Strong Dependence of Flattening and Decoupling of Graphene on Metals on the Local Distribution of Intercalated Oxygen Atoms

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CONTENTS

| Computational details | S3 |
|--|-----|
| Detailed time-line of electronic decoupling | S4 |
| Details of the LEED pattern | S9 |
| Electronic decoupling studied through $(\sqrt{3} \times \sqrt{3})$ R30° modulation | S10 |
| Complete STS spectrum | S11 |
| References | S12 |

COMPUTATIONAL DETAILS

All simulations have been performed using the VASP code [1] with a plane-wave basis set with an energy cutoff of 400 eV to ensure a proper convergence. The PAW method [2, 3] was used to construct pseudopotentials of all species and a Generalized Gradient Approximation was used in the exchange and correlation functional as described by Perdew, Burke and Ernzerhof (PBE) [4]. A semi-empirical correction (D2 by Grimme [5]) was added to the final energy in order to take into account dispersion forces between the metallic surface and G. In this kind of system, London forces have a crucial role in the physics of the problem so neglecting them led to a significantly larger corrugation values [6]. The supercell used in the simulations, with a total of 230 atoms excluding oxygen atoms, consists in the superposition of a four-layer slab $(6 \times 6)_{Rh}$ cell in Rh(111) and a $[(\sqrt{43} \times \sqrt{43}) - R7.6^{\circ}]_G$ reconstruction in graphene with more than 14 Å of vertical spacing between periodical images. Details of the lattice parameters, strains and the procedure to build this cell avoiding the mismatch between lattices are explained in our previous work [7]. Each structure, containing different number of oxygen atoms, was subjected to ionic relaxation following a conjugate gradient algorithm until forces upon atoms were less than 0.01 eV/Å. During these relaxations the two deepest layers of the slab were kept fixed while all the rest, including oxygen atoms, were allowed to relax. The reciprocal space was sampled by a minimal $2 \times 2 \times 1$ Monkhorst-Pack grid [8] when relaxing structures and it was increased to a $11 \times 11 \times 1$ grid when calculating densities of states. It is worth noting that before starting calculations of the oxygen intercalation, we tested the pseudopotentials and functionals by studying the adsorption of atomic oxygen on the Rh(111) surface both in the 2×2 and 2×1 reconstructions comparing with previous theoretical calculations [9] in good agreement with experimental results [10].

DETAILED TIME-LINE OF ELECTRONIC DECOUPLING

In figure 3 of the main text we have shown a representative selection of the total intercalated structures studied. In this section we show the complete set of those structures for different coverage degrees. In table S1 we collect the main structural parameters of each structure labeled in the same way as in the following figures. In each figure we show a detailed height map of the structure together with a PDOS of some atoms compared with the DOS of the free-standing graphene. As it is explained in the main text we show this wide selection of structures to highlight that decoupling has not a simple linear dependence with the oxygen coverage. Only those structures with enough coverage and some oxygen atoms located in the most unfavorable adsorption positions, like O–c6tri1, O–ctri2, O–c6rows, lead to partially-decoupled systems. On the contrary structures with all oxygen atoms located under the higher areas of the moiré pattern, like O–c4 or O–c6, do not show a significant electronic decoupling.

TABLE S1. Relevant structural parameters of the graphene/O/Rh(111) for different 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 with respect the top of the metallic surface.

| Structure | z_{av} (Å) | σ_z (Å) | z_{min} (Å) | z_{max} (Å) | C_G (Å) | Θ_O |
|--------------------------------|--------------|----------------|---------------|---------------|-----------|------------|
| | | | | | | |
| O-1 | 2.47 | 0.40 | 2.01 | 3.36 | 1.35 | 1/36 |
| O–c3 | 2.58 | 0.46 | 2.01 | 3.51 | 1.50 | 1/12 |
| O-c4 | 2.66 | 0.47 | 1.98 | 3.55 | 1.57 | 1/9 |
| O–c4cro | 2.74 | 0.42 | 1.96 | 3.40 | 1.44 | 1/9 |
| O–c6 | 2.71 | 0.49 | 2.06 | 3.59 | 1.53 | 1/6 |
| O–c6tri2 | 3.27 | 0.24 | 2.66 | 3.59 | 0.93 | 1/6 |
| O-c6tri1 | 3.30 | 0.21 | 2.83 | 3.62 | 0.80 | 1/6 |
| O–c6rows | 3.31 | 0.21 | 2.96 | 3.59 | 0.62 | 1/6 |
| $\mathrm{O}\text{-}(2	imes 2)$ | 3.60 | 0.023 | 3.54 | 3.65 | 0.11 | 1/4 |
| O-(2 	imes 1) | 3.93 | 0.028 | 3.87 | 3.98 | 0.11 | 1/2 |



FIG. S1. Height map of the carbon atoms in the equilibrium structure of with out oxygen (w/o–O) with the PDOS of the highlighted atoms compared with the PDOS of the free-standing graphene. Notice how in the absence of intercalated species in this strongly-interacting system the electronic properties of G are completely destroyed due to the G-metal interaction.



FIG. S2. Height map of the carbon atoms in the equilibrium structures of O–1, O–c3, O–c4 and O–c4cro with the PDOS of the highlighted atoms compared with the PDOS of the free-standing graphene. In these structures the coverage is low so it is not observed a significant decoupling.



FIG. S3. Height map of the carbon atoms in the equilibrium structures of O–c6, O–c6tri2, O–c6tri1 and O–c6rows with the PDOS of the highlighted atoms compared with the PDOS of the free-standing graphene. In these structures the coverage is medium and depending on the distribution of O atoms we observe a different decoupling degree.



FIG. S4. Height map of the carbon atoms in the equilibrium structures of $O(2 \times 2)$ and $O(2 \times 1)$ with the PDOS of the highlighted atoms compared with the PDOS of the free-standing graphene. In these structures the coverage is high so a complete decoupling is observed recovering the characteristic linear dispersion of the pristine graphene with a slight positive shift of the Dirac cone due to charge transfer.

DETAILS OF THE LEED PATTERN

Enlargement of the LEED pattern presented in the inset of Fig. 1e of the main text. The structure marked in blue in the figure matches with either a (2×2) oxygen structure or a (2×1) with three rotational domains.



FIG. S5. LEED pattern observed when a complete oxygen coverage is achieved. Graphene periodicity is marked with a green circle while Rh(111) is in orange and oxygen $(2 \times 2)/(2 \times 1)$ is in blue (E = 55 eV).

ELECTRONIC DECOUPLING STUDIED THROUGH $(\sqrt{3} \times \sqrt{3})$ R30° MODULA-TION



No $(\sqrt{3}x\sqrt{3})$ R30° modulation

 $(\sqrt{3}x\sqrt{3})R30^{\circ}$ modulation

FIG. S6. On the left, a boundary between two rotational domains of graphene on Rh(111). No modulation different from the atomic one is observed. On the right, the same kind of boundary on graphene/oxygen/Rh(111). In both the image and its zoom in, two periodicities are observed: far from the boundary, the typical atomic modulation. Near the boundary, the electronic modulation coming from the intervalley scattering is observed. Parameters of G/Rh(111) images: (15×19) and (6×6) nm² respectively, $V_s = 38$ mV, $I_T = 11$ nA. Parameters of G/oxygen/Rh(111) images: (27×34) and $(6\times6)~{\rm nm}^2$ respectively, $V_s=280$ mV, $I_T=2$ nA.

COMPLETE STS SPECTRUM



FIG. S7. Complete numerical dI/dV spectrum taken at room temperature.

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