

# SYNTHESIS AND CHARACTERIZATION OF GRAPHENE OXIDE BY MODIFIED HUMMERS METHOD

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**Abstract:** The carbon based nanomaterial graphene oxide is emerged as an alternate path for the synthesis of graphene. From the structural point of view, graphene oxide is similar to that of graphene sheet with the oxygen-containing groups on its base which can be removed easily by dissolving it in water or other water like solvents. There are a numbers of methods reported in literature for the synthesis of graphene oxide, which satisfies its own pros and cons. Here in the present work, we have reported successfully the employment of an easy and important method known as the improved or modified version of Hummers' method for the synthesis of graphene oxide. The formation of graphene oxide in the experimentation is confirmed by the appearance of strong characteristic peak of graphene oxide at the two theta value of  $9.08^\circ$  and oxygen containing functional groups during the XRD and FTIR characterization, respectively.

**Index Terms -** Graphene oxide, Hummers' method, XRD, FTIR, graphite

## I. INTRODUCTION

Graphenes are the two-dimensional hexagonal structures that are arranged in stacks in a vertical direction [1] under the influence of weak Van der Waals force to form one of the important allotropes of carbon that is graphite. The graphene is renowned for being the strongest and thinnest known material in the universe. Due to these attractive properties graphene are proposed to be used in various domains of medical and electronic industries namely as biosensors [2], electrodes [3], supercapacitors [4], bioelectronics [5], etc. For the synthesis of this novel carbon based material graphene, different kinds of approaches were employed by various groups of researcher [6-11] around the globe. The approach for the synthesis of single layer graphite had been initiated in the early part of 1975, [6] where the author reported [6] the fabrication of mono and multi-layered graphite on the Pt substrates by the process of thermal disintegration of carbon. However, the first ever successful approach for the isolation of single graphene layer was carried by Novoselov et. al in the year 2004 [7]. In their work, they have isolated the graphene layer by undergoing a simple mechanical peeling method, where the exfoliation of graphite surface was carried out with scotch tape. The reported [7] method was proved to be a simple one, but the yield of graphene produced through this procedure is not up to date marked for the industrial applications. As an alternative to this method, scientist have been reported some other popular methods such as chemical vapour deposition (CVD) [8, 9], thermal decomposition [10], solvent stripping [11] etc. Although the above mentioned processes provide a better option for the synthesis of graphene oxide, but they are not free from demerits. For example, in case of CVD method, a very thin layer of graphene sheet can be obtained but the impurity elements are sitting on the graphene layer creates problem in achieving a clean environment for the application. Another method, namely, the thermal decomposition of SiC layer embraces the advantage of having uniform sheet with non requirement of transfer to other insulating medium but due to the lack of continuous and uniform film deposition the production rate of thermally decomposed graphene layer is still at the lower limit side. On the other hand, solvent stripping process provides the merit of production of defect free graphene layer with the disadvantage of lower production yield in the prospect of industrial application. Apart from these important processes, another popularly used method for the fabrication of graphene is the redox method [12, 13]. The method follows three main steps where initially the oxidation of graphite is happened in the presence of strong oxidizing agent and then followed by graphene oxide aqueous dispersion and reduction, respectively. It is note worthy to mention here that from structural point of view graphene oxide and graphene sheet are similar only difference is that the graphene oxide contains base having oxygen-containing groups. Also these groups attain a high affinity to the water molecules and hence easily dissolved in water and other water like solvents. Therefore, the synthesis of graphene oxide provides an alternative path for the synthesis of graphene by following any relatively easy and short procedure. In recent years, many methods, like Brodie [14], Staudenmaier [15], and Hummers [16] had been invented to carry out the oxidation process of graphite for obtaining the graphene oxide. Out of those, due to the properties, like non-toxicity and shorter time span environment the Hummers method finds an extra advantage to use in oxidation process popularly among the scientists [16]. Moreover an improvement or modification of Hummers method was reported in 2010 by a group of researcher at Rice University [17]. The team reported the advantage of this improved or modified method in terms of more intact graphitic basal plan and higher hydrophilic degree of produced graphene oxide with better temperature control than the conventional Hummers method. Keeping this key advantage in our mind, here in this work for the synthesis of graphene oxide we have employed the improved or modified version Hummers method [18] for carrying out the current experimentation. After synthesis of graphene oxide, those are characterized mainly by structural characterizing tools such as X-ray Powder Diffraction Method (XRD) and Fourier-transform infrared spectrum (FTIR) to know whether our procedure really able to provide the successful results.

## II. EXPERIMENT AND METHODS

### 2.1. Raw materials

Flake graphite power,  $\text{KMnO}_4$ , concentrated  $\text{H}_2\text{SO}_4$ , concentrated  $\text{H}_3\text{PO}_4$ , aqueous  $\text{H}_2\text{O}_2$ , dilute HCl, deionized water and ice for water bath.

## 2.2. Graphene oxide preparation

As mentioned earlier, here in this current work we have used improved Hummers method [18] for the synthesis of graphene oxide. Initially 1.5 gm graphite powder and 9.0 gm  $\text{KMnO}_4$  were consecutively added into a 9:1 mixer of concentrated  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$  (180:20ml) under continuous stirring environment at an elevated temperature of  $50^\circ\text{C}$ . In this process,  $\text{KMnO}_4$  is used as an oxidizing agent on the other hand  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  are used to improve yield of graphene oxide and elimination of production of any toxic gases (such as  $\text{NO}_2$ ). After the continuous stirring at temperature  $50^\circ\text{C}$  for 12 hours, the solution was then cooled to room temperature and then the solution was poured into ice bath with 30%  $\text{H}_2\text{O}_2$  (3ml). Here in the experiment,  $\text{H}_2\text{O}_2$  was used to stop the oxidation process or in otherword to remove the excess amount of  $\text{KMnO}_4$  that was present in the solution. After completion of above procedure, we observed the bright yellow color of the solution that infers the high oxidation level of the graphite. The suspension of the solution was then filtered by using filter paper and then the solid mixture was washed with the deionised water, 30% of  $\text{HCl}$  (3ml) solution and ethanol. The solid product thus obtained on the surface of filter paper was finally dried at  $80^\circ\text{C}$  for duration a of 24 hours to obtain the reduced graphene oxide. That graphene oxide was then grinding with the help of a mortar to obtain in a final powder form that is graphene oxide powder for carrying out various characterisations. Fig.1, shows the photographs of experimentation at different stages.

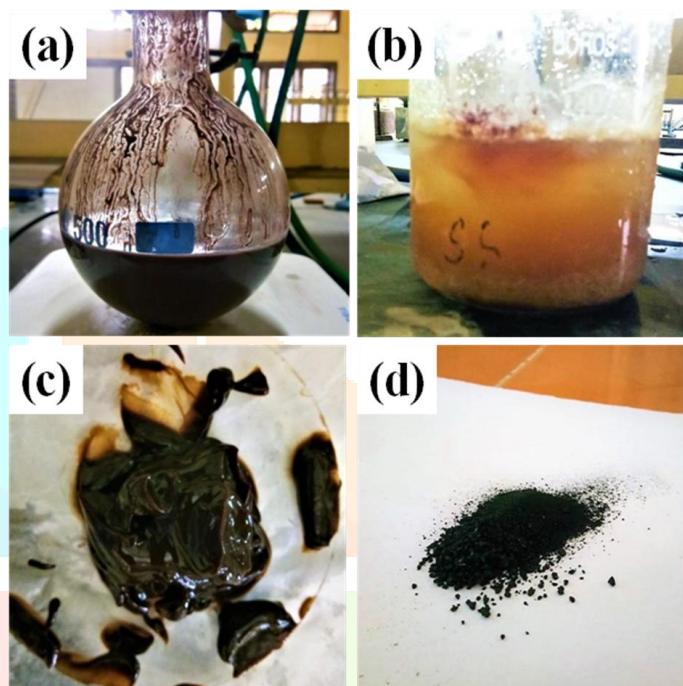


Fig. 1: (a) Mixer of graphite powder,  $\text{KMnO}_4$ , conc.  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  at  $50^\circ\text{C}$ , (b) After 12 hour of heating the solution was poured into ice with 30 %, (c) Paste of graphene oxide before it is converted into powdered form and (d) After dried at  $80^\circ\text{C}$  final powdered form of reduced graphene oxide.

## 2.3. Characterization

The crystal features of graphene oxide was obtained by XRD at SAIF, Guwahati with two theta values ranging from  $0$  to  $90^\circ$  by using a PANalytical make Empyrean model machine. The FTIR spectrum was recorded by using IRAffinity-1 FTIR, Shimadzu, within the range of  $4000\text{--}400\text{ cm}^{-1}$  at the college.

## III. RESULT AND DISCUSSION

For structural characterisation, XRD is an important and rapid analytical technique used for the identification of various phase of crystalline material. The XRD plot of our synthesised graphene oxide for the two theta value ranging from  $0$  to  $90^\circ$  is displayed in Fig. 2. From the plot it is evident that a sharp peak at the two theta value  $9.08^\circ$  is observed. The peak is identified as the plane (001) of graphene oxide and its corresponding basal plane spacing is calculated as  $0.09727\text{ nm}$ . This value of interlayer spacing is found to be increased significantly in comparison to the d-spacing of natural flake graphite. Hence the formation of graphene oxide is confirmed in our experimentation. The increase in the interlayer or basal plan spacing is supposed to arise from the intercalation of oxygen functional group inside the graphite layers [19]. A similar kind of observation in the case of XRD characterisation is also reported in [17, 19-21]. Ning Cao and Yuan Zhang have reported [19] the existence of the most intense peak of graphene oxide at two theta  $9.8^\circ$  with the d-spacing of  $0.88160\text{ nm}$ . On the other hand, Song et. al. [21] and Bykkam et. al.[20], had found the strongest peak of graphene oxide at the two theta value of  $10.2$  and  $9.09^\circ$  with the corresponding d-spacing value of  $0.84369$  to and  $0.961\text{ nm}$ , respectively.

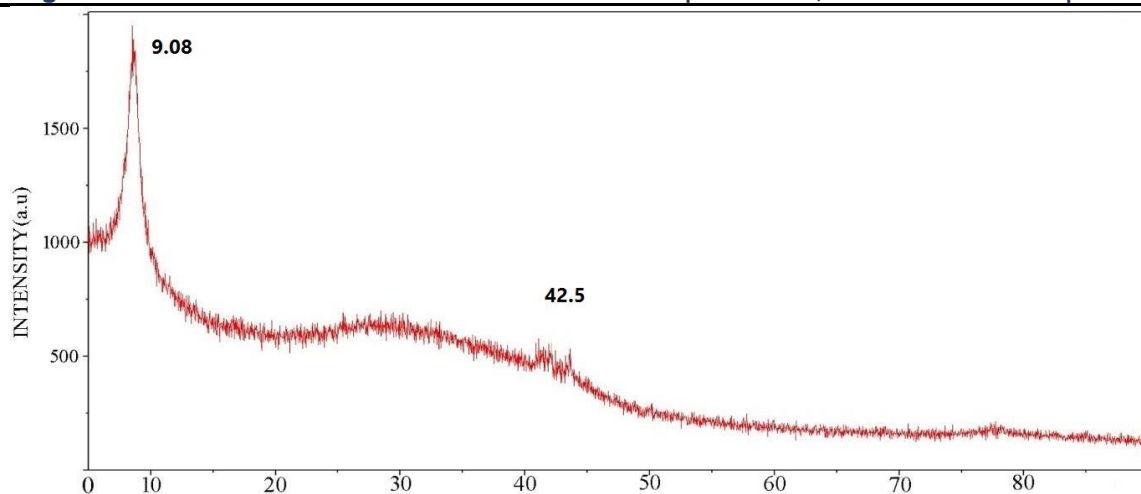


Fig. 2: XRD plot of synthesised graphene oxide.

Again from Fig. 2, it is also observed in the XRD pattern that along with the most intense (001), another feeble peak is observed at two theta value of  $42.5^\circ$ . Similar kind of peak is also noticed by Ning Cao and Yuan Zhang [19], they mentioned that this peak has arisen due to the incomplete oxidation process.

To investigate the structural and functional groups of synthesized material, we have carried out the FTIR characterization. The FTIR spectrum of prepared graphene oxide powder is shown in Fig. 3.

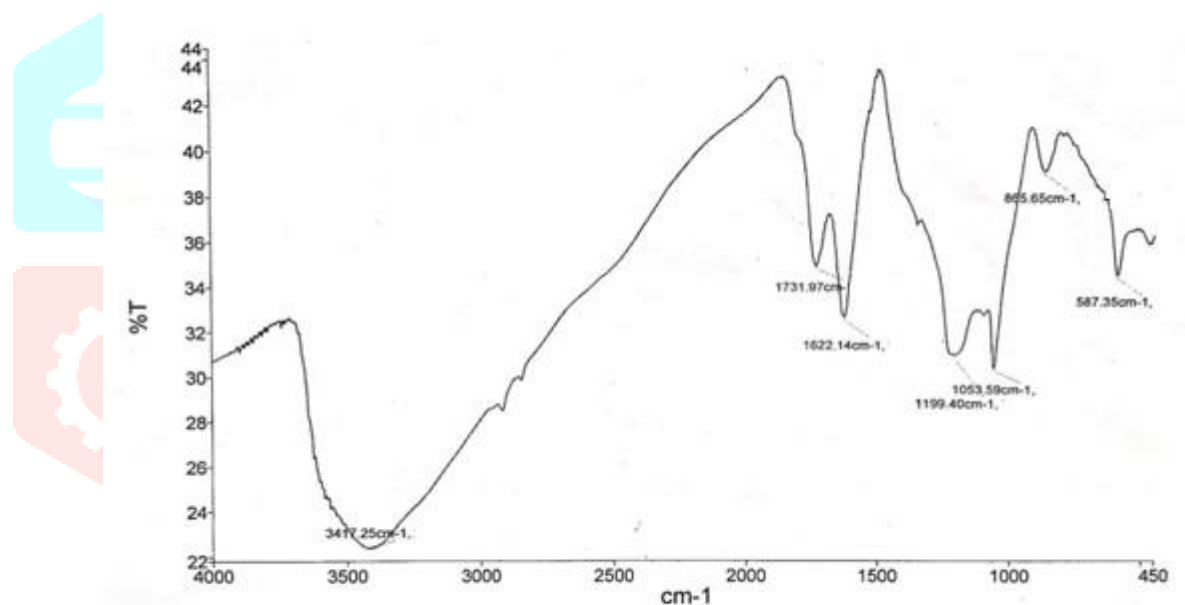


Fig. 3: FTIR spectrum of synthesized graphene oxide powder.

The spectrum exhibits the presence of carbon oxygen functional groups of graphene oxide. A broad and wide peak is observed at  $3417.25 \text{ cm}^{-1}$ , which is proposed to attribute as the O-H stretching vibrations of the C-OH groups and water [20]. Apart from this broad peak, some other important peaks, namely characteristic peaks of C=O, C-OH, and C-O at  $1622.14$ ,  $1199.40$  and  $1053.59 \text{ cm}^{-1}$ , respectively are also noticed which are believed to be attributed to carboxylic acid and carbonyl groups [21]. The presence of oxygen functional groups in the synthesis material confirms the formation of graphene oxide from the flake graphite powder in our current experimentation.

#### IV. CONCLUSION

In the present work graphene oxide is synthesized by following the improved Hummers method. After synthesis the production of graphene oxide is confirmed with the help of XRD and FTIR. The presence of strong characteristic peak and expansion of interlayer spacing in case of XRD provides the evidence of formation of graphene oxide. On the other hand the presence of various oxygen containing functional groups at the FTIR spectrum also confirmed the synthesis of graphene oxide. Thus we can conclude that the improved or modified Hummers' method is an easy and cost effective method for the formation of graphene oxide in an appropriate amount along with a non-toxic environment. The graphene oxide synthesized through our experimentation can further be forwarded in the line of studying it as a base material for the water purification, biosensors and supercapacitors etc direct application based experimentation.

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