



Preparation of Graphene by Oxidation-Reduction Method†

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Graphene nano sheets and graphene oxide were synthesized from natural flake graphite with Hummers and modified Hummers methods. By comparison the infrared spectrums of graphene, we found graphene oxide prepared by the modified Hummers method, in which a slight excess of concentrated sulfuric acid and excessive hydrogen peroxide was used to reduce the residual oxidant, could be reduced more completely and contains less oxygenated functional groups than Hummers method, showing that by controlling the experimental conditions and parameters of oxidation-reduction preparation process that we can reduced graphene oxide completely and get more perfect graphene crystal.

Keywords: Graphene, Modified hummers method, Preparation.

INTRODUCTION

Graphene is one of the carbon nano-materials which has two dimensional hexagonal honeycomb lattice structure consisting of carbon atoms closely stacked by sp^2 hybrid system, pure graphene is only one atom thick crystal, the thickness is *ca.* 0.35 nm. Its basic structural unit is the most stable benzene six-member ring of organic materials. This special structure makes it demonstrate excellent electrical properties (conductivity is as high as 35100 s/m), high strength (Young's modulus up to 1.0 TPa), good thermal conductivity (the thermal conductivity is 3000 W/(m K)), high surface area (2965 m²/g), *etc.*¹. These significant properties make it extensive application prospects in catalysis, composite materials, super capacitor, lithium ion battery, electron field emitters, transparent conductive film, field effect transistor, *etc.*

As graphene has these unique and exceptional performances, it is widely concerned since the discovery in 2004 and the preparation and performances have been made a large number of extensive research. At present, the methods for preparing graphene with graphite mainly include micro-mechanical cleavage², epitaxial growth method³, chemical vapor deposition⁴, oxidation-reduction method^{5,6}. Compared with other three methods, the oxidation-reduction method has relatively low production cost, simple operation and easily realization of large-scale production and thus become a hot research topic in the preparation of graphene.

Oxidation-reduction method is firstly to react natural graphite with strong acid and strong oxidizing substances in ultrasonic dispersion, then remove the surface oxygenated groups of graphene oxide by adding a reducing agent (such as hydrazine) to obtain the reduced graphene. The preparation methods of graphene oxide generally have three types: Brodie method⁷, Staudenmaier method⁸ and Hummers method⁹. Hummers method has the advantages of simple, convenient, less time consuming, high safety, less pollution to the environmental, so Hummers has become the main method to prepare graphene oxide.

The only disadvantage of oxidation-reduction method is that the prepared graphene oxide has some defects. In the preparation of graphene oxide, the graphite sheet layer has some oxygen containing groups, such as -OH-COOH. The graphene oxide that is modified on the surface is often difficult to reduce completely during the process of reduction, which leading to residual oxygen-containing functional groups in the prepared graphene oxide. These structural deficiencies will destroy the crystal structure of graphene, causing partial loss of graphenes electrical properties, which limited the application of graphene. So we hope to prepare the graphene sheets with perfect crystal structure which is reduced sufficiently by comparing the different experimental parameters and conditions of oxidation-reduction method. In this paper we use the Hummers method and the improved Hummers to prepare graphene oxide

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and made the graphene in different experiment parameters and process. With the help of infrared spectroscopy (FT-IR) test methods and other test methods for comparative analysis of graphene oxide and graphene.

EXPERIMENTAL

Oxidation-reduction method is used to synthesize water-soluble graphene with process of oxidation, stripping and reduction of the natural graphite. The graphene achieved mono-disperse condition and could get homogeneous suspension in aqueous solution. The synthetic process was shown in Fig. 1. Mainly through three steps: (1) graphite is oxidized and layer spacing increased (2) graphene oxide is sonicated and exfoliated into graphene oxide sheets in water, electrostatic repulsion made it stable and uniform dispersed in the polar solvent; (3) reduction of graphene oxide with hydrazine hydrate.

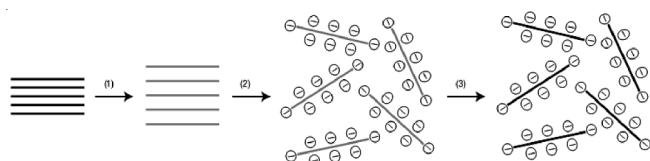


Fig. 1. Synthesis process of graphene

Experimental materials: Natural graphite powder, concentrated sulfuric acid (95-98 %), concentrated hydrochloric acid (36 %), potassium permanganate, sodium nitrate, hydrogen peroxide (30 %), hydrazine hydrate (85 %) and so on, the ingredients are AR.

Preparation of graphene oxide and graphene nano sheets by Hummers: Graphite powder was employed as the raw material. In a typical preparation process, the mass ratio of graphite, sodium nitrate, potassium permanganate was 2:1:6. 1 g of graphite flake and 0.5 g of sodium nitrate were precisely weighed and then dissolved in 23 mL of concentrated sulfuric acid in the ice-bath with continuous stirring. After the complete dissolution of the added salts, 3 g of potassium permanganate was also added and dissolved by stirring below 10 °C for 1 h. Then the mixture was diluted by 50 mL of deionized water by stirring at 35 °C and a large amount of heat was released in this process. Raise the temperature to 98 °C and continue the reaction for 15 min, the colour of the mixture turn brown to yellow. 200 mL of deionized water was added for further dilution and then 10 mL of 30 % H₂O₂ (10 mL) was added for reduction of KMnO₄. Finally, the mixture was washed by 5 % HCl (400 mL) and filtering, in which process the metal ions were removed away. The removal of acid was carried out by the deionized water, then the obtained powder was dried at 60 °C for 2 h. The obtained 0.1 g graphene oxide was added to 100 mL water for ultrasonic dispersion 1 h, then added 5 mL hydrazine hydrate (85 %) in oil bath 100 °C for 1 day, 2 days and 3 days, respectively, the resulting black flocculent precipitate, washed with water, filtration and drying, the obtained powder was graphene.

Preparation of graphene oxide and reduction by modified Hummers method: The experimental procedure was similar with the previous Hummers method. The difference was that increasing the amount of concentrated sulfuric (23-

40 mL) in the oxidation process and increasing the use of H₂O₂ (10-14 mL) in the reduction of residual oxidant KMnO₄ and extending the low temperature reaction time.

RESULTS AND DISCUSSION

Modified Hummers method: Due to the concentration of oxidants and oxidation time have greatly impact on the size and thickness of graphene films. The modified Hummers method by extending the low temperature (10-15 °C) reaction time and in the high temperature phase, control the temperature below 100 °C by adding water continuous, to facilitate hydrolysis of deep oxidation of graphite intercalation compound, generating high oxidation degree of the graphene oxide to improve the reaction efficiency. Facilitate the next step synthetic graphene oxide using hydrazine reduction of graphene. Modified Hummers method can obtain graphene oxide effectively and get high quality nano graphene sheets.

Infrared spectroscopy of the graphene prepared by Hummers method is shown in Fig. 2. As can be seen from the Fig. 2 that graphite crystal has a stretching vibration peak of *sp*² structure at 1620 cm⁻¹, which is the sign peak of graphite. Graphene oxide curve has a series of infrared absorption peaks. Absorption peak at 1113 cm⁻¹ was attributed to the vibration absorption peak of C-O-C. Absorption peak at 1388 cm⁻¹ was corresponding to deformation vibration absorption peak of water molecules. Stretching vibration absorption peak at 1641 cm⁻¹ belongs to C=O that was on carboxyl of graphene oxide. In the range of 3700-3000 cm⁻¹ range appeared a wide and strong absorption peak, which is the stretching vibration peak of -OH; the residual water molecules in graphene oxide also affect the absorption peak. Judging from the infrared spectrum of graphene by Hummers method exist some functional groups, such as -OH, -COOH, -C=O, -CH(O)CH-, which makes graphene oxide easy to form hydrogen bonds with the water molecules and thus keep a good hydrophilic. The epoxy groups of graphene are different with functional groups, like hydroxyl or carboxyl, epoxy groups produces stress on the C-C key at the three atoms epoxide ring. When some epoxy groups arranged in rows, the graphene sheets can be stacked to form a fold, part of the folds can release energy chain, so that this configuration can exist stable. Therefore, epoxy groups tend to form long chains entangled on the surface of graphene by synergistic in the graphite oxidation. In the rapid thermal expansion process of graphene, oxygen-containing functional groups decomposed into carbon dioxide and escaping and some residual water in graphene oxide layers escaped at the same time. Although the water of graphite layers was accompanied by generating carbon dioxide gas, the process played an important role in stripping process. In fact, the presence of water will affect the stripping effect, because the water was evaporating endothermic reaction that produced a cooling effect. The pressure to strip graphene was mainly from the carbon dioxide produced by exothermic reaction of the epoxy and hydroxyl groups. The pressure can make the graphite sheets to overcome the van der Waals force between the layers and eventually stripping into a single layer of graphite. Graphite oxide was reduce by hydrazine and appeared absorption peak of C=C around 1620 cm⁻¹, which indicating that the graphene oxide has been restored. Only a

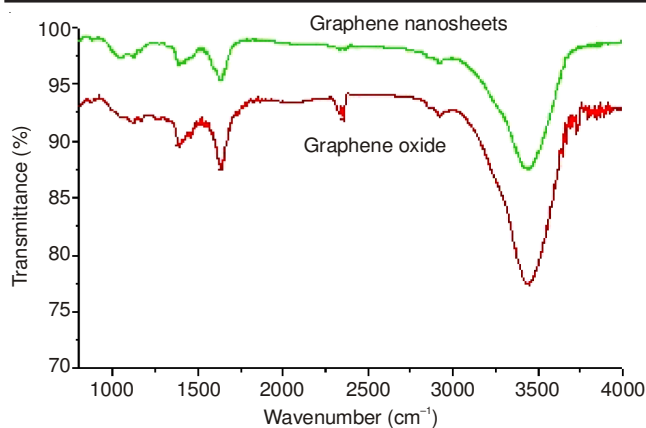


Fig. 2. IR of graphene oxide and graphene nanosheets with Hummers method

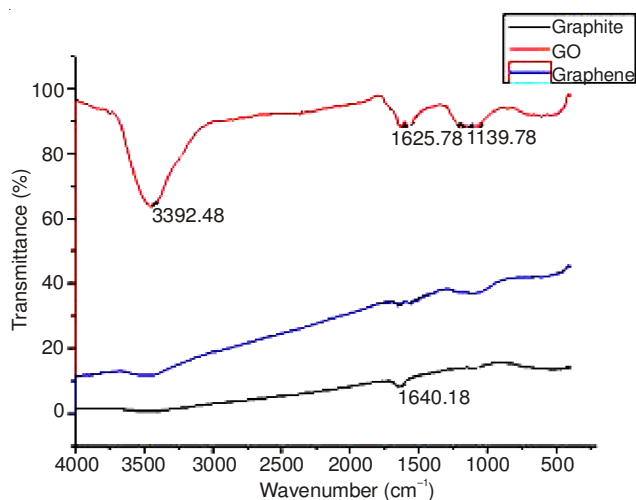


Fig. 3. IR of graphene by modified Hummers

relatively weak and narrow peak appears in 3700-3000 cm^{-1} , which is probably caused by a small fraction of haven't being reduced -OH and the adsorption water molecules. In addition, in the place of the oxygen-functional groups' peak that the shape of graphene was very weak or flat curve showed that the oxygen-containing groups were taken off basically.

Fig. 3 is the infrared spectra of graphene of modified Hummers compared with graphene oxide and graphite. The infrared spectrum of graphene was very similar to graphite. The difference was graphite has a sharp absorption peaks at 1640.18, which was the C=C telescopic peaks with sp^2 hybridized, but graphene's transmissivity was higher than that of graphite. Compared graphene with graphene oxide, it is clear that graphene oxide has typical absorption peaks. The absorption peak occurred at 1139.78 cm^{-1} was belonged to the vibration absorption peak of C-O-C. The absorption peak at

1625.78 cm^{-1} was belonged to stretching vibration peak of C=O on the carboxyl group of graphene oxide. At 3392.48 cm^{-1} , appeared a wide, strong absorption peak, which was the free vibration peak of -OH. Thus it can be seen that the functional groups, like -OH, -COOH, -C=O, -CH(O)CH-, on the surface of graphene oxide, can form hydrogen bonds with the water molecules, so that the graphene oxide has a good hydrophilic.

Comparing Fig. 2 with Fig. 3 it can be found that the graphene prepared in Fig. 2 still have oxygen containing groups that graphene oxide was reduced incompletely. The graphene prepared by modified Hummers have fewer and smaller absorption peaks, indicating the reduction of graphene oxide was more completely. The experimental conditions of Fig. 3 was different in the use of a slight excess of concentrated sulfuric acid and excess hydrogen peroxide to reduce the residual oxidizing agent, it may promote the subsequent reducing effect.

Conclusion

Graphene and graphene oxide are prepared by Hummers and modified Hummers method. In the modified Hummers method, a slight excess of concentrated sulfuric acid and excessive hydrogen peroxide are used to reduce the residual oxidant, so we can get graphene that contains less oxygen-containing functional groups than Hummers method. Therefore by controlling the experimental conditions and parameters of oxidation-reduction preparation process, graphene oxide can be reduced much more completely and made into the graphene with more perfect structure.

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