

Electronic Supplementary Information

Top down method for Synthesis of Highly Conducting Graphene by Exfoliation of Graphite Oxide using Focused Solar Radiation

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Experimental section

1. Preparation of Graphite Oxide

GO was prepared according to Modified Hummers method. SP-1 (Bay Carbon) graphite was used as the starting material. Briefly, graphite was grounded with NaCl and washed with DI water followed by filtration. After drying, the filtrate was stirred with conc. H₂SO₄ for 8 h. 6 g of KMnO₄ was gradually added while keeping the temperature less than 20 °C. The mixture was stirred at 35 to 40 °C for 30 min and 65 to 80 °C for 40 min. 92 ml water was added to the above solution and heated to ~ 100 °C. This was diluted by adding 280 ml of water followed by the addition of 30% H₂O₂. The mixture was washed followed by repeated centrifugation and filtration (first by 5 % HCl and then with water). The final product was washed and dried in vacuum.

2. Reduction and Exfoliation of Graphite Oxide

GO was spread over petri dish and kept under sunlight. A convex lens of diameter 90 mm was used to focus the incoming radiation from the sun and its power at different wavelengths are shown in the table S1. A series of experiments have been performed with lenses of different diameters 50 mm, 75 mm, 90 mm and 100 mm. The efficient exfoliation has been achieved using 90 mm and 100 mm diameter lenses even at moderate intense sunlight. Hence further experiments have been carried out using 90 mm converging lens. The power of the focused radiation was ranging from 1.77 - 2.03 W and temperature raised to more than 150° C (figure S1).

Wavelength (nm)	Power of focused EM radiation (W) using 90 mm converging lens
400	1.83-2.09
470	1.90-1.95
500	1.89-2.04
600	1.98-2.12
700	2.01-2.13

Table S1: Power of focused EM radiation at different wavelengths using 90 mm converging lens

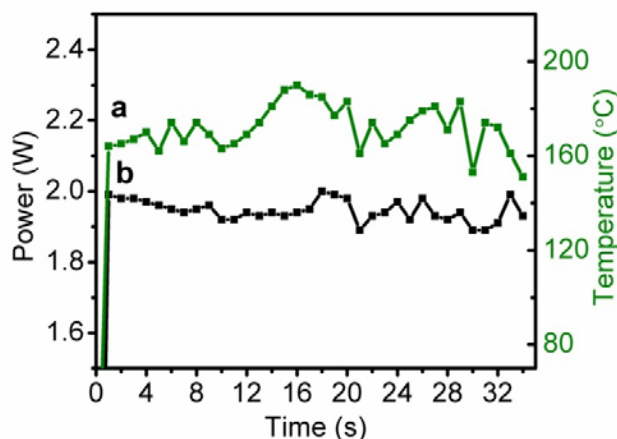


Fig. S1. Power and temperature profile of the focused solar radiation with respect to time during exfoliation of Graphite oxide.

3. Characterization Techniques

The XRD measurements were performed with a PANalytical X'Pert Pro X-ray diffractometer with nickel-filtered Cu K α radiation as the X-ray source. The pattern was recorded in the 2θ range of $5^\circ - 40^\circ$ with a step size of 0.016° . Raman spectroscopy was performed on Witec Raman microscope using green (532 nm) laser excitation, with excitation energy of 2.33 eV. Scans were taken on an extended range ($500-3000\text{ cm}^{-1}$) for an exposure time of 60 s. The samples were sprinkled over cleaned glass slides for observation and viewed under a maximum magnification of $\times 20$. FTIR was performed on Perkin Elmer spectrum one spectrometer in the range of $400-4000\text{ cm}^{-1}$ using KBr pellet method. Thermo gravimetric spectra were recorded with NETZSCH analyzer from ambient temperature to 800°C in N_2 atmosphere with temperature heating of $10^\circ\text{C}/\text{min}$. Field emission scanning electron microscopy (FESEM, Quanta 3D) imaging was used to examine the morphology of the synthesized samples. Samples were mounted on a standard aluminium specimen stub using double sided conductive carbon tape. The microscope was operated at an accelerating voltage of 5-30 kV depending on different imaging purposes. EDX spectra was recorded with Li doped Silicon X-ray detector equipped with FESEM. High resolution micrographs were obtained with FEI Tecnai G² transmission electron microscope operated at 200 keV. The samples were dispersed in ethanol and drop cast over holey carbon coated copper grid (200 mesh). The samples were dried over night in ambient atmosphere. The AFM measurements were performed in tapping mode using Park systems XE-100. For imaging, samples were placed on freshly cleaved HOPG surface by spin coating from a suspension at 2000 rpm for 20 s. Suspensions were prepared by mixing 1 mg of sG with 10 ml of DMF by ultrasonication for 15 min. This suspension was diluted to a concentration of 0.02 mg/ml. Model 842.PE Newport optical thermopile based power meter was used to measure the power of radiation. Agilent thermocouple based temperature sensor was used to measure the temperature of the focused radiation.

A comparative study describing different synthesis techniques of graphene by either reduction or exfoliation of GO and the experimental conditions involved has been depicted in table S2. The table clearly shows that, most of the techniques for exfoliation of GO involved sophisticated instruments, man power, poisonous chemicals and time consuming processes. But in the present study, there are no chemicals involved and the ease of preparation makes it an excellent green approach for the synthesis of graphene.

Method	Experimental conditions	Reference and year
GO reduction by alkaline conditions	100 W, 40 kHz, 1 h intense ultrasonication and centrifugation of GO suspension for 2h at 23,000 rpm and heating in alkaline solutions.	[1], 2008
Solvothermal reduction method	Sonication at 50° C for 60 min and diluted with NMP, degassed for 60 min, bath sonication at 240° C for 24 h under argon atmosphere, centrifuge at 4500 rpm and annealed at 250, 500 and 1000°C	[2], 2010
Thermal exfoliation	The dried graphite oxide is charged into a quartz tube and purged with argon. Rapid heating (>2000 °C/min) to 1050 °C	[3], 2006
Arc discharge exfoliation	GO was rapidly heated by arc discharge in a mixed buffer gas of H ₂ (≤10 kPa pressure) and argon (90 kPa pressure). High-temperature discharge between the two electrodes were generated by a direct current mode ranging from 100 to 150 A. The resulting exfoliated graphite (10 mg) was dispersed in 10 mL of NMP for 2 h by sonication. Suspension was centrifuged at 15000 rpm for 5 min to remove thick graphene sheets and nonexfoliated graphite, and to retain thin GSs in the supernatant.	[4], 2009
Vacuum exfoliation	The asprepared GO was put into a quartz tube connected to vacuum pump. The tube was heated at the rate of 50 °C/min under a high vacuum (<1 Pa) and kept at 200 °C for 5 h	[5], 2009
Chemical reduction	GO (100 mg) dispersion was sonicated using ultrasonic bath cleaner (150 W). Hydrazine hydrate (1.00 mL, 32.1 mmol) was then added and kept in oil bath at 100 °C under a water-cooled condenser for 24 h over which the reduced GO gradually precipitated and isolated by filtration and washed with water and dried.	[6], 2007
Laser reduction	Graphene formation using pulsed (~9 ns, 20 Hz) irradiation was carried out using the frequency-doubled (532 nm) and -tripled (355 nm) outputs of a Nd:YAG laser from Raman	[7], 2010

	microscope.	
Microwave reduction	20 mg of GO were dispersed into 6 mL water under mild ultrasound. Then 30 mL of DMAc was added and sonicated for few minutes and suspension was obtained in the mixture of DMAc/H ₂ O. For the microwave thermal reduction experiment, 36 mL of the prepared GO suspension in DMAc/H ₂ O (0.56 mg mL ⁻¹) was put into a microwave oven (Galanz, G70D20ASP-DF, China) under dry nitrogen gas, and it was treated for different time in the range of 1–10 min at 800 W. After washing with ethanol for three times then the mixture was freeze dried at 80 °C for 24 h.	[8], 2010
Flash reduction	Flash reduction of free-standing GO films can be done with a single, close-up (<1 cm) flash from the Xenon lamp equipped on a common digital camera. Most experiments were done with a Sunpak 383 stand-alone flash unit with a larger window size of around 30 mm × 50 mm	[9], 2009
Hydrothermal	25 mL of 0.5 mg/mL GO aqueous solution was transferred to a Teflon-lined autoclave and heated at 180 °C for 6 h.	[10], 2009
Electrochemical method	The electrochemical reduction of GO in a three-electrode system (Pt as counter electrode, saturated calomel electrode as reference electrode, GO film coated over GCE as working electrode). Electrochemical reduction experiments were performed on a CHI at a constant potential (–1.5 or –1.3 V vs SCE) in 10 mmol/L pH 5.0 PBS (K ₂ HPO ₄ /KH ₂ PO ₄) under stirring for 2 h	[11], 2009
Solar exfoliation	GO powder in a petri dish irradiated with focused solar radiation using a converging lens undergone exfoliation within a few seconds.	Present technique

Table S2: Comparison table for various synthesis methods for the reduction of graphite oxide.

4. Raman Fingerprints

Raman spectroscopy gives information about the existence of sp^2 and sp^3 bonds present in any carbon nanostructure. From the Raman spectra it is clear that graphite is having most sp^2 hybridization bonds due to its basic conjugated π electrons as the intensity of its D-band is minimal.¹²⁻¹³ In the case of GO, which is deformed structurally having more defects due to the incorporation of epoxide, carbonyl and hydroxyl functional groups which is clear from the broadening of the spectra. After exfoliation of GO by solar radiation, the graphite oxide loses its functional groups and the reduced graphene (*sG*) gains conjugated electrons, which is evident from the reduction in peak intensity of D band in *sG*. Further, the defects induced in solar exfoliated graphene is much lower compared with that observed during chemical reduction methods such as reduction of graphite oxide by Fe,¹⁴ sodium borohydride,¹⁵ hydrazine hydrate,¹⁶ and hydrothermal reduction.¹⁰

The ratio of intensities of D and G bands has been compared in table S3. The I_D/I_G ratio is normally used as an indication of the level of chemical modification in graphitic carbon. Raman spectrum of *sG* shows a minimal I_D/I_G value, indicating its less defective nature.

S. No	Method of Reduction of GO	I_D/I_G	Reference
1	NaBH ₄	>1	[15]
2	Hydrothermal	0.90	[16]
3	Hydrazine	1.63	[10]
4	Fe	0.32	[14]
6	Hydroquinone	>1	[17]
7	Solvothermal	~0.86	[18]
8	Electrochemical	>1	[11]
9	arc discharge	0.26	[19]
10	Microwaves	0.96	[8]
11	Solar EM radiation	0.20	present

Table S3: I_D/I_G comparison of graphene prepared by different methods.

5. Fourier Transform Infrared Spectra

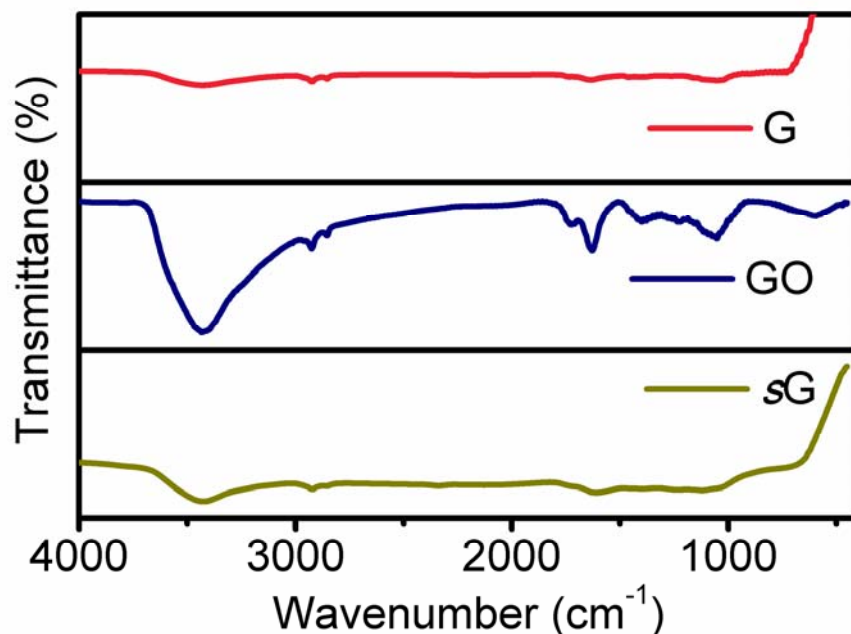


Fig. S2: FTIR spectra of Graphite, Graphite Oxide and Solar graphene

It is observed that the spectrum of graphite is deficient of any functional groups except O-H stretching vibrations (3427 cm^{-1}) whereas GO identified the presence of following functional groups. O-H stretching vibrations (3432 cm^{-1}), CH_2 asymmetric and symmetric stretching vibrations (2924 and 2852 cm^{-1}), C=O stretching vibrations (1725 cm^{-1}), C=C from unoxidized sp^2 bonds (1627 cm^{-1}), O-H bending deformation (1408 cm^{-1}) and C-O vibrations (1049 cm^{-1}). This confirms the presence of hydroxyl, epoxide and carbonyl functional groups in GO as shown in the figure S2. On the otherhand, the spectrum of *sG* exhibits a broad O-H band (3436 cm^{-1}) which can be due to adsorbed moisture. The absence of any other oxygen containing functional groups in *sG* clearly validates the exfoliation process.²⁰

6. Elemental Mapping, Morphology and Composition Analysis

FESEM and EDX analyses of irradiated samples over different regions have been performed for the quantification of oxygen content. The elemental mapping as well as the full and reduced area EDX recorded is displayed in figure S3, S4 and S5. Carbon and oxygen mapping using red and green colours provides the visualization of almost negligible oxygen content present after deflagration of GO by solar irradiation. The carbon and oxygen peaks observed at 0.265 eV (K_α) and 0.514 eV (K_α) can be seen from figures S4 and S5.

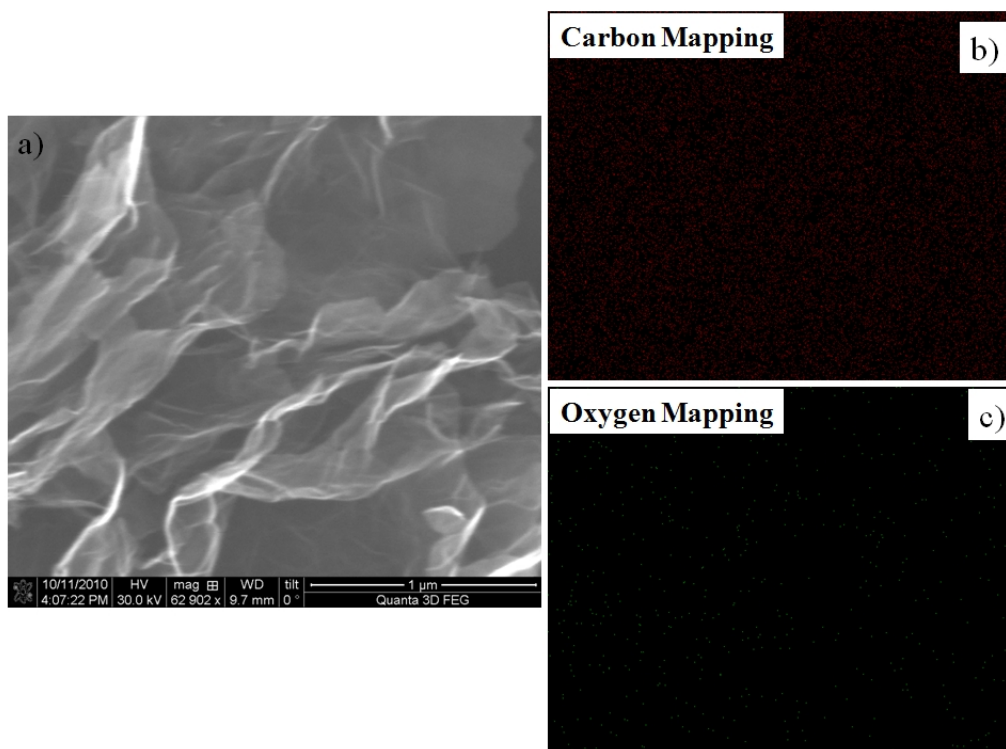


Fig. S3. a) FESEM image of *sG* and (b & c) elemental mapping of Carbon (Red dots) and Oxygen (Green dots)

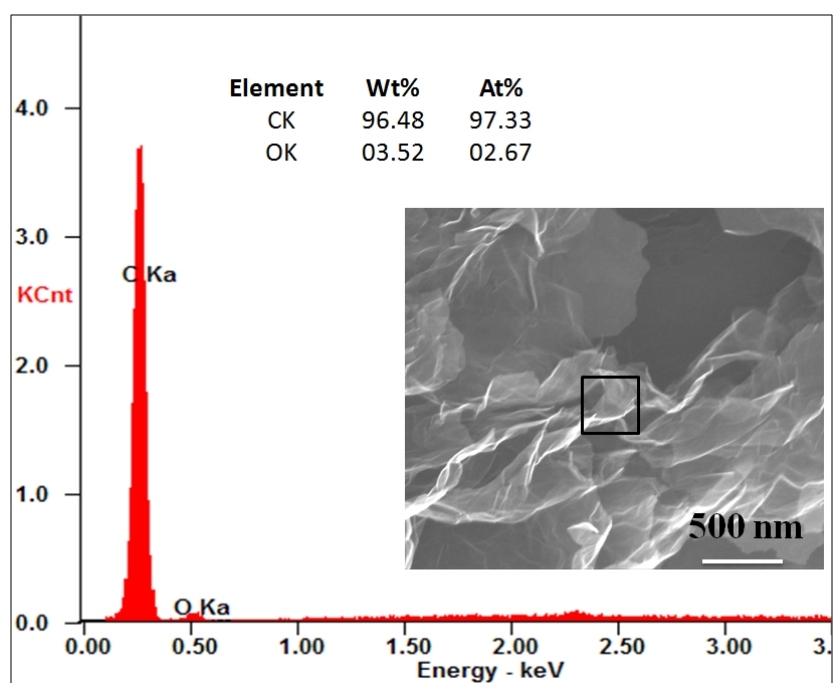


Fig. S4: Energy dispersive spectra (EDX) of solar graphene (Reduced area scan)

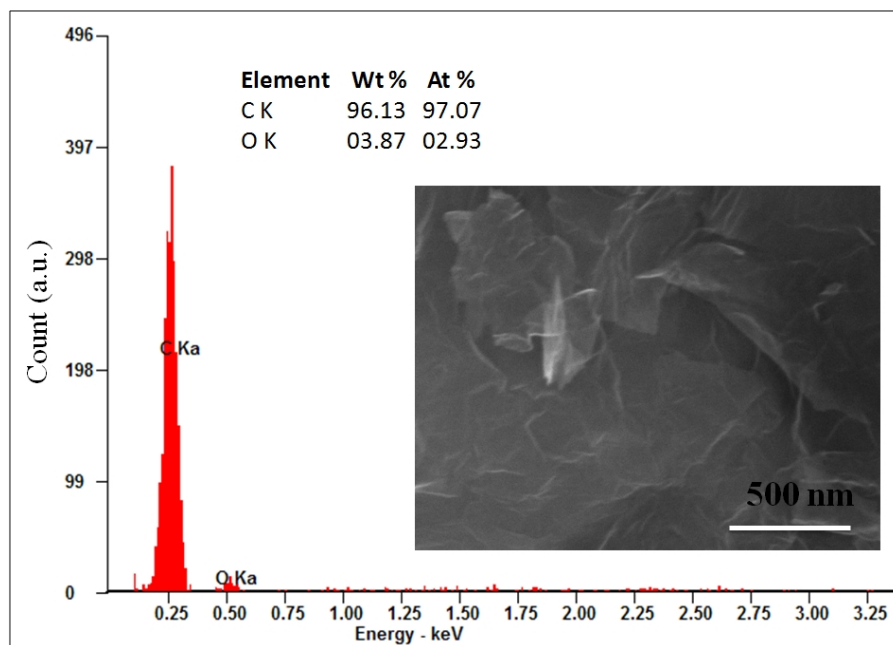


Fig. S5: Energy dispersive spectra (EDX) of solar graphene (Full area scan)

The histogram plotted by taking a number of EDX spectra at different locations of solar graphene has been depicted in figure S6. The efficient deflagration of GO resulted in negligible oxygen functionalities in solar graphene. The remaining 2-6 wt % of oxygen may be due to the presence of minute quantity of adsorbed functional molecules. This result can be justified by comparing with the literature report of modeling of the structure²¹ of GO where the difficulty in complete reduction of GO has been demonstrated.

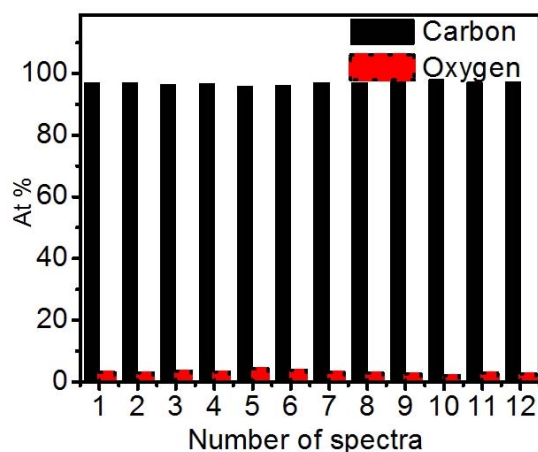


Fig. S6. Quantification of atomic carbon and oxygen content analyzed using EDX spectra of *sG*.

7. Electrical conductivity

Two probe method was employed for measuring electrical conductivity of the GO where as for Graphite and Graphene, collinear four probe technique was used in order to avoid contact resistance, lead resistance etc. Positive constant current was applied to the 1st and 4th terminal and corresponding voltage was measured between 2nd and 3rd terminals. Similarly negative constant current was applied and corresponding voltage was measured. Positive and negative currents were applied in order to avoid voltage generation due to thermoelectric effects. All input and measured parameters were substituted in equations 1, 2 and 3 for calculating conductivities of the samples G, GO and sG.

Two probe technique, electrical resistivity ($\Omega\text{-m}$)

$$R = \frac{\rho l}{A} \text{-----} (1)$$

Where R is the measured resistance between the two probes (Ω)

l is the probe separation (m)

and A is the area of current distribution (m^2)

Four point collinear probe technique

$$\rho = \frac{\pi t}{\ln 2} \frac{(V_+ - V_-)}{2I} k \text{-----} (2)$$

Where ρ is electrical resistivity ($\Omega\text{-m}$)

t is the thickness of the sample (m)

I is the applied current (A)

$k = k_1 k_2$ is the correction factor due to finite size and dimensions

V_+ is the measured voltage for applied positive current (V)

V_- is the measured voltage for applied negative current (V)

Reciprocal of resistivity is known as conductivity (σ)

$$\sigma = \frac{1}{\rho} \text{ (S/m)-----} (3)$$

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