Electronic Supplementary Information

Persian waxing of graphite: towards green large scale production of graphene

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OUTLINE

1. Materials and methods:

Natural graphite flakes and graphite foil (0.13 mm thick) were purchased from Sigma Aldrich and Alfa Aesar, respectively.

Exfoliation and dispersion was obtained using a three-roll mill (80E EXAKT GmbH, demo version, Germany) equipped with silicon carbide (SiC) cylinders. The speed ratio is 1:3:9 between N_1 (feed roll): N_2 (center roll): N_3 (apron roll).

Sugar wax. 50 gr of commercially available refined saccharose, 25mL of distilled water and 50mg of citric acid were mixed into a 100 mL beaker. The mixture was gently stirred with a spatula and heated up on a hot plate at 300 °C until the mixture reached a temperature of 130 °C. Then the beaker was removed from the hotplate and 7 mL of glycerol (15 mL for loading test) were added to the hot wax and mixed gently with a spatula until homogenous. The gold coloured wax was then cooled down at room temperature using a water bath.

Exfoliation and dispersion protocol. Persian wax was spread on the feed roll (N_1). The roll-to-roll distance (gap size) was fixed at 5 µm and speed at 30 rpm. The excess of resin collected from the knife was removed until a thin adhesive film (< 5 µm) was homogeneously covering all the rolls and the knife was collecting no more resin. Then, the gap between the apron roll and the center roll was increased to the maximum (134 µm) and graphite foil (130 µm thick) was attached to the feed roll. The exfoliation was carried out in force mode (1.0 N/mm) between N_1 and N_2 while keeping the apron roll at the maximum distance (N_2/N_3 gap = 134 µm). The initial excess of graphite which was transferred to the apron roll (N_3) and removed from the knife was discarded. The apron roll was then further cleaned with a wet piece of paper. After 1h of exfoliation, Persian wax was added to the feed roll (N_1) and the N_2/N_3 gap was moved from 134 µm to force mode (1 N/mm) in order to collect the exfoliated material.

High loading test: the process was done by mixing graphite flakes (from 300 mg up to 6 gr) with 60 gr of the hot Persian wax (15 mL of glycerol) with a spatula before cooling it down to room temperature with a water bath. Then approximatively 10 gr of the mixture was fed into the TRM. The exfoliation was carried out in force mode (fixed applied force of 1.0 N/mm or 3.0 N/mm) at the minimum speed (30 rpm apron roll) for 1 hour, by continuously removing the mixture collected on the knife and feeding it again on the feed roll. The resulting black wax was then collected and characterized.

Preparation of the Samples for AFM and Raman. A small amount of wax containing the exfoliated material was firstly coated on VWR Weighing Paper, then the exfoliated material was transferred directly from the wax to Si/SiO2(90 nm) commercial substrates by pressing the paper onto the substrate surface. To remove the paper and the wax from the substrate this was soaked in warm water until the paper was spontaneously detached. The substrates were further rinsed with water to remove any trace of the wax.

Preparation of samples for STEM and HR-TEM analysis: a Lacey carbon-coated copper grid was gently immersed in the sugar-based paste. Later, sugar is washed away in a hot water bath.

Preparation of samples for XPS: drop-casting of a graphene dispersion in ethanol obtained after several washing steps of the paste with water and ethanol by centrifuge (7000 rpm) in order to solubilize and remove the sugar. The dispersion has been deposited on native silicon substrates.

XPS analysis were carried out using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer equipped with an aluminium X-ray source (energy 1.4866 keV) and working at pressure of 10-8-10-9 mbar in the main chamber. X-ray spot size was settled at 400 µm. Survey spectra were recorded as result of 10 scans with a pass energy of 200.00 eV and a step size of 1 eV; high-resolution spectra are average of 10 scans with a pass energy of 50.00 eV and a step size of 0.1 eV.

Raman spectra were recorded by a Renishaw microscope with a 100x objective, laser excitation wavelength of 532 nm and laser power of 1%.

AFM imaging was carried out in tapping mode using a Bruker Multimode V AFM, equipped with Nanoscope 5 controller.

2. Characterization of exfoliated material by microscopy techniques:

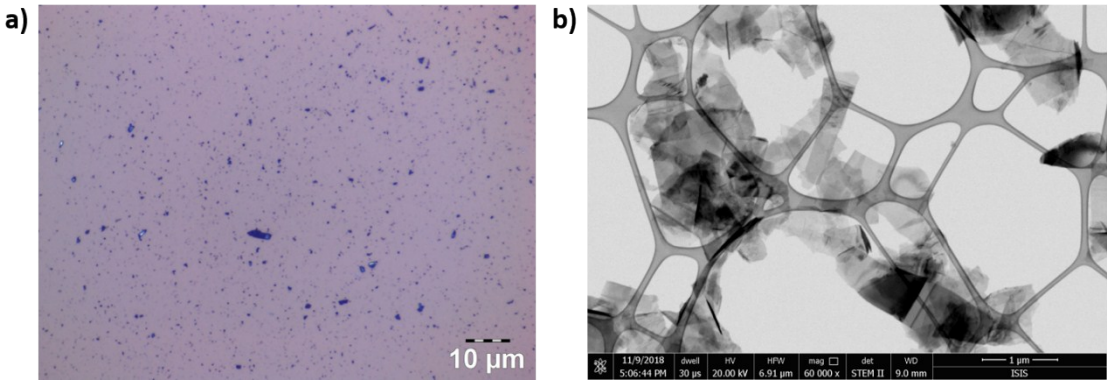

Figure S1. Characterization of graphene thin flakes by microscopies: a) optical microscopy; b) Scanning transmission electron microscopy (STEM).

3. Statistical thickness and flake size analysis by AFM and HR-TEM

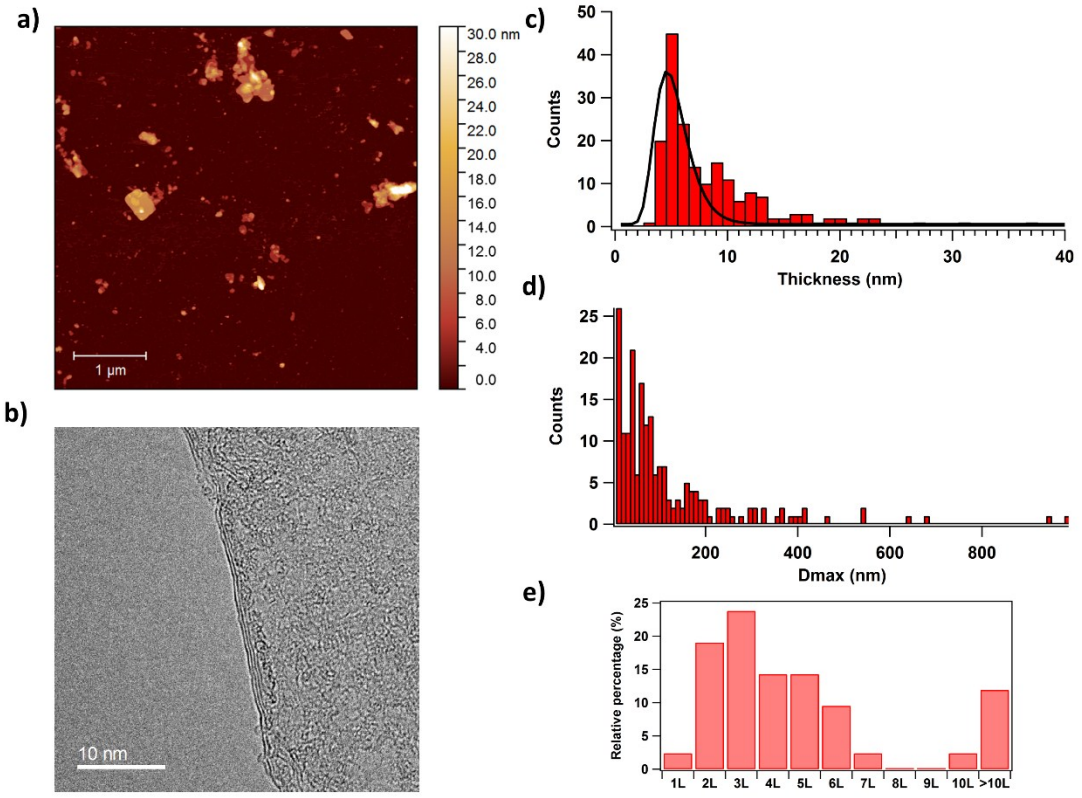

Figure S2. Characterization of material produced in high loading test (30% in weight of graphite flakes; fixed applied force of 1.0 N/mm): representative AFM; (a) and HR-TEM images (b) of FLG; Distributions of flakes thicknesses (c) and lateral sizes (d) measured by AFM. Lateral sizes are expressed as D_{max} that is the maximum dimension of the analysed particle in the horizontal plane; (e) Distribution of number of layers per sheet as determined by HR-TEM.

4. XPS characterization: a comparison with starting materials

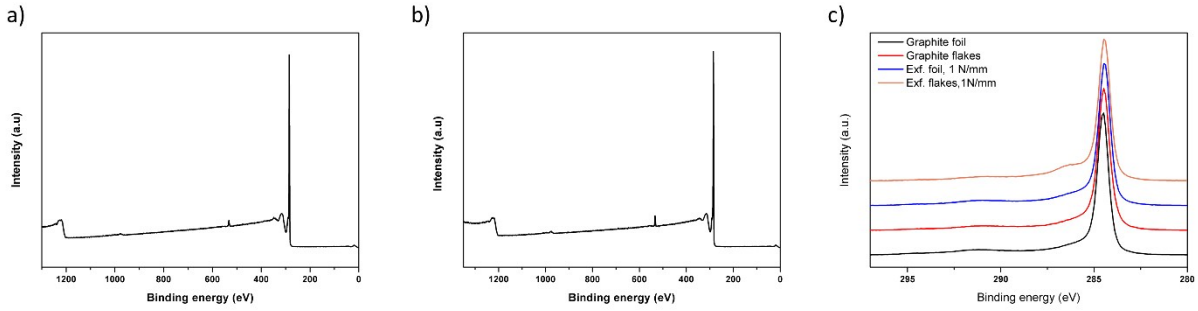

Figure S3. XPS characterization: survey of (a) graphite foil and (b) exfoliated flakes; (c) C1s spectra: comparison between exfoliated and starting bulk materials.

5. Raman spectroscopy

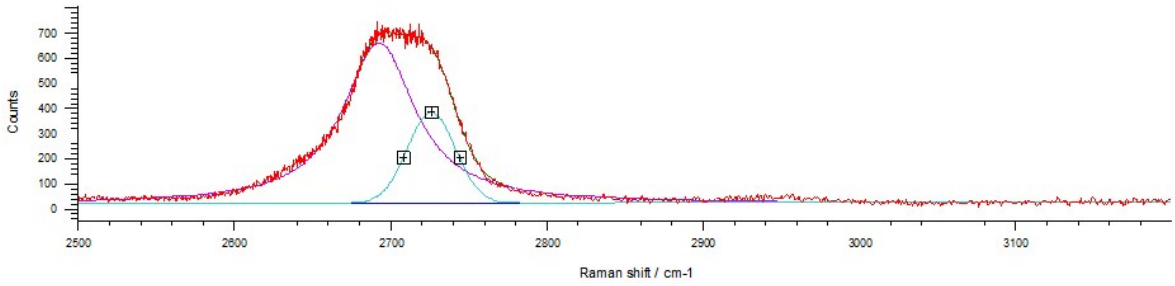

Figure S4. Magnification of Raman 2D band for FLG and its deconvolution in the two components $2D_1$ and $2D_2$.