# Supporting information for: Substrate-Induced Stabilization and Reconstruction of Zigzag Edges in Graphene Nanoislands on Ni(111)

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### Substrate induced symmetries on graphene nanostruc-

#### tures

When considering the structure of a graphene nanoisland on Ni(111), both the stacking and edge type have a determinant influence on its final shape. In nanostructured systems, the edge energy is an important part of the total energy and can affect the final stacking with the substrate. For this reason several combinations of stacking and edge have to be considered in order to determine the possible system structures. As seen in Figure S1, zz edges with top-fcc and top-hcp stacking have threefold-edge symmetries; however zz edges with bridge-top stacking do not obey to the same symmetry rules.



Figure S1: Graphene zz edges on Ni(111). Edges with top-fcc stacking, which have a threefold symmetry, are shown on the left. Top-hcp, which have the same symmetries as top-fcc, are shown in the middle. Zz edges with bridge-top stacking have complicated symmetries represented by colors.

Figure S2 shows the structure of triangular graphene nanoislands exhibiting only ZZ edges with top-fcc, top-hcp and bridge-top stacking. Other stackings, such as fcc-hcp, bridge-fcc, and bridge-hcp, have not been considered since it is unlikely that the energy cost can be compensated by the most stable edge configuration.



Figure S2: Different zz edge configurations of graphene nanoislands depending on their shape and stacking.

While TGI with top-fcc and top-hcp stacking are composed of a single type of zz edges, TGI with bridge-top stacking are composed of one  $zz_{\gamma}$  edge and two  $zz_{\alpha}$  ( $zz_{\beta}$ ) edges. Considering the edges structure we would expect different properties for  $zz_{\gamma}$  and  $zz_{\alpha}$  ( $zz_{\beta}$ ) edges, such as stability, growth rate, reactivity. In the case of our experimental observations there is no statistically relevant variation of the length of one edge with respect to the others in TGI and they possess a marked threefold symmetry. For this reason we discard bridge-top stacking as a possible candidate. We also note that the orientation of a TGI depends on the combination of the stacking with the edge type. For example, islands with top-fcc stacking and  $zz_h$  edges have the same orientation as islands with top-hcp stacking and  $zz_t$  edges. Changing either the stacking or the edge type alone results in a change of the orientation of the triangular graphene nanoisland.

HGI exhibit 3  $zz_h$  and 3  $zz_t$  edges for top-fcc and top-hcp stacking. In the case of brigde-top stacking they would posses 2  $zz_{\alpha}$ , 2  $zz_{\beta}$ , and  $zz_{\gamma}$  edges. The existence of the reconstruction in 3 edges indicates that the stacking of HGI can only be top-fcc or top-hcp, consistent with our conclusion for TGI.

## **First-principles simulations**

#### Details of the theoretical methods

Spin-polarized density functional theory (DFT) calculations with SIESTA<sup>S1</sup> are performed using the generalized gradient approximation for exchange-correlation with the Perdew, Burke and Ernzerhof (PBE) functional<sup>S2</sup> and a cutoff of 310 Ry for the real-space grid integrations. The basis set consists of double- $\zeta$  plus polarization orbitals for all the atomic species. The corresponding Ni lattice parameter is 3.506Å. Spin-polarized calculations are required due to the ferromagnetic character of the substrate and to the presence of unsaturated carbon bond and/or edge states at the carbon edge. Our calculations yield the correct state for the Ni substrate, with a bulk magnetic moment of  $0.66\mu_B$ . All the systems investigated (described below) are relaxed until forces are smaller than 0.04 eV/Å.

Simulations with ANT.G<sup>S3</sup>, a DFT code based on a cluster embedded Green's function formalism<sup>S4,S5</sup> which interfaces with the GAUSSIAN09 package<sup>S6</sup>, are done using the LanL2DZ<sup>S7</sup> basis set and Becke's exchange functional<sup>S8</sup> complemented with the correlation functional of Perdew, Burke and Ernzerhof<sup>S2</sup>.

In this work, we have decided not include the effect of van der Waals (vdW) forces, although they are known to be an issue for graphene/Ni(111) system.<sup>S9–S12</sup> In particular, we

expect that the vdW interaction will be important to determine the absolute value of the adsorption energy. However, here we are mainly concerned with the description of the weak covalent interaction among the under-coordinated carbon atoms in the edge of the nanoisland and the underlying Ni(111), i.e. the saturation of the carbon dangling-bonds in the graphenic structures by the Ni atoms in the substrate. We expect PBE to be able to account for this weak covalent interaction. Furthermore, with our computational scheme and PBE we obtain an adsorption distance (~ 2.1Å) in good agreement with that obtained with higher level calculations.<sup>S10,S11</sup> As explained below, for the optimization of the graphene nanostructures on Ni(111) we also fix this distance to the substrate for those atoms deep inside the ribbon (bulk graphene atom), which will guarantee that the mechanical boundary conditions for the relaxations of the edges will be correctly described. All in all, and in absence of a consensus about the performance of the different DFT-vdW functionals available, we firmly believe that PBE is sufficient to tackle the particular problem we are considering here, i.e. that of the structure and stability of the edges of graphene on Ni(111).

#### Estimation of edge energies using triangular nanoislands

For the description of triangular graphene nanoislands on Ni(111) using SIESTA, we considered an  $8 \times 8$  supercell made up of a 3 layer Ni(111) slab, with a vacuum region of more than 10 Å between both surfaces, and a graphene island containing 22 C atoms placed on one of the surfaces. A  $2 \times 2 \times 1$  Monkhorst-Pack mesh is used for the k-point sampling of the three-dimensional Brillouin zone. Geometry optimizations are performed with the bottom Ni layer fixed, and both on-top/fcc and on-top/hcp stacking of graphene on Ni(111). The optimized TGIs are shown in Figure 3 of the paper.

We have verified that adding a fourth Ni layer introduces differences of less than 10%, in the calculated energies. For example, the energy difference between TGIs with  $zz_h$  and  $zz_t$  edges changes from 183 meV to 199 meV when increasing the slab width from 3 to 4 Ni layers. However, these energy differences are small enough as to provide an overall correct picture of the problem, so that we can be confident about the conclusions extracted from our calculations. Besides, a similar number of Ni layers has been employed in previous DFT calculations for graphene on Ni(111).<sup>S13,S14</sup>

We have also studied larger triangular graphene nanoislands, containing 33 C atoms, using ANT.G. These TGIs are placed on a Ni(111) surface described by a cluster with 2 Ni layers (140 Ni atoms). Relaxed geometries, together with the energy differences per carbon atom, are shown in Figure S3. We can expect that the structure of the central part of these larger triangle is closer to that of extended graphene on Ni(111) and, thus, the energy difference with respect to the extended layer reflects more faithfully the effect of the edges. Although these larger calculations required using a cluster that only contains (explicitly) two Ni layers, due to the fact that ANT.G uses a model self-energy to account for the presence of a semi-infinite substrate underneath, the corresponding results are not expected to be much less accurate than SIESTA calculations from the point of view of the finite size effects. In any case, we reckon these calculations to be somewhat less accurate in reflecting the differences among top/fcc and top/hcp stacking.

The main purpose of including ANT.G calculations in this work was two-fold: on the one hand, to compare the results obtained using two different approaches, and on the other hand, to compare the conclusions regarding the edge effects extracted from the calculations for triangular nanoislands of different sizes. Notably, from the results summarized in Figure 3 and Figure S3, we see that the overall picture extracted from the two sets of results is the same, which we believe is a further indication that our DFT calculations for smaller triangles are correct and reliable.

From the energies per carbon atom obtained using graphene triangles in different conformations (Figure 3 and Figure S3), we can estimate the energy difference between  $zz_h$  and  $zz_t$  edges. We use this method, rather than deriving this difference from our calculations of adsorbed graphene nanoribbons, due to the impossibility to obtain a nanoribbon that presents only one type of edge (either  $zz_h$  or  $zz_t$ ) and, simultaneously, maintains the correct



Figure S3: Relaxed structure of TGIs containing 33 carbon atoms on Ni(111) as obtained with ANT.G. The corresponding energies per carbon atom, measured with respect to the most stable TGI, are also given.

top/fcc stacking.

The most stable triangle island always exhibits  $zz_h$  edges and has top-fcc stacking [Figure 3 (a) and Figure S3 (a)]. It is also quite clear from Figure 3 (a) and (b), as well as from Figure S3 (a) and (b), that the effect of stacking is only minor and the main energy differences are related to the different edges.

To illustrate how we estimate the edge energies let us first consider the triangle island in Figure S3 (a). It has three  $zz_h$  edges, each of them with 4 edge C atoms. Additionally, there

are another 3 uncoordinated "edge-like" C atoms on the vertices of the triangle. However, while the atoms in the edges are in hollow positions, the atoms in the vertices occupy top positions. Therefore, if  $E_h$  and  $E_t$  are the edge energies per atom associated with, respectively,  $zz_h$  and  $zz_t$  edges, we can estimate the total edge energy of the island in Figure S3 (a) as  $3 \times (4 E_h + E_t)$ . Here we have assumed that the energy penalty associated with having a C atom either in the edge or in one of the vertices is similar and only depends on the stacking (hollow or top) of that particular atom with the metal substrate below. Correspondingly, the edge energy of the island in Figure S3 (c) can be estimated as  $3 \times (4 E_t + E_h)$  and the difference between them is  $\Delta E_{edge}^{triangle} = 9 \times (E_t - E_h)$ .

For a general triangle island with  $N_e$  edge C atoms (plus 3 C atoms in the vertices) the difference of edge energy between a triangle island with  $zz_t$  edges and another one with  $zz_h$ edges reads

$$\Delta E_{edge}^{triangle} = (N_e - 3) \times (E_t - E_h). \tag{1}$$

Then, multiplying by the linear density of edge atoms in a zz edge,  $\lambda_{zz}$ , the energy difference per unit length between  $zz_t$  and  $zz_h$  edges is obtained as

$$\Delta E_{zz} = \frac{\Delta E_{edge}^{triangle}}{(N_e - 3)} \times \lambda_{zz}.$$
(2)

For the triangular nanoislands under consideration here  $\lambda_{zz}$  is ~ 0.40Å<sup>-1</sup>.

We now take the total energy differences given in Figure 3 in the paper and in Figure S3 for islands with identical stacking but different edge configurations. Notice that these energies are given per C atom, so they must be multiplied by the total number of C atoms in the islands before using them. If we assume that these energy differences (for triangles with the same stacking) are solely due to the different edges, we can identify them with  $\Delta E_{edge}^{triangle}$  in Eq. 2.

For the islands containing 22 C atoms we obtain an edge energy difference between  $zz_t$ 

and  $zz_h$  edges ( $\Delta E_{zz}$ ) of 0.26 eV/Å and 0.27 eV/Å, respectively, for islands with top/fcc and top/hcp stackings. These values might be somewhat overestimated, since for triangles of this size different edge types might induce quite different relaxations in the inner part of the islands. This effect, if present, must be mitigated in the larger triangles from which we obtain edge energy differences of 0.21eV/Å and 0.16 eV/Å, respectively, for top/fcc and top/hcp stackings. Hence, we have decided to use the average value of all these calculations as our estimate of  $\Delta E_{zz}$ , which amounts to ~ 0.22 eV/Å. Finally, from the maximum (0.27 eV/Å) and minimum (0.16 eV/Å) values, we estimate an error of ±0.05 eV/Å.

# Estimation of the energies of reconstructed edges using nanoribbons

For graphene nanoribbons on Ni(111), a 4x8 supercell made of a 3 layer Ni(111) slab is employed, with a vacuum region of more than 10 Å between both surfaces, and a graphene ribbon containing 40 C atoms placed on one of the surfaces. A 5x2x1 Monkhorst-Pack mesh is used for the k-point sampling of the three-dimensional Brillouin zone. Geometry optimizations are performed with the bottom layer fixed. Only initial configurations in which the bulk of the graphene nanoribbon has on-top/fcc stacking with respect to the underlying Ni(111) are considered. All the calculations are performed using the SIESTA code.

With the aim of extracting edge formation energies, geometry optimizations are done in various steps. First, we tried to relax carbon ribbons with all different combinations of edge terminations. In these relaxations, we only fix the atoms in the bottom Ni layer and the height of the central rows of C atoms over the Ni surface. We force this height to remain similar to that found for an extended graphene layer on Ni(111). This last point is important to mimic the limit of large graphene islands. Unfortunately, due to the small width of the ribbons, during the relaxations some of the ribbons move significantly from the initial position over the Ni(111) surface. Thus, the final stacking does not always correspond to the nominal initial one. However, it was possible to stabilize two nanoribbons in which the final relaxed structure could be assigned unambiguously to two different edge combinations:  $zz_h(57)/zz_t(57)$  and  $zz_h/zz_t(57)$  [see Figure S4(a) and (c)]. These ribbons only allow to compare the stability of the reconstructed and zigzag hollow edges. It is interesting to note that the  $zz_t$  edge does not appear in these "stable" nanoribbons. One could interpret this as an indication of the unfavorable character of the  $zz_t$  edges. As we see below, this suspicion is confirmed by later calculations.

In order to discern the importance of the stacking with the underlying substrate it is necessary to proceed further. Therefore, in a second step and based on the  $zz_h(57)/zz_t(57)$ and  $zz_h/zz_t(57)$  nanoribbons stabilized so far, we set up new model nanoribbons by "unreconstructing" one of the edges (the lower half of the ribbons (a) and (c) in Figure S4 ) while keeping the atoms in the other edge fixed. Hence, we end up with four different nanoribbons:  $zz_h(57)/zz_t(57)$ ,  $zz_h(57)/zz_t$ ,  $zz_h/zz_t(57)$  and  $zz_h/zz_t$ . By construction, the first two nanoribbons [(a) and (b) in Figure S4] have identical  $zz_h(57)$  edges, whereas the other two [(c) and (d) in Figure S4] have identical  $zz_h$  edges. These model systems are then relaxed fixing the bottom Ni layer and the C atoms in the upper half of the ribbons (rows 1 to 5). In the lower half of the ribbons, only the height of the inner C atoms (rows 6 to 8) is fixed. The relaxed geometries of the two new ribbons are shown in Figure S4 (b) and (d).

Once the energies for the relaxed model systems are calculated, we can proceed with the estimation of edge formation energies. With that purpose, and given that each nanoribbon contains two different edge types, we define the following energy equation:

$$(E_{zz1} + E_{zz2})L = E - E_{Ni} - N * E_g,$$
(3)

where  $E_{zz1}$  and  $E_{zz2}$  represent the edge formation energies of the two types of graphene edges contained in each nanoribbon and L the edge length, E is the total energy of the system, Nthe number of C atoms,  $E_g$  the energy per C atom for extended graphene on Ni(111) and  $E_{Ni}$  the energy of the substrate. It should be emphasized that Eq. 3 can be used to express



Figure S4: Model graphene nanoribbons on Ni(111) used to extract the edge energies. In panel (a) we have included the row numbering used to describe the relaxation procedure.

the formation energy for any carbon structure on Ni(111), where the chemical potential is fixed to that of extended graphene on Ni(111).

An alternative expression to Eq. 3 can be derived by taking into account that the adsorption energy of the graphene nanoribbon can be expressed as

$$E_{ribbon}^{ads} = -(E - E_{Ni} - E_{ribbon}^{gas}), \tag{4}$$

where  $E_{Ni}$  and  $E_{ribbon}^{gas}$  are the equilibrium energies of the substrate and the free standing ribbons, respectively. Note as well that the adsorption energy as defined in Eq. 4 is positive when the adsorption is more favorable, i.e. when the total energy becomes more negative. Besides, the energy per C atom for extended graphene on Ni(111) can be written as

$$E_g = E_{graph}^{gas} - E_{graph}^{ads},\tag{5}$$

where  $E_{graph}^{gas}$  is the energy of the free standing graphene and  $E_{graph}^{ads}$  is the adsorption energy of graphene on Ni(111). Then, Eq. 3 can be expressed as

$$(E_{zz1} + E_{zz2})L = E_{ribbon}^{gas} - E_{ribbon}^{ads} - N * (E_{graph}^{gas} - E_{graph}^{ads}).$$
(6)

In the calculation of the adsorption energies we use the standard counterpoise corrections to reduce the effect of the basis set superposition error (BSSE).<sup>S15</sup> This correction to the adsorption energy is standard when basis sets of atomic orbitals are used, and allows improving considerably the calculated adsorption energies.

Employing the total energies of the four model nanoribbons described above, Eq. 3 and 6 permit us to obtain the following energy relationship between reconstructed and unreconstructed edges of hollow or top type:

$$E_{zzt(57)} = E_{zzt} - 0.15 \,\text{eV/Å}$$

$$E_{zzh(57)} = E_{zzh} + 0.16 \,\text{eV/Å}$$

$$E_{zzh(57)} + E_{zzt(57)} = 1.07 \,\text{eV/Å}$$
(7)

This information is very relevant in order to understand the relative stability of different edge types. It shows that, for top edges it is energetically favourable to undergo a 57reconstruction  $(E_{zzt(57)} < E_{zzt})$ , whereas the opposite is true for hollow edges  $(E_{zzh(57)} > E_{zzh})$ . From Eq. 7 we can also compute the average (over the hollow and top stackings) of the zigzag edge energies. For the unreconstructed egde we obtain  $E_{zz}=\frac{1}{2}(E_{zzh}+E_{zzt}) \sim$ 0.53 eV/Å, which is identical to the value reported by Gao *et al.*<sup>S13</sup> for the zigzag edge energy on Ni(111) (computed without discriminating the edge stacking) from plane-waves calculations using the same exchange-correlation functional that we use here (PBE-GGA).<sup>S2</sup> Our average value for the 57-reconstructed edge energies is  $\sim 0.54 \text{ eV/Å}$ , which is somewhat lower than the 0.60 eV/Å reported by Gao *et al.* for the 57 edges, but still in very close agreement.

In order to extract absolute edge formation energies additional information is required. In a first attempt, we considered using a symmetric nanoribbon with either  $zz_h$  or  $zz_t$  edges. However, it is quite difficult to obtain relaxed structures which, simultaneously, are truly symmetric and whose edges correspond faithfully to the most stable structure of each type of edge. In this regard, it is interesting to note that relaxed structures with asymmetric edges, as those shown in Figure S4, are much easier to obtain. Consequently, the relative formation energies described by Eq. 7, that reflect the effect of the stacking with the substrate, provide robust results.

To overcome the problems with constructing symmetric nanoribbons we finally decided to employ our estimation of the edge energy difference between  $zz_h$  and  $zz_t$ ,  $\Delta E_{zz}$ , obtained from the calculations of triangle islands. Table S1 shows our results for the energies of the different zigzag edges, with and without reconstruction.

Table S1: Energies (in eV/Å) of zigzag edges in graphene islands on Ni(111). The energy difference between  $zz_h$  and  $zz_t$  edges ( $\Delta E_{zz}$ ) is obtained from calculations for triangle islands of different sizes. The average, maximum and minimum values of  $\Delta E_{zz}$  in our calculations are, respectively, 0.22, 0.27 and 0.16 eV/Å. Using this information and the results of the calculation for nanoribbons with reconstructed and unreconstructed edges (Eq. 7) we find the values reported in this table.

Calculated zigzag edge energies (eV/Å)				
$\Delta \mathbf{E}_{zz} = \mathbf{E}_{zzt} - \mathbf{E}_{zzh}$	$E_{zzt}$	$E_{zzt(57)}$	$E_{zzh}$	$E_{zzh(57)}$
0.22 (average)	0.64	0.49	0.42	0.58
0.16  (minimum) 0.27  (maximum)	$\begin{array}{c} 0.61 \\ 0.67 \end{array}$	$\begin{array}{c} 0.46 \\ 0.52 \end{array}$	$\begin{array}{c} 0.45 \\ 0.39 \end{array}$	$\begin{array}{c} 0.61 \\ 0.55 \end{array}$

Finally, we have proved that for graphene on Ni(111) the (57) reconstruction of the  $zz_t$  edge is more stable than the zz(ad) reconstruction. With this aim, we have optimized

a graphene nanoribbon with  $zz_h$  and zz(ad) edges on Ni(111). Following the procedure described above, we have obtained the minimum, average and maximum formation energies for the zz(ad) edge to be 0.52 eV/Å, 0.55 eV/Å and 0.58 eV/Å, respectively. Therefore, we can conclude that for graphene on Ni(111) the zz(ad) reconstruction of the  $zz_t$  edge is less stable than the (57) reconstruction.



#### Equilibrium shapes of graphene nanoislands on Ni(111)

Figure S5: Wulff constructions for graphene islands on Ni(111) taking into account the effect of the stacking with the substrate of the zigzag edges, as well as their possible reconstruction [in panels (d), (e) and (f)]. The energy of the ac-ad edge is taken from PBE-GGA calculation reported in Ref. 10. Red dashed lines correspond to the interpolated edge energies for arbitrary edge orientations following the recipe in Ref. 11. Panels (b) and (e) correspond to the shapes in the insets of Figure 6 in the paper.

We now proceed to investigate the equilibrium shape of graphene nanoislands on Ni(111) using the information provided in Table S1. For this purpose, in addition to the energies of the zigzag edges, we also need those of the armchair edges. Given the good agreement between our average results for the zigzag edges and the edge energies reported by Gao *et al.*<sup>S13</sup> using the same PBE-GGA functional, in this section we will use the armchair edge energies calculated by these authors. It is interesting to note that, in constrast to the

situation for zigzag edges, there is only one type of armchair edges for graphene on Ni(111). Ref. S13 reports an armchair (ac) edge energy on Ni(111)  $E_{ac} \sim 0.60 \text{ eV/Å}$ , which is clearly higher than the average energy of zigzag edges and substantially higher that our most stable  $zz_h$  edge. A more stable edge can be obtained by attaching an additional carbon atom to one of the edge atoms (ac-ad edge), reducing it edge energy to  $E_{ac-ad} \sim 0.53 \text{ eV/Å}$ , which is now competitive with the zigzag edges. Artyukhov *et al.*<sup>S14</sup>, using the local density approximation for the exchange-correlation functional, also calculated a similar difference of ~0.07 eV/Å for the energies of the ac and ac-ad edges.

The Wulff constructions presented in Figure S5 report the equilibrium shapes obtained once the effect of the stacking of the zigzag edges and their possible reconstruction are taken into account. The dashed red lines present the edge energies interpolated for an arbitrary edge orientation using the scheme proposed by Artyukhov *et al.*<sup>S14</sup> Slightly different shapes are obtained using values of zigzag edge energies within the uncertainty of our calculations (corresponding to different values assigned to  $\Delta E_{zz} = E_{zzt} \cdot E_{zzh}$ ). However, the absence of the unreconstructed  $zz_t$  edges and the transition from triangle-like to hexagonal-like shapes when the 57 reconstruction of the  $zz_t$  is allowed are robust features. Shapes in panels (b) and (e) correspond to edge energies and shapes reported in Figure 6 of our paper.

#### Edge energy of graphene nanoislands on Ni(111)

From the computed edge energies and the calculated equilibrium shapes, we can now compute the edge-energy differences between triangle-like or hexagon-like islands depending on their size. Figure S6 exhibits the magnitude of these edge-energy differences. For a 10 nm<sup>2</sup> graphene island we estimate an edge-energy difference of  $\sim 3$  eV. Being proportional to island perimeter, this energy difference is proportional to the square-root of the island area.



Figure S6: Size dependence of the estimated edge-energy difference between islands with  $zz_t(57)$  edges (hexagon-like, HGI) and those that do not exhibit reconstructed zz edges (triangle-like, TGI). The inset shows the edge energy for each island shape as a function of the island area. The shapes used for this calculation correspond to those shown in the insets of Figure 6 in the paper and panels b) and e) in Fig. S5.

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