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Strong dependence of flattening and decoupling of graphene on metals on the local distribution of intercalated oxygen atoms

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ABSTRACT

We show that the flattening of a highly corrugated graphene layer grown on Rh(111) is linked to its decoupling from the metal substrate taking place during oxygen intercalation in the lowest moiré sites. We have been able to track this process at the atomic scale by combining scanning tunneling microscopy experiments and first-principles calculations. Initially, intercalated and non intercalated areas can coexist through a careful experimental control of the oxygen dosage and temperature. This allows a direct comparison of the corrugation profiles of both areas. Although the corrugation increases for very low coverages, higher oxygen concentrations provoke the occupation of the lowest moiré sites leading to a flattening of the graphene sheet. This mechanism is confirmed by calculations and scanning tunneling spectroscopy measurements reveal that the flattening of the graphene layer is linked with the local uncoupling from the metal induced by the increasing oxygen concentration. This process, completed only when the lowest moiré sites are filled with oxygen, finally converts a strongly coupled system into a free-standing like p-doped graphene layer.

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1. Introduction

During the 60's and 70's, hundreds of graphite intercalation compounds were synthesized [1]. These materials were produced by the insertion of layers of different chemical species between the atomic planes in the graphite host material. The driving force for this work was the possibility of tuning properties like the electrical conductivity from an almost insulating behavior along the c-axis in certain acceptor compounds to in-plane superconductivity in some alkali metal donor compounds. Many years later, after the isolation of a single graphite layer, graphene [2], and the discovery of its extremely unique properties [3–6], it is not surprising that the study of intercalation in graphene-substrate systems has become a hot topic. The motivation for intercalating atoms or small molecules between graphene and the substrate was to preserve the characteristic electronic properties of the graphene monolayer (G) after deposition.

One of the first successful attempts was achieved on G grown on the SiC(0001) surface, where the intercalation of hydrogen [7] led to the production of enhanced transistors [8]. After that, many examples with different intercalated species like oxygen [9], gold [10], lithium [11], germanium [12] or fluorine [13,14] were reported. All these cases showed the recovery of the typical linear dispersion near the Dirac point, that was slightly shifted due to the charge doping with a sign depending on the electronegativity of the intercalated species.

Intercalation has been also explored in graphene-metal systems, both in the weakly and strongly interacting cases. In the first group, the G is not highly coupled with the metallic surface and it presents a small geometrical corrugation. The intercalation of both electropositive (silicon [15], caesium [16,17] and europium [17–19]) and strongly electronegative atoms (mainly atomic oxygen [20,21]) has been studied in the representative G/Ir(111) case. For strongly interacting systems, most efforts have been focused on the highly







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corrugated G/Ru(0001) [22–30] case, with only one study in G/ Rh(111) [31]. Again, besides the examples with silicon [22,23], Ar [24] and metal species [25–28], it is also possible to intercalate atomic oxygen on G/Ru(0001) [29,30]. The first successful O intercalation [29] already included a simple explanation of the process and latter contributions have tried to go further in the elucidation of the mechanism, particularly refs. [22] and [23] that combine experiments with first-principles calculations. The emerging consensus is that intercalation should occur via adatom diffusion through point defects or grain boundaries in G, but none of these studies, dealing only with the initial and final stages of the intercalation process, has been able to provide conclusive information about the intermediate steps in order to achieve an atomic-scale description of the whole process.

In this work, we characterize the oxygen intercalation process in G/Rh(111), following its evolution as a function of the oxygen coverage. High-resolution Scanning Tunneling Microscopy (STM) measurements and a precise control of the experimental conditions (O dosage and temperature) allow us to study how corrugations and electronic properties change at the atomic-scale during the process. Density Functional Theory (DFT) simulations of the equilibrium geometries for different O concentrations explain the evolution of the corrugation found in the experiments. The corresponding changes in the electronic properties of the G, revealed by first principles calculations, shows how the electronic decoupling is taking place only when oxygen atoms are placed under the graphene areas closest to the metal. This means that corrugation and decoupling not only depend on the oxygen coverage but also on the specific intercalation sites.

2. Results and discussion

Epitaxial graphene was grown on Rh(111) under ultra-high vacuum (UHV) conditions via chemical vapor deposition (CVD) of low pressure ethylene (C_2 H₄). Samples were then transferred in situ (under UHV) to a home-built STM [32,33] where data were measured at room temperature (RT) using the WSxM software [34]. Although many different moiré periodicities could be formed [35] during this preparation, Fig. 1a shows that the metal is mostly covered by a 12×12 graphene moiré aligned with a commensurate 11×11 supercell in the Rh(111) surface. This large and highly corrugated moiré has been well characterized previously by experiments and first principles calculations [35,36]. The G-metal distance varies significantly within the moiré unit cell, from less than 2 Å in the most coupled areas (bridge position) to more than 3 Å in the highest ones (top position) [35]. The oxygen intercalation was carried out after graphene growth and required a careful experimental control in order to study the different steps during this process. It consists on exposing the sample to oxygen gas $(6 \times 10^{-7} \text{ Torr})$ while the temperature is kept at around 570 K, paying special attention to small variations of this parameter in order to avoid graphene oxidation [37]. The amount of oxygen atoms intercalated was varied by changing the exposure time from 30 to 100 min. With this procedure, we have been able to follow the intercalation process with STM imaging from the very first steps to nearly a complete monolayer (Fig. 1). In the first stage, an increase of the corrugation due to intercalation of oxygen in the most detached parts of graphene, i.e., top positions, is observed (see Figs 1b and 2c). As a second step in the intercalation process Fig. 1b clearly shows how oxygen starts spreading beneath graphene by linking these top areas and creating strands, always trying to avoid, as much as possible, the occupation of strongly coupled bridge positions. As the oxygen exposure time is increased, larger areas of the surface are intercalated, creating either triangular islands or longer strands (Fig. 1c and d). All of these structures not only follow the



Fig. 1. a) 25×25 nm² (-450 mV, 2.0 nA) typical graphene on Rh(111) surface where the $(12 \times 12)_G$ on $(11 \times 11)_{Rh}$ moiré pattern is observed. Inset: 6×5 nm² image where the moiré pattern is atomically resolved (-410 mV, 2.0 nA). b-e) Typical structures formed by the oxygen intercalated on graphene on Rh(111): b) 25×25 nm² (100 mV, 8.6 nA) the intercalation process starts by linking high areas of the moiré pattern with thin stripes and triangular structures; c) 25×25 nm² (140 mV, 7.8 nA) triangular islands of intercalated oxygen with a threefold symmetry; d) 50×50 nm² (95 mV, 8.6 nA) thicker stripes of intercalated oxygen where only the closest areas of the graphene to the metal (bridge positions) are still coupled; e) 50×50 nm² (70 mV, 6.0 nA) almost the saturation coverage of the surface of intercalated oxygen is achieved. Inset: LEED pattern (55 eV) where the graphene, the Rh(111) and the $2 \times 2/2 \times 1$ oxygen structures can be observed when the oxygen saturation coverage is achieved. (A colour version of this figure can be viewed online.)

moiré orientation but also its periodicity. This is consistent with the fact that the intercalation seems to proceed by first connecting the highest areas, using as few bridge areas as possible. Both strands and triangular shapes are structures in which top areas are linked in such a way that the bridge positions occupied by oxygen are as few as possible. If the amount of oxygen is further increased, the lower parts of the moiré start detaching and the intercalated paths become thicker, leaving just few bridge graphene positions coupled to the substrate (Fig. 1e). For large oxygen coverage, a LEED pattern (inset of Fig. 1) was observed corresponding to a $2 \times 2/2 \times 1$ oxygen structure with respect to the metal surface.

A systematic study of the experimental apparent corrugation (Fig. 2) provides insight into the intercalation process. As observed in Fig. 2a the apparent height of the graphene layer increases when oxygen is located in the interface. For comparison, the typical apparent corrugation of the G/Rh(111) moiré, without oxygen, is



Fig. 2. Variation on the topography images corrugation. a) $13 \times 10 \text{ nm}^2$ (150 mV, 8.5 nA) topography image where it is clearly observed the variation on the graphene corrugation with the oxygen intercalation on different positions of the moiré pattern; b) $9.2 \times 8 \text{ nm}^2$ (40 mV, 11 nA) typical corrugation found on graphene/Rh(111), with no oxygen intercalation; c) $9.2 \times 8 \text{ nm}^2$ (100 mV, 5.9 nA) at low coverage, the atop position of the moiré increases with the oxygen intercalation. The line profile illustrates the comparison between the corrugation of intercalated (the two moiré half-cells on the right) and non-intercalated (the half-cell on the left) areas; d) $9.2 \times 8 \text{ nm}^2$ (1.2 V, 3 nA) at high coverage the corrugation of the graphene decreases to ~10 pm. (A colour version of this figure can be viewed online.)

shown in Fig. 2b (~0.6 Å). For low oxygen coverage (Fig. 2a and c), the G top areas with oxygen atoms beneath are higher with respect to other top areas with no oxygen intercalated. The strand structures have also a larger corrugation. For high enough coverage, where the lower areas of the moiré pattern start being filled with oxygen, this trend is reversed and the corrugation decreases as the intercalation proceeds. In the final stages (Fig. 2d), the whole graphene layer completely detaches from the metal surface and the apparent corrugation of the moiré pattern is minimal (lower than 15 pm).

We have used DFT simulations in order to gain insight into the atomistic mechanisms behind the intercalation and the graphene flattening processes observed experimentally and its relationship to the resulting electronic structure. The calculations have been performed with the VASP code [38] using the PBE [39] exchange-correlation functional supplemented with semi-empirical van der Waals D2 interactions [40], PAW pseudopotentials [41,42] and a plane-wave basis set of 400 eV (see Ref. [35] and Supporting Information for further details).

Our approach to simulate the experiments is based on the characterization of the equilibrium structures of the G/O/Rh(111) system for different oxygen coverage. Performing these large set of calculations on the $(12 \times 12)_G$ on $(11 \times 11)_{Rh}$ moiré is not feasible, so we have restricted our study to the $[(\sqrt{43} \times \sqrt{43})-R7.6^\circ]_G$ on $(6 \times 6)_{Rh}$ moiré, that shares the main features of the larger moiré and has been experimentally found and characterized in our previous study of the G/Rh(111) system [35].

We have performed a series of simulations placing a different number of oxygen atoms between G and the Rh surface. O atoms were always put in fcc-hollow (fcc) sites, as our calculations show that these are the most energetically favorable adsorption positions even in the presence of G. Our $(6 \times 6)_{Rh}$ cell has a total of 36 fcc sites. We have explored this huge phase space, with particular attention to low coverage, by studying multiple combinations of 1, 3, 4, 6, 9 and 18 intercalated atoms. The last two cases correspond to the 2×2 and 2×1 reconstructions identified by LEED.

The structural parameters of the most representative cases for different coverages are collected in Table 1 (all the structures are characterized in Supporting Information). For a single intercalated atom (O-1 in Table 1), there is a clearly preferential adsorption site:

just below the higher parts of the moiré. Simulations where G was free to move in the *xy* plane reveal a clear displacement of the whole G layer in order to adjust the higher area right above the O adatom. We can quantify this preference with calculations where only the *z* coordinates were allowed to relax. In this way we showed that all alternative sites were clearly unfavorable (0.25 - 1.50 eV higher). The corrugation of this single-atom structure increases from 1.07 Å to 1.35 Å. Adding two more oxygen atoms in the surrounding positions ($\Theta_0 = 1/12$, structure O–c3), the corrugation increases even further to 1.50 Å (see the corrugation color maps in Fig. 3).

Notice that the absolute values of the geometrical corrugation obtained by DFT are larger than the STM apparent corrugation due to the important contribution of electronic effects to the tunneling process [35], but we can still use their changes to follow the evolution of corrugation during the intercalation process. From the calculations, it is clear that, in the initial stages, the G corrugation increases. However, for $\Theta_0 = 1/6$ (6 atoms in our 6×6 cell), the original corrugation value has been recovered but only in those cases where 0 atoms start to occupy the most unfavorable positions like in the O-c6tri2 structure (see other structures in Supporting Information). And most importantly, for higher coverage (1/4 and 1/2), a flattening transition occurs and the corrugation almost disappears (~10 pm). These results are fully consistent with the evolution seen in the experiments (Fig. 2).

As we will show, there is a direct relationship between

Table 1

Relevant structural parameters of the G layer on the G/O/Rh(111) system for different O coverages (Θ_O): average adsorption distance z_{av} , height dispersion σ_z , minimum z_{min} and maximum heights z_{max} and corrugation C_G . All distances are in Å and referred to the top of the Rh(111) surface.

Structure	Zav	σ_z	Z _{min}	Z _{max}	C _G	Θ_0
w/o-0	2.49	0.35	2.07	3.14	1.07	0
0-1	2.47	0.40	2.01	3.36	1.35	1/36
0-c3	2.58	0.46	2.01	3.51	1.50	1/12
O-c6tri2	3.27	0.24	2.66	3.59	0.93	1/6
0-(2 × 2)	3.60	0.023	3.54	3.65	0.11	1/4
$0-(2 \times 1)$	3.93	0.028	3.87	3.98	0.11	1/2



Fig. 3. Electronic and structural properties of the G/O/Rh(111) system as a function of O coverage (Θ_0). For each coverage value we present: i) a height-map (in Å) of the carbon atoms belonging to the graphene monolayer and the positions of the intercalated oxygen atoms in red with black edges, ii) a schematic ball-and-stick model with the side view of the unit cell (only the uppermost layer of the metallic slab is shown) and the values of the graphene corrugation and the average adsorption distance and iii) the projected density of states of the carbon atoms highlighted in different colors compared with the PDOS of a free-standing G. (A colour version of this figure can be viewed online.)

corrugation, observed both through experiments and calculations, and the graphene layer electronic structure. We have analyzed the correlation between the intercalation structures and the electronic state of the G atoms using the projected density of states (PDOS). Fig. 3 shows five different steps of the process. In G/Rh(111), the characteristic linear dispersion around the Dirac Point has been completely destroyed ($\Theta_0 = 0$ in Fig. 3). There are no significant changes in the PDOS for $\Theta_0 \leq 1/12$, what is consistent with the small structural changes in the G layer (see Table 1). However, for $\Theta_0 = 1/6$, the PDOS of the atoms in the G higher areas begin to resemble the one of pristine G. Although the corrugation is still very similar to the initial state, the partial decoupling takes place because of the increment in average adsorption distance, from 2.49 Å to 3.27 Å. This decoupling is very local and depends strongly on the detailed distribution of the O intercalated atoms. The electronic decoupling is provoked by the occupancy of the most unfavorable adsorption sites that leads to a reduction in the corrugation: our calculations show how structures, like O-c6tri2, are more uncoupled than others, like O-c6 in Supporting Information, which despite having the same coverage, oxygen atoms are all placed under the higher parts of the moiré. The same tendency is observed in the corrugation of these two structures.

In the final stages, when the interface is filled with a 2×2 ($\Theta_0 = 1/4$) or 2×1 ($\Theta_0 = 1/2$) structure of oxygen and the graphene surface is almost completely flattened (~10 pm), these PDOS show the complete recovery of the characteristic linear dispersion. Also, there is a shift of 0.45 eV for the first structure or 0.63 eV in the second case in the Dirac point due to the charge taken from the G π -states by the O/Rh underneath substrate.

The electronic decoupling of graphene observed in the calculated PDOS for coverages above the flattening transition has also been verified experimentally. A first evidence can be obtained from Fig. 4a that shows a low bias STM image measured at high oxygen intercalation coverage where one atomic-size surface defect is observed. This defect is surrounded by a $(\sqrt{3} \times \sqrt{3})$ R30° (R3 in the following) pattern that extends a few nm. In ideal graphene, atomic-size impurities give rise to intervalley scattering processes [43] that lead to modulations of the local DOS with R3 periodicity (see also Fig. S6 in Supporting Information). These R3 modulations have been observed in well-decoupled graphene layers as epitaxial graphene on SiC [44] or graphite [45], among others. Therefore the existence of well-extended R3 patterns on our oxygen intercalated G surface can be explained as a direct consequence of the electronic uncoupling. A further direct evidence has been obtained by measuring scanning tunneling spectroscopy (STS) data on intercalated surfaces. Fig. 4b shows STS data that reveal the characteristic V-shape corresponding to the linear dispersion of ideal G (the complete spectrum is shown in Fig. S7 in Supporting Information). Its minimum can be identified with the Dirac point experimentally located at ~0.65 eV. This behavior corresponds exactly with what was obtained from the electronic structure calculations of the PDOS of the $O-(2 \times 1)$ reconstruction below G (Fig. 4b).



Fig. 4. Two different experimental observations bear out graphene decoupling: a) $4.7 \times 4 \text{ nm}^2$ image of the graphene/oxygen/Rh(111) where one surface defect is observed. This defect gives rise to the typical $(\sqrt{3} \times \sqrt{3})$ R30° electronic modulation of defects in uncoupled graphene due to intervalley scattering (20 mV, 9.5 nA); b) numerical dl/dV curve obtained at the graphene/oxygen/Rh(111) surface at room temperature compared with the theoretical PDOS of $G/O-(2 \times 1)/Rh(111)$. (A colour version of this figure can be viewed online.)

3. Conclusions

In summary, the combination of STM experiments and first principles calculations allowed us to get new insights in the study of intercalation processes in graphene-metal systems. Intermediate stages of the process have been described as a function of the oxygen coverage thanks to a careful control of the experimental conditions. We have studied in detail the changes in corrugations on the G from the initial stage in a highly corrugated coupling state to a completely flat and uncoupled quasi-free-standing graphene. Finally, we have demonstrated how these changes in corrugation and adsorption distance are directly correlated with the step-bystep electronic decoupling of the G, showing that decoupling takes place only when the lowest moiré areas, the sites where the G bonds to the metal, are occupied by oxygen atoms and therefore the graphene layer is flattened. As a final perspective, our work shows that coupled and uncoupled graphene areas can coexist on the same G surface when a well-controlled intercalation procedure is experimentally applied. The coexistence of such regions opens up new possibilities in further graphene studies.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.01.079.

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