Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ELECTRONIC SUPPLEMENTARY INFORMATION

"Probing plasma fluorinated graphene via spectromicroscopy"

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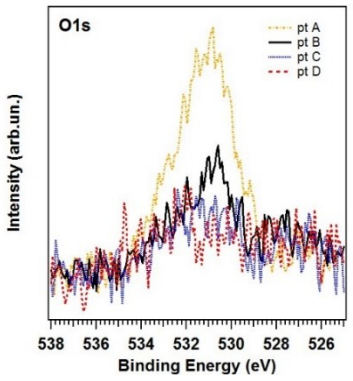

Figure S1 O1s spectra acquired on different ROIs at the sample surface: bare Cu surface (pt A), monolayer (pt B), bilayer (pt C) and multilayer graphene (pt D). The decrease in the intensity of the XPS signal for increased number of graphene layers indicates that O atoms are mainly located at the Cu surface.

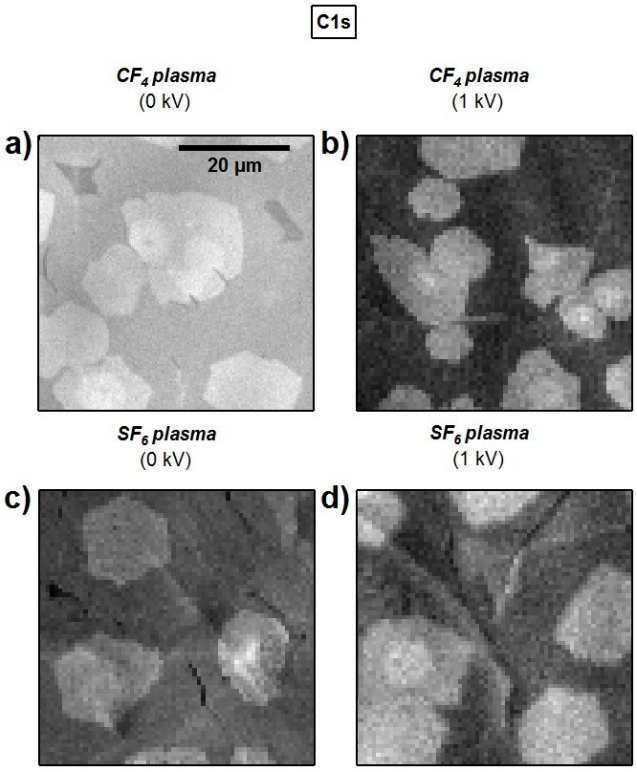

Figure S2 SPEM images (50×50 µm^2) of the fluorinated samples obtained by recording the C1s signal after fluorination. The light grey areas correspond to the graphene flakes whose dimension extends from 10 to 20 µm^2. Regions of multilayer graphene can be individuated as brighter islands. The flakes are preserved at µm scale for the used plasma parameters, as indicated in the figure.

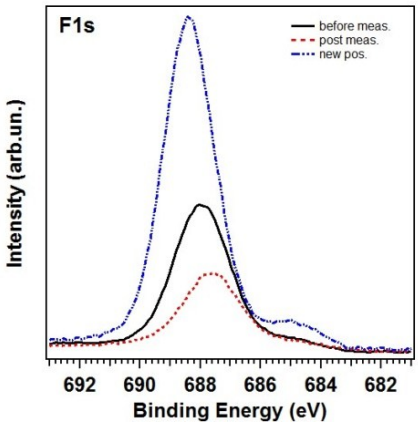

Figure S3 F1s spectra acquired after CF_4 fluorination (0 kV). The dotted blue and black continuous line spectra are recorded at different points of the sample surface using the same acquisition parameters. The difference in the intensity and the energy shift of the main peaks indicate that the fluorination is not spatially homogenously distributed; this is associated to a non-homogenous sample surface composed of islands with different numbers of graphene layers, ripples, wrinkles and bare Cu areas. The dotted red spectrum is recorded at the same region as the black one, after irradiation with a focused X-ray beam to 120 nm, viz. a high photon flux (number of photons per second per unit area). The energy shift in the main structure of the spectrum and the intensity decrease suggest that the resulting functionalization is sensitive to the photon flux.

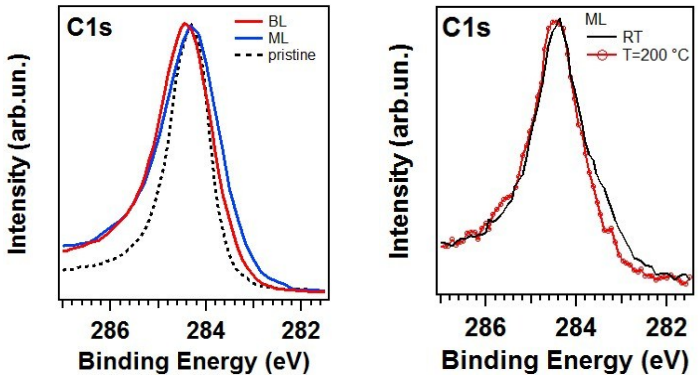

Figure S4 Micro XPS C1s spectra acquired on the sample surface after CF_4 fluorination (1 kV). (left) The black dotted line refers to the pristine sample, the blue one is acquired from monolayer (ML) while the red one from a bilayer (BL) area after plasma exposure. As discussed in the text, the carbon vacancies contribute to the intensity at lower binding energy side, indicating that the plasma treatment creates a higher C vacancy amount in thinner graphene layer. (right) C1s spectra

acquired from the as-functionalized monolayer (black continuous curve) and after heating it at T= 200 °C (red curve with circles). The reduced width of the red curve indicates that the vacancies generated by the ions during the plasma fluorination are partially filled up during the heating treatment.

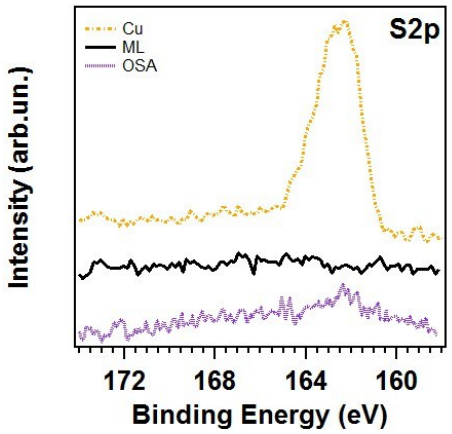

Figure S5 S2p spectra are acquired on SF_6 fluorinated graphene (0 kV). The S signal is only detected, by using the focused beam, on the bare Cu surface (yellow dotted line), while the monolayer area is sulfur-free (black continuous line). For comparison, the S2p spectrum collected with a non-focused beam spot (violet dotted curve) is added to the figure: the signal is slightly noticeable as the surface area of the Cu is almost fully covered by graphene.

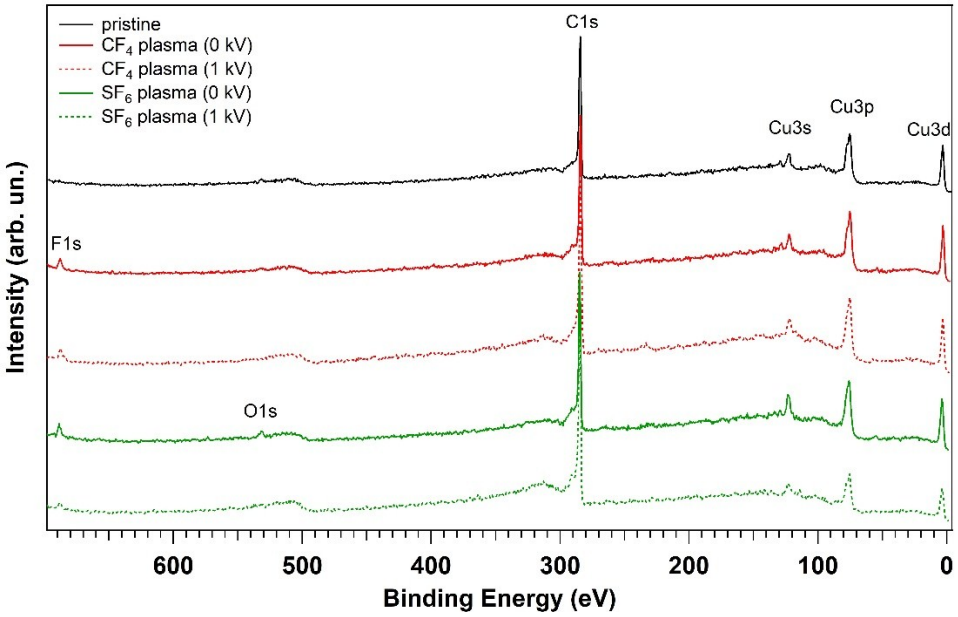

Figure S6 Survey spectra are acquired on pristine and plasma fluorinated samples using CF_4 and SF_6 plasma treatment with 0 and 1 kV.