

Supporting Information

Characterization

The structures of the HG and the PEEG powders were examined using a D2 X-ray diffractometer equipped with a Cu K α tube and a Ni filter ($\lambda = 0.1542$ nm). Raman spectra of these samples were recorded using a high-resolution confocal Raman microscope (HORIBA, Lab RAM HR) and a 514.5 nm Ar laser source. High-resolution transmission electron microscopy (HRTEM) images were recorded using a JEOL 2100F apparatus operated at 200 kV; for HRTEM measurement, a few drops of the HG or PEEG dispersion were placed on a Cu grid presenting an ultrathin holey C film. Scanning electron microscopy (SEM) was performed using a JEOL JSM-6500F scanning electron microscope operated at 15 kV. For preparation of the SEM sample, a PEEG dispersion was filtered through an AAO membrane (Anodisc; diameter: 47 mm; nominal pore size: 0.02 μ m); the solids were then dipped in EtOH to remove residual NMP; the flakes that floated on the surface of the EtOH were collected on a Si substrate for SEM measurement. The sheet resistance (R_s) of the vacuum-filtered graphene films was measured using four-probe method (Accent HL5500 Hall System).

S1 Detailed experimental conditions

The electrolytic solution, comprising KOH (5%, 200 mL) and (NH $_4$) $_2$ SO $_4$ (2.5%, 40 mL) at a pH of approximately 12, was preheated to an initial temperature of 70 °C. A cylindrical high-purity graphite rod (HG) was used as the cathode connected to a voltage supply unit (negative voltage output); the cathode diameter and length were 6 and 100 mm, respectively. Another HG rod (diameter: 6 mm; length: 150 mm) was used as the anode in the electrochemical system for the plasma-assisted electrochemical exfoliation process (PEEP). The HG tip surface cathode was placed about 1 mm above the surface of the electrolytic solution, while the anode was submerged in the electrolytic solution. Both electrodes were connected to a regulated DC power supply (TES-6220) with the bias voltage increased gradually to 60 V, resulting in discharging plasma in the area adjacent to the HG tip surface cathode and the electrolytic solution. The temperature of the solution within the beaker was measured during the process using a conventional mercury thermometer; it was maintained at approximately 70–80 °C. To enhance exfoliation and the homogeneity of the reaction, a magnetic stirrer was placed in the beaker with its rate of spinning maintained at 200 rpm. When a sufficiently high potential of 60 V was applied across the two

electrodes, electrochemical oxidation reactions were triggered with the simultaneous release of gases on the surface of anode and the generation of plasma on the HG tip surface cathode (see movie in SI); as a result, the surface of the graphite electrodes slowly disintegrated into micrometer-sized sheets and dispersed into the electrolyte. The tip position of the cathode was lowered to maintain an approximate current range from 0.6 to 1.2 A. The length of time in which the samples experienced simultaneous treatment was 5 min. Fig. 1a provides a schematic representation of the equipment setup. After cooling to room temperature, the resulting exfoliated graphite flakes were collected through vacuum filtration of the solution through PVDF membranes (average pore size: 0.2 μm) supported on a fritted glass holder. The prepared products were washed with DI water and dried at 50 $^{\circ}\text{C}$ under vacuum for 24 h. After peeling off the PVDF membrane, the powder prepared from PEEP, described herein as plasma-electrochemically exfoliated graphene sheets (PEEG) was stored in a drying box at 50 $^{\circ}\text{C}$ until required for use.

Preparation of PEEG dispersion

The obtained PEEG (15 mg) was added to N-methyl-2-pyrrolidone (NMP, 15 mL) to create PEEG dispersion (1 mg/mL) when treated with an ultrasonic cleaning bath, operated at 20 kHz and a power of 130 W for 10 min.

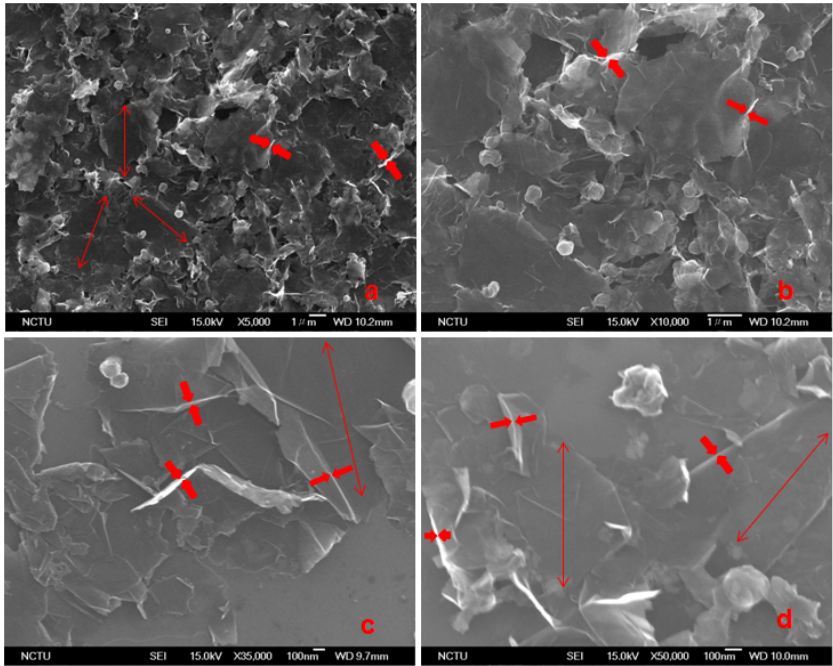
Table 1 lists the calculated amounts of the various functional groups in the HG and PEEG samples, based on the areas under these XPS peaks. The atomic percentage ratio of oxygen to carbon atoms in the PEEG [as determined from the small content of C–O bonds (ca. 4.2%)] was approximately 1:22.8, confirming that very slight oxidation occurred during our PEEP.

Table 1 Relative atomic percentages of carbon atoms in various functional groups in HG and PEEG, estimated based on the areas under the C 1s peaks.

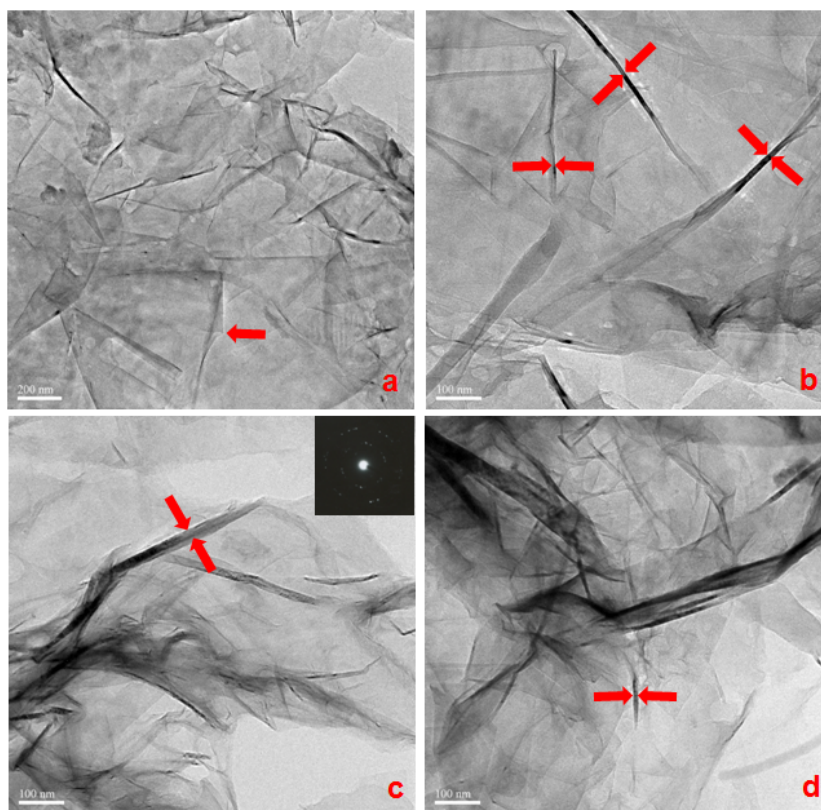
C=C (%)		C–C (%)	C–O (%)
HG	84	16	
PEEG	68	27.8	4.2

Table 2 Graphene sheets produced with plasma-assisted and conventional electrochemical exfoliation methods

Electrochemical method	Experimental conditions KOH (5%, 200 mL) and (NH ₄) ₂ SO ₄ (2.5%, 40 mL), 80°C, 5 min	Average graphene sheet diameter (μm)	Thickness of a single nanoplatelet (nm)	Potential applied	Yield of product (filtrated with 200nm PVDF)
Plasma- assisted	HG tip cathode barely above the surface of electrolyte. HG rod anode submerged in electrolyte.	2.5	2.5	-60 V (I ~ 1.2 A)	32 mg
Conventional	HG rod submerged in electrolyte.	2.0	3.5	9.3 V (I ~ 3.1 A)	5 mg



S.2 (a) SEM images of PEEG, (b, c, d) high-magnification images; Two arrows pointing in opposite directions indicate the thickness of PEEG that was on the surface of the Si/SiO₂ substrate.



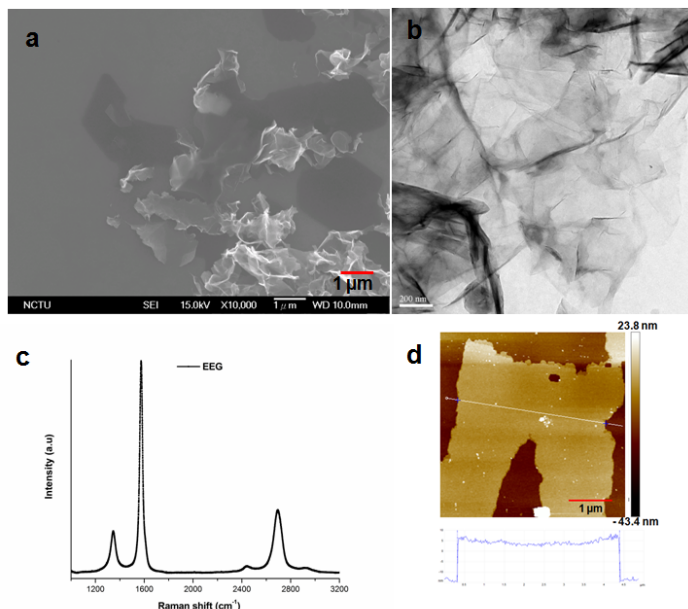
S.3 TEM images of PEEG, inset: corresponding SAED pattern. Two arrows pointing in opposite directions indicate the thickness of PEEG that was on the top of the copper grid.

In the TEM images, the graphene sheets display flattened or scrolled feature that were conformably on a copper grid (Indicated by arrows in Fig. 2c, 2d and S.2, S.3 in IS). In addition, two sets of diffraction patterns can be identified in the SAED (inset of S.3c), resulting from the folded layers with different crystalline orientations. Furthermore, the X-ray diffraction pattern of the graphene sheets in the powder form show the same lattice structure as that of the original graphite, see Fig. 3a. Nevertheless, the diffraction peak of the platelets relating to (0 0 2) plane becomes significantly weaker than that of the graphite, and the peaks of (100), (101), and (004) plane is indiscernible, indicating that the thickness of platelet is largely reduced compared to that of the original graphite. These results indicate that the obtained material is a mixture of graphene sheets and graphite nanoplatelets with graphene sheets dominating.

S4. Demonstration movie

Demonstration movie 1: plasma-assisted electrochemical method.

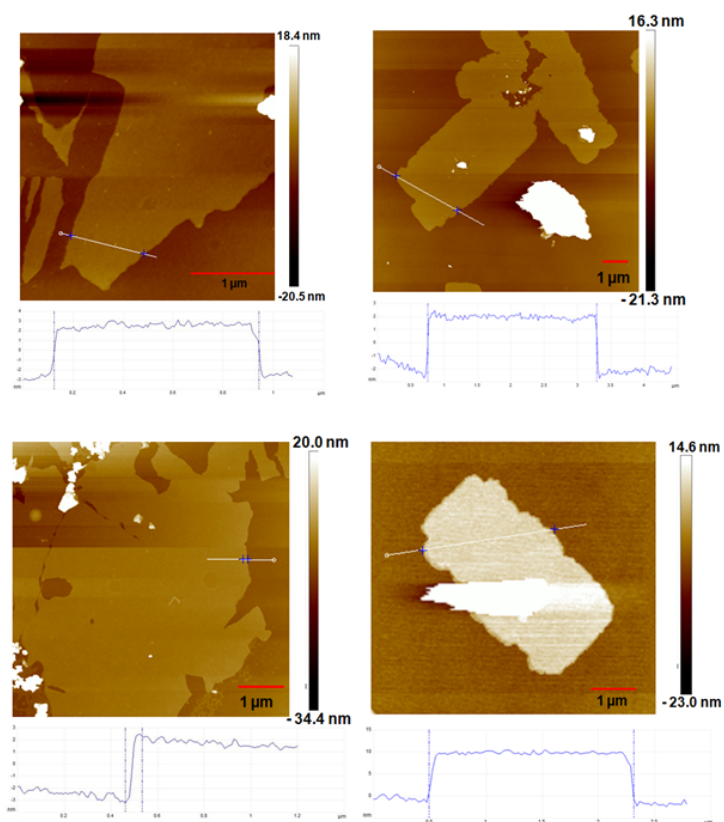
Demonstration movie 2: conventional electrochemical method.



S.5 (a) SEM high-magnification and (b) TEM images of electrochemically exfoliated graphene sheets (EEG), (c) Raman spectra of EEG, and (d) AFM image and height profile of a EEG sample deposited on a Si/SiO₂ substrate.

Fig.S5a and 5.b shows SEM and TEM images of electrochemically exfoliated graphene sheets (EEG) on the top of Si/SiO₂ and the copper grid, respectively, where they were rippled and entangled with each other. Image analysis calculations based on EEG nanosheets revealed that the average lateral dimensions was approximately 2.0 μm, with a thickness of approximately 10–30 nm, similar to that of PEEG, based on cross-sectional imaging of the folded edges of EEG. Note that, folded platelets depict an intrinsic to graphene nanosheets.

Fig. S.5c displays Raman spectrum of the EEG sample, revealing a weak D (defect) band, a prominent G (graphite) band, and an intermediate 2D (doubly generated G) band at 1343, 1576, and 2695 cm⁻¹, respectively. The 2D band of EEG had the high symmetry and shifted to a lower frequency relative to that of HG, suggesting the formation of graphene structures in EEG after electrochemical exfoliation.



S6. AFM image and height profile of a PEEG samples deposited on a Si/SiO₂ substrate.