Graphyne on metallic surfaces: an improved graphene

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We showed how a structural modification of graphene, which gives a 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 the further modification of the energy gap which occurs via the charge transfer mechanism. We performed the calculation based on the density functional theory with the novel non-local vdW-DF correlation of the adsorption of graphyne on Cu(111), Ni(111) and Co(0001) surfaces and showed the dependence of the gap change on the charge transfer in the system. The binding of graphyne appears to be stronger than 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 of a single layer graphene has boosted a tremendous interest in its physical properties. The most prominent feature of this two-dimensional material is its exceptional electronic structure with linear band dispersion in the vicinity of the Dirac point. Graphene shows a huge mobility of charge carriers, high conductivity of electrons and holes and a ballistic charge transport, what makes it a promising candidate for a number of applications in nanoscale electronic devices.

However, what seems to be a graphene strongest side is also its weakest point. Namely, graphene band structure has no band gap what makes it unsuitable in building some of basic electronic elements. 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 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 already, such as using graphene-substrate interaction, lateral confinement, uniaxial strain and breaking the inversion symmetry in bilayer graphene.

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 section II where the freestanding graphyne is discussed. In section III we report for the first time the graphyne adsorption on three representative metallic surfaces showing the features of binding of graphyne on Co(0001), Ni(111) and Cu(111). Finally, in section IV we give conclusions and perspectives of graphyne.

II. FREE STANDING GRAPHYNE

Graphyne, shown in Fig. 1(b), is a 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 the one-dimensional linear polymer chain consisting of strongly interacting coplanar \( p_z \) orbitals, each of which contributes one electron to the resultant continuous \( \pi \)-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

FIG. 1. (Color online). Structure and energy bands. (a) Graphene, (b) Graphyne, (c) Reciprocal lattice, (d) Energy bands for different lattice constant (see text). Circles in (a) and (b) denote the substitution in graphene that creates graphyne.
FIG. 2. (Color online). Graphyne adsorbed on Cu(111) in top row and Ni(111) in bottom row, (a) and (d) top view, (b) and (e) side view, (c) and (f) charge rearrangement (isosurface of 0.04 e/Å³ plotted, depletion in blue, accumulation in red), angle view, only the top layer of surface atoms are plotted.

...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 with 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 $\Gamma$ 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 $\pi$ 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.(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 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, the change of the periodicity of the system and lifting of the degeneracy at the K points. The resulting graphyne has a high electron density at the Fermi level like the graphene, but most importantly it has a well defined direct bandgap of 1.1 eV at the M point of the Brillouin zone as displayed in Fig.(d).

Graphyne and similar non-natural carbon allotropes can be assumed to be chemically stable, in spite of having a triple bond in their structure. Finite building blocks have being synthesized and steps towards a preparation have been developed. In fact, a graphdiyne, an allotrope with diacetylenic linking chain, has already being synthesized but only as a multi-layer film and a nanowire with the diameter of 30 nm. There is no report of a free standing or supported monolayer material. The calculation of the band structure of single layer graphyne and graphdiyne have been reported, 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 a hybrid structure of graphene and ferromagnetic surfaces, for example, brings a promise for a spin-filtering device. In that respect graphyne as a semiconductor with different charge distribution locally is a new element, possibly a new building block in nanoelectronics.

The change it brings can be best verified 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, as they provide the possibility for physisorption and chemisorption due to a hybridization of carbon orbitals with metallic states. Graphyne is expected to have a large polarizability, which together with the polarizability of metallic surfaces may result in a significant van der Waals interaction. To calculate the structure and electronic properties we use the state of the art approach of density functional theory (DFT) as implemented in the VASP 5.1. computer code and vdW-DF correlation with the
optB88 exchange. To describe the bonding, from physisorption to chemisorption, accurately we used a recent selfconsistent implementation of the nonlocal vdW-DF functional following the method of Róman-Pérez and Soler. 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 by 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) for several percents in order to make its unit cell commensurate with the (3x3) cell of the substrate metal. It resulted in minor changes of band energies, Fig.2(d).

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

Recalling that the values of adsorption energy per C atom for graphene on the Cu(111) surface is 38 - 68 meV, graphene with 145 meV, as seen in Table I, evidently binds more strongly. It is a consequence of a different distribution of charges locally in a graphyne plane. One expects a stronger interaction with Cu atoms located under the acetylenic link, then 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 of 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. It is quite the opposite compared to the adsorption on Ni and Co surfaces. Adsorption energies per carbon atom on those surfaces, 351 meV and 376 meV respectively, are also larger compared to those of graphene (67 meV for Ni(111) and 77 meV for Co(0001) surfaces). But Ni and Co surfaces are harder and do not relax as much as Cu surface. Their interaction with graphyne is evidently stronger compared to Cu as their average distance to graphyne plane is considerably shorter.

Graphyne on Ni(111), Fig.2(b), and on Co(0001) (not shown here), therefore suffers a strong corrugation, what is an indication of an 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 acetylenic carbon and hexagonal carbon atom. That have a consequence on the interaction in the graphyne backbone itself, as we have discussed before, leading to the change of 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, the 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 Cu(111) surface, Fig.2(c) top. Surprisingly, on Co(0001) the charge transfer (not shown here) is very similar to that on Ni(111) surface although the surfaces are different. The graphyne adsorption is governed by the vdW interaction with a typical nonlocal correlation interaction features. In addition, a strong orbital hybridization of graphyne orbitals with the states of metal occurs, consistent with a small distances of less than 2 Å, Fig.2(b).

The calculated energy bands show a strong change compared to free standing 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 the hybridization

| Adsorp. site | E_{ads} / C atom | d_{CC3} |
|--------------|----------------|--------|
| free graphyne | | 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 |
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 free standing graphyne we conclude on relative downshift of graphyne’s levels and crossing at Fermi level which renders graphyne metallic rather than semiconducting.

On Ni(111) surface due to its ferromagnetic property different electronic structures are induced for majority and minority spin states as seen in Fig. 4. The 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 gives 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, shown in Fig. 5 the band structures are very similar to those on Ni(111) surface taking the fact that the d-band of cobalt is wider.

One notices that the length of a triple carbon bond, given in Table I, is longer in adsorbed then in free standing graphyne (d = 1.225 Å) and increasing from 1.309 Å for Cu to 1.383 Å for Ni and 1.401 Å for Co surfaces. The increase is accompanied with the accumulation of charges between acetylenic and hexagonal carbon atom as mentioned before. According to our discussion in section II, it implies the change of the bonding with hexagonal carbon tending to a more symmetric bonding between hexagonal atoms and its neighbors and consequently should be followed by the reduction of energy gaps at the K points. Indeed, the inspection of the structure of energy bands in Fig. 3., 4. and 5. supports the conclusion. The structure is partly blurred by the hybridization induced rather strong redistribution of energy levels in the vicinity of Fermi level, but apparently the energy gap is the most reduced at the K points and the reduction of the gap is increasing from Cu(111) to Ni(111) and Co(0001) surfaces.
IV. CONCLUSIONS

We have shown how a structural modification of graphyne 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 the density of states comparable to that of graphene, a 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 vdW-DF functional which explicitly includes nonlocal correlations. The binding of graphyne appears to be several times stronger than that of graphene on the same surfaces and a way above typical thermal fluctuations at room temperature ($\sim 25\text{meV}$), what makes a graphyne less prone to desorption. In conclusion our results show that a graphyne can complement and even overcome the graphene as a building block in future nanoelectronic components.

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