

Chemical route to the formation of graphene

Farman Ali, Neeraj Agarwal, Pabitra K. Nayak, Ranjan Das and N. Periasamy*

Department of Chemical Sciences,
Tata Institute of Fundamental Research, Homi Bhabha Road,
Colaba, Mumbai 400 005, India

A possible chemical route towards the formation of graphene is via water soluble graphite oxide (GO), which can be reduced chemically or thermally to carbon. GO prepared by Hummer's method is shown to be EPR-active with $\sim 10^{16}$ electron spins/g. Heating GO increased the free radical concentration at $\sim 140^\circ\text{C}$, together with the elimination of CO_2 and water, and finally produced black, diamagnetic graphitic material at high temperature. Significant loss of carbon in the thermal process implies that the chemical route to graphene via Hummer's GO is less attractive.

Keywords: Electron paramagnetic resonance, graphene, graphite oxide.

GRAPHENE, a single layer of graphite, was discovered to be stable in 2004 (ref. 1). Since then a number of theoretical and experimental studies have demonstrated its outstanding electron transport properties^{2,3}. So far, graphene is obtained by mechanical methods and these methods have very low productivity⁴. There is no method known for the large scale production of graphene. Large cohesive energy between the layers in graphite does not allow easy separation nor allows a suspension of graphene to be stable in liquids. Chemical methods provide a stable suspension of sheets of graphite oxide (GO; in high concentration) in water, which can be subsequently reduced to graphene⁵⁻⁷. Hydroxy, epoxy and carboxyl groups in GO impart water solubility to the individual sheets⁸. GO has been used to fabricate paper-like films with excellent mechanical properties⁹, as well as electrically conductive polymer¹⁰ and in the fabrication of transparent electrode¹¹. Importantly, the electrical conductivity of reduced GO and its composite formulations was found to be enhanced¹¹ due to increase of conjugation. Thermal treatment is shown to be an efficient reduction method for conversion of GO to a black graphitic material¹¹. This suggests that a single graphene sheet could be obtained by thermal reduction of a single sheet of GO deposited on a suitable substrate. Hence, it is important to understand the mechanism of reduction in the thermal treatment of GO. To the best of our knowledge, there is no report on free radicals in GO and their role in thermal reduction. Here we report temperature dependent

EPR, thermogravimetric and chemical analysis which give insight into the mechanism involved in the reduction of GO by thermal treatment.

Commercially available microcrystalline graphite powder ($<25\ \mu\text{m}$, Aldrich) was subjected to extremely oxidizing conditions to give water soluble GO, by using modified Hummer's method¹². In this method graphite is treated with potassium permanganate and sodium nitrate in H_2SO_4 for five days, and processed further to produce yellow coloured GO¹². GO contains a number of oxy-functional groups (epoxy, carboxylic and hydroxyl) which are identified in the FT-IR spectrum of GO⁵. X-ray diffraction (XRD) of GO powder revealed that the inter-layer spacing in GO has increased to $9.33\ \text{\AA}$ as compared to $3.35\ \text{\AA}$ in graphite. Upon sonication, single sheets of GO are stabilized in the suspension, which can be drop-cast on a substrate such as mica. Average thickness of GO sheet is $1\ \text{nm}$ as seen in the atomic force microscope (AFM) topograph image (Figure 1).

Thermal treatment of the yellowish GO powder resulted in a black graphitic powder. Thermogravimetric analysis (TGA) of GO indicated a weight loss of $\sim 55\%$ (Figure 2 inset): weight loss of $\sim 15\%$ at $<110^\circ\text{C}$, a sharp weight loss at $\sim 140^\circ\text{C}$, followed by a further weight loss up to 300°C . Simultaneous thermogravimetric and mass spectrometric (TG-MS) analysis of GO is shown in Figure 2. TG-MS indicated that weight loss of water occurred throughout whereas simultaneous loss of CO_2 and water occurs only at $\sim 140^\circ\text{C}$. The initial weight loss ($\sim 15\%$) is due to physically adsorbed water while the subsequent weight loss ($\sim 40\%$) is due to co-elimination of water and

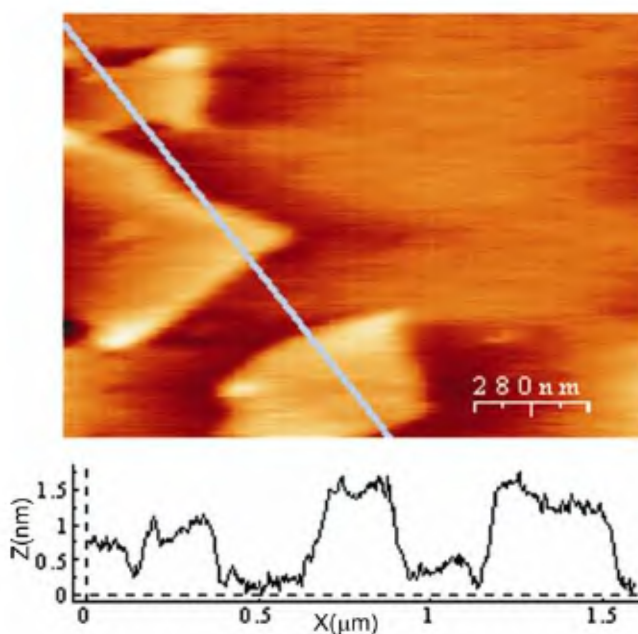


Figure 1. AFM topograph image of graphite oxide (GO) sheets on mica obtained by noncontact mode. GO in water ($0.5\ \text{mg/ml}$) was sonicated for 1 h and dropcast on freshly cleaved mica.

*For correspondence. (e-mail: peri@tifr.res.in)

CO₂. We propose that elimination of CO₂ at ~140°C increases hydrophobicity which leads to co-elimination of water bound to hydrophilic sites.

Formation of CO₂ and water on heating of GO was confirmed by simple chemical tests. In this, solid GO,

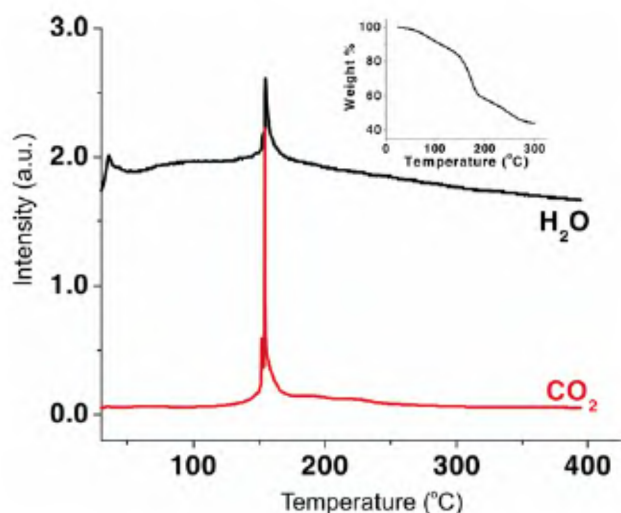


Figure 2. TG-MS of GO showing mass peaks of water and CO₂ at 140°C, and thermogram of GO, % weight loss vs temperature (inset).

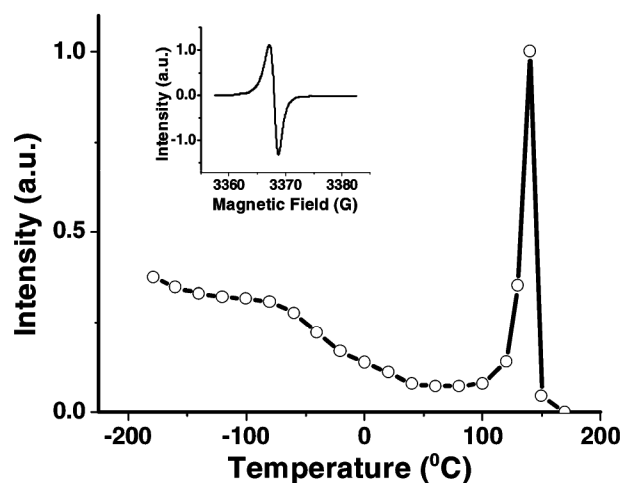


Figure 3. EPR signal of powdered GO at room temperature (inset) and variation of the doubly integrated derivative EPR signal with temperature.

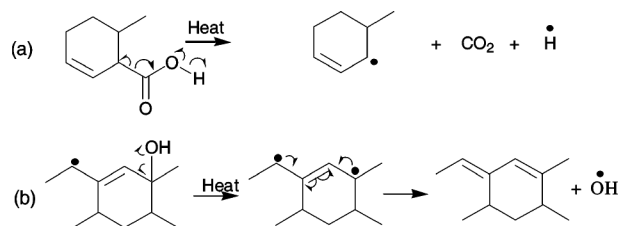


Figure 4. Proposed mechanisms for the formation of CO₂, free radical intermediates and double bonds in GO on thermal treatment.

kept in a long glass tube, was gradually heated (10°C/min) at the bottom end up to 180°C. Colourless liquid condensed in the cooler part of the top end of the tube at around 85°C. Anhydrous copper sulphate when added to the colourless liquid changed to blue confirming that the liquid was water. Brisk evolution of a gas was observed at ~135°C. The gas when passed into freshly prepared lime water turned it milky, which confirmed CO₂.

GO was found to be paramagnetic. The EPR spectrum of GO powder showed a single line with *g*-value of 2.0028 (Figure 3, inset). The number of spins per gram of GO was calculated by comparing its integrated intensity with a standard reference compound, diphenyl picryl hydrazyl (DPPH) dispersed in calcium carbonate¹³. Spins per gram in GO was calculated to be about 10¹⁶. Figure 3 shows the variation of the doubly integrated derivative EPR signal of GO recorded at different temperatures. At low temperature (<25°C), the intensity increased with the decrease in temperature. This is due to increase in the population difference between the Zeeman-split levels involved in the EPR transition. The intensity at -173°C was about three times that recorded at room temperature (22°C). Above room temperature, the intensity first decreased, became constant after 50°C, and then there was a steep increase in the intensity at ~140°C. The intensity at ~140°C was about 10 times higher than at room temperature. As shown earlier, CO₂ and H₂O were co-eliminated at ~140°C. Therefore, the increase in the EPR intensity at ~140°C is due to the formation of free radicals accompanying elimination of CO₂ and H₂O. At ~150°C and above, the EPR signal was completely lost and the compound became black. This change was irreversible.

Based on the thermogravimetric, chemical analysis, and EPR results, we propose indicative mechanisms (Figure 4) which could explain the elimination of CO₂ and the generation of free radicals as intermediates. Increase in double bonds is explained by the elimination reactions and recombination of free radicals. It may be noted that the free radicals which were present initially are also destroyed upon heating. The black colour of the final product and the absence of the peaks of hydroxyl and carboxyl groups in the FT-IR spectrum suggest that graphene regions had developed in GO.

The change in free radical concentration in GO by chemical reduction route was studied by exposing GO (powder) to hydrazine vapour at room temperature. The EPR signal was found to increase with time. After 5 h, EPR signal showed a 10-fold increase in the free radical concentration. Hydrazine vapour treated GO with 10-fold higher concentration of free radicals was kept in a sealed EPR sample tube and heated to ~80°C, the EPR signal intensity decreased eight-fold; at ~100°C, the EPR signal disappeared completely. A colourless liquid (water) condensed in the upper part of the EPR sample tube. Thus, the process of hydrazine vapour chemical reduction of

GO follows free radical mechanism and shows features (increase in concentration, elimination of water) that are similar to thermal reduction.

In summary, our results show that graphite oxide prepared by Hummer's method is EPR-active. Thermal treatment leads to co-elimination of CO₂ and H₂O and a large enhancement in transient free radicals, finally leading to EPR-inactive graphitic material. It appears possible that single sheets of GO deposited on mica substrates may be thermally converted to graphene-like molecule. However, significant loss of carbon occurs in the thermal process and therefore the path towards pure graphene via Hummer's GO is less attractive.

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ACKNOWLEDGEMENT. We thank Prof. S. Ramakrishnan, IPC Department, Indian Institute of Science, Bangalore, for TG-MS data.

Received 15 September 2008; revised accepted 7 July 2009

Radioactivity associated with common salt and estimation of ingestion dose to the general public

P. Prema Kumari^{1,*}, C. G. Maniyan²,
A. P. Lipton³, M. Chandran⁴ and K. Esai Selvan⁵

¹Department of Chemistry, N.M.S. Kamaraj Polytechnic College, Pazhavilai 629 501, India

²Health Physics Unit, IREL, Manavalakurichi 629 252, India

³Centre for Marine Science and Technology, Manonmaniam Sundaranar University, Rajakamangalam 629 502, India

⁴Department of Chemistry, Vivekananda College, Agasteeswaram 629 701, India

⁵Environmental Assessment Division, IREL, Manavalakurichi 629 252, India

The sea brine and sub-soil brine used for the manufacture of common salt contain several chemical and radioactive elements. This study estimated the gross alpha and gross beta activities from the sea and sub-soil brine at two salt works at Kovalam and Puthalam in Kanyakumari District, Tamil Nadu. The activity of the sea brine was higher than that of the sub-soil brine. The gross activity was increasing at subsequent stages of production due to the concentration of brine. The sediments and gypsum samples collected at different stages were also subjected for estimation of different types of activity. ⁴⁰K activity was found to increase, source to bittern, from 8.6 to 162.16 Bq l⁻¹ at Kovalam and 8.59 to 198.98 Bq l⁻¹ at Puthalam. The ingestion dose due to consumption of salt was calculated to be 13.61 µSv per year, the highest contribution (12.42 µSv) coming from ²²⁶⁺²²⁸Ra. This study shows the influence of natural high-background radiation areas on the radioactivity in common salt and calls for setting limits for radioactivity contents in it.

Keywords: Alpha–beta activity, gypsum, salt works, sea and sub-soil brine, sediments.

COMMON salt (NaCl) has several applications in the chemical industry, which consumes 94% of the salt produced, and the rest (6%) is consumed by the human population¹. Manufacture of common salt from sea water or natural brine using solar energy and wind is a popular process. The brine is pumped to large reservoirs of 3–4 m depth and made to flow through underground trenches to a distance of 3 km and stored there. This brine is sent to primary, secondary and tertiary condensers, arranged in series, for evaporation. The concentrated brine from condensers is let into crystallizers, for production of salt, using solar energy². The original volume of the water reduces to 3%, when bittern (the supernatant liquid obtained after the precipitation of NaCl) is formed³. The brine density expressed as salinity Baume (°Be), is a

*For correspondence. (e-mail: prema2008phd@gmail.com)