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First-principles study of the alkali earth metal atoms adsorption on graphene

Minglei Sun [a], Wencheng Tang [a,*], Qingqiang Ren [b], Sake Wang [c], JinYu [d,e], Yanhui Du [a], Yajun Zhang [f]

[a] School of Mechanical Engineering, Southeast University, Nanjing 211189, Jiangsu, China
[b] State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, Hunan, China
[c] Department of Physics, Southeast University, Nanjing 210096, Jiangsu, China
[d] School of Materials Science and Engineering, Southeast University, Nanjing 211189, Jiangsu, China
[e] Jiangsu Key Laboratory of Advanced Metallic Materials, Southeast University, Nanjing 211189, Jiangsu, China
[f] Department of Engineering Mechanics, School of Aeronautics and Astronautics, Zhejiang University, Hangzhou 310027, Zhejiang, China

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ABSTRACT

Geometries, electronic structures, and magnetic properties for alkali earth metal atoms absorbed graphene have been studied by first-principle calculations. For Be and Mg atoms, the interactions between the adatom and graphene are weak van der Waals interactions. In comparison, Ca, Sr and Ba atoms adsorption on graphene exhibits strong ionic bonding with graphene. We found that these atoms bond to graphene at the hollow site with a significant binding energy and large electron transfer. It is intriguing that these adatoms may induce important changes in both the electronic and magnetic properties of graphene. Semimetal graphene becomes metallic and magnetic due to n-type doping. Detailed analysis shows that the *s* orbitals of these adatoms should be responsible for the arising of the magnetic moment. We believe that our results are suitable for experimental exploration and useful for graphene-based nanoelectronic and data storage.

1. Introduction

In recent years, graphene [1,2] have attracted a surge of interest due to their potential applications in nanoscience and condensed matter physics. Thanks to its unique electronic, mechanical, thermal and other outstanding properties [3–7], graphene has been successful manipulated to enable catalysis [8,9], to assist in energy storage [10–12], to fabricate nanoelectronic devices [13,14], spintronics [15,16], and sensors [17]. Structurally, with planar sp^2-bonding and π-bonding between perpendicular p_z orbitals, graphene is a nonmagnetic semimetal [4] and its band energy dispersion is linear near the Fermi level. In order to broaden the application of graphene, many strategies have been adopted to achieve new functionalities. For instance, defect formation with electron or ion beam [18–21] can induce magnetism in graphene. Creating of graphene nanoribbons [22–25] is also widely adopted. Recently, many works also focus on the graphene nanomesh [26] and doping [27–29]. Moreover, because of the diversity of elements and the availability of experimental techniques [30], the adsorption of adatoms on graphene is a widely used and efficient strategy to provide new functionalities in nanoscale applications.

Numerous previous theoretical works on this subject has been focused on metal adatoms adsorption on graphene. Yagi et al. [31] studied Fe, Co, and Ni adsorption on graphene and single wall carbon nanotubes (SWCNTs). The hollow site was the most stable site for all elements after optimization. The magnetic moments of the transition metal (TM) atoms were found to be considerably reduced due to the promotion of *4s* orbitals electrons to the *3d* orbitals. Chan et al. [32] implemented a comprehensive study on the adsorption of 12 different metal adatoms on graphene. From groups I–III of the Periodic Table, the results are consistent with ionic bonding, and the adsorption is characterized by minimal change in the graphene electronic states and large electron transfer. For transition, noble and group IV metals, the calculations are consistent with covalent bonding, and the adsorption is characterized by strong hybridization. Valencia et al. [33] studied the functionalization of graphene and (8,0) SWCNTs with individual *3d* transition metal (TM) atoms by density functional theory (DFT) calculations. The structural geometry, magnetism, and binding energies were analyzed. They found that Sc, Ti, Fe, and Co metals could be isolated

* Corresponding author.
E-mail address: 101000185@seu.edu.cn (W. Tang).

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on the graphene surface, whereas all other *3d* TM atoms diffused. Gao et al. [34] studied the group IV metal adatoms adsorption on graphene. They found that semimetal graphene becomes metallic and attains a magnetic moment. Detailed analysis shows that the magnetic moment comes from the localized *p* orbitals of group IV metal adatoms.

Among the vast amount of studies on graphene, some works have been studied the behaviors of alkali earth metal (AEM) adsorption on graphene. Ciraci et al. [35] published a study on hydrogen storage of Ca atoms adsorbed on graphene. They found that Ca adatom is chemisorbed on graphene and the graphene becomes metallic. Zhou et al. [36] carried out a study on strain-engineered adsorption of Ca atoms on graphene. The adsorption energy increased significantly with the application of strain. Liu et al. [37,38] found that Mg adatom exhibits physisorption character. In contrast, Ca adatom is found to transfer substantially to graphene and leads to ionic bonding. So far, systematic first-principles study on the adsorption of alkali earth atoms, including Be, Mg, Ca, Sr and Ba, on the graphene is still absent. Therefore, a theoretical study is timely at present.

In the present paper, we analyzed the trends in the geometric parameters, adsorption energies, electronic structures and magnetic moments of AEM atoms (Be to Ba, five different metal adatoms) on graphene by means of first-principle calculations. The paper is organized as follows. In Section 2, the computational details are described. The main numerical results and discussions are elaborated in Section 3. Finally, in Section 4, a conclusion is presented.

2. Computational details

The geometric, electronic and magnetic properties is calculated by the density functional theory (DFT) in the generalized gradient approximation (GGA) implemented in the Vienna ab-initio simulation Package (VASP) [39,40] in which the projected augmented wave method (PAW) [41] and Perdew, Burke, and Ernzernhof (PBE) [42] of exchange-correlation are used. PAW-PBE method has been shown to be very effective for cluster [43,44] and surface [45–48] calculations. It is well known that the GGA tends to underestimate the binding in the configurations, so if the atoms bind in GGA, they will definitely bind in a real configuration. A kinetic energy cutoff of 550 eV was used for valence electron wave functions. A $4 \times 4 \times 1$ supercell of graphene is built for the adsorption on graphene. This supercell is found to be adequate because many previous works also use this supercell to perform their studies [49–53]. Brillouin zone is sampled within Gamma scheme by $7 \times 7 \times 1$ mesh points. A large vacuum region is set as 20 Å to eliminate the influence between the atoms in the supercell and its replica. Convergence precision of total energy between two self-consistent steps is taken to be 10^{-6} eV. After the ionic relaxation, the Hellmann–Feynman forces are smaller than 0.01 eV/Å. All calculations were performed in the spin unrestricted manner and all the parameters in the calculations are carefully tested.

3. Results and discussions

A. Adsorption energy and geometric structure

The first question one has to address is, of course, whether the AEM adatoms can form strong bonds with graphene. Because of the high symmetry hexagonal structure of graphene, the possible adsorption sites can be reduced into three types: the adatom directly above one of carbon atom in graphene (T), above the middle of the C—C bond (B), and above the center of the hexagon (H), as shown in Fig. 1.

The adsorption energy (E_{ad}) in our calculations is defined as follows:

$$E_{ad} = (E_G + E_a) - E_T \quad (1)$$

In formula (1), E_{ad} is the adsorption energy; E_G is the total energy of graphene; E_a is the energy of an isolated AEM adatom; E_T is the total energy of the configuration. Of all the three adsorption sites mentioned above, the site with the largest E_{ad} is referred to as the most stable site.

Adsorption energy (E_{ad}), bond length (d_{ac}), graphene distortion (Δh) electron transfer (Δq) and magnetic moments (M) were summarized in Table 1.

Unfortunately, it is noteworthy that from Table 1, for Be and Mg adatoms adsorbed on graphene, the E_{ad} in all the three cases (adsorption on T, B and H site) is vanishingly small, which implies that the interactions between these adatoms and graphene are most likely to be physisorption and they are dominated by van

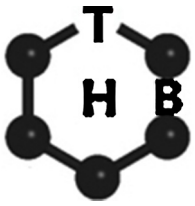

Fig. 1. Three adsorption sites of AEM adatom adsorbed on graphene: top (T) site, bridge (B) site, and hollow (H) site.

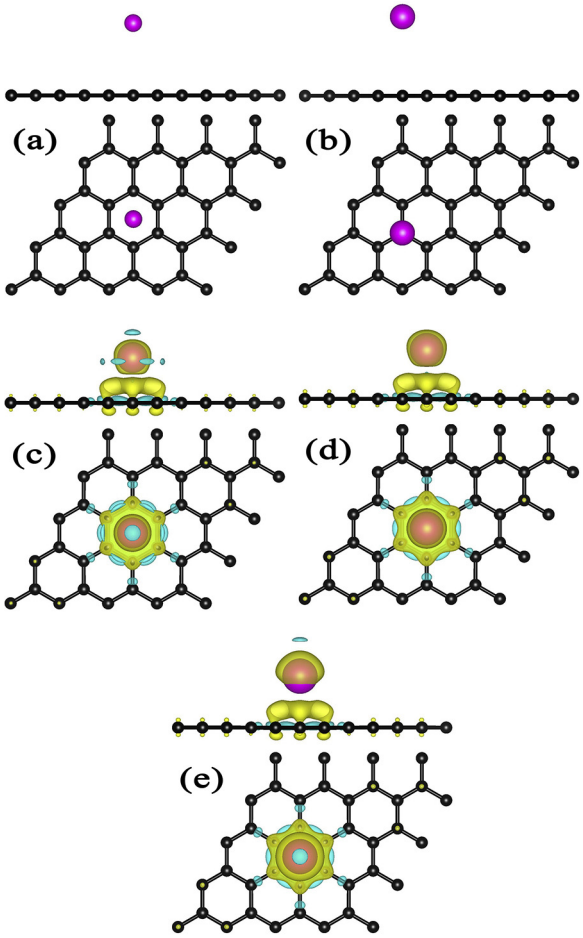

Fig. 2. Charge difference for (a) Be adatom adsorption on the H site in a graphene sheet (denotes as Be&H hereafter), (b) Mg&T, (c) Ca&H, (d) Sr&H and (e) Ba&H.