



# Noble metal chain adsorption on graphene sheet

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## ABSTRACT

Van-der-Waals dispersion force plays a crucial role in physisorption mechanisms. Using density functional theory, the adsorption of noble metal (Cu, Ag, and Au) chains on graphene sheet was studied within two possible adsorption geometries, the zig-zag and the preferred armchair one. In order to take the portion of non-local correlations into account, we applied both semi-empirical and ab-initio van-der-Waals functionals in our calculations. The interaction leads to a charge transfer at the physisorption interface and makes graphene p-doped. Not only does the Fermi level shifts with respect to the Dirac point, but also a small band gap opening is predicted. Work function calculations confirm the presence of physisorption mechanism at the interface.

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## 1. Introduction

Graphene is a two dimensional nanostructure formed in a honeycomb lattice. The Fermi level is situated at the corner of the first Brillouin zone where  $\pi$  and  $\pi^*$  bands are found to touch each other at the point that is called the Dirac point [1]. Therefore, it has aroused an enormous interest in theoretical and experimental works [2,3]. The long mean free path of graphene heralds promising applications in electronic devices [4]. Even if, indium tin oxide (ITO) is widely used in electronic products, graphene has outstanding electronic properties and thus, it has the potential for significant applications in prospective devices [5]. Characterization of metal–graphene contacts leads to fabrication of graphene-based devices with higher performances. Some good examples of what is mentioned above are electronic transport measurements through metal electrodes [6].

High mobility of graphene in room temperature turns it to an ideal material for transistor fabrications. On the other hand, band gap engineering is necessary to have a high on–off ratio. The creation of a band gap is obtained by spatial confinement, e.g. graphene nanoribbons [7]. A gap opening due to breaking the inversion symmetry of the graphene lattice is more readily achievable in bilayer graphene [8,9]. For extended graphene sheets, gap engineering relies on hydrogenation [10] and adsorption [11,12]. It should be noted that band gaps could be opened via interaction with various substrates [13].

It is known that metal–graphene contacts involve chemical adsorption (chemisorption) and physical adsorption (physisorption) regimes which correspond strong and weak interactions respectively. Since electronic properties of the system are modified due to the interaction between metal and graphene [14,15], physical phenomena at

metal–graphene interfaces are well worth scrutinizing [16]. In the case of chemisorption, where strong chemical bonding occurs at the interface, the adsorption mechanism is governed by the strong bonding between metal and graphene [17]. In contrast, in the matter of physisorption no bonding occurs at the interface, resulting in large adsorption distance and low adsorption energy, so that long-range (non-local) dispersion forces such as van-der-Waals (vdW) attraction force play a dominant role in determining adsorption distance and adsorption energy [18]. It should be noticed that there are even some cases of strong chemical bonding in which vdW force contribution is critically important [19].

Today, density functional theory (DFT) is widely used to study the electronic structure of solids. Current exchange–correlation functional approximations provide an accurate description of covalent and ionic bondings. Nevertheless, they would lead to failure for the systems in which long-range dispersion forces are present [20]. For the systems in which vdW force dominantly accounts for determining the strength of interactions happening in the interface between adsorbent and adsorbate, the two common DFT approximations, i.e. the local density approximation (LDA) and the generalized gradient approximation (GGA) usually overestimate and underestimate the adsorption energy, respectively, as compared with experimental results [21]. Therefore, it is necessary to apply some functionals containing non-local correlations. In DFT calculations the portion of vdW forces can be generally regarded in two different approaches. The recently semi-empirical correction to the DFT in Kohn–Sham formulation, DFT-D2, that is used for description of the electronic structure of layered systems, improves LDA and GGA results in term of accuracy [22]. Besides the semi-empirical method, some newly developed ab-initio methods can also improve the description of vdW interactions [23–26]. However, LDA is found not to give overestimate bonding between graphene and metal (111) surfaces [27].

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Charge transfer at the metal–graphene interface results in *p*-type or *n*-type doping of the graphene sheet, causing the Fermi level to move away from the graphene conical point [16]. By means of DFT (using vdW-DF) and  $G_0W_0$  method, it has been reported by Vanin et al. that physisorption of graphene on Ag and Cu metal (111) surfaces leads to the Fermi level shifts downward and also results in an upward shift for Au with respect to the Dirac point. No opening gap at the *K* point has been observed for these combined systems [21].

Here we report the changes in structural and electronic properties of a combined system containing noble metals (NMs) on graphene sheet in the presence of vdW force. For this aim, in the first approach the non-local dispersion energy correction is added to Kohn–Sham energy through semi-empirical DFT-D2 calculations [28,29] as below:

$$E_{DFT-D} = E_{DFT} + E_{disp}, \quad (1)$$

where  $E_{DFT}$  is the self consistent energy and  $E_{disp}$  is the semi-empirical correction that is given by [28]

$$E_{disp} = -s_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_{ij}}{R_{ij}^6} f_{dmp}(R_{ij}). \quad (2)$$

Here,  $s_6$  is a global scaling factor,  $C_{ij}$  denotes the dispersion coefficient for atom *i* paired with atom *j*, whereas; the interatomic distance is  $R_{ij}$ . The summations are over  $N_{at}$  that is the number of atoms in the combined system. To ensure that no singularities occur for small values of *R*, defining of a damping function is required

$$f_{dmp}(R) = \frac{1}{1 + e^{-\alpha(R/R_0 - 1)}} \quad (3)$$

where  $R_0$  is the sum of atomic vdW radii. One must consider that Eq. 3 for  $E_{disp}$  tends to zero for small *R*. The above-mentioned tendency toward zero is reasonable in order for the strength of usual bonding not to be affected by dispersion forces.

In the second approach, ab-initio van-der-Waals density functional (vdW-DF) method, the non-local correlation energy is given by [24]

$$E_c^{nl} = \int d^3r \int d^3r' n(r) \phi(r, r') n(r') \quad (4)$$

which is included in the exchange–correlation energy through the form

$$E_{xc} = E_x^{GGA} + E_c^{LDA} + E_c^{nl}. \quad (5)$$

In this paper, we studied the bonding mechanism at the metal–graphene interface due to adsorption of a noble metal chain (NMC) on a single layer of graphene. Adsorption energy, adsorption distance, Fermi level shift relative to the Dirac point of graphene, and band gap opening are calculated through various types of functionals. In the last section of the paper, work function (WF) and charge density calculations are performed to investigate the physisorption interface and the doping mechanism.

## 2. Computational details

Calculations have been performed by Quantum ESPRESSO (QE) which is based on DFT and pseudopotential technique [30]. In this code the valence electronic wave functions are expanded in a plain wave basis set. We performed total energy and electronic structure calculations within local density approximation of Perdew and Zunger (PZ) [31], and generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) [32]. The long-range dispersion correction for PBE approximation is implemented in QE within a DFT-D2 approach of Grimme [28]. Moreover, vdW corrections are included in

pure first-principles calculations via vdW-DF and vdW-DF2B86R functionals [23,26]. An optimal lattice constant of 2.45 Å was determined for pristine graphene. The NMC bond length is adapted to the corresponding C–C bond length of graphene sheet. Since NMC is a one dimensional structure and a zero force has been calculated in our study, this consideration is reasonable.

The configuration of an armchair (A) nano chain adsorbed on one layer graphene is illustrated in Fig. 1. Our calculations yield negative formation energy for nano chain, suggesting that this structure may form. Therefore, such configuration is worth investigating. As it is shown in Fig. 1, the growth of a nano chain on graphene sheet is considered along the *x* axis. A supercell with dimensions  $2.45 \times 12.75 \times 14.72 \text{ \AA}^3$  is chosen, so that each one contains twelve carbon atoms and one noble metal atom. Thus, in-plane nano chains are separated by a large enough space. In addition, a vacuum space is provided along the *z* axis in order to avoid spurious interactions between adjacent supercells. A zig-zag (Z) chain is also considered to figure out which adsorption configuration is preferred for NMs on graphene. The corresponding supercell was generated with dimensions  $4.25 \times 12.27 \times 17 \text{ \AA}^3$ , containing twenty carbon atoms and two NM atoms (Fig. 2).

For A supercell, a uniform Monkhorst-Pack  $30 \times 6 \times 1$  *k*-point mesh is used to sample the first Brillouin zone, including the  $\Gamma$ , *K*, and *M* high symmetry *k*-points [33], while the Z supercell is sampled with a  $24 \times 9 \times 1$  *k*-point grid. The kinetic energy cutoff is set to 65 Ry, while the cutoff for the electron density is set to 450 Ry. For better convergence, the electronic self-consistency criterion is set to  $10^{-8}$  eV. For  $C_6$  and  $R_0$ , we adopted the parameters proposed by Grimme *et al.*, while they found the scaling parameter  $s_6$  to be 0.75 for the PBE functional [28]. In order to obtain adsorption energy, self consistent calculations are performed separately for graphene, NMC, and combined system in an identical supercell. According to the sixfold rational structure of graphene, three possible adsorption sites could be considered for A nano chain: hollow site (H) which is placed in the middle of the hexagon, between two neighbor carbon atoms which is labeled as bridge site (B), and top site (T) right above the carbon atom (Fig. 1). Finally, the stability of the combined system is analyzed. The atomic positions are fully relaxed until the convergence of forces acting on ions reaches 0.001 Ry/au. Since the systems of interest are nonmagnetic, no magnetic term should be considered in the exchange–correlation Hamiltonian.

## 3. Results and discussion

The calculated structural and electronic properties of combined systems are listed in Table 1, including equilibrium adsorption distance between NMC and graphene sheet,  $d_{eq}$ , maximum C–C bond length variation,  $\Delta d_{C-C}$ , Fermi level shift with respect to the Dirac point due to electronic state interactions of carbon and NMs,  $\Delta E$ , band gap opening at the Dirac point,  $\Delta E_o$ , and adsorption energy,  $E_{ads}$ , which is obtained using the following equation

$$E_{ads} = E_{Gr-ch} - E_{Gr} - E_{ch} \quad (6)$$

where the three terms on the right side represent the total energy of combined system, pristine graphene, and NMC, respectively.

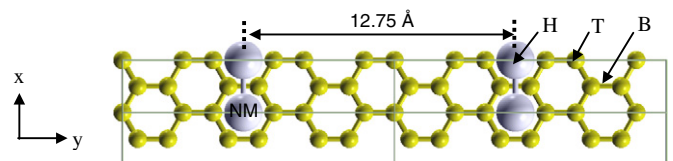


Fig. 1. The growth of an armchair NMC on graphene sheet along the *x* axis (top view). Three possible NMC adsorption sites: hollow (H), bridge (B), and top (T).

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