

SYNTHESIS OF GRAPHENE AND GRAPHENE OXIDE BASED NANOCOMPOSITES AND THEIR CHARACTERIZATION

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ABSTRACT

Graphene is a material that has generated enormous research interest and activity in the past few years due to its remarkable properties and wide applications in fields, such as nanoelectronics, sensors, nanocomposites, batteries, supercapacitors, hydrogen storage, transparent conductors and energy storage materials. The synthesis of graphene was mainly carried out using chemical methods. In our studies we investigated the conversion of pristine vein graphite into graphite oxide by modifying the existing Hummer's method. Prepared graphite oxide was characterized using Fourier Transform – Infrared Spectroscopy (FT-IR) and X-ray Diffractometry (XRD) and obtained results were in good agreement with the previously reported data. Synthesized graphite oxide was then dispersed in water medium using bath sonication method to prepare graphene oxide dispersion. This dispersed graphene oxide was subsequently reduced to graphene using sodium borohydride. Synthesized graphene was characterized using FT-IR spectroscopy. In addition, the synthesis of graphene/Poly vinyl pyrrolidone (PVP) nanocomposite was also carried out by combining PVP to graphene. The product obtained was characterized using FT-IR, XRD and particle size analyzer (PSA). Results indicated that graphene was combined with the PVP polymer. As a conclusion it can be stated that this is very fast and low cost method to synthesize graphene from graphite.

Key words: Graphene, Graphene oxide, Graphite, Hummers method

1. INTRODUCTION

Graphite is inexpensive and they are available in large quantities [1]. There are three main types of Graphite namely, Crystalline Flake Graphite (flake graphite), Lump Graphite (Vein graphite) and the Amorphous Graphite. These three types are different in their structure and morphology. Although Graphite made out of graphene it does not readily give individual graphene sheets out, and as a result of this, graphene does not exist naturally [1]. Therefore graphene is prepared using chemical methods through the synthesis of graphene oxide followed by reduction to reduced graphite oxide (so called graphene). There are four main methods to synthesize Graphene. First method is the chemical vapor deposition and epitaxial growth [2] and second method is micromechanical exfoliation of graphite, this is also known as the "Scotch Tape method" or the peel off method [2], third method is epitaxial growth on electrically insulating surfaces, [2] fourth method is based on creation of colloidal suspensions [2]. Graphite oxide is the intermediate for most of the chemical synthesis of graphene from graphite.

Graphite oxide is one of the most important compounds for the formation of Graphene. Graphite Oxide is made up of large number of layers of graphene oxide. Graphite oxide consists of sp^2 hybridized carbons and as well as sp^3 hybridized carbons [3]. Graphite oxide consists of hydroxyl groups, epoxide groups, carboxyl groups and carbonyl functional groups [3]. And these groups are arranged in different ways. Hydroxyl and epoxide groups are arranged in the top and the bottom of the each sheet [3]. Also the carbonyl functional groups and carboxyl functional groups are arranged in sp^2 hybridized carbons in the sheets of graphene oxide. There are interlayer hydrogen bonds between the layers of graphene oxide [3]. Graphite oxide preserves the parent structure of graphite but the interlayer distance is two times greater than the interlayer distance in graphite. Graphene oxide can simply be made using the sonication method. Most of the electrical properties will lose when modulating graphite to graphite oxide. When converting graphite oxide to graphene electrical conductivity can be

restored [3]. Reduction is achieved in many ways, namely, chemical reduction, thermal reduction or electrochemical reduction [3]. Main objective of this work is to prepare Graphene from graphite using a fast and a simple method.

2. MATERIALS AND METHODOLOGY

2.1 Synthesis of Graphite Oxide from Pristine Vein Graphite

Magnetic stirrer (Stuart heat-stir, CB 162) was used for the heating and stirring purposes. FT-IR Spectrophotometer (Varian 660-IR, USA), analytical balance (Precisa, XB-120A), XRD (Bruker D8 FOCUS X-ray diffractometer, $\lambda=1.5418\text{\AA}$), SEM Hitachi SU 6600, resolution 1.2 nm, magnification X10X600000). Pristine vein graphite (purity degree > 99.5%, $\sim 30\ \mu\text{m}$) was used to synthesize graphite oxide. Potassium permanganate (KMnO_4 , 99%), concentrated sulfuric (H_2SO_4 , 95%-97%), concentrated hydrochloric acid (HCl, 37%) and sodium nitrate (NaNO_2 , >99.0%) purchased from Sigma Aldrich were used. Hydrogen peroxide (H_2O_2 , 30%) purchased from price marketing services, Sodiumborohydride purchased from DAEJUNG, ammonium hydroxide (NH_4OH , 25%) was purchased from Analytical Rasayan and Methanol was purchased from Sigma Aldrich. Double distilled water was used during the whole procedure. The synthesis of graphite oxide was carried out using an already established method. [4] This method is called the modified Hummer's method. A 5 g of vein graphite was mixed with 115.0 ml concentrated H_2SO_4 acid and 2.50 g NaNO_3 in ice bath for half an hour using a magnetic stirrer. A 15.00 g of KMnO_4 was slowly added (small amount at each time) into the mixture within 1 hour while keeping the temperature of the mixture not exceeding 5°C . Then the mixture was heated up to 60°C and was maintained at 60°C for 30 min, then 230.0 ml of double distilled water was added into the mixture and heating was continued for additional 30 min at the same temperature. Finally, the oxidation reaction was terminated by the addition of 700.0 ml of double distilled water and 50.0 ml 30% H_2O_2 solution. Then the mixture was filtered and the product was washed several times with 5% hydrochloric acid followed by double distilled water and dried in a vacuum oven for 24 hours.

2.2 Synthesis of graphene oxide dispersion

A 0.1000 g of dried graphite oxide was measured using an analytical balance. Measured graphite oxide was dissolved in 100.0 ml of double distilled water using magnetic stirrer (stirring was carried out until whole solid was dissolved). Then the suspension was sonicated using a bath sonicator for 1 hour and the solution was kept to precipitate for 24 hours. Then the supernatant part of the suspension was used for the characterization purposes.

2.3 Synthesis of graphene

Graphite oxide dispersion (1mg/ml) prepared in above experiment 1.1.2 was transferred to a 250 ml conical flask and 1.000 g of sodium borohydride was added to the graphene oxide dispersion followed by 350 μl of ammonium hydroxide solution. Then pH was adjusted to 10. Then the solution was stirred for few minutes and was heated to 95°C for 1 hour. The solution was filtered through a filter paper and precipitate was washed with double distilled methanol for several times.

2.4 Synthesis of graphene/PVP nanocomposite

For a 100.0 ml of graphene oxide dispersion (prepared in section 1.1.2) added 1 g of PVP powder. Solution was homogenized for few minutes until PVP powder was dissolved. An amount of 1.0000 g of sodium borohydride was added and stirred for few minutes. Then the 350 μl of ammonium hydroxide was added to the solution to adjust pH to 10. The resulted solution was heated up to the 95°C and this temperature was maintained for one hour. After one hour graphene get started to aggregate with PVP, then the solution was further heated at 95°C until the suspension forms a slurry.

3. RESULTS

Figure 1, figure 2, figure 3, figure 4 shows the FT-IR spectra of Graphite, Graphene oxide and Graphene

and XRD of graphite oxide respectively.

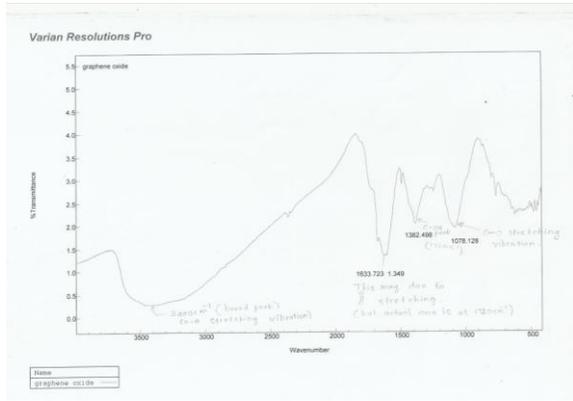


Figure 1: FT-IR spectrum of graphite oxide

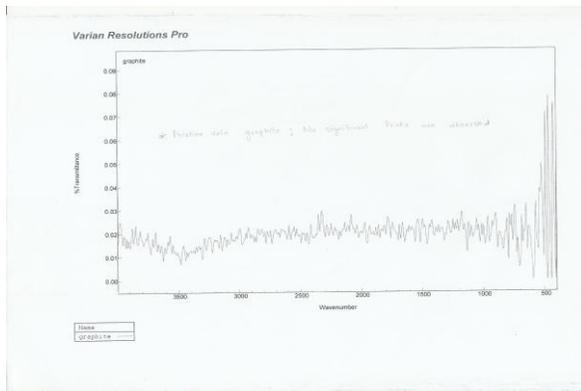


Figure 3: FT-IR spectrum of graphite

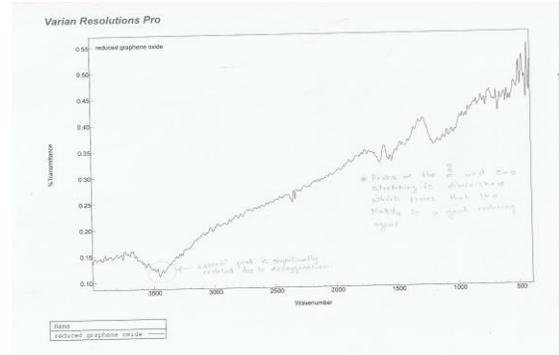


Figure 2: FT-IR spectrum of Graphene

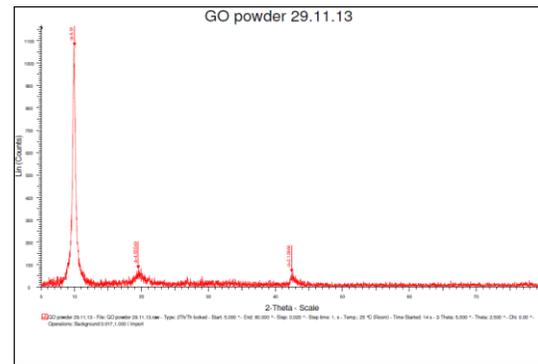


Figure 4: XRD spectrum of graphite oxide

FT-IR spectrum of graphite oxide the broad peak at 3400 cm^{-1} is relevant to the stretching vibrations of hydroxyl group. Peak at 1633 cm^{-1} corresponds to the stretching vibrations from carbonyl group. Peak at 1600 cm^{-1} corresponds to skeletal vibrations from non oxide graphitic domains. [5] Also the peak at 1382 cm^{-1} and 1078 cm^{-1} corresponds to C-OH stretching vibrations and C-O stretching vibrations [5].

In the spectra of graphite and grapheme there are no significant peaks that are relevant to any functional groups. When reducing graphene oxide to graphene the functional groups have disappeared. This is clearly reflected via FT-IR spectrum for not having bands corresponding to any functional groups.

In Figure 4 there is a sharp and strong peak at $2\theta = 11$ which is very significant peak for graphite oxide [6]. This indicates the presence of oxygen functionalities.

4. CONCLUSION

In conclusion, graphite oxide was successfully prepared by modified Hummers method. FT-IR spectrum of the graphite oxide clearly proved the chemical structure of GO. By increasing the oxidation time was possible to obtain the graphite oxide with carbon and oxygen composition which exactly matches with the literature. Preparation of graphene oxide dispersion was carried out using the bath sonication method where the energy associated with sound wave help to break the weak vanderwaales bonds between the graphene oxide sheets. This method was successful for exfoliation of graphite oxide. The minimum particle size reported was 110.1 nm. Synthesis of graphene was carried out by reduction of graphene oxide to graphene using sodium borohydride. The FT-IR spectrum of graphene clearly shows that the peaks that were observed for graphite oxide were vanished when it reduced to graphene. This implies that this reduction method is suitable for the synthesis of graphene. This method was easy and very efficient but the major problem associated with this was the use of NaBH₄ with graphene oxide in 10:1 ratio. The XRD pattern of graphene/PVP nanocomposite shown that graphene and PVP are chemically bound thus these spectra shows the extra functionalities than pure graphene and PVP. The direct liquid phase sonication and then reduction was easy and rapid method for the synthesis of graphene.

5. REFERENCE

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