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Graphyne on metallic surfaces: A density functional theory study

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We show how a structural modification of graphene, which gives the carbon allotrope graphyne, can induce an energy gap at the K point of the Brillouin zone. Upon adsorption on metallic surfaces, the same mechanism is responsible for a further modification of energy bands which occurs via the charge transfer mechanism. We perform the calculation based on the density functional theory with the novel nonlocal van der Waals–density functional correlation of the adsorption of graphyne on Cu(111), Ni(111), and Co(0001) surfaces and show the dependence of the band change on the charge transfer in the system. The binding of graphyne appears to be stronger than that of graphene on the same surfaces.

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I. INTRODUCTION

Carbon nanostructures, and graphene in particular, are becoming unavoidable materials in the growing field of nanoelectronics. The experimental realization [1,2] of single-layer graphene has created tremendous interest in its physical properties. The most prominent feature of this two-dimensional material is its exceptional electronic structure, with a linear band dispersion in the vicinity of the Dirac point. Graphene shows great mobility of charge carriers, high conductivity of electrons and holes, and ballistic charge transport, which makes it a promising candidate for a number of applications in nanoscale electronic devices.

However, what seems to be graphene's strongest characteristic is also its weakest point. Namely, the graphene band structure has no bandgap, which makes it unusable for building some basic electronic elements. The graphene field-effect transistor, for example, cannot be turned off effectively due to the absence of a bandgap. Creating a bandgap in graphene is one of the most important research topics in the graphene community since it may ultimately enable new applications in electronics, nanospintronics, and infrared nanophotonics. A number of approaches have been proposed or implemented to create a bandgap in graphene, such as using graphene-substrate interaction [3], lateral confinement [4], and uniaxial strain [5] and breaking the inversion symmetry in bilayer graphene [6,7].

Here, an alternative approach is proposed: the use of another allotrope of carbon instead, a graphyne. Our presentation is organized as follows. The motivation for our studies is further supported in Sec. II, where the freestanding graphyne is discussed. In Sec. III we report for the first time graphyne adsorption on three representative metallic surfaces, showing the features of binding of graphyne on Co(0001), Ni(111), and Cu(111). Finally, in Sec. IV we give conclusions and perspectives on graphyne.

II. FREESTANDING GRAPHYNE

Several forms of graphyne are possible [8]. The form we consider, shown in Fig. 1(b), is known as γ-graphyne. In the rest of the paper we refer to it simply as graphyne. Graphyne is the result of a structural change in the two-dimensional graphene plane which opens a gap at the K point, i.e., lifts the degeneracy caused by the symmetry of the hexagonal structure. It can be easily understood by making a comparison with a one-dimensional linear polymer chain consisting of strongly interacting coplanar p_z orbitals, each of which contributes one electron to the resultant continuous π-electron system. The chain should behave essentially as a one-dimensional metal with a half-filled conduction band and show Peierls distortion and a metal-insulator transition. By introducing a bond alternation (alternating single long and double short bonds) and consequently doubling the lattice constant, such a chain can efficiently lower its energy. This reduces the extent of electronic delocalization that can take place along the backbone but opens an energy gap in the electronic structure of the polymer.

In a graphene each carbon atom, too, has one out-of-plane p_z orbital with one electron. The peculiarity of graphene, dictated by the backbone hexagonal structure, is that each atom is surrounded by three equivalent neighbors and cannot make such a transition with bond alternation. The periodic crystal potential is such that it causes a band splitting at the Γ and M symmetry points but degeneracy (zero bandgap) at the K points of the first Brillouin zone, making graphene a zero-bandgap semiconductor as shown in Fig. 1(d).

One way to lift that degeneracy is then to introduce an inequivalent neighbor to the hexagonal atom. In a π conjugated system this is easy to achieve by forcing a single bonding to the neighboring atom, as discussed for the case of a linear polymer. In Fig. 1(b) it is achieved by introducing an acetylene in the hexagonal structure. The p_z orbitals of the acetylene atoms are involved in a triple bond and the acetylene atom can only form a single bond with the hexagonal atom. The consequence of the formation of a single bond is thus an inequivalent neighbor, a change of the periodicity of the system, and a lifting of the degeneracy at the K points. The resulting graphyne has a high electron density at the Fermi level like graphene, but most importantly it has a well-defined direct bandgap of 0.59 eV at the M point of the Brillouin zone as displayed in Fig. 1(d). The effective masses at characteristic points, labeled m_1, m_2, and m_3 in Fig. 1(d) are equal to -0.3, 0.4, and -0.2 of the electronic mass m_e, respectively.

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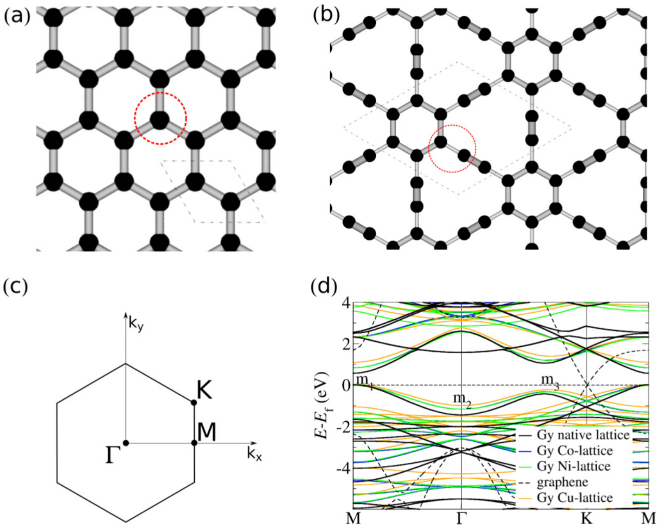

FIG. 1. (Color online) Structure and energy bands. (a) Graphene; (b) graphyne; (c) reciprocal lattice; (d) energy bands for different lattice constants (see text). Circles in (a) and (b) denote the substitution in graphene that creates graphyne.

TABLE I. Graphyne (Gy) adsorbed on Cu, Ni, and Co surfaces: Energetically favored adsorption sites, adsorption energy per carbon atom, and length of the triple bond (acetylenic link).

	Adsorption site	E_{ads}/C atom	d_{CC3}
Free Gy			1.225 Å
Gy/Cu(111)	H1	145 meV	1.309 Å
Gy/Ni(111)	H2	351 meV	1.383 Å
Gy/Co(0001)	H2	376 meV	1.401 Å

Graphyne and similar non-natural carbon allotropes can be assumed to be chemically stable [9], in spite of having a triple bond in their structure. Finite building blocks have being synthesized [10,11] and steps towards a preparation have been developed [10,12]. In fact, a graphdiyne, an allotrope with a diacetylenic linking chain, has already being synthesized [13,14], but only as a multilayer film and a nanowire with a diameter of 30 nm. There is no report of a freestanding or supported monolayer material.

Calculation of the band structure of single-layer graphyne and graphdiyne has been reported [15–18], but to the best of our knowledge, the adsorbed monolayer on any surface has not yet been investigated.

III. GRAPHYNE ON METALLIC SURFACES

Support of surfaces and coupling to metal contacts play a fundamental role in technological applications and may bring a new property resulting in novel devices. In spintronics the hybrid structure of graphene and ferromagnetic surfaces, for example, holds promise for a spin-filtering device [19]. In this respect graphyne as a semiconductor with a different charge distribution locally is a new element, possibly a new building block in nanoelectronics.

The change it brings can be best verified by investigating its adsorption on transition metal surfaces. We choose Cu(111), Ni(111), and Co(0001) surfaces, studied a lot in the context of graphene adsorption [20–23], as they provide the possibility for physisorption and chemisorption due to the hybridization of carbon orbitals with metallic states. Graphyne is expected to have a large polarizability [24], which, together with the polarizability of metallic surfaces, may result in a significant van der Waals (vdW) interaction. To calculate the structure and electronic properties we used the state-of-the-art approach of density functional theory (DFT) as implemented in the

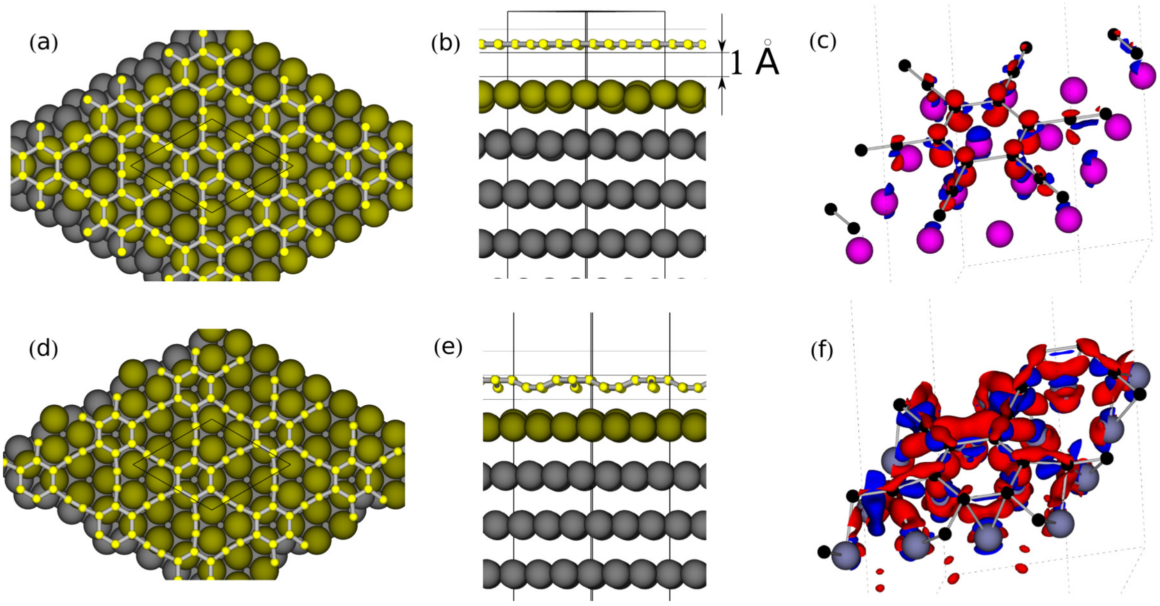

FIG. 2. (Color online) Graphyne adsorbed on Cu(111) (a–c) and Ni(111) (d–f). (a, d) Top view; (b, e) side view; (c, f) charge rearrangement (isosurface of 0.04 $e/\text{Å}^3$ plotted; depletion in blue, accumulation in red), angle view—only the top layer of surface atoms is plotted.

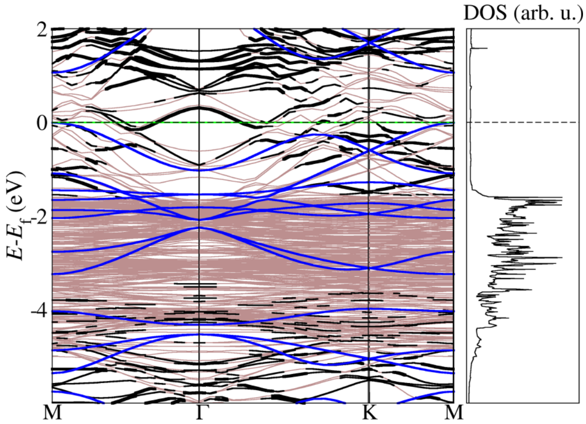

FIG. 3. (Color online) Left: Energy bands of graphyne/Cu(111). The contribution of Cp_z orbital projection is shown in black; free graphene bands, in blue. Right: Density of states (DOS) of clean Cu (right).

VASP 5.1. computer code [25] and vdW–density functional (DF) correlation [26,27] with the optB88 exchange [22]. To describe the bonding, from physisorption to chemisorption, accurately we used a recent self-consistent implementation [28,29] of the nonlocal vdW-DF following the method of Róman-Pérez and Soler [30]. We employed a plane-wave cutoff of 500 eV and dipole correction. All structures were allowed to relax until the atomic forces were below 1 meV/Å. The metallic slab was simulated with five layers of atoms, all of which were allowed to relax, and an additional 22 Å of vacuum to avoid periodic image interaction. We have enlarged the graphyne lattice constant ($a = 6.95$ Å) by several percent in order to make its unit cell commensurate with the (3×3) cell of the substrate metal [31]. This resulted in minor changes of band energies [Fig. 1(d)].

Four high-symmetry positions of adsorbed graphyne were calculated: H1, H2, TOP, and BRIDGE. In H1 and H2 the center of grapyne's hexagonal ring was positioned above the FCC and HCP hollow sites of the unit cell, respectively. For all three substrates H1 and H2 proved to be the best adsorption sites, as reported in Table I. The total energies for H1 and H2 structures on a Cu(111) surface were virtually identical, H1 being just slightly lower. For Ni(111) and Co(0001) surfaces, H2 appeared to be energetically favored.

Recalling that the value of the adsorption energy per C atom for graphene on a Cu(111) surface is 38–68 meV [32], graphyne, with 145 meV, as reported in Table I, evidently binds more strongly. This is a consequence of the different distribution of charges locally in the graphyne plane. One expects a stronger interaction with Cu atoms located under the acetylenic link than under the carbon ring. But even though the interaction is different locally the graphyne plane does not show any corrugation, as shown in the top panel in Fig. 2(b). The corrugation is shown in the substrate Cu plane instead, where the Cu atoms located under the acetylenic link are slightly pulled out of plane. This is quite the opposite compared to the adsorption on Ni and Co surfaces. Adsorption energies per carbon atom on these surfaces, 351 and 376 meV, respectively, are also higher compared to those of graphene (67 meV for Ni(111) [22,33] and 77 meV for Co(0001) [33,34]). Ni and Co surfaces are harder and do not relax as much as the Cu surface. Their interaction with graphyne is evidently stronger compared to that of Cu, as their average distance to the graphyne plane is considerably shorter. Graphyne on Ni(111) [Fig. 2(b)] and on Co(0001) (not shown) therefore suffers a strong corrugation, which is an indication of inequivalent bonding to surfaces locally.

The extent of the variation of interaction can be better understood by looking at the charge transfer in the system presented in Fig. 2(c). From the shapes of the charge depletion (blue) and charge accumulation (red) regions, we conclude that there are several types of charge transfer. There is some accumulation of charges along the line between the acetylinic carbon and the hexagonal carbon atom. This has a consequence on the interaction in the graphyne backbone itself, as we have discussed before, leading to the change in the gap at the K point of the Brillouin zone. There is a charge transfer between acetylenic carbon and the underlying substrate atoms, too, with the accumulation of charges into the carbon p_z orbital coming mostly from the d orbital of the underlying substrate atom. In addition, polarization along the graphyne plane as well as of the substrate atoms takes place, which is a clear fingerprint of a vdW-bonded π-conjugated system. All of these effects are more pronounced for graphyne on Ni(111) [Fig. 2(c), bottom] than on a Cu(111) surface [Fig. 2(c), top]. Surprisingly, on

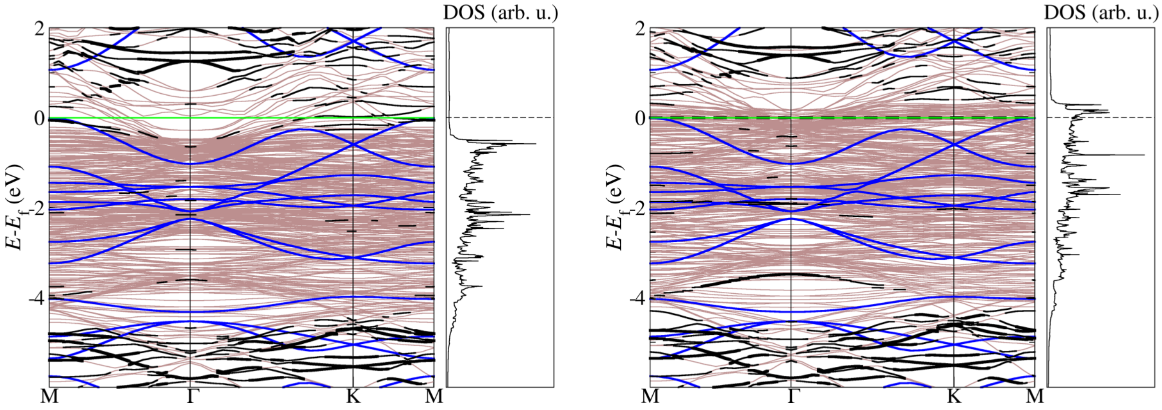

FIG. 4. (Color online) Energy bands of graphyne/Ni(111) and density of states of clean Ni for majority (left) and minority (right) spin. The thickness of black lines shows the projection weight on carbon atoms. Blue lines: freestanding graphyne.

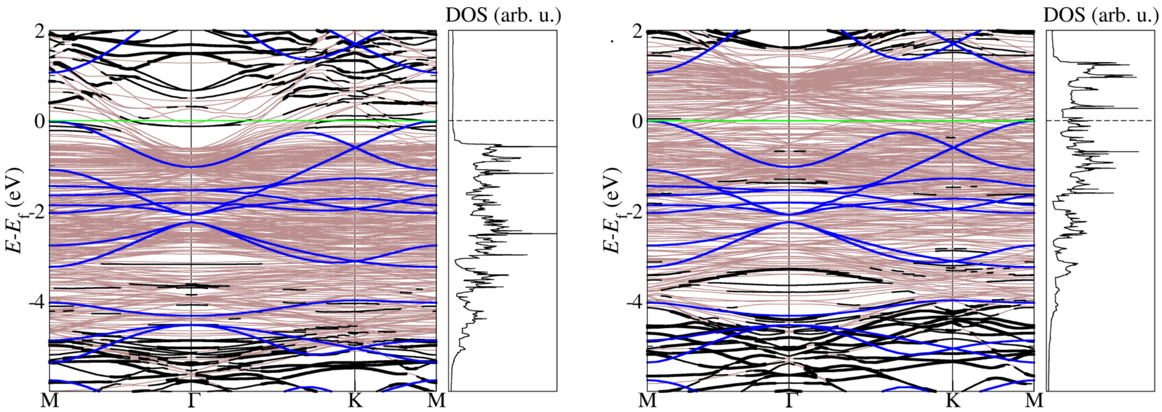

FIG. 5. (Color online) Energy bands of graphyne/Co(0001) and density of states of clean Co for majority (left) and minority (right) spin. The thickness of black lines shows the projection weight on carbon atoms. Blue lines: freestanding graphyne.

Co(0001) the charge transfer (not shown here) is very similar to that on the Ni(111) surface, although the surfaces are different. Graphyne adsorption is governed by the vdW interaction with typical nonlocal correlation interaction features. In addition, strong orbital hybridization of graphyne orbitals with the states of metal occurs, consistent with small distances, less then 2 Å, [Fig. 2(b)]. The calculated energy bands show strong changes compared to the freestanding graphyne bands. In order to follow the details of the electronic structure changes in the figures the contribution of C p_z states is made proportional to the thickness of the line.

As shown in Fig. 3 for graphyne on Cu, hybridization is particularly strong in the range of the metal *d*-band energy region, where the graphyne states are virtually dispersed over the band. Comparing the thicker band lines with the lines of freestanding graphyne we conclude that there is a relative downshift of graphyne's levels and crossing at the Fermi level which renders graphyne metallic rather then semiconducting.

On the Ni(111) surface (Fig. 4), due to its ferromagnetic property, different electronic structures are induced for majority and minority spin states. An overall downshift of graphyne's levels for both spins appears, similar to the Cu(111) surface. Due to the fact that the *d* band straddles the Fermi level the level repulsion of hybridized and unoccupied graphyne states makes no crossing at the Fermi level and the majority spin states around the Fermi level are mostly metallic *d* states. There are pronounced gaps at *K* and *M* points of the Brillouin zone. On the ferromagnetic Co(0001) surface (Fig. 5) the band structures are very similar to those on the Ni(111) surface considering the fact that the *d* band of cobalt is wider.

The hybridization of graphyne with the substrate changes the magnetization of the system, particularly the magnetic moments of the metal atoms at the surface. In Table II we list the magnetic moment per atom averaged over the layer of graphyne and the substrate layer of ferromagnetic Co(0001) and Ni(111) slabs. The true values differ from site to site, dependent on the position of the C atom on the surface and its bonding to neighboring C atoms.

TABLE II. Average magnetic moment per atom (in μ_B) for graphyne adsorbed on Ni(111) and Co(0001) surfaces: five metallic layers and graphyne are listed, numbered from the graphyne (C), positioned on top.

	6	5	4	3	2	1 (C)
Ni	0.594	0.611	0.576	0.425	0.228	0.005
Co	1.708	1.646	1.607	1.583	1.114	−0.022

One notes that the length of a triple carbon bond, listed in Table I, is longer in adsorbed than in freestanding graphyne ($d = 1.225$ Å) and increases from 1.309 Å for Cu to 1.383 Å for Ni and 1.401 Å for Co surfaces. The increase is accompanied by the accumulation of charges between acetylenic and hexagonal carbon atoms as mentioned before. According to our discussion in Sec. II, this implies a change in the bonding with hexagonal carbon, tending to a more symmetric bonding between hexagonal atoms and their neighbors, and consequently should be followed by a reduction in energy gaps at the *K* points. Indeed, inspection of the structure of energy bands in Figures 3–5 supports the conclusion. The structure is partly blurred by the hybridization-induced rather strong redistribution of energy levels in the vicinity of the Fermi level, but apparently the energy gap is most reduced at the *K* points and the reduction of the gap increases from Cu(111) to Ni(111) and Co(0001) surfaces.

IV. CONCLUSIONS

We have shown how a structural modification of graphene induces an energy gap and that the gap of the new allotrope graphyne can be modulated via the charge transfer upon adsorption on different metallic surfaces. As a semiconductor with a density of states comparable to that of graphene, graphyne can become a valuable material in the field of nanoelectronics. We have calculated the adsorption of graphyne on Cu, Ni, and Co surfaces using a DFT method with a self-consistent implementation of the vdW-DF which explicitly includes nonlocal correlations. The binding of graphyne appears to be several times stronger than that of graphene on the same surfaces and way above typical thermal fluctuations at room temperature (∼ 25 meV), which makes graphyne less prone to desorption. We have shown a change in surface magnetization of Ni and Co substrates upon graphyne adsorption. With different substrates the magnetic moments of additional ferromagnetic atoms adsorbed on top of graphyne could be so controlled, as recently reported by Donati *et al.* [35] for graphene complexes.

Due to the stronger hybridization graphyne complexes might be more efficient. In conclusion, our results show that graphyne can complement and even overtake graphene as a building block in future nanoelectronic components.

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