

Electronic Supplementary Information

## The nature of the Fe-graphene interface at the nanometer level

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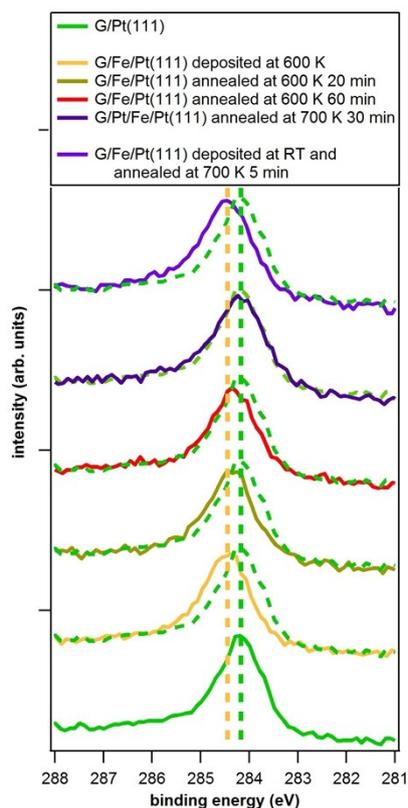
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### Additional XPS data on alloy

Fe-Pt alloy formation was investigated by photoemission spectroscopy using C 1s core level, since C 1s binding energies (BEs) can be used as diagnostic tool to determine if Fe is in contact with Fe, Pt or an alloy. The spectra reported here have a lower resolution than those shown in the paper because they were acquired using a conventional Mg K<sub>α</sub> x-ray source (Fig. S1).

As reported in the manuscript, the C 1s BE of G in contact with Fe, either as NPs deposited above G or as a flat intercalated layer, is centered at 284.4 eV, whereas for the G/Pt(111) interface, the C 1s peak maximum is positioned at 284.15 eV.



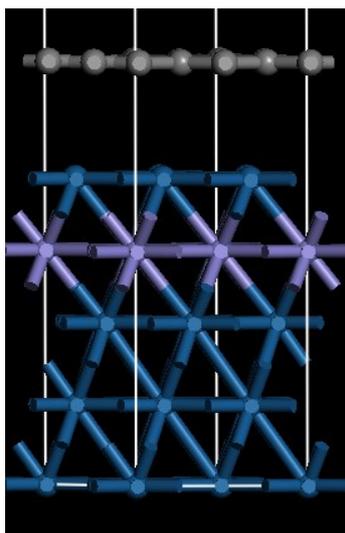
**Fig. S1.** C 1s photoemission lines corresponding to 1 ML Fe deposited on G/Pt(111) following different routes (deposition at RT and 600K), and subjected to different thermal treatments.

By annealing the sample it is possible to convert the interface from G/Fe/Pt(111) to G/Pt/Fe/Pt(111) since Fe tends to diffuse into the bulk of Pt leaving a Pt skin on the surface.

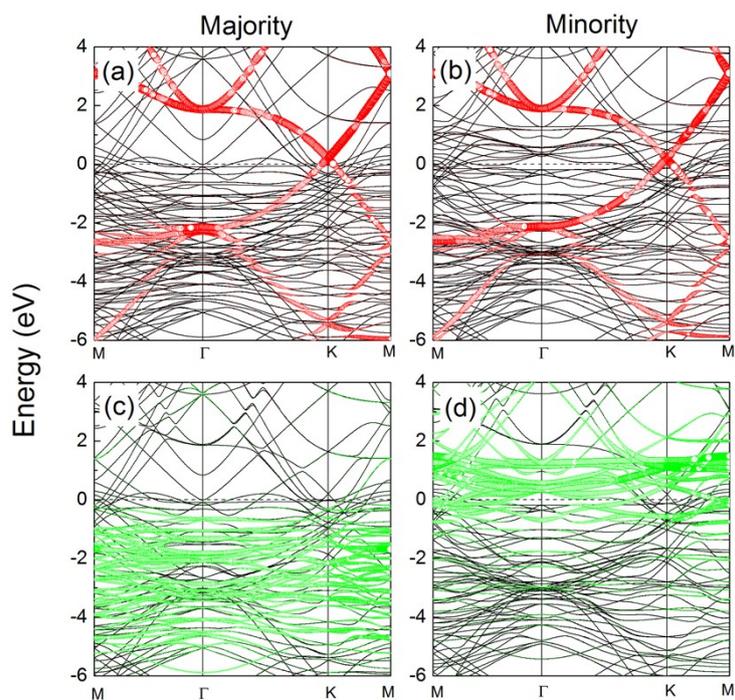
The kinetics of the process can be followed as a function of time by monitoring the shift in the BE of the C 1s photoemission peak. As observed in the data reported in Figure S1, for short annealing time, Fe is pinned at the interface with G, whereas longer annealing treatments promote its dissolution into the bulk Pt.

### DFT calculations on G/Pt/Fe/Pt(111)

To study the structure of G on Fe-Pt alloy with Pt skin, we simulated a system with Fe buried into the second layer of Pt(111), see Fig. S2 for the atomic structure. The calculated energy of this G/Pt/Fe(1ML)/Pt(111) system is 0.76 eV/Fe atom lower than G/Fe(1ML)/Pt(111). Plotted in Fig. S3 is the band structure for this system. As shown, the calculated band structure is very similar to that of G/Pt(111) (see Fig. 4 in the main text). C  $2p_z$  and Fe  $3d$  states do not interact due to the presence of the Pt layer. The dispersion of the  $\pi$  band is linear around the K point and the Dirac point can be observed about 0.25 eV above the Fermi level, which is slightly lower than on G/Pt(111) (0.5 eV).



**Fig. S2.** Optimized structure of G/Pt/Fe(1ML)/Pt(111) with one monolayer Fe buried below 1 ML of Pt. Gray, purple, and dark blue spheres indicate C, Fe, and Pt atoms, respectively.



**Fig. S3.** Band structures of the intercalated system G/Pt/Fe(1ML)/Pt(111). (a) Majority spin and (b) minority spin band structures with the contributions of carbon  $2p_z$  states are highlighted in red. The contributions of Fe  $3d$  states to (c) majority and (d) minority spin band structures are highlighted in green. The Fermi level is set at zero.