

Synthesis of Graphene Oxide using Modified Hummer's Method and its Reduction using Hydrazine Hydrate

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Abstract: Graphene is a hot area of research because of its unique and remarkable properties. These properties have invoked researchers to use this form of carbon in various potential applications. One of the bottlenecks in developing such application is mass production of graphene. Hummer's Method is one of the easiest and economical methods to synthesize huge amount of reduced graphene oxide (RGO) sheets. Graphene Oxide (GO) was prepared from graphite powder using modified Hummer's method, followed by reduction of exfoliated GO with hydrazine hydrate which resulted in formation of high surface area two dimensional structure consisting of RGO flakes and nanosheets. To obtain porous and layered structure of RGO, hydrothermal reduction was performed at an elevated temperature. The synthesized reduced GO was characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) to investigate the morphological and physicochemical changes occurred in exfoliated graphite. In XRD results, it was found that $2\theta = 26.4^\circ$ peak with interplanar spacing (d_{002}) of 0.335nm of graphite powder disappeared, while another significant peak observed at $2\theta = 11.95^\circ$ with interplanar spacing of 0.754 nm demonstrated successful oxidation of graphite and formation of GO. A diffraction peak obtained at $2\theta = 22.5^\circ$ clearly indicated that upon hydrothermal reduction, reduced GO flakes were formed. SEM results also support the formation of RGO since particle size lies in nanometric range (6-20 nm).

Keywords: Exfoliation Reduced Graphene Oxide, Hydrothermal Reduction, SEM, XRD, Substrate.

I. INTRODUCTION

Graphene is a one atom thick layer of graphite having a two dimensional crystal structure. It is a mother of all graphitic material in which sp^2 hybridized carbon atoms are bonded in honey comb structure [1]. It has grabbed the attention of researcher due to its unique properties which is enhanced surface area, excellent conductivity, high mechanical strength, high electron mobility etc. These unique properties of graphene are being exploited by the researchers in various potential applications such as biosensors, super-capacitors, photovoltaic cells. Single layered

Graphene can be synthesized by variety of methods including exfoliation through chemical route, micromechanical method, chemical vapour deposition, solar exfoliation, thermal exfoliation and many more [2]. One of the promising strategy for synthesis of graphene is chemical oxidation of graphite followed by reduction of graphene oxide (GO) through reducing agents such as hydrazine hydrate, potassium hydroxide, sodium boron hydride etc [3-5]. Chemical method is a practical approach for mass production of graphene. In this method, strong oxidizing agents are used to oxidize graphite to obtain graphite oxide which is highly non-conducting and hydrophilic material. In 1859, Brodie was the first to demonstrate synthesis of graphite oxide by adding potassium chlorate to slurry of graphite in fuming nitric acid [4]. Later on, in 1898, Staudenmaier improved this method by adding concentrated sulphuric acid to fuming nitric acid followed by gradual addition of potassium chlorate. Highly oxidized graphite oxide was obtained through this process. However, amount of GO produced was very small [6]. Afterwards, in 1958, Hummer used an alternative method for mass production of graphene oxide (GO). He used $KMnO_4$ and $NaNO_3$ for synthesis of GO [2, 4, 7]. This paper describes the synthesis of graphene oxide (GO) using modified hummer's method. The GO was reduced hydrothermally using hydrazine hydrate as a reducing agent.

II. EXPERIMENTAL WORK

A. Materials Used

Graphite Powder (Extra pure), Sodium Nitrate ($NaNO_3$), Sulphuric Acid (H_2SO_4), Potassium Permanganate ($KMnO_4$), Hydrogen peroxide (H_2O_2), Hydrochloric acid (HCl), Hydrazine Hydrate ($N_2H_4.H_2O$), Methanol were of analytical grade and used without further purification. High quality deionised water was used throughout the experimental work.

B. Synthesis of Graphene Oxide

Graphene Oxide was prepared from graphite powder using modified hummer's method [8-10]. In a typical synthesis, 0.5 g graphite and 0.5 g $NaNO_3$

was added to 24 ml concentrated sulphuric acid (H_2SO_4). The mixture was ultrasonicated for 1 hour, keeping temperature approximately $5^\circ C$ using ice bath. Then 3 g of potassium permanganate was added gradually keeping the temperature of mixture below $15^\circ C$. Then a mixture was stirred by ultrasonication using ultrasonic bath (power: 150 W and frequency: 33 KHz) for 2 hours to get a homogeneous mixture. 50 ml DI water was added (gradually) to mixture followed by ultrasonication for 1 hr. The brown colour of the mixture was observed as shown in fig 1. The mixture was removed from ice bath and stirred magnetically for one hour and temperature was increased to $35^\circ C$. The colour of the mixture changed to light brown. Subsequently another 100 ml DI water was added to mixture and temperature was increased to $90^\circ C$ and stirred for 1 hour. Finally a solution of 10 ml hydrogen peroxide and 100 ml DI water was added to obtain a light yellow suspension. When H_2O_2 was added, the residual $KMnO_4$ and MnO_2 formed in the solution was also reduced to colourless soluble salts and the colour changes from brown to light yellow as shown in fig 2.



Fig 1. Dark Brown Suspension of Graphite



Fig 2. Light Yellow Suspension of Graphite Oxide

The suspension so obtained was filtered with high quality wattman filter and washed with 10% HCl to remove metal ions and finally washed with DI water till pH becomes neutral. The filtrate was then mixed with DI water and ultrasonicated for one hour to obtain dispersion of Graphene Oxide (GO)

solution. The nature of synthesized GO was hydrophilic. The dispersion was then centrifuged at 5000 rpm for 30 min to remove unexfoliated graphite and other impurities. This solution was then, filtered and dried. Finally a brown coloured graphene oxide (GO) powder was obtained (1.5 g approx.).

C. Reduction of Graphene Oxide (GO) Using Hydrazine Hydrate

The next step was to reduce graphene oxide (GO). This was achieved by a one-step hydrothermal approach [2, 10-12]. For this, graphene oxide was dispersed in DI water (1 mg/ml) followed by ultrasonication for 1 hour to obtain homogeneous dispersion keeping temperature below $50^\circ C$. Afterwards, 2 ml of Hydrazine hydrate was added into 50 ml dispersion of GO and pH was adjusted to 10. This solution was kept in oven at $90^\circ C$ for 24 hours.

Hydrothermal method resulted in the formation of dense precipitate which ensured successful completion of the reduction process. After the hydrothermal reaction, the obtained reduced graphene oxide (RGO) flakes were washed thoroughly with distilled water and methanol. The procedure was repeated until pH~ 7. Then RGO flakes were dried in hot air oven at $60^\circ C$ in order to remove water content. The colour of RGO flakes was dark black.



Fig 3. Reduced Graphene Oxide Flakes

These RGO flakes were dispersed in DI water (1mg/ml) followed by ultrasonication for 1 hour to obtain homogeneous dispersion. High quality glass substrate was used to deposit RGO dispersion. Before coating, the glass substrate ($2.5 \times 2.5 \text{ cm}^2$) was cleaned by Trichloroethylene (TCE) and methanol, followed by DI water for 10 minutes. Then the glass substrate was cleaned in a mixture containing H_2SO_4 and H_2O_2 (3:1) for 15 min and thereafter rinsed with DI water several times. The substrate was dried in oven at $100^\circ C$. Then dispersion of RGO was deposited by spin coater at a rate of 1500 rpm for 30 seconds.

The RGO coated glass samples were dried in oven at 90°C for 10 minutes. This process was repeated four times to obtain uniform deposition of the film.

D. Annealing

Annealing is a process in which sample is heated at high temperature and then cooled slowly. It alters the microstructure of the film thereby causing change in its properties. This process relieves film from internal stress introduced during deposition. Finally, the samples were annealed at 400°C for half an hour on hot plate to remove water content and other volatile impurities. At an elevated temperature, atoms re-orient themselves to have minimum surface energy. Two different samples of RGO, one with annealing and another without annealing were prepared and further characterized using XRD and SEM.

III.CHARACTERIZATION TECHNIQUES

A. X-Ray Diffraction (XRD)

It is a characterization tool to analyse crystal configuration and orientation of the nanomaterials. A diffraction pattern is formed when X-rays come in contact with crystalline phase of the film. It also provides information about different orientation and interlayer spacing of the atomic layers. The X-ray diffraction of the synthesized reduced GO was recorded on XPERT-PRO diffractometer system equipped with a Cu_{Kα} radiation source (λ=1.5406 Å).

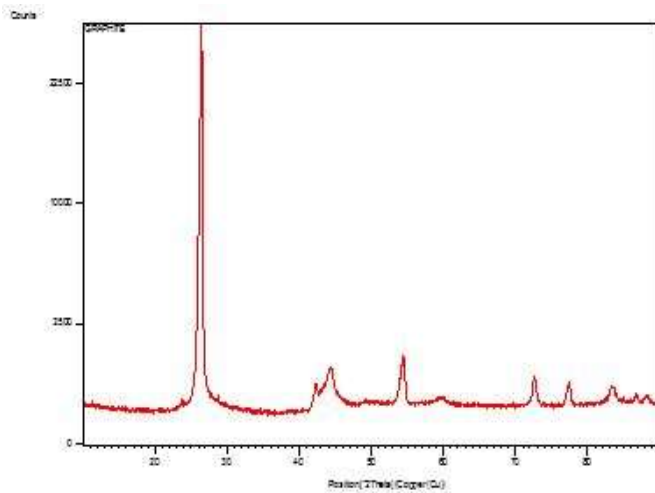


Fig 4: XRD of Natural Graphite Powder

To calculate grain size, Debye-Scherrer’s formula was used. It is given as:

$$D=0.9 \lambda / \beta \cos \theta$$

where,

- D=Crystallite Grain Size (nm)
- λ= Wavelength of X-rays (Å)
- β=Line Broadening of full width at half maxima (FWHM in radians)
- θ=Bragg’s Diffraction angle in degrees

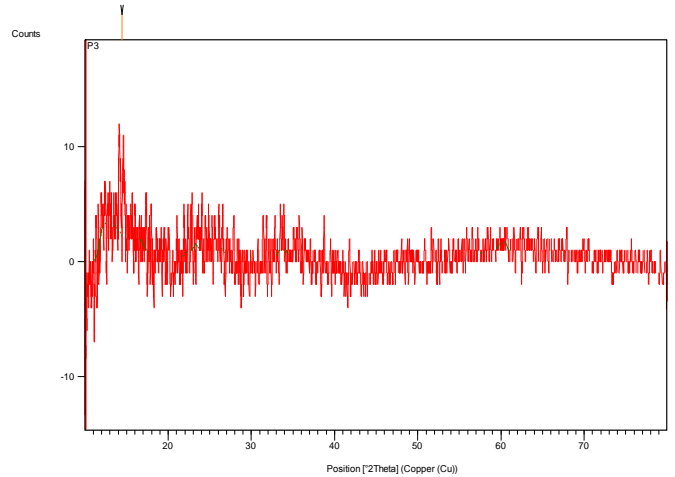


Fig 5: XRD of Reduced Graphene Oxide on Glass Substrate (without annealing)

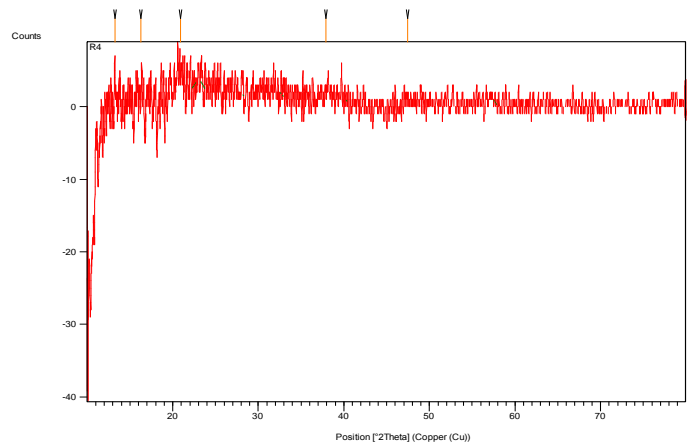


Fig 6: XRD of Reduced Graphene Oxide on Glass Substrate (Annealed)

B. SEM

The prepared RGO samples were characterized using scanning electron microscope to study physicochemical changes occurred in graphite. SEM is a tool to visual the images of the order nm to μm. The details of the surface of the exfoliated graphite were analysed from SEM characterization.

The SEM images of prepared RGO at different magnifications are shown in Fig 7. (a - d):

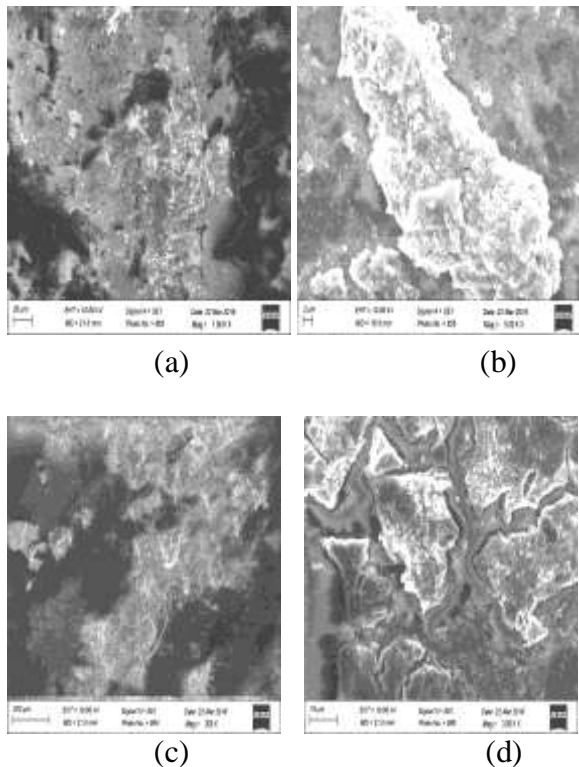


Fig 7.(a) SEM image of RGO flake at 1K magnification (b) SEM image of RGO nanosheets at 5K magnification (c) SEM image of RGO at 2K magnification (d) SEM image of RGO at 3K magnification

IV. RESULTS AND DISCUSSIONS

In the present work, a chemical method for the synthesis of reduced graphene oxide was employed. Moreover, graphite was oxidized to graphene oxide followed by exfoliation into reduced GO flakes and nanosheets in accordance with modified Hummer's method [2]. It demonstrated a less hazardous and more economical method for graphite oxidation. A brown coloured slurry of GO was obtained which include exfoliated sheets along with non-oxidized graphitic particles and residue of the oxidizing agents in the reaction mixture. The unwanted ions and impurities were removed after centrifugation from GO suspension. The brown-yellowish coloured GO was reduced with hydrazine hydrate which resulted into dense black coloured reduced GO flakes and nanosheets simultaneously.

Fig.4 shows XRD results of natural graphite powder which clearly demonstrates that graphite is a highly oriented carbon material. The diffraction peaks corresponding to (002), (100), (101), (004), (103), (110) crystalline planes of graphite were observed [13]. Fig 5 represents XRD of RGO sample (without annealing). A strong diffraction peak at $2\theta = 12.5^\circ$ with increased interplanar distance of 0.61nm corresponding to (001) crystalline plane was

observed [1,4]. This peak shows that oxygen was introduced into graphite layer by oxidizing agents thereby increasing its interplanar distance. This resulted into successful oxidation of graphite.

Fig.6 demonstrates XRD pattern of annealed reduced Graphene Oxide (RGO) film deposited on glass substrate. This figure clearly shows that main intense peak of graphite at $2\theta = 26.56^\circ$ corresponding to interplanar distance (d_{002}) of 0.335 nm has disappeared after exfoliation. Also an additional peak at lower angle $2\theta = 11.95^\circ$ having interplanar distance of 0.754 nm corresponding to (001) crystalline plane was observed. The increase in interplanar distance of Graphene Oxide (GO) is due to the formation of oxygen containing functional groups such as epoxy, carboxyl and hydroxyl. Another significant peak observed at $2\theta = 22.5^\circ$ corresponding to (002) crystalline plane clearly, shows the formation of reduced GO [2, 10, 14]. Apart from this, weaker diffraction peaks at 37.8° and 47.4° corresponding to (020), (040) crystalline plane were also observed. It demonstrates the poly crystalline nature of exfoliated graphite. The obtained XRD results are in near concord with results reported in literature. Moreover, the particle size of nanoparticles of RGO at different diffraction peaks calculated from Scherrer's formula varies from 7 to 12 nm. Hence modified Hummer's Method is one of the easiest and an economical method for synthesis of Graphene Oxide.

The morphology and structure of reduced GO nanosheets were investigated through SEM observation. Fig 7. (a-d) shows SEM images of Reduced GO at different magnifications. The RGO flakes are however layer structured, folded and irregular as shown in SEM image of fig 1.(a). Here, Fig 7. (b) depicts the representative SEM image of free-standing GO nanosheets, revealing a crinkled and bubbled structure which was the result of deformation upon the exfoliation and restacking processes [14]. Fig 7. (c,d) showed few layers of RGO with lots of wrinkles. The intrinsic nature of reduced graphene oxide is suggested by corrugation and scrolling, because 2D structures are thermodynamically stable via blending. The SEM images display various scaled particle size. It can be noticed that the particles as small as 6 nm and as big as 20 nm are observed. The particle size calculated from Scherrer's formula as already explained in XRD results, has approximately same range as that of SEM results. Thus the exfoliation and morphological changes of graphite is confirmed from XRD and SEM results.

V. CONCLUSIONS

The exfoliation of graphite and formation of graphene oxide is confirmed from XRD results. Addition of oxygen containing functional groups via Hummer's Method into layers of graphite increases its interplanar distance which is responsible for formation of reduced

graphene oxide. Further SEM analysis shows various particle sizes claiming exfoliation of graphite by hydrothermal method. Thus it can be stated that the reduced GO with extraordinary properties has been synthesized from this method successfully. To avoid recombination of reduced graphene oxide nanosheets, process of reduction should be done carefully under optimum condition of temperature. One of the advantage of this process is quantity of RGO produced is very high as compared to graphene synthesized by ultrasonication method.

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