

Supporting information for

A facile and fast electrochemical route to produce functional few-layer graphene sheets for lithium battery anode application

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Figure S1 : Electropolymerization curve of acrylonitrile in DMF containing TEAP (0.05 M) at 20 mV.S⁻¹

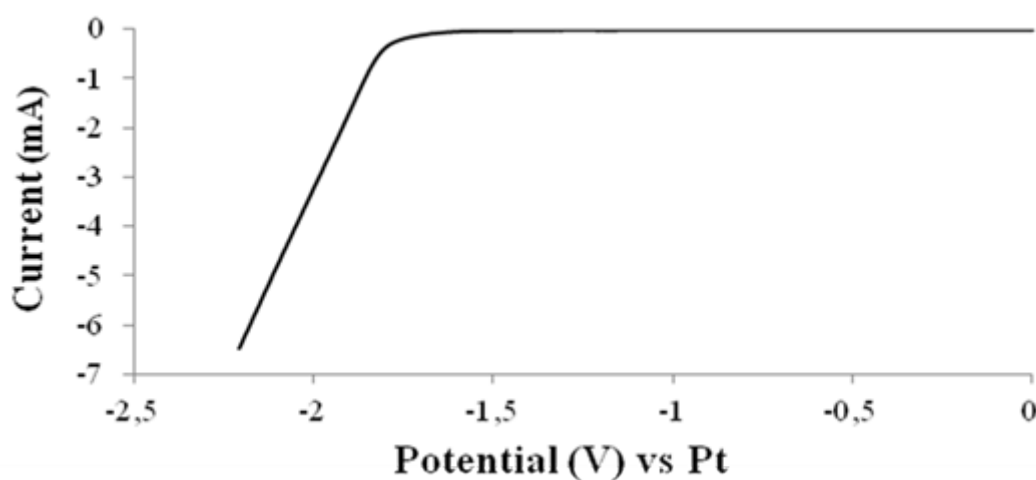


Figure S2: TGA analysis of pure PAN.

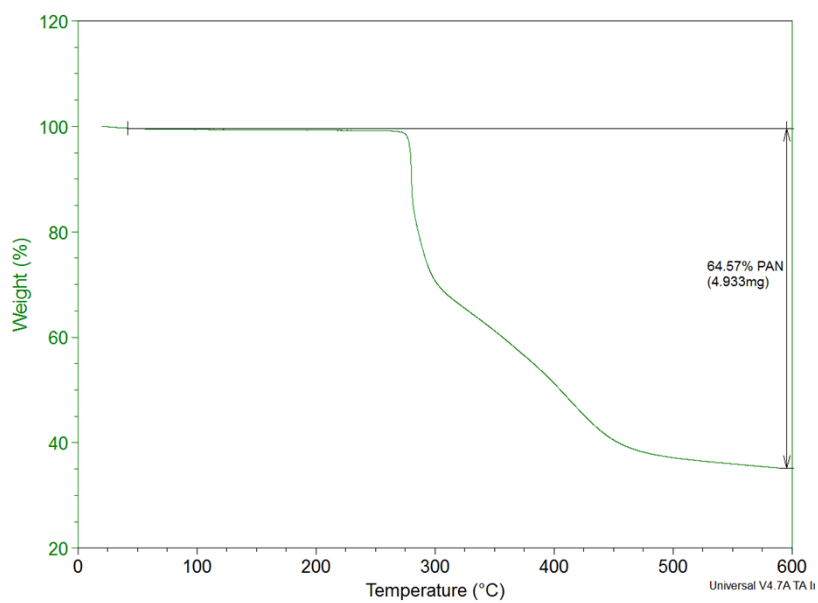


Figure S3: Large area AFM images acquired in the acoustic intermittent contact mode of exfoliated graphene sheet solution (0.1 mg/mL in DMF) spin-coated onto a mica substrate, (a) height and (b) phase.

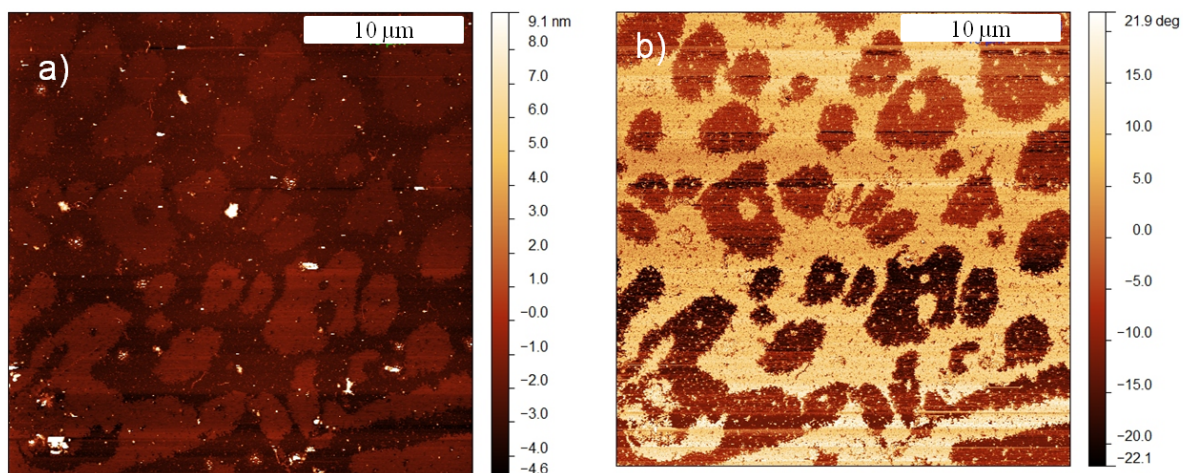


Figure S4: XRD spectra of pristine HOPG and of chemically exfoliated Gr-g-PAN.

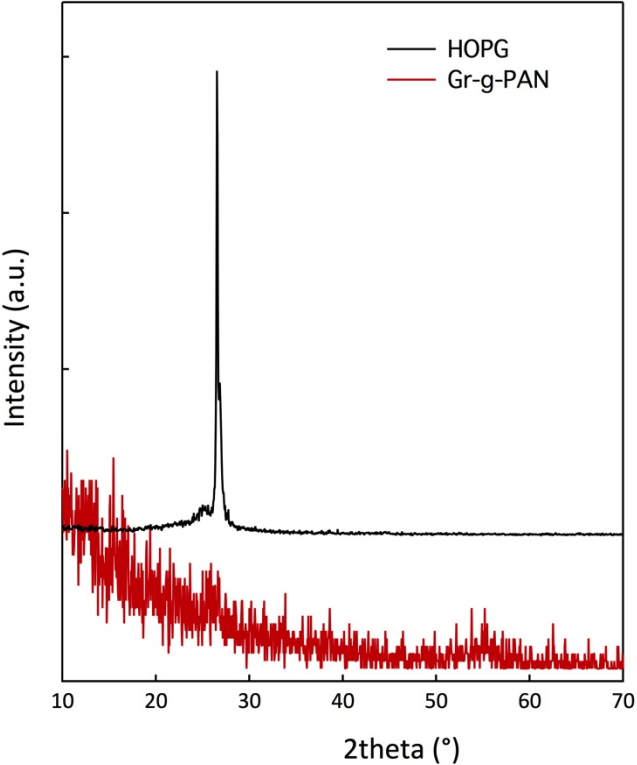


Figure S5: Scanning electronic microscopy image of graphene sheet film deposit on glass substrate (film thickness: 370 nm).

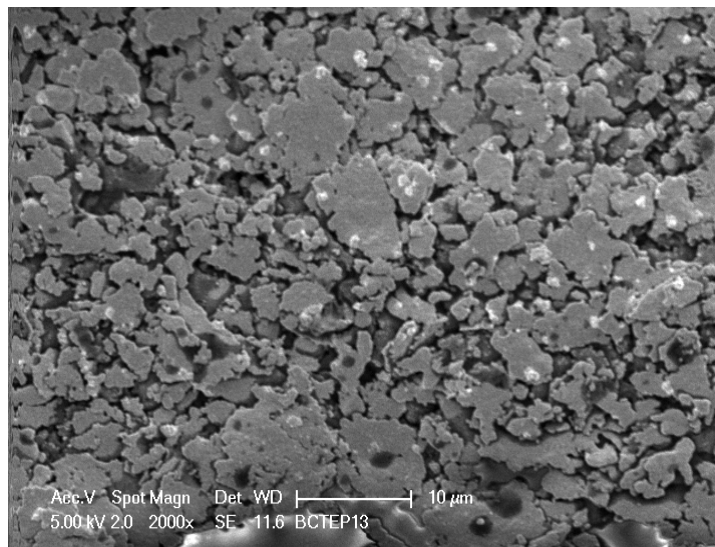
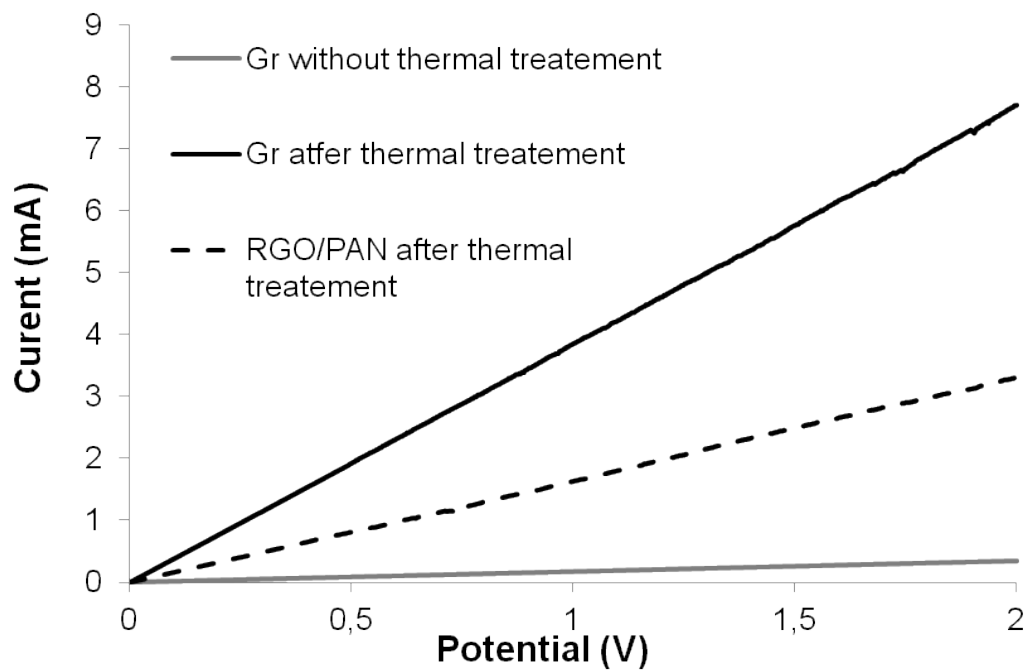


Figure S6 : I-V curves of exfoliated graphene (Gr-g-PAN) sheet film deposit on glass substrate before (grey) and after (dark) thermal treatment at 250°C superposed with composite reduced Oxide graphene (RGO)/PAN (10% of PAN) thermally annealed at 250°C.



Experimental section

Chemicals were obtained from Aldrich, and used as received. Solvents were distilled over standard drying agents under dry nitrogen. Highly oriented pyrolytic graphite (HOPG) (1 cm × 0.5 cm × 1 mm) was purchased from the SPI Co. Ltd.

Electrochemical exfoliation of graphene: an HOPG flake was employed as an electrode and source of graphene for electrochemical exfoliation. The HOPG was inserted as anode into acrylonitrile solution in DMF (1M), placed parallel to the Pt wire as counter-electrode with a separation of 2 cm and Pt as pseudo-reference electrode. The electrochemical exfoliation process was carried out by applying potential between the initial potential at open circuit (-0.1V) and -2 V, and kept constant at that value for 6 h. The exfoliated HOPG electrode was dispersed in DMF under ultrasonication (Branson 2510 Ultrasonic Cleaner, 40kHz) for 30 min. The dispersed graphene in DMF, after ultrasonication, was fractioned by centrifugation at different speed rates. Non-exfoliated graphene was eliminated with centrifugation at low speed rate (1000~2000 rpm) and, in the end of the centrifugation process, only the ultrathin modified graphene sheet remained in the DMF solution. The exfoliated graphene sheets were recovered by filtration on 0.45 μm filter and washed 5 times by DMF before drying under vacuum over night at 100°C.

Characterization:

Thermogravimetric analysis (TGA) was performed under nitrogen from room temperature to 600 °C with a Hi-Res TGA Q500 from TA Instruments at a heating rate of 40 °C/min. Transmission Electron Microscopy (TEM) observation was carried out on a TEM, Philips CM100. No staining was used since the graphene sheets were contrasting enough in the polymer matrix. Raman scattering spectroscopy was performed with a LabRam Spectrometer (Jobin-Yvon) equipped with a confocal microscope and an Andor BR-DD CCD detector. The excitation was carried out at 647.1 nm using a Spectra Physics Krypton laser. X-ray diffraction (XRD) patterns of Gr-g-PAN films deposited on SiO₂ substrate and HOPG sheet were measured by using a Bruker AXS D8 collecting the diffraction data in a 2θ range of 10–70°. Atomic Acoustic intermittent contact mode Atomic Force Microscopy (AFM) measurements were performed in air at room temperature using a PicoPlus 5500 microscope (Agilent Technologies, Inc.) and silicon cantilevers (PPP-NCH, Nanosensors, nominal spring constant 42 N/m). Gwyddion SPM data analysis software was used to analyse the data. The thickness of the graphene layer deposited onto a glass surface was evaluated between the average level of the layer and the average level of the substrate in a border area where the film had been mechanically removed. This measurement was repeated in seven different areas. Electrochemical measurements were carried out with a PAR EG&G potentiostat (model 273A) in a three-compartment cell equipped with a Pt pseudoreference electrode and a Pt counter electrode. All the electrochemical experiments were carried out in a glovebox under dry nitrogen. Scanning electron microscopy images were carried out with FEG-ESEM XL 30 microscope from FEI operated at 5 kV in high vacuum conditions

Preparation of thin film electrode: The graphene solution with the concentration of 1 mg/mL in DMF was dropped (0.1 mL) onto the cleaned glass substrate, followed by adding a drop (20 μ L) of deionized (DI) water. The thin graphene film was then self-aggregated at the solution surface. After that, the substrates were heated on a hot plate at 150°C for 30 min to evaporate the residual DMF. The operation of the deposition is repeated 4 times. For the thermal annealing process, the samples were loaded into a quartz tube in a furnace and heated at 250°C for 1 h under air conditions. RGO/PAN film was prepared by mixing RGO methanol solution with PAN DMF solution. The mixture was dropped onto glass substrate and heated at 250°C for 1 hour.

Conductivity measurements: The electrical conductivities of exfoliated graphene sheet were measured by the method of volume resistivity with a VMP3 biologic potentiostat. The resistance of the film was measured by cyclic voltammetry, applying a tension of 0 to 2V across the film and measuring the resulting current. The resistivity was calculated from the geometry of the graphene film (rectangle : 4 \times 7 mm) and its thickness (370 nm). To ensure a good contact between the electrode and the film, two copper threads were stuck on the film surface by silver paint (AGAR Scientific G3649 Electrodag 1415).

Electrochemical measurements: The working electrode was prepared by drop-casting of Gr-g-PAN DMF solution (1mg/mL) on Cu Foil, followed by adding a few drop of deionized (DI) water. After that, the substrates were heated on a hot plate at 150°C for 30 min to evaporate the residual DMF. The operation of the deposition is repeated 4 times and finally the working electrode was vacuum dried at 55°C for 12h. Disks of 2cm in diameter were used as working electrodes. Coin-cells were assembled using Li-metal foil as counter and reference electrode and a microporous polypropylene separator (CelgardP). The cell was activated by adding few drops of 1M LiPF₆ in 1:1 (v/v) mixture of ethylene carbonate and diethyl carbonate. Galvanostatic charge discharge cycling was performed using an Arbin Instruments BT-2043.