

## Supporting Information.

### Solutions of Negatively Charged Graphene Sheets and Ribbons

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**S1. Preparation of the graphite intercalation compound (GIC).** Graphite powder is mixed with a potassium-naphtalene solution, using a molar ratio C/K=8 and using THF as solvent.[S1-1] The reaction is maintained under mechanical stirring under inert atmosphere. After 24 hours it is filtered under vacuum over PVDF membranes (0.45 microns) to recover the carbonaceous material. It is then washed with THF and dried.

S1-1 Pénicaud, A., Poulin, P., Derré, A., Anglaret, E., Petit, P., *J. Am. Chem. Soc.* **127**, 8-9 (2005).

**S2. Preparation and chemical analysis of the solution of the GIC in NMP.** The GIC is mixed with NMP (ca 0.5 mg/ml) under inert atmosphere, at room temperature under stirring. After 24 hours, the solution is centrifuged at 4000 rpm for 60 minutes to separate the non-soluble material from the solution of graphite salt in NMP. The coloured supernatant constitutes the solution of graphene layers in NMP. This solution becomes colourless in contact with air (see Figure S3-1).

Analysis: The K content of the reduced graphene solution was determined at the Analytical Service Center of the Gorlaeus Laboratories, Leiden University, on a Perkin-Elmer 3100 atomic absorption (AAS) and flame emission spectrometer using a linear calibration method. The experimental error that should be considered in such determination is of the order of 5%.

### S3. Optical microscopy image of the solutions.

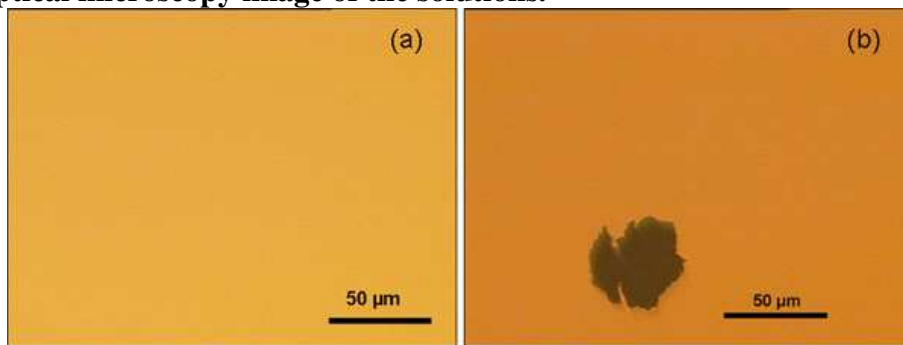


Figure S3-1. Optical microscopy image of the solution (left) showing no aggregates above optical detection limit, ca 0.5 microns and the oxidized solution (right) showing large aggregates. Colors on the images are a result of varying aperture and contrast and do not represent the true color of the solution (which appears colorless at this thickness (0.1 mm thick capillaries)).

### S4. Preparation and imaging of deposits of the solution onto substrates:

Deposits of the solution were prepared onto different kind of substrates by dip-coating in the solution for ca 15-30 minutes under argon atmosphere, then washing with NMP, acetone, water and isopropanol (still under Ar atmosphere); finally, the deposits were taken out of the gloves-box to be completely dried under vacuum at 200 °C for 48 hours.

Interferometry: the graphene sample was deposited by dip-coating on a molecularly smooth, freshly cleaved, muscovite mica piece of uniform thickness smaller than 4 mm, which was previously back-coated with a 45nm thick silver layer (Sigma-Aldrich 99.9999%) by thermal evaporation. To favor the adsorption of the negatively charged graphene flakes the mica surface was previously immersed 30 minutes in a 100 mM  $\text{NiCl}_2$  solution, in order to promote the ionic-exchange of  $\text{Ni}^{2+}$  with naturally occurring  $\text{K}^+$  ions on exposed cleavage surfaces thus positively polarizing the mica surface.[S4-1] The mica-graphene stack was then coated by evaporation of a second semi-reflective silver layer, as illustrated in the inset of Figure 4.

AFM: deposits were prepared in the same way except for the silver covering steps and imaged on a multimode AFM (Veeco) in tapping mode.

Ambient STM: deposits were prepared onto freshly cleaved HOPG (highly oriented pyrolytic graphite) by drop-casting. The HOPG surface was imaged right before deposition to ensure quality and cleanliness. Low and high resolution images were obtained respectively on Nanoscope III and II instruments.

Optical microscopy: deposits were prepared by dip-coating onto special Si/SiO<sub>2</sub> wafers (“Surfs”, Nanolane, France)

S4-1. Ill, C. R., Keivens, V. M., Hale, J. E., Nakamura, K. K., Jue, R. A., Cheng, S., Melcher, E. D., Drake, B. & Smith, M. C. *Biophys. J.* **64**, 919–924 (1993).

**S5. Details of the Interferometry measurements:** To determine the thickness of the mica-graphene layer, a beam of collimated white light is sent through the multilayer system at normal incidence, undergoing multiple reflections between the semi-reflective silver films. The emerging light is focused onto the entrance slit of a spectrometer. Fringes of equal chromatic order (*FECO*) are recorded at the exit port of the spectrometer. The sharp fringes are due to constructive interference of the reflected light, and contain the information about the optical thickness between the two silver layers.[S5-1] A small increase of the optical thickness of the multilayer is translated into

a small shift to greater wavelengths of the *FECO*. The thickness profile of the section of the multilayer system focused on the entrance slit can then be determined with sub-angstrom height sensitivity and a lateral resolution of about 2  $\mu\text{m}$ .

The condition for constructive interference and maximal transmittance of a mica sheet silver-coated in both sides is given by:

$$n\lambda_n = 2\mu_M(\lambda_n)Y_M + \frac{2\phi(\lambda_n)}{2\pi}\lambda_n$$

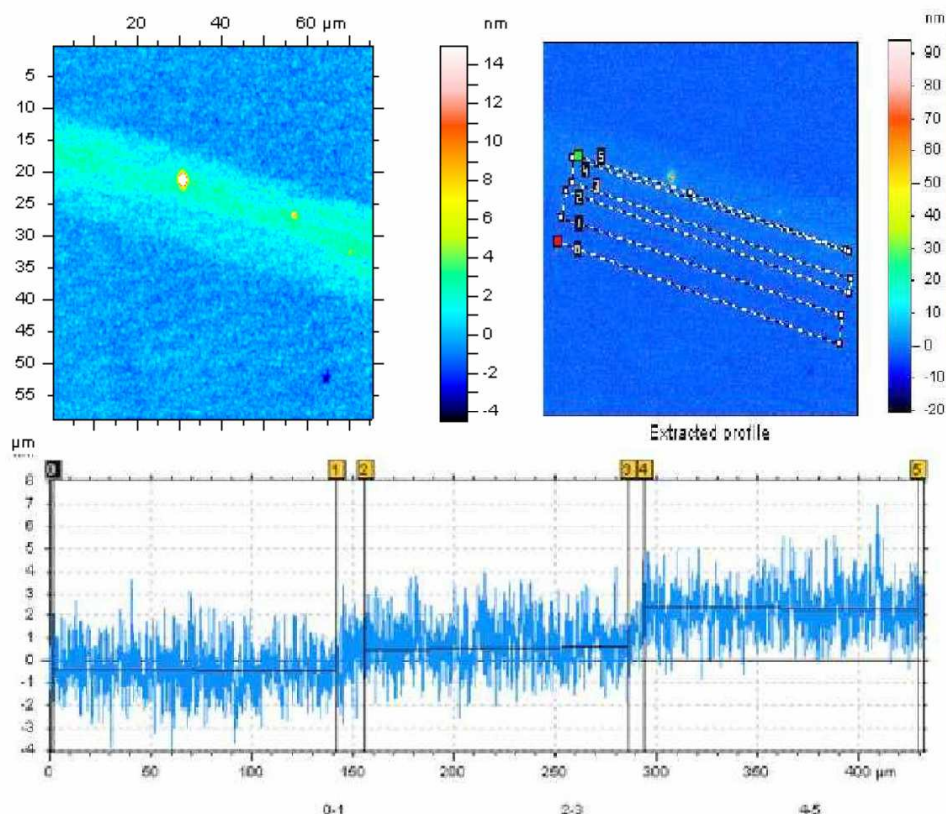
where  $n$  is the order of the chromatic fringe at wavelength  $\lambda_n$ ,  $\mu_M(\lambda_n)$  is the mica refractive index at the same wavelength,  $Y_M$  is the thickness of the mica and  $\phi(\lambda_n)$  is the optical phase change upon reflection at the mica-silver interface. From this equation,  $Y$  and  $n$  can be easily determined by measuring the wavelength of at least two *FECO*, all the other quantities being known. This resonance condition is modified when the optical distance between the semi-reflective silver mirrors is altered, e.g. by interposing a graphene layer between the mica and the silver layer. An extra term, corresponding to the optical thickness of the grapheme layer ( $\mu_G(\lambda_n).Y_G$ ), has to be added. A small increase of the optical thickness of the multilayer is translated into a small shift to greater wavelengths of the *FECO*.

Several algorithms have been proposed to determine the variation of the optical thickness between the mirrors from these shifts. The exact equations describing the transmittance of the three layers interferometer have been derived in the past.[S5-2] Other possibility is to use the Multilayer Matrix Method [S5-3,S5-4] to describe the propagation of the light through the stratified media. Measuring the wavelength of enough *FECO* allows determining a number of parameters (i.e. thickness and refractive index) of the multilayer system. We obtained identical results by both methods.

- S5-1. Tolansky, S. *Multiple Beam Interferometry of Surfaces and Films* (Oxford University Press, Oxford, 1948).
- S5-2. R. G. Horn and D. T. Smith, "Analytic solution for the three-layer multiple beam interferometer," *Appl. Opt.* **30**, 59- (1991)
- S5-3. M. Born and E. Wolf, *Principles of Optics*, 6th ed. (Pergamon, Oxford, 1980).
- S5-4. M. T. Clarkson, *J. Phys. D* **22**, 475 (1989).

## **S6. Differential interference contrast (DIC) optical microscopy.**

The flakes deposited on a modified Si/SiO<sub>2</sub> wafer (Surf, Sarfus<sup>TM</sup> technology) have been imaged by differential interference contrast (DIC) optical microscopy in a manner similar to the procedure on Si/SiO<sub>2</sub> substrates. By comparison with standards of known heights and correcting for the optical index of graphene (2.20 [S6-1]), height measurements can be performed on such images.[S6-2, S6-3] This procedure yielded heights of 0.3 and 0.7 nm for the two color tones of the long object of Figure S6-1 with respect to the substrate.



**Figure S6-1.** Sarfus image of a deposit on a Surf wafer. The bottom curve shows the height profile along the dotted line. After correction by the optical index of graphene (2.2), heights of 0.3 nm and 0.7 nm are found respectively for the zones between markers 2-3 and 4-5 with respect with the substrate.

S6-1 McCartney, J.T. & Ergun, S., *J. Opt. Soc. Am.* **52**, 197-200 (1962).

S6-2 Ausserré, D. & Valignat, M.-P., *Nanolett.* **6**, 1384-1388 (2006).

S6-3 Souplet, V., Desmet, R., Melnyk, O., *J. Pept. Sc.* **13**, 451-457 (2007).

## S7. Additional STM images

Those images have been taken in conditions similar to Figure 1, i.e. by drop casting a solution of filed-down graphite onto HOPG.

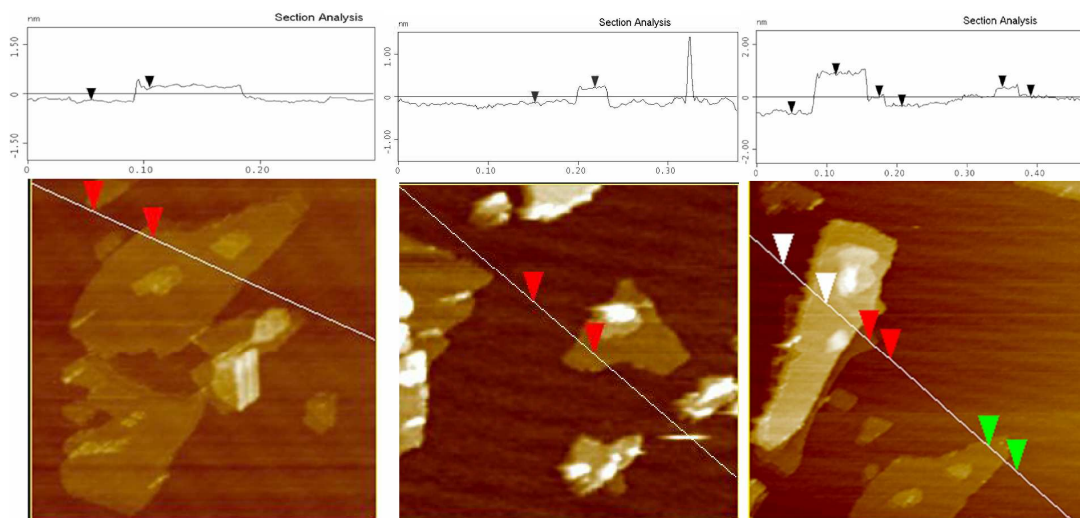


Figure S7-1

Figure S7-2

Figure S7-3

## S8. Additional AFM images

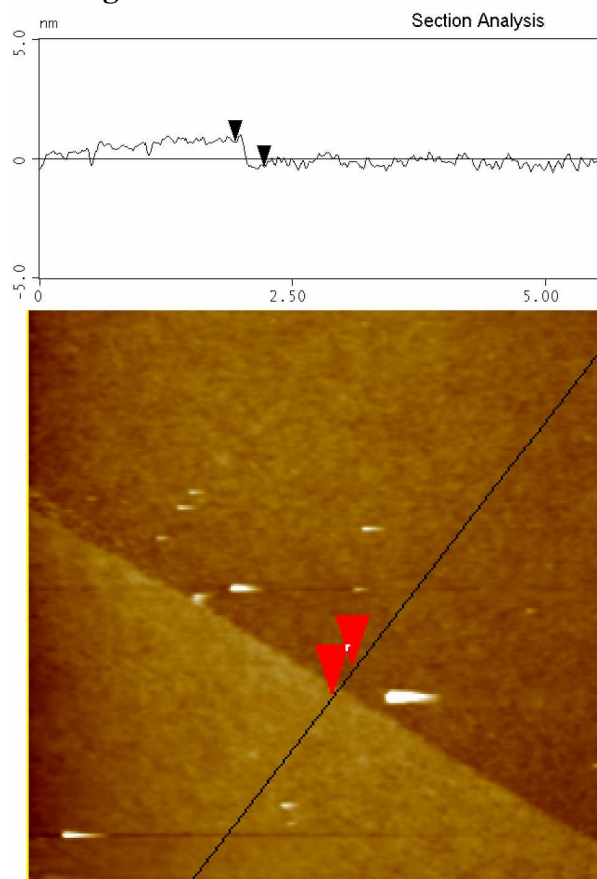


Figure S8-1 Part of a graphene flake (lower left) laying on Si/SiO<sub>2</sub> substrate (upper right).

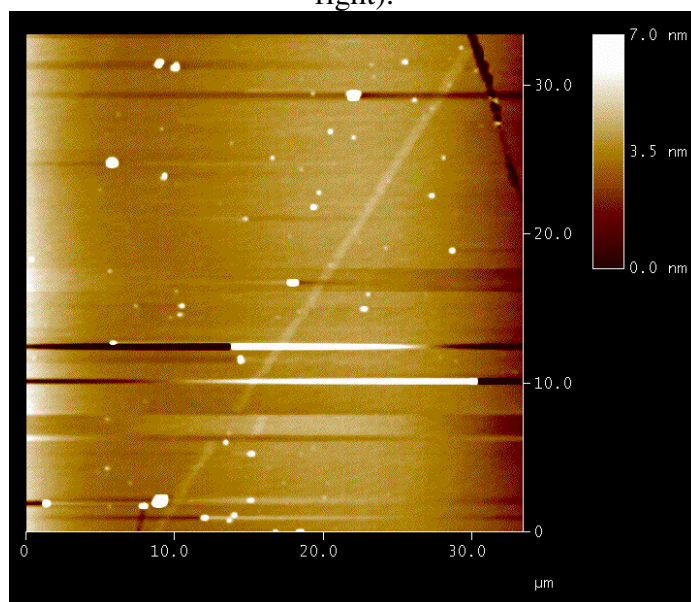


Figure S8-2: Large scan AFM image of the ribbon of Fig. 3, laying on mica, showing its length is over 40 microns.



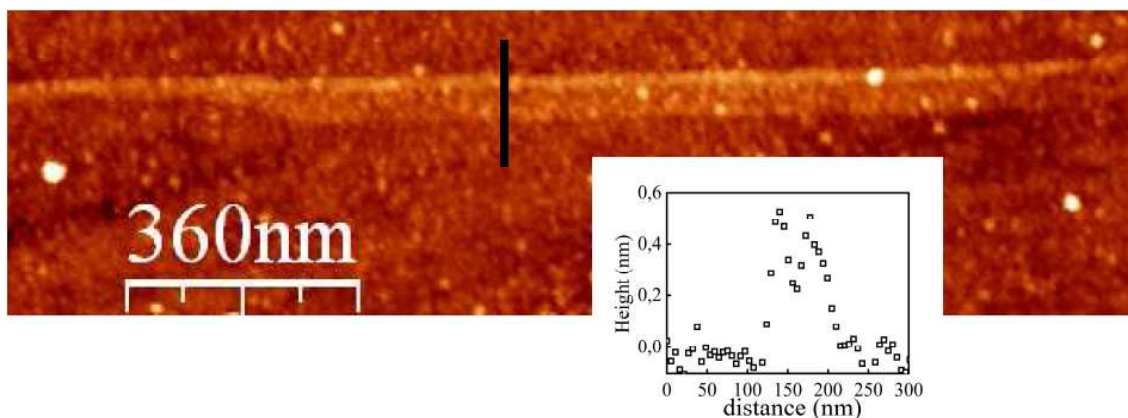


Figure S8-3: Another graphene ribbon laying on mica. Inset: height profile along the black line.

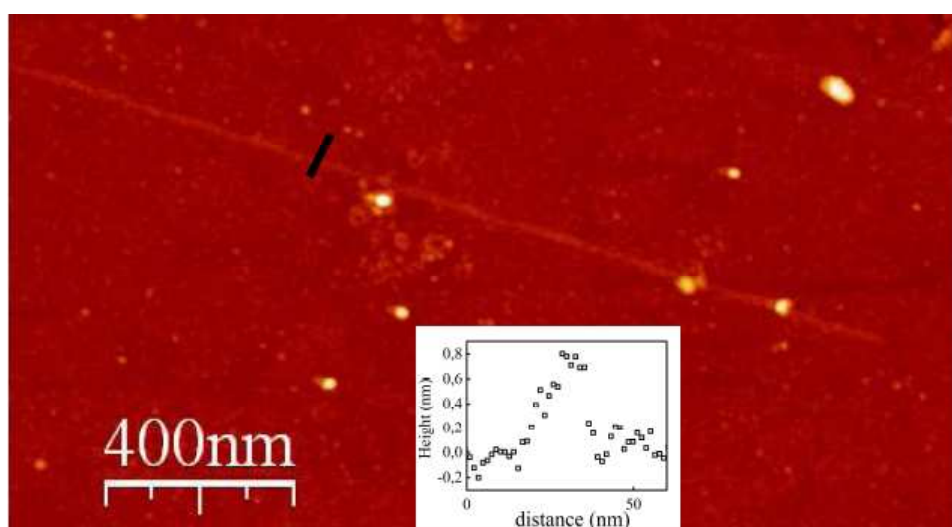


Figure S8-4: Another graphene ribbon laying on mica. Inset: height profile along the black line. Lateral distance has not been corrected from tip convolution.

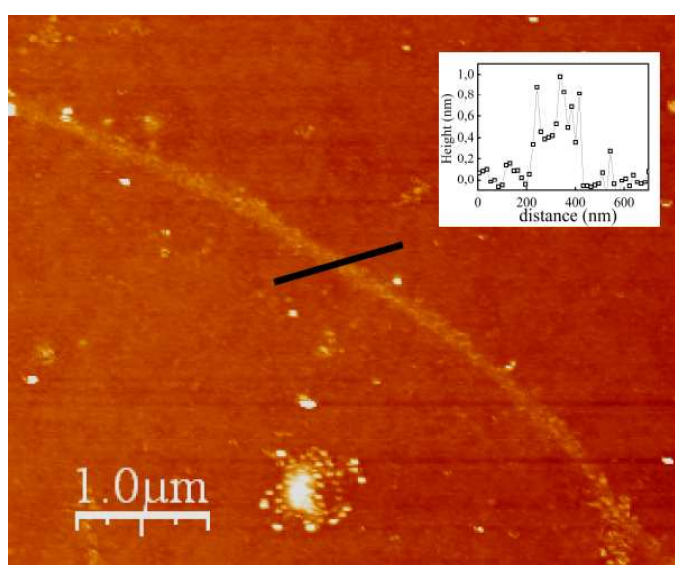


Figure S8-5: Another graphene ribbon laying on mica. Inset: height profile along the black line.

### S9. X-ray photoelectron spectroscopy

XPS analysis of deposits on a Si/SiO<sub>2</sub> wafer (Figure S9-1) and HOPG (Figure S9-2) repeatedly showed the absence of any detectable peak of nitrogen and potassium. This implies that all NMP and the potassium salts expected to form upon ambient air exposure of the deposits, by analogy with C<sub>60</sub> [S9-1] and carbon nanotubes,[S9-2] are removed by the rinsing procedure used. The carbon C1s peaks observed for all deposits on Si/SiO<sub>2</sub> wafers are very similar, centered on 284.6 to 285 eV and quite symmetric, while they correspond to varying amounts of C, e.g. from ca. 11 to 25 atomic % (4 samples, several positions analyzed, Figure S9-3). These features are not those of amorphous carbonaceous material usually found on SiO<sub>2</sub> surfaces (asymmetric peak with a higher energy shoulder, lower amounts, [S9-3]). Altogether, the XPS data thus indicate the deposition of varying amounts of graphitic-like un-oxidized carbon.

Experimental: measurements were performed with a VG 220 i.XL ESCALAB spectrometer. All spectra were taken using a Mg non-monochromatized source (1253.6 eV) at 200 W. The spot size was approximately 25 μm. The typical operating pressure was 2×10<sup>-7</sup> Pa. The reported data for graphene deposits are extreme surface ones (no sputtering was performed). The range of depth information is 1 to 10 nm, in agreement with the detection of the deposition surface used (HOPG and SiO<sub>2</sub>). The detection limit is of the order of 0.1 atom%. Typical binding energies were taken from The Handbook of Monochromatic XPS Spectra, The Elements and Native Oxides, B. V. Crist, Wiley, 2000.

- S9-1 Stinchcombe, J. , Pénicaud, A. , Bhyrappa, P. , Boyd, P.W.D. , Reed, C.A. *J Am Chem Soc* **115**, 5212–7 (1993)
- S9-2 Pénicaud, A.; Valat, L.; Derré, A.; Poulin, P.; Zakri, C.; Roubeau, O.; Maugey, M.; Miaudet, P.; Anglaret, E.; Petit, P.; Loiseau, A.; Enouz, S. *Compos. Sc. Technol.* **67**, 795-797 (2007).
- S9-3 a) The Handbook of Monochromatic XPS Spectra, The Elements and Native Oxides, B. V. Crist, Wiley, 2000 ; b) M. P. Seah, S. J. Specer, *J. Vac. Sci. Technol. A* **2003**, 21, 345-352

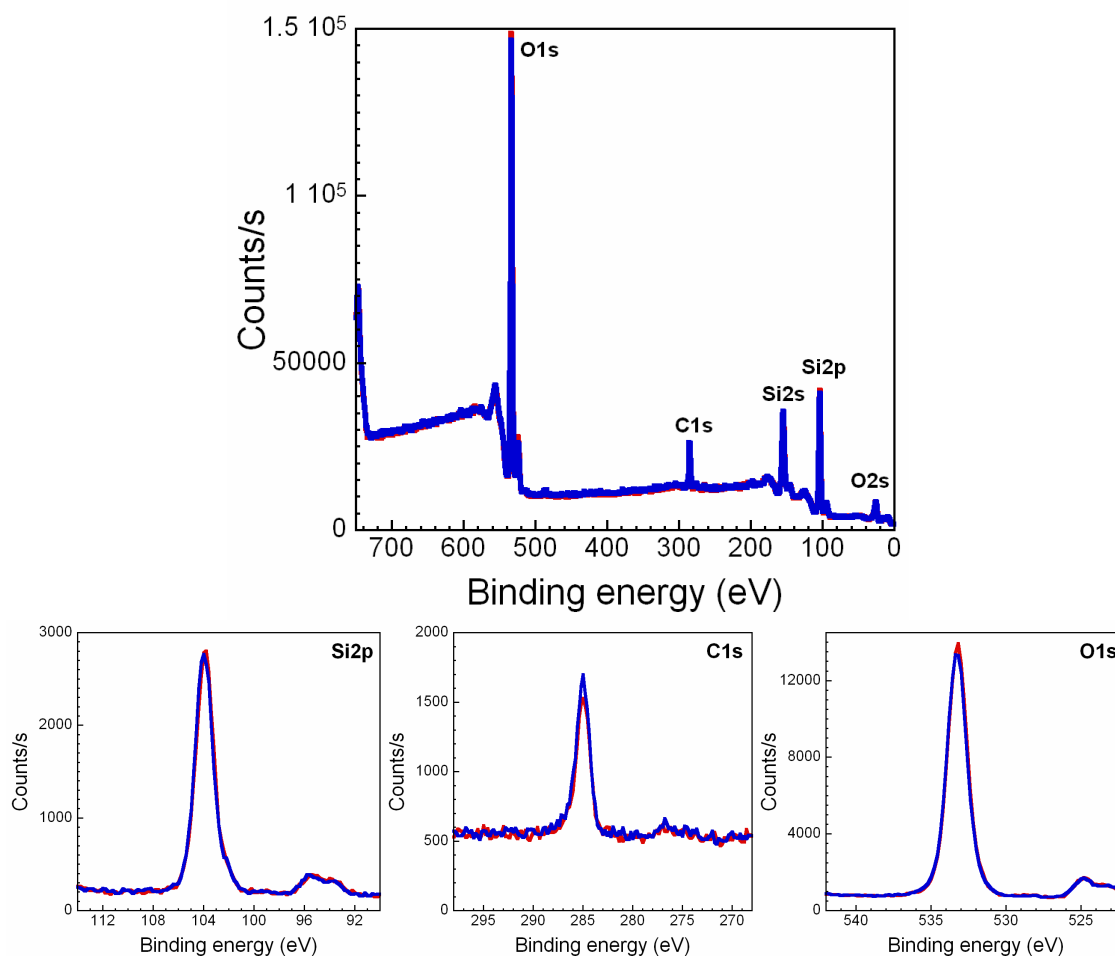


Figure S9-1 : XPS data of potassium-graphene salt solution dip-coated over Si/SiO<sub>2</sub> wafer (Surf, Sarfus<sup>TM</sup> technology), washed and dried. Red and blue curves correspond to two different analysis positions on the surface. The survey (top) shows the absence of any detectable amounts N (strongest XPS band is N1s usually found between 400 and 407 eV depending on the chemical environment), indicating that the NMP solvent has been removed efficiently. The higher resolution data of the C1s and K2p area (bottom, left) confirms the absence of any detectable amounts of K (strongest XPS bands are 2p<sup>3</sup> and 2p<sup>1</sup> usually expected at respectively 292.9 and 295.7 eV). Semi-quantitative analysis of the higher resolution data (bottom) taking into account the relevant atomic sensitivity factors gives the following atomic percentages respectively for the two positions : C, 10.8 / 12.8 ; O, 59.7 / 57.7; Si, 29.5 / 29.5. The C1s band is found at 285.0 eV, very close to the expected 284.5 eV of graphitic carbon (HOPG). Its rather symmetric shape together with the absence of a significant shoulder at higher binding energies confirms the deposited carbon is not at all oxidized (C1s for C-OR, C=O and COOR environments are respectively expected at 285.5, 287.8 and 288.9 eV).



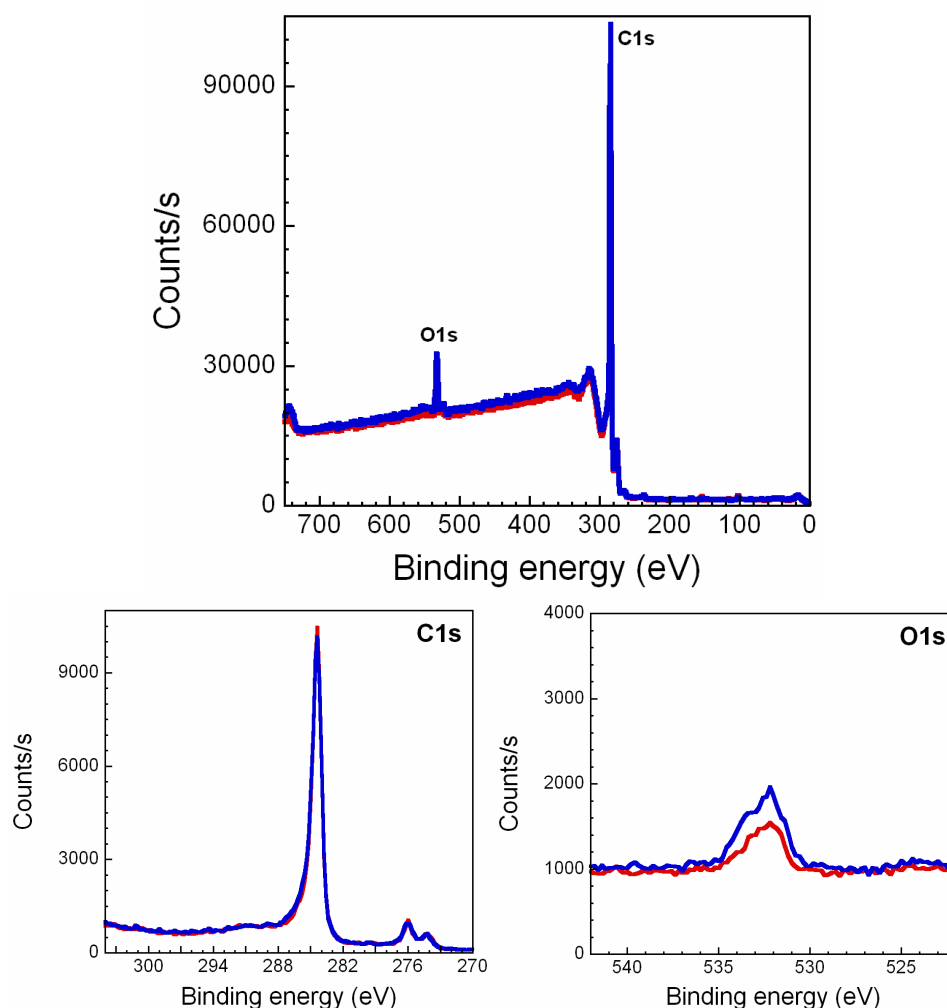


Figure S9-2 : XPS data of potassium-graphene salt solution dip-coated over HOPG, washed and dried. Red and blue curves correspond to two different analysis positions on the surface. The survey (top) shows the absence of any detectable amounts N (strongest XPS band is N1s usually found between 400 and 407 eV depending on the chemical environment), indicating that the NMP solvent has been removed efficiently. The higher resolution data of the C1s and K2p area (bottom, left) confirms the absence of any detectable amounts of K (strongest XPS bands are  $2p^3$  and  $2p^1$  usually expected at respectively 292.9 and 295.7 eV). Semi-quantitative analysis of the higher resolution data (bottom) taking into account the relevant atomic sensitivity factors gives the following atomic percentages respectively for the two positions : C, 96.5 / 94.3 ; O, 3.5 / 5.6. The amount of oxygen found is not significantly higher than that found on pure HOPG, in agreement with non-oxidized deposited graphene. Analysis of the C1s peak (found at 284.5 eV as expected for HOPG) is senseless as the deposited graphene will at most represent a very small fraction of the detected C.

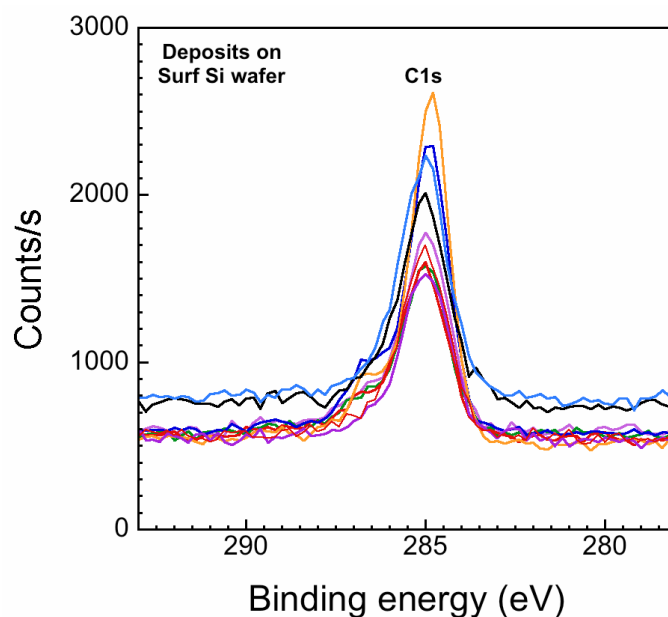


Figure S9-3 : C1s area for four different samples (nine positions analyzed in total) of deposits on Si/SiO<sub>2</sub> wafer (Surf, Sarfus<sup>TM</sup> technology), showing reproducible binding energy (284.6 to 285 eV) and shape (symmetric, almost no high energy shoulder).

## S10. Raman spectroscopy characterization of graphene solutions and deposits

The presence of graphene materials in both our solutions and deposits was characterized by Raman spectroscopy. For the samples used in this experiment, the air-sensitive graphene solutions were transferred to a quartz cuvette under argon atmosphere inside a glove box and flakes were also deposited from those solutions on a modified Si/SiO<sub>2</sub> wafer (Surf, Sarfus<sup>TM</sup> technology). Raman spectra were collected with a JY Horiba Labram II micro-Raman system with excitation laser wavelength of 1064 nm for solutions and 514 nm for deposits. The spot size of the laser was  $\sim 2 \mu\text{m}$  using a 100x objective and the incident power was kept well below 3mW to avoid sample damage or laser-induced heating.

We have studied solutions and deposits from different graphite sources and spectral features associated with sp<sup>2</sup> carbons have been seen for all samples. As an example, we show in Figs S10-1 and S10-2 1st (1500 – 1700 cm<sup>-1</sup>) and 2nd order (2400–2900 cm<sup>-1</sup>) Raman scattering for respectively graphene solution obtained from highly oriented pyrolytic graphite (HOPG) and graphene deposits (sheets and ribbons) obtained from expanded graphite. In those figures, we also show the spectrum for the original bulk graphite for comparison. The features near  $\sim 1580 \text{ cm}^{-1}$  and between 2500 and 2700 cm<sup>-1</sup> in sp<sup>2</sup> carbons are referred to as G and G' (or 2D) bands. Recent works [S10-1 to 3] suggest that G and G' Raman bands change in shape, position and relative intensity with the number of graphene layers and could be used to clearly distinguish a monolayer or few layers from several graphene layers or bulk graphite. Initially, when peeling off the penultimate layer, G band was showed to slightly upshift, I(G')/I(G) was observed to significantly increase and G' was shifted and fitted by just one Lorentzian with a full width at half maximum (FWHM) of 24 cm<sup>-1</sup>. More recently [S10-4 to 6], however, it was showed that the criterium based on the shape of the G' band still stands, but that of G and G' peak position and I(G')/I(G) are also dependent on the presence of defects and

doping effects. In our case, G band is upshifted and G' band is downshifted with respect to the original bulk graphite for both graphene solution and deposits. Besides, even though G' band shows low intensity, it can be fitted by just one Lorentzian, indicating a higher symmetry compared to the raw material (Figure S10-3). These results confirm the presence of graphene materials in both solution and deposits. For the ribbons (Fig. S10-2), the intense D-band scattering ( $\sim 1350\text{ cm}^{-1}$ ) could be related to edges and mainly finite crystallite size effects [S10-7]. A more detailed work is being carried out in our group to better understand the Raman spectral features of reduced graphene sheets in solution and after deposited on substrates and will be addressed in a separate report.

#### References:

- S10-1 Ferrari, A.C. et al., Phys. Rev. Lett. **97**, 187401 (2006).
- S10-2 Gupta A. et al., Nano Lett. **6**, 2667 (2006).
- S10-3 Graf, D. et al., Nano Lett. **7**, 238 (2007).
- S10-4 Ferrari A. C., Solid State Commun. **143**, 47 (2007).
- S10-5 Casiraghi, C. et al., Appl. Phys. Lett. **91**, 233108 (2007).
- S10-6 Das A. et al., arXiv:0710.4160v1 [cond-mat.mtrl-sci] (2007).
- S10-7 Kim U. J., Carbon **46**, 729 (2008).

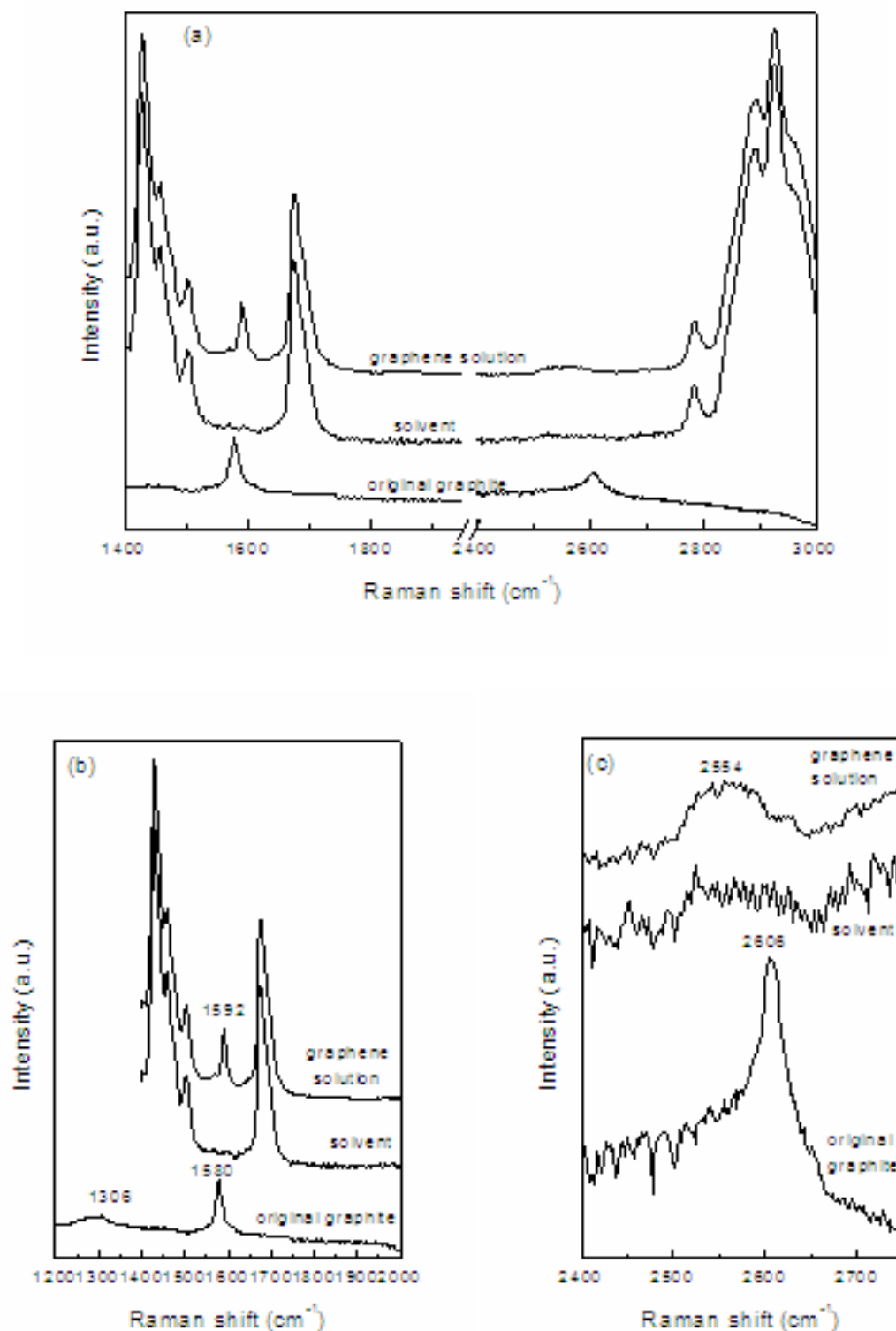


Fig. S10-1: Raman spectrum ( $\lambda = 1064 \text{ nm}$ ) for graphene solution obtained from highly oriented pyrolytic graphite (HOPG) in the G band  $1500 - 1700 \text{ cm}^{-1}$  region (a and b) and G' band  $2400 - 2900 \text{ cm}^{-1}$  region (a and c). Spectra for the bulk HOPG and the pure solvent (NMP) were also plotted for comparison.

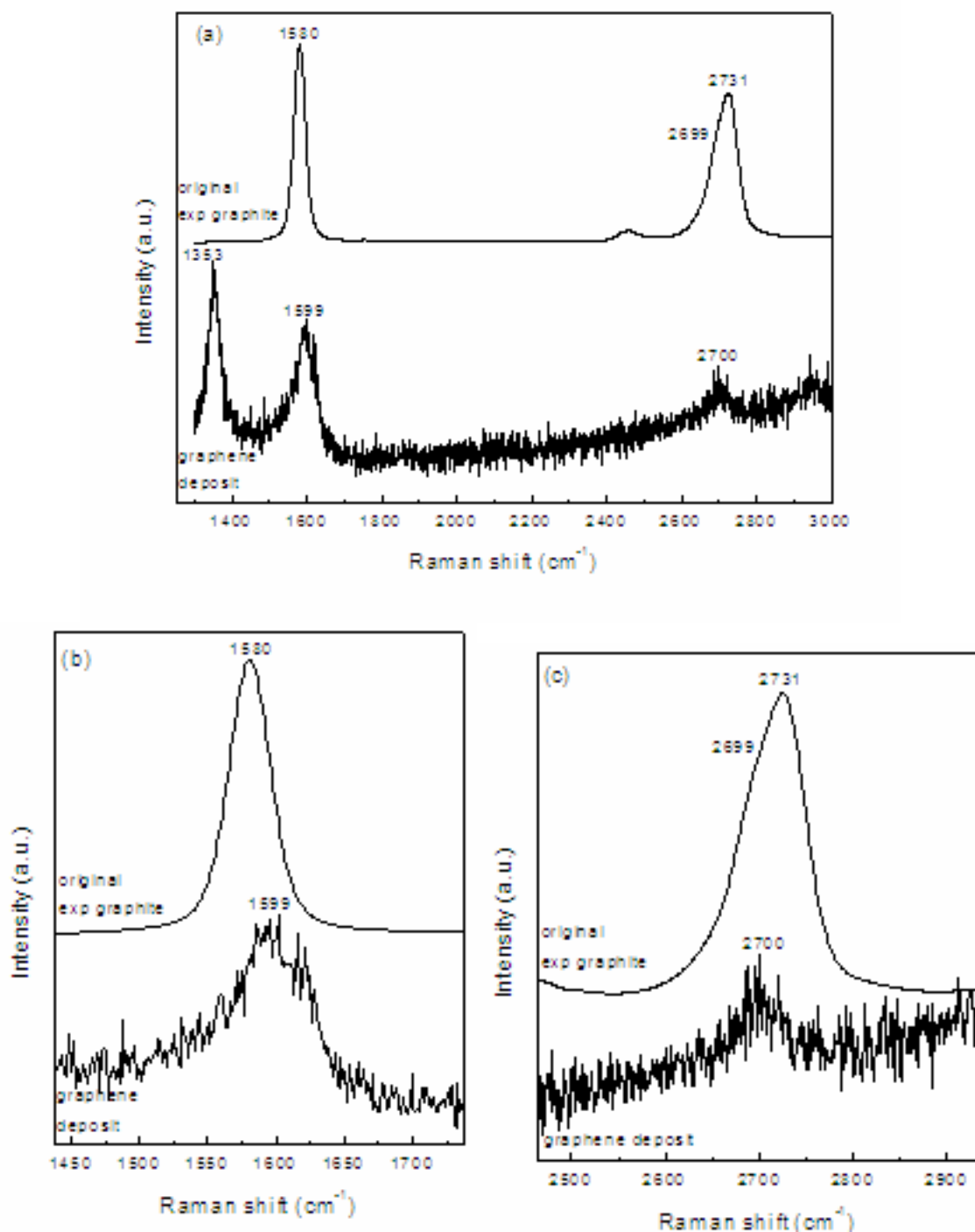


Fig. S10-2: Raman spectra ( $\lambda = 514 \text{ nm}$ ) in the G band  $1500 - 1700 \text{ cm}^{-1}$  (a and b) and G' band  $2400 - 2900 \text{ cm}^{-1}$  (a and c) spectral ranges for a graphene ribbon, obtained from expanded graphite, deposited on Si/SiO<sub>2</sub> substrate. Spectrum for the bulk expanded graphite was also plotted for comparison.



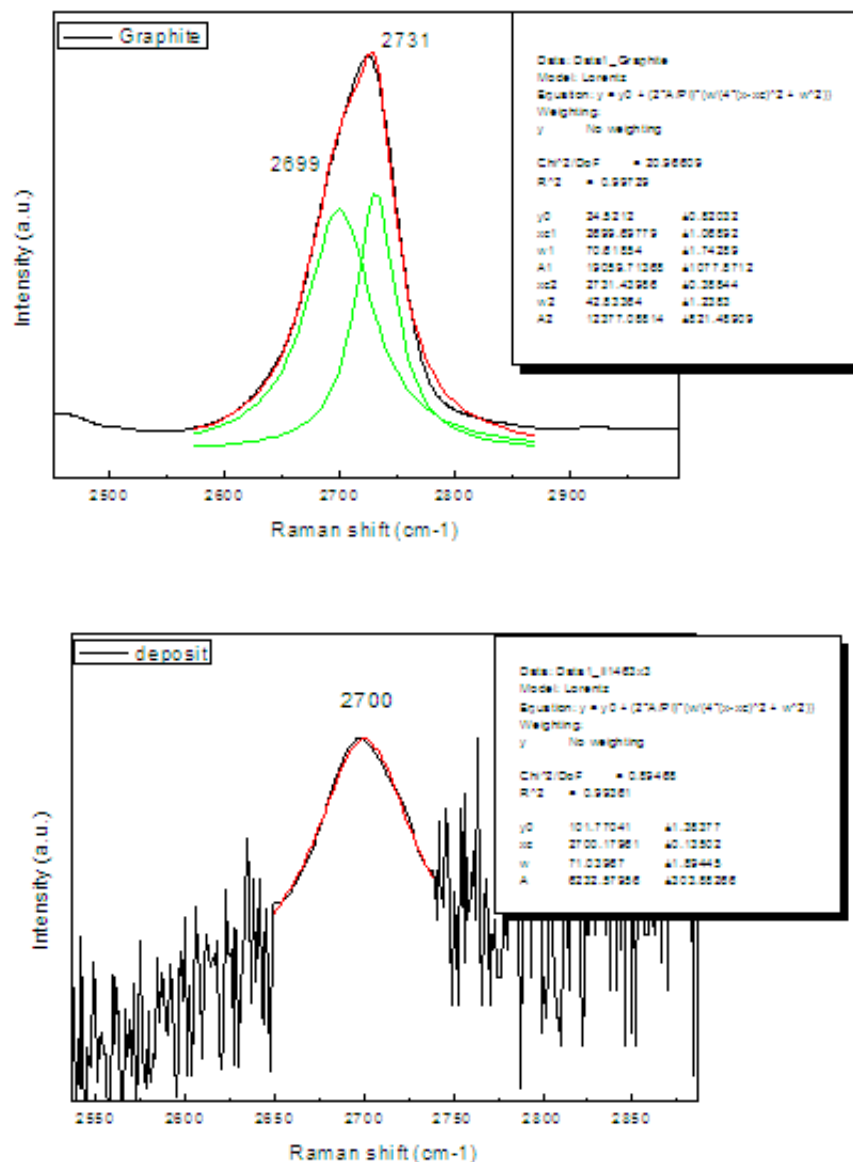


Figure S10-3. Deconvolution of the G' band for starting graphite (top) and deposit (bottom) from expanded graphite (same as Figure S10-2). The graphite signal is fitted by two Lorentzian lines centered at 2699 and 2731  $\text{cm}^{-1}$  whereas the signal for the deposited ribbon is fitted by a single Lorentzian line centered at 2700  $\text{cm}^{-1}$ , i.e. the low energy component, as expected for a graphene deposit (refs S10-1 to S10-3).

## S11. TEM measurements:

TEM investigation was done using 80kV beam energy, i.e., below the energy threshold for atoms displacement in hexagonal carbon lattice which is 87kV.[S11-1] A specific electron optical set-up allows for the usage of the Cs-corrector at lower voltage, providing corrections up to fifth-order aberrations, corresponding to so-called aberration-free imaging. Using these conditions, sufficient resolution for imaging the carbon atoms distributed according to the honeycomb lattice while preserving the crystal structure from damage is achieved. The determination of the number of graphene layers in the flakes deposited over a holey carbon film is done directly by inspection of the HRTEM images and counting the number of 002 graphite fringes in a folded border, as displayed in Fig. 5c in the article text. Whether the flakes are single or multi-graphenes can be determined or confirmed by inspection of the electron diffraction peak intensity profiles (see an example in Figure S11-1).

The flake imaged in Fig 5a in the main article has been deposited onto regular holey carbon coated copper grid for TEM, from a droplet of the expanded graphite solution. Fig. 5b shows the diffraction pattern of the flake seen in Fig. 5a, performed at the same low voltage, under Kholer imaging conditions to obtain a spatially limited and parallel probe with size of few tenth nanometres. Since the pattern was taken from the suspended tip region where the flake is unfolded, the hexagonal pattern of the stacked graphenes is clearly visible and the diffraction peaks were labelled using Miller-Bravais (hkil) indices.[S11-2 to 3] The diffracted intensity recorded along the line indicated in Fig. S11-1a is displayed in Fig. S11-1b, and shows that both  $I_{-2110}/I_{-1010}$  and  $I_{1-210}/I_{0-110}$  ratios are higher than one. This is consistent with reports about multi-graphenes piled up according to the Bernal (AB) stacking (typical of genuine graphite), while  $I_{-2110}/I_{-1010} < 1$  for a single graphene.[S11-4] This result confirms both the multi-graphene nature for the flake and the AB stacking order.

### References:

- S11-1 B. W. Smith and E. Luzzi. Electron irradiation effects in single wall carbon nanotubes. *J. Appl. Phys.*, **90**, 3509 (2001).
- S11-2 Meyer, J. C. *et al.* The structure of suspended graphene sheets. *Nature* **466**, 60-63 (2007).
- S11-3 Meyer, J. C. *et al.* On the roughness of single- and bi-layer graphene membranes. *Solid State Commun.* **143**, 101-109 (2007).
- S11-4 Horiuchi, S. *et al.* Carbon nanofilm with new structure and property. *Jpn. J. Appl. Phys. Lett.* **42**, L1073-L1076 (2003)

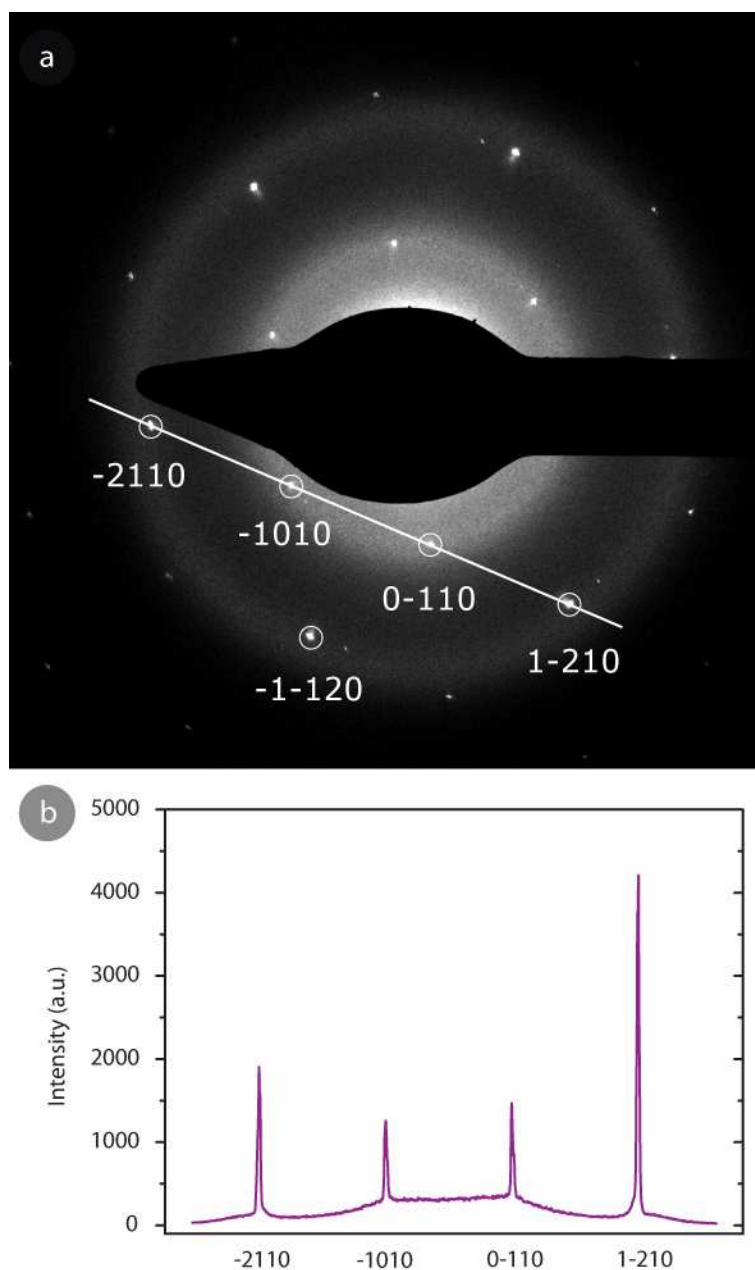


Figure S11-1. (a) Same electron diffraction pattern as in Figure 5b from the unfolded tip region of the flake shown in Figure 5a, displaying the line along which the intensity profile shown in (b) was recorded.

### S12. Complete ref. 12:

Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z.; De, S.; McGovern, I.; Holland, B.; Byrne, M.; Gun'ko, Y.; Boland, J.; Niraj, P.; Duesberg, G.; Krishnamurthy, S.; Goodhue, R.; Hutchison, J.; Scardaci, V.; Ferrari, A. C.; Coleman, J. N. *Nature Nanotech.* **3**, 563-568 (2008).

### S13. Conductivity measurements:

Interdigitated electrodes were dip-coated in the graphene solutions, rinsed and dried, according to the procedure described in section S4. Two different experiments gave

respective resistance values of 235 (Figure S13-1) and 370 Ohms. Distance between the electrodes was 12 microns.

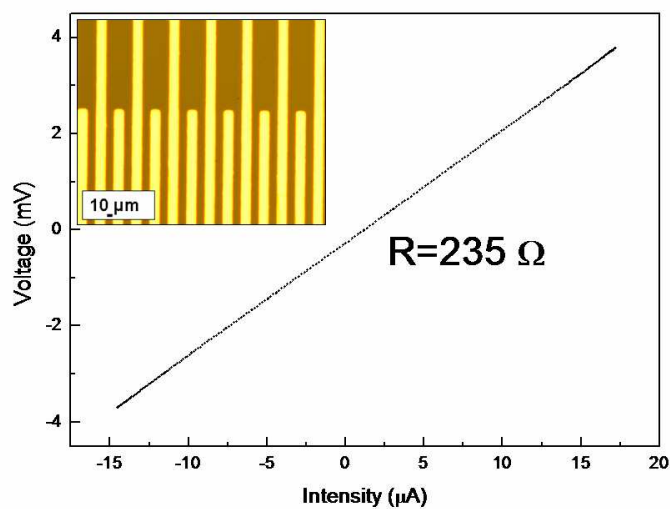


Figure S13-1. I(V) curve for a graphene deposit on interdigitated electrodes. Inset: photograph of the electrodes.