Supporting Information

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Reversible Hydrogenation and Bandgap Opening of Graphene and Graphite Surfaces Probed by Scanning Tunneling Spectroscopy

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Supplementary information:

Reversible hydrogenation of graphene and graphite probed by scanning tunneling spectroscopy

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**Argon plasma treatment**

We have studied the role of the Ar ions impact (occurring during the Ar/H₂ plasma treatment) in the changes of the electronic properties of graphite and graphene. The samples are exposed for 40 min. to pure Ar plasma. After the treatment we perform a statistical analysis of 2000 scanning tunneling spectra acquired at 50-100 different spots in the samples surfaces. We have found that after a pure Ar plasma treatment the samples do not present the semiconducting behavior (accumulation of counts in the zero differential conductance region of the 2D histograms) observed in samples treated with Ar/H₂ plasma.
Figure S1. Two dimensional histograms of the differential conductance as a function of the tip bias voltage measured for pristine, Ar/H$_2$ plasma-treated and Ar plasma-treated samples: HOPG (a) and CVD graphene (b). The changes on their electronic properties are probed after the different treatments, measuring 2000 STS spectra at 50-100 different positions on the surface. The hydrogenation step is carried out by a 40 min. exposure to an Ar/H$_2$ plasma. The effect of Ar ion impacts on the electronic properties is studied by exposing the samples for 40 min. to an Ar plasma. For both the HOPG and CVD graphene samples, after the Ar/H$_2$ treatment, the 2D histograms show a semiconducting behavior (accumulation of data points around zero differential conductance value). Samples treated with the pure Ar plasma do not show this behavior.

While the samples treated with Ar/H$_2$ plasma present a high accumulation of traces with a flat region with zero differential conductance (indicating the opening of a bandgap), the samples treated with pure Ar plasma maintain a conducting behavior with only some residual traces with zero differential conductance which can be attributed to the presence of some adsorbed insulating molecules or lattice defects (see Figure S2).

Figure S2. One dimensional histograms extracted from a profile along the dashed line (zero differential conductance) in the two dimensional histograms of Figure S1 for samples treated with the Ar/H$_2$ plasma (light blue) and Ar plasma (dark blue). Left panel corresponds to the HOPG and right panel to CVD graphene sample.
2D histograms of IV traces

The 2D histograms shown in Figure 2 of the manuscript are obtained by numerical differentiation of current vs. tip bias voltage traces (IV traces). Here we show the 2D histograms employing the IV traces without differentiation. From Figure S3, it is clear that the most probable IV traces for samples treated with the Ar/H₂ plasma show a flat region with zero current, indicating the opening of a bandgap around the Fermi level.

![HOPG 2D histograms](image)

![CVD graphene 2D histograms](image)

**Figure S3.** Two dimensional histograms of the tunneling current as a function of the tip bias voltage measured for HOPG (a-e) and CVD graphene (f-j) at different stages of the hydrogenation/dehydrogenation treatments. These 2D histograms are composed by 2000 of current vs. voltage traces measured at 50-100 different spots on the samples. The 2D histograms shown in Figure 2 of the manuscript have been prepared by numerical derivation of the IV traces employed in these histograms.

2nd hydrogenated CVD graphene sample

Here we show the results obtained for another graphene sample grown onto nickel. The main features shown in Figure 2 of the manuscript are also shown in this sample. After the plasma treatment, the sample shows a semiconducting behaviour which disappears after a moderate thermal annealing. Eventhough the higher heterogeneity of the CVD graphene samples the semiconducting behavior shown after Ar/H₂ plasma and the conducting behavior after annealing are robust results.
**Figure S4.** Two dimensional histograms of the differential conductance as a function of the tip bias voltage measured for another CVD graphene sample (different that the one used in the manuscript figures) at different steps of the hydrogenation/dehydrogenation process (a-c).