

## Studies on Synthesis, Optical and Thermal Properties of Graphene Oxide

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### Abstract

Graphene has emerged as an exotic material of the 21st century and received world-wide attention due to its exceptional charge transport, thermal, optical, and mechanical properties. In the present study, graphite oxide was prepared by oxidizing graphite following modified Hummers method. The graphene oxide (GO) was prepared by graphite oxide exfoliating in distilled water with ultrasonic waves. It is proven that redox method is promising ways to synthesize GO on a large scale. Comprehensive characterizations of the properties of GO were investigated with help of various characterization techniques. The tests of UV-VIS spectrometer and TGA analyzer indicated that GO sheet possessed excellent optical response and exceptional thermal stability.

**Keywords:** Graphene oxide, Characterization, spectroscopy.

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### INTRODUCTION

Graphene oxide (GO) have recently emerged as anew carbon - based nanoscale material that provides an alternative path to graphene. As early as 1947, Wallace [1] first proposed the concept of graphene and studied the electronic properties of graphene using tight-binding model. It is concluded that graphite is a semiconductor without activation energy, because of the small portion of valence band of graphite extended to the conduction band, in which data established a foundation for the use of the physical properties of graphite. However, since several decades, the study of graphene is still just staying at the level of theory [2–5].

Until 2004, Novoselov and Geim [6] in the University of Manchester separated the single graphene from graphite for the first time through simple mechanical peeling method. Graphene was increasing more and more attention in various areas of science and technology due to its remarkable physicochemical properties.

As a one-atom-thick, two-dimensional crystal, graphene has been considered as basic building block for all  $sp^2$  graphitic materials including fullerenes, carbon nanotubes, and graphite [6]. Owing to the special two-dimensional structure, graphene possessed many unique properties different than carbon materials, including a high specific surface area (theoretically  $2630 \text{ m}^2/\text{g}$ )

for single-layer graphene) [7], extraordinary electronic properties and electron transport capabilities [8–10] and high thermal conductivity ( $\approx 5000 \text{ W m}^{-1} \text{ K}^{-1}$ ) [11,12].

Currently, many methods had been explored to prepare graphene. Novoselov and Geim [6] firstly observed a single layer of graphene from highly oriented pyrolytic graphite using micromechanical exfoliation method. It is a simple way to prepare graphene, but the yield of graphene was very low, and one cannot achieve high-quality industrial production. Srivastava et al. [13] prepared “petal” graphite sheet with  $\sim 20 \text{ nm}$  thickness by chemical vapor deposition (CVD). Even though thickness of graphite sheet prepared by CVD method significantly decreased than ever, more impurities of Ni element in graphite sheet was another new problem. Solvent stripping method [14] is a new approach that emerged in recent years. Its principle is destroying Van Der Waals Force between the graphite layers in a solvent to obtain graphene sheets. Method of solvent stripping did not destroy the structure of the graphene and presented no surface defects in the graphene sheet. However, the low yield of graphene was still a problem. Redox method [15–21] is the most popular method to prepare graphene and graphite oxide. During the oxidation process, graphite crystal was treated with strong oxidizing agents and carried oxygen-containing functional groups into graphite oxide sheet. After ultrasonic treatment, the oxygen-containing functional groups were removed and obtained the graphene sheet. Production of graphene can be very high using redox method, and introduction of functional groups in the oxidation process provided advantages of combining the compound to improve the compatibility of matrix composite. Therefore, redox method was suitable for the preparation of graphene-based composite materials.

In summary, in order to turn graphene applications into reality, one must fabricate the material. The redox method is considered to be a very promising way to prepare graphene, and graphite oxide (GO), as intermediate product of preparation process has a crucial influence on the quality of graphene. Therefore, exploration for properties of graphite oxide is essential and imminent. In view of these issues, this study successfully synthesized graphene oxide (GO) by the modified Hummers method, as the precursor for preparing graphene. A UV spectrometer (UV-VIS) was used to measure the optical absorption properties of the GO. Thermal stability of GO was determined through the thermal gravimetric analyzer (TGA).

## **MATERIALS AND METHODS**

In the present study, graphene oxide was synthesized by Hummers’ method. The chemicals used for synthesis are Graphite powder, Sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%), potassium permanganate ( $\text{KMnO}_4$ , 99.9%), hydrogen peroxide ( $\text{H}_2\text{O}_2$  30%). All chemicals were of analytical reagent grades and used as received.

### **Synthesis of graphene oxide**

Graphene oxide (GO) was synthesized from graphite powder using modified Hummer’s method. In brief, 1 g of graphite and 0.5 g of sodium nitrate were mixed together followed by the addition of 23 ml of conc. sulphuric acid under constant stirring. After 1 h, 3 g of  $\text{KMnO}_4$  was added gradually to the above solution while keeping the temperature less than  $20^\circ\text{C}$  in ice bath to prevent overheating and explosion. The mixture was stirred for half an hour. The mixture was stirred at  $35^\circ\text{C}$  for 12 h and the resulting solution was diluted by adding 500 ml of water under

vigorous stirring. To ensure the completion of reaction with  $\text{KMnO}_4$ , the suspension was further treated with 30%  $\text{H}_2\text{O}_2$  solution (5 ml). The resulting mixture was washed with HCl and  $\text{H}_2\text{O}$  respectively. The color of mixture was changed to bright yellow indicating a high oxidation level of graphite. The solution was filtered and washed several times with water to remove the remaining impurities. The washing process was carried out using a simple decantation of the supernatant with centrifugation technique at 5000 rpm for 30 minutes which result in formation of graphene oxide [22,23].

### Characterization

UV spectrometer (UV-VIS; Hitachi inc., U-3900) was used to measure the optical absorption properties of GO. Thermo gravimetric analyzer (TGA; Perkin Elmer Inc., STA6000) was used to determine the thermal stability of samples.

## RESULTS AND DISCUSSION

Synthesis of graphene oxide was achieved by placing graphite in concentrated acid in the presence of an oxidizing agent. Hummer's method demonstrated a less hazardous and more efficient method for graphite oxidation. This and its modified versions are presently the most commonly used methods for the oxidation of graphite. Individual sheets of GO can be viewed as graphene decorated with oxygen functional groups on both sides of the plane and around the edges. Due to ionization of carboxyl groups, which are primarily present at the edges of sheet, GO can be electrostatically stabilized to form a colloidal suspension in water, alcohols, and certain organic solvents without surfactants. Exfoliation of graphite oxide into individual sheets can be facilitated by ultrasonic agitation or rapid heating but excessive ultra-sonication can result in the decrease of lateral dimensions. Oxidation of graphite results in a brown-colored viscous slurry, which include graphite oxide and exfoliated sheets along with non-oxidized graphitic particles and residue of the oxidizing agents in the reaction mixture. After repeated centrifugation, sedimentation, or dialysis, salts and ions from the oxidation process was removed from GO suspensions. To achieve a suspension of monolayer GO, non-oxidized graphitic particles and thick graphite oxide platelets were precipitated out by further centrifugation. Suspensions of GO flakes that are mono-dispersed according to their lateral size were also obtained by density-gradient centrifugation.

The synthesized GO sheet was characterized using UV-VIS spectrometer. The UV-VIS spectrum of the GO sheet is shown in Figure1.

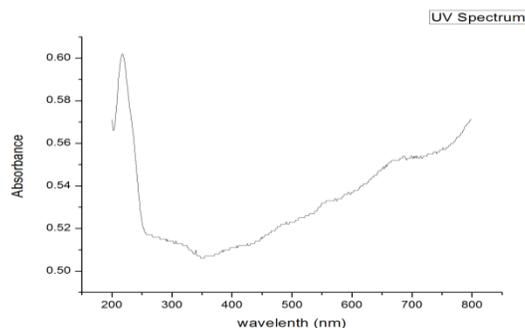
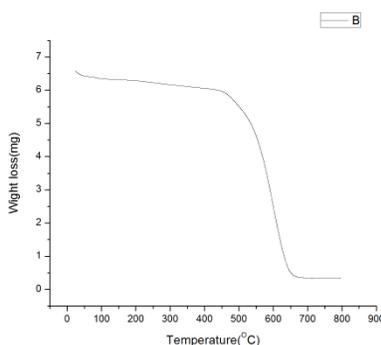


Figure 1: UV-Visible spectrum

The results indicate that graphene oxide possessed a good absorption in the visible range (380~800 nm), but absorption in the ultraviolet range was also slightly decreased. The maximum absorption peak at ~220 nm attributable to  $\pi$ - $\pi^*$  transition of the atomic C-C bonds and shoulder peak at ~300 nm due to  $n$ - $\pi^*$  transitions of aromatic C-C bonds. The results showed the good photoresponse of GO sheet not only in ultraviolet range but also in visible range, which implied the enormous potential for optical application.

Thermogravimetric analysis (TGA) of graphite, graphene oxide and reduced graphene was carried out under N<sub>2</sub> flow using TA Instrument Thermogravimetric Analyzer Q50 and their masses were recorded as a function of temperature. The samples were heated from room temperature to 800 °C at 5 °C/min. The results are shown in Figure 2.



**Figure 2: TGA analysis**

Graphene oxide shows slight mass decrease from room temperature to 400 °C and significant decrease from 400 °C to 650 °C. The mass of graphene oxide further slowly decreased up to 800 °C. The major mass reduction at ~ 400 °C was caused by pyrolysis of the oxygen-containing functional groups, generating CO, CO<sub>2</sub> and steam.

## CONCLUSION

The graphene oxide was prepared by oxidizing purified natural flake graphite via modified Hummer's method. This method was carried out with the highest conversion level of graphite flakes to graphene oxide and shows that pure graphene oxide is formed. UV-vis spectrum of GO exhibits maximum absorption peak at ~220 nm attributed to  $\pi$ - $\pi^*$  transitions of the C-C bonds. The TGA analysis of graphene oxide indicated that GO sheet possessed excellent thermal stability.

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