Supplementary Information

Graphene synthesis via hydrogen induced low temperature exfoliation of graphitic oxide

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1. Experimental Details

1.1 Materials
Graphite (99.99% SP-1, Bay carbon) used was having a particle size of 45μm. Sodium Nitrate (NaNO₃, 99.5%), Potassium Permanganate (KMnO₄, 99.5%) and concentrated Sulphuric acid (98%) were purchased from Rankem chemicals, India. Sodium Chloride (NaCl, 99.9%) was purchased from SRL, India. Hydrogen Peroxide (30%) was procured from S D Fine-Chem ltd. India. DI water was used for all reactions.

1.2 Characterizations
Powder X-ray diffraction studies were carried out using a PANalytical X’PERT Pro X-ray diffractometer with nickel-filtered Cu Kα radiation as the X-ray source. The pattern was recorded in the 2θ range of 5° to 90° with a step size of 0.016°. Identification and characterization of functional groups were carried out using PerkinElmer FT-IR spectrometer in the range 500–4000cm⁻¹. The samples were prepared by KBr pellet method. The Raman spectra were obtained with a WITec alpha 300 Confocal Raman system equipped with a Nd:YAG laser (532 nm) as the excitation source. Field emission scanning electron microscopy and transmission electron microscopy images were obtained using FESEM, FEI QUANTA and JEOL TEM-2010F.
instruments. Brunauer-Emmett-Teller (BET) surface area analysis was determined by recording nitrogen adsorption/desorption isotherms at 77 K using a static volumetric technique with a Micromeritics ASAP V3.01 G 2020 instrument. Differential scanning calorimetry was carried out on DSC 200 PC, PHOX, NETZSCH under N\textsubscript{2} atmosphere and a heating rate of 5\textdegree C/min. Surface roughness of the HEG-200 was obtained by using atomic force microscope (AFM, Dimension 3100, Nanoscope IV Digital Instruments, USA) in tapping mode. The sample for AFM was prepared by dispersing the graphene powder in N-methyl 2 pyrrolidinone (NMP) by ultrasonication and spin coated on a cleaned glass substrate. The sample was then heated to remove the solvent. XPS analysis was performed with SPECS GmbH spectrometer (Phoibos 100MCD Energy Analyzer) using Al K\textalpha radiation (1486.6 eV). The residual pressure inside the analysis chamber was in $10^{-10}$ mbar range. The spectrometer was calibrated by using photoemission lines of Ag (Ag 3d3/2 = 367 eV with reference to Fermi level). Peaks were recorded with constant pass energy of 20 eV at 100 W power. XPS signals were analyzed using CASA XPS software.

1.3 Synthesis of graphitic oxide and graphene

We prepared graphitic oxide from purified natural graphite using two methods, Hummers\textsuperscript{1} method and a modified Hummers method\textsuperscript{2} (MH method). Though the Hummers method is simpler, the resulting GO and hydrogen exfoliated graphenes (HEG) are identical. We have named the samples used and obtained by modified Hummers method with a prefix MH.

In Hummers’ method\textsuperscript{1}, 2 g of graphite was added to 46 ml of conc. H\textsubscript{2}SO\textsubscript{4} under continuous stirring in an ice bath. 1 g NaNO\textsubscript{3} and 6 g KMnO\textsubscript{4} were added gradually and successively. The ice bath was removed and suspension was allowed to come to room temperature. 92 ml of water was then added to above mixture. After 15 min, the above mixture was diluted to 280 ml using warm water. Following this, 3\% H\textsubscript{2}O\textsubscript{2} was added till the solution turned bright yellow. The suspension was filtered and the filter cake was washed with warm water, repeatedly. The residue was diluted using water and the resulting suspension was centrifuged. The final product was dried under vacuum and stored in vacuum desiccators, until further use.
In MH method, GO (MHGO) was prepared as in ref. 2 with the exception that SP-1 graphite was used instead of expandable graphite. Graphite was grounded with NaCl and washed with DI water followed by filtration. After drying the filtrate was stirred with conc. H$_2$SO$_4$ for 8 h. 6 g of KMnO$_4$ was gradually added while keeping the temperature less than 20 ºC. The mixture was stirred at 35 to 40 ºC for 30 min. and 65 to 80 ºC for 40 min. 92 ml water was added to the above solution and heated to ~ 100 ºC. This was diluted by adding 280 ml of water followed by the addition of 30% H$_2$O$_2$. The mixture was washed by repeated centrifugation and filtration (first by 5 % HCl and then with water). The final product was washed and dried in vacuum.

Exfoliation of GO was carried out as follows. The sample was taken in a quartz boat and placed inside a tubular furnace. The furnace was sealed at both the ends with end couplings having provision for allowing gas. The furnace was flushed with Ar for 15 min. The temperature of the furnace was then raised to ~ 200 °C (slightly above). High pure H$_2$ gas was allowed at that temperature. Within 1 minute exfoliation occurred which could be seen visibly.

2. Results and discussions

It is interesting to note that graphite (Gr), GO and graphene can be primarily distinguished based on their physical appearance alone. Graphite is grey in color, while graphitic oxide is brownish yellow and graphene is a highly dark material. Secondly, GO contains a large quantity of water. As a result an increase in the mass by ~ 1.7 – 1.8 times is observed after the synthesis. The mass of graphene obtained is always less than that of the graphite present in the GO, excluding the losses occurring during the synthesis. This is because graphene synthesis from GO occurs largely by the removal of water and oxygen as mentioned earlier. Additional losses can be due to the removal of carbon containing functional groups as carbon dioxide. The most important physical characteristic however is the huge volume expansion that accompanies during the synthesis of graphene. The photograph in figure 3 symbolically represents these features of graphite, GO and hydrogen exfoliated graphene. Nearly 55 mg of grey colored graphite gives ~ 100 mg of GO and this would result in 40-45 mg of graphene.
As discussed in the main text, the intensity ratio of the D and G bands gives indications regarding the number of defects present in the samples. This ratio decreases as we go from GO to graphene indicating a partial restoration of the basal planes in graphene. This is also supported by the shift in the positions of the D and G bands, as indicated in the table S1.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>D-band (cm⁻¹)</th>
<th>G-band (cm⁻¹)</th>
<th>I_D/I_G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gr</td>
<td>-</td>
<td>1585</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>1360</td>
<td>1609</td>
<td>0.9902</td>
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<tr>
<td>HEG-200</td>
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<td>HEG-300</td>
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<td>1589</td>
<td>0.8510</td>
</tr>
</tbody>
</table>

Table S1 The positions of G and D bands in Gr, GO and HEG obtained by Hummers method GO. The intensity ratios of these bands are also given.

The XRD pattern and the Raman spectra of samples prepared via modified Hummers method are presented here. They are similar to ones obtained by Hummers method, thus showing the universality of our method.
Fig. S2 The XRD patterns of (a) MH GO and (b) graphene (MH HEG -200) produced from MH GO at 200 °C.

Fig. S3 The Raman spectrum of (a) MH GO and (b) MH HEG-200. The Raman spectra obtained in this case was similar to that obtained by Hummers method.
The Nitrogen adsorption and desorption curves for the same are presented below. A BET surface area of 442.9 m$^2$/g was obtained for our graphene which is comparable to the vacuum exfoliated graphene$^3$ (~400 m$^2$/g). We had also prepared graphene via thermal exfoliation and its surface area was ~469 m$^2$/g, a value comparable to the surface area of our graphene. Graphene prepared by other techniques like CVD have given lower surface area values.$^4$

![Graph showing Nitrogen adsorption desorption curves](image)

Fig. S4 Nitrogen adsorption desorption curves for determining BET surface area.
The DSC curves of GO and HEG-200 are presented in Fig. S5. GO shows an exothermic peak at ~ 200°C corresponding to the removal of oxygen containing functional groups and an endothermic behavior below 100°C indicating the removal of adsorbed water. In the case of graphene, both these processes are absent as both the adsorbed water and the oxygen moieties are removed during the exfoliation process.

AFM studies were carried out to determine the thickness profile of the prepared graphene. The AFM images (Fig. S6) reveal a complex morphology that depends somewhat on the deposition conditions and the type of graphene. The AFM images along with thickness profile show a uniform thickness distribution with a height ~ 3.5 nm. However, this data cannot be used to determine the number of layers, especially in the case of graphenes prepared from GO. Schniepp et al.\textsuperscript{5} showed that the exfoliated graphenes due to their wrinkled nature may not sit flatly on substrates. As a result, the thickness profile is not an accurate measurement for determining the number of layers. Fig. S7 presents the XPS spectrum of HEG-200. The peaks corresponding to C1s appears at 285 eV which suggests a good restoration of C=C after exfoliation. Small amount of oxygen still remains after exfoliation which probably corresponds to the carbonyl groups.

Fig. S5 Differential scanning calorimetry (DSC) curves of GO and HEG-200.
present in graphene. Elemental analysis further confirms the increase in C/O ratio from ~1 to ~4, as is to be expected in the case exfoliated graphene.⁶

Fig. S6 AFM image and the corresponding thickness profile of HEG-200 dispersed in NMP. The HEG-200 sample shows a main peak at 284.5 eV, indicating the presence of $sp^2$ hybridized C-C bonds. This peak at 284.5 eV is a signature of graphitic carbon.

Fig. S7 XPS spectra of HEG -200.
References


