

## Preparation and Characterization of Graphene

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**Abstract.** The homogeneous-dispersed graphene oxide was prepared by the improved Hummers method, which would be reduced to graphene with the reducing agent called hydrazine hydrate. The X-ray diffraction, Infrared spectroscopy, Raman spectra and Transmission electron microscopy were used to analysis the phase, morphology and structure of the graphene and graphene oxide. The results show that the graphene oxide and reduced graphene oxide prepared via this method, whose degree of oxidation and reduction are high; Also obtained a higher well-disperses and less structural imperfection of the graphene that was manufactured in the reducing system that added ammonia reduction

### 1 Introduction

Graphene is a kind of two-dimensional cellular crystal tightly packed into by the monolayer of carbon atoms, and the perfect graphene which is formed by sp<sup>2</sup> hybridization presents a stable two-dimensional structure, it only has a hexagonal cells. It's another new form of carbon structure that is different from that of the fullerenes and carbon nanotubes [1]. Of course, it is founded after them. 2004, University of Manchester, professor Geim got the high quality of graphene by the method of tape tearing [2]. Since then, graphene has attracted much more researchers to study for its unique properties. Such an approximately perfect structure, such as the electricity [3], thermology [4], mechanism [5], etc., that make graphene own a bright application prospect in the transparent electrode, solar cells, sensors, supercapacitors, energy storage and catalyst carrier, and other fields. Now, the preparation of high quality graphene and the improvement application of graphene has become a hot area of research, also it is the best way to advocate energy-saving environmental protection and social development. Based on the concept of low-cost and large-tonnage, the improved Hummers method is adopted to prepare graphene, and the change of the phase, structure and morphology is studied under the different control condition.

### 2 Experiment

#### The preparation of graphite oxide.

The experiment used the improved Hummers method. Measuring 100 ml of concentrated sulfuric acid in the 250 ml beaker and stirring with the 0 °C ice water bath, after of the operation, 1.0 g sodium nitrate was added in the

mixture. When it dissolved adequately and stirred uniformly, 3.0 g flake graphite would be added in batches. 10.0 g potassium permanganate should be joined in the mixtures slowly after it was stirring for 30minutes to prevent the explosion due to the high local temperature caused by instantaneous heat release. Continuing to reaction 1hour, the beaker was transferred into the 40 °C water-bath with constant temperature and kept stirring for 2 hours. During high-temperature stage, the reaction was under the conditions of room temperature and agitation. 140 ml distilled water would be added in the form of droplets to maintain the solution under 100 °C. Finally, the oxidation reaction was finished by the addition of 400 ml distilled water and 5~10 ml 30% hydrogen peroxide to make the color of solution change into golden yellow. The resultant mixture product was filtered while it still hot and washed with 5% sulfuric acid and distilled water in less frequent way and dried at 60 °C under vacuum for 48 hours.

#### The preparation of graphene.

0.1 g graphite oxide was dissolved in 50 ml distilled water and ultrasonicated with power of 100W for 2 hours until the solution turned into brown. So the graphene oxide solution was got. And then the graphene oxide aqueous solution was heated up to 80 °C, at the same time, 2 ml85 % hydrazine hydrate was added. The mixture would maintain that temperature and stir for 6 hours. All that remains was to filter, wash and dry under vacuum to get the graphene.

### 3 Results and discussion

#### X-ray diffraction analysis.

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As shown in figure 1, it can be seen that the graphite oxide show a very obvious (001) peak at  $10.3^\circ$  for a typical characteristic peak with a layer spacing of 0.859 nm significantly larger than that of graphite of 0.335 nm. The phenomenon is attributed to the introduction of a large number of oxygen groups of the graphite oxidation make graphite intercalating space larger. The (001) diffraction peak disappeared after reduction of the graphite oxide, thus opposite is appearing a diffraction peak at around  $24.5^\circ$  which is similar to graphite that is at  $26^\circ$ , but the diffraction peak of graphene is more widely obviously. For the size of graphite is smaller by the reduction reaction and the degree of deficiency and disorder of graphite will increase via the two stages that is oxidation and reduction.

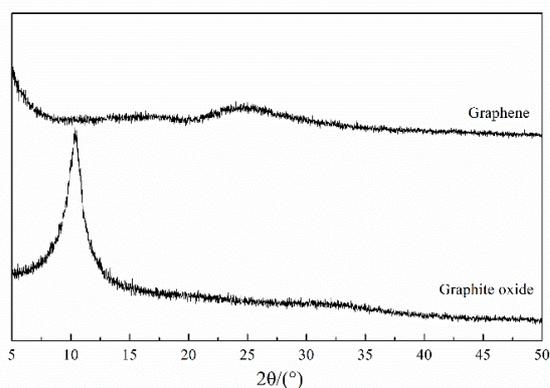


Figure.1. XRD patterns of graphene and graphite oxide

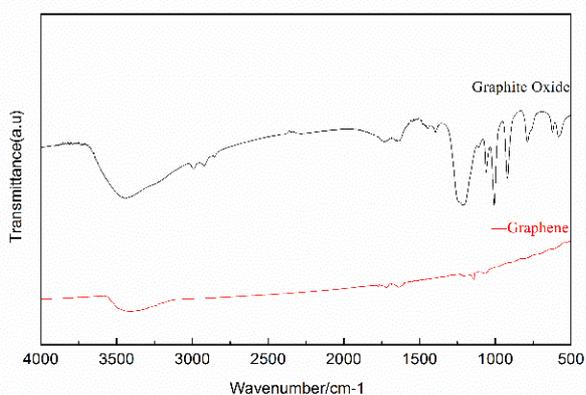


Figure.2. Infrared spectra of graphite oxide and graphene

### Infrared spectroscopy analysis.

The infrared spectra from  $500\sim 4000\text{ cm}^{-1}$  of the graphene and graphene oxide are shown in figure 2. It is shown that the peak at about  $3430\text{ cm}^{-1}$  attributed to OH stretching vibration in the high frequency area, and at  $3000\sim 3700\text{ cm}^{-1}$  owing to a wide spectrum peak that mainly because of OH bending vibration in the water molecules that the graphite oxide absorbs. The peak at about  $2900\text{ cm}^{-1}$  attributed to the C-H stretching vibration of  $\text{CH}_2$  groups, at about  $1730\text{ cm}^{-1}$  belong to the COOH stretching vibration of carboxyl groups of edge of graphite oxide, at about  $1640\text{ cm}^{-1}$  refer to the C=C. The peak at the range

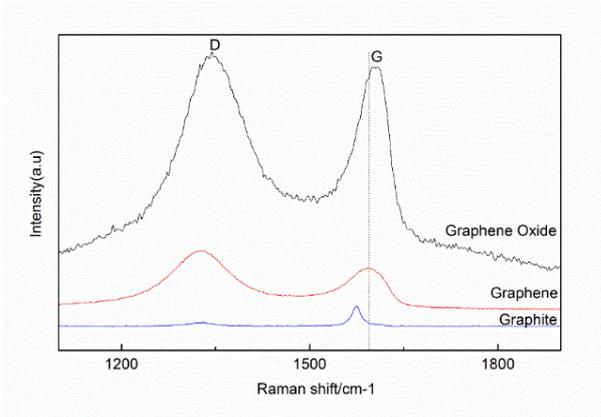
of  $1500\sim 900\text{ cm}^{-1}$  might be related to C-O-C stretching vibration on the surface of graphite oxide entirely. Besides the band at  $1390\text{ cm}^{-1}$  ascribed to  $\gamma\text{C-O-C}$ , at  $1200\text{ cm}^{-1}$  belong to  $\beta\text{C-O-C}$ , at  $1100\sim 900\text{ cm}^{-1}$  and  $780\text{ cm}^{-1}$  are corresponded to  $\alpha\text{C-O-C}$  and C-O-C. These existing oxygen containing groups show that graphite has been oxidation and the degree of oxidation is very high. This is the reason graphite oxide has good hydrophilicity due to the existence of oxygen containing groups. Furthermore, a delamination effect could occur within alkaline solution to apply to the synthesis of composite materials under certain conditions.

Compared with graphite oxide, the absorption peak of oxygen-containing groups vibration of graphene are all disappeared. It is also shown that the reduction degree of graphite oxide is so high.

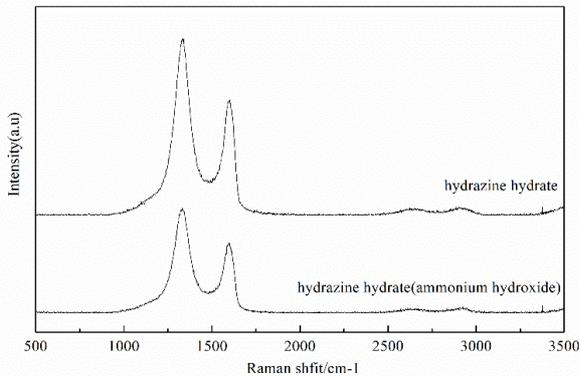
### Raman spectrum analysis.

The Raman spectrum of graphite, graphite oxide and graphene are shown in figure 3. The most obvious and important characteristic peak of the single atomic layer graphene is the G band at about  $1580\text{ cm}^{-1}$  caused by the first-order  $\text{E}_{2g}$  phonons planar vibration of carbon atoms. The D band is produced on the edge defects or lattice structure damage in the process of preparation of graphene, otherwise known as defect peak at about  $1350\text{ cm}^{-1}$ . It is shown that the G band of graphite is at  $1570\text{ cm}^{-1}$  and blue shift relative to that of the graphene. This is because the D band comes from the lattice defects, for the breakage of graphite, it is Raman inactive, namely graphite itself almost does not exist defects. The oxidation make its edge and surface introduce a large number of oxygen-containing groups and change the bond of C=C, thus the graphite oxide has the Raman active and a strong D defect peak at  $1350\text{ cm}^{-1}$ . At the same time, the destruction of C=C and the change of lattice structure make the part of the carbon atoms turn  $\text{sp}^2$  hybridization into  $\text{sp}^3$  hybridization, the result is the attenuation of  $\text{sp}^2$  hybridization and the rise of lattice disorder. So that it has a wide G band at  $1600\text{ cm}^{-1}$  and redshift to the graphite.

Relate to graphene oxide, the graphene blue shift and its G band, D band respectively at  $1580\text{ cm}^{-1}$  and  $1340\text{ cm}^{-1}$ . The ratio of  $I(\text{D})/I(\text{G})$  is larger than that of graphene oxide, it also shows a part of  $\text{sp}^3$  hybridization have converted to  $\text{sp}^2$  after the reduction. The figure shows that graphene oxide have been fully reduced basically, it also means the loss of a large amount of oxygen-containing groups make chemical bonds have further changes and the increase of lattice structure defect.



**Figure.3.** Raman spectrum of graphite, graphene oxide and graphene

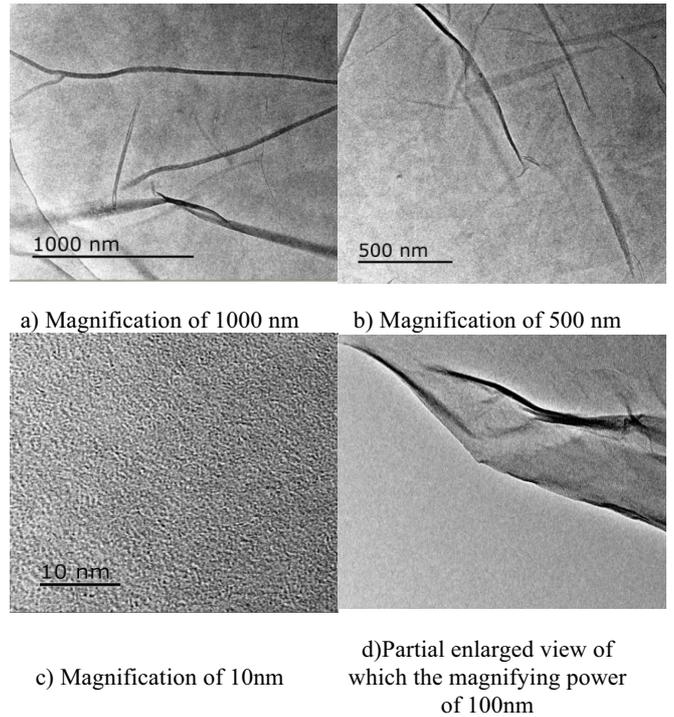


**Figure.4.** Raman spectrum of graphene with and none ammonium hydroxide

As shown in figure 4, there is no obvious difference in the position of G and D band between the two kinds conditions of preparation of graphene. In the process of preparation, the addition of hydrazine hydrate excessive and alkaline to make the solution present alkaline. But the addition of ammonia did not play an obvious role in adjusting the PH of solution. On the other hand, compared with both the ratio of I(D)/I(G), we can see the ratio of I(D)/I(G) decrease when add ammonia. It also illustrates the regulation of ammonia can make solution environment become "mild", oxygen containing groups are more likely to fall off, the damage of lattice structure is smaller. All these reflected on the Raman spectrum is the decrease of the ratio of I(D)/I(G). In the experiment, it expresses a better dispersion.

**Transmission electron microscopy analysis.**

According to information of the picture, the morphology of graphene oxide can be described as flake-like, transparent gauze texture, curly edge and some fold phenomenon. The structure of graphene oxide that is prepared by oxidation – reduction method is hard to avoid some defects that may create incomplete and unsmoothed lamellar structure.



**Figure.5.** TEM picture of graphene oxide

**4 Conclusion**

The degree of oxidation and reduction of the graphene oxide and graphene prepared by improved Hummers method are high and the dispersion of graphene is good. What obtained in this experiment is exactly what we want. Besides, the operation process is not simple, but also it is easy to control.

However, the defects of graphene oxide and graphene are serious and the number of graphene layers more than five. And the reduction mechanism of graphene has not been fully understood. So it requires researchers exert more effort to do further deeper research.

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**References**

1. Avouris P, Chen Z, Peter beinos V. Nat.Nanotechnol, 2007, 2:605.
2. Sarma S D, Adam S, Hwang E H, et al. Electronic transport in two-dimensional graphene[J]. Reviews of Modern Physics, 2011, 83(2): 407.
3. Kim T Y, Ruoff R S. High Surface Area Graphene-Based Materials for Electrochemical Energy Storage[C]//Meeting Abstracts. The Electrochemical Society, 2014 (28): 1147-1147.

4. Balandin A A. Thermal properties of graphene and nanostructured carbon materials[J]. Nature materials, 2011, 10(8): 569-581.
5. Chae H K, Siberio-Perez D Y, Kim J, et al. A route to high surface area porosity and inclusion of large molecules in crystals[J]. Nature, 2004, 427(6974): 523-527.