

The nature of the Fe-Graphene interface at the nanometer level.

Mattia Cattelan, Luca Artiglia, Emanuele Cavaliere, Marco Favaro, Stefano Agnoli, Alexey Barinov, Silvia Nappini, Elena Magnano, Federica Bondino, Luca Gavioli and Gaetano Granozzi

Department of Chemical Sciences, University of Padova, via Marzolo 1, 35131, Padova, Italy

mattia.cattelan.1@studenti.unipd.it

Abstract

The study of the interface between Graphene (G) and metals is gaining more and more interest thanks to the growing industrial application of G in flexible electronics [1] and future use in high frequency transistors and thin film logic devices. G is also emerging as the ideal platform for future spintronics since it combines long spin lifetime and excellent electron velocity [2],[3]. In this context, the possibility to manipulate the local properties of the G/metal interface by the introduction of other species through the *intercalation* process, represents an easy method to obtain tailored interfaces [4],[5].

The aim of our work is to study how Fe interacts with the G/Pt(111) system either after *in-situ* UHV deposition at room temperature (RT) or at T=600 K. In this way two complementary systems can be investigated: supported Fe nanoparticles (NPs) (i.e. Fe/G/Pt(111)) and *intercalated* Fe layers (i.e. G/Fe/Pt(111)). Moreover, the oxidation of these systems was investigated by dosing oxygen at RT in the range of 10^{-6} mbar. To understand the electronic properties of G in contact with Pt(111) and Fe, photoemission spectroscopy from core-levels, near edge x-ray absorption fine structure (NEXAFS) and angle resolved photoelectron spectroscopy (ARPES) were carried out using synchrotron radiation. We also performed scanning tunneling microscopy (STM) to obtain a precise view of G lattice morphology at the atomic scale.

G was grown on Pt (111) by dosing of C_2H_4 at 1100 K obtaining a quasi free-standing layer [6]; Fe was deposited on G/Pt(111) by physical vapor deposition (PVD) at RT. Fig. 1*a,b,c,d* shows the evolution of the C 1s photoemission line as a function of the Fe coverage (0, 0.5, 1 and 1.5 equivalent ML). Three different components can be clearly identified: the peak at 284.16 eV is due to the unperturbed G atoms (as for G/Pt(111)), whereas the two components at 284.40 eV and 285 eV are associated to the sp^2 atoms in contact with Fe and to a partial rehybridization of G to sp^3 driven by the strong Fe-C interaction [7], respectively. STM data acquired upon Fe deposition at RT show a rough G morphology, in good agreement with the XPS data and the hypothesis of a G local rehybridization.

The intercalated system, G/Fe/Pt(111), was prepared by depositing Fe at 600 K or heating the Fe/G/Pt(111) system at this temperature. In this case STM data (Fig. 3) show the formation of ML thick islands of Fe on the Pt surface, covered by a continuous unperturbed layer of G. This extraordinary continuity suggests that the combination of these two metals can be one of the best choices for future spintronic studies and devices. The flatness of the Fe layer *intercalated* below G was confirmed also by photoemission (Fig. 1*f*): the peak at 284.16 eV, which is the fingerprint of G in contact with Pt(111) is completely suppressed.

ARPES measurements show major differences in the G band distribution for G/Pt(111) and G/Fe interfaces. In the G/Pt(111) case (Fig. 2*a*), G is scarcely interacting with the Pt 5*d* states; around the K point the π band of G has a linear dispersion as in quasi free-standing layer [8]. On the contrary, when G is in contact with Fe, either in the Fe/G/Pt(111) (Fig. 2*b*) or G/Fe/Pt(111) (Fig. 2*d*) case, a relevant

hybridization of its π band with Fe $3d$ states can be observed. At about 4 eV the band deviates from the linear dispersion typically observed around the K point, and it bends remaining pinned at about 2.6 eV below the Fermi level. Similar features in C $1s$ and ARPES spectra are reported in the literature for G interacting with other not-noble d -metals, such as Ni(111) [4].

To study the oxidation of our system O_2 was dosed on Fe/G/Pt(111), obtaining a defective oxide referenced as FeO_x . Both photoemission from core levels and ARPES show that this oxide does not interact with G. In the C $1s$ photoemission line related to $FeO_x(1.5 \text{ ML})/G/Pt(111)$ (Fig. 1e), we observed a decrease of the component of Fe/G and an increase of the one related to unperturbed G. Surprisingly, also the component at 285 eV is strongly suppressed after oxidation, demonstrating that the local hybridization to sp^3 is reversible.

From ARPES measurements it is clear the absence of an interaction between the FeO_x and G. The π band is no more hybridized with the Fe $3d$ states (Fig. 2c), it has very similar structure of the G/Pt(111) (Fig. 2a). The attempt to oxidize the G/Fe/Pt(111) system with O_2 at RT was unsuccessful, indicating that this system can be a good platform to grow arrays of intercalated ferromagnetic islands that could be protected from air oxidation.

References

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Figures

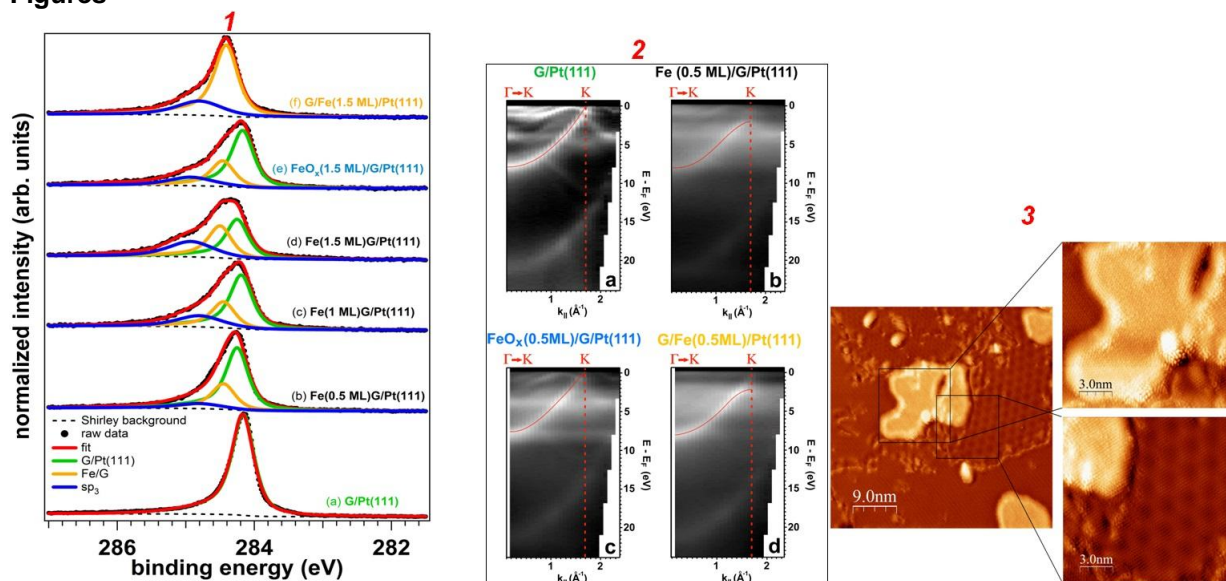


Figure. (1) C $1s$ photoemission line ($h\nu=550 \text{ eV}$) deconvoluted into single chemical shift components for (a) G/Pt(111) system (b,c,d) after Fe deposition, (e) oxidation and (f) intercalation at 600 K. (2) ARPES acquisition in the Γ to K direction of G for (a) G/Pt(111) system (b) after Fe deposition, (c) oxidation and (d) intercalation at 600 K. Dashed red line are for the theoretical position of the G K point in a free-standing layer. (3) STM image of a Fe island on Pt(111) intercalated below a G layer.