Ripple morphology of graphitic surfaces: a comparison between few-layer graphene and HOPG

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Supplementary information

1. Coexistence of SP and LP ripples

Dropping a molecular solution on HOPG occasionally resulted in the formation of coexisting SP and LP rippled domains. The amplitude TM-AFM image in figure SI-1a shows parallel SP and LP ripples coexisting on HOPG after L-Methionine dropping. The analysis of the corresponding height image (not shown) indicates that the two domains lie on adjacent terraces, with SP and LP ripples on the lower and upper terrace, respectively. Another example of coexisting domains is shown in figure SI-1b which shows an amplitude TM-AFM image of a HOPG surface after lysozyme dropping. In this case SP and LP domains are rotated by 30° and coexist on the same terrace as can be inferred from the analysis of the corresponding height image. We note that 30° rotated SP and LP domains were previously observed on adjacent exposed planes after dropping of a β-lactoglobulin solution [1].
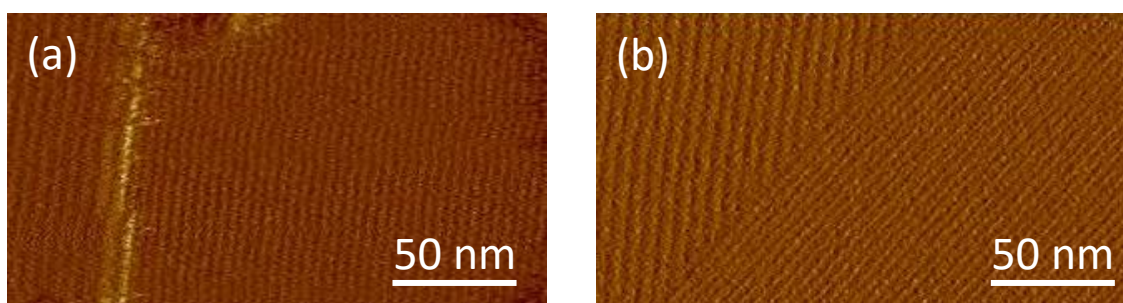

Fig. SI-1 Amplitude TM-AFM images of HOPG after dropping of (a) L-Methionine and (b) lysozyme solution. In panel (a) SP (right) and LP (left) ripples lie on two adjacent terraces separated by a step. In (b) SP and LP domains coexist on the same terrace.

2. Surface morphology of FLG after sonication and exfoliation in DMSO

Sonication of FLG in DMSO solution results in disordered surfaces with the complete removal of ripples as shown by AFM analysis at the nanoscale (Figure SI-2). The surface is decorated with small irregular debris up to 1 nm in height. On such a disordered surface no ripples could be detected.
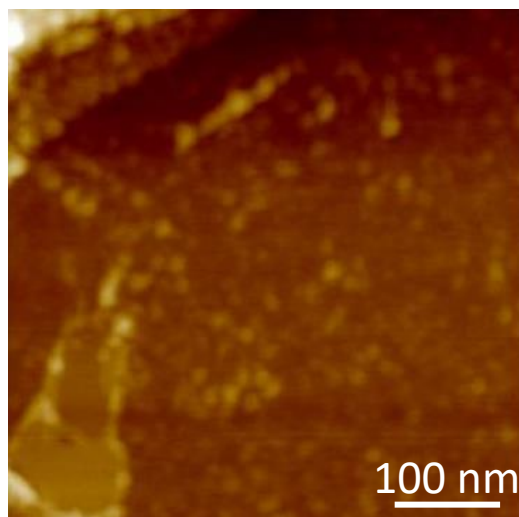
Figure SI-2. TM-AFM height image of FLG after sonication in DMSO solution, z-scale: 8 nm.

3. XPS measurements

XPS analysis flanked Raman spectroscopy in order to characterize thickness and quality of the FLG film before and after treatments in solution, and to verify exfoliation effects. For all samples we measured survey (wide-scan) spectra in different zones. Then for selected zones we measured higher resolution spectra focusing on narrow spectral regions (typically around C1s, Si2p, O1s peaks).

Note that in the experimental procedure the samples are taken in and out of the UHV chamber twice. Though care has been taken to perform the measurements under similar conditions regarding photon intensity, geometry of incidence and detection, detection efficiency and zones of the sample probed, we think that caution has to be considered to evaluate small intensity changes.

FLG before treatments

Representative XPS results in figure SI-3 show C1s and Si2p core level spectra for the FLG film before any treatment. Spectra obtained on a bare SiC substrate are reported for comparison. The graphical choice adopted for the y-scales emphasizes the difference among the two cases. The figure shows data (symbols) after a background (linear + Shirley-type) subtraction, the best fit (red line) and the decomposition in sub-components (in different colours). Details on fitting are given below, for each panel.

Regarding FLG before treatments in solution, the C1s spectrum, figure SI-3a, is dominated by the intense, well-defined C_G peak which exhibits the clear asymmetry toward higher binding energies typical of graphitic systems [2]. The peak was fitted by a Doniach-Sunjic (DS) line shape function (green line). The position, at 284.4±0.1 eV, is in agreement with previous works on FLG [3]. The FLG film is thick enough to suppress the detection of photo-electrons belonging to the substrate. Only a faint component at about 282.5 eV (blue line) is reminiscent of the spectrum of SiC, which is shown in Fig. SI-3c. The C1s spectrum of bare SiC is indeed characterized by two main sub-components which have been fitted by Voigt functions. The higher BE component C_A, located at 284.9±0.2 eV,

was assigned to sp3 adventitious carbon and used as reference. The C_S component, at 282.8±0.2 eV, was attributed to the SiC substrate after comparison with previous reports [3,4].
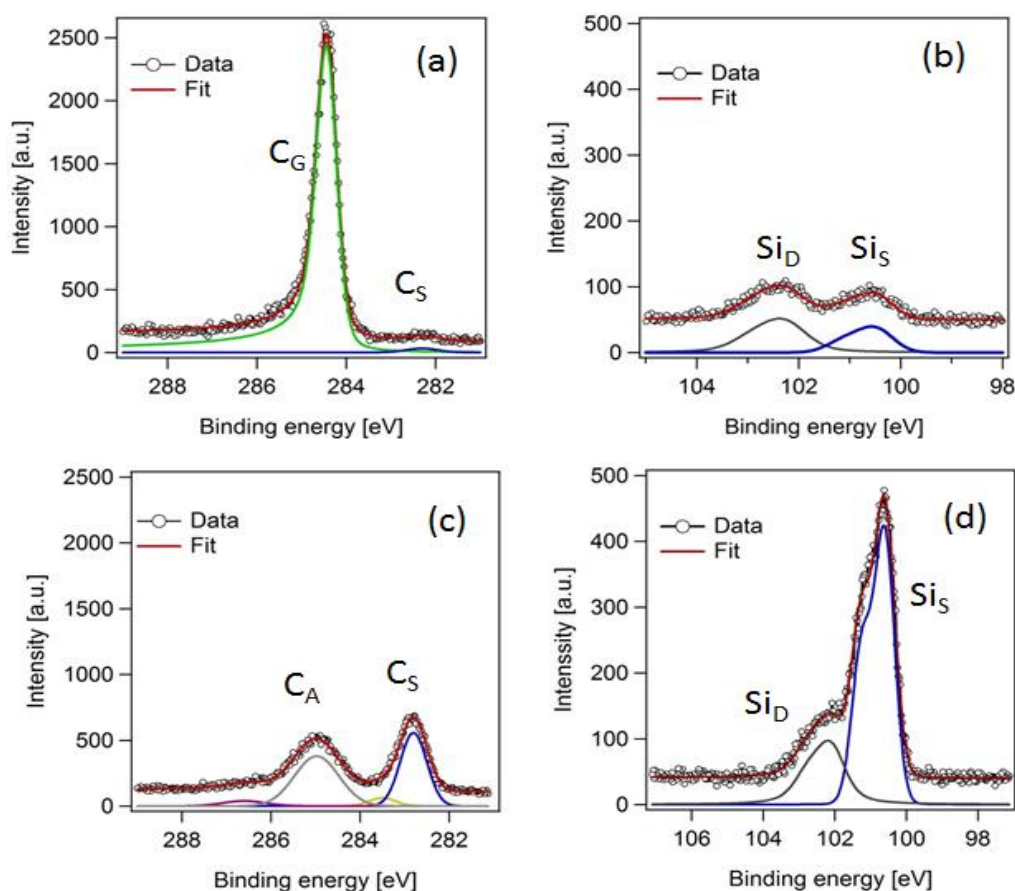

Figure SI-3. XPS core level spectra. Left panels: C1s spectral region. Right panels: Si2p spectral region. (a-b) FLG, untreated (c-d) SiC substrate. The spectra are shown as a function of binding energy (BE): the scale was referenced to the C1s signal of C-C adventitious carbon on the SiC substrate set at 284.9 eV. The take-off angle was 45°. Symbols: experimental data. Red line: best-fit curve. Sub-components are shown in different colors. For the meaning of labels see the text.

Two additional weak components at ~ 286.5 eV and 283.5 eV were included for a more accurate reproduction of the experimental profile. The former is perceptible also on raw data and can be likely assigned to contaminants. The latter, much weaker and correlated to the choice of background, is tentatively assigned to SiC faults.

Passing to the Si2p spectral region, the FLG spectrum (Figure SI-3b) shows two peaks which appear severely attenuated with respect to their counterparts in pristine SiC (cfr. Fig. SI-3d). The 2p doublets have been modelled with Voigt functions, with a branching ratio of 1:2 and a spin orbit splitting of 0.6 eV. The doublet structure is fully evident only on the most intense Si_S peak in Fig. SI-3d: the $2p_{3/2}$ sub-component is located at 100.6±0.1 eV BE and can be assigned to SiC [4,5]. The weaker component Si_D is located at 102.1±0.2 eV BE. The severe broadening of Si_D suggests the convolution of several contributions from defects.

We have applied well-known formulas [5,6,7] to determine the thickness of the FLG film based on the intensity of the FLG- and SiC-related XPS peaks (from C1s and Si2p spectra), taking into account the photoelectron emission angle, attenuation lengths and elemental sensitivity factors.

The initial FLG film thickness was estimated of the order of 3.5 nm (~ 12 layers), assuming a value for the attenuation length in FLG of 2 nm for photoelectrons with kinetic energies of 1200-1300 eV [5].

FLG after treatments

<u>Mild treatment</u>

Spectra obtained after dropping molecular solutions (either L-Methionine or DMSO) on FLG resembled those of pristine samples, regarding intensity and line-shapes.

Fig. SI-4 presents three representative survey (wide-scan) spectra obtained on different regions of the same sample. In panel A and B the spectra are practically superimposed. Some small changes we observed in some zones of the sample (e.g. panel C of the figure) were assigned to the systematic uncertainty of the measurements. No clear message of exfoliation, such as a decrease of the C1s state related to graphene accompanied by an increase of the substrate-related signal, was obtained.
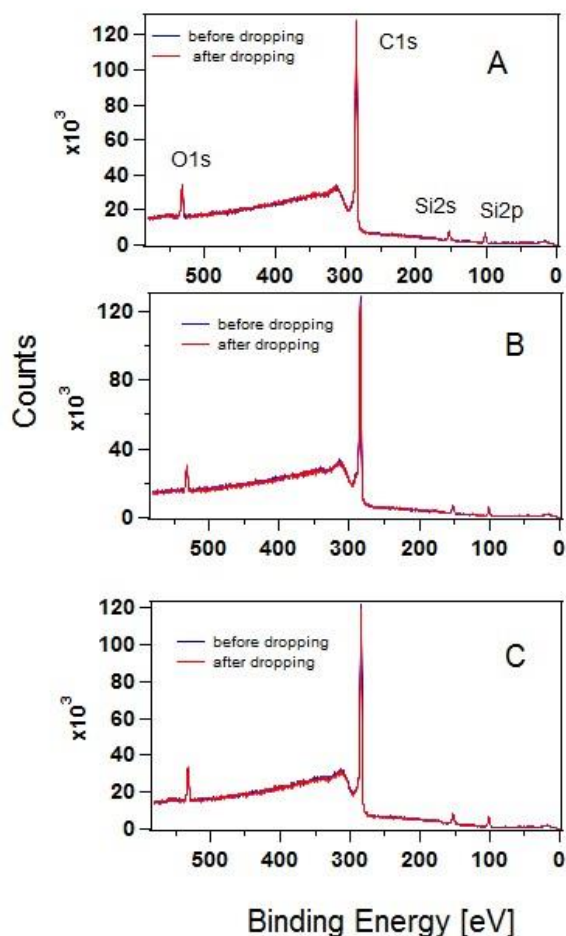

Figure SI-4. Representative survey (wide-scan) spectra obtained on different regions of the same FLG sample before and after dropping (L-Methionine solution).

Exfoliation

In the case of sonication treatment survey spectra (not shown) already showed significant differences.

High resolution XPS spectra obtained on FLG after sonication in DMSO are shown in Figure SI-5. The best fit positions for the C_G and the C_S components were found at 284.6±0.1 and 282.8±0.2 eV, respectively. The C_G peak maintains the Doniach-Sunjic line-shape. According to literature its small upward BE shift is also consistent with the thinning of the FLG film [3,4,8,9].

The neat decrease of the C_G peak intensity and the counterpart increase of the substrate-related peaks (C_S and Si_S) fairly testify a significant reduction of the FLG film thickness, related to exfoliation, in agreement with Raman measurements. We exploited the intensity of FLG- and SiC-related peaks derived from C1s and Si2p spectra to obtain an estimate of such reduction of thickness. 1h sonication in DMSO reduced the FLG thickness to ~40% of the initial thickness.

Note that the Si_D component appears much less affected by the sonication treatment. We may speculate that part of SiC faults could have hindered the formation of FLG.
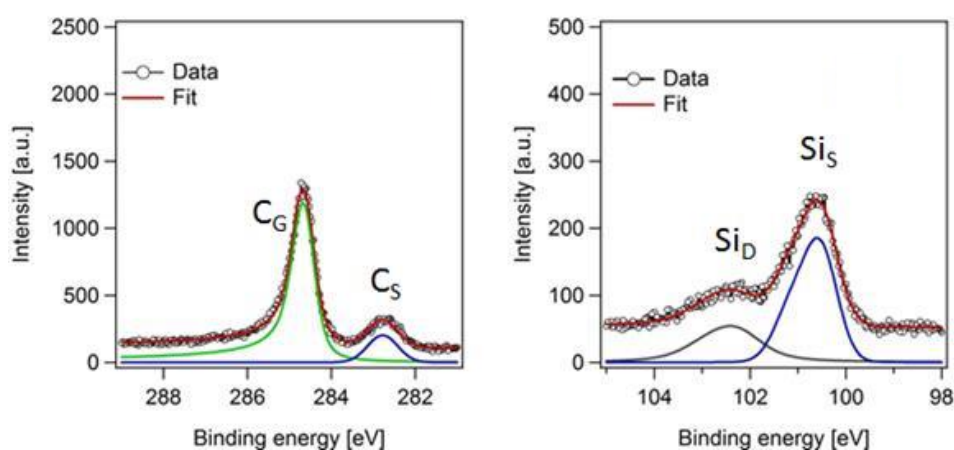

Figure SI-5. XPS core level spectra of the FLG film after sonication in DMSO. Left: C1s spectral region. Right: Si2p spectral region. The spectra are shown as a function of binding energy (BE). The take-off angle was 45°. The intensity scale in each panel is the same of Fig. SI-3 to help the comparison with FLG before sonication. Symbols: experimental data. Red line: best-fit curve. Sub-components are shown in different colors. For the meaning of labels see the text.

4. **HOPG exfoliation**

Exfoliation of graphite was characterized through an UV-Vis absorption spectroscopy analysis of the solution after sonication in DMSO. In order to obtain a sufficient quantity of exfoliated products we resorted to sonicate macroscopic flakes obtained by peeling HOPG samples. The HOPG flakes were let to deposit and the dispersions were repeatedly diluted in Milli-Q water to minimize scattering losses during the absorption measurements. As shown in figure SI-6 the absorption spectra of the diluted solution exhibit a maximum at ~ 270 nm, indicative of the π conjugated electronic structure of the graphene sheets [10]. The absorption measurements indicate a successful dispersion of graphene sheets, even at the very low solution concentration used in the present work.
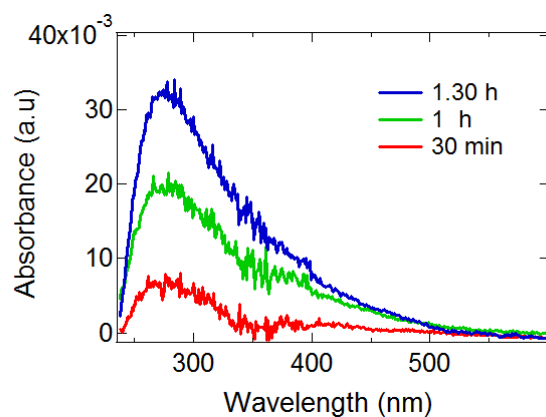
Figure SI-6. UV-Vis absorption spectroscopy of the solution after sonication in DMSO of macroscopic flakes obtained by peeling HOPG samples. Spectra obtained as a function of sonication time are shown.

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