Top down method for synthesis of highly conducting graphene by exfoliation of graphite oxide using focused solar radiation†

Varlla Eswaraiah, Sasidharannair Sasikaladevi Jyothirmayee Aravind and Sundara Ramaprabhu*

Received 23rd February 2011, Accepted 22nd March 2011
DOI: 10.1039/c1jm10808e

Herein we report a rapid, chemical free and low temperature method
for high throughput production of graphene by exfoliation
of graphite oxide using focused solar radiation. The simple method of
preparation, easy scalability, cost effectiveness and high electrical
conductivity (1.5 × 10^4 S m^-1) of solar graphene hold great promise
for true practical applications.

The novel 2D material in the carbon family, graphene, has stimulated
wide interest due to its intriguing properties such as high mobility of
charge carriers, unique transport performance, high mechanical
strength, and extremely high thermal conductivity. These fascinating
properties render graphene suitable for many promising applications such as graphene based electronics, photonic devices, molecular gas sensors, energy storage and conversion devices and composite materials. All of these engineering applications demand massive production of high quality graphene by a rapid, economic and energy efficient process. The major synthesis methods of graphene reported till now include micromechanical cleavage of graphite, chemical vapor deposition (CVD), epitaxial growth, super acid dissolution, arc discharge method, thermal exfoliation, chemical reduction of graphite oxide (GO) and hydrogen exfoliation. Among these, the most promising methods for the large scale production of graphene are based on the chemical reduction of GO using hydrazine, hydroquinone, or NaBH₄ as reducing agent. Unfortunately these reducing agents are poisonous and explosive and hence require great care. GO is intrinsically defective and electrically insulating and must be reduced to make it electrically active. Chemical and thermal treatments for reduction of GO reported failed to retain the electrical conductivity of pristine graphene due to the attachment of additional functional groups introduced during chemical reduction. Direct conversion of graphite to graphene by liquid phase exfoliation of graphite has been reported for large scale production of graphene. The reducing methods that do not involve the use of any chemicals or high temperature for the exfoliation would maximize the applicability of the produced graphene. In this regard, the attempts aimed at using photographic camera flash for photo-thermal heating and deoxygenation of GO as well as laser induced reduction of GO were highly appreciated but the applications are limited to either ignition or patterning. Given the lack of reliable top down, chemical free methods for high quality production of graphene, the present study demonstrates a novel technique for the synthesis of graphene by exfoliation of GO using focused solar electromagnetic radiation.

GO was prepared from graphite (G) by the modified Hummers method. The proof of concept for the preparation of graphene from GO by focused solar radiation is shown in Fig. 1. Incoming solar radiation was focused using a convex lens of 90 mm diameter (Fig. 1a). Highly intense focused solar radiation directed towards GO (Fig. 1b) imparts sufficient energy needed for exfoliation. The rapid exfoliation resulted in the colour change of GO from light brown to dark black and also a large volume expansion has occurred, as visible from the optical photograph of solar graphene (sG) in Fig. 1c. Fig. 1d compares the volume expansion of synthesized solar graphene (sG) with graphite (G) and graphite oxide (GO).
When radiation is absorbed by a body, the photoacoustic effect takes place and the thermal expansion of the body that occurs when optical radiation is converted to heat causes mechanical motion of the body, which, in turn, discharges a popping sound wave into the surrounding medium.\textsuperscript{32} The phenomena (a.mpg video file is available in the ESI\textsuperscript{†}) are similar to the flashing of carbon nanotubes.\textsuperscript{33} The effect is thought to be arising from the high temperature chemical reaction between the surface carbon and surrounding water.\textsuperscript{44} Due to localized thermal excitation of GO by focused solar radiation, the temperature increases suddenly (in 1–2 s) to 150–200 °C (see ESI\textsuperscript{†}) which causes the exfoliation of GO into graphene. The reduction mechanism of GO can be understood as follows: when focused sunlight falls on GO, rapid heating of the material occurs. The exposure to the focused sunlight causes the decomposition of insulating functional groups over basal planes of GO, known as deflagration of GO.\textsuperscript{27} During this process, GO decomposes to graphene and the most thermodynamically stable oxide of carbon, CO\textsubscript{2}. Along with this, H\textsubscript{2}O also forms as a minor product. It is interesting to note that the rapid colour change and volume expansion observed in addition to change in the nature from dense to fluffy after immediate exposure to the focused solar radiation, indicate the deoxygenation of GO.

The temperature of the solar radiation rose to 150–200 °C from ambient temperature and the power changed drastically to ~2 W from 60 mW after focusing by converging lens. In the complete visible region (400–700 nm), the power of the focused radiation was varying from 1.90 W to 2.13 W (see ESI\textsuperscript{†}). Schniepp et al.\textsuperscript{14} reported thermal exfoliation of GO by rapid heating it to (>2000 °C min\textsuperscript{-1} or >33 °C s\textsuperscript{-1}) 1050 °C. At that high temperatures, exfoliation of GO occurred with the evolution of CO\textsubscript{2}. But in the present solar exfoliation technique, the heating rate was more rapid (>100 °C s\textsuperscript{-1}) and hence, exfoliation took place at much lower temperature (150–200 °C) than thermal exfoliation, with the decomposition of the functional groups and the evolution of CO\textsubscript{2} immediately after irradiation. In other words, the pressure developed between graphitic layers during solar exfoliation could easily overcome the van der Waals force between them and hence resulted in rapid exfoliation.

We have characterized the graphene sheets prepared by solar irradiation by a number of techniques that clearly reveal the unique nature of the material. An X-ray diffraction pattern of G, GO and sG is displayed in Fig. 2a. The crystalline peak in graphite at 26° corresponds to reflections from C (002) plane. The spectra of GO exhibit a single peak at 10.6° for 2θ corresponding to an inter layer d spacing of 8.36 Å. The increase in d value of GO can be due to the evolution of 3.4 Å spacing between typical graphene sheets in graphite to integrate the water molecules trapped between oxygen containing functional groups in GO sheets.\textsuperscript{38} The absence of any peak at a 2θ value of 26° reveals that the produced GO is devoid of any graphite. Due to the rapid heating of GO in the presence of sunlight, the decomposition rate of the oxygen-containing groups of GO exceeds the diffusion rate of the evolved gases back to the material, thus yielding pressure that surmounts the van der Waals force holding the graphene sheets together in GO.\textsuperscript{36} The XRD of sG gives the first confirmation of complete reduction of GO, as it does not have a peak at 10.6°, yet shows a weak and broad peak C (002) around 25°. The width of the sG peak in the XRD pattern can be attributed to two factors. It can be either due to the small size of the layers or a relatively short domain order of the stacked sheets, each of which broadens the XRD peak.\textsuperscript{35} The Raman spectrum of graphene is characterized by two prominent features: a G band at ~1567 cm\textsuperscript{-1} arising due to first order Raman scattering of the E\textsubscript{2g} phonon at the Brillouin zone center of sp\textsuperscript{2} carbon atoms\textsuperscript{39} and a D mode arising from the breathing mode of k-point phonons of A\textsubscript{1g} symmetry at 1356 cm\textsuperscript{-1} which requires a defect for its activation.\textsuperscript{39} The Raman spectra of G, GO and sG are shown in Fig. 2b. The Raman spectrum of GO displayed an intense D band at 1368 cm\textsuperscript{-1} and a broad G band at 1604 cm\textsuperscript{-1}, exhibiting a rightward shift in frequencies (blue shift) with respect to those of graphite. The broadening and increment in frequency (nearly 37 cm\textsuperscript{-1}) of G band of GO may be due to the reduction in size of the in plane sp\textsuperscript{2} domains possibly due to strong oxidation of graphite.\textsuperscript{39} After exfoliation of GO by solar irradiation, the position of G band (1567 cm\textsuperscript{-1}) of graphene exactly matches with that of graphite. The intensity ratio of D to G band (I\textsubscript{D}/I\textsubscript{G}) of GO is about 1.16, which is very much higher than that of graphite, possibly due to more defects introduced by disruption of the aromaticity caused by the presence of various functional groups. For sG, I\textsubscript{D}/I\textsubscript{G} is 0.20, which approximates closely with the I\textsubscript{D}/I\textsubscript{G} of pure graphite (0.07). The decrease in I\textsubscript{D}/I\textsubscript{G} of sG can be due to the restoration of sp\textsuperscript{2} network during exfoliation of GO. The perfect matching of the G peak (1567 cm\textsuperscript{-1}) position for both G and sG clearly indicates the efficient and fast healing of sp\textsuperscript{2} conjugated electrons during solar exfoliation. This illustrates that graphene sheets undergo annealing during the exfoliation process, corroborating the atomistic mechanism of graphite defect annealing.\textsuperscript{40}

We used a field emission scanning electron microscope (FESEM) and a high resolution transmission electron microscope (HRTEM) to analyze the structural morphology of sG and observed that the most of the GO were efficiently exfoliated to form separated, ultrainthin, transparent sheets (Fig. 3a–d). Also TEM images show wrinkled nature of the graphene sheets. Energy dispersive X-ray (EDX) analysis reflects the extent of oxygen removal (see ESI†). The histogram plotted by recording EDX over different regions of sG determined the percentage of oxygen content as ~2 to 6% (see ESI†). This value agrees well with the ~6 wt% mass loss observed during thermogravimetric analysis (TGA) of sG at less than 200 °C due to the decomposition of oxygen functionalities. The thickness of graphene sheets measured using HRTEM lattice imaging came out to be ~1 nm,\textsuperscript{39} indicating the bilayer nature of the present solar exfoliated graphene sheets. Atomic Force Microscopy (AFM) is considered to be best suited for the measurement of surface roughness and thickness of graphene sheets. Hence in the present study, the number of layers of sG has been analyzed by AFM (Fig. 3e–f). Multiple cross-sections of sG deposited onto a HOPG substrate were recorded, and a number of step heights were measured across the relief of the sample. The average step heights measured between the surface of the

![Fig. 2](image-url)
sheets and the substrate were found to be \( \sim 0.9 \) to \( 1.4 \) nm, proving them to be two atoms thick. This corroborates the bilayer nature observed from HRTEM lattice imaging. The discrepancy in thickness compared to the theoretical value for graphene suggests the presence of some residual oxygen functionalities on the sheets.\(^7\) Also for several sheets of sG measured, we found that the average lateral dimension of sG was \( \sim 0.1 \) \( \mu \)m.

Thermo-gravimetric analysis (TGA) of graphene shows good thermal stability even after 800 °C as shown in Fig. 4a. GO is thermally unstable and starts to lose mass upon heating below 100 °C due to moisture and water, but severe mass reduction occurs at 190 °C probably due to pyrolysis of the labile oxygen-containing functional groups, yielding CO, CO\(_2\), and steam.\(^4\)\(^5\)\(^6\)\(^7\) Hence, the thermal decomposition of GO can be accompanied by a vigorous release of gas, resulting in a rapid thermal expansion of the material. This is very clear from the video, where upon irradiation with sunlight, rapid generation of gases is visible. Irradiation imparts thermal stability to the reduced GO with the removal of thermally labile oxygen functional groups. Apart from a 6 wt% loss below 200 °C, which can be due to the release of remaining oxygen functionalities, no significant mass loss is detected when the solar graphene is heated up to 600 °C. Probably the extent to which deflagration of GO occurred can be visualized more clearly by measuring the electrical conductivities of the materials. Fig. 4b shows the electrical conductivity values of graphite, graphite oxide and solar graphene. Graphite shows a conductivity of \( 2.318 \times 10^4 \) S m\(^{-1}\) whereas GO is insulating as its conductivity is \( \sim 10^{-5} \) S m\(^{-1}\). The obtained conductivity value of 1.494 \times 10^3 \) S m\(^{-1}\) (see ES\(\text{I}^1\)) for sG almost reaches that of the parent material (graphite). This implies the efficient healing of sp\(^2\) conjugated network in solar graphene after exfoliation. In other words, the present combination of photoacoustic and photothermal effect of exfoliation of GO to sG leads to excellent restoration of the electrical conductivity in a short period of time (\( \sim 5 \) min). The high electrical conductivity of present solar graphene sheets can contribute percolated pathways for electron transfer making electrically conducting graphene reinforced polymer composites and hence a promising tool in the arena of composite materials for energy, environmental and structural applications.

**Conclusions**

In conclusion, we have demonstrated a rapid and green chemical method for high throughput production of graphene by a simple and economical method. The present solar exfoliated graphene with negligible oxygen functionality and high electrical conductivity is the simplest and fastest top down converted material produced to date. The use of natural resource makes the present technique extremely ingenious and the properties of the solar exfoliated graphene can be utilized in a multitude of applications. Above all, the present natural solar electromagnetic irradiation method stands above the reported chemical and high temperature thermal treatments as the former is instantaneous, chemical free and energy efficient. Further, the vast natural resource can be exploited with the use of a solar tracker-lens system for large scale production of high quality graphene.

**Notes and references**


