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Graphite exfoliation in cellulose solutions

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Supplementary Information

Materials: Microcrystalline cotton linter cellulose (high purity grade) from Sigma-Aldrich, NaOH (≥98% purity) from Vetec and graphite powder (≥98% purity) from Synth.

1. Zonal sedimentation

Sedimentation in a density gradient was used to separate particles from all samples by size and density. A CsCl aqueous solution gradient was used to separate graphite or graphene mixed with cellulose. A gradient was prepared by mixing two CsCl aqueous solutions containing 1% NaOH, where the top layer was a 30% CsCl solution (1.29 g/cm³ density) and the bottom layer was a 60% CsCl solution (1.79 g/cm³ density). When an aqueous mixture containing cellulose and exfoliated graphite is placed on top of the gradient, the larger particles sediment faster than the smaller ones, leaving smaller particles at the top. Zonal sedimentation was thus used to isolate and collect the smaller particles for examination in microscopes (Figure 3).

2. Transmission Electronic Microscopy

TEM measurements were performed using a Carl Zeiss Libra 120 instrument operated at 80 kV accelerating voltage with a tungsten filament. The microscope was equipped with an in-column omega filter. Brightfield images with low chromatic aberration were collected with a 15 eV-width energy slit selected to zero loss. The same configuration was also used to obtain 25 eV energy loss filtered images (EFTEM). The samples collected in the sedimentation experiments were diluted thousand-fold in water and a droplet of the dilute dispersion was placed over a parlodion-carbon coated TEM microscope grid. All data were registered using an Olympus Cantega G2 CCD camera (2048x2048 pixels) controlled by iTEM software.

Thicknesses of representative areas were estimated by collecting and analyzing energy loss spectra at selected regions. The spectra were acquired using the TEM in imaging-mode (EELS diffraction coupled) with a collection angle of 15 mrad. Based on relevant microscope settings and the mean atomic number of the sample, the iTEM software calculates an approximate electron inelastic mean free path, 92.37 nm. This value is used as a reference in the log-ratio method used to estimate thickness. Using this methodology, the thickness values estimated for aggregates of cellulose and exfoliated graphite vary between 20 and 286 nm (total of 37 measurements, Fig. S1). It is important to note that these thicknesses are not related to single graphitic particles and they refer to the sample fraction collected for TEM analysis.

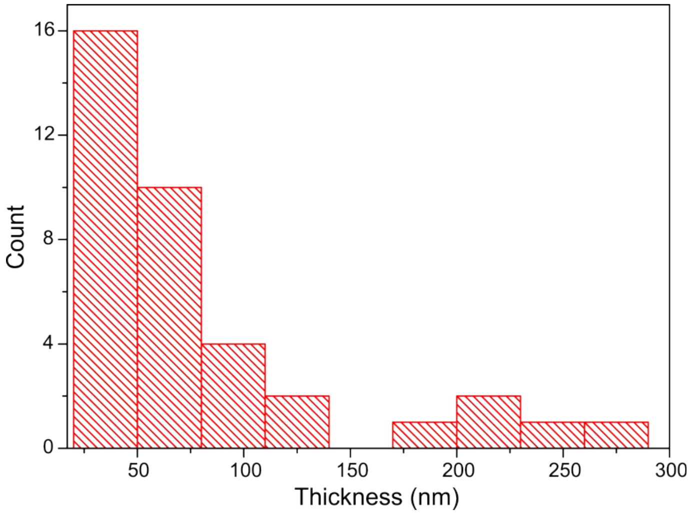

Fig. S1 Cellulose and exfoliated graphite aggregate particle thickness histogram (minimum 20 nm, maximum 286 nm).

3. Atomic Force Microscopy

Samples *g* and *k* were diluted thousand-fold in water, as in the TEM experiments, and deposited on one-side polished silicon wafers (Ted Pella) and then scanned using the intermittent contact and phase contrast modes (Shimadzu 9600 instrument). Phase mode was imaged with a silicon tip Nanoworld NCHR (resonance frequency = 300 kHz and force constant = 40 N/m).

KFM images were acquired in the same scanning probe microscope, with a silicon tip Nanoworld EFM-20 (resonance frequency = 79 kHz and force constant = 2.6 N/m). The KFM scanning system was enclosed within an environmental chamber to control temperature (25 ± 1ºC) and relative humidity (55%) during electric potential scanning. Topographic, phase mode and KFM images (512x512 pixels) were obtained at 0.25 Hz scan rate.

4. Thermogravimetric analysis (TGA)

Cellulose and exfoliated graphite particles from sample *i* were washed with deionized water and centrifuged at 10000 rpm, for 20 min at 20°C, until pH = 7. The remaining neutral particles were dried at 60°C to remove the excess of water. TGA was conducted at Ar flow of 100 mL/min, heating rate of 20°C/min, using a TGA 2950 (TA Instruments). The sample mass used was 12.9100 mg. In the beginning of the curve (Fig. S2), the weight loss of approximately 0.5% is related to residual water evaporation. At 300°C, there is a considerable weight loss (ca. 60%), due to cellulose pyrolysis,[1] indicating that cellulose stays adsorbed on exfoliated graphite particles. TGA data confirms that, in the micrographs, the plastic film that covers the graphitic particles is cellulose.

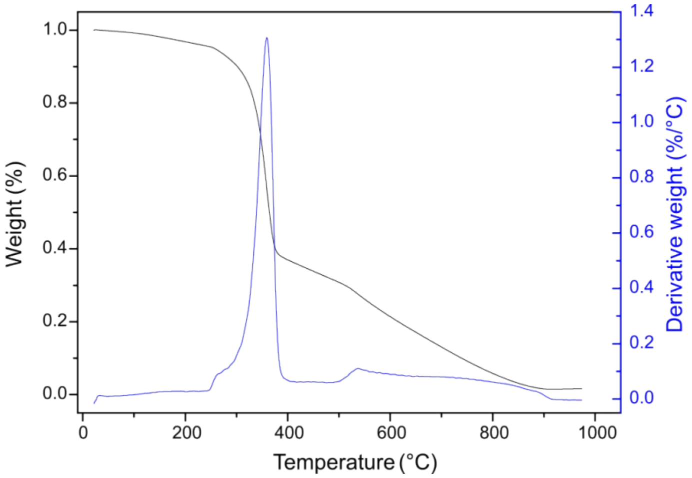

Fig. S2 Thermogram of exfoliated graphite and cellulose particles from sample "*i*", after NaOH removal.

5. X-ray Diffraction (XRD)

Thin particles were separated from sample *i* using centrifugation at 6000 rpm, for 1 h at 20°C. The supernatant containing exfoliated graphite particles, cellulose and NaOH was washed with deionized water and centrifugated at 10000 rpm, for 20 min at 20°C, until pH = 7. The remaining neutral particles were dried at 60°C to remove the excess of water. XRD was conducted using a diffractometer XRD7000 (Shimadzu), equipped with a Cu target operating at 40 kV and 30 mA. The scanning was made at 2°/min and step size of 0.02°. The region from 2θ = 18-28° was scanned at 0.5°/min for higher resolution. For comparison, the original graphite used in this work was also analyzed. Fig. S3 show peaks that correspond to cellulose II pattern[2] (2θ = 12, 20 and 22°) and a low intensity signal from graphite (2θ = 26.5°).

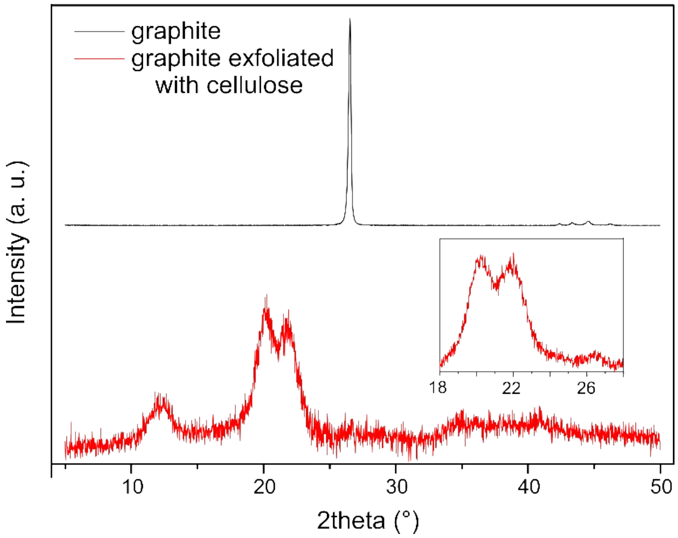

Fig. S3 XRD pattern of graphite (black) and graphite exfoliated with cellulose (red) from sample i, after NaOH removal.

6. Raman Spectroscopy

Thin particles were separated from sample *i* using centrifugation at 6000 rpm, for 1 h at 20°C. The supernatant containing exfoliated graphite particles, cellulose and NaOH was deposited on a Si/SiO_2 substrate. To remove NaOH, the sample drop on the substrate was washed with deionized water and gently dried with filter paper, many times. Pristine graphite and cellulose were dispersed in water and deposited on a Si/SiO_2 subtract and also analyzed, for comparison. Raman Spectroscopy was conducted using an XploRA spectrometer (HORIBA) equipped with a 100x objective, a 532 nm laser and 1 µm spot size.

7. Control experiments with pristine graphite

Self-supporting films containing the graphitic starting material (without cellulose) were prepared via dispersing graphite powder in isopropyl alcohol (Synth) up to a concentration of 10% in weight and immediately filtering the dispersion. After drying, a film of stacked graphite particles is formed on top of the filter paper. These particles are mildly attached to each other and the overall layer is loosely attached to the supporting paper. Samples from the films were characterized with SEM (Fig. S4) and AFM analyses (Fig. S5). SEM images were acquired in a JEOL JSM-6340F equipment operating at 5 kV accelerating voltage and spot size 40. Samples were fixed with carbon tape on a stub and sputtered with Au-Pd (8 nm). For TEM, the graphitic dispersion was centrifuged at 1000 rpm during 10 min and the upper fraction was characterized (Fig. S6).

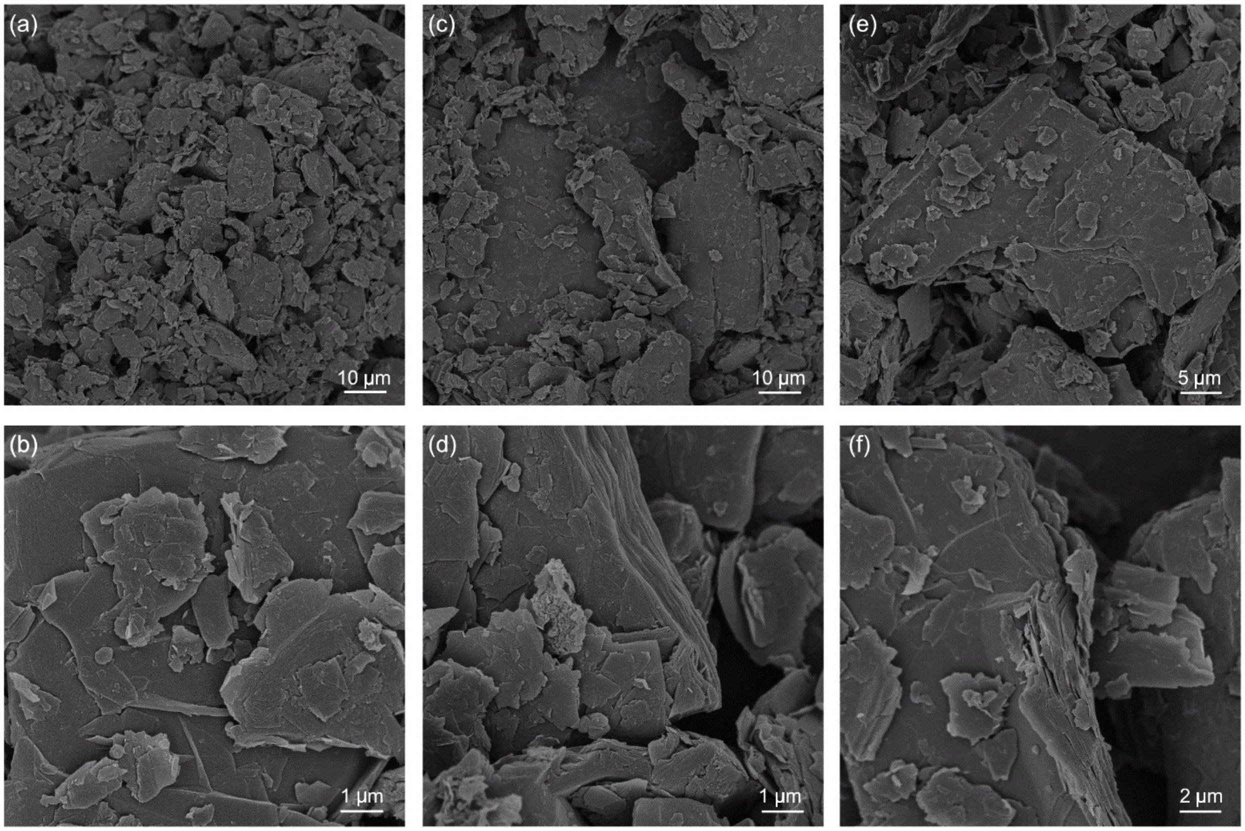

Fig. S4 Scanning electron micrographs of pure graphitic films. The images display relevant morphologic features found at different magnifications. Acceleration voltage of 15 kV.

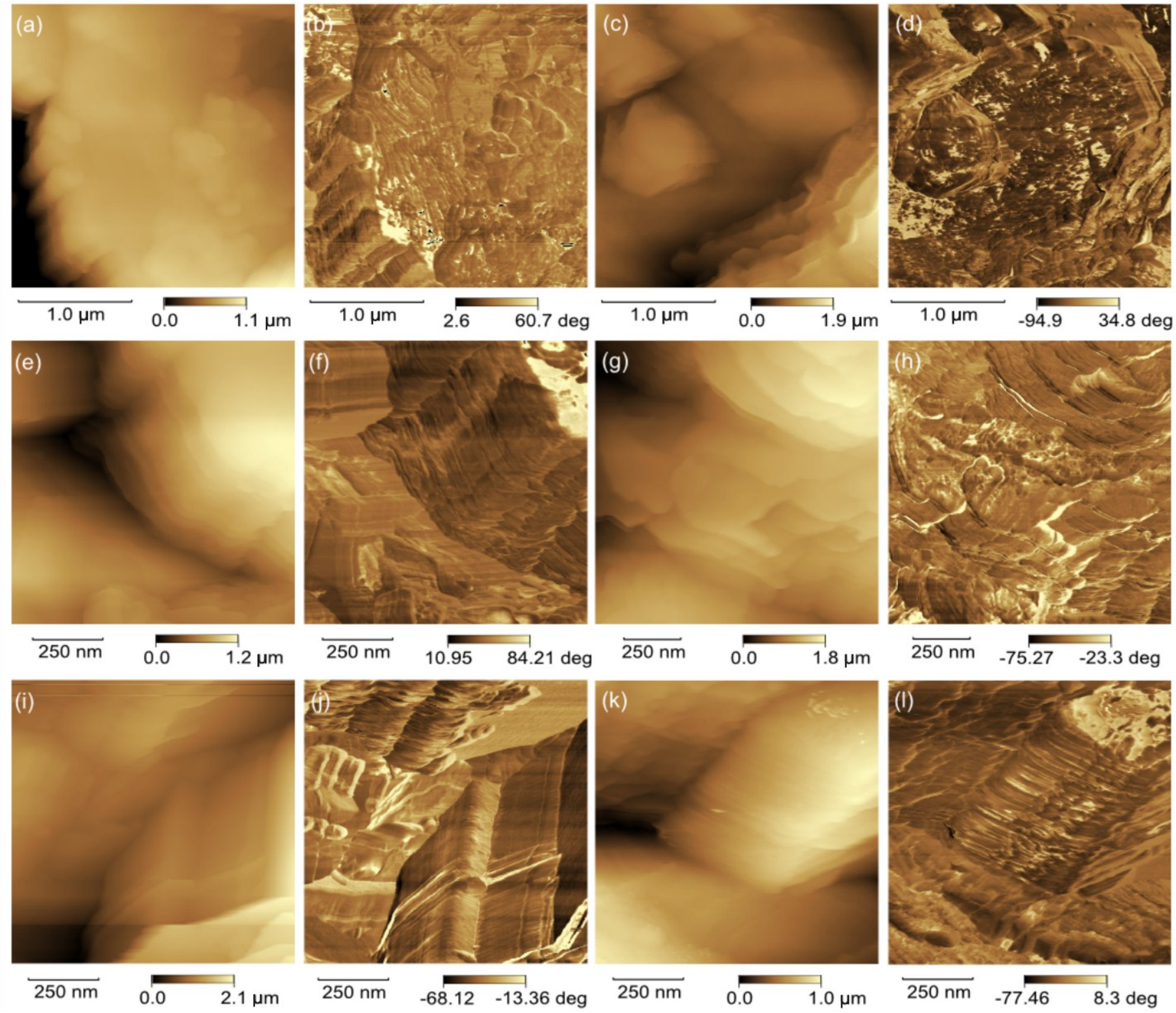

Fig. S5 Topographic and phase contrast images of pure graphitic films. The AFM images display relevant morphologic features found at different magnification levels.

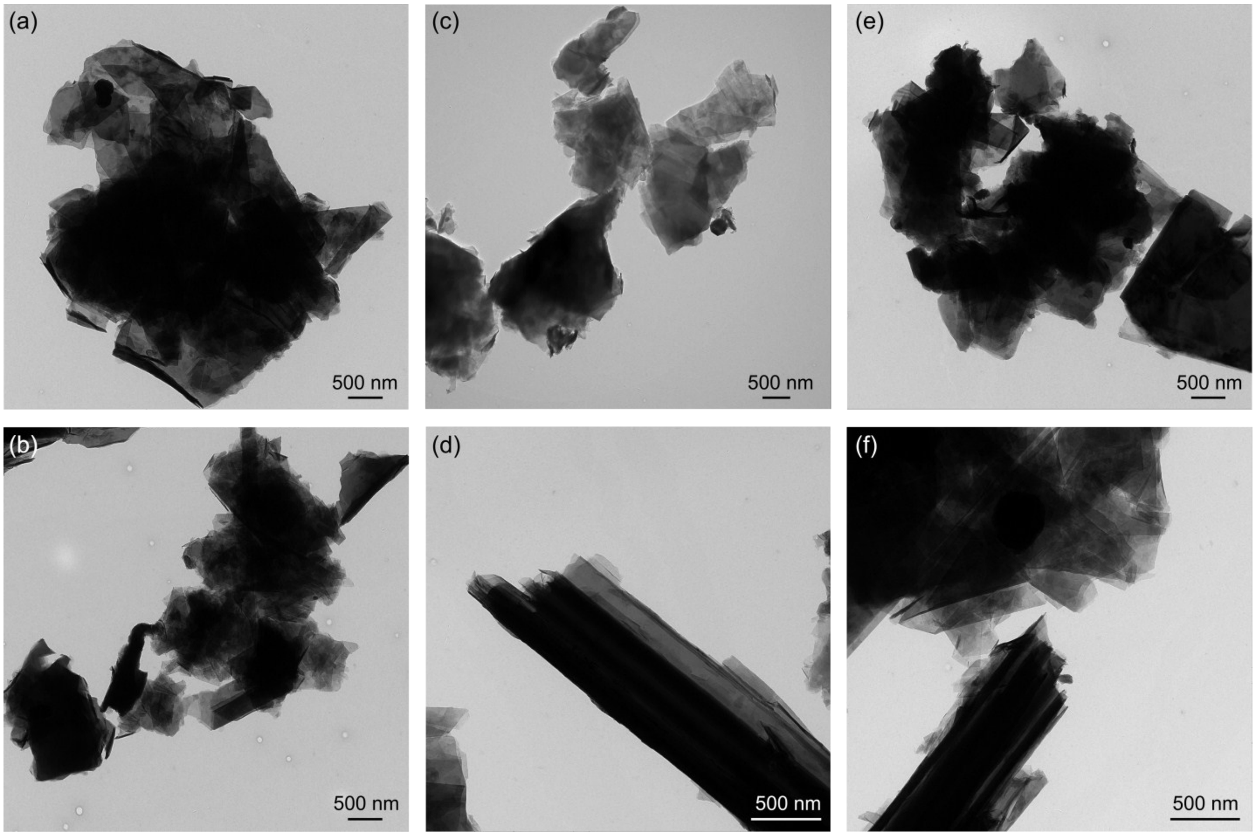

Fig. S6 Brightfield transmission electron micrographs of the graphitic starting material.

8.Rheology

Rheological properties of aqueous mixtures of cellulose and graphite were analyzed using a viscometer DV-II+ Pro (Brookfield). Samples *k* and *l* were kept at 20.0 ± 0.1°C using a water bath during 12 h. Shear stress measurements were conducted at 20.0°C ± 0.1°C, using 0.50 mL of each sample and a plate geometry (model CP52, Brookfield) at different speeds.

9.Surface Resistance

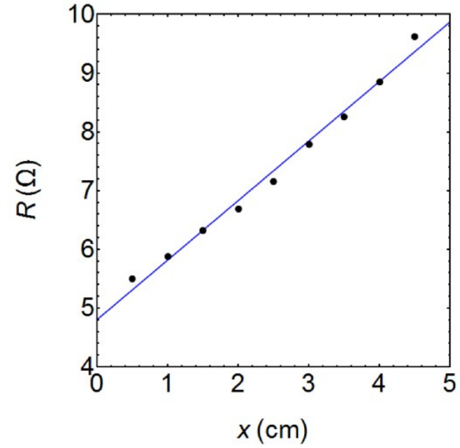

Fig. S7 Surface resistance (R) as a function of the distance (x) along a 6 x 1 cm film stripe (see Fig. 7). An almost linear increase in the measured values indicates a uniform graphite coverage on top of the filter paper. The calculated sheet resistance is 1 Ω/□. Graphitic film thickness is 20 µm and the resistivity is ρ = 4 10^{-5} Ω.m. The low sheet resistance value indicates its suitability for many electrical applications.

(1) Antal, M. J.; Várhegyi, G.; Jakab, E. Ind. Eng. Chem. Res. 1998, 37 (4), 1267–1275.
(2) A. D. French, *Cellulose*, 2014, **21**, 885–896.