FTIR, Raman and XRD analysis of graphene oxide films prepared by modified Hummers method

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Abstract—Graphene oxide (GO) is a promising material for energy storage device applications. Modified Hummers method (MHM) has been used to prepare GO films from graphite flakes by Sol-Gel method. With the aid of bridging agent dimethyldichlorosiline, structurally fine GO films were prepared. Fourier transform and infra-red (FTIR) spectrum of the GO thin film possesses absorption bands at 461, 594, 670, 803, 1020, 1243, 1457, 1544, 1627, 2850, 2926 and 3429 cm⁻¹. A sharp OH⁻ absorption band was revealed at 3429 cm⁻¹. Two vibrational bands were noticed in the Raman spectrum for pure graphite flakes at 1578 and 2718 cm⁻¹. However, for GO, five Raman vibrational bands were unveiled at 413, 1344, 1597, 2697 and 2945 cm⁻¹. Among these bands, the mode at 1344 cm⁻¹ was assigned to D-band and 1597 cm⁻¹ was assigned to G-band. Compared to D-band, G-band was dominated for the GO films. Several times of centrifugation and ultra-sonication process have aided to obtain more intensity of G-band. In addition, 2D and D + G bands were also revealed in the GO films. X-ray diffraction (XRD) analysis was confirmed that a sharp peak at 10.64 degrees leads to formation of GO thin film.

Keywords: Graphene oxide films, Modified Hummer’s method, Structural properties

1. Introduction
Carbon based materials are suitable for energy storage devices like batteries [1], super capacitors [2], mechanically useful materials such as composites [3], paper like materials [4], conductive ink [5] and electrochemical systems like nano-electro-mechanical systems/micro-electro-mechanical system (NEMS/MEMS) [6] etc. Among these, research on graphene plays a crucial role for battery applications. Now-a-days researchers focus on sodium ion batteries (SIBs) because of abundance of sodium in earth crust and cost effective compared to lithium. In SIBs, the transition metal doped graphene layer releases sodium ions for energy storage applications [7].

The GO film consists of sp² hybridized two-dimensional (2D) monolayer carbon atoms tightly packed by forming a honeycomb-like structure which derived from 3D graphite [9]. GO has unique physical properties, good mechanical flexibility, large specific surface area, higher thermal/chemical stability and excellent electrical conductivity [10]. GO is an atomic sheet of graphene decorated by several oxygenated functional groups on its basal planes and its edges, resulting in a hybrid structure comprising a combination of sp² and sp³ hybridized carbon atoms [11].

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Graphene can be synthesized by two different types of approaches: top-down and bottom-up. In top-down approach, the separation of the stacked layers of graphite occurs and yields into a single graphene sheet, whereas in bottom-up method, graphene is synthesized from alternative carbon containing sources [12]. In top down approach, chemical reduction is a reliable method to produce Graphene. In general, GO has been synthesized using modified Hummer’s method [MHM] [13]. In the present work, synthesis and structural characterization of GO is discussed. Purified graphite flakes, sulfuric acid, sodium nitrate and potassium permanganate are mixed in a sequence followed by addition of deionised water (DIW) and forms a graphite solution. The resultant solution was filtered and washed with 10% HCl. After obtaining a brown color solution, decanted the supernatant and the precipitate was dried in an oven. The obtained GO film was characterized by FTIR, Raman and XRD analysis.

2. Experimental procedure
2.1. Chemicals and materials
Graphite flakes (natural, −325 mesh) with a purity of 99.8% was purchased from Sigma-Aldrich, sodium nitrate (NaNO₃) with a purity of 98% purchased from Alfa Aesar, ACS sulfuric acid (H₂SO₄) with a purity of 98%, EMPLURA potassium permanganate (KMnO₄) with a purity of 98.5%, qualikem hydrofluoric acid (HF) with a purity of 40%, EMPARTA hydrogen peroxide (H₂O₂) with a purity of 30%, fisher scientific hydrochloric acid (HCl) with a purity of 35-37%, acetone, deionized water (DIW) and distilled water.

2.2. Synthesis of GO films
2.2.1. Purification of graphite flakes
25 ml of HF acid was taken in a plastic beaker. For which a 2 g of graphite flakes (GF) was added to HF. Then mechanical stirring was performed for one hour at 35 °C with 600 rpm. Sufficient time was given to settle down the GF in HF. This process is known to be sedimentation. After sedimentation to decant the HF, some quantity of distilled water was added to wash off the acid content in the GF. The same procedure was continued until the pH of the solution becomes neutral [7]. Then some DIW was added to perform ultrasonication for 30 min for proper mixing of GF with DIW. The solution was left in one day to settle down the graphite flakes in DIW to decant the water. Then the obtained residue was added to a small amount of acetone was added to obtain a residual solution and it was dried in an oven at around 100 °C for 20 min.

2.2.2. Synthesis of GO by using MHM
2 g of pure graphite flakes, 1 g of NaNO₃ and 45 ml of sulfuric acid were reserved in a 500 ml conical flask. The conical flask was kept in an ice-bath with stirring continuously for 30 min by monitoring the temperature not exceeding 15 °C. After obtaining a homogenized mixture, 6 g of KMnO₄ was added to the mixture. Later, when the ice-bath was removed, the temperature gradually increases in the mixture. This was maintained for 30 min until the mixture starts to thicken and become a dark green paste. Later 80 ml of DIW was added slowly while stirring. At the same time violet effervescence and a rapid increase of temperature were observed. The mixture was stirred for 30 min at 90 °C with the aid of a hot plate. 200 ml of DIW was added again to dilute the solution. When 3 ml of H₂O₂ is added then the color of the solution was changed to luminous yellow. The formation of yellow color indicates that the graphite oxide was formed and the brown color layer was formed at the top of the solution. The mixture was centrifuged and washed with 100 ml of 10% HCl for several times to remove the metal ions present in the solution. This solution was centrifuged for 20 min at 4000 rpm to discard supernatant. This procedure was repeated several times until the pH reaches to neutral [7]. The obtained graphite solution was exfoliated to GO by using ultra sonication. Finally, GO solution was poured in a petri dish at 50°C and maintained the same temperature for 24 h. In order to avoid humidity, the GO film was stored in a vacuum desiccator.
### Results and Discussions

#### 2.3.1 FTIR spectra

FTIR spectrum of GO layer is shown in Fig.1. The spectrum consists of vibrational groups of GO layer that includes carbonyl (C = O), aromatic (C = C), carboxyl (COOH), epoxy (C-O-C) and hydroxyl (O-H) groups are prescribed in Table 1. It is observed that a sharp peak at 3429 cm\(^{-1}\) corresponds to the carboxyl groups (O-H) due to water molecules, and the absorption peaks at 2926 cm\(^{-1}\) and 2850 cm\(^{-1}\) represents the asymmetric and symmetric stretching vibrations of CH\(_2\) bonds [14]. The peak at 1627 cm\(^{-1}\) is due to ketone group (C=O) and the main graphitic domain of the peak at 1544 cm\(^{-1}\) is due to sp\(^2\) hybridization [15]. This similar peak was also observed in Raman spectrum. The band at 1457 cm\(^{-1}\) reveals the C-O, 1243 cm\(^{-1}\) indicates about the C - O stretching of epoxy groups. The mode at 1020 cm\(^{-1}\) gives information about C - O - C stretching of alkoxy groups [16]. The absorption peak at 803 cm\(^{-1}\) belongs to aromatic C - H deformation [17]. Spikes at 670, 594 and 461 cm\(^{-1}\) arises from C-H bending vibrations [18].

#### Table 1. Characteristic vibrational modes and their energies of GO

| Wave number (cm\(^{-1}\)) | Functional group | Ref. |
|---------------------------|------------------|-----|
| 3429                      | -OH              | [14]|
| 2926                      | CH\(_2\)         | [14]|
| 2850                      | CH\(_2\)         | [14]|
| 1627                      | C = O            | [15]|
| 1544                      | C = C            | [15]|
| 1457                      | C - O            | [16]|
| 1243                      | C - O - C        | [16]|
| 1020                      | COOH             | [16]|
| 803                       | C - H            | [17]|
| 670                       | C - H            | [17]|
| 594                       | C - H            | [17]|
| 461                       | C - H            | [17]|

**Fig. 1.** FTIR spectrum of GO films prepared by MHM
2.3.2. Raman analysis of graphite and GO

Raman spectrum of GF contains bands marked as G and 2D bands as shown in Fig. 2 (a). These two highest intense peaks are the G peak at about 1578 cm\(^{-1}\) and the 2D peak at about 2718 cm\(^{-1}\). Among these the former one is the aforementioned G band, the only allowed first order Raman band. The G band is prominent for \(sp^2\) carbon networks. The second band is the result of a higher order process involving two phonons, and is known as 2D band.

In the Raman spectrum of GO layer contains bands marked as D, G and 2D bands. The Raman spectrum of GO is shown in Fig. 2 (b). The first-order D and G peaks are arising from the vibrations of \(sp^2\) carbon appeared at around 1344 cm\(^{-1}\) and 1597 cm\(^{-1}\), respectively. The D-band reveals that disorders of crystalline materials and defects associated with vacancies and grains [18]. It is noticed that the shape and the position of D peak shifts as the thickness of GO changes. In fact, a blue shift is observed to decrease of the thickness of GO. The shift and shape of the overtone of the D peak, called as 2D peak around 2697 cm\(^{-1}\), correlated to the set of graphene layers. The G peak corresponds to the optical \(E_{2g}\) phonons at the Brillouin zone center resulting from the bond stretching of, \(sp^2\) carbon pairs in both rings and chains [19].

![Raman spectra of (a) GF and (b) GO film](image)

Fig. 2. Raman spectra of (a) GF and (b) GO film

2.3.3. XRD analysis of GO

![X ray diffraction spectrum of GO](image)

Fig. 3. X ray diffraction spectrum of GO
A diffraction peak of GO was observed at 10.64° corresponding to an interlayer spacing (d) of 0.817 nm with indices (001) as shown in Fig. 3. One more broad diffraction peak was observed at 26.3° corresponding to an interlayer spacing of about 0.34 nm with an indices of (002) [20]. The main peak (002) of graphite is vanished totally in case of dried GO [21]. This peak was broader and very lower in intensity than the natural graphite and represents the graphene with reduced layers.

3. Conclusion
The GO films have been synthesized by modified Hummers method (MHM). The functional groups and structure of GO films were characterized with the help of FTIR, Raman and XRD analysis. From FTIR spectrum, the oxygen containing functional groups such as hydroxyl, carbonyl, carboxyl and epoxy groups was revealed. With the help of the Raman spectrum, it is concluded that the GO film has less defects as the G band is dominated to D band. Finally, XRD spectrum revealed that the changes in the interlayer spacing may be indicative of the perturbation of the oxygen-containing functional groups bound to the GO film.

Reference
[1] V.H. Pham, T.V. Cuong, T.T. Dang, S.H. Hur, B.S. Kong, E.J. Kim, E.W. Shin, and J.S. Chung, Superior conductive polystyrene – chemically converted graphene nanocomposite J. Mater. Chem., 21,11312 (2011).
[2] Stoller, M. D., Park, S., Zhu, Y., An, J. & Ruoff, R. S. Graphene-based ultracapacitors. Nano Lett. 8, 3498–3502 (2008).
[3] Stankovich, S., Dikin, D. A., Dommett, G. H. B. Kohlhaas, K. M. J., Z. E. Stach, E. A. Piner, R. Nguyen, S. T., Ruoff, R. S, Graphene-based composite materials, Nature, 442, 282–286(2006).
[4] Dikin, D. A. Stankovich, S. Zimney, E. J. Piner, R. Dommett, G. H. B. Evmenenko, G. Nguyen, S. T. Ruoff, R. S, Preparation and characterization of graphene oxide Paper, Nature, 448, 457 – 460(2007).
[5] L. Huang, Y. Huang, J. Liang, X. Wan, and Y.Chen. Graphene-Based Conducting Inks for Direct Inkjet Printing of Flexible Conductive Patterns and Their Applications in Electric Circuits and Chemical Sensors, Nano Res., 4, 675 (2011).
[6] Bunch, J. S. v. d, Zande, A. M., Verbridge, S. S.Frank, I. W. Tanenbaum, D. M. Parpia, J. M. Craighead, H. G. McEuen, P. L, Electromechanical Resonators from graphene Sheets , Science, 315, 490–493(2007).
[7] lamuel David, Romil Bhandavat, and Gurpreet Singh, MoS2/Graphene Composite Paper for Sodium-Ion Battery Electrodes, ACS Nano, vol. 8, no.2,1–13 (2014).
[8] A.K. Geim, K.S. Novoselov, The rise of Graphene, Nat. Mater. 6, 183 (2007).
[9] Niyogi, E. Bekyarova, M.E. Itkis, J.L. McWilliams, M.A. Hamon, R.C. Haddon, Solution Properties of Graphite and Graphene, J. Am. Chem. Soc. 128, 7720 (2006).
[10] Dikin DA, Stankovich S, Zimney EJ, Piner RD, Dommett GH, Evmenenko G, et al. Preparation and characterization of graphene oxide paper, Nature, 60, 448- 457(2007).
[11] Nisha Bagotia, Harshal Mohite, Nidhi Tanaliya, D.K. Sharma, A Comparative Study of Electrical, EMI Shielding and Thermal Properties of Graphene and Multiwalled Carbon Nanotube Filled Polystyrene Nanocomposites, polymer composites, 1-12 (2017).
[12] William S. Hummers, JR., and Richard E. Offeman, Preparation of Graphitic Oxide, Journal of the American Chemical Society, 80, 1339-1339 (1958).
[13] Tarko Fentaw Emiru, Delele Worku Ayele, Controlled synthesis, characterization and reduction of graphene oxide: A convenient method for large scale production, Egyptian Journal of Basic and Applied Sciences, 111, 1-6 (2016).
[14] Sudesh, N Kumar, S Das, C Bernhard and G D Varma, Effect of graphene oxide doping on superconducting properties of bulk MgB2, Supercond. Sci. Technol. 26 (2013) 095008 (8pp).
[15] Dongning He, Zheng Peng, Wei Gong, Yongyue Luo, Pengfei Zhao and Lingxue Kong, Mechanism of a green graphene oxide reduction with reusable potassium carbonate, RSC Adv., (2015), 5, 11966.
[16] Wang Z, Huang B, Dai Y, Liu Y, Zhang X, Qin X, Wang J, Zheng Z, Cheng H: Crystal facets controlled synthesis of graphene@TiO2 nanocomposites by a one-pot hydrothermal process. Cryst Eng Comm, 14(5)1687–1692(2012).

[17] A.V. Ramya, B. Manoj and Anu N. Mohan, Extraction and Characterization of Wrinkled Graphene Nanolayers from Commercial Graphite, Asian Journal of Chemistry; Vol. 28, No. 5, 1031-1034 (2016).

[18] A. C. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon. Phys. Rev. B 61, 14095-14107(2000).

[19] Leila Shahriary, Anjali. Athawale, Graphene Oxide Synthesized by using Modified Hummers Approach, IJREEE, volume 2, 58-63(2014).

[20] Sanjeev Rao, Jahnavee Upadhyay, Kyriaki Polychronopoulou, Rehan Umer and Raj Das, Reduced Graphene Oxide: Effect of Reduction on Electrical Conductivity, J. Compos. Sci., 2, 25 (2018).

[21] Hu Meng, Wei Yang, Kun Ding, Liang Feng and Yafeng Gua, Cu2O nanorods modified by reduced graphene oxide for NH3 sensing at room temperature, J.Mater.Chem. A, 3, 1174-1181(2015).