Effect of Different Reduction Methods on the Structure of Graphene Oxide

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Abstract. The samples of graphene oxide were prepared by Hummers method, and then they were reduced and dried by different methods. The effects of different treatment methods on the graphene oxide’s morphology, size and oxygen content were analysed by IR, Roman and TEM. The results show that the reduction method of increasing temperature can effectively reduce the oxygen content of graphene oxide but increase the defect density. However, the ultrasonic cell pulveriser can effectively reduce the oxygen content of graphene oxide in the reduction process and has little effect on the defect density. Therefore, low-defect and low-oxygen reduced graphene oxide can be quickly obtained by an ultrasonic cell pulveriser.

1. Introduction
In 2004, British scientist professor A. Geim and his team used the method of mechanical stripping to successfully prepare graphene in experiments for the first time [1]. Since then, graphene has attracted extensive attention because of its excellent properties. Graphene is a type of carbon elemental substance. Carbon atoms of graphene form two-dimensional materials with hexagonal structural units through sp² hybridization. Due to its special two-dimensional structure, graphene has excellent electrical, optical, thermodynamic and mechanical properties, which make it widely used in many fields. Reduced graphene oxide has properties between graphene and graphene oxide [2]. Reduced graphene oxide can be combined with a variety of materials due to its surface containing a variety of oxygen-containing functional groups, making it applicable for biomedical applications [3-4]. Graphene oxide can be reduced by reducing agents, heating and electrochemical reduction methods. During the reduction process, graphene oxide will lose a large number of oxygen-containing functional groups on the surface of graphene oxide, making its C/O ratio increased [5-8].

In this paper, different treatment methods such as ultrasonic, microwave, drying and freeze-drying were used respectively or together in the reduction process of graphene oxide. Through comparing their effects on the reduction degree of graphene oxide, effective methods are proposed to prepare certain type of graphene oxide to prepare for subsequent application.

2. Experimental section

2.1. Materials
Graphite powder (C, AR, >98.0%) were supplied by Tianjin Dengke Chemical Reagent Co., Ltd. Potassium Permanganate (KMnO₄, AR, >99.5%), Concentrated Sulfuric Acid (H₂SO₄, AR, 95.0% – 98.0%), Hydrochloric Acid (HCl), Hydrogen Peroxide (H₂O₂, GR, 30%), all above chemicals were used directly without further purification.

### Table 1. Different treatment conditions of graphene oxide.

| Graphene oxide | Microwave (1 min | 3 times) | Ultrasonic (30min) | Untreated | Untreated | Ultrasonic cell disrupter (30 s | 3 times) |
|----------------|-----------------|-------------|-------------------|-----------|-----------|-------------------------------|------------|
| Freeze drying  |                 |             |                   | 7-1       | 7-2       | 7-3                           | 7-4        |
| Drying at 60°C |                 |             |                   |           |           |                               | 7          |

#### 2.2. Preparation of Graphene oxide and reduced graphene oxide
Graphene oxide was prepared from graphite by a modified Hummers method[9]. Take 2.5 g of graphite powder and slowly add it into the beaker with 80mL of concentrated sulfuric acid under the condition of ice water bath, then add 7.5 g of potassium permanganate into the beaker and stir for 10 minutes, the solution turns dark green. Add the magnetic rotor to the beaker and stir it for 6 hours. After 6 hours, the solution turns to dark green viscous substance, slowly add 110 mL distilled water to the beaker, the solution starts to turn yellow, then add 15 mL of 10% hydrogen peroxide solution to oxidize the incomplete reaction substance, and the solution turns to golden yellow after complete oxidation. Wash the golden yellow liquid with 5% hydrochloric acid solution for 3 times, and then wash it with distilled water until there is no sulfate ion in the washing solution to get wet graphene oxide sample.

Table 1 shows the symbolisms of samples. No.7 sample was dried directly at 60 °C. No.7-1 sample was freeze-dried after microwave treatment for 3 times. No.7-2 sample was freeze-dried after ultrasonic treatment for 30 minutes. No.7-3 sample was freeze-dried in original solution. No.7-4 sample was freeze-dried after ultrasonic cell pulverizer treatment for three times. No.7-5 sample was 99% high-purity graphene as control.

#### 2.3. Characterization
The Transmission Electron Microscopy (TEM) were characterized by JEOL JEM 2100, with TEM running at an accelerating voltage of 200 kV. The Raman spectra were obtained by a microscopic confocal laser Raman spectrometer (in Via Reflex), with a Spectra-Physics argon ion laser and excited by the 514.5 nm line. Fourier-transform Infrared Spectroscopy (FT-IR) was recorded on a Bruker
TENSOR27 IR spectrometry. The structural analysis of the samples was characterized by powder X-ray Diffraction (XRD) using a Bruker D8-advance with Cu Kα (λ = 1.5418 Å). The size and morphology were obtained by a scanning electron microscopy (SEM, Hitachi S-4800).

3. Results and discussion

3.1. Infrared test results of different samples
In the infrared spectrum, the broad bands at around 3440 and 1384 cm\(^{-1}\) are assigned to the stretching vibration and deformation vibration of hydroxyl (-OH) from oxygen-containing functional groups and water molecules. The asymmetric and symmetric stretching bands of -CH\(_2\) are performed with two bands at 2926 and 2855 cm\(^{-1}\). The peak of 1717 cm\(^{-1}\), 1633 cm\(^{-1}\), 1053 cm\(^{-1}\) are caused by the stretching vibration of carboxylic (C=O), the aromatic ring vibrations from graphene skeletal (C=C) and the symmetrical stretching vibration of epoxy groups (C-O-C) respectively\(^{10}\). It can be seen from Figure 2 that the peaks of high-purity graphene (sample 7-5) in 3440 and 1384 cm\(^{-1}\) (-OH), 1717 cm\(^{-1}\) (C=O) and 1053 cm\(^{-1}\) (C-O-C) are not obvious with respect to the freeze-dried original sample (7-3), and the peaks of the samples after different treatments are all changed, but the changes of sample 7-1 and 7-2 are not obvious, but the changes of sample 7 and 7-4 are obvious, indicating the increased temperature and ultrasonic cell pulverizer can promote the removal of oxygen-containing groups more easily, and the ultrasonic cell pulverizer has a very good effect on the removal of oxygen-containing groups in a relatively short period of time.

![Figure 2. IR spectra of different samples.](image)

3.2. Raman test results of different samples
In Raman spectrum, G- peak is the main characteristic peak of graphene, which is caused by the in-plane vibration of sp\(^2\) carbon atom. It appears near 1580 cm\(^{-1}\). The peak reflects the number of graphene layers. The intensity of G- peak increases approximately linearly with the number of layers. The D- peak is the disordered vibration peak of graphene, which can be used to characterize the
structure defect or the edge defect of graphene. Generally, the defect density in graphene is characterized by the intensity ratio ID / IG of D-peak and G-peak and the half width of G-peak \cite{11}. It can be seen from figure 3 that the ID/IG ratio of sample 7-5 high purity graphene is the smallest, and the lines of sample 7-2, 7-3 and 7-4 almost coincide, while the ratio of sample 7 is the largest. The comparison showed that the defect density of go increased during heating and microwave reduction, but did not increase during ultrasonic reduction.

3.3. TEM test results of different samples
The SEM view of sample 7 (Figure 4) shows that the size of the stripped go is about 10 microns. Dried and reduced flakes of go look like wrinkled-paper, which correlates to the imperfect C=C bonds and thermal instability influenced by the oxygen functional groups in the sp^3 hybridization model due to incomplete reduction during the hydrothermal route \cite{12}.
4. Conclusions
In this paper, the effect of the reduction graphene oxide prepared by hummers under different conditions is reported. It can be concluded from the experimental comparison that the reduction method with elevated temperature can effectively reduce the oxygen content of graphene oxide but increase the defect density. The ultrasonic cell pulverizer can effectively reduce the oxygen content of graphene oxide while reducing the defect density. Therefore, low-defect and low-oxygen reduced graphene oxide can be quickly obtained by an ultrasonic cell pulverizer.

Acknowledgment
This work was supported by Innovation and Scientific Research Project for Postgraduates of General Institutions of Higher Learning in Hainan Province (Hys2018-54)

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