

Tractable Synthesis of Graphene Oxide by Electrochemical Exfoliation Method

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Abstract. The aim of this work is electrochemical exfoliation of pyrolytic graphite for mass production of few-layer oxygen-functional graphene, commonly known as graphene oxide (GO). It is synthesized by intercalation of graphite sheets in the 1M concentration of nitric acid electrolyte by application of positive bias. The voltage is gradually increased with an increment of 0.5V upto 8V and an interval of 3 minutes. The X-ray diffraction peaks corresponding to GO ((001) plane) and graphene sheet ((002) plane) were observed at 2θ positions of 26.35° and 13.56° respectively. The morphology of as-synthesized GO is characterized by field emission scanning electron microscopy. The transparent layers of GO are observed in transmission electron microscopy. AFM topography revealed that the thickness of the few-layer GO nano sheets are in the range of 3-5nm only. The hexagonal ring structure of GO sheets was identified by selected area diffracted pattern. Through FTIR studies, the presence of functional groups of O-H and C-O has been identified. The synthesized material can be used as a base material for the future applications such as desalination of sea water, supercapacitors, sensors, solar cells, and coatings.

Keywords: Pyrolytic graphite, Electrochemical, Intercalation, exfoliation, Graphene oxide nano sheets, AFM, TEM.

1 Introduction

Graphene is one of the allotropes of carbon consisting of single layer thick carbon atoms in a hexagonal lattice. It has the association of both the thermal and electric conductivities at remarkably great [1]. Some of the remarkable characteristics of graphene like thermal conductivity makes astonishing values i.e. 4.9×10^3 to 5.35×10^3 W/mK [2], Young's modulus of $E = 1.0$ Tpa [3], intrinsic mobilities in the level of $200,000$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ at an electron density of $2 \times 10^{11} \text{cm}^{-2}$ [4], [5]. Graphene has very low electrical resistance with an optical transmittance of about 85%, so graphene sheets are being used as thin transparent conducting electrodes [6], [7]. Based on aforementioned characteristics graphene finds applications in display technology and medical science as well.

Graphene can be synthesized by different techniques, but at first, it was synthesized by the famous scotch tape method. High-quality samples of graphene were delivered by above mentioned technique for initial investigations. Later several methods have been developed with different approaches and technologies to synthesize few-layer graphene nano sheets. These methods can be categorized into two approaches 1) top-down and 2) bottom-up approaches. Based on the practices they have some advantages and disadvantages as well. In order to select a particular method, it is important to have quantity and quality of the graphene produced.

Gas-phase microwave production and chemical vapor deposition, epitaxial growth techniques and thermal annealing of silicon carbide were embraced for the bottom-up approach for the synthesis of graphene nano sheets (GNSs) [8]. Nanomechanical cleavage of graphite was one of the classical methods, it derives high-quality graphene but yields small films in order of a few tens of micrometers and hence is not a productive one [9]. High amounts of reduced graphene oxide (RGO) sheets have been produced by chemical reduction of exfoliated graphite oxide layers, but it resulted in damage of graphene lattice and defects. Due to defects in the lattice, the synthesized GNSs electrical properties were reduced. RGOs were further reduced to GNSs by dispersion technique [10], but productivity was low, and also films produced were not continuous. Hence they do not meet the requirement for many specialized applications.

In competition with these classical approaches electrochemical exfoliation is one such method, which can offer several advantages, like the ease of experiment, cost-effective, eco-friendly and can operate at ambient temperature. Electrochemical exfoliation technique is still under developing stage because of generation of defects in the final graphene lattice. In this method, pure graphite is used as a working electrode with protic ionic electrolytes at an appropriate DC bias. Due to applied potentials (may be positive/negative) to the graphite electrode, anionic/cationic intercalate from the electrolyte start intercalate the flaky graphite by breaking the weak van der Waals force between the two adjacent layers. Hence corresponding redox reactions primes to the evolution of gases at the electrode outer surfaces, leading to in-situ stress formation. This phenomenon could also create a surface blistering of the flaky graphite substrate [11]. Subsequently, single to few-layer thin sheets of flakes gets spread in the solution. Many findings with different anionic intercalants like polystyrene sulfonate ions, perchlorate ions, tetrafluoroborate ions, dodecyl sulfate ions, sulfate ions, nitrate ions,

hexafluorophosphate ions have been explored and reported. The rate of intercalation and quality of sheets finally produced depends on these anionic intercalates primarily. Cathodic intercalation has also played a major role in synthesizing of graphene, which is a conventional technique than cathodic intercalation. Due to intercalation process, some of the gases evolve around the electrode (Graphite). Mainly oxygen and carbon dioxide gases were evolved during anodic intercalation, whereas hydrogen gas was evolved in cathodic intercalation. It is believed that with an increase in the volume of gas evolved during the anodic process[12], exfoliation is expected to be higher. But there is a high chance of functional group (epoxy, carboxylic and hydroxyl) attachment onto graphene nano sheets which formed freshly. These could be minimized by proper optimization of parameters (applied potentials, electrolyte).

Following the above observations, in the present study, a fast and easy approach is used to the synthesize graphene oxide nano sheets in an electrolyte, from pyrolytic graphite sheets by applying suitable potentials by anionic intercalation. Also, the structure and topography of GO were characterized by XRD, FESEM, AFM, and TEM.

2 Experimental Works

Analytical grade HNO_3 had been used as an electrolyte, the double distilled water was used as a solvent for all the experiment. Super fine grain and high-quality pyrolytic graphite sheet of full dimension (10 x 15 x 3) mm (by Asbury Graphite Mills), IPG 15 was employed as both the counter and working electrodes in this experiment. A regulated DC power supply by APLAB, model number 7103, was engaged in applying DC potential between electrodes. All the experiments were done at atmospheric pressure and temperature only.

The electrodes were kept vertically and facing each other at a separation of 1 cm. This setup was held in a beaker with the help of a stand. Initially, the WE was connected as cathode and CE as an anode. After the proper connection, a DC bias of 10V for 30 sec was applied, this treatment will serve a dual purpose i.e. to clean the surface of the electrodes by removing the impurities and create the availability of surface and lattice pores of graphite electrode for effective intercalation.

After the cathodic pre-treatment, the electrodes were switched i.e., WE electrode was connected as anode and CE were connected as a cathode. Subsequent exfoliation was started by raising the DC bias from 0 to 8V with an increment of 0.5 V and an interval of 3 minutes. As a result of electrolysis, in an acidic electrolyte the hydrogen ions (H^+) and NO_3^- ions were redounded. The H^+ ions are materially adsorbed onto graphite lattice surface (Eq. 1) and successively released in the form of molecular hydrogen gas (Eq. 2).

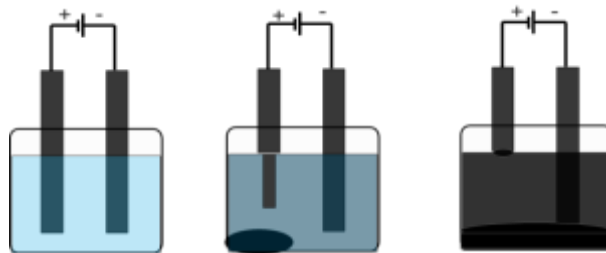
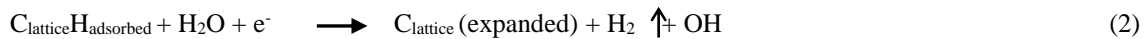


Fig. 1 Schematic diagram of electrochemical intercalation and exfoliation process.

The Oxidation reactions will occur at anode due to the intercalation process, which was carried out by NO_3^- ($d = 0.358\text{nm}$) intercalants. It will result in exfoliation of a mixed phase multilayer of graphite to few layers of graphene nano sheets. These exfoliated graphite layers were then dispersed in the electrolyte and also large particles were slowly deposited at the bottom of the beaker. After that, the electrolytic bath which consists of exfoliated graphite flakes was thoroughly washed with double distilled water to remove any acid contents, ionic forms and undissipated particles. The obtained mixed phase of graphene oxide nano sheets further fragmented by the ultrasonification process at a frequency of 20 KHz for 20 minutes[13]. The resulted colloidal was centrifuged at 4500 rpm for 30 minutes. Due to centrifuging the large particles were collected at bottom of the flask and GO were in colloidal form. The attained colloidal was dried in hot air oven at 100°C for 24 to 48 hours. The dried flakes were collected for additional characterizations.

The as-synthesized flakes were then subjected to characterization. The Ultima IV system using a monochromatic Cu K α radiation ($\lambda = 0.154$ nm) was used for the X-ray diffraction (XRD) spectrum, from a 5-60 $^\circ$ range of 2θ . FEI Nova NanoSEM 450 FESEM along with EDS and a JEM 1200 JEOL operated at 200kV TEM were used to investigate surface Morphology. The Shimadzu IR Prestige-21, FTIR instrument, was used to investigate the details about the various functional groups bonded to the exfoliated GO in the range of 4000-750 cm^{-1} . The SPM lab programmed Veeco diInnova MultiMode Scanning Probe Microscope with tapping (non-contact) mode was used for AFM topographical analysis of GO.

3 Results and Discussion

3.1 XRD Analysis

The XRD spectrum of as-synthesized GO nano sheets is shown in figure 2 (a). In the figure, the blue line corresponds to Graphene oxide nano sheets and black one corresponds to pristine graphite in powder form. The peak at $2\theta = 26.25^\circ$ refers to the (002) orientation with the lattice space (d) equal to 3.392 \AA which confirms a highly oriented layer structure in both the Graphite powder as well as in GO. The size of intercalant (NO_3^-) is very close to the interlayer spacing of graphene sheets in the graphite electrode. Therefore, these anions should effectively interstice the graphite lattice. The effective intercalation leads to the high expansion of the graphite lattice along with higher oxidation. It has been observed that the sharp basal plane peaks centered at 26.35° for PGr has been broadened and shifted to 25.99° . This shows the increase in interlayer spacing from 3.378 to 3.426 nm in the (002) planes. Due to intercalation, the lattice space of graphite is increased and broad peak could be observed at $2\theta=26.35^\circ$. The diffraction peak at $2\theta = 13.56^\circ$ refers to the (001) plane which confirms the oxidation of graphite. The broad peak at (001) plane is due to the existence of further functional groups within the lattice space, hence the corresponding lattice space (d) at the plane (001) is 6.53 \AA . The remaining diffraction peaks at 42.40° , 44.37° , and 54.44° (2θ values) correspond to (100), (101), and (004) reflections respectively as shown in figure 2 (a). The abovesaid planes are common in both XRD spectrum of the graphite powder and GO,[14] so it may be confirmed that some un-exfoliated graphite particles were present in as-synthesized samples.

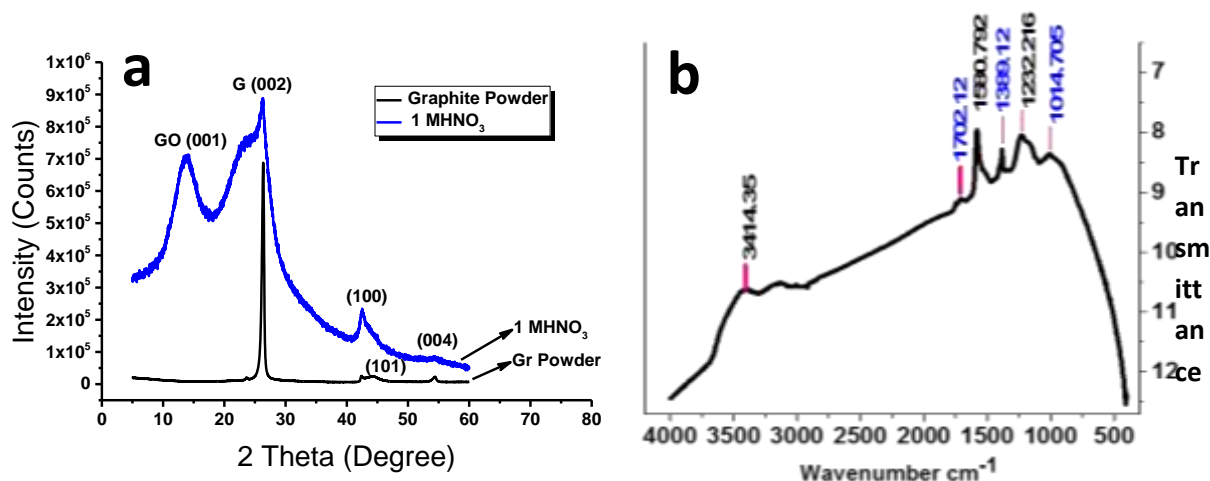


Fig. 2 a) XRD spectrum of Graphite powder and as synthesized GO. b) FTIR transmittance spectrum of as-synthesized GO.

3.2 FTIR Spectral Analysis

The electrochemically exfoliated GO nano sheets are expected to be endowed with several oxygen functional groups with the carbon atoms that causing from the protic solvent media with applied potential. Furthermore, the carbon structure and different functional groups attached to the GO nano sheets have been analyzed by fourier transform infrared spectroscopy (FTIR). The extent of these functional groups has been studied by FTIR spectrum of GO nano sheets dispersed in KBr. Figure 2(b), shows the FTIR spectra of GO nano sheets, which illustrates the infrared transmittance peak at 1015 cm^{-1} corresponding to carbonyl (C=O), and the peak at 1232.21 cm^{-1} corresponding to epoxy group C–O–C. The peak at 1389.12 cm^{-1} is corresponding to COO–H/CO–H group. The peak at 1580.79 cm^{-1} was recognized as rising from C–C vibrations of the graphitic province. A peak at 1702.12 cm^{-1} is observed as carboxylic acid group C=O. The pretty broad peak at 3414 cm^{-1} may be due to the adsorbed water on the surface of the GO nano sheets. Followed by the above observations it is confirmed that the quality of

3.3 Morphological Studies

To acquire the morphological and topographical evidence of the GO nano sheets the FESEM, TEM and AFM investigations were carried out. The FESEM observations revealed the structure of graphite and confirmed the stratified nature of the planner graphitic crystal planes as shown in figure 3a (inset). A number of layers stacked

as bundles in a lateral direction with small pores in between the grains of graphitic layers. These pores act as easy intercalate sites for ions/ intercalants for uniform intercalation throughout the electrodes. The structure of GO nano sheets, that a few layers of sheets stacked together with curl edges are observed and are shown in figure 3 (a,b). Same as its parent material graphite, but here the layers look like tot fragments. Also found that unexfoliated layers of graphite of size $1\ \mu\text{m}$ to $3\ \mu\text{m}$ are stacked with each other. TEM images of GO, which are deposited on the copper grid shown in figure 3(c). The TEM image reveals that as prepared GO transparent sheets have a lateral size of $0.5\ \mu\text{m}$ to $1.5\ \mu\text{m}$. The small unexfoliated graphite particles are also combined with the transparent GO nano sheets. The SAED pattern of GO is confirming the XRD data. The ring-like structure is analyzed and found that the planes (001), (100) and (002), which are already discussed in the XRD spectrum shown in figure 3 (d). The crystallographic structure of the as-synthesized GO could be confirmed from the above results and discussions.

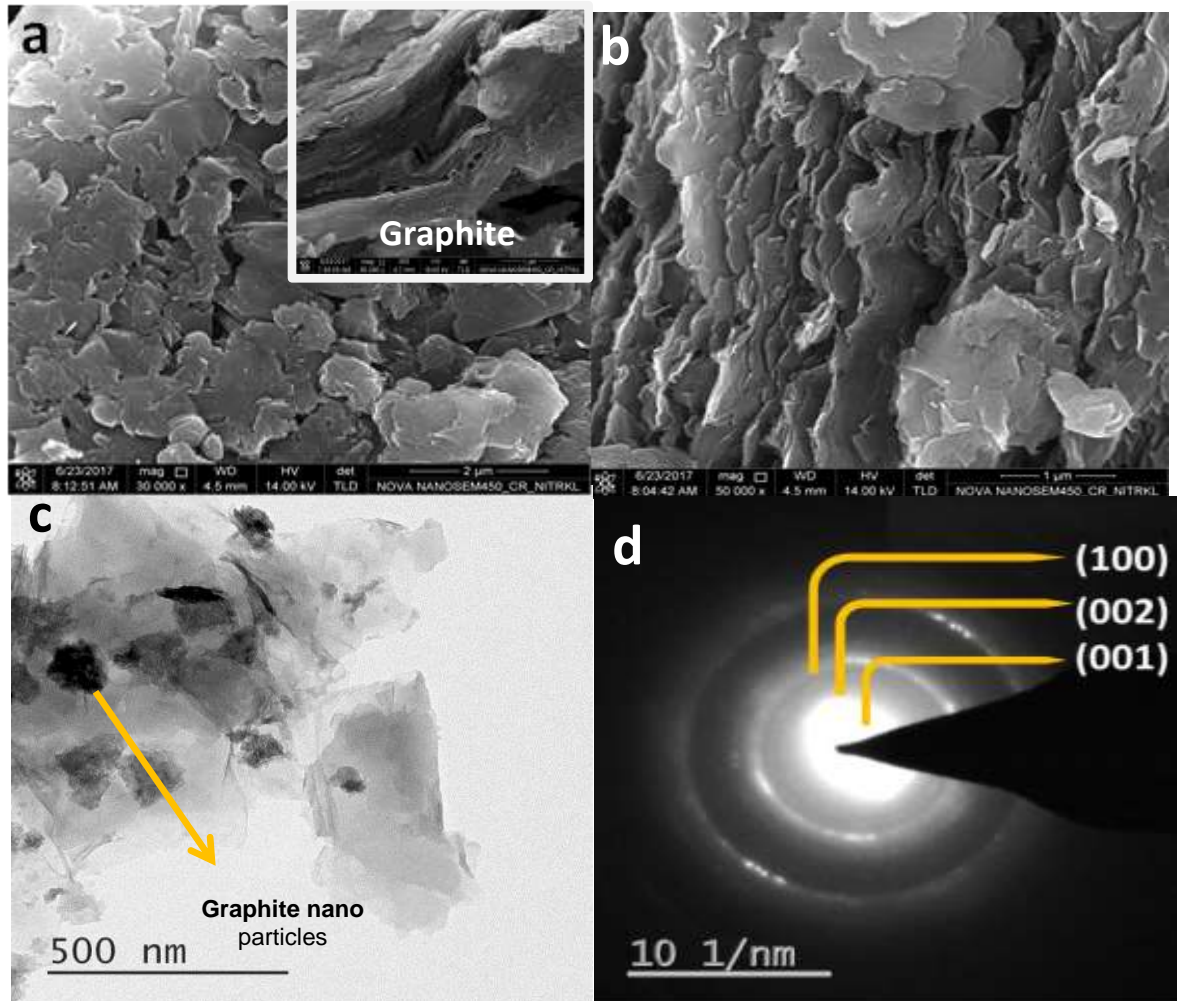


Fig. 3 **a,b)** FESEM images of GO. (inset) Graphite powder. **c)** TEM image of GO. **d)** SAED Pattern of GO.

The exfoliation of graphite to Graphene takes place in the vicinity of the anode along with the rapid evolution of H_2 gas at an anode and oxygen at the cathode. During intercalation, the exfoliated graphene oxidizes to graphene oxide due to the presence of dissolved oxygen. The presence of single to few layers of graphene oxide is confirmed by the TEM image analysis. Along with single layer (SL) and few-layer GO can be observed, also the presence of some exfoliated graphite nanoparticles as a by-product. The formation of graphite nanoparticles ($\approx 15\ \text{nm}$) might be due to the defects induced during the exfoliation process resulting in the formation of nano dimension graphite particles. In most of our experiments, we observed the presence of graphite nanoparticles. Hence it is conclusive that the formation of SLGO/FLGO and graphite nanoparticles takes place simultaneously during exfoliation.

3.4 Atomic Force Microscopy Observations of GO on Mica Substrate

Broad AFM investigations are done to characterize the GO nano sheets, which are deposited onto mica surface. The AFM sample preparation is made by mixing the GO powder with 10 ml of double distilled water at the rate of 1 mg/mL. The solution is sonicated for 45 minutes at room temperature by using bath sonicator. As-synthesized and well dispersed GO nano sheets are dropcast on to an atomically flat freshly cleaved mica sheet so that evenly distributed GO nano sheets are obtained and dried in ambient conditions [14]. The AFM observations are performed in tapping (non-contact) mode of action using quadrilateral silicon cantilevers with a spring constant (k) of $\sim 40 \text{ Nm}^{-1}$ and general resonance frequencies between 300 and 370 kHz. The typical imaging is aided by tip-sample interaction, recording topography (height) and phase images simultaneously.

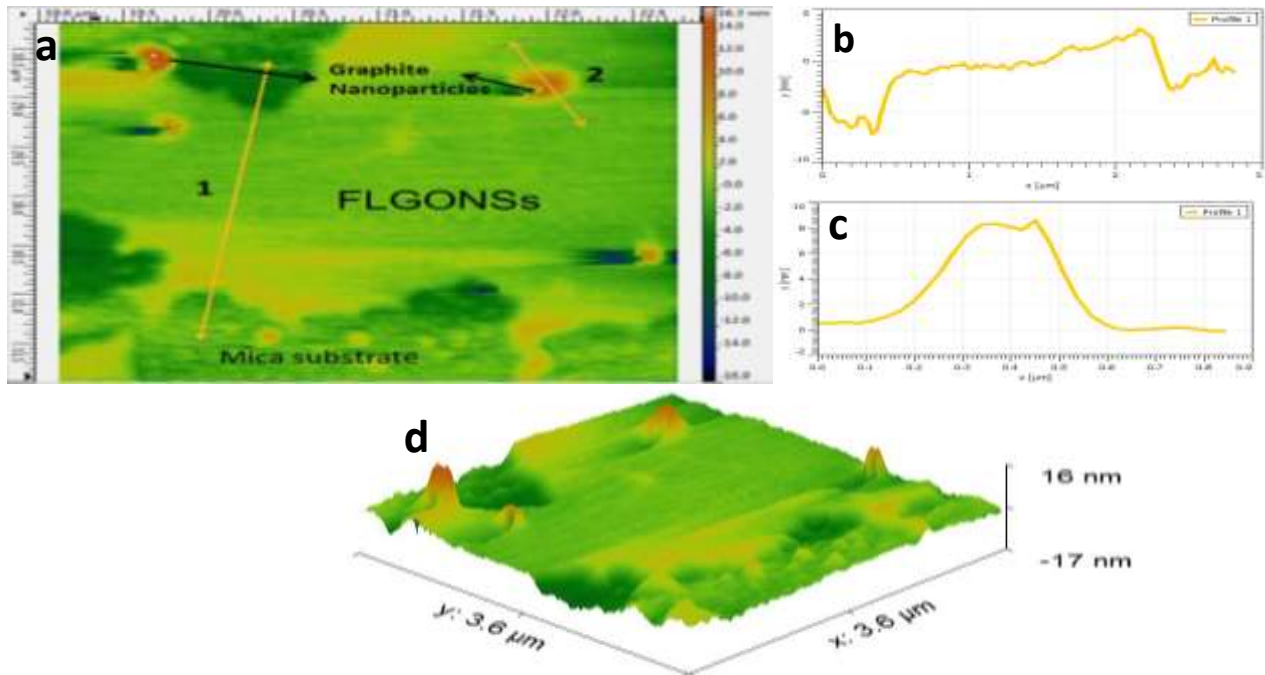


Fig. 4 a) AFM topography of well dispersed GO on the surface of freshly cleaved mica. b) Height profiles respected to line profile 1. c) Height profile respected to line profile 2. d) Three-dimensional topography of GO and Graphite nanoparticles.

The AFM topography shows that a 1 to $3 \mu\text{m}$ dimensioned GO nano sheet is detected and is shown in figure 4 (a). The lateral thickness of as-synthesized GO nano sheets is observed in the range of 2 to 5 nm as shown in the height images of figure 4 (b,c). Two height profiles were observed at two different locations, first height profile across the GO it showing flat few-layers of nano sheets of thickness in the range of 3 nm to 5 nm only (figure 4b). The second height profile showing the thickness of the graphite nano particles of the size 10 nm (figure 4c) i.e. the same characterization also observed in the TEM characterization as well. The AFM topography has also revealed an evidence for the presence of unexfoliated Graphite nano particles. The three-dimensional histogram is also shown in figure 4d, it shows the size of graphite particles are in the range of 10 nm to 16 nm.

4 Conclusions

An efficient, green and scalable method for synthesis of GO nanosheets by electrochemical intercalation and exfoliation of pyrolytic graphite sheets has been discussed in this paper. The as-synthesized GO has low quality due to impurities, like graphite nano particles.

1. The exfoliation of graphite in HNO_3 electrolyte has found very rapid, due to the small size of intercalates (NO_3^-), so they can easily perforate into the lattice of the graphite and increases the rate of exfoliation.
2. The FESEM observations revealed that few layers of graphene oxide nanosheets in the range of 1- 3 μm .
3. FTIR studies confirm that the existence of the functional groups, but they could be removed by using a simple chemical reduction process.
4. A 1- 2 transparent layers Graphene oxide can be observed in the TEM analysis.
5. The TEM observations and AFM observations are showing that the existence of both the GO and graphite nano particles.

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