Supplementary materials

Synergy of Oxygen and Piranha Solution for Eco-Friendly Production of Highly Conductive and "Clean" Graphene Dispersions

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The Greenness of the present Graphene Fabrication technique can be attributed to the following pointers:

1. Metal oxidizing agents such as $KMnO_4$,[1] $KClO_3$,[2] $NaNO_3$,[1] etc are not used in this synthesis technique and hence the additional solvents (HCl, H_2O_2) needed to wash away the unreacted metals can be excluded.
2. Since the as-fabricated graphene sheets are highly conductive, post treatment is not necessary where either a reductions process or thermal annealing is required to render the GO conductive.
3. The energy needed for the reaction to proceed is 1.8×10^4 Joules of energy (5kWh) using the CEM discover microwave (300W of power is used for 60sec) which is very low when compared to the traditional heating in an oil bath which requires approximately around 3.79×10^5 Joules of energy (103KWh) (where 630W of power is used for 10mins to reach 100^0C and then the power is used accordingly to maintain the temperature for as long as

2hrs to 5days). This makes the microwave approach an energy saving and economical approach.

4. In this ecofriendly approach mentioned, toxic gases such as CO, NO_2, N_2O_4 are not produced and the filtrate does not contain any small molecules which pose as a hazard to the environment.[3]
5. In this ecofriendly approach mentioned, the time required for graphene fabrication is very short *i.e* 60sec when compared to the traditional GO synthesis 2hrs to 5days and in addition they need to be further reduced to be converted to rGO.[4]

Supplemental Experimental results

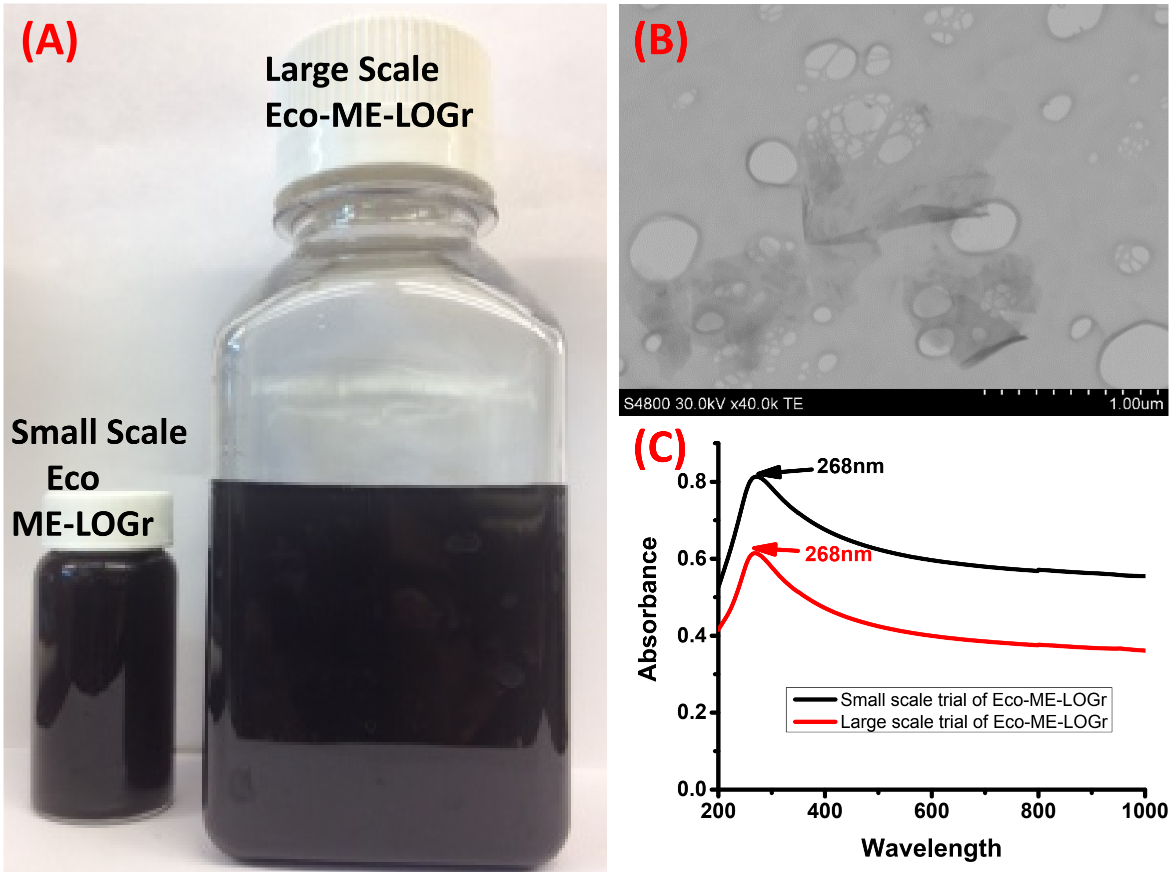


Figure S1: (A). Digital photographs of the stable Eco-ME-LOGr dispersions in water from small and larger scale production. (CEM discover, 300 watts for small scale, and Synthwave from Milestone, 900W for larger scale production, see details in the experimental section) in a piranha solution. (B) A representative STEM image of the graphene sheets from larger scale production achieved via Synthwave from Milestone. (C) UV-Vis-NIR spectra of the Eco-ME-LOGr in water from small and larger scale production. The similar lateral sizes of the graphene sheets, and the overlapping of the two UV-Vis-NIR spectra indicate that similar quality of graphene sheets were obtained, demonstrating that this Eco-Friendly approach can be easily scaled up for mass production.

Table S1 Concentration and production yield of the Eco-ME-LOGr in various solvents

Solvent	Concentration (mg/ml)	Total weight in the solution	Initial weight(mg)	% yield
Ethylene glycol	0.40	16.12	20	80.6
NMP	0.29	11.43	20	57.2
Water	0.22	10.27	20	51.4
DMF	0.20	8.02	20	40.1
Chloroform	0.19	7.56	20	37.8
THF	0.071	2.84	20	14.2
Acetone	0.026	1.05	20	5.3

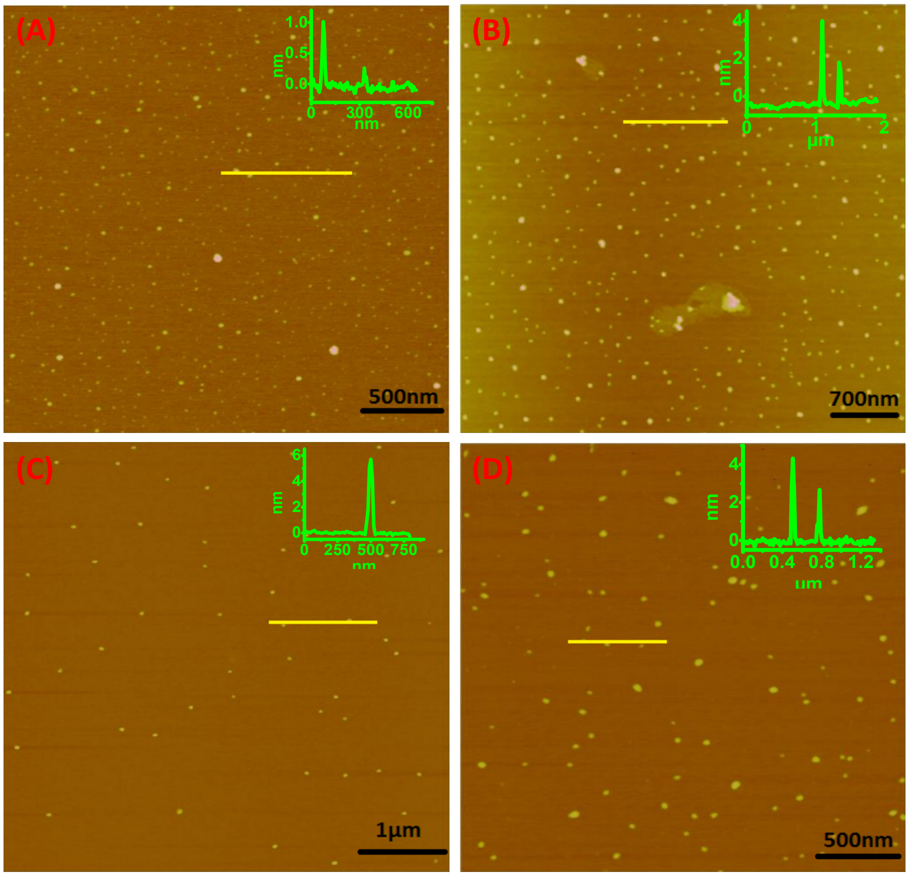


Figure S2. AFM images of graphene sheets prepared from fresh GIC without O_2 purging (A); GIC purged with 20 minutes O_2 (B); GIC with 5 minutes O_2 purging, but longer microwave irradiation (75 second, instead of 60 seconds) (C); GIC with 5 minutes O_2 purging with traditional heating instead of microwave heating (D).

Table S2. Weights of Graphite and GICs with/ and without purging with 5 min of O_2 after washing with water.

Reaction mixtures	Initial weight(mg)	Weight after washing(mg)
Fresh GIC	40.1mg	40.2mg
Fresh GIC purged with O_2	40mg	41.6mg

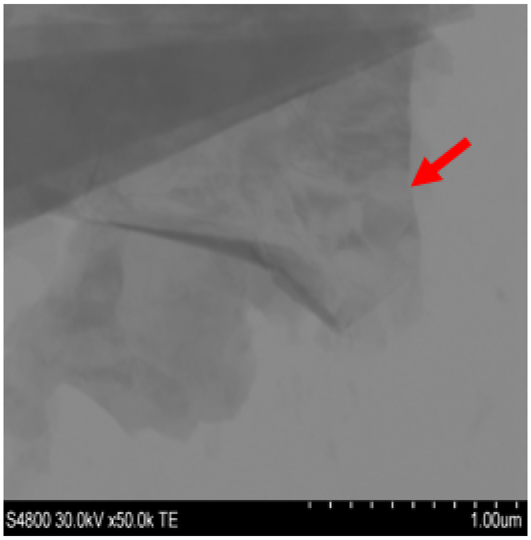


Figure S3. A typical STEM images of graphene structures obtained by microwave irradiation of oxygen purged GIC without further addition of piranha solution. The image shows thick graphene sheets with straight edges indicated by the arrow.

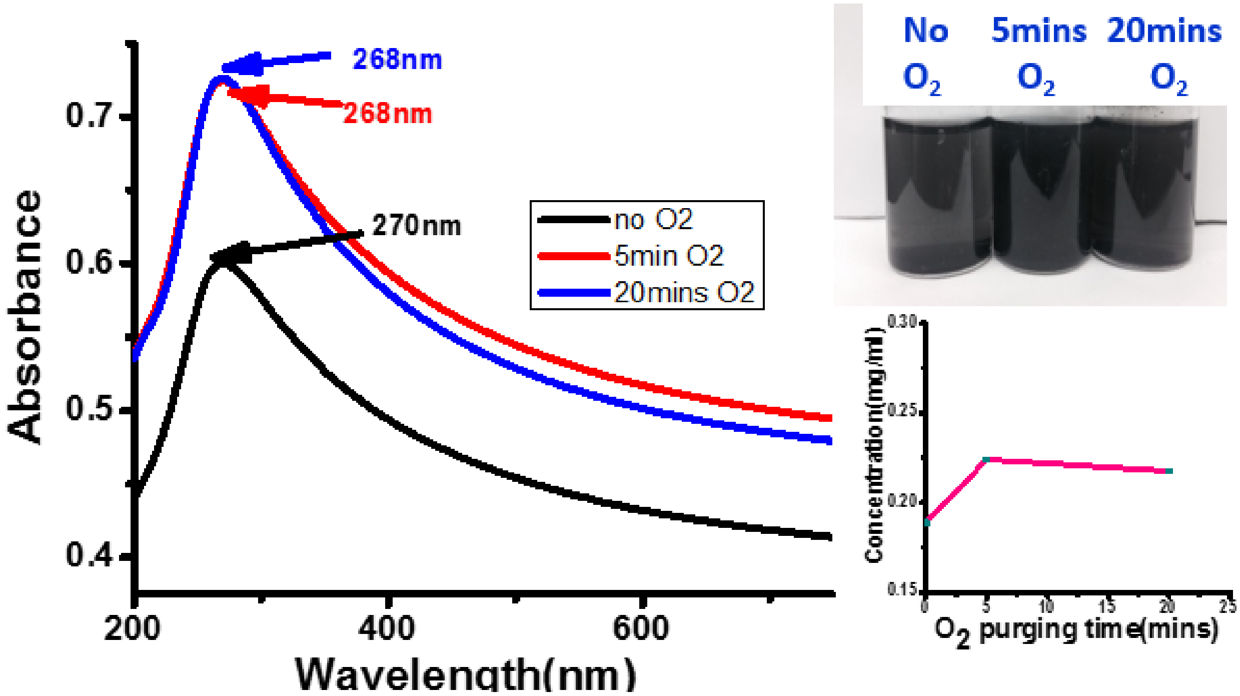


Figure S4. UV-Vis spectra and digital pictures of the dispersed graphene solution to show the yield of the products depends on the O_2 purging time with the same microwave power (300 W).

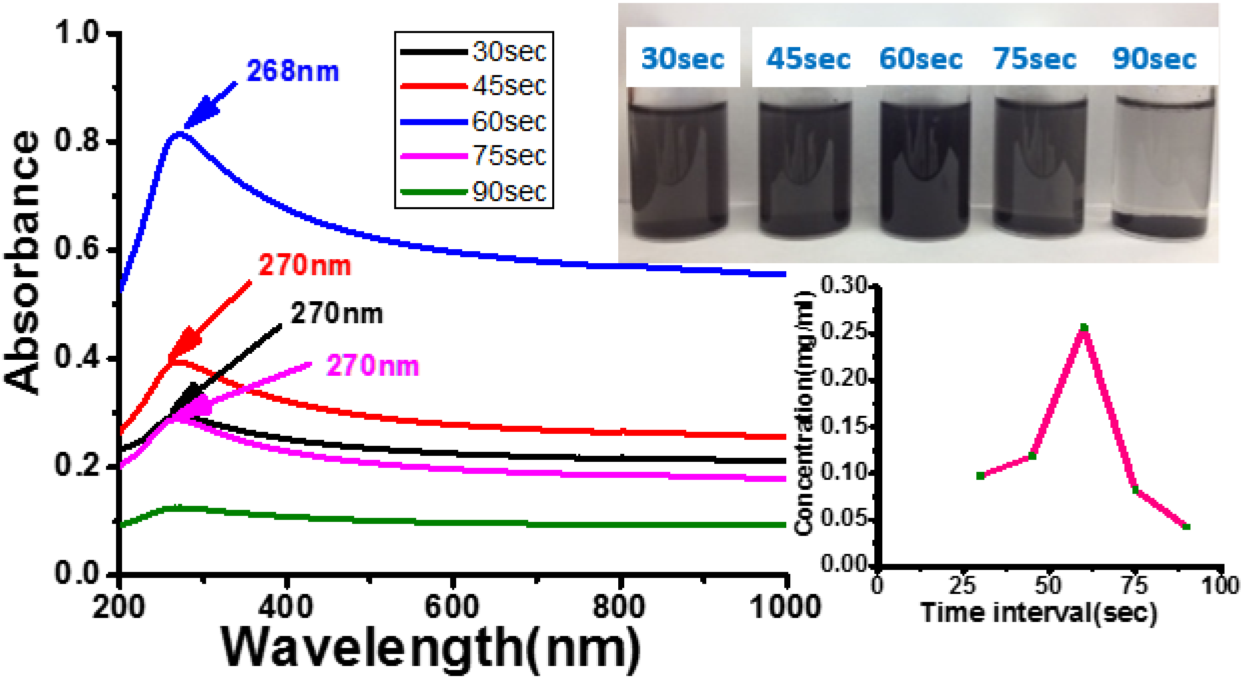


Figure S5. UV-Vis spectra and digital pictures of the dispersed graphene solution to show the yield of the products depends on the microwave irradiation time with the same microwave power (300 W). With 60 second of irradiation, the concentration of the dispersed graphene sheets reached the maximum.

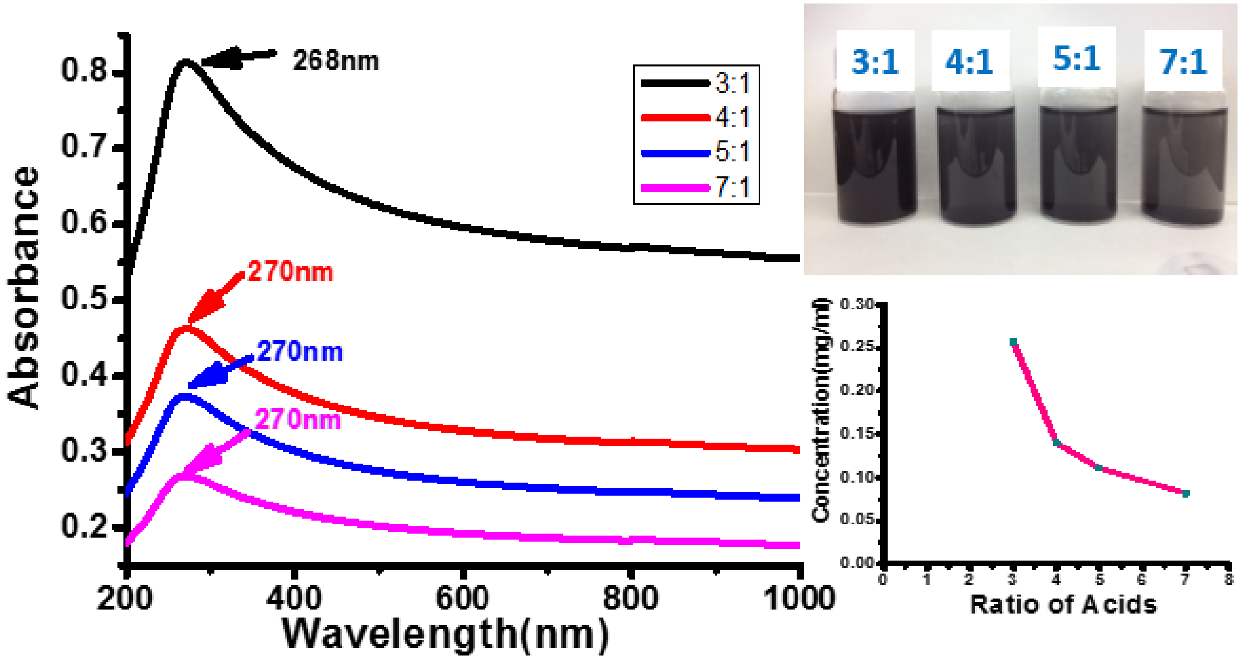


Figure S6. UV-Vis spectra and digital pictures of the dispersed graphene solution to show the yield of the products depends on the ratio of H_2SO_4 to H_2O_2 of the piranha solutions, with 3:1 ratio giving the highest production yield (Microwave irradiation time 60 seconds and microwave power of 300 W).

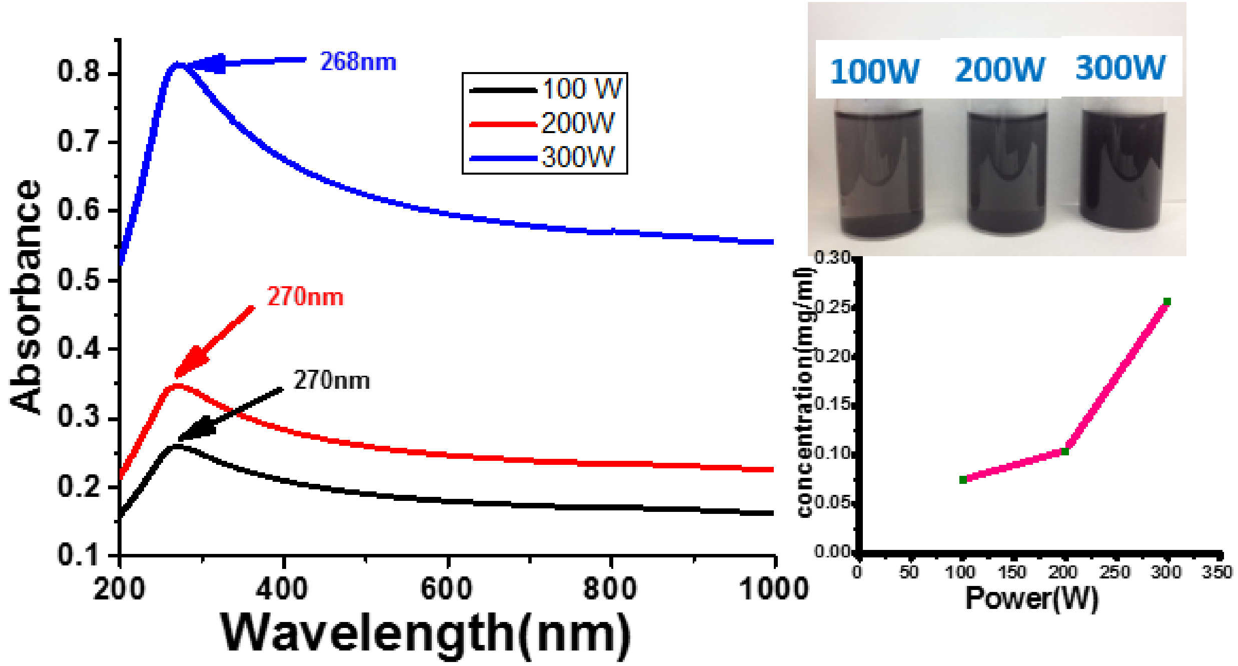
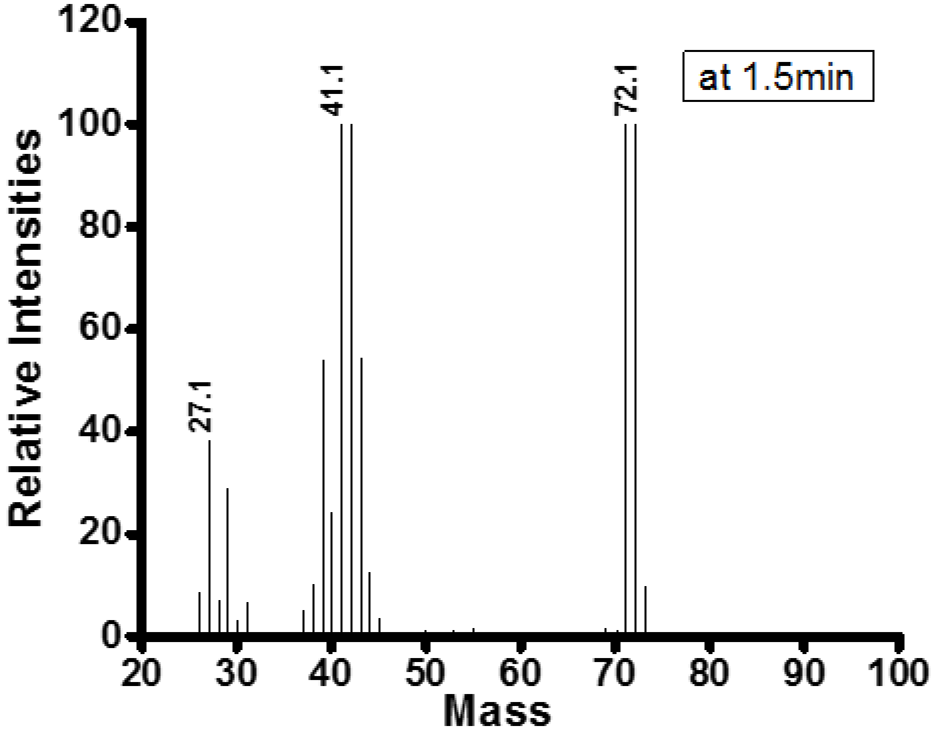
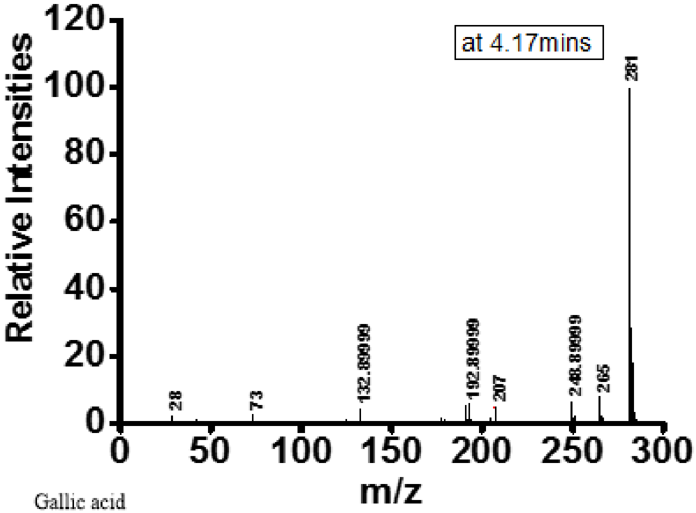


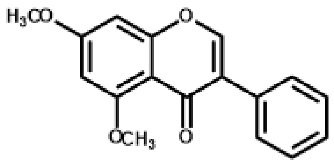
Figure S7. UV-Vis spectra and digital pictures of the dispersed graphene solution to show the yield of the products depends on the microwave power.

Figure S8. Mass Spectra at different retention time in the GC spectrum showing in Figure 6B.





5,7 dimethoxy isoflavone
score 0.71
hit 24
C17H14O4



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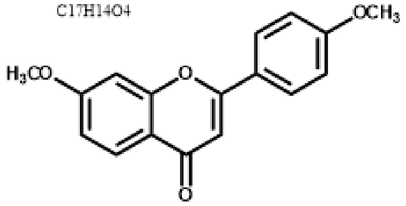

Gallic acid
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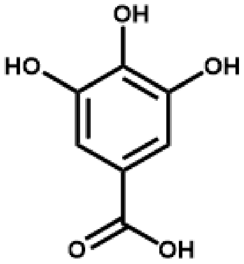
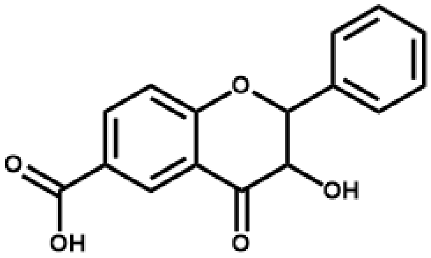
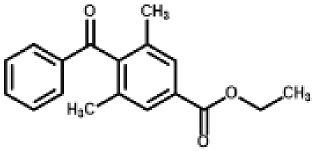
C7H6O5
score 0.64
hit36

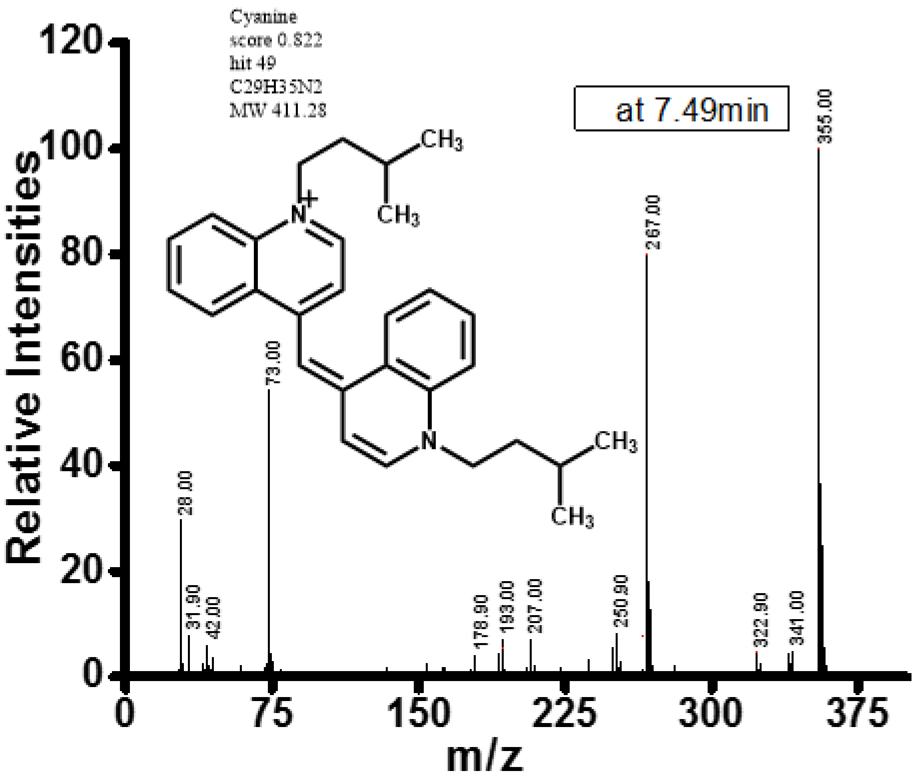


6- carboxy flavanol
Mw 282.053
C16H10O5
score 0.76
hit 23



Ethyl 4 benzoyl 3,5 dimethyl benzoate
Mw 282.126
C18H18O3
Score 0.79
hit 46




Cyanine
score 0.822
hit 49
C29H35N2
MW 411.28
at 7.49min
CH3
N+
CH3
N
CH3
CH3
Relative Intensities
120
100
80
60
40
20
0
0
75
150
225
300
375
m/z
28.00
31.90
42.00
73.00
178.90
193.00
207.00
250.90
267.00
322.90
341.00
355.00

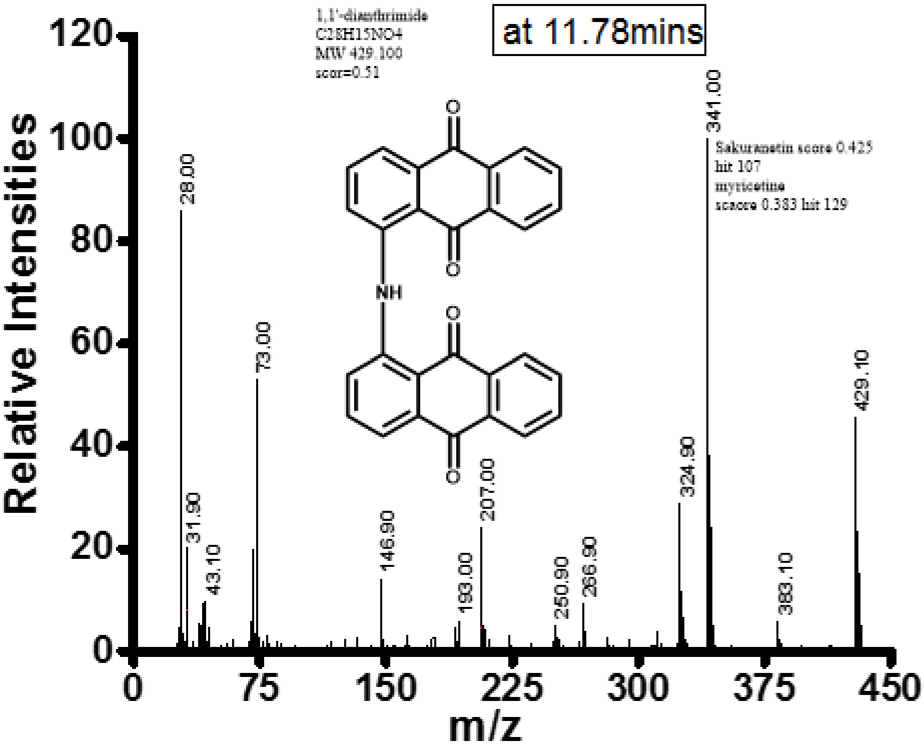
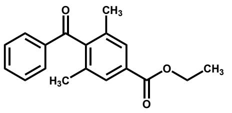
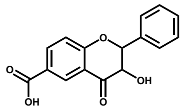
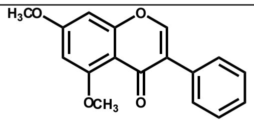
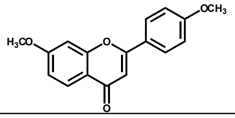
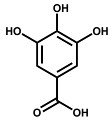
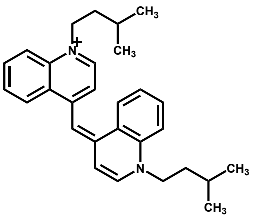
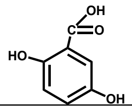
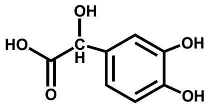
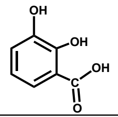

1,1'-dianthrimide
C28H15NO4
MW 429.100
scor=0.51
at 11.78mins
O
O
NH
O
O
Sakuranetin score 0.425
hit 107
myricetine
scaore 0.383 hit 129
Relative Intensities
120
100
80
60
40
20
0
0
75
150
225
300
375
450
m/z
28.00
31.90
43.10
73.00
146.90
193.00
207.00
250.90
266.90
324.90
341.00
383.10
429.10

Table S3 Detailed molecular structures and their score compared to the mass spectra in the mass bank database.

Name	Molecular weight	Mass Bank Score	Structure
Ethyl 4 benzoyl 3,5 dimethyl benzoate	282.126	0.79	
6-Carboxy Flavanol	282.053	0.77	
5,7 dimethyl isoflavone	282.089	0.71	
4',7 dimethoxy isoflavone	282.089	0.66	
Gallic acid	170.02	0.65	
Cyanine	411.280	0.82	
Gentisic acid	156.027	0.82	
3,4 di hydroxy mandelic acid	184.15	0.81	
2,3 dihydroxy benzoic acid	154.12	0.80	

Sample Preparation for characterization:

Surface Morphology:

Atomic Force Microscopy (AFM): AFM helps to determine the size and thickness (height) of the graphene sheets synthesized. The AFM samples were prepared by dropping 1-2µl of the dispersed graphene solution onto freshly cleaved mica surface and then allowing it to dry. The sample after drying is washed with water drop by drop to remove the dirt on the sample if by any chance accumulated and again dried. This sample is scanned using a Nanoscope IIIa multimode SPM (Digital instruments) with a J scanner for small scan size and G scanner for larger scan size operated in "Tapping mode". The AFM tips for imaging were 160 µm long rectangular silicon cantilever/tip assembly from AppNano was used with a resonance frequency of 160 kHz and a spring constant of approximately 7.7N/m with a tip radius of less than 10nm.

Scanning Electron Microscopy (SEM) and scanning Transmission Electron Microscopy (STEM): SEM samples were prepared by dropping 1-2µl of the sample onto silica substrate. The silica substrate is cleaned initially with piranha solution and then water and then dried with N_2 gas. The sample solution is dropped onto silica substrate and then allowed to dry for 2-3mins and then dried in N_2 gas to spread the sample throughout the substrate. The SEM images were captured using a Hitachi S-4800 Field Emission Scanning Electron Microscope (FE-SEM, Hitachi Co.Ltd.) under an accelerating voltage of 1-2KV and a probe current of 10µA to obtain images with high contrast. STEM samples were prepared by dropping 1µl of the sample on the Cu grid. After the samples are dried in air, they are imaged with a Hitachi S-4800 FE SEM under high accelerating voltage of 30KV and a probe current of 10-15µA with a working distance of 15mm.

X ray photoelectron Spectroscopy (XPS): XPS was pursued by depositing graphene solution onto a gold film of 1 × 1 cm^2 surface area. The deposited film has a thickness roughly 50nm. XPS data was acquired using a thermo scientific Kα system with a monochromated Al Kα X-ray source (hv=1486.7ev).

Raman Spectroscopy: Raman spectra is a more direct and non-destructive method which gives useful information about the quality of the graphene sheets. Raman spectra from films deposited on Alumina membranes were collected with a Kaiser Optical Systems Raman Microprobe with a 785nm solid state diode laser, the collection time is 60sec for each spectrum and collected three times on an average.

Optical and Electronic properties:

Cary UV-VIS spectroscopy 5000: The optical properties of the graphene dispersions were measured by the UV-VIS NIR spectroscopy. The spectra were obtained from Cary-5000 Ultra violet-Visible-Near Infrared Spectroscopy operated in double beam with 200-1000nm wavelength range.

Conductivity measurements:

First the sheet resistance of graphene films with controlled thicknesses was prepared by a vacuum filtration method through alumina anodic membranes **(**Whatman Ltd) with 0.2 µm pores. These films were dried in vacuum for 1 day to remove the residual solvent before conductivity measurements. The sheet resistance is measured by a manual four point resistivity probe from Lucas Laboratories, model 302. The conductivity of the films is calculated from the sheet resistance and thickness by the formula:

$$\text{Conductivity} = \frac{1}{Sheet\ resistance \times thickness}$$

This formula can be used to measure the films with thickness not more than half of the probe spacing (the distance between two probes of the four point probe instrument). The error in this case is less than 1%.

Rutherford Back Scattering technique for thickness measurement: The thickness of the film to obtain the conductivity in S/m for a given film of known sheet resistance is determined by Rutherford backscattering technique (RBS). Rutherford back scattering (RBS) was performed using a 2 MeV He2+ ion beam produced in a tandem accelerator with an ion current of 2–3 nA. Spectra were collected in the back scattering geometry and simulations were performed using the SIMNRA program (see detail in supplementary materials). The samples were prepared via vacuum filtration on Anodisc membranes and then transferred onto Si surface after etching the membrane in a strong base NaOH (4M), followed by washing with excess water until the pH of the solution becomes neutral. After transferring to Si surface, the samples were dried in vacuum and then the thickness of them is measured using RBS.

Gas Chromatography-Mass Spectrometry (GC-MS). The gas evolved during the reaction process is carefully collected through a syringe and 1ml of the gas sample taken from the headspace (total headspace volume: 5 mL) was injected into an Agilent HP6890 system, which was equipped with a HP-5-MS capillary column. For the filtrate, 10µl of the THF extracts was injected into the same GC-MS system by sampling through the septum of one of the four vials (THF extracts of the filtrate from nitronium oxidation approach, the filtrate from this Eco-friendly approach, and the filtrate from a control experiment *via* the Eco-friendly approach without adding graphite particles, and pure THF solvent. A temperature program was performed, starting at 50 °C held for 1 min, followed by temperature ramping at a rate of 10 °/min to a final temperature of 300 °C and held for an additional 1 min.

Rutherford Back Scattering (RBS)

For a given film of known sheet resistance, the conductivity can be analyzed as a function of its thickness. The thickness measurement of such thin films is characterized by the Rutherford backscattering spectroscopy (RBS) technique. Eco-ME-LOGr samples with varying thickness on silicon-oxide/silicon were analyzed. The measurements provided the elemental composition and the thickness of the various films under study.

Principle: For RBS measurement, we used a well collimated monoenergetic beam of He^{2+} ions directed onto and scattered from the target atoms (in the sample) due to columbic repulsion between the nuclei. The kinematics of the collision determine the energy of the scattered He^{2+} ion, which is less than its energy prior to collision (with the excess energy going into the recoiled atom/ion). We used an incident energy of approximately 2MeV. The He^{2+} ion energy loss during scattering depends on the mass of the target nucleus and the scattering angle. Additional energy is lost while passing through the film which gives rise to the depth sensitivity. Thus by monitoring the number of backscattered ions as a function of energy, the elemental composition and the depth distribution of elements can be determined. SIMNRA software is used to simulate the experimental spectra. If there is a good correlation between experimental and simulated data, then the simulation can be used to offer an accurate determination of the film thickness.

Eco-ME-LOGr samples with varying thicknesses on silicon-oxide/silicon were analyzed. The thickness of these films varied from 90 to 20nm depending on the quantity of the deposited material. With decreasing thickness the sheet resistance increased, as anticipated.

Data treatment

To illustrate the data treatment, a sample spectrum (Eco-ME-LOGr film on the substrate) is considered as shown in Figure S9. The spectrum shows the backscattered He^{2+} ions displayed in terms of energy channels. For the thickness calculation, the following procedure is utilized.

The *target* parameter in SIMNRA[5] software is the main parameter in controlling the simulated spectrum. For the sample, a total of 3 layers is considered with its elemental composition as follows: (1) Layer 1 consists of Eco-ME-LOGr hence the elemental composition are made of C and O (2) Layer 2 consists of Si and O (3) Layer 3 consists of Si (large thickness) from the substrate. The thickness and concentration parameters under *target* are varied to simulate the experimental data. Once a good fit is obtained under the *density calculation* parameter in SIMNRA, specifying the abundant element in the topmost layer (Layer1) displays the atomic density and this value is used for the thickness calculation. Thus, the product of the atomic density and the displayed layer thickness in terms of areal density provides a good approximation of the film thickness. There is some uncertainty in our total quantification due to small amount of oxygen present, which is not considered in the density but this is small and included as error in the thickness determination.

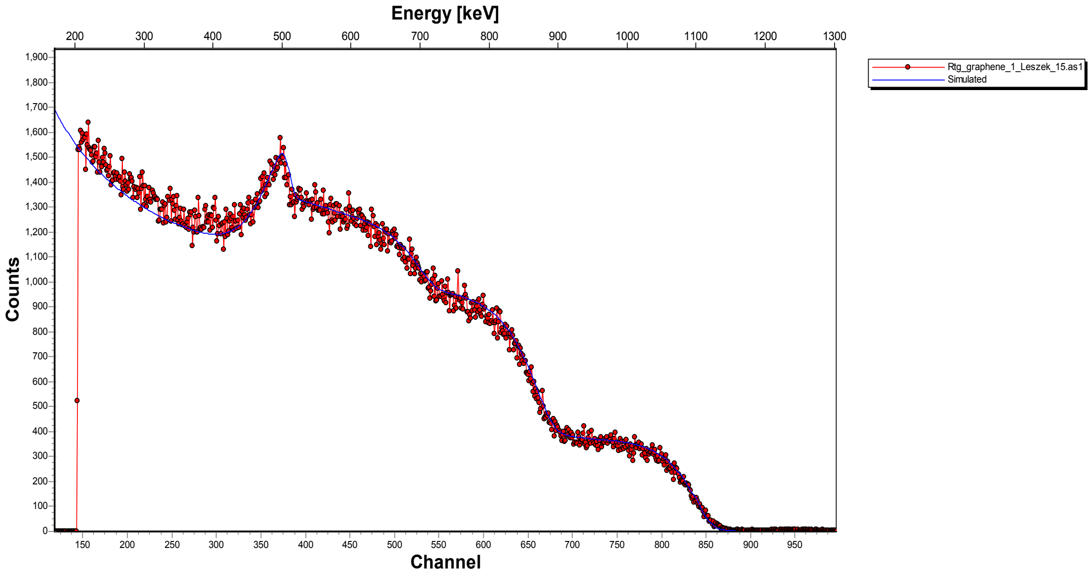


Figure S9 – SIMNRA simulated curve (blue) fitted to experimental data (red) with different elements in the sample

In another Ion beam based method to obtain the thickness, the difference in the leading edge between the pure substrate and the substrate with Eco-ME-LOGr film is analyzed as shown in Figure S10. The energy shift between the leading edges along with the stopping factor (from SRIM) gives the film thickness.

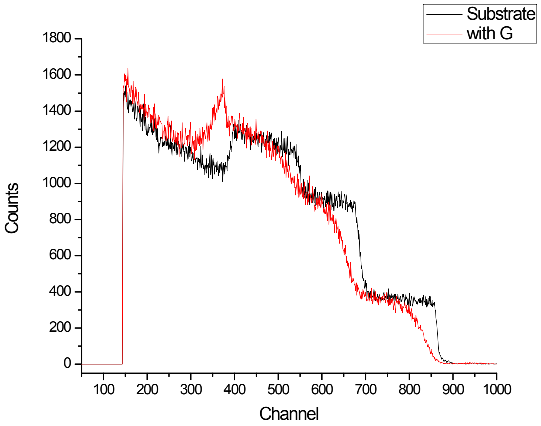


Figure S10 – Pure substrate (black) and substrate and film (Red) overlay of RBS spectra

Both these methods display a similar trend in the analysis of the various samples and the trend for the different thicknesses are shown in Table S4. The error for samples with thinner films is a little higher (8%) relative to the samples with thicker films (5%).

Thickness calculation of Eco-ME-LOGr film		
Sample	From SIMNRA (nm)	Using leading edge (nm)
1	88 ± 4	84 ± 3
2	75± 4	66 ± 3
3	66 ± 3	46 ± 2
4	44 ± 2	31 ± 1
5	42 ± 2	33 ± 1
6	26 ± 2	18 ± 1

Table S4. Thickness calculation of Gr film using two different methods.

X-ray Photoelectron Spectroscopy (XPS)

XPS characterization was performed after depositing Eco-ME-LOGr solution onto a gold film (The solution was drop casted onto the gold substrate repeatedly until sufficient thickness is achieved). XPS spectra were acquired using a Thermo Scientific K-Alpha system with a monochromated Al Kα x-ray source (hν = 1486.7 eV) and a hemispherical analyzer. The energy calibration was performed in-situ with respect to the Au substrate with the sample. The reference value of Au 4f 7/2 peak centered at a binding energy of 84.2 eV with a FWHM of 1.0 eV was used for calibrating the Au substrate. Energy shifts for normalizing with respect to the calibrated Au peak were not required as no charging was observed.

Casa XPS was used for the peak-fitting. For all the spectra, a Shirley background removal was applied followed by a Gaussian-Lorentzian hybrid function to fit individual peaks. The FWHM of deconvoluted peaks are a combination of intrinsic photoelectron core-hole lifetimes, instrumental broadening and film heterogeneity. Therefore; the FWHM was allowed to float within a narrow range to accommodate these effects. For carbon peaks, 0.9-1.2 eV was utilized whereas 1.6-1.9 eV was used for oxygen. Relative binding energies for the different carbon species were obtained from the work of Briggs and Beamson, and are related to the absolute energy value for adventitious carbon, as noted above[6]. The graphitic carbon peak was assigned a fixed energy of 284.2 as per the literature value of HOPG.[7] Further analysis was performed to analyze the specific bonding present in each material. The oxygen free carbon is mainly derived from the C 1s peak of aromatic rings (284.2 eV), and that of the aliphatic rings and/or linear alkylinic carbon chains (284.7 eV). The peaks for oxygen containing carbon with various functionalization are assigned as follows: C-

OC and C-OH (285.8 eV), C-OC=O (287.5 eV), C=O and O-C-O (288.7 eV), O-C(=O)-O (289.7 eV) [3].

References

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