

Synthesis of Reduced Graphene Oxide Using Novel Exfoliation Technique and its Characterizations

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For processing of graphene based composite materials Graphene oxide is considered to be the main precursor. Though epitaxial growth and chemical vapor deposition techniques have been utilized to get monolayers of graphene, wet chemical process have been used for its large scale synthesis. For the extraction of graphene monolayer the chemical route relies on the weakening of the Van der Waals cohesive force upon the insertion of reactants in the inter layer space as a consequence sp^2 lattice is partially degraded into a sp^2 - sp^3 sheet that possesses a less π - π stacking stability. The method described here uses a novel chemical exfoliation technique. The graphite from the pencil lead is used as the precursor and it is treated with alcohol-ketone-surfactant mixture and mechanically agitated so as to get the golden brown colored suspension. The material was characterized by Fourier Transform Infra Red spectroscopy. The absence of 1570 cm^{-1} peak clearly indicates the oxidation of $C=C$ bonds. The SEM images confirmed the presence of the nanoplatelets of graphene oxide. The AFM analysis confirmed the sheet thickness of the graphene oxide sheets to be $< 5\text{ nm}$. The sheet resistance of the sheets of thermally treated graphene oxide or reduced graphene oxide on Si wafer (p-type, $4\text{-}6\ \Omega/\text{cm}$) was measured as $200\text{-}300\ \Omega/\square$. The Ellipsometric characterisations also matches with that of the thermally reduced graphene oxide films formed.

Keywords: Graphite, Graphene, Reduced Graphene oxide, Nano-sheets, Oxidation, Exfoliation.

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1. INTRODUCTION

Graphene is a special class of two-dimensional carbon nanostructure which is so unique that it holds to be a promising material for potential applications in many technological fields such as Nanoelectronics, sensors, nanocomposites, batteries, super capacitors and hydrogen storage [1, 2, 7, 8, 13 and 14]. In spite of such potential applications the major challenge is in the synthesis and processing of bulk-quantity of Graphene sheets. Graphite consists of a stack of flat Graphene sheets. It is much cheap and is available in large quantities. Though mechanical cleavage of graphite had originally led to the discovery of Graphene sheets, its low productivity makes it unsuitable for large-scale use. In such a case chemical conversion appears to be a much more efficient approach to bulk production of Graphene sheets at low cost. In such method the exfoliation of graphite in liquid phase to Graphene like materials include the oxidation and subsequent exfoliation of graphite to give Graphene oxide.

Ruoff and co-workers [11, 12, 18] demonstrated a solution based route involving chemical oxidation of graphite to hydrophilic graphite oxide (GO), which can be readily exfoliated as individual Graphene oxide sheets by ultrasonification. Graphene oxide can be converted back to conducting Graphene by chemical reduction using hydrazine or by thermal methods. But the Graphene sheets so produced by this method had a tendency to form irreversible agglomerates owing to their hydrophobic nature. To overcome this defect stabilization using selected polymers or surfactants has to be done [3, 9, 10, 15]. The study is particularly based on pencil lead which is a low cost, easily available graphite precursor. Here a

chemical and mechanical exfoliation has been done. The polar solvent-surfactant and mechanical stirring has been combined with heating resulting in fast exfoliation of the graphite sheets Fig. 1 and 2. As the method does not use any salt and acid there is no criticality to stability of the sheets developed. On the other hand hydrazine being highly toxic and its use has to be minimized the reduction process by thermal heating has been used. In addition the presence of the polymeric nature of the non-ionic surfactant used reduces the tendency of agglomeration upon the evaporation of solvent. On study of the FTIR spectra of the specimen so developed by the method indicates the absence of peaks associated with, $C=C$, $C-OH$ and $-COOH$ groups showing that the material is completely oxidized and is a defect free material.

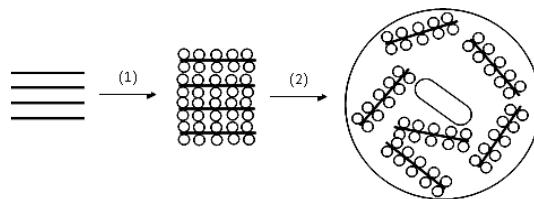


Fig. 1 – Possible mechanism of reduced graphene oxide formation (1) Oxidation of graphite to graphite oxide and (2) Exfoliation of graphene oxide under stirring. Under thermal treatment the material reduces to reduced graphene oxide

2. EXPERIMENTAL DETAILS

1 gm of pencil lead is grinded by mortar and pestle for about 1 hour to a fine consistency. About 0.2 gms of the material is magnetically stirred with ethanol-acetone (1:1) and Triton X-100 and refluxed for about an hour at temperatures above $100\text{ }^\circ\text{C}$. Solvent is

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Fig. 2 – From pencil to reduced graphene oxide

removed under vacuum from the dispersion and again heated in a hot air oven at 200 °C and is then centrifuged above 6000 rpm. The supernatant is a yellow-brown colored suspension which is separated and studied. This suspension turned black when heated to high temperature above 400 °C indicating the reduction of the graphene oxide under vacuum. Solid samples and film prepared by drop casting the material so obtained were dried and were characterized.

FTIR spectra were studied using Thermo Nicolet, Avatar 370. SEM micrographs were taken using Energy dispersive spectrometers JEOL Model JSM-6390LV. The sheet resistance was measured by coating the suspension on Si wafer (p-type, 4-6 ohms/sq) and then using automated Keithley 4 point probe system. The film thickness and optical property were measured using Spectrometric ellipsometer SE 800. The sheet thickness was measured using PARK systems Atomic force microscope.

3. RESULTS AND DISCUSSIONS

3.1 Structural characterisations

3.1.1 Fourier Transform Infra red spectroscopy

Total transmittance FTIR spectra as shown in Fig. 3 of the final sample were measured. The spectra shows the deformation of water molecules at 1630 cm^{-1} and alkoxy C-O stretching vibrational modes at $\sim 1043\text{ cm}^{-1}$. Further the bands at 1448 cm^{-1} corresponds to =CH in-plane vibrations and 780 cm^{-1} corresponding to -CH out-of-plane vibrations. A broad peak at 3400 cm^{-1} which can be assigned to the vibrations of the adsorbed water molecules or may also contain skeletal vibrations corresponding to unoxidised graphitic domains [4, 5, 6, 18]. The spectra does not

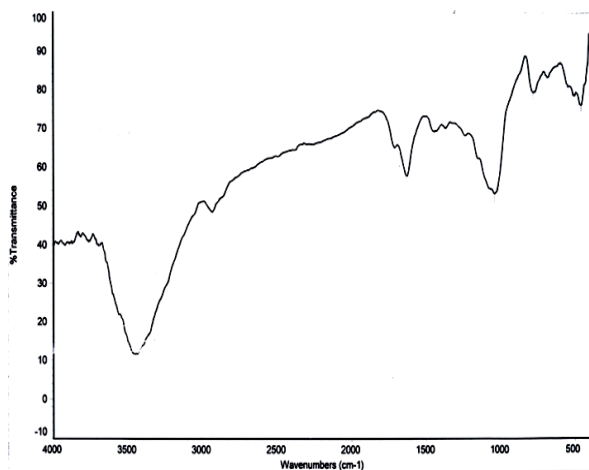


Fig. 3 – FTIR spectra of reduced Graphene oxide

contain any peaks associated with C-OH ($\sim 1340\text{ cm}^{-1}$), C = C ($\sim 1570\text{ cm}^{-1}$) and -COOH ($\sim 1710\text{-}1720\text{ cm}^{-1}$) groups. The C = C bonds missing indicates a strong oxidation to have taken place [19]. This spectrum is in contrast with the spectra for reduced graphene oxide or chemically derived Graphene.

3.1.2 Atomic force Microscopy

The GO dispersion were deposited on hydrophobic substrates such as Si wafer (p-type, 4-6 ohms/sq) by drop casting the suspension and then annealing at 480 °C. The average height of 2.5 nm were observed with atomic force microscopy (AFM) given by the Fig. 4. Color change from golden brown to deep brown and then to black is also noted.

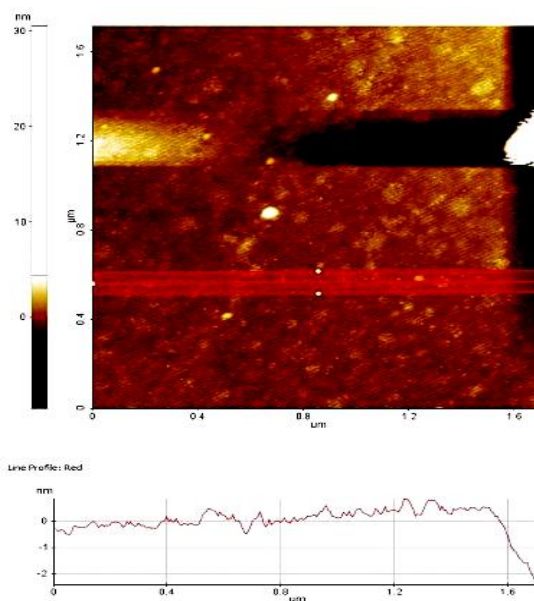


Fig. 4 – Reduced graphene oxide film and its height profile

3.1.3 Scanning electron Microscopy

Fig. 5 shows the SEM images of the material after thermally treating it after drop casting it on glass cover slips. It can be seen from the SEM images that many of the flakes are smaller in diameter ($< 1\text{ }\mu\text{m}$). Some flakes are found to be larger in size [16, 17].

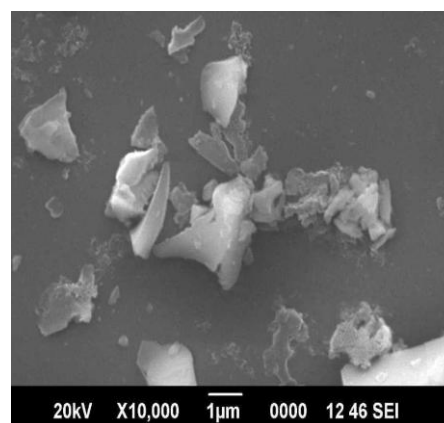


Fig. 5 – SEM micrograph of Reduced graphene oxide

3.2 Optical characterizations

3.2.1 Spectroscopic Ellipsometry

The reduced graphene oxide film was studied using a spectroscopic ellipsometer. The Ellipsometric data was recorded (Fig. 6) and the optical properties and thickness of the multilayer stack were fitted by modeling with a Cauchy function [20].

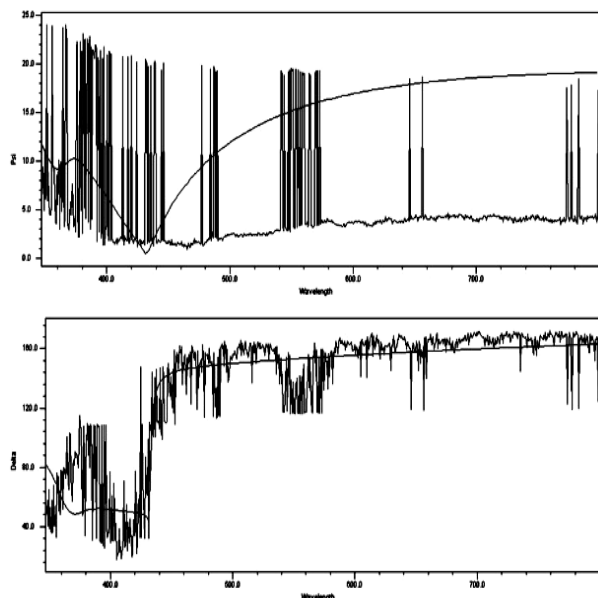


Fig. 6 – Spectroscopic Ellipsometric data of reduced graphene oxide after thermal treatment

3.3 Electrical characterisations

The sheet resistance (R_s) of a 50 nm thick graphene film prepared was measured using a four point probe

method and the average sheet resistance was calculated to be about $230 \Omega/\square$. Such low sheet resistance is subsequently due to the annealing and removal of oxygenated groups in Graphene Oxide films.

4. CONCLUSIONS

A method has been developed to disperse graphite from pencil lead in surfactant-polar solvent solutions. The results show that exfoliation and oxidation of graphite to graphene oxide can be done in a much simpler way and also with a much common precursor easily available to everyone. The films of reduced graphene oxide of good conductivity can be prepared by simple drop casting the suspension on a surface and further by thermal treatment. This film made from the material has been utilized as the counter electrode in dye sensitized solar cell using natural dyes and also for developing immunosensor. Further studies are intended in the defects study of the material.

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