



Synthesis and Thermal Investigation of Graphene from Natural Graphite Flakes

C. L. Tumbade and G. R. Dhokane
Department of Physics, Arts, Science and
Commerce College, Chikhaldara Dist. Amravati
Email: chandrakant.tumbade@rediffmail.com

Abstract:

Graphene is a rapidly rising star on the horizon of materials science and condensed-matter physics. Its extended honeycomb network is the basic building block of all other graphitic carbon allotropes of different dimensionality. Single basal plane of Graphite is called Graphene. Graphene is a 2D crystal made up of single atomic layer of carbon atoms arranged in honey comb structure making bonds with three neighbour atoms by sp^2 hybridization. Graphite is a stacked bunch of single layer Graphene attached with each other by weak Wan-der-Wals forces. The graphine was prepared by oxidizing purified natural flake graphite via modified Hummers method.

Keywords: carbon, graphite flakes, composites, graphene, chemical synthesis

Introduction:

Graphene is a rapidly rising star on the horizon of materials science and condensed-matter physics. This strictly two-dimensional material exhibits exceptionally high crystal and electronic quality [1]. Graphene is a parent form of all graphitic structures of carbon. With the discovery of Graphene researchers from many field found good scope of research in the field of Graphene. In very simple words, its extended honeycomb network is the basic building block of all other graphitic carbon allotropes of different dimensionality. Single basal plane of Graphite is called Graphene. Graphene is a 2D crystal made up of single atomic layer of carbon atoms arranged in honey comb structure making bonds with three neighbor atoms by sp^2 hybridization. Graphite is a stacked bunch of single layer Graphene attached with each other by weak Wan-der-Wals forces. Nanotubes and fullerene can be thought of as rolled and wrapped structure of Graphene plane respectively having stitched ends.

Brodie first demonstrated the synthesis of Graphene in 1859 by adding a portion of potassium chlorate to a slurry of graphite in fuming nitric acid [2]. In 1898, Staudenmaier improved on this protocol by using mixture of concentrated sulfuric acid and fuming nitric acid followed by gradual addition of chlorate to the reaction mixture. This small change in the procedure provided a simple protocol for the production of highly oxidized GO [3]. In 1958, Hummers reported an alternative method for the synthesis of graphene oxide by using $KMnO_4$ and $NaNO_3$ in concentrated H_2SO_4 [4]. GO prepared by this method could be used for preparing large graphitic film [5]. In the present paper, attempts have been made to synthesize graphene with few layers by modified the hummer's method.

Experimental:

Chemicals and reagents:



Bulk Graphite flakes, H_2SO_4 , $NaNO_3$, H_2O_2 (30%), $K_2S_2O_8$, P_2O_5 and $KMnO_4$ were purchased from Sigma-Aldrich. All the chemicals were of analytical reagent grades and used as received, without further purifications. The aqueous solutions were prepared in Milli-Q water.

Synthesis of Graphite Oxide (GO):

Chemical oxidation of natural graphite is one of the easy method for synthesis of graphene from natural graphite and chemically oxidized graphite named as graphite oxide (GO) [6-8]. 1 g Graphite flakes (GF ARC) were mixed with mixture of concentrated H_2SO_4 (36 mL), $K_2S_2O_8$ (1 g), and P_2O_5 (1 g) at $70^\circ C$. The mixture was kept at $70^\circ C$ for 4.7 h using hotplate. Successively, the mixture was cooled to room temperature and diluted with 0.5 L of distilled water and filtered by Buckner Funnel. Successively washes of distilled water were given till neutral pH observed and confirmed by pH paper. Washed Graphite flakes were dried in ambient condition overnight. Product obtained by above reaction was dull blackish flakes with reduced shining. This product was abbreviated as Pre-Oxidized Graphite (POG).

1.5 g pre-treated (or Pre-Oxidized) graphite powder was mixed with cold ($0^\circ C$) concentrated H_2SO_4 (36 mL). Then, $KMnO_4$ (3 g) was added gradually under stirring and the temperature of the mixture was kept below $21^\circ C$ by cooling. Successively, the mixture was stirred at $35^\circ C$ for 24 hr, and then diluted with distilled water (250 mL). Because the addition of water in concentrated Sulphuric acid medium releases a large amount of heat, the addition of water was carried out in an ice bath to keep the temperature below $21^\circ C$.

After adding all of the 250 mL of distilled water, the mixture was stirred for 2 h, and then additional 1 L of distilled water was added. Shortly after the dilution with 1L of water, H_2O_2 (30 %) was added to the mixture, until the colour of mixture changed into brilliant yellow along with bubbling. Bright golden coloured suspended graphite flakes were observed.

Above suspension was washed by centrifugation and decantation cycles until neutral pH observed. Neutral pH point was confirmed by pH strip. As the pH tends to neutralization it was observed that color of particles changes to reddish brown and mixture becomes slurry instead of dispersion of big particles. Obtained slurry type product was abbreviated as Graphite Oxide (GO) slurry.

Graphene from graphite oxide

Graphene was synthesized from GO by ultrasonication treatment. GO slurry was diluted in water as 1mg/1ml. This diluted GO suspension was ultrasonicated by using ultrasonic cleaner bath for 30 min.

Results and discussion:

FTIR analysis of Graphite Oxide:

FTIR analysis of pristine graphite, POG, GO Dried were carried out to observe changes in functionality type after oxidation of graphite in various stages like after pre oxidation and after complete oxidation. Sample of pristine graphite was taken as such. POG was dried at $100^\circ C$ for 2 hr before analysis and GO Slurry also dried at $120^\circ C$ for 2 hr. for sample preparation. Dried GO was abbreviated as Dried GO and analysed.

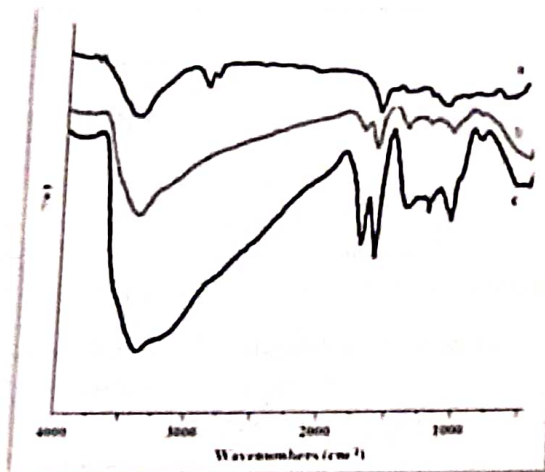
FTIR spectra of pristine graphite, POG and Dried GO show strong peak at $\sim 1650\text{ cm}^{-1}$ for aromatic C=C stretching in the case of pristine graphite, POG and Dried GO as shown in Fig.1. This is because of back bone skeleton of graphene planes. GF ARC and POG shows aromatic

substituted functionality by showing absorption peaks in between $1000-1500\text{ cm}^{-1}$ which can be because of the naturally present functionalities in Graphite. In case of Dried GO upon final oxidation aromatic Carbon-Carbon double bonds absorption peak shifted to lower wavenumbers showing more over decrease of double bonds between carbons. It can be because of substituted functionality on back bone skeleton structure of graphitic planes. It was confirmed by strong and broad peak at $\sim 1570\text{ cm}^{-1}$ in the case of Dried GO which shows presents of substituted aromatic back bone.

Another interesting peak is at $\sim 1650\text{ cm}^{-1}$ showing possibility of carboxylic acid functionality. Interestingly it is absent in pristine graphite and increases little bit in POG but it increases tremendously in Dried GO. Carboxylic acid functionality was confirmed from peak at $\sim 880\text{ cm}^{-1}$ along with peak at $\sim 1470\text{ cm}^{-1}$ in finger print region. Broad and strong peaks in between $\sim 3100 - 3500\text{ cm}^{-1}$ show presence of $-\text{OH}$ functionality. This was confirmed by strong peak at $\sim 1030\text{ cm}^{-1}$ in finger print region. Peaks between $1000-1080\text{ cm}^{-1}$, $1400-1460\text{ cm}^{-1}$, $3100-3500\text{ cm}^{-1}$, $3500-3700\text{ cm}^{-1}$ shows possibility of primary alcohols presents in pristine graphite. While all these peaks gets broadened and strengthened in case of POG, along with primary aliphatic hydroxyl functionality there is presence of aromatic phenolic $-\text{OH}$ showing peak between $1150-1290\text{ cm}^{-1}$ in both case i.e. pristine graphite and POG.

Peak at $\sim 1260\text{ cm}^{-1}$ shows presence of epoxide groups. It gets enhanced as oxidation proceeds in pristine graphite, POG and Dried GO successively. Ionized carboxyles also shows probably presence because of peak present between $1400-1450\text{ cm}^{-1}$ and $1550-1650\text{ cm}^{-1}$.

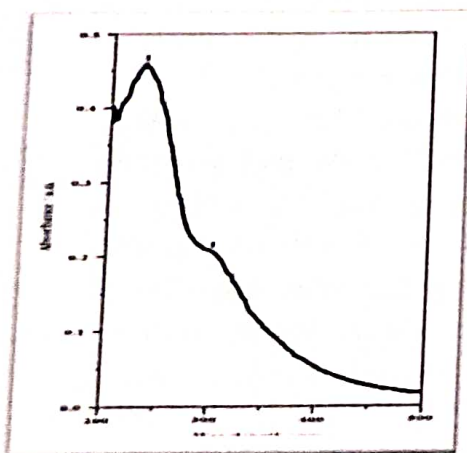
Fig: 1 FTIR spectra of (a) pristine graphite, (b) pre-oxidized graphite (POG) (c) and graphite oxide (GO)



From above discussion we can say that pristine graphite contains functional groups but these groups are not sufficient to interact with any solvent and hence graphite remains undissolved or undispersed in various media especially in water. Upon oxidation more oxygen functionalities like carboxylic, hydroxyl, epoxide etc get attached to the graphitic planes by chemical oxidation of graphite with strong oxidizing acids. Upon this reaction backbone skeleton structure of graphitic planes having aromatic double bond converts to substituted aromatic structure. As a result more functionality containing oxygen enables graphitic planes to make stable dispersion in water as well as other solvents.

UV-Vis analysis of Graphene:

UV-Visible Spectroscopic analysis was carried out to analyze exfoliated Graphene dispersed in water. Graphene slurry was diluted with distilled in water with the ratio 1:20 (G: Water). One part of sample was filtered and filtrate was used as reference media for above analysis. UV-Vis. Absorption spectrum of exfoliated Graphene Slurry with reference to



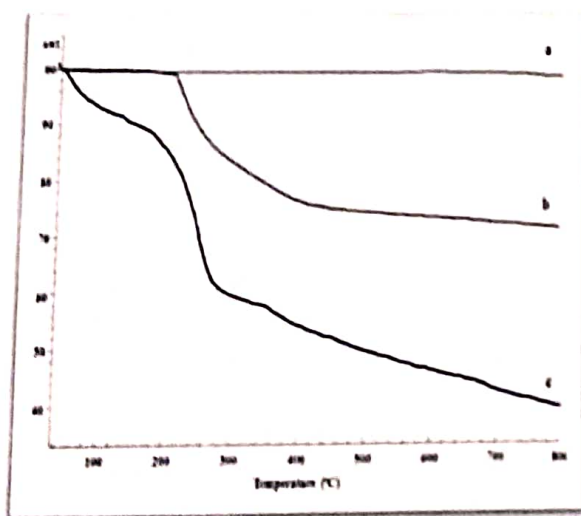
filtrate of Gslurry is shown in Fig.2. The spectrum shows sharp peak at $\lambda = 230$ nm indicating $\pi-\pi^*$ transition of C = C (aromatic) of hexagonal rings of Graphene planes. It shows that there is no effect of ultrasonication on oxygen functionalities which is attached to graphene sheets.

Fig.2 UV-Vis spectrum of exfoliated graphene

Above result match with findings of FTIR analysis that upon oxygen fictionalization still graphene planes retain their aromatic nature after exfoliation.

TGA analysis of Graphite Oxide:

As prepared graphite oxide is thermally unstable because of presence of physically adsorbed water and large number of oxygen containing functionalities. Thermal analysis of pristine graphite, pre-oxidized graphite (POG) and graphite oxide (GO) was carried out from 35°C to 400°C in nitrogen atmosphere to study thermal stability after oxidation of graphite. Fig.3 shows TGA curves of graphite at above different stages. TGA results show that, no weight loss is observed in pristine graphite. But in case of pre-oxidized graphite and graphite oxide weight loss is observed.



POG is the first stage of oxidation of graphite and at this stage small amount of oxygen functionalities attached to the graphite planes and make it active for further oxidation. GO is the final stage of oxidation and at this stage large number of oxygen functionalities attached to graphite planes.

Fig.3 TGA curves in nitrogen of (a) pristine graphite, (b) pre-oxidized graphite (POG) and (c) graphite oxide (GO)

In case of POG, the weight loss was observed between 110°C to 200°C. This weight loss shows the attachment of oxygen with graphite

layers. The major weight loss occurred near about 250°C. After 350°C steady weight loss was observed up to 400°C.

On the other hand GO is thermally unstable and starts to lose weight upon heating even below 100°C. Large weight loss was observed between 150°C to 270°C and the major weight loss occurred at near 230°C, presumably due to pyrolysis of the labile oxygen-containing functional groups, yielding CO, CO₂ [9].

The deoxygenation of GO during thermal analysis is roughly divided into four stages like (I) from 30 to 130°C, the physically adsorbed and intercalated water is evaporated ("physical" water); (II) from 130 to 300°C, the intermolecular dehydration takes place between neighbouring carboxylic and/or hydroxyl groups, to generate thermally stable lactones, anhydrides, ethers, and carbonyls as well as release abundant H₂O ("chemical" water). Meanwhile, the decarboxylation of individual carboxylic groups release abundant CO₂ [10], (III) from 170 to 300°C, the anhydrides decompose to evolve both CO₂ and CO, while the individual phenols decompose to release CO and (IV) from 200 to 400°C, the lactones and individual ether desorb as CO₂ and CO, respectively [11-12].



Conclusion:

Modified Hummer's Method was used to synthesize graphene followed by exfoliation by ultrasonication of GO to get dispersion of oxygen functionalized graphene in water. GO and dispersion of graphene were characterized by various techniques.

FTIR analysis shows increase in functionality as degree of oxidation increases. In this oxidation method, mainly carboxylic groups, hydroxyl groups and phenolic groups were found to have attached to graphene sheets.

It was found that graphite oxide (GO) is a bunch of planes instead of single layer of graphene and after exfoliation it was in form of single to few layer graphene.

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