Synthesis of Graphene Nano Sheets by the Rapid Reduction of Electrochemically Exfoliated Graphene Oxide Induced by Microwaves

Arshad Hussain Wazir* and Imran Waseem Kundi
Carbon Materials Laboratory, Department of Chemistry, University of Science and Technology,
Bannu, Khyber Pukhtunkhwa, Pakistan.
arshadwaziri@gmail.com*

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Abstract: Graphene has been produced by various methods and techniques from various precursors. Here we demonstrate a simple and fast method of electrochemical exfoliation of graphite to graphene oxide (GO) and then its rapid reduction to graphene nano-sheets (GNs) with the help of microwaves. The samples prepared by this method were characterized with different techniques such as Ultra Violet-Visible spectrophotometry (UV-Vis), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and Atomic force microscopy (AFM) to confirm their characteristic properties. The UV spectra of GO and GNs showed a sharp and intensive peaks centered at 266.5 nm and 230 nm. The FTIR spectra confirmed the oxidation of graphite and deoxygenation of the GO. Similarly, XRD analysis also confirmed the comparative layer structures of GO and GNS. The typical AFM morphology of GNs drop-casted on glass substrate ascertained the presence of few layers of graphene. This electrochemical exfoliation method and microwaves reduction offers a low-cost and efficient route to produce high quality graphene with high yield.

Keywords: Electrochemical exfoliation, Microwave reduction, Graphene oxide, Graphene, Atomic force microscopy

Introduction

Graphene is a flat monolayer of carbon atoms arranged into a two-dimensional (2D) honeycomb lattice [1]. Recently, graphene emerged as wonder material of the 21st century, and received world-wide attention due to its exciting properties such as high Young's modulus (~1.0TPa) [2], mechanical strength, a large theoretical specific surface area (2630 m^2g^{-1}), high inherent mobility (200,000 $cm^2v^{-1}s^{-1}$) [3, 4], high thermal conductivity (~5000 $Wm^{-1}K^{-1}$) [5] and is an optically transparent material which absorbs only 2.3% of visible light and optical transmittance of (~97.7) [6]. A wide potential application of graphene in various specialized areas have been utilized such as graphene based electronics [7], composite materials [8], molecular gas sensors and energy storage and conversion [9, 10], biosensors [11], fuel cells [12, 13], solar cells [14, 15], transistors [16] and etc.

The demand for newer materials has been increased in modern applied technologies such as electronics, composite materials, molecular gas sensors and energy storage/conversions. Wherein, carbon-based nanomaterial exhibit unique chemical, electrical, magnetic and physical properties as compared to conventional bulk carbon materials. In order to realize and produce better-quality materials, devices and systems, the conventional bulk materials are converted into nano scale materials. So far, different techniques have been performed to synthesize graphene sheets such as micromechanical exfoliation of graphite [17], chemical vapor deposition (CVD) [18], solvothermal synthesis [19], epitaxial growth on electrically insulating surface [20], the reduction of graphene oxide (GO) [21], unzipping of carbon nanotubes [22], and microwave synthesis [23]. Among the various methods of graphene synthesis, electro chemical method is one of the simple, fast and high-yielding methods [24, 25]. By applying the same method, Wang et al. prepared a stable graphene/polymer suspension by carrying out the electrolytic exfoliation of graphite in poly (sodium-4-styrenesulfonate) as an effective electrolyte [26]. Dryfe and co-workers produced few layer graphene through intercalation of tetra alkyl ammonium cations into pristine graphite during electrochemical exfoliation [27]. Alanyalıoglu et al. also reported an electrochemical route to produce a stable colloidal graphene/sodium dodecyl sulfate (SDS) suspension from the electrochemical intercalation of SDS as surfactant into graphite followed by electrochemical exfoliation of a SDS-intercalated graphite electrode [28]. Similarly, Salavagione and co-workers studied the synthesis of high-quality few layer graphene by electrochemical intercalation and microwave-assisted expansion of graphite [29].

In the present study we demonstrate a novel two-step approach for production of high-quality

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[*] **To whom all correspondence should be addressed.**

graphene nano sheets by electrochemical exfoliation of graphite and its successive microwave irradiation reduction.

Experimental

For electrochemical exfoliation purposes, two graphite rods (55mm in length and 7 mm in diameter) collected from wasted dry battery cells, were used as electrodes and ionic solution of H_2SO_4 in deionized water (DI) as an electrolyte. The ionic solution used was prepared by dissolving 2.4g (98%) H_2SO_4 in 100ml deionized (DI) water [25]. The graphite rods were adhered to a zinc wire as a second electrode in the electrolytic cell filled with ionic solution and both were placed parallel at a distance of 2 cm from each other as shown in Fig. 1a. The process of electrochemical exfoliation was carried out by applying DC bias of +10 V to graphite electrode. The exfoliated graphene oxide sheets as filtrate were collected by Wattman filter paper (Grade 42) which were washed with DI water and then with ethanol and finally were dried in an oven at temperature of 105°C. The obtained graphene oxide powder was then reduced into graphene by microwave (*Dawlance*, Model EC-20, Korea) treatment in ambient conditions at various powers of Watts (W) for different time intervals. The obtained graphene powder was further dispersed in DI water and sonicated for one hour at room temperature. Finally, the system was centrifuged at 2500 rpm for five minutes to remove unwanted large particles. Thus the supernatant found after centrifugation was used to make thin film on glass substrate. The glass substrates were first cleaned with Piranha solution to remove undesired impurities for making the surfaces hydrophilic. The graphene solution (0.01mg/ml in DI water) was drop casted on the cleaned substrate where the thin graphene film was then self-aggregated at the substrate surface. For characterization purposes, the substrate samples were heated on a hot plate at 120°C for 30 min to evaporate the residual DI water.

The characteristic properties of the samples obtained were characterized by using the UV-Visible absorbance spectra (UV-1800 UV-Visible spectrophotometer, Japan). The FTIR spectra were obtained using (IR Prestige-21, Japan) spectrometer. The XRD measurements were carried out using JEOL X-ray diffractometer (JDX-3532, Japan) equipped with a copper target. The AFM images were performed in a NanoWizard II JPK AFM (JPK Instruments AG, Berlin, Germany).

Results and discussion

The electrochemical exfoliation of graphite was performed to obtain graphene oxide (GO) by submerging two graphite rods parallel at a distance of 2 ± 0.1 cm from each other in an electrolytic cell filled with an electrolyte solution, as shown schematically in Fig. 1(a). Wherein, during the electrochemical exfoliation, the anodic electrode was corroded as black precipitate and gradually appeared in the Electrolytic cell as dispersion that can be observed in Fig. 1(b).

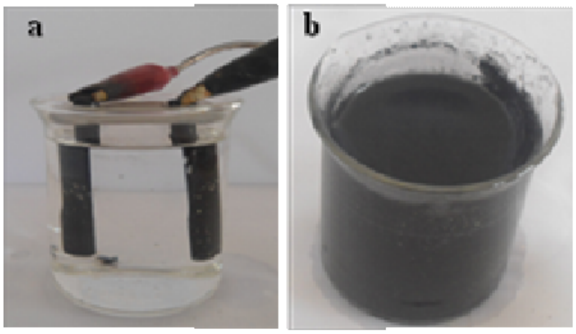

Fig. 1: (a) Experimental Set up and (b) exfoliated graphite.

The dispersed precipitate was collected from electrolytic cell and then filtered. The collected filtrate was then washed with DI water until the pH of the filtrate became neutral and finally dried at 105°C in an oven for two hrs to get graphene oxide powder as shown in Fig. 2. In the course of electrochemical exfoliation of graphite using H_2SO_4 solution, the process was observed to be time dependent where the amount of exfoliated graphite was found to be increased with the increase in time duration of exfoliation.

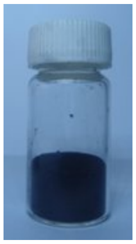

Fig. 2: GO prepared during electrochemical exfoliation of graphite.

The Graphene oxide powders prepared by electrochemical exfoliation were treated in a microwave oven at optimum conditions of given power (800Ws) for time period of 30 seconds. Upon microwave reduction, a little volume expansion of the GO powders was observed, accompanied by lighting and violent fuming. A glass bottle containing the reduced graphene oxide as black and fluffy powders obtained by this method can be seen in Fig. 3, as described earlier in the literature [30-33]. Wherein, the mass loss after the microwave process was found to be 30%.

Fig. 3: Microwave assisted reduced GO.

The UV-Vis spectra of graphene oxide and graphene nano sheets are shown in Fig. 4. Where the absorption peaks in spectra (a) at 230 nm and a small shoulder at 300nm correspond to the л-л* transition of aromatic C–C bonds and the n-л* transition of C=O bonds, respectively, indicating that the graphite get oxidized during the electrochemical exfoliation [34, 35]. While the absorption peak in spectra (b) at 266.5 nm confirms the reduction of graphene oxide due to the restoration of electronic conjugation within the graphene nano sheets that red shifted from 230 nm to 266.5 nm [36, 37] during the microwave irradiation.

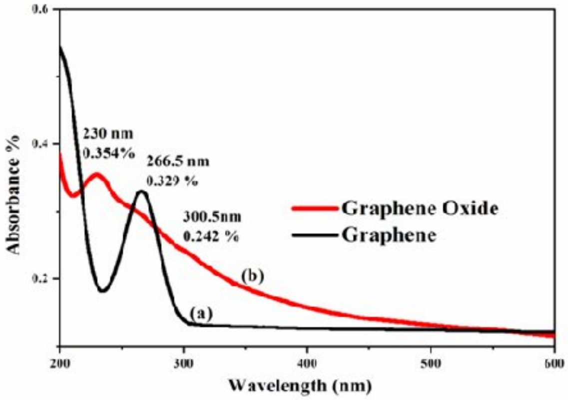

Fig. 4: UV-Vis absorption spectra of graphene oxide (0.5 mg/ml) and reduced graphene (0.1mg/ml) in DI Water.

The FTIR spectra of graphite, graphene oxide and reduced graphene nanosheets are shown in Fig. 5. In the graphite sample no significant peak was found while in the FTIR sample of graphene oxide, the presence of different type of oxygen functionalities were observed at various wavelengths such as at 3425.5 cm^{-1} (O-H stretching vibrations), a broad peak of hydrophilicity at 2885 cm^{-1} to 3715 cm^{-1} as contributed by the O-H stretch of H_2O molecules [37], at 1760 cm^{-1} (stretching vibrations from C=O) and occurrence of aromatic stretching vibrations at 1643.3 cm^{-1}confirms the existence of C=C bond that still remained before and after the oxidation process. Similarly, the peaks at 1388.7 cm^{-1} (C-OH stretching vibrations), and at 1095.5 cm^{-1} (C-O stretching vibrations) also confirmed the presence of oxide functional groups were created during the oxidation process [38]. Most of the peaks in the FTIR spectra of reduced graphene showed the decrease in intensities at 3425.5 cm^{-1} (O-H stretching vibrations) and at 1760 cm^{-1} (C=O stretching vibrations) due to deoxygenation which is further confirmed with the help of XRD analysis.

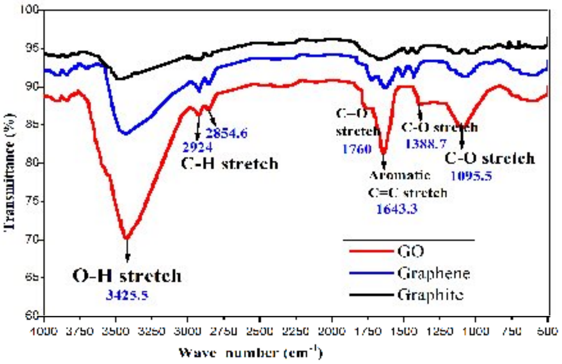

Fig. 5: The FT-IR spectra of Graphite, GO and Graphene.

The XRD pattern of graphite, GO and GNs are shown in Fig. 6. The peaks indexed for (100) at 42.80°, (004) at 54.9° signify the crystalline structure of graphite. The distinguishable (002) peak of graphite at 26.5° has inter planar distance (d_{002}) of 0.334 nm that is showing a highly ordered carbon structure of graphite. Similarly, the XRD pattern of graphene oxide shows the shifting of 002 peak to lower angle at $2\theta=9.96^\circ$, representing an increase in d-spacing from 0.34 nm to 0.87 nm. This increase in the interlayer distance between consecutive carbon basal planes is attributed to the intercalation of oxygen functional groups and water molecules into carbon layer structure [30, 39]. The characteristic peak of graphite of 002 at 26.5 ° doesn't vanish but reduced considerably, showing that the graphite is not completely oxidized during electrochemical exfoliation but retains partially its graphitic structure.

The XRD pattern of GNs sample shows a broad peak at 2θ=26.50°, corresponding to an interlayer distance of 0.339 nm, which may be attributed to the graphene layers due to high degree of exfoliation that achieved during the microwave irradiation reduction of GO [40]. It is considered that the obtained product consists of few-layer graphene, having a new lattice structure and is absolutely different from the graphite and graphene oxide.

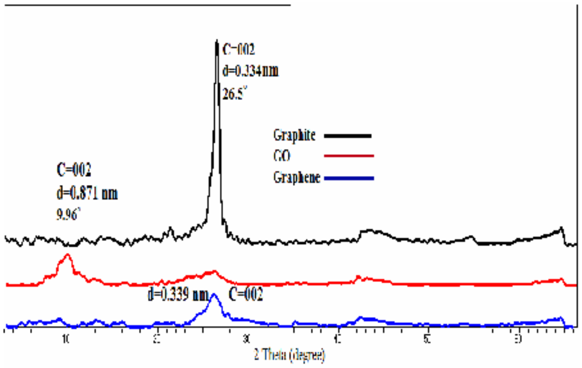

Fig. 6: The X-Ray Diffraction pattern of Graphite, GO and Graphene.

AFM image of graphene nanosheets drop-casted on glass substrate by Intermittent Contact (air) mode is shown in Fig. 7(a). The average thickness of graphene film was found to be 1.354 nm with an intersheet distance of 0.35 nm which concludes that the reduced graphene is completely exfoliated into individual sheets [41]. The cross section, designated by line-1 in Fig. 7(a) selected for layer analysis of graphene thin film is graphically represented in Fig. 7(b). Where in, the cross section along the indicated line reveals a single layer graphene with a height of 0.338 nm followed by a bi-layer graphene with a height of 0.71 nm and tri-layer grapheme with a height of 1.16 nm [42]. The increased height in many of the nanosheets can be observed from the image that also appears as a rough surface and has been reported earlier as solvent trapped between the graphene layer and the substrate [43]. The 3D surface morphology of the image is also shown in Fig. 7(c). The histogram as shown in Fig. 7(d) confirms the presence of thinner layers. Thus the statistical analysis confirmed the graphene nanosheets with its lateral size of about 0.1 μm and with its thickness of about 1.354 nm.

As it is known that GO by itself has poor microwave absorption capacity while the unoxidized graphitic portions present in GO act as the microwave absorbents that initiate the microwave-induced deoxygenation process as mentioned earlier in the literature [44].

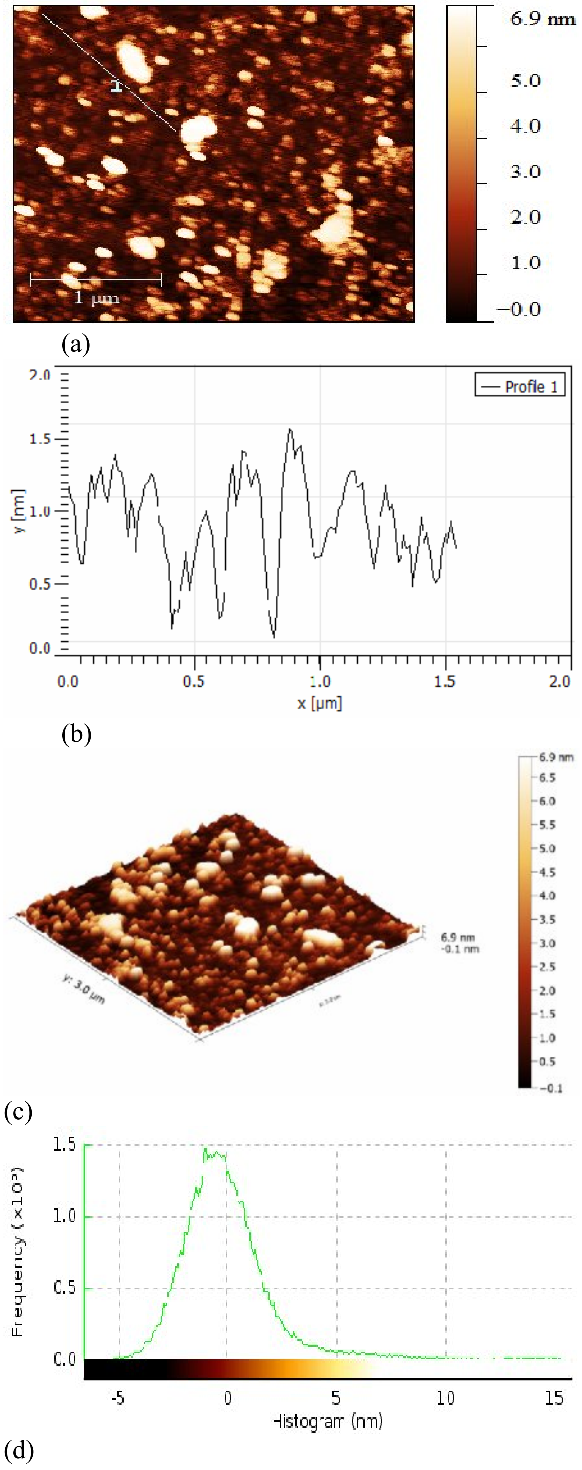

Fig. 7: (a) AFM image of graphene film drop-casted on glass substrate, (b) Graphical presentation of cross-sectional analysis of graphene, (c) Three dimensional image of graphene nano-sheets drop-casted on a glass

Conclusions

In this work, a simple method is developed to prepare graphene by microwave assistant rapid reduction of electrochemically exfoliated GO. The reduction of GO can be successfully achieved in time scale of minutes at a given power of 800 W. The yield of graphene prepared by this method is very high and production in large scale is easily attained. Thus, the present work provides an efficient approach to obtain high quality and cost-effective production of graphene powder which will really pave the way to their future applications in fabricating composite materials, flexible electronics and etc.

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