrometer, using the

514.5 nm line of Ar-ion laser with a power of 4.7 mW, and the beam spot was $\sim 3 \mu\text{m}$.

3. Results and discussion

3.1. FTIR spectra

As shown in Fig. 2, FTIR spectra were used to qualitatively validate the very existence of introduced oxygen functional groups on the surface of T-GNS. In the original T-GNS sample, the characteristic feature was the peak at 1580 cm^{-1} , which correspond to $\text{C}=\text{C}$ [34]. After ozone treatment, the peak of $\text{C}=\text{C}$ was slightly weakened, and peaks of $\text{C}-\text{H}$ appeared at 2750, 2530 and 960 cm^{-1} . Meanwhile, clear peaks appeared at 3100 and 1380 cm^{-1} , which correspond to the functional group of OH [35]. These peaks were not observed before ozone treatment and became more intense with increasing the ozone treatment time and temperature. More in detail, characteristic $\text{C}=\text{O}$ peaks (1950 , 1760 and 1600 cm^{-1})

Table 3
Element content of all T-GNS samples.

Sample	C1s (%)	O1s (%)
T-GNS	94.66	5.34
T-GNS 25-5	87.28	12.72
T-GNS 25-10	84.93	15.07
T-GNS 25-20	83.74	16.26
T-GNS 50-5	86.81	13.19
T-GNS 50-10	82.23	17.77
T-GNS 50-20	80.78	19.22
T-GNS 80-5	86.32	13.68
T-GNS 80-10	80.81	19.19
T-GNS 80-20	66.54	33.46

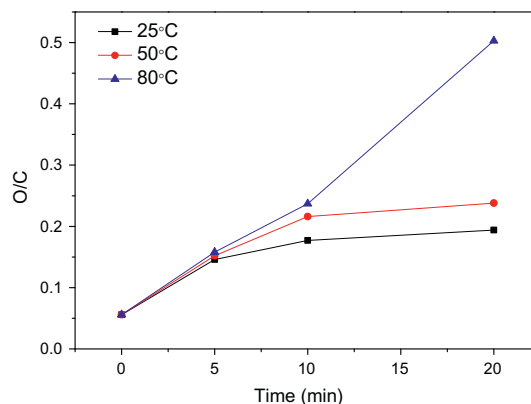


Fig. 3. The O/C atomic ratio of T-GNS as a function of ozone treatment time under different temperature.

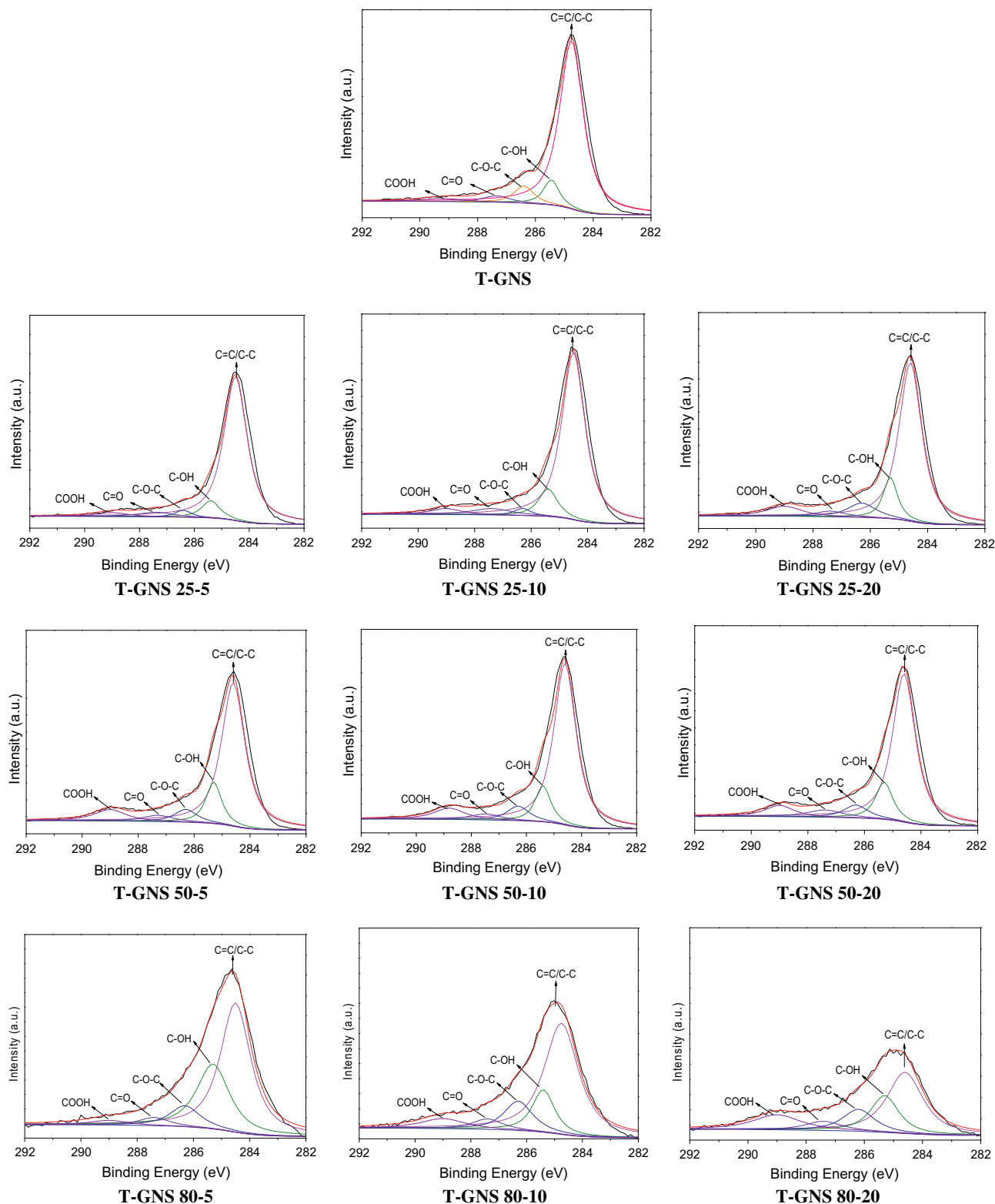


Fig. 4. High-resolution of C1s spectra of all T-GNS samples.

and C–O peaks (1100 cm^{-1}) appeared after ozone modification [34,35], corresponding to the stretching mode of the carboxylic acid group (–COOH). The present FTIR spectra revealed that large extent oxygen functional group of –OH, C–O and C=O, which was originated from –COOH groups, was introduced on the surface and it could be attributed to ozone oxidation effect. Li et al. [36] reported that ozone attacking on the C=C was responsible for the

oxidation of carbon surface. C=C would be firstly converted to –C–OH which was then oxidized to –COOH finally.

3.2. XPS analysis

The element contents of all T-GNS samples were listed in Table 3, and the O/C atomic ratio of T-GNS samples was shown

in Fig. 3. Compared with the three curves in Fig. 3, it could be concluded that with the treatment time increasing, the degree of oxidation is gradually increased, and the atomic ratio of O/C is also increased. More in detail, Fig. 3 also reveals that in the same treatment time, the higher the temperature, the larger the atomic ratio of O/C. The O/C atomic ratio of T-GNS 80-20 is plus a factor of 5 higher than that in the original T-GNS. Fig. 3 contradicts common ideas, as ozonation at elevated temperature is expected to increase surface oxygen content.

For the detailed studies of functional groups, peaks of C 1s were studied. We use XPSPEAK41 software to fit the peaks and analyze the C 1s spectra. And then we calculate the chemical composition of all the T-GNS samples by calculating the relative ratios of each chemical group's peak area. Fig. 4 and Table 4 show C 1s peaks of XPS spectra of the T-GNS samples before and after ozone treatment. The C1s spectra of all samples were deconvoluted into five peaks corresponding to C=C/C-C in aromatic rings (284.5–284.8 eV), C-OH bond (285.2–285.5 eV), an epoxide group (286.2–286.4 eV), a carbonyl group (287.3–287.5 eV), and an additional carboxylate group (288.6–290.0 eV) [25,37].

Due to the ozone treatment process, the percentage of C=C/C-C was lower whereas the percentage of oxygen-containing groups were higher than the untreated T-GNS, which was also consistent with the O1s spectra of T-GNS (Fig. 5). Comparing the C1s spectra for all T-GNS samples, it can be easily observed that ozone treatment at room temperature increased the C-OH, C=O and COOH species with a simultaneous reduction in the C=C/C-C. The most unexpected result is a decrease in C-O-C species when the treatment time was 5 or 10 min, and with the further extension of time, the C-O-C increased. This may be due to the reason that the C-O-C species was first decomposed at the beginning of ozone oxidation reaction, and the surface of T-GNS was re-oxidized as the ozone treatment continues. Then, with the treatment temperature increasing to 50 °C, the change of oxygen functional groups becomes not obvious even though we extended treatment time. However, when the temperature was elevated to 80 °C, the oxygen functional groups on the surface of T-GNS vary significantly. In the first 5 min, a large number of C-OH groups generated on the surface of T-GNS samples after ozone treatment. When ozone treatment was taken for 10 min, some of the C-OH groups converted into C-O-C and COOH species. Especially when ozone modification was performed at 80 °C for 20 min, C-OH, C-O-C and C=O species increased to 20.77%, 13.90% and 6.68%, respectively. The most worthy of our attention is that the percentage of carboxyl group was more than 10 times increased compared to original T-GNS, which suggests that different functional groups are formed during ozone treatment at elevated temperatures. This hypothesis is partially supported by reports on ozone treatment of different carbon materials [28,35,26].

3.3. AFM observations of T-GNS

In order to characterize the surface topography changes of T-GNS samples before and after ozone modification, AFM measurements were used in the contact mode. According to the FTIR and XPS results, the effects of ozone treatment mainly depend on temperature. Moreover, combined with the atomic ratio of O/C mentioned above (Fig. 3), we can easily find that when the ozone modification of T-GNS samples was taken for 20 min, a better oxidation degree could be obtained. So we take four typical samples (T-GNS, T-GNS 25-20, T-GNS 50-20 and T-GNS 80-20) to investigate the surface change of the T-GNS samples. As can be seen in Fig. 6a and b, there is an obvious difference between the original T-GNS and T-GNS 25-20. The thickness of the original T-GNS is about 1.37 nm, however, after ozone treatment, the thickness of the ozone modified T-GNS samples is raised to 2.27 nm (T-GNS

Table 4
Chemical composition of all T-GNS samples.

Sample	Functional group (%)				
	C=C/C-C	C-OH	C-O-C	C=O	COOH
T-GNS	83.82	6.75	5.64	2.36	1.43
T-GNS 25-5	82.60	7.69	2.76	4.00	2.95
T-GNS 25-10	78.18	10.58	2.37	5.22	3.65
T-GNS 25-20	70.15	11.54	7.96	3.51	6.84
T-GNS 50-5	69.09	13.49	5.89	4.17	7.36
T-GNS 50-10	71.77	11.26	6.46	3.62	6.89
T-GNS 50-20	68.65	13.03	6.37	5.43	6.52
T-GNS 80-5	55.48	29.75	8.89	3.44	2.44
T-GNS 80-10	58.15	16.96	12.08	4.92	7.89
T-GNS 80-20	44.28	20.77	13.90	6.68	14.37

25-20), 2.38 nm (T-GNS 50-20) and 2.95 nm (T-GNS 80-20), respectively (Fig. 6b–d), which indicates that the T-GNS samples are covered by the introduced oxygen-containing groups. Moreover, notched edges and porous defective nanostructure appears on the T-GNS 50-20 and T-GNS 80-20 (Fig. 6c and d). These results further reveal that graphene could be successfully ozonated at a moderate temperature. These results indicated that the oxygen functional groups were incorporated onto the surface of T-GNS evenly and uniformly. The sharp increase of the thickness is due to the oxygen-containing groups generating onto the basal plane of T-GNS, which is also in good agreement with the FTIR and XPS characterization. The presence of morphological changes in ozonated T-GNS gives evidence of a partial decomposition of the carbon structure due to synergetic effects of ozone oxidation and treating temperature. Therefore, ozone treatment may increase the specific surface area of the T-GNS samples and create new nano-hole structures in basal plane of T-GNS, which would be expected to be useful in further applications such as polymer composites [13].

3.4. Raman spectra of T-GNS

To further characterize the structural changes of T-GNS before and after ozone modification, Raman analysis were applied. We also selected these typical samples (T-GNS, T-GNS 25-20, T-GNS 50-20 and T-GNS 80-20) to investigate. The Raman spectra in Fig. 7 convey important information on the structural damages induced in the T-GNS samples after ozone treatment. The G band (sp^2 -hybridized carbon) at $\sim 1590\text{ cm}^{-1}$ and the D band (sp^3 -hybridized carbon) at $\sim 1355\text{ cm}^{-1}$ are recorded [38–42]. The intensity ratio of D band to G band (I_D/I_G) of T-GNS is shown to

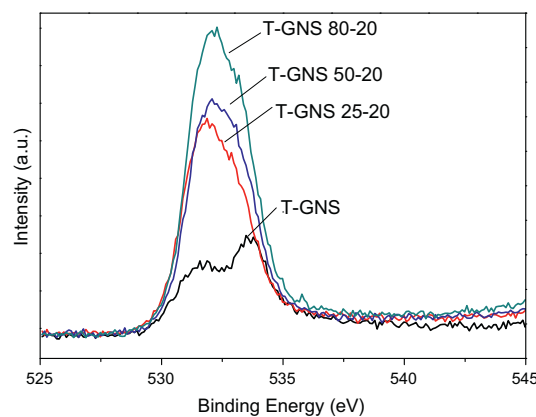


Fig. 5. The O1s spectra of T-GNS before and after ozone treatment.

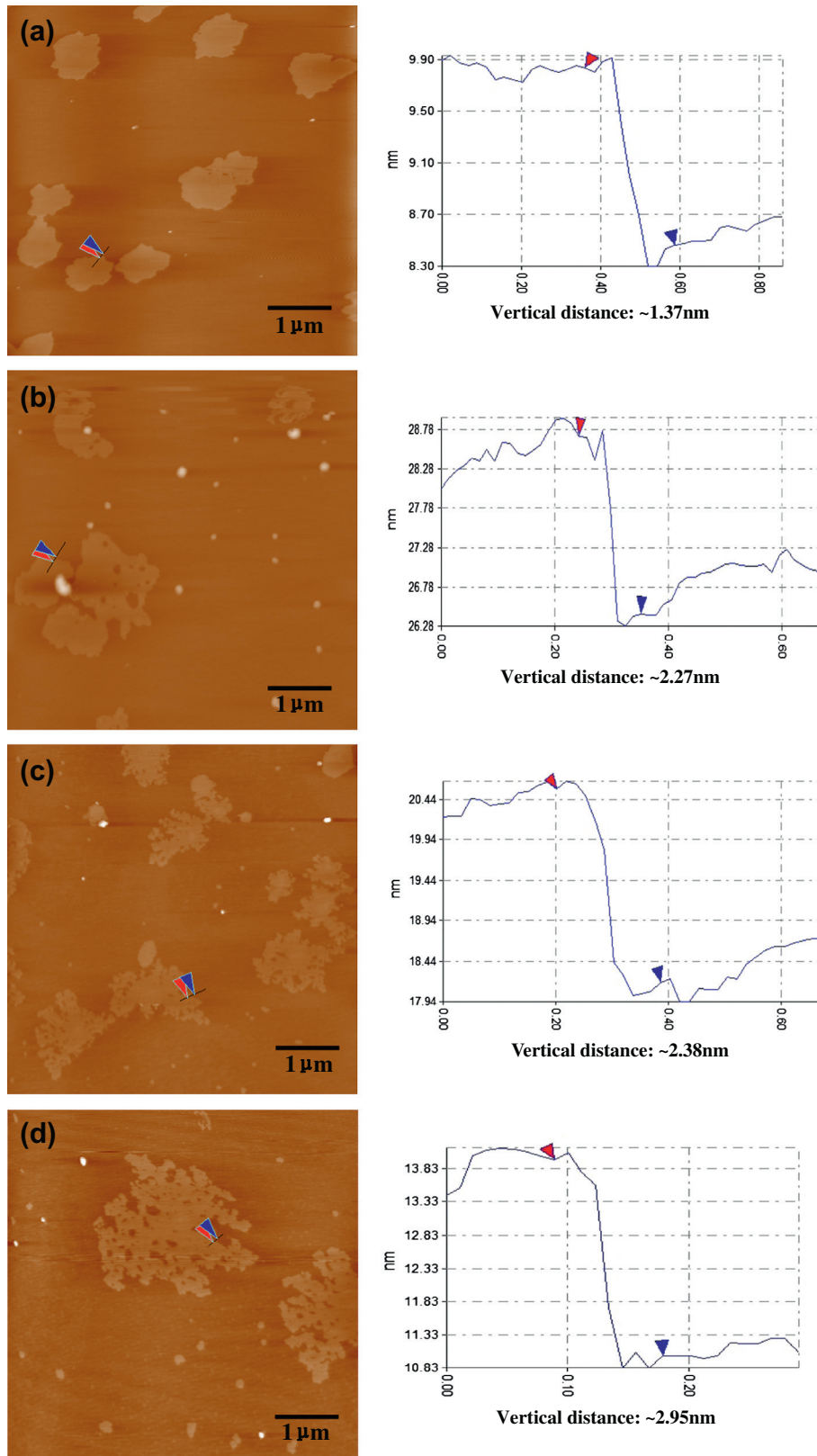


Fig. 6. AFM images of T-GNS before and after ozone treatment: (a) original T-GNS, (b) T-GNS 25-20, (c) T-GNS 50-20 and (d) T-GNS 80-20.

be increased from 0.735 to 0.753 (T-GNS 25-20), 0.810 (T-GNS 50-20) and 0.816 (T-GNS 80-20) after ozone treatment, suggesting a decrease in the average size of sp^2 carbon domains, which is induced by the increased number of smaller graphitic domains

formed during ozone modification process. Therefore, as the temperature elevated, the structure defects in basal plane of T-GNS also increased. These increases may also suggest the introduction of oxygen-containing groups on T-GNS and support the edge

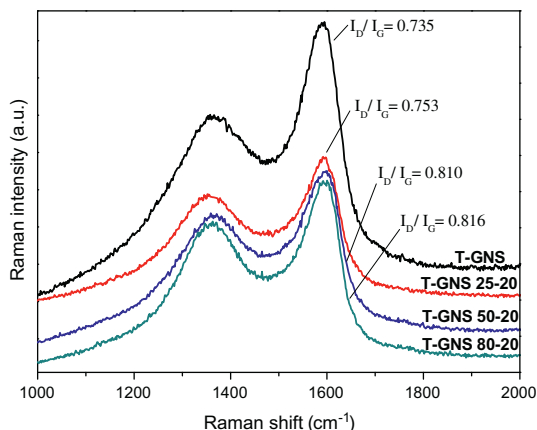


Fig. 7. Raman spectra of T-GNS samples before and after ozone treatment for 20 min.

etching and porous structure effects (from the AFM results) under ozone treatment.

3.5. Dispersion properties

To investigate the dispersion properties of T-GNS after ozone modification, all samples were dissolved in distilled water at 0.1 mg/ml. Compared with the original T-GNS, the ozone-treated T-GNS samples have a very good dispersion in aqueous solution. As can be seen in Fig. 8, T-GNS after ozone treatment disperse well in aqueous solution and do not form aggregation at the bottom of the bottle after 30 min ultrasonication (Fig. 8a). According to Fig. 8b, it can be seen from the picture that there are black sediments at the bottom in T-GNS 25-5, T-GNS 25-10 and T-GNS 25-20, which indicated that the dispersibility of T-GNS samples treated under room temperature became unstable after settling for 24 h. In contrast, other samples treated at a higher temperature perform better and do not form deposition even after settling for 24 h, which clarifies that the oxygen-containing groups introduced on the surface of the T-GNS via ozone treatment are almost hydrophilic. In brief, the dispersion properties of ozone-treated T-GNS are significantly improved especially in 80 °C. These results are also consistent with FTIR, XPS, AFM and Raman analysis.

4. Conclusion

In conclusion, a facile and efficient method to modify graphene nanosheets via ozone treatment with moderate temperature is presented in this article. The results revealed that the edge etching, porous and highly reactive graphene nanosheets could be prepared. The analysis results of FTIR and XPS indicated that ozone treatment time and temperature jointly affect the atomic contents and structure properties of T-GNS. Moreover, treatment temperature is crucial for the final results. The O/C atomic ratio of T-GNS treated under 80 °C for 20 min reached 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, AFM results show that ozone oxidation above 50 °C will cause the edge etching and form more pore structure on the surface of T-GNS, and thus will greatly improve its reaction activity. Raman spectra also confirm that structure defects occurred on the T-GNS samples during the ozone treatment. As a result, the dispersion of T-GNS in deionized water is improved by ozone treatment in an intermediate temperature. Ozone treatment under a moderate temperature is a simple method to obtain high-reactive T-GNS, which makes T-GNS be conveniently used for further functionalization and broadens their application in other fields.

Acknowledgments

The work was funded by the National Natural Science Foundation of China (11175130, U1362108), China Postdoctoral Science Foundation (2012M520578) and the Jiangsu Planned Projects for Postdoctoral Research Funds (1202067C).

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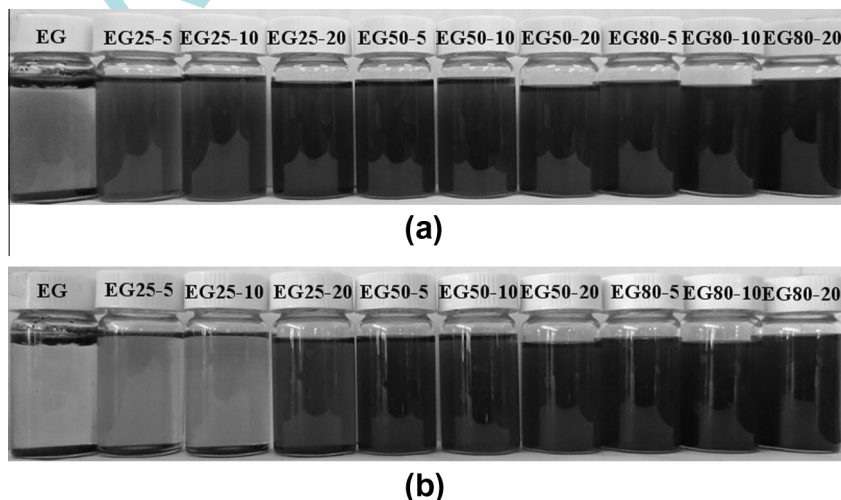


Fig. 8. Dispersion properties of T-GNS samples (0.1 mg/ml in distilled water) before and after ozone treatment: (a) after ultrasonication for 30 min and (b) and then after settlement for 24 h.

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