# Biomass derived solvents for scalable production of single layer graphene from graphite#

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**Experimental Section:**

**Materials:**

Graphite nano powder (average particle size: 400 nm) was purchased from SRL Chemicals, Mumbai, India. Bio-solvents such as levulinic acid (LA), ethyl lactate (EL), ɣ-valero lactone (GVL) and formic acid (FA) were used for the exfoliation of graphite to graphene. These bio-solvents were purchased from TCI Chemicals, Tokyo, Japan and Merck Chemicals Pvt. Ltd., Mumbai, India, respectively. All chemicals are analytical grade and were used as received.

**Method of the exfoliation of graphite:**

To prepare the respective sample for the exfoliation of graphite, 100 mg of graphite powder was added to a glass vial containing 20 ml of bio-solvents (LA/FA/EL/GVL). The solution was then sonicated for the desired time (typically 30 min, 60 min, 90min and 120 min) using a ultrasonic water bath. After that, centrifugation was performed at a velocity of 5000 rpm (optimised) for 1 hour using an Tarsons Spinwin centrifuge machine. After completing the vial was removed carefully and typically the upper layer solution was transferred to a another clean vial containing graphene. The solution was then washed with milli-Q water followed by centrifugation at 13000 rpm for 15 min. for several times to remove the residual solvents and stay in desiccator under reduced pressure to obtained dried graphene.

In case of exfoliation of graphite using LA, the graphite dispersion after sonication for 120 min (optimised) was kept at room temperature for 24 h. During this period formation of graphene doped crystal of LA was found. Thereafter, this crystal was melted followed by centrifugation at 5000 rpm to obtained single layered graphene.

**Characterization:**

UV-Vis absorbance spectra were recorded on a CARY 500 Varian 8.01 UV-Vis spectrophotometer. Transmission electron microscope (HRTEM) images were recorded on a JEOL HR-TEM (JEOL JEM 2100, Japan) instrument operated at accelerating voltage of 200 kV. Atomic force microscopy (AFM) imaging was carried out on an Ntegra Aura atomic force microscope (NTMDT, Moscow) instrument in semi-contact mode using an NSG 01 silicon probe. Powder X-ray diffraction patterns were

recorded at 298 K on a PANanalytical system using Cu anode, Ka radiation (λ = 0.15405 nm) with $2\theta$ range from 5º to 80º at a scan speed of 0.1º $s^{-1}$. Fourier transform infrared (FT-IR) was performed on a Perkin-Elmer FT-IR machine (Spectrum GX, USA) using KBr pellets in the range 4000–400 $cm^{-1}$. Raman spectroscopy measurements were taken using a micro-Raman system (Horiba Jobin-Yvon LabRAM HR800 UV-Vis m-Raman) with argon sourced laser excitation at 514.5 nm employing power 10 mW in the scanning range of 100–4000 $cm^{-1}$. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Multilab-2000 (Thermo-scientific UK) spectrometer using a monochromic AlKα X-ray source (1486.6 eV) with scan 1 eV to 1100 eV.

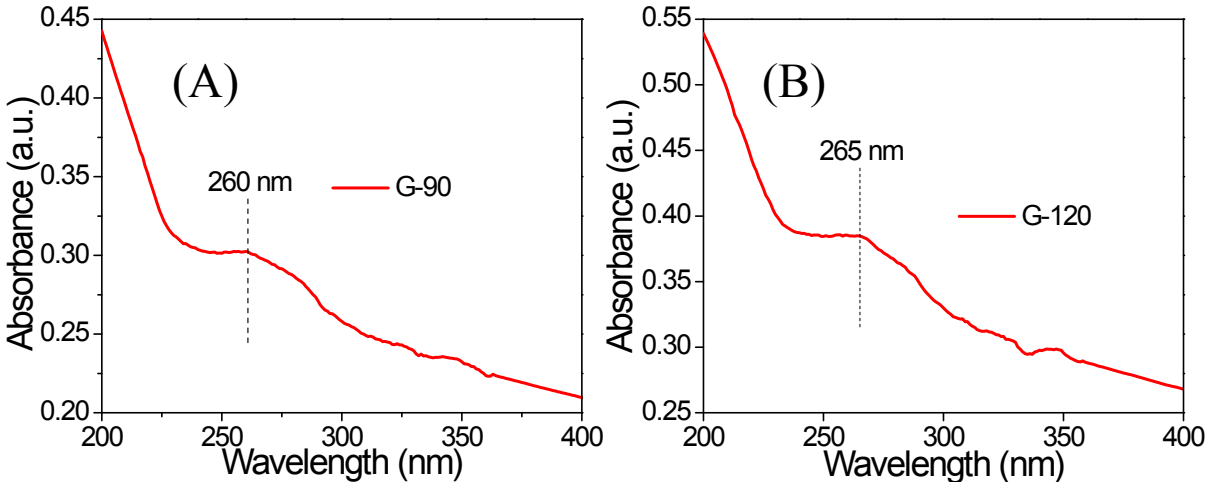


**Figure S1:** UV-Vis spectra of graphene obtained via sonication in levulinic acid for ultrasonication duration of 90 min (A) and 120 min (B).

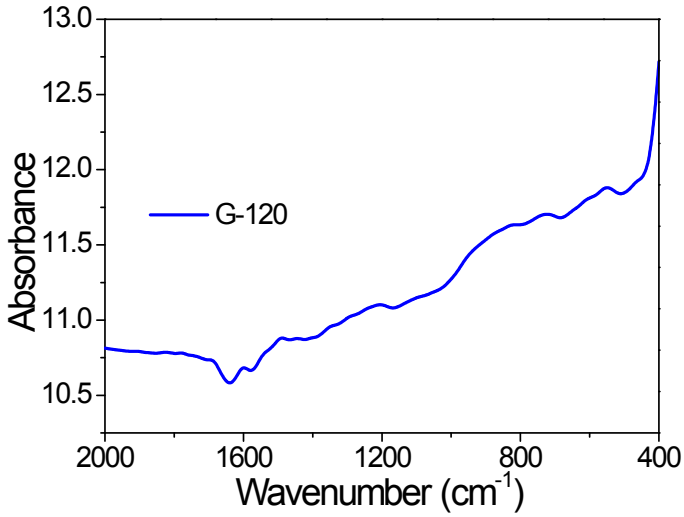


**Figure S2:** FT-IR spectra of graphene (G-120) obtained after ultrasonication of graphite in LA for 120 min.

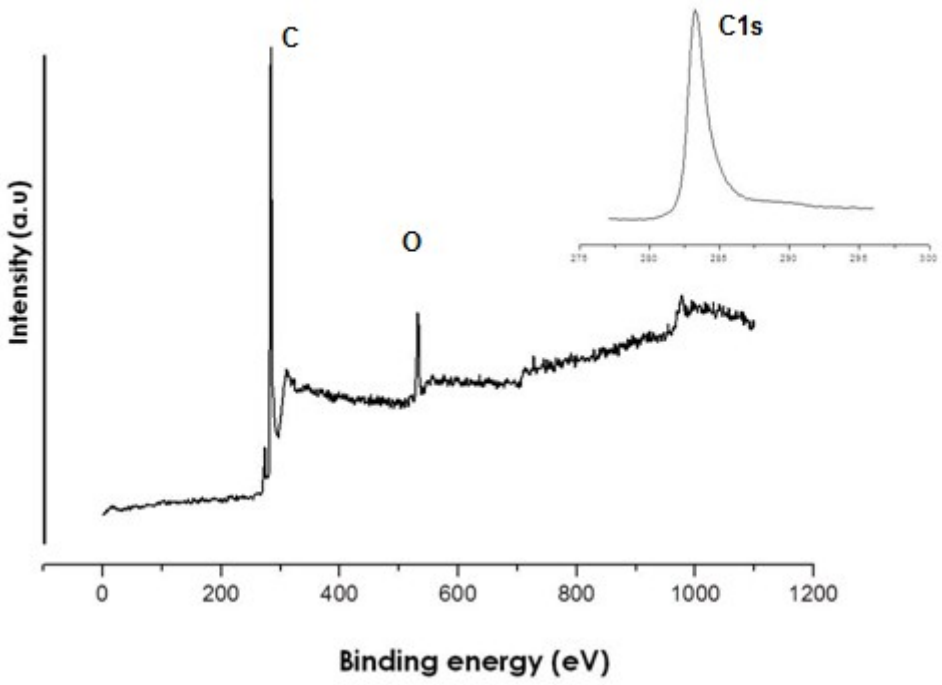


**Figure S3** : XPS survey spectra and high resolution C1s spectra of graphite.

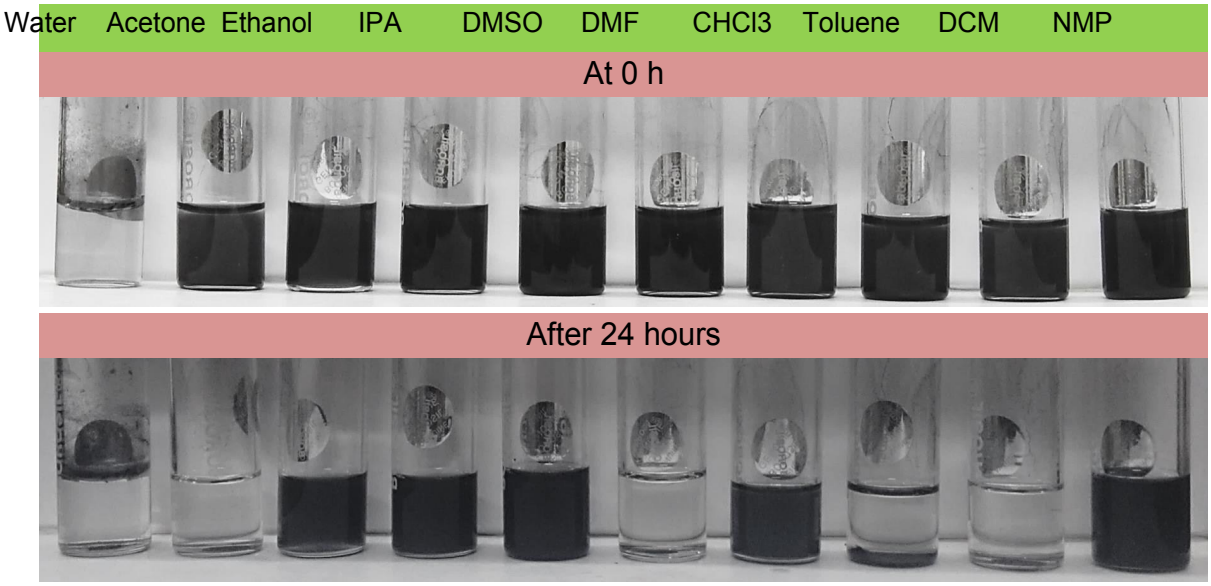


**Figure S4:** Dispersion of graphene (G-120) in different organic solvents at 0 h (top raw) and after 24 h keeping at room temperature (bottom raw).

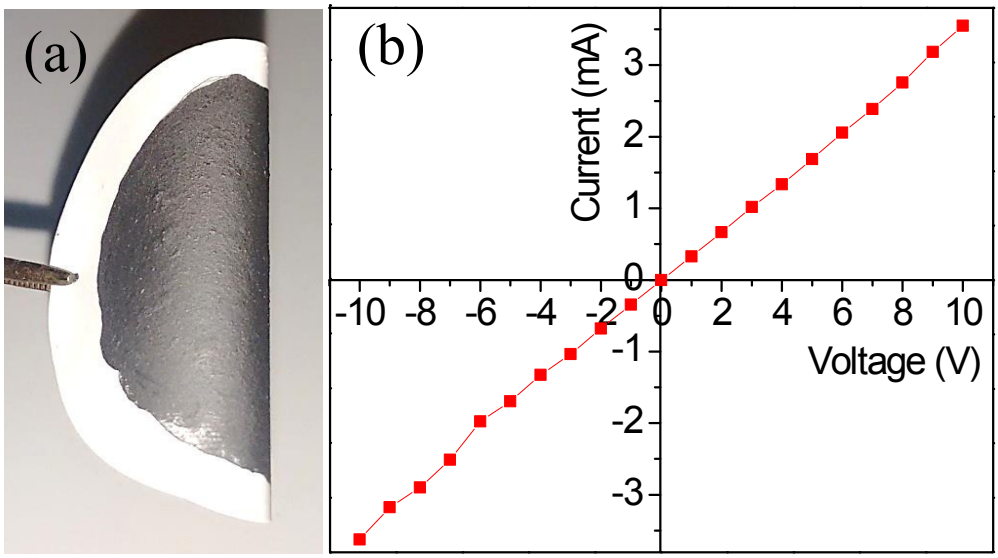


**Figure S5:** (A) Graphene paper (G-120) prepared on PVDF membrane; and (B) Its electrical conductivity.

**Table S1:** List of solvents used for the exfoliation of graphite to graphene using ultrasonication technique.

| Entry | Solvent | Method/ Time (h) | Conc. of exfoliated graphene ($mg.mL^{-1}$) | No. of graphene layers | $I_D/I_G$ ratio | Ref. |
|---|---|---|---|---|---|---|
| 1 | *N*-methyl-2-pyrrolidone (NMP) | Sonication / 0.5 | 0.01 | Monolayer (~1 wt%) | – | 1 |
| 2 | Aqueous NaOH (pH = 11.0) | Sonication / xx | 0.002–0.02 | Multilayer | 0.52 | 2 |
| 3 | Pentafluorobenzonitrile ($C_6F_5CN$) | Sonication / 1.0 | 0.1 | Multilayer | – | 3 |
| 4 | Hexafluorobenzene ($C_6F_6$) | Sonication / 1.0 | 0.07-0.08 | Multilayer | – | 3 |
| 5 | Octafluorotoluene ($C_6F_5CF_3$) | Sonication / 1.0 | 0.05 | Multilayer | – | 3 |
| 6 | Pentafluoropyridine ($C_5F_5N$) | Sonication / 1.0 | 0.05 | Multilayer | – | 3 |
| 7 | NMP | Sonication / 460 | 1.2 | Monolayer (~4 wt%) | – | 4 |
| 8 | NaOH + NMP | Sonication / xx | 0.07 | Few-layer | – | 5 |
| 9 | NaOH + *N,N*-dimethylacetamide | Sonication / xx | 0.06 | Few-layer | – | 5 |

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|---|---|---|---|---|---|---|
| | (DMA) | | | | | |
| 10 | NaOH + Benzylamine (BA) | Sonication / xx | 0.06 | Few-layer | – | 5 |
| 11 | NaOH + Cyclohexanone (CYC) | Sonication / xx | 0.05 | Few-layer | – | 5 |
| 12 | Chloroform | Sonication / 0.5 | 0.0034 | ≤ 5 Layers | – | 6 |
| 13 | Isopropanol (IPA) | Sonication / 0.5 | 0.0031 | ≤ 5 Layers | – | 6 |
| 14 | Acetone | Sonication / 0.5 | 0.0012 | ≤ 5 Layers | – | 6 |
| 15 | Chloroform | Sonication / 48 | 0.07 | ~10 Layers | – | 7 |
| 16 | IPA | Sonication / 48 | 0.07 | ≤ 5 Layers | – | 7 |
| 17 | Acetone | Sonication / 48 | 0.01 | ~10 Layers | – | 7 |
| 18 | CYC | Sonication / 48 | 0.2 | ~10 Layers | – | 7 |
| 19 | NMP | Sonication / 48 | 0.2 | ~10 Layers | – | 7 |
| 20 | DMF | Sonication / 48 | 0.2 | ~10 Layers | – | 7 |
| 21 | 1-Propanol | Sonication / 0.33 | 0.025 | Monolayer | – | 8 |
| 22 | Water-ethanol (40%) | Sonication / 1.0 | 0.01 | ~10 Layers | – | 9 |
| 23 | Water-IPA (55%) | Sonication / 1.0 | 0.02 | ~10 Layers | – | 9 |
| 24 | Ortho-dichlorobenzene (ODCB) | Sonication / 0.5 | 0.03 | Fewlayer/monolayer | – | 10 |
| 25 | Levulinic acid | Sonication / 2.0 | 0.065 | Monolayer | 0.57 | Present study |
| 26 | Levulinic acid | Sonication / 1.5 | 0.049 | Few layer | 0.49 | |

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