First-principles investigation on the bonding mechanism between graphyne and the (111) surface of Cu, Ag and Au

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Abstract
A series of adsorption configurations with less than 2% lattice mismatch of graphyne adsorbed at different sites on the (111) surface of Cu, Ag and Au are obtained by a systematic rotation of the graphyne sheet. Besides, all the non-equivalent adsorption configurations of graphyne on metal surfaces are obtained by a structure screening method based on the translation of graphyne sheet and the calculation of the atomic overlapping area at the interface. The most stable adsorption configuration of graphyne on each metal surface is obtained by optimizing these non-equivalent adsorption configurations with a small computational cost. Then the adsorption energy, differential charge density, and partial density of states are calculated using a first-principles method in order to investigate the bonding mechanism between graphyne and the (111) surface of these three metals. The results show that the adsorption types of graphyne on the (111) surface of Cu, Ag and Au are chemisorption, chemical and physical mixed adsorption and pure physisorption, respectively. In detail, when a metal (Cu or Ag) atom is below a C atom, the C-p\(z\) orbital will interact with the s and d orbitals of the metal atom and then form a covalent bond with the metal atom. In particular, when a Cu atom lies below two carbon atoms joined by an acetylene bond, the s and d orbitals of the Cu atom hybridize with each other to form two identical sd orbitals and then form two covalent bonds with two C-p\(z\) orbitals. Our results not only provide a structure screening method for obtaining the most stable configuration with a very small lattice mismatch but also reveal the interface bonding mechanism between graphyne and metals, which will provide help for the preparation of graphyne and its application in composite materials.

1. Introduction
Graphyne and the graphyne-family members were first proposed theoretically by Baughman et al in 1987 [1], which are novel carbon allotropes with one-atom-thickness and consist of sp and sp\(^2\) hybridized carbon atoms. Graphdiyne (GDY), a typical member of the graphyne family, was first fabricated on the surface of copper via a cross-coupling reaction in 2010 by Li et al [2]. Experimental and theoretical studies confirm that graphdiyne essentially displays excellent structural, mechanical, electronic, and thermal properties [3]. Now, GDY [4–14], \(\beta\)-GDY [15, 16] and Carbon Ene-Yne [17, 18] are also fabricated on different metal substrates experimentally, which makes the graphyne family applied in a broad range of fields, such as electronic devices, filtration, desalination, lithium batteries, hydrogen storage and catalysis etc [19]. It’s obvious that the interactions between graphyne and metals will have a significant impact on the properties of graphyne-metal composite materials. Therefore, understanding the interaction mechanism between graphyne and metal surfaces will play a crucial role in the preparation of graphyne and its application in composite materials.

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Theoretical studies on graphyne contacted to metals have been reported in a few works [20–23]. However, the adsorption mechanism of graphyne on metal surfaces is not clear enough. From an experimental point of view, graphyne (GY) is the most typical and stable one in the graphyne-family members [1, 24], but it has not been fabricated successfully so far. Therefore, we investigated the interactions between graphyne and the (111) surface of Cu, Ag and Au commonly used in the cross-coupling reaction by using a first-principles calculation at the level of density functional theory to promote the preparation of graphyne successfully in experiment. In addition, two main challenges in the first-principles calculation of the graphyne-metal interface are as follows. Firstly, the unit cell of graphyne is large due to the existence of acetylene bonds, which results in a relatively large lattice mismatch between graphyne and metal surfaces. Multiplying the unit cells of GY and metal surfaces to construct the interfacial structure can reduce the lattice mismatch but greatly increase computational difficulty. Secondly, graphyne consists of sp and sp² hybridized carbon atoms, which makes the interaction at the interface more complicated. As a result, the most stable configuration of graphyne on metal surfaces can’t be obtained if only the highly symmetrical adsorption sites of graphyne on metal surfaces are considered, namely top site, bridge site and hollow site.

Therefore, the research contents of this paper are as follows to solve the above model construction problems and reveal the bonding mechanism between graphyne and metal surfaces. Firstly, a series of adsorption configurations with less than 2% lattice mismatch of graphyne adsorbed on the (111) surface of Cu, Ag and Au are obtained by a systematic rotation of the graphyne sheet. Still, all the non-equivalent adsorption configurations of graphyne on metal surfaces are obtained by a structure screening method based on the translation of graphyne sheet and the calculation of the atomic overlapping area at the interface. Thirdly, the most stable adsorption configuration of graphyne on each metal surface is obtained by optimizing these non-equivalent adsorption configurations with a small computational cost. Finally, we calculated the adsorption energy, differential charge density and partial density of states of the most stable adsorption configuration by using a first-principles calculation at the level of density functional theory to investigate the bonding mechanism between graphyne and the (111) surface of Cu, Ag and Au. The results obtained by the present study not only provide a time-saving structure screening method that can obtain the most stable adsorption configuration with less than 2% lattice mismatch of graphyne on the (111) surface of face-centered cubic metals, but also reveal the bonding mechanism of graphyne on the (111) surface of Cu, Ag and Au.

2. Most stable model construction

As far as we know, the lattice mismatch of graphyne adsorbed on metal surfaces is relatively large and excessive lattice mismatch will cause the initial stress in the graphyne interior. As a result, it’s impossible to determine whether the buckling of graphyne after adsorption on metal surfaces is due to the interaction between graphyne and the metal surface, or due to the release of the initial stress in the graphyne interior. Still, we need to find the most stable adsorption configuration in order to better investigate the bonding mechanism between graphyne and the (111) surface of Cu, Ag and Au. In this paper, we will solve the above problem from the following aspects.

Firstly, a systematic rotation of the graphyne sheet will be used to obtain a series of adsorption configurations with less than 2% lattice mismatch of graphyne adsorbed on metal surfaces. Then, the matching period of graphyne on the (111) surface of metals can be obtained by a systematic translation of the graphyne sheet and the calculation of the atomic overlapping area at the interface. And we can obtain all the non-equivalent adsorption configurations according to this period. Finally, we optimize these non-equivalent adsorption configurations by using a first-principles calculation and compare the adsorption energy. As a result, the adsorption configuration with the largest adsorption energy is the most stable one. It’s worth noting that the model construction processes are performed in a programming way in order to eliminate the effects of human error on the final results. And all the codes in the programming process are shown in the supporting information.

2.1. Model rotation

The (111) surface of metals is fixed and then the whole graphyne is rotated to match the metal substrate. For each rotation angle given, a new adsorption configuration will be obtained by rotating graphyne on metal surfaces. However, it is a very time-consuming and error-prone task to find all the adsorption configurations by human observation. we proposed a kind of novel method to solve the above issue well and the specific operations are as follows in the following paragraphs.

The configuration of the Cu(111) surface is shown in figure 1(a), where the red line frame represents the primitive cell. The structure of graphyne with a hexagonal symmetry can be viewed as a 2D network of hexagonal carbon rings (sp² hybridized) connected by acetylenic linkages (sp hybridized), as presented in figure 1(b), where the red line frame represents the primitive cell. We find both the (111) surface of face-centered cubic metals and graphyne have a hexagonal symmetry, which shows the lattice constants in two directions of the graphyne...
supercell are equal, that is, \( |\mathbf{a}| = |\mathbf{b}| \). So is the metal substrate. Therefore, the matching mode of graphyne on metal surfaces can be determined once their supercell lattice constants are determined in one direction.

The abstract lattice diagram of graphyne is shown in figure 1(c), where the circle represents the basis and the red line frame represents the primitive cell. As far as we know, the lattice constants of supercell can only be the nearest neighbour distances in the lattice, so the lattice constant of the rotated graphyne supercell must be the 1st to nth neighbour times of the length of its primitive cell as shown in figure 1(c) by the black arrows. So does the (111) surface of metals. As a result, the configurations obtained by matching the nearest neighbour distances of the graphyne sheet with the nearest neighbour distances of the (111) surface of metals are the same as those obtained by rotating graphyne on metal surfaces directly.

Graphyne supercells that are with different nearest neighbour distances as lattice constants are matched with metal substrates one by one in order to obtain a series of interface matching structures with less than 2% mismatch. Table 1 shows the detailed matching results between graphyne and the (111) surface of metals. The threshold value of the supercell lattice constant is no more than 4 times of the primitive cell lattice constant of graphyne. In addition, the lattice constants of primitive cells of graphyne, Cu, Ag and Au used in this part are 6.89\( \text{Å} \) [25], 2.542, 2.873 and 2.872 Å [26].

The lattice mismatch in this paper was calculated by the underlying formula

\[
\delta = \frac{a_M - a_{GY}}{a_{GY}}
\]

where \( \delta \), \( a_{GY} \) and \( a_M \) represent the lattice mismatch, the supercell lattice constants of graphyne and the (111) surface of metals, respectively. A positive \( \delta \) indicates graphyne will be stretched, otherwise, graphyne will be compressed.

The supercell configurations with the smallest lattice constants are taken from the red line frame areas in table 1 for the next translation operation are shown in figure 2, where graphyne is rotated 54.79°, 57.00° and 57.00° with respect to the metal substrate, respectively.

### 2.2. Model translation and atomic overlapping area calculation

The different adsorption sites of graphyne on metal surfaces have an important effect on the interface structure. Therefore, we will translate graphyne comprehensively to find the most stable adsorption site. As we all know, the most straightforward method to obtain the most stable adsorption configuration is to calculate the

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**Table 1.** Detail matching results between graphyne and the (111) surface of metals. \( \delta \), \( a_{GY} \) and \( a_M \) represent the lattice mismatch, the supercell lattice constants of graphyne and the (111) surface of metals, respectively. The vector column represents two lattice vectors of the metal surface supercells relative to their primitive cells.

| Metal | Structure | \( a_{GY} \) (Å) | \( a_M \) (Å) | \( \delta \) (%) | Vector |
|-------|-----------|-------------------|----------------|-----------------|---------|
| Cu    | \( \sqrt{3}GY\cdot2\sqrt{3}Cu \) | 18.229 | 18.331 | 0.558 | (5.2)%(-2.8) |
|       | 3GY-3Cu   | 20.670 | 20.336 | -1.614 | (8.0)%(-0.8) |
|       | 3GY-\( \sqrt{6}\)Cu | 20.670 | 20.808 | 0.666 | (7.2)%(-2.9) |
|       | 2\( \sqrt{3}GY\cdot\sqrt{3}Cu \) | 23.868 | 24.250 | 1.600 | (9.1)%(-1.10) |
| Ag    | \( \sqrt{3}GY\cdot3\sqrt{3}Ag \) | 18.229 | 17.942 | -1.577 | (5.2)%(-2.7) |
|       | 3GY-3Ag   | 26.707 | 26.717 | 0.329 | (6.3)%(-3.8) |
|       | 2\( \sqrt{3}GY\cdot\sqrt{3}Ag \) | 23.868 | 23.516 | -1.472 | (7.2)%(-2.9) |
| Au    | \( \sqrt{3}GY\cdot3\sqrt{3}Au \) | 18.229 | 17.933 | -1.626 | (5.2)%(-2.7) |
|       | 3GY-3Au   | 26.707 | 20.707 | 0.180 | (6.2)%(-2.8) |
|       | 2\( \sqrt{3}GY\cdot\sqrt{3}Au \) | 23.868 | 23.505 | -1.521 | (7.2)%(-2.9) |

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**Figure 1.** The structure of Cu(111) surface and graphyne. (a) The structure of Cu(111) surface. (b) The structure of graphyne. (c) The lattice of graphyne.
adsorption energy of graphyne on different adsorption sites and the configuration with the largest adsorption energy is the most stable one. Taking the Cu(111) surface as an example, there are about $5.6 \times 10^2$ adsorption sites in the primitive cell with an interval of 0.1 Å as shown in figure 1(a). However, it must be a very time-consuming task if every adsorption configuration is optimized. Fortunately, there are lots of equivalent structures after graphyne is adsorbed on the different sites on the (111) surface of metals because both graphyne and the (111) surface of metals have a hexagonal symmetry. Therefore, we need to find out the non-equivalent structure to reduce the computational costs. In order to solve the issue, we select the atomic overlapping area value at the interface as the unique marker to identify the structure on different adsorption sites after graphyne is translated on the (111) surface of metals. And we obtained the matching period of graphyne on the (111) surface of metals by calculate this maker. Therefore, we can gain all the non-equivalent adsorption configurations according to the period. Importantly, it will be a very time-saving approach to obtain the most stable adsorption configuration by a systematic translation of the graphyne sheet and the calculation of the atomic overlapping area at the interface. The detailed steps are as follows.

Firstly, the (111) surface of metals is fixed and then the whole graphyne is translated in the rectangular shaded region as shown in figure 3(a). The grid is drawn at interval of 0.02 Å in the rectangular area while the vector for each translation will point at the grid point. In other words, each grid point is an adsorption site. At this point, the overlapping areas between each carbon atom and its nearest metal atoms are calculated as shown in the shaded region in figure 3(b). Therefore, the overlapping area of graphyne adsorbed at each adsorption site can be obtained by adding areas of all shaded regions. The radii of C, Cu, Ag and Au atoms used in the calculation are 0.70, 1.35, 1.60 and 1.35 Å, respectively [27]. Similarly, the pattern of overlapping area values of graphyne at different adsorption sites can be obtained by translating graphyne to each grid point as shown in figure 4(a). As we can see, the pattern has a period. Once the period is determined, we can obtain all the non-equivalent adsorption sites. We will implement the following analysis in order to find out this period.

Secondly, the circular region in figure 4(a) is enlarged to find out the smallest irreducible area of adsorption sites during the translation of graphyne as shown in figure 4(b). Two kinds of structures can be found when the graphyne is translated to the valley points in figure 4(b). The first one is that the hexagonal ring of graphyne is directly above the Cu atom illustrated by the schematic diagram A on the left part in figure 4(b), which is the configuration of the corresponding structures of graphyne adsorbed on A, B, C and D adsorption sites on the right part in figure 4(b). The second one is that the hexagonal ring of graphyne is at the hollow site of the Cu(111)...
surface as shown in the schematic diagrams O and O’ on the left part in figure 4(b). The two structures are equivalent to each other when the interactions between carbon and metal atoms are considered owing to the same three-fold symmetry. As a result, the adsorption region $\Delta ABC$ is equivalent to the $\Delta ACD$. In summary, the region corresponding to diamond ABCD is the ‘primitive cell’ of adsorption sites and the region $\Delta AOB$ is the smallest irreducible area of adsorption sites during the translation of graphyne on the Cu(111) surface because the region $\Delta ABC$ has a three-fold symmetry. The translation vectors corresponding to A, B, O are $(0.050, 0.960)$, $(0, 0)$ and $(0.295, 0.460)$ Å, respectively.

The overlapping areas at the graphyne-Ag(111) and the graphyne-Au(111) interfaces satisfy similar periodicity with the above analysis method. As a result, a series of non-equivalent adsorption configurations will be obtained by translating graphyne with a step size of 0.1 Å in the smallest irreducible area on each metal surface like the $\Delta AOB$ region in figure 4(b). Subsequently, we use a first-principles calculation to optimize these non-equivalent adsorption configurations and obtain the adsorption configuration with the largest adsorption energy, that is, the most stable one as illustrated by the top row in figure 5. The translation vectors of graphyne for the most stable structure on the (111) surface of Cu, Ag and Au are $(0, 0)$, $(0.2, 0.3)$ and $(0.1, 0.9)$ Å, respectively.

2.3. Computational details
Calculations of the structural optimization and the total energy based on a double-$\zeta$ polarization quality Gaussian basis sets (DZVP-MOLOPT-SR-GTH) of 500 Ry cut-off energy were performed with the freely available program package CP2K [28] using a mixed Gaussian and plane wave (GPW) approach [29]. The
generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerh (PBE) [30] was used to describe the exchange correlation effect. And the DFT-D3 semi-empirical dispersion correction scheme was adopted due to the Van der Waals force (vdW) between graphyne and metals. A dipole correction was applied to avoid spurious interactions between periodic images of the slab. The electronic self-convergence criterion is set to $1 \times 10^{-5}$ Ry and the forces on all the atoms are converged to within $4.5 \times 10^{-4}$ Ry/Bohr with respect to ionic relaxation.

Also, the electronic structure calculations based on the plane-wave basis sets of 450 eV cut-off energy were performed with the Vienna ab initio simulation package (VASP) [31]. The exchange correlation effect was described within the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerh (PBE). Monkhorst-Pack scheme was employed to discretize the Brillouin-zone (BZ) integrations with a sampling density of 0.2 Å. The electronic self-convergence criterion is set to $1 \times 10^{-4}$ eV.

The supercell used to model the graphyne-metal interface is constructed from a slab consisting four layers of metal atoms, with a graphyne layer adsorbed from the top side of the slab and a vacuum region of 25 Å. Considering the metal substrate is usually much thicker than the upper layer film and the film trends to match the lattice constant of the metal substrate in the experiment. Therefore, the lattice constant of metal unit cells is fixed to construct the interface supercell. In this paper, the $\sqrt{7} \times \sqrt{7}$ graphyne unit cell is adjusted to the $2\sqrt{13} \times 2\sqrt{13}$ unit cell of Cu(111) surface; the $\sqrt{7} \times \sqrt{7}$ graphyne unit cell is adjusted to the $\sqrt{39} \times \sqrt{39}$ unit cell of the (111) surface of Ag and Au. The interplanar spacing of the metal (111) plane is selected as the initial interfacial distance to ensure the sufficient interaction between graphyne and the metal substrate. And the initial interfacial distances between graphyne and three metals (Cu, Ag and Au) are 2.071, 2.362 and 2.399 Å, respectively.

Finally, the post-processing calculations were performed by VASPkit [32] and VESTA [33].

### 3. Results and discussion

#### 3.1. Graphyne-metal binding

The local configurations of graphyne adsorbed on the (111) surface of Cu, Ag and Au are shown in figure 5, where the top row is the top views before optimization, while the middle row and the bottom row are the top views and the side views after optimization, respectively. It can be seen that the graphyne sheet shows no significant change from the top view but a large of buckling from the side view after graphyne is adsorbed on the Cu(111) surface. In addition, it can be found all the sp hybridized C atoms are closer to the Cu(111) surface than the sp$^2$ hybridized C atoms. Also, the Cu atoms near the sp hybridized C atoms also move upward from their original positions. The above results show the interaction between graphyne and the Cu(111) surface is very strong. A similar phenomenon can be observed after graphyne is adsorbed on the Ag(111) surface but the buckling range is obviously reduced, illustrating the interaction between graphyne and the Ag(111) surface is weaker than that between graphyne and the Cu(111) surface. However, both the graphyne sheet and the Au(111) surface still remain planar after graphyne is adsorbed on the Au(111) surface, indicating the interaction between graphyne and the Au(111) surface is weakest.

The detailed structural information of all the graphyne-metal interface configurations is shown in table 2, where $\delta$ represent the lattice mismatch which can be calculated by formula (1).

$E_{\text{ads}}$ is the adsorption energy of graphyne on different metal substrates which can be calculated by underlying formula

$$E_{\text{ads}} = \frac{(E_C + E_M - E_{C-M})}{N}$$

(2)

where $E_C$, $E_M$ and $E_{C-M}$ represent the total energy of the isolated graphyne, the bare slab and the adsorption system, respectively. $N$ is the total number of C atoms. According to the definition, a positive $E_{\text{ads}}$ indicates the adsorption system should be stable.

| $\sqrt{7}$ GY- | $\sqrt{7}$ GY- | $\sqrt{7}$ GY- |
|----------------|----------------|----------------|
| $2\sqrt{13}$ Cu | $\sqrt{39}$ Ag | $\sqrt{39}$ Au |
| $\delta$ (%) | $d$ (Å) | $E_{\text{ads}}$ (meV per C) |
| 0.314 | 2.480 | 107.0 |
| $-0.909$ | 3.140 | 95.9 |
| 0.656 | 3.337 | 93.8 |
In our calculations, the approximation made by the matching procedure is reasonable since the mismatch with the lattice constant of graphyne is less than 1%. All the graphyne-metal interface modes can be also confirmed to be stable according to the definition of the adsorption energy. In addition, the adsorption energy of graphyne on the Cu(111) surface is much larger than that on the (111) surface of Ag and Au. Besides, the average equilibrium interfacial distance of graphyne adsorbed on the Cu(111) surface is 2.480 Å, which is smaller than 3.140 Å and 3.337 Å after adsorbed on the (111) surface of Ag and Au. In conclusion, the interaction between graphyne and the Cu(111) surface should be strongest, followed by the Ag(111) surface and the Au(111) surface.

We will calculate the differential charge density in order to determine the adsorption types of graphyne on the (111) surface of these three metals (Cu, Ag and Au) in the following paragraphs.

3.2. Differential charge density
The differential charge density plots induced by the adsorption of graphyne on the (111) surface of Cu and Ag are shown in figures 6−7, respectively. The differential charge density results at the graphene-metal interface can be analyzed according to the following three cases. The first case is that the metal atom lies below the two C atoms joined by an acetylene bond as shown in the region I. The second one is that the metal atom is below a C atom as shown in the region II. The last one represents the general adsorption of graphyne on the metal surface as shown in the region III. As is known to all, there must be a covalent bond formed if there’s charge accumulation near the center of two adjacent atoms, otherwise, there’s no covalent bond formed.

In the case of the graphene-Cu(111) interface as shown in figure 6, when the Cu3 atom lies below the C67 and C81 atoms joined by an acetylene bond (I region), there’s lots of charge accumulation near the center of the Cu and C atoms, showing there are two covalent bonds formed. However, the s orbital of the Cu3 atom does not participate in bonding with the C67 and C81 atoms. Therefore, we infer the s orbital and an inner d orbital of the Cu3 atom first hybridize with each other in order to form two identical sd orbitals, and then form two covalent bonds with the pz orbitals of the C67 and C81 atoms. When the Cu1 atom is below the C64 atom (II region), a large amount of charge accumulation can be found near the center of the Cu and C atoms, which indicates there’s a covalent bond formed, that is, the Cu1 atom forms a covalent bond with the p orbital of the C64 atom. When it comes to the general case (III region), a small amount of charge accumulation can be found near the center of the Cu and C atoms, which illustrates the interactions between the Cu and C atoms are...
weak chemical force. In conclusion, the adsorption type of graphyne on the Cu(111) surface is pure chemisorption.

As far as the graphyne-Ag(111) interface is concerned as shown in figure 7, when the Ag1 atom is below the C65 atom (II region), there’s a lot of charge accumulation near the center of the Ag and C atoms, which indicates the Ag1 atom forms a covalent bond with the pz orbital of the C65 atom. Similarly, when the Ag3 atom lies below the C36 and C51 atoms joined by an acetylene bond (I region), a small number of charge accumulation can be found near the center of the Ag and C atoms, which illustrates the interactions between the Ag and C atoms are weak chemical force. However, when it comes to the general case (III region), there’s no charge redistribution around the atoms and there’s also no charge accumulation near the center of the Ag and C atoms, showing there is also no covalent bond formed. Notably, regions with charge accumulation at the graphyne-Ag(111) interface are significantly less than those at the graphyne-Cu(111) interface as shown in the top view in figure 7. It can be concluded that the adsorption type of graphyne on the Ag(111) surface is chemical and physical mixed adsorption but physisorption plays a more important role.

It’s worth noting that there is no charge redistribution around the atoms and there’s also no charge accumulation near the center of the Au and C atoms when the isosurface corresponds to $2.5 \times 10^{-3}$ e Å$^{-3}$ after graphyne is adsorbed on the Au(111) surface, illustrating the interactions between the Au and C atoms are only Van der Waals force. That’s to say, the Au atoms don’t form covalent bonds with the C atoms. Therefore, the adsorption of graphyne on the Au(111) surface is only physisorption. Also, the differential charge density plot induced by the adsorption of graphyne on Au(111) surface is shown in figure S1 is available online at stacks.iop.org/MRX/7/065603/mmedia of the supporting information.

To sum up, the adsorption types of graphyne on the (111) surface of Cu, Ag and Au can be determined according to the differential charge density results. Next, we will calculate the partial density of states (PDOS) in order to investigate the bonding mechanism between graphyne and the (111) surface of Cu, Ag and Au in the following paragraphs.

### 3.3. Partial density of states (PDOS)

The structural optimization results show the C atoms close to the metal surface in graphyne are mainly sp hybridized C atoms. Besides, the differential charge density results show charge accumulation mainly exists near the center of the metal and sp hybridized C atoms. Therefore, sp hybridized C atoms play more important role in the interaction between graphyne and the metal surface. For this reason, we focus on the partial density of states of sp hybridized C atoms before and after adsorption. Here, we carried out the partial density of states analysis of the chemisorption regions on the (111) surface of Cu and Ag in order to investigate the interfacial bonding mechanism.

As far as the graphyne-Cu(111) interface is concerned, when the Cu3 atom lies below the C67 and C81 atoms joined by an acetylene bond (I region), the strong orbital coupling effect is found between the s and d orbitals as shown in figure 8(a) in the energy range from $-2$ to $0$ eV after adsorption, proving the s and d orbitals of the Cu3 atom hybridize with each other in order to form two identical sd orbitals. It can be seen that the density of states of the C67-p$_s$, Cu3-s and Cu3-d orbitals as shown in figure 8 changes significantly after adsorption. Also, there are lots of overlapping peaks found between the C67-p$_s$ orbital and the Cu3-s and Cu3-d orbitals below the Fermi energy as shown in figures 8(b) and (c), that is, there exists the strong orbital coupling effect between the C67-p$_s$ orbital and the nearest Cu3-s and Cu3-d orbitals, confirming the C67-p$_s$ orbital forms a covalent bond with one sd orbital. In the same way, the C81-p$_s$ orbital forms a covalent bond with the other sd orbital.

When the Cu1 atom is below the C64 atom (II region), there exists the strong orbital coupling effect between the C64-p$_s$ orbital and the Cu1-s and Cu1-d orbitals after adsorption as shown in figures 9(a) and (b), proving
the C64-pz orbital forms a covalent bond with the Cu1 atom. When it comes to the general case (III region), the degree of orbital coupling effect between the C38-pz orbital and the Cu6-s and Cu6-d orbitals in figures 10(a) and (b) is inferior to that in the I and II regions, especially in the energy range from $-1$ to $1$ eV, which indicates the interaction between the C38 and Cu6 atoms is weak chemical force.

In terms of the graphene-Ag(111) interface, when the Ag1 atom is below the C65 atom (II region), many overlapping peaks are found between the C65-pz orbital and the nearest Ag1-s and Ag1-d orbitals below the Fermi energy as shown in figures 11(a) and (b), showing there is the strong orbital coupling effect between the C65-pz orbital and the nearest Ag1-s and Ag1-d orbitals, that’s to say, the C65-pz orbital forms a covalent bond with the Ag1 atom.

Similarly, when the Ag3 atom is below the C36 atom (I region), the orbital coupling effect between the C36-pz orbital and the Ag3-s and Ag3-d orbitals can be found in figures 12(a) and (b), illustrating the C36-pz orbital forms a covalent bond with the Ag3 atom. In addition, the PDOS in the unbonded region (region III) is shown in figure S2 of the supporting information.

Figure 9. The PDOS of the C64-pz, Cu1-s and Cu1-d orbitals in the II region before and after adsorption. (a) The PDOS of C64-pz and Cu1-s orbitals before and after adsorption. (b) The PDOS of C64-pz and Cu1-d orbitals before and after adsorption.

Figure 10. The PDOS of the C38-pz, Cu6-s and Cu6-d orbitals in the III region before and after adsorption. (a) The PDOS of C38-pz and Cu6-s orbitals before and after adsorption. (b) The PDOS of C38-pz and Cu6-d orbitals before and after adsorption.

Figure 11. The PDOS of the C65-pz, Ag1-s and Ag1-d orbitals in the II region before and after adsorption. (a) The PDOS of C65-pz and Ag1-s orbitals before and after adsorption. (b) The PDOS of C65-pz and Ag1-d orbitals before and after adsorption.
4. Conclusions

The most stable configuration with less than 2% lattice mismatch of graphyne on the (111) surface of face-centered cubic metals can be obtained with a small computational cost by a structure screening method based on a systematic translation of the graphyne sheet and the calculation of the atomic overlapping area at the interface. This kind of model construction method has a certain portability and can be applied in constructing the interface formed by two kinds of hexagonal symmetrical materials. Our calculation results show that the adsorption types of graphyne on the (111) surface of Cu, Ag and Au are chemisorption, chemical and physical mixed adsorption and pure physisorption, respectively. In detail, when a metal (Cu or Ag) atom is below a C atom, the C-pz orbital will interact with the s and d orbitals of the metal atom and then form a covalent bond with the metal atom. In particular, when a Cu atom lies below two carbon atoms joined by an acetylene bond, the s and d orbitals of the Cu atom hybridize with each other to form two identical sd orbitals and then form two covalent bonds with two C-pz orbitals. Our results reveal the interfacial bonding mechanism between graphyne and metals, which will provide help for the preparation of graphyne and its application in composite materials.

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