Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Avoiding oxidation with coating: graphene protected magnesium surfaces†

Jimena A. Olmos-Asar*[a,b] and Marcelo M. Mariscal[a,b]

Supporting Information

Determination of a proper unit cell

The unit cell of the magnesium surface and graphene have different areas. When performing computer simulations with plane waves, periodic boundary conditions are implemented. For this reason, a proper unit cell must be constructed with a compromise between the total size of the system (computational cost) and the strain caused in the materials. There are many ways of accommodating graphene on Mg. Taking in consideration this compromise, we simulate a 4x4 supercell of a 4 layer slab of magnesium covered by a 5x5 supercell of graphene, totalling 114 atoms. We have chosen to keep the Mg slab in its most stable lateral size, compressing the graphene layer. This represents a strain on graphene of about -3.74%. The energy increase by C atom when compressing graphene is shown in Figure S1.

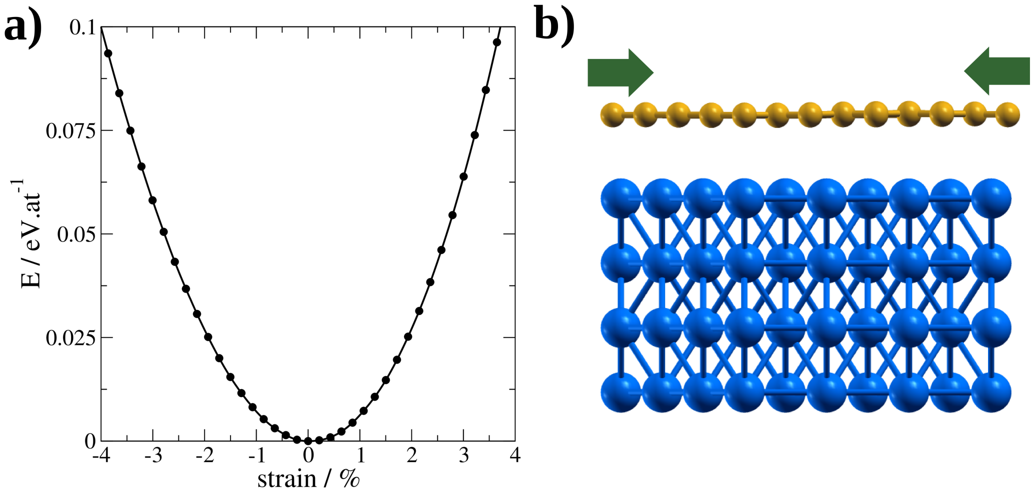

Figure S1 Straining graphene. a) Energy increase per carbon atom during compression. b) Representation of the generated strain.

Larger cells with smaller strains have been tested to corroborate that the electronic structure of the system does not change significantly. In particular, we tested a 7x7 supercell of Mg covered by a 9x9 supercell of graphene. For this system, the strain is reduced from 3.74% to 0.86%, at the expenses of an increase in the computational cost to almost double. As we found that the main behaviour is very similar (Mg-graphene distance, interlayer energy, Mg relaxation under defective graphene and charge transfer) we chose to use the smaller cell.

With the aim of finding even smaller unit cells, we have also tested some rotated structures (see Figure S2 for a 20°rotation, with a strain of -2% on graphene). However, the adsorption energy of graphene (-0.027

[0a] *Instituto de Investigaciones en Físico-Química de Córdoba (INFIQC) - CONICET.; E-mail: jimena.olmos.asar@unc.edu.ar*

[0b] *Departamento de Química Teórica y Computacional, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Argentina.*

eV·at^{-1}) is smaller than in the non-rotated case (-0.045 eV·at^{-1}). This is because, when rotated, some C-Mg interactions are lost (there are less C atoms directly on-top of Mg atoms).

To find the optimal structure of the chosen unit cell, we have performed a full relaxation of the system (keeping the lowest Mg layer fixed to mimic the bulk), starting from a laterally displaced graphene layer in different positions (see below lubrication results to compare energies). Also, we have started from Mg-graphene distances of 3.3 and 3.0 Å, in both cases arriving to the same final structure. Finally, this optimal interlayer distance was validated with the compression calculations, as presented below.

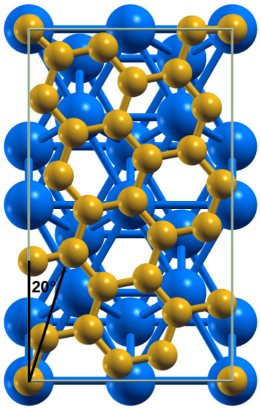

Figure S2 Example of a cell with rotated graphene.

Lubrication and shock absorption

Graphene layer may act as a lubricant on the magnesium surface. When the sheet is laterally displaced in the zig-zag direction, the energy barrier for the process is very small: $7 \cdot 10^{-4}$ eV.at^{-1} (see Figure S3a). This means that under some external agent which may cause wear due to friction, graphene would answer translating with almost no barrier.

On the other hand, when a perpendicular external force is applied, graphene can act as a shock absorber. In Figure S3b it can be observed how the energy per area rises as pressure (compression) is applied.

To construct this plot, we have proceeded in this way: a force perpendicular to the surface is simulated by compressing the topmost atomic layer of each system. For the case of bare Mg, we compressed the topmost metallic layer of the surface, while in the heterostructure we compressed the graphene sheet. At each compression step, the rest of the system is allowed to relax freely, except for the lowest Mg layer to mimic bulk. At each step, the total energy is informed by unit area, normalising the results. As can be extracted from the Figure, when compressing bare Mg the energy increases much faster than when graphene is protecting the surface. This means that the graphene is acting as a shock absorber when the force is applied.

Electronic band structure

When the Mg-gr heterostructure is constructed, a small charge transfer happens from the metallic surface to the graphene layer. We have calculated the band structure of the heterosystem, shown in Figure S4. The Dirac cone of graphene (placed at the K point of the Brillouin zone) is moved around 1 eV below the Fermi energy, which means it is n-doped. It corroborates the results of the Projected Density of States (pDOS) discussed in the main article.

Bare magnesium oxidation

When magnesium is exposed to oxygen, spontaneous oxidation occurs. We have estimated the adsorption energies as -0.57 eV for the molecular case and -4.47 eV.at^{-1} for the dissociative case. Both final structures are displayed in Figure S5.

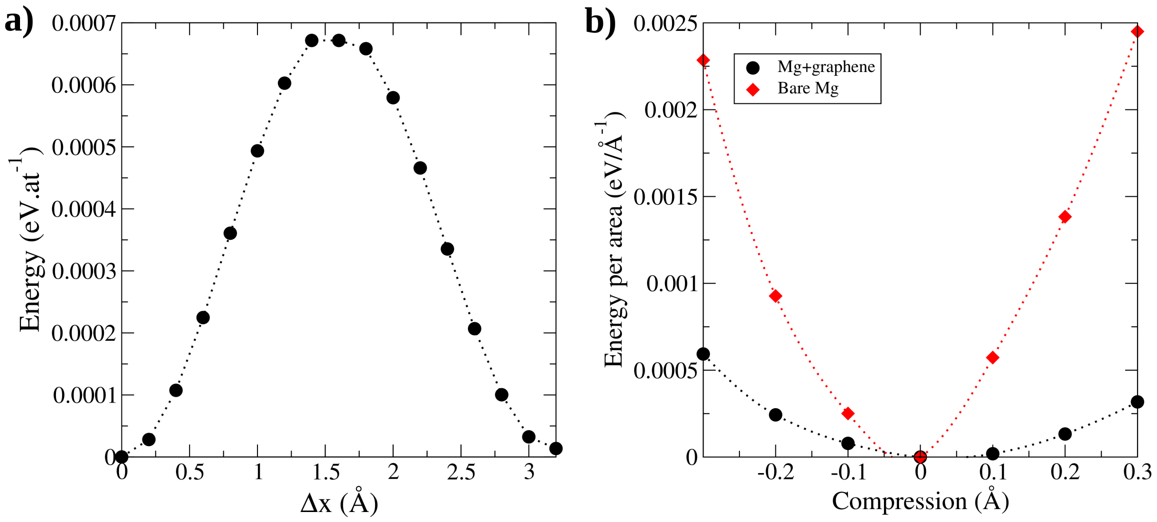

Figure S3 Mg-gr mechanical properties. a) Energy as a function of lateral displacement of graphene with respect to magnesium. b) Energy as a function of compression for bare magnesium (red curve) and graphene covered Mg (black curve).

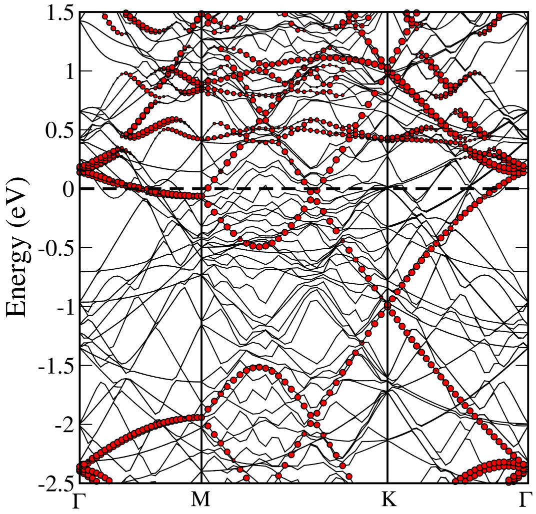

Figure S4 Mg-gr electronic band structure. In red symbols, the projection of the graphene states, with proportional size.

Oxygen penetration accross graphene

We have estimated the energy barrier for an oxygen molecule to penetrate through free-standing and supported perfect and defective graphene. During the process, the graphene sheet is kept fixed, and the oxygen molecule is forced to go down across a carbonaceous hexagon or heptagon, depending on the case, and kept at its most stable O-O bond distance. The energy profiles are displayed in Figure S6. As can be observed, penetration is not likely to occur at room temperature. For the case of perfect graphene, both free-standing and supported on Mg(0001), the energy barrier for penetration of an oxygen molecule is around 33 eV. For the case of a Stone-Wales heptagon the estimated energy barrier is about 18 eV.

Oxygen adsorption on Mg-DV

When the graphene layer on Mg(0001) contains a double vacancy defect, a magnesium atom goes up to bind the dangling bonds of carbon. If an oxygen molecule is in the environment, it can adsorb non-dissociatively onto this magnesium atom. The charge density difference analysis shows the formation of two covalent bonds

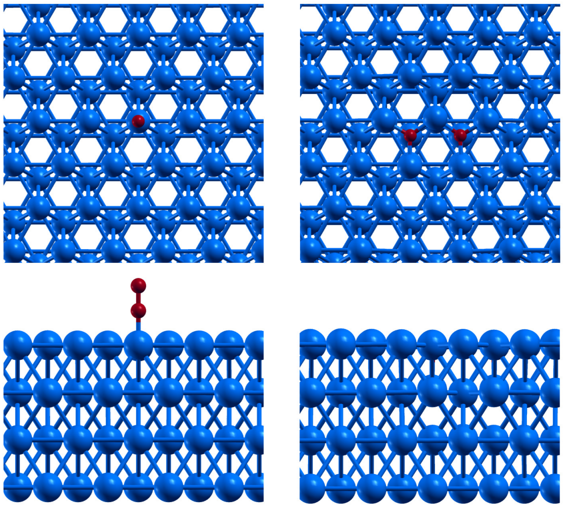

Figure S5 Bare magnesium oxidation. The final structures for molecular (left) and dissociative (right) adsorption of oxygen are shown from a top (top) and side (bottom) view.

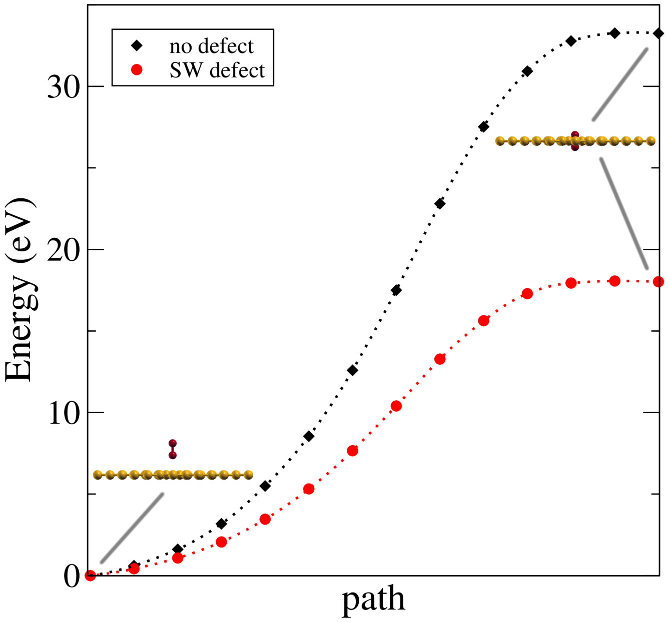

Figure S6 Oxygen penetration accross perfect graphene and a Stone-Wales heptagon. The energy profile is shown, as well as initial and final snapshots.

between the oxygens and the magnesium atom, as shown in Figure S7.

Molecular dynamics simulations were performed to observe the spontaneous attachment of a O_2 molecule from the environment into the defect. At room temperature, some oxygen molecules were distributed randomly near the surface. After 1 ps we observe that the closest oxygen molecule adsorbs on the exposed Mg atom (see Figure S8). On the other hand, we have studied the stability of the Mg-O bonds once the molecule is adsorbed. We observe that the molecule remains attached under these thermal conditions.

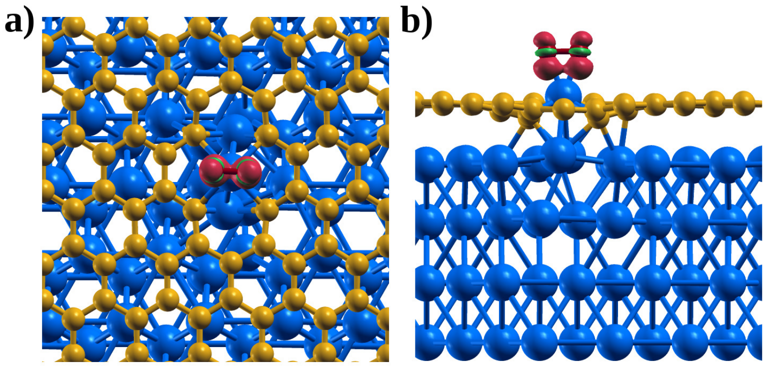

Figure S7 Oxygen adsorption to a Mg atom surrounded by a double vacancy defect in graphene. Isovalue: 0.01 e^{-1}. Pink is for charge accumulation and green is for depletion.

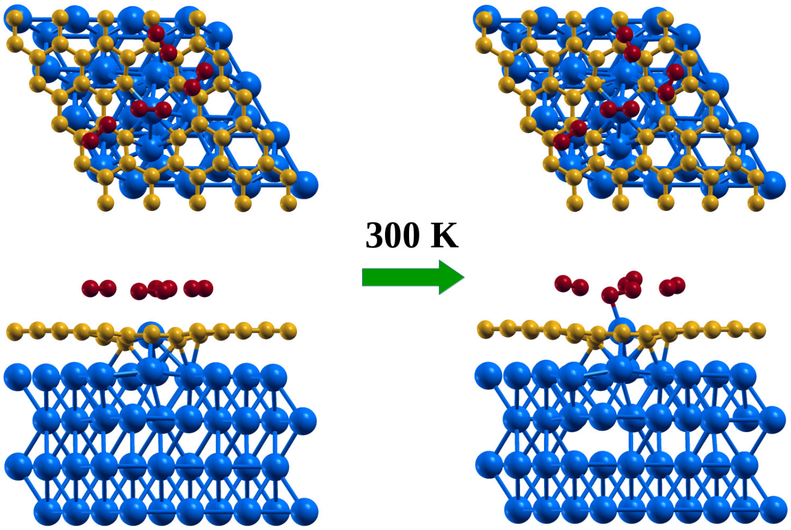

Figure S8 MD simulation of O_2 molecules near a DV defect. The closest molecule adsorbs to the exposed Mg atom. Top (top) and side (bottom) views of the initial (left) and final (right) states.