

# Graphene-Based Membranes Fabricated Using High Purity Natural Vein Graphite (NVG)

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*Abstract—The multilayer graphene oxide membranes (MGOMs) are fabricated using graphite oxide synthesized using a rare form of high purity natural vein graphite (NVG) and are characterized using FE-SEM, AFM and C 1s and O 1s core level photoemission (ESCA) for their properties. It is observed that NVG based MGOM can be thermally reduced energy efficiently to obtain graphene-like membranes.*

**Keywords**—graphene oxide, vein graphite, graphene based membranes, ESCA

## I. Introduction

The multilayer graphene oxide membrane (MGOM) is a material that can microscopically be visualized as having number of single layers of graphene oxide (GO) cradled through a network of hydrogen bonding interceded by water molecules. It comprises discontinuous and distorted regions of GOs resulting in voids within the membrane having dimensions varying from nano to submicron scale [1]. There are number of possible applications for MGOM in many different fields. In particular, the expanded interlayer distance of MGOM is useful for fabricating energy storage devices, such as super-capacitors and batteries as the electrolyte ions can easily intercalate between the expanded layers [2]. Recently, photoflash and laser-reduced free-standing GO membrane has been found to be an excellent anode material to generate high power lithium ion batteries [3]. Further MGOM can easily be fabricated in a relatively simple and cost-effective manner, which is scalable.

Although the structural and electronic properties of single layer GO have been investigated well (e.g., Ref.4), such properties for the MGOM are not well known and the information available in the literature is limited [5, 6]. Given the higher potential use of MGOM in wide spectrum of applications, it is important that properties of such membranes are investigated in detail as such information can be used to better understand their functions. This necessity becomes imperative when MGOMs are produced using source materials that are not ubiquitous and inherits distinct properties (e.g. such as natural vein graphite (NVG)) [7]. We have demonstrated

earlier that NVG is an ideal source material to produce single walled and multi walled carbon nanotubes (SWCNT and MWCNTs) [8, 9]. In this work, we investigate the aptness of NVG to produce MGOM and single layer graphene oxide (SLGO), which is a precursor to the next generation wonder material “graphene”, and their properties. We employ scanning probe microscopy (FE-SEM and AFM) and photoemission spectroscopy (ESCA Al K $\alpha$  radiation @ 1486.6 eV) to probe topographical and electronic properties of NVG based SLGO, MGOM and thermally reduced form of MGOM in UHV.

## II. Material and Methodology

Graphite oxide was synthesized using improved Hummers (IM) method, as reported in the literature [10] using natural vein graphite (NVG). The purity of as-supplied precursor graphite, obtained from the international vendor [11] and estimated by ash content (ASTM D 6349-09) using Atomic Absorption Spectroscopy (AAS), was better than 99.95%. The graphite oxide slurry resulting in from the chemical oxidation of NVG was thoroughly washed with laboratory grade distilled water until the pH of the solution became neutral. A small aliquot of pH neutral graphite oxide slurry was then diluted sufficiently with distilled water (~1mg/1ml) and was exposed to ultrasound (150 W, Grant, UK) for 30 min. Following the exposure to ultrasound, the graphite oxide dispersion was kept under stirring (at 120 rpm) at room temperature for at least 24 hours. This procedure resulted in single layers of GO having average lateral dimension ~ 2 microns and thickness ~ 1 nm as was observed in atomic force microscopy (NC-AFM, Park Systems XE 100, Korea).

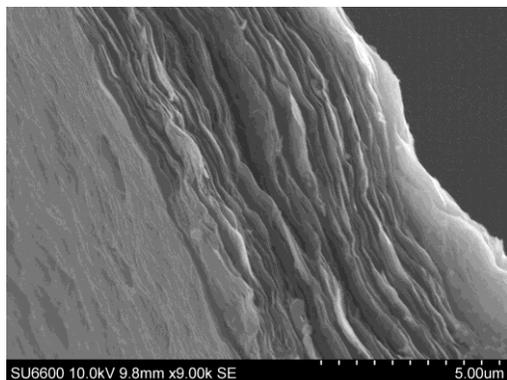
The MGOM was fabricated using pH neutral graphite oxide slurry by a self-assembling process. After fabrication, the samples were stored in an air-tight transparent sample container. Field emission scanning electron microscopy (Hitachi, SU6600 FE-SEM) was used to examine the cross section of the membrane. Room temperature C 1s, O 1s and survey spectra were recorded at Materials Science beamline (MSB), ELETTRA Synchrotron, Trieste. Italy. The MGOM

was then thermally annealed in the range of 450 K - 600 K in UHV to investigate the reduction process. Although it is true that the high temperature (>1300K) thermal reduction in UHV is effective in producing significantly high C/O ratio in GO [12], we, however, avoided the high temperature option because it is unlikely to be compatible with any fabrication techniques used for most applications. Further high temperature annealing is not an energy efficient process, hence not economically viable at large scale. All spectra recorded using Al K $\alpha$  were aligned to the binding energy (BE) of the adventitious C at 284.5 eV. The background of all core level spectra was subtracted using 4<sup>th</sup> order polynomial function and the core level spectra were fitted using a simple Voigt function. All spectra were acquired using a SPECS Phoibos 150 hemispherical electron energy analyzer with a 1D-DLD detector. Thermal annealing of MGOM was carried out by gradual heating the MGOM sample in UHV.

### III. Results and Tables

#### SEM and AFM of multilayer GO membrane

Fig.1 shows FE-SEM image acquired from the cross section of MGOM. The sample for SEM was prepared by sectioning a small piece from MGOM and holding it vertically upright in the SEM sample holder, which allowed the electron beam to be incident laterally across the sectioned edge. Fig. 1 clearly shows that the GO membrane is composed of layers and their orientation.



**Fig.1** shows FE-SEM image recorded from the cross section of the multilayer GO membrane.

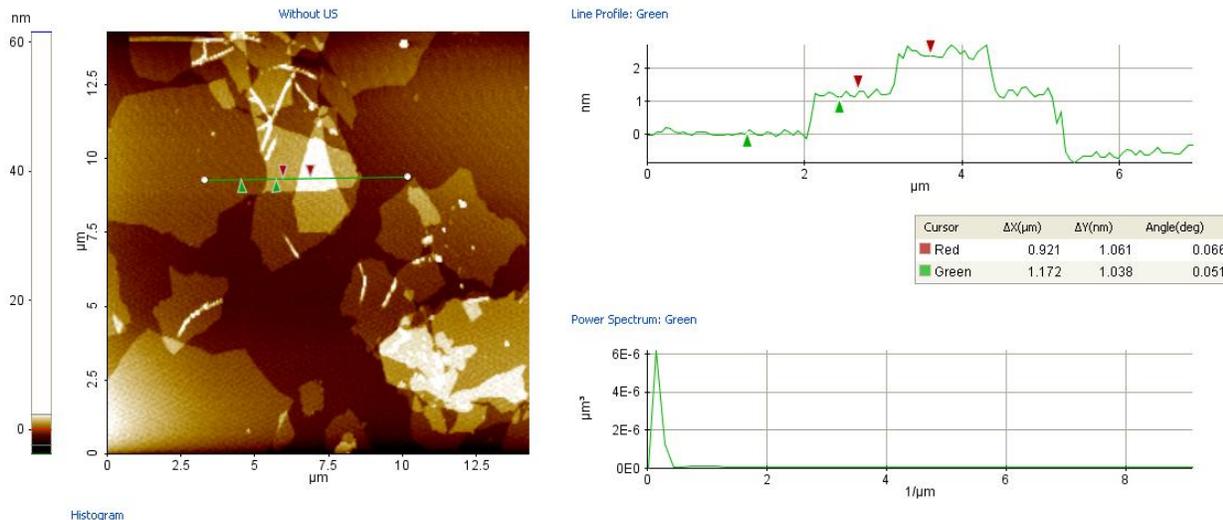
The FE-SEM image was captured in secondary electron imaging (SEI) mode and the average thickness of the GO membrane is about 7.0  $\mu\text{m}$ . The discontinuous and crimped-like nature of GO layers are clearly visible in the FE-SEM image which suggest that such feature are fundamental to MGOMs despite their preparation method and other physical properties such as thickness [1]. Fig.2 displays AFM image acquired from single layer GO in NC-AFM mode. The typical height for a single GO layer ( $\sim 1$  nm) is observed in the image which clearly illustrates that the NVG based graphite oxide undergoes

a complete exfoliation. The statistics across the line profile chosen from an arbitrary location in Fig 1 (b) are also shown in the figure.

#### C and O core level spectra of multilayer GO membrane

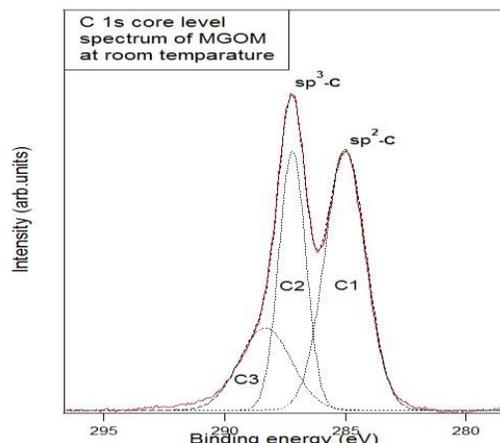
Shown in Fig.3 is the C 1s core level spectrum recorded from MGOM using an Al K $\alpha$  source with photon energy 1486.6 eV. The spectrum was recorded at RT and with X-rays striking the sample at grazing (30 degrees off to the sample normal) angle in a fixed geometry. The spectrum exhibits well-defined double peak formation with a pronounced peak present at the higher binding energy (BE) side of the main peak, which is a clear signature of a higher degree of oxidation in GO. The best fit of the spectrum is obtained using three components (C1, C2 and C3), with the main component, C1, lying at a BE of 285 eV, the second component C2 at a BE of 287.2 eV (i.e., 2.2 eV higher to the main peak) and the third component C3 at a BE of 288.4 eV (i.e., 3.3 eV higher to the main peak), confirming the presence of different types (i.e., chemical environment) of carbons in the MGOM. Consequently, the component C1 lying at a BE of 285.0 eV originates from the sp<sup>2</sup> bonded carbon atoms, i.e., -C=C- [13]. The component C2 at a BE of 287.2 eV originates from hydroxyls and epoxy groups with sp<sup>3</sup> hybridized orbitals [13, 14, 15-18]. The higher BE peak C3 located at 288.4 eV originates from carbonyls (-C=O-) in either ketones or carboxylic groups [16-18]. The broad full width at half maximum (*fwhm*) of the component C1 indicates it has contributions not only from sp<sup>2</sup> type carbons but also from other types of carbons such as C-H or C vacancies [13,14]. The BE values for individual peaks observed here are similar to those reported in a recent investigation on MGOM by Kim *et.al* [14].

Fig 4 shows the O 1s core level spectrum recorded from MGOM. The spectrum was recorded in the same geometry used for collecting the C 1s spectrum. The best fit for the spectrum is found with three components (O1, O2 and O3) lying at BEs of 530.9.0 eV, 533.0 eV and 535.1 eV, respectively. The component at a BE of 533.0 eV, i.e., O2, dominates the spectrum with trivial contributions from other two. By reference to the C 1s peak assignments, we assign the component at a BE of 533.0 eV to contributions from hydroxyl (-OH) and epoxy (-O-) groups. The kinetic energies of the O1s photoelectrons are lower than those of the C 1s. Therefore the O 1s sampling depth is smaller than the C 1s and the O 1s spectrum is somewhat surface specific [19] than the C 1s, hence the observed enhancement of the peak at a BE of 533.0 eV. Similar to the C 1s core level data, our O 1s data are also in good agreement with the work done by Kim *et. al* [14].

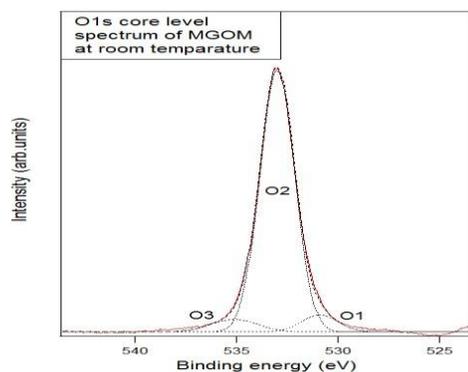


**Fig. 2** displays the plan view of an image acquired from a single layer of GO by AFM in noncontact mode (NC-AFM). The typical height for a single layer of GO (~ 1 nm,  $\Delta y$  in the line profile statistics) is observed.

In such circumstances, the X-rays probe surface sensitive molecular signatures attached to the basal plane of GO.

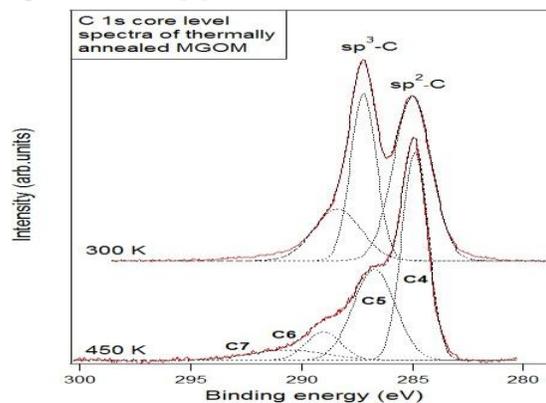


**Fig.3** shows the C 1s spectrum of MGOM at room temperature recorded using Al K $\alpha$  source at grazing incidence. Peak fitting and the background subtraction procedures are described in the text

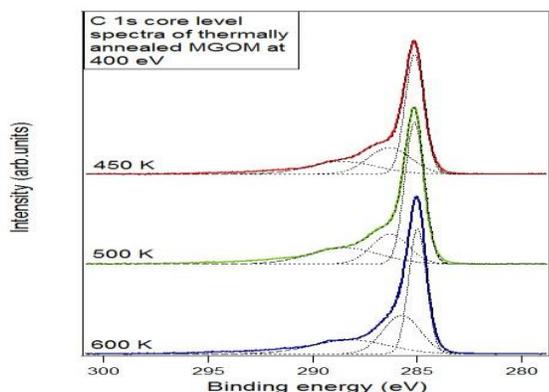


**Fig. 4** shows O 1s core level spectrum recorded from MGOM at room temperature using Al K $\alpha$  source at grazing incidence.

The contribution of oxygen moieties into the structure of GO can be estimated by finding the C/O atomic ratio which is calculated by dividing the area under C 1s peak with that under O 1s peak (shown in Fig. 4) and multiplied by the ratio of photo-ionization cross section of the two elements. This is found to be equal to 1.75 here, with C contribution of ~ 64%. The sp<sup>2</sup> carbon fraction is another important parameter that can be used to characterize the degree of oxidation in GO, which is estimated by dividing the area under sp<sup>2</sup> peak with that of C 1s total peak-area. Here we found that the sp<sup>2</sup> fraction of GO is about ~ 48%, which means a sizable fraction of un-oxidized C atoms is still present on the graphene layers of NVG which may explain why NVG has the highest cohesive energy of all natural graphite material [8].



**Fig.5** displays the comparison of C 1s spectra of MGOM at room temperature and at 450 K. The spectra were acquired using Al K $\alpha$  source at grazing incidence.



**Fig.6** C 1s core level spectra of NVG based MGOM at different annealing temperatures.

### C 1s core level spectra of thermally annealed multilayer GO membrane

Fig. 5 shows C 1s core level spectra of thermally annealed MGOM at 450 K. For comparison, room temperature (RT) spectrum has also been shown in the figure. The best fit for the spectrum at 450 K was obtained with three components C4, C5 and C6 at BEs of 284.9 eV, 286.7 eV and 288.9 eV and a small but broad component C7 at a BE of 290.6 eV. The peaks C4, C5, C6 are arising from  $sp^2$  bonded carbon (284.9 eV), epoxy and/or hydroxyl groups surviving on the carbon plane (286.7 eV), and carbonyl and/or carboxylic groups still present in the carbon plane (288.9 eV) [20]. The peak at a BE of 290.6 eV is assigned to a  $\pi$  to  $\pi^*$  shake-up satellite peak [21]. Following thermal annealing at moderate temperature, a substantial reduction in the intensity of all  $sp^3$  bonded carbon peaks, which is about  $\sim 41\%$  of its initial value, is observed. Simultaneously, the intensity of the  $sp^2$  bonded carbon peak also increases by about 21% from its initial value. The formation of high density of lattice defects on GO planes is observed here as the percentage loss of  $sp^2$  carbon is higher. However, an interesting observation was made in this work (Fig.6) when the annealing temperature was at 600 K, i.e., the spectral line shape of the C 1s of MGOM became almost similar to that of NVG [8] implying that the restoration of  $sp^2$  bonded carbon network on GO planes. Therefore, it seemed that it is possible to achieve  $sp^2$ -bonded-carbon network at lower temperatures on the graphene oxide planes of NVG based MGOM which is an important property of this material in terms of applications.

## IV. Conclusion

We have successfully produced single layer graphene oxide (SLGO) and multilayer graphene oxide membrane (MGOM) using a rare form of precursor graphite, NVG, and characterized them using FE-SEM, AFM and core level photoemission. The observation that MGOM restores  $\pi$ -conjugated graphitic structure following thermal annealing at a moderate temperature while retaining a fraction of functional groups (carbonyls and hydroxyls) is important as reduced GOs with higher conductivity is sought after as they are amenable for device fabrication.

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