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Stability of edge magnetism in functionalized zigzag graphene nanoribbons

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Abstract

Graphene nanoribbons are attractive candidates for future technological applications due to exceptional electronic and magnetic properties. We investigate the stability of edge magnetism in the zigzag graphene nanoribbons with indene-type functionalized edges, recently synthesised on Au(111) in our laboratory. Using density functional theory (DFT) calculations, we show that the functionalized nanoribbons preserve most electronic properties of the pristine ribbon, with band modifications making edge magnetism sensitive or unstable to environmental influences. The tendency towards such instability already emerges when the system is investigated with a simple mean field Hubbard model where the on-site Coulomb repulsion can be parametrically tuned. It becomes fully evident in DFT calculations when the mostly dispersive interactions between the nanoribbon and the metal substrate are modeled using different van der Waals correction schemes. One of such schemes gives results in agreement with spectroscopy experiments in which the highest occupied and lowest unoccupied states locate on the unmodified and modified zigzag edge sections, respectively. When a different dispersion correction approach is considered, theory predicts, despite a very similar adsorption geometry, an inversion of occupied/unoccupied states and a 60 % reduction in absolute magnetization. Such sensitivity with

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respect to small perturbations is discussed.

1. Introduction

The unique electronic properties of graphene, an atom-thick carbon sheet of sp^2 -bonded carbon with an electrostatically tunable carrier density [1], make it an attractive material for applications in nanoelectronics [2, 3]. It is characterized by a linear dispersion around the charge neutrality or Dirac point and a remarkably high electron mobility at room temperature [4]. Furthermore, graphene possesses unique optical, thermal [5] as well as mechanical properties [6]. However, it lacks a sizeable electronic energy gap, which limits its use in field effect transistor devices for digital electronics. A possible solution to this problem is to confine the charge carriers in one-dimensional structures called graphene nanoribbons (GNRs) to open a gap [7, 8]. Accordingly, graphene nanostructures and especially GNRs have become the focus of an intense research activity (see, e.g., [9] and references therein). Recently, sub-10 nm GNRs with smooth edges have shown to be semiconductors with an inverse relation between band gap and ribbon width [10], in agreement with theoretical predictions [7].

Additionally to the band gap, GNR edges can give rise to unconventional electronic and magnetic properties. In this respect GNRs with zigzag edges (ZGNRs) are of particular interest, because of the presence of localized edge states, which are at the origin of theoretically predicted spin polarization [11]. Signatures of this spin polarization at the edges of ZGNR have been reported recently [12, 13]. Due to their energetic position at the Fermi level and their localized nature, these edge states are susceptible to a Stoner instability resulting in a spin polarized ground state. Here the driving force is the Coulomb repulsion of the electrons and accordingly many-body interactions need to be considered for the description of this phenomenon [14]. Theory predicts a semiconducting, antiferromagnetic ground state with ferromagnetism along each edge, where the energetic difference to the metallic, non magnetic state goes to zero with in-

creasing width of the ZGNR. Because magnetism and edge states are intimately connected to each other, the requirement of smooth and atomically precise edges is of great importance, since spin polarization can be largely suppressed in the presence of edge modifications and impurities [15]. This makes the experimental investigation of the edge magnetism highly challenging as, unfortunately, top-down engineered samples (for example produced via lithography or chemical etching) generally contain a rather high density of structural defects at the edges. Furthermore, real GNRs are usually supported by a substrate, which can affect the edge magnetism through hybridization or screening, where the latter acts on the strength of the Coulomb repulsion [16, 17, 18, 19].

Very recently defect-free 6-ZGNRs could be synthesized on Au(111) [20] by the bottom-up coupling of appropriate precursor molecules following a strategy developed by Cai et al. in 2010 [21],[22],[23].

In this paper we examine the electronic properties of these experimentally available ZGNRs and discuss in detail the mechanism by which indene-type modifications to their edges influence the spin polarization, specifically rendering it less robust. We show how small perturbations in the environment and electronic screening can lead to a reordering of the edge bands, and in principle to suppression of edge magnetism. Such a perturbation can be the modification of the interaction of the GNR with a Au(111) surface upon a small (0.05 nm) difference in adsorption height.

2. Computational Details

Density functional theory (DFT) calculations are carried out using the CP2K code [24] for geometry optimization, and the PWSCF code of the Quantum-ESPRESSO package [25] for electronic structure calculation. In the CP2K case, the core electrons and nuclei are represented using the pseudopotential recommended by Goedecker, Teter, and Hutter (GTH) [26] and the valence electrons are treated with triple- ζ valence basis set with two sets of p -type or d -type polarization functions (TZV2P) [27]. In Quantum Espresso a plane wave basis set and ultrasoft pseudopotentials [28] are used (SCF calculation). The

exchange-correlation is treated using the PBE functional. The atomic positions are optimized until the forces on each ion become less than 0.005 eV/Å. A vacuum region of ~ 15 Å is added along the direction perpendicular to the ribbon. The energy cutoffs for the wave-function and charge-density are 30 and 240 Ryd, respectively. We used a Monkhorst-Pack [29] $2 \times 6 \times 1$ k -point grid in the reciprocal space for the self-consistent (SCF) calculation. Due to the small screening length in metals we employ a four-layer slab of gold to describe the interaction between ZGNR and the surface. One side of the slab is saturated with H to avoid interactions between the two Au surface states.

To study organic molecules on coinage metals, an accurate description of weak van der Waals interactions is needed [30]. For this work we compare two correction schemes called DFT-D3 [31] and DFT-D2+ [32], both based on atom-atom interactions asymptotically decaying like the sixth inverse power of the distance. A dispersion method developed by Grimme *et. al*, DFT-D3, captures the effects from the environment and accordingly modifies the C_6 coefficients based on the knowledge of the coordination number of each atom. The maximum number of neighbors leads to “squeezing” of the atom and thereby decrease in C_6 coefficient, which depends on the atomic polarization. Therefore, in order to capture the effects from the chemical environment, a range of pre-calculated C_6 coefficients for element pairs in different reference (hybridization) states need to be considered [33]. Depending on the hybridization state, the C_6 coefficient for an atom can also change continuously [34, 35, 30, 31]. The transition metal substrates show significant dispersion screening effects which can be considered via the many-body collective response theory [36, 37].

In DFT-D2+ treatment, we adopted dispersion parameters for element Au from Ref. [32]. These parameters were obtained by combining Tkatchenko-Scheffler pairwise corrections with the Lifshitz-Zaremba-Kohn theory for the nonlocal Coulomb screening within the bulk. The dielectric screening within the inorganic substrate reduces the dispersion coefficients of Cu, Ag, and Au species. With these parameters, Ruiz *et. al.* found quantitative agreement between theory and experiment for the binding energy and the binding distance

of PTCDA on metal surfaces. For the other elements, we used the DFT-D2 parametrization by Grimme with a standard combination rule [38].

Mean-field Hubbard model calculations are carried out in the single-band scheme by considering only the nearest neighbor hopping parameter of $t = 3$ eV in the tight binding term of the Hamiltonian, and a on-site Coulomb repulsion term [39] with tunable U parameter (see below). Half filling, i.e. charge neutrality is assumed for all calculations. The calculation for pristine ZGNRs considers a non-primitive unit cell consisting of 6 primitive ones in order to keep the axial size of the unit cell the same as for the edge-modified ribbon, similarly as in the DFT calculations. The iterative self-consistent solution of the Hubbard Hamiltonian is initiated with a weak antiferromagnetic (AFM) bias on the edges of $0.05 \mu_B$ per atom in all cases.

3. Results

The basic structure of the GNR studied here is shown in Fig. 1(b). It consists of a 6-ZGNR (the number 6 denotes the number of diagonal C-C bonds across the ribbon), which is functionalized on the upper and lower edges by phenyl rings rotated by 30° to the GNR carbon rings and fused to the 6-ZGNR edge via a five-membered ring, thus forming an indene-type edge extension. We will refer to this GNR structure as a 6-ZGNR+.

3.1. Synthesis procedure to edge-modified ZGNRs (6-ZGNR+)

Fig. 1 a) and b), adapted from Ref. [20], shows the reported bottom-up approach to synthesize edge-modified zigzag GNRs (6-ZGNR+). The surface-assisted polymerization and subsequent cyclization of molecular precursors, shown in green color in Fig. 1 (a), provide atomically precise ribbons with smooth edges. During cyclodehydrogenation (STEP 2), the additional phenyl group protruding at the zigzag segment, has an equal probability to tilt right or left and undergoes a ring closure to form a five membered ring with the backbone as shown in Fig. 1 (b). Since the additional ring closure can occur to either of the neighboring zigzag edge carbon atoms, no fully periodic arrangement of the

external phenyl groups can be expected (Fig. 1e). However, there are always two edge groups per unit cell (14.76 Å length). We have verified that the results of the calculations (at the mean field Hubbard level) do not significantly depend on the assumption of a periodic or aperiodic arrangement of edge groups and therefore we will discuss only the periodic sequence in the remainder of the paper.

The constant height, nc-AFM frequency shift images (Fig. 1e) reveal the anticipated atomically precise structure of the 6-ZGNR+. Constant-height differential conductance (dI/dV) mappings at -150 meV and 150 meV (Fig. 1c and 1d respectively) show characteristic features at the edges of the 6-ZGNR+, whose relevance we will discuss later.

3.2. *Electronic properties of edge-extended 6-ZGNR+*

The well-known properties of pristine ZGNRs [8, 11, 14, 20] with flat bands and a Stoner gap [40] opening at the Fermi level for $k > 2\pi/3a$, are summarized in Fig. 2a, c, d.

For the pristine ZGNR each carbon atom is bonded exclusively to carbon atoms of the complementary sublattice, i.e. atoms of sublattice A bond exclusively to atoms of sublattice B and vice versa. The presence of the indene-type edge modification is associated with a geometric frustration, because it involves a bond between atoms of the same sublattice (AA or BB, indicated in Fig. 2 b), and an increase of the unit cell size from $a = 2.46\text{\AA}$ to $6a = 14.76\text{\AA}$. At the mean field Hubbard model level of theory the coupling of identical sublattice atoms leads to a breaking of the particle-hole symmetry of the system.

We will see in the following that the 6-ZGNR+ retains several electronic features of the parent 6-ZGNR, but with its (quasi)periodic arrangement of modifications and loss of particle-hole symmetry, the nature of the edge state is changed, offering the opportunity to study the competition between two mechanisms that lift the degeneracy of the frontier bands. One is the Stoner mechanism, the other stems from the effect of the edge extension on the energetic position of the edge states. It is important to notice that these two effects act

Figure 1: Synthesis procedure to edge-modified ZGNRs with zigzag edges (6-ZGNR+): a) Monomer (shown in green color) with an additional phenyl group at the zigzag segment is designed to produce an edge-modified 6-ZGNR+ (width $N = 6$) upon polymerization (STEP 1) and subsequent cyclization. b) Possible cyclodehydrogenation product assuming ring closure at the external phenyl groups (STEP 2). c) Constant height dI/dV map of the occupied state at $V = -150$ meV and d) Constant height dI/dV map of the unoccupied state at $V = 150$ meV. e) Atomic force microscopy frequency shift map of the 6-ZGNR+ ribbon. Figure adapted from [20].

differently on the magnetic properties: whereas the first induces the antiferromagnetic spin polarization observed in the pristine 6-ZGNR, the second can stabilize a non-magnetic ground state. It is in this sense that the competition between the two effects needs to be understood. In a very recent paper, Ortiz et al. [42] have studied the effect of the pentagon edge modifications on the spin exchange along the edges. The authors found that the presence of the modification may introduce a locally antiferromagnetic coupling along the edges. At the mean-field Hubbard level, they found that the latter arrangement is energetically favored, with a choice of parameters of $U = t$, which we found here not to reproduce the DFT result in the gas phase. We tried, at the DFT/PBE level,

Figure 2: Magnetization plots, primitive cell representation of the band structures, and Kohn-Sham orbitals; The primitive cell length along the ribbon axis for the 6-ZGNR is set to $a = 2.46\text{\AA}$. Top-left panel: Magnetization plots for pristine 6-ZGNR (a) and edge-modified 6-ZGNR+ (b). The two equivalent graphene sublattices are labeled as A and B. In (b), the green oval indicates two same sublattice sites (AA or BB) linking to each other in the 6-ZGNR+ system. The simulation cell with periodicity of $6a = 14.76\text{\AA}$ along the ribbon axis is indicated by a dashed rectangle. Scale bar indicates magnetization (μ_B) per site. Bottom-left panel: Primitive cell representation (c) and folded band structure (d) for 6-ZGNR along with the 6-ZGNR+ band structure (e) and unfolded effective band structure (f) simulated using the cells indicated in a), b) and postprocessed according to the recipe described in [41]. The Fermi energy is set to zero. Right panel: isosurfaces of the probability density for Kohn-Sham states at the points marked by the numbers 1-4 in the band structure at $k = \frac{5\pi}{6a}$. The blue color is used for occupied and the red color for unoccupied states. The isovalue used is $0.001 \text{ e}/\text{\AA}^3$.

configurations in the gas phase with antiferromagnetic coupling along the edges, and found that such configurations are energetically unfavorable (by about 100-160 meV/double unit cell). Such configurations will not be further considered in the present paper.

Bhattacharjee [43] previously studied with DFT the influence on the electronic structure of the perturbation of a single ZGNR edge with a set of topological modifications. In particular, the author discussed the inclusion of a pentagonal modification (the same present also in the 6-ZGNR+ considered here): such topological modification breaks the bipartite nature of the graphene lattice. The resulting magnetic frustration leads to two main effects, a reduction of the on-site magnetism and a spatial separation between the states localized on the unmodified edge and the ones localized at the pentagon. This leads to a complex pattern of occupied and unoccupied frontier bands, whose ordering eventually dictates the magnetic characteristics of the system.

Four questions arise from this scenario: (i) What is the mechanism of the modification-induced band splitting at the edges? (ii) Will this band splitting preserve the magnetism induced by the Stoner mechanism, or work against it? (iii) Is the ordering of the bands dependent on electronic correlations? (iv) Can the ordering of the bands be affected by the substrate, and to which extent?

In Fig. 2. we compare the DFT electronic structures of the pristine 6-ZGNR (Fig. 2c) and the 6-ZGNR+ (Fig. 2e). For a better comparison it is convenient to unfold the band structure of the 6-ZGNR+ by a method for transforming the eigenstates computed for the “perturbed structure” in a supercell into an effective band structure (EBS) in the primitive cell of the unperturbed (pristine ZGNR) system using spectral decomposition [41]. The spectral weight in the unfolded band structure (Fig. 2 f)) resembles the dispersion of the pristine ZGNR (Fig. 2 c)), with some significant changes: at $k = 5\pi/6a$ (the value where the nodes in the Kohn-Sham states have an appropriate periodicity matching the modification repetition pattern) the spectral function has a discontinuity indicating energy lowering for some of the states originated by the edge modification resulting in a reduction of the band gap.

This analysis based on the unfolded band structure of the 6-ZGNR+ thus provides an answer to question (i) above. Close to the Fermi energy, we have four low dispersive bands which are related to edge states. The analysis of the corresponding Kohn-Sham states (Fig. 2g) shows that there are two different types of bands. For the first type, the Kohn-Sham state has low amplitude on the atoms connecting the edge phenyl group to the ZGNR edge and large amplitude between the edge extension (see state 2 and 4). For the second type, the Kohn-Sham state has large amplitude on the atoms connecting the edge phenyl group to the zigzag edge and low amplitude between the edge extension (see state 1 and 3). The states of “type two” receive a down shift in energy due to the high amplitude on the 3-fold coordinated edge atoms which connect to the edge phenyl ring. They are threefold coordinated with other C atoms, and thus can profit from the energy lowering due to π_z bonding more than pristine zigzag edge atoms.

Regarding question (ii), it needs to be stressed that the band splitting mechanism discussed above works against the spin polarization by lowering the energy of the “type two” states (1 and 3 in Fig. 2) as compared to the “type one” states (2 and 4 in Fig. 2). If the ordering were such that the “type two” states are filled (below E_f) and the “type one” states are empty (above E_f) no significant AFM spin polarization would occur. Indeed, in order to obtain significant AFM spin polarization, one “type one” band (e.g. spin up on the upper edge) must be filled and the complementary one (e.g. spin down on the upper edge) must be empty. The same must hold true for the “type two” bands. Looking at the ordering of the bands in Fig. 2 we see that this is exactly the case. This means that, although the edge modifications work against the Stoner type spin polarization by lifting the degeneracy of the edge state bands, the effect is not strong enough to reorder the states in such a way that the spin polarization is suppressed.

The spatial charge density plots at the four principal peaks in the projected DOS (I-IV in Fig. 3a), shown in Fig. 3b, reveal the above discussed edge state ordering. The occupied state (II) near the Fermi energy is localized predomi-

Figure 3: 6-ZGNR+ in the gas phase calculated with DFT. (a) Projected density of states of the C p_z orbitals. Electronic density of states projected on edge C atoms (black) and contribution from all C atoms (red). Fermi energy is set to zero (dashed blue line). The edge states are indicated by I, II, III and IV. (b): localized DOS at a height of 1.65 Å for states I (-0.48 eV), II (-0.10 eV), III (0.17 eV) and IV (0.53 eV). A Gaussian broadening of 0.1 eV is used.

nantly between the indene-type edge modifications (i.e. is of “type one”) while the unoccupied state (III) has maximum contribution on the pentagonal ring (i.e. is of “type two”). Referring to the frontier bands as valence band top (VT) and conduction band bottom (CB), we note that VT-1 and CB look similar, as is the case also for VT(II) and CB+1 (IV). The edge defect-induced separation between VT and CB is consistent with the result of Bhattacharjee[43], who finds VT on the pristine edge and CB in the vicinity of the defect.

As to the magnetic properties of the edge-modified 6-ZGNR+, the absolute magnetization for the AFM state of 6-ZGNR+ is $5.40 \mu_B/\text{unit cell}$ and the spin-polarization of the unmodified edge (zigzag segment between two indene units) remains similar to the 6-ZGNR case. Thus, the absolute magnetization per cell is decreased by $0.60 \mu_B$ as compared to the pristine ZGNR.

In order to illustrate the critical competition between the edge modification induced band splitting and the Stoner AFM polarization, we investigate the system in the mean-field Hubbard description, where we can tune the ratio between the nearest neighbor hopping term t and the Coulomb repulsion U that relates both effects to each other. Fig. 4(a) shows the dependence of the

absolute magnetization of the pristine 6-ZGNR and 6-ZGNR+ as a function of the strength of the Coulomb repulsion expressed by the mean field Hubbard U (given here in units of the nearest neighbor hopping term t). For the pristine ZGNR, the large DOS at the Fermi level leads to a strong expression of the Stoner mechanism leading to an AFM spin polarization on the edges starting from very small values of U . The situation is different for the 6-ZGNR+. Here no significant magnetic ordering can be observed for $U < 0.7t$. Above this threshold a weak AFM behavior is observed with a steep increase at about $U = 1.35t$. The spin polarization for three selected situations is plotted in Fig. 4(b). Panels A and B show the magnetic ordering for $U = 1.0t$ for the pristine ZGNR and the 6-ZGNR+, respectively. The weaker spin polarization of the 6-ZGNR+ is readily observed, with a particular suppression at the edge atoms linking to the indene-type functionality. The corresponding absolute magnetization is $4.88 \mu_B/\text{unit cell}$ and $0.93 \mu_B/\text{unit cell}$ for the pristine ZGNR and the 6-ZGNR+ respectively. Increasing U to $1.6 t$ (panel C) shows a sharp increase of the absolute magnetization to $6.75 \mu_B/\text{unit cell}$ for the 6-ZGNR+ ($7.93 \mu_B/\text{unit cell}$ for the pristine case).

In order to understand this behavior it is instructive to examine the bands close to the Fermi energy (Fig. 4c) and the corresponding wave functions (Fig. 4d) in detail. Increasing U from zero to $1t$ does not change the bands drastically. The four X-point frontier states for the *up*-spin are displayed in Fig. 4(d). The occupied states are characterized by amplitude concentrated on the edge atoms of the indene unit (thus corresponding to “type two” discussed above), and the unoccupied states by amplitude located in between the edge modifications (“type one”). Spin degeneracy is still preserved, but *up* and *down* spin of the same energy state have their main weight on opposite edges. This leads to the situation that the *up* spin wave function of state 1 has nearly the same amplitude distribution as the *down* spin of state 2 on the same edge. On the opposite edge the same happens for *down* spin state 1 and *up* spin state 2, and therefore no significant spin polarization results. By increasing U to $1.6t$, state 2 and 3 exchange their order in energy at the X-point as can be seen from Fig.

4(d) right panel. Now the occupied *up* spin states of state 1 and 2 lay on the same edge and the corresponding *down* spin states on the opposite edge. This situation drives the strong spin polarization and marks the transition in absolute magnetization at $U = 1.35t$. As it is evident from the comparison among Figs. 2 and 3 (DFT) and Fig. 4(d) (Hubbard), for a value of $U = 1.6t$, the mean field Hubbard results match well the DFT ones for the isolated ribbon in terms of band structure, spin polarization, and frontier orbital spatial distribution (see Fig. 2 and 3).

One can then repeat the “Gedankenexperiment” of gradually increasing the on-site Coulomb repulsion with ribbons where the indene-type edge modifications are at different distances d . In the experimentally considered case (6-ZGNR+), we have $d = 6$ (in units of the zigzag edge periodicity of $2.46 \text{ \AA}$). As it is evident from Fig. 5, the largest effect (and the largest step of magnetization) is observed when the edge state periodicity and the splitting due to the functional unit are compatible, which occurs for $d = 8$. If the spacing is much smaller the splitting due to the different carbon environments cannot occur in a very pronounced manner because the edge state has not the required low wavelength components. If it is larger, such splitting can be very effective due to this wave length matching. It only affects two bands, and as d increases there will be many “backfolded” edge state bands which remain unaffected leading to less pronounced criticality. There is still the step in the magnetization present at about $U = 1t$, however, the magnitude of the step is largely reduced.

The criticality of the value of U on the appearance of an accentuated AFM state is here of particular interest. The U parameter that we consider in our implementation of the mean field Hubbard model has to be regarded as an effective Coulomb interaction comprising on-site U_{00} and non-local interactions U_{0j} (j indexing neighboring sites), where the latter is influenced by screening [44, 45]. The effective Coulomb interaction can then be approximated by $U = U_{00} - U_{01}$ [45]. According to M. Schüler et al. $U_{00} = 3.63t$ and $U_{01} = 2.03t$ yielding $U = 1.6t$ [45]. This value is consistent with our observation that the AFM ground

Figure 4: Absolute magnetization and band structures in the mean field Hubbard model. a) Dependence of the absolute magnetization on the Hubbard U parameter for the pristine ZGNR and the 6-ZGNR+. b) Magnetization plot for three selected situations indicated by the numbered arrows in a). c) Band structures ($\gamma_0 = 3$ eV) of an edge-functionalized (6-ZGNR+) nanoribbon as a function of the Hubbard U parameter. d) Representation of the up -spin wave functions of the 6-ZGNR+ at the X point for the bands labeled 1 to 4, considering two different values of the U parameter. Marker size represents wave function amplitude and colors represent the phase ($[0, \pi]$: blue and $[-\pi, 0]$: red).

state of the 6-ZGNR+ obtained from the DFT calculations requires an effective U in the mean field Hubbard above $1.35t$. Considering the value of the absolute magnetization resulting from DFT calculations in the gas phase of $5.4 \mu_B/\text{unit cell}$, the effective U should thus not exceed $1.6t$ (which yields $6.75 \mu_B/\text{unit cell}$).

In the approximate relation for the effective Coulomb interaction $U = U_{00} - U_{01}$, the non-local interaction (U_{01}) should be more susceptible to screening, and will lead to increase the effective U parameter and therefore drive the system towards the strong AFM states. It may seem counterintuitive at first that the presence of a screening metallic substrate should stabilize the edge magnetism in the 6-ZGNR+. However, this consideration does not take into account the hybridization of the GNR and substrate states. In order to get a realistic picture of the substrate induced influence on the edge magnetism, all electronic effects need to be considered, which calls for a DFT level investigation of the 6-ZGNR+/substrate system.

3.3. Functionalized ZGNR on Au(111)

As we have shown above, the magnetism of 6-ZGNR+ depends on the delicate competition between Stoner type spin polarization on one hand and band splitting and reordering due to the edge modifications on the other. For the free standing 6-ZGNR+ the Stoner mechanism is dominant, however not by a large margin. Therefore, we will discuss in this section whether this situation still holds true if the 6-ZGNR+ is adsorbed on a Au(111) surface, as is the case in the experimental synthesis process and subsequent STM characterization.

We observe that the adsorption configuration obtained from DFT is very sensitive to the dispersion correction scheme adopted. Accordingly, we have tested two such schemes, DFT-D2+ and DFT-D3 (see above in the Methods section) in detail. The equilibrium geometries for both cases are shown in Fig. 6. The two methods deliver different lowest energy configurations: whereas in DFT-D2+ [32] the configuration with the central carbon ring of the 6-ZGNR+ on top of a

Figure 5: Effect of increasing the on-site Coulomb repulsion U on the ribbon magnetization for different spacings d between the fused indene-type units. The largest effect is observed for $d = 8$.

Figure 6: Structure of the 6-ZGNR+ on Au(111). Left: DFT-D2+ scheme. Right: DFT-D3 scheme. The simulation cell used is indicated by the red box. Color scale indicates the buckling/bending (in Å of the ribbon with respect to the average height). Lower panel: Magnetization plots for 6-ZGNR+ using DFT-D2+ and DFT-D3 schemes respectively. Scale bar indicates magnetization (μ_B) per site.

Au atom is more stable as compared to the central ring positioned on a hollow site by 128 meV/unit cell, the situation is reversed for DFT-D3 [31]. Here the hollow site configuration is more stable by 460 meV/unit cell. We also find a significant difference in the mean separation of the 6-ZGNR+ to the Au(111) surface, namely 3.08 Å (DFT-D3) versus 2.89 Å (DFT-D2+) with corrugations of 0.30 Å and 0.39 Å, respectively. This difference in adsorption configuration is accompanied by a drastic difference in total magnetization, namely 4.50 μ_B /unit cell (DFT-D3) versus 1.90 μ_B /unit cell (DFT-D2+). Similar to the free-standing ribbon, the magnetization on the edge C atoms increases away from the indene unit as shown in the lower panel of Fig. 6. The difference in adsorption configuration and total magnetization resulting from the DFT-D3 and DFT-D2+ calculations is also reflected in the density of states near the Fermi energy. This difference concerns particularly the edge states as can be seen from Fig. 7 a) and c) where the projected DOS at a constant height of 1.65 Å above the topmost C atom are displayed for the two dispersion correction schemes. Whereas the DFT-D3 case shows an edge state DOS signature very similar to the one of the free standing 6-ZGNR+ the situation for the DFT-D2+ case is markedly different. As for the free standing case, the edge state DOS signature for the DFT-D3 is characterized by 4 low dispersive bands at E_f with the same sequence of alternating LDOS on the pristine (I and III) and the indene modified (II and IV) edge regions (compare to Fig. 7 d). This alternation is in agreement with our recent experiments [20] where the highest occupied states show contribution on the edges (Fig. 1 c) and the lowest unoccupied states (Fig. 1 d) are concentrated on the indene-type site.

It must be noted that the difference between “type one” (I and III) and “type two” (II and IV) bands is not as pronounced as in the gas phase case (Fig. 3). This smoothening of the site separation of the edge bands is also present in the experimental images (Fig. 1 c,d) and is to be attributed to screening and/or hybridization effects by the substrate. This evidence leads to the conclusion that the DFT-D3 parametrization leads to a more faithful description of the adsorbed 6-ZGNR+ system.

Figure 7: 6-ZGNR+ on Au(111): Projected density of states of the p_z orbitals of C atoms: Electronic density of states projected on edge C atoms (brown curve: right edge, red curve: left edge) and contribution from all C atoms (purple curve), as well as the contribution from Au atoms beneath the ribbon (black line) and far from the ribbon (green line). The edge states are indicated by I (-0.26 eV), II (-0.14 eV), III (0.24 eV) and IV (0.38 eV) and their spatial distribution is shown in the right panel. Fermi energy is set to zero. Gaussian broadening of 0.1 eV is used.

The clear distinction of 4 frontier edge state bands is not possible in the DFT-D2+ case anymore, also there is a slight asymmetry between the DOS of the right and left edge. We now observe a strong VT (state I) with the DOS concentrated on the indene modification sites. In contrast, the CB is rather weak with the DOS located primarily on the pristine edge regions (Fig. 7b). This ordering (not the intensity) is reminiscent of the low Hubbard U value ($U < 1.2t$) case discussed in the mean-field Hubbard scheme shown in Fig. 4, where only a weak spin polarization can be observed. These findings underline the criticality of the spin polarization for the 6-ZGNR+, where rather small changes

in the adsorption configuration, as obtained from different implementations of the dispersion forces in the DFT calculation, can drastically change the magnetic properties of the Au(111) supported nanoribbon.

From the discussion above we can conclude that in order to obtain DFT results, which compare well with the experimental findings, it is required that advanced implementation schemes of the dispersion forces are used. In the present case the dispersion scheme based on semiempirical atom pairwise interactions using the DFT-D3 method described in Ref. [31] proves to be superior to the DFT-D2+ approach owing to the environment-dependent atomic dispersion coefficients. The DFT-D3 method, which includes fixed or environment-independent dispersion coefficients is indeed expected to lead to significant improvements in the predictions of structural properties with respect to the purely (semi)local functionals.

It would be worthwhile -yet beyond the scope of this paper- to compare also more advanced schemes with the present experimental findings. Such schemes include the approach by Dion et al. [46] which includes non-local correlations and the more recently developed many-body dispersion method developed by Maurer et al. [47], which appears particularly suitable for adsorbates on metal surfaces.

Generally, when an organic molecule is adsorbed on an inorganic substrate, the electronic gap changes due to the screening of mobile charge carriers from the substrate [48]. Such screening also affects the effective on-site Coulomb repulsion, which is the driving force of the spin polarization in zigzag GNRs. Furthermore, the interaction between a molecule and the underlying surface causes broadening and splitting of the molecular states [49, 50]. It is thus appealing to connect the band exchange observed in the mean-field Hubbard model calculations (see above) upon parametric modification of U , and the effect of tiny changes in the substrate/ribbon structure. All these sources of external perturbation are barely affecting the nanoribbon geometry, but severely the electronic structure: an exchange of frontier bands leads to a strong suppression of antiferromagnetism, underlining the marginal stability of the ribbon under

study, ultimately due to the particular periodicity of the edge modification units as seen from Fig. 5.

4. Conclusion

In this work we have presented a DFT-based description of the electronic properties of a functionalized zigzag graphene nanoribbon experimentally obtained on Au (111) via a bottom-up synthesis approach. Our results show that two different sets of dispersion parameters lead to changes in ribbon-substrate distance of 0.20 Å and in corrugation across the ribbon of 0.10 Å. In agreement with the recent experimental results, the VT state shows main contribution on the pristine edges using the DFT-D3 scheme. We observe instead an inversion of VT and CB states when modified dispersion coefficients are considered.

The main message of the paper is to show that and why the particular functionalization of the zigzag edges with the observed periodicity along the edge leads to a relatively robust occurrence of the edge states also when the ribbon is adsorbed on the gold surface, but to a reduction of the stability of the edge magnetism. On the basis of comparison between DFT calculations and experimental results, we conclude that in studying organic molecules on a coinage metal like gold, a careful choice of dispersion parameters is needed. This is a necessary condition for a correct prediction of equilibrium structure and stability, and electronic properties of supported organic molecules. Therefore, the dispersion scheme DFT-D3 by Grimme *et al.*, gives more accurate results owing to the environment-dependent atomic dispersion coefficients and seems to offer a better performance within the simplest class of C_6 -based corrections.

A small modification in the structure originates a different ordering of the frontier bands, and this may lead in turn to a dramatic reduction of the absolute magnetization of the nanostructure. Both effects can be ascribed to the compatibility of the edge states periodicity in the pristine ZGNR with the periodicity of the edge modification in the 6-ZGNR+, which allows the splitting of the frontier bands into two components localized along the zigzag segment and other two around the indene-type edge modification. Whereas the lowest of the

four bands is stabilized by coordination, the ordering of the two bands that are closer to the Fermi energy is prone to being affected by external perturbations. Modeling the latter by tuning the effective Coulomb interaction parameter U in the mean-field Hubbard Hamiltonian, we observe a jump in magnetization for the 6-ZGNR+ case upon crossing a critical value of $U = 1.35t$. Considering the substrate as a source of electronic screening and hybridization, we observe within our DFT calculations a similar sensitivity of edge magnetism to tiny changes in the structure.

Our analysis reveals yet another perspective of the bottom-up strategy that allows to obtain atomically precise nanoribbons, namely the opportunity to affect the edge electronic and magnetic properties in a predictive manner, with potential applications in nanoelectronics and spintronics.

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