

Synthesis of High Yield Graphene Oxide Nano-Sheet at Room Temperature for Supercapacitor Application

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ABSTRACT: Graphene oxide and Graphene based Nano Composites are under intense spotlight of Scientific Community due to their unparalleled unique properties. This work describes a simple Room temperature method for the synthesis of Graphene oxide nanosheet. Successful Graphene oxide formation was confirmed by XRD Studies and Raman Spectra studies (D and G band). The d spacing was also calculated using XRD information. Morphology of the prepared sample was observed from the HRSEM images. The test of UV-VIS spectrometer indicated that GO sheet possessed excellent optical response. Electrochemical performance of the Graphene oxide electrode was analyzed by cyclic voltammetry, which showed the capacitive behavior of Graphene oxide. This investigation highlights the importance of the preparation of Graphene oxide sheets using simple room temperature method, which finds use in supercapacitor applications.

Keywords: Electrochemical, Graphene Oxide, Raman, XRD.

I. INTRODUCTION

The demand for various innovative materials is increasing day by day to meet the technological needs of the modern society. Graphene based materials have attracted researchers in many fields, due to its vast applications. Graphene oxide is one such material, that has been in the limelight in the field of materials science due to its wonderful characteristics such as excellent structural [1], electrical [2], mechanical [3] and optical [4] properties and with promising applications in the field of supercapacitor application [5]. GO has also enhanced the electrocatalytic performance [6]. Graphene oxide has shown promising device applications, such as in the development of energy storage capacitors [7], field effect transistors [8], energy related materials [9], sensors [10], drug delivery and biomedical applications. GO has repeatedly been investigated using different experimental techniques.

Brodie first demonstrated the synthesis of GO in 1859 by adding a portion of potassium chlorate to a slurry of graphite in fuming nitric acid [11]. 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 [12]. 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 [13]. GO prepared by this method could be used for preparing large graphitic film [14].

Graphite is a naturally occurring material available in abundance. By using oxidizing reagents, exfoliated graphite oxide could be obtained. The carbon atoms plane in graphite oxide would be heavily decorated by oxygen-containing groups. When the oxidizing agents react with graphite the interlayer distance increases. [15]. Graphene oxide is effectively a by-product of this oxidation. The completely oxidized compound can then be dispersed in a base solution such as water, and graphene oxide is thus produced. These oxidized layers can be exfoliated in water under moderate ultrasonication. GO, acquire multiple defects and the degree of the defects is subject to the additive

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Amount of oxidant and the oxidizing time, GO has been synthesized by various methods [16]. But the requirement of ice bath or temperature controlled devices would be expensive in synthesizing GO. Hence a simple and cost effective method is the need of the day. In this work a simple room temperature modified hummers method is employed in synthesizing GO. Graphite powder has been used as the starting material. After oxidation, the oxygen containing functional groups were introduced between the layers of the Graphite. The successful formation of GO was achieved and confirmed by relevant studies. The focus of this paper is to study the electrochemical response of the GO prepared under simple room temperature modified hummers method in, for supercapacitor application.

II. MATERIALS AND METHODS

The chemicals used for synthesis are Purified natural Graphite Powder (99.9995%), Sodium nitrate (NaNO_3) Sulfuric acid (H_2SO_4 , 98%), potassium permanganate (KMnO_4 , 99%), Hydrogen peroxide (H_2O_2 , 30%), Hydrochloric acid.

2.1. Synthesis of Graphene Oxide

GO nanosheets were obtained by different chemical treatments on purified natural graphite powder. GO was prepared by Modified Hummer's Method at room temperature. 1 gram of graphite and 0.5 gram of NaNO_3 were added to 23 ml of high concentration H_2SO_4 . 3 gram of Potassium Permanganate as oxidizing agent was further added into the mixture under constant stirring. While adding the Potassium permanganate into the mixture the temperature tends to increase. To avoid the sudden raise of temperature in the reaction, KMnO_4 was added gradually and gently for 6 hours. This helps the oxidation of graphite to form uniformly with time. The mixture was stirred at room temperature for upto three days to achieve high degree oxidation. After this process, 100 ml of deionised water was added in the mixture under stirring. Following this a raise in temperature was seen. Under this raised temperature stirring is continued for another one hour. Finally 3 ml of H_2O_2 was added in the suspension to stop the oxidation process. During this process the colour of the suspension changed from dark brown to bright Yellow. This indicates the high oxidation level of graphite. Subsequently centrifugation of 4000 rpm was carried out for 15 minutes to separate the supernatant. Washing with HCl was necessary to remove the sulphate ions from the product at this stage. The supernatant was discarded and the precipitate was then washed with HCl two times followed by deionised water until the resultant pH was around 5 to 6. By washing with deionised water repeatedly the Graphite oxide experienced exfoliation which resulted in the thickening of the Graphene oxide solution forming a GO gel. The resulting gel was dispersed with deionised water in an ultrasonic bath for 30 minutes and then dried at 60°C for 6 hours.

III. RESULT AND DISCUSSION

XRD STUDIES: Figure 1a shows xrd pattern of Graphite. The sharp peak in $2\theta = 26.56^\circ$. The d Spacing could be calculated by Bragg's law $n\lambda = 2d \sin\theta$. The corresponding d spacing of graphite is 0.336 nm. Figure 1b shows the xrd pattern of GO. The main diffraction peak appears at 10.14° with a (FWHM) of approximately 0.31. The corresponding interlayer distance in GO is 0.871 nm. The corresponding reflections of GO is (001). This value is higher than interlayer spacing of graphite (d-spacing = 0.336 nm, $2\theta = 26.56^\circ$), due to the presence of oxygenated functional groups and intercalated water molecules [18]

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MORPHOLOGY INVESTIGATIONS: Figure 2. Shows HRSEM images of GO sheets with different magnification, which appears as closely arranged thin sheets randomly aggregated with distinct edges. Wrinkled surface and folds are also seen. Layered and exfoliated structure with length in microns of GO is present in the image.

RAMAN ANALYSIS: Raman spectroscopy is a commonly used method to characterize carbon based materials. The D and G Band of GO is shown in the Figure 3. D and G bands were observed clearly at 1342cm^{-1} and 1585cm^{-1} respectively. The intensity ratio of ID/IG was calculated to be 1.151. Increase in ID/IG ratio implies the increase in the number and size of sp^2 clusters. The intensity of D/G band is a measure of the defects present in Graphene structure. The D peak of GO located at 1342cm^{-1} arises from a defect-induced breathing mode of sp^2 rings due to oxidation [19]. The intensity of the D band is related to the size of the in-plane sp^2 domains and an increase in the D peak intensity indicates formation of more sp^2 domains [20]. This method was employed to weaken the van der Waals forces of graphite by introducing oxygen functional groups there by promoting complete exfoliation of GO sheets in aqueous media.

UV-VISIBLE SPECTROPHOTOMETRIC ANALYSIS: Figure 4 shows the absorption spectra for a Graphene Oxide sheets in aqueous solution. UV-VIS. absorption spectra of aqueous GO solution show sharp absorption peak at 230 nm and a shoulder in the range 300 nm - 310 nm. It is observed that GO peak in 230 nm attributed to $\pi-\pi^*$ transition of the atomic C-C bonds and shoulder peak at 300 nm due to $n-\pi^*$ transition of aromatic bonds. We assign this broad shoulder in the range 300-310 nm to the $n-\pi^*$ transition due to presence of epoxide (C-O-C) and peroxide (R-O-O-R) like linkage [15] [16] [17]. The broad shoulder becomes very predominant when the spectrum was recorded. This is due to the formation of large number of peroxide like linkages in multilayered GO.

CYCLIC VOLTAMMETRY: Cyclic voltammetry is a predominant technique widely used to determine the capacitance behavior of the electrode material. Figure 5. shows the typical CV curve of GO recorded at various scan rates in 1M of H_2SO_4 from -0.5 V to 0.65V potential window. Materials with high energy density is economically important. The large potential window was obtained at 5mVs^{-1} Scan rate which indicates the

high energy density. Though there is an increase in the scan rate there is not much shift in the peak position which implies lower polarization effect in the electrode material[8]. The Specific Capacitance of GO is calculated from the equation $SC = \frac{1}{V} \int m (v_a - v_c) \cdot i dv$. A maximum specific capacitance of 144 F/g was calculated at 5 mVs^{-1} scan rate. The Specific Capacitance values of GO obtained at various Scan rates are further shown in the Chart Diagram (5b).

IV. FIGURES

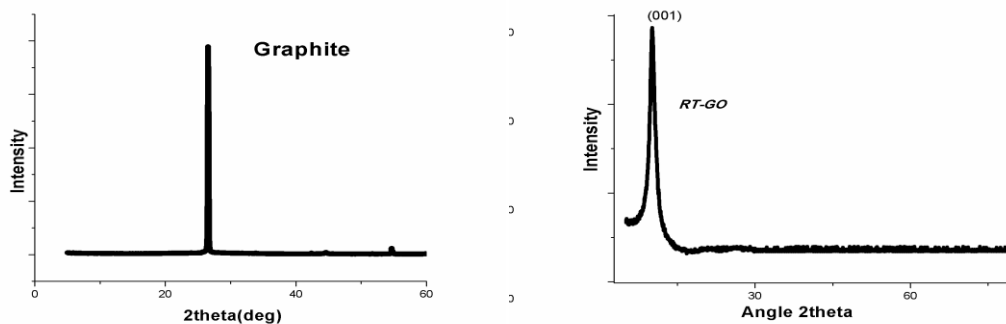


Figure 1a : XRD pattern of graphite

Figure 1b: XRD pattern of Graphene Oxide

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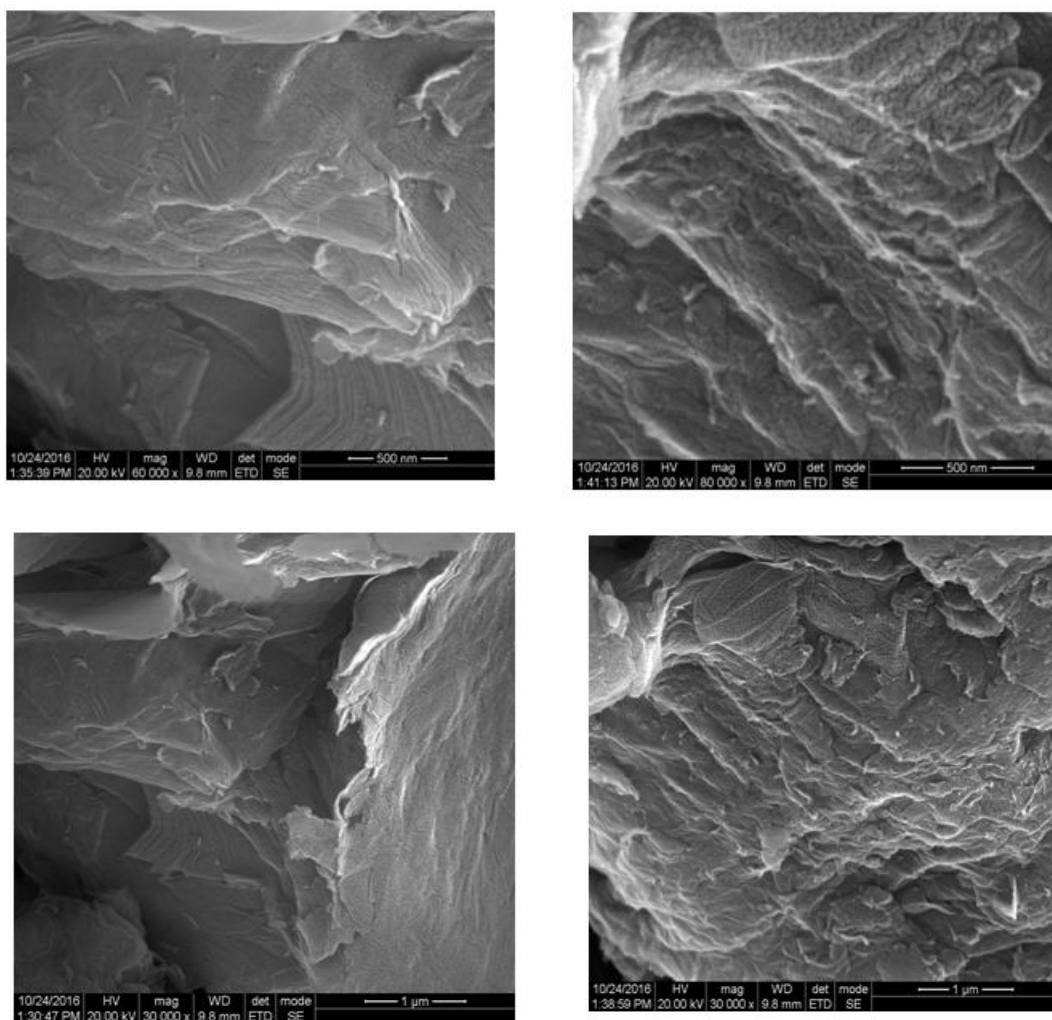


Figure 2 :HRSEM image of GO with different magnifications.

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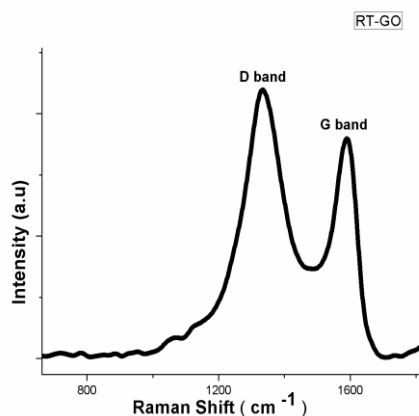


Figure 3 . Raman spectra of GO

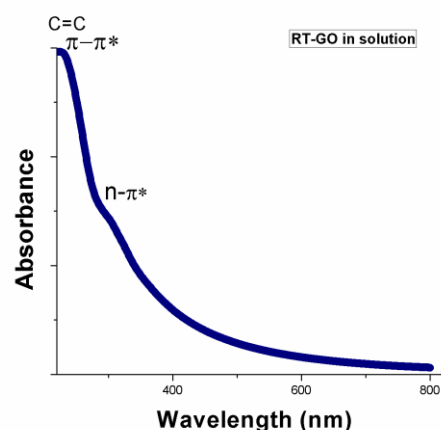


Figure 4: Absorption spectra of GO

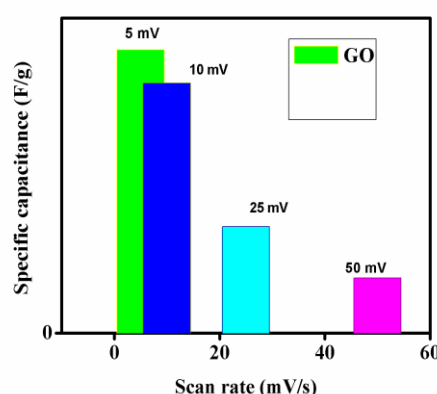
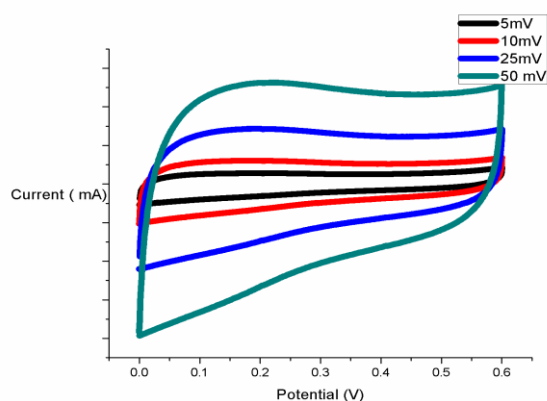


Figure 5a: exhibits the cyclic voltammety recorded for various scan rates. Figure 5 b: The Specific Capacitance values of GO at various Scan rates are shown in the Chart Diagram.

V. CONCLUSION

In this work GO sheets were synthesized using modified hummers method in room temperature. Hence, this method does not require any ice bath or temperature control device. This sample low cost synthesis process could lead to new opportunities for cost effective production of GO. In this work, the XRD result shows the main diffraction peak of GO, $2\theta = 10.14^\circ$ with d spacing of 0.871 nm. HRSEM images demonstrate thin and layered exfoliated structure.

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UV-VIS spectrum of GO exhibited maximum absorption peak at 230 nm. D peak was observed at 1342 cm⁻¹ and G peak at 1585 cm⁻¹ by Raman result. The intensity ratio of ID/IG was calculated to be 1.151. The maximum specific capacitance of GO, 144 F/g was calculated at 5 mVs⁻¹ scan rate. This could provide information regarding defects and disorders. In summary we have presented a cost effective and feasible technique for the rapid and large scale synthesis of exfoliated GO sheets. With promising and excellent electrochemical property, this material finds a vital usage as an energy storage material in Supercapacitors.

ACKNOWLEDGEMENT

The authors acknowledge the funds provided through "Anna Centenary Research Fellowship (ACRF)" by Anna university for carrying out this work.

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