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Full Length Article

Spin polarization properties of benzene/graphene with transition metals as dopants: First principles calculations

X.B. Yuan [a,*,1], Y.L. Tian [a,1], X.W. Zhao [a], W.W. Yue [a,b], G.C. Hu [a], J.F. Ren [a,b,*]

[a] School of Physics and Electronics, Shandong Normal University, Jinan, 250014, China
[b] Institute of Materials and Clean Energy, Shandong Normal University, Jinan 250014, China

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ABSTRACT

First principles calculations are used to study the spin polarization properties of benzene molecule adsorbed on the graphene surface which doped with transition metals including Mn, Cr, Fe, Co, and Ni. The densities of states (DOS) of the benzene molecule can be induced to be spin split at the Fermi level only when it is adsorbed on Mn-, and Cr-doped graphene. The p-orbital of the benzene molecule will interact with the d orbital of the doped atoms, which will generate new spin coupling states and lead to obvious spin polarization of the benzene molecule. The spin-polarized density distributions as well as the differential charge density distributions of the systems also suggest that Mn-doped graphene will induce bigger spin polarization than that of Cr-doped graphene. Benzene molecule could be spin-polarized when it is adsorbed on the graphene surface with transition metal dopants, which could be a new method for researching graphene-based organic spintronic devices.

1. Introduction

As a two-dimensional honeycomb structure, graphene has attracted great attentions since its first discovery in experiments in 2004 [1–6]. Graphene has other high performance in addition to its unique two-dimensional structure. For example, it has unique physical and chemical properties, such as excellent electrical, optical and mechanical properties, et al. Because of its excellent properties, graphene has been widely applied in various fields, such as electronic circuitry elements, energy production, and field-effect transistors [7–11]. In addition to the remarkable intrinsic electronic and mechanical properties of pure graphene, the structure and properties can also be modified and controlled by molecule adsorptions and atom-dopants [12–15]. The interactions between graphene and the adsorbed molecules or the atom-dopants will change the electronic structures of the graphene and then its properties will also be changed, these already have been experimentally and theoretically proved. Graphene could be selected to turn into a particular material towards molecular adsorption and separation processes or as a support for different catalysts owing to their tiny dimensions and great surface area [16].

Graphene has been widely used in spintronic devices based on the small spin-orbit coupling and small hyperfine interactions as well as the excellent charge carrier mobility. The effective injection of spin-polarized carriers from graphene to organic materials is of critical important in developing organic spintronic devices by taking advantage of the potential spin transport properties of graphene [17]. Graphene are regarded as building blocks in next-generation nano electronic devices due to the exotic electronic properties and potential applications [18]. The band structure of pure graphene is spin degenerate, so it is needed for people to make graphene spin polarized by various physical and chemical modifications. Cutting graphene into nanoribbons is a good way to improve the spin polarization properties in graphene-based spintronic devices. Even though the band structure of the graphene nanoribbons is spin degenerated at ground states, the electron density is spatially spin-polarized, so breaking the symmetrical distribution of spin density is regarded as a good way to realize spin polarization in graphene. In the past studies, graphene nanoribbons are regarded as hot objects in graphene-based spintronic devices [19–21]. On the other hand, the electronic and band structures of graphene can be changed by doping atoms. Doped with transition metals in graphene will change the electronic structure of graphene and induce magnetic moment. Therefore, graphene doped with transition metals is another object to research the spin polarization properties of graphene [22–25]. At the same time, for spin polarization in organic materials, people

* Corresponding authors at: School of Physics and Electronics, Shandong Normal University, Jinan, 250014, China (J.F. Ren).
E-mail addresses: yxb@sdnu.edu.cn (X.B. Yuan), renjf@sdnu.edu.cn (J.F. Ren).
[1] These authors contributed equally to this work.

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usually choose representative organic molecules which contain p_z-electron systems such as thiophene, benzene, cyclopentadienyl radical, and cyclooctatetraene as spin injection materials because of their significant different characteristics [26,27]. By using graphene with transition metal dopants as electrode to achieve spin polarized injection and transportation in organic molecules becomes hot topics in organic spintronics.

In this article, spin polarization properties of benzene molecule adsorbed on the surface of graphene doped with transition metals including Mn, Cr, Fe, Co, Ni are studied theoretically. Transition metal dopants in graphene will induce magnetic moments, so the electronic structures of benzene/graphene will be changed and the spin polarization of benzene molecule can be induced. Adsorb organic molecules on graphene with transition metal dopants can be a new method for researching graphene-based organic spintronic devices.

2. Theoretical model and computational details

We use density functional theory (DFT) with the vdW-DF method to determine the adsorption energy and atomic structures. All DFT calculations are performed by using VASP with the projector augmented wave (PAW) basis sets and periodic boundary conditions [28,29]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional is used [30], and the plane-wave cut off energy is set to 500 eV throughout the calculations. Each simulated system consists of a 4×4 graphene supercell (32C atoms) with one transition metal atom substitutes a C atom. A single benzene molecule is adsorbed on the graphene surface with transition metal dopants. In the direction parallel to the graphene surface, the supercell is extended for 20 Å in order to avoid the interference. The Monkhorst-Pack k-point grid of $5 \times 5 \times 1$ is adopted for the Brillouin zone integration [31]. All the atoms are allowed to relax during the structural optimizations and the convergence criteria for the total energy and the force are 10^{-4} eV and 0.02 eV/Å, respectively.

There are two different adsorption types for benzene, i.e., a hollow and a stack adsorption sites, which are shown in Fig. 1. For hollow adsorption, the hexagon ring of the benzene molecule is placed parallel to the hexagon ring in graphene and the carbon atoms in benzene molecule are placed directly above the corresponding carbon atoms and the transition metal dopants in the graphene. In the case of stack adsorption, the hexagon ring center of benzene molecule is placed above the doped transition metals and three carbon atoms in the benzene molecule are placed directly above the corresponding carbon atoms of the graphene, the other three C atoms are placed above the centers of the graphene hexane rings. The total energies of the two different adsorptions are calculated, and according to the results, it is found that the total energy is lower when the benzene molecule is adsorbed on the stack site than that of the hollow site. Stack adsorption is the stable adsorption and is adopted in the following calculations.

3. Results and discussion

The most stable full relaxed stack adsorption configurations of benzene/graphene with different transition metal dopants are shown in Fig. 2. It is found that the graphene structures have been changed and the doped atoms protrude out of the graphene plane when the dopants are Mn, Cr, and Fe. However, the doped atoms concave down out of the graphene plane when the dopants are Co and Ni. Different dopants induce different adsorption structures, which make spin polarization properties of the adsorption systems different.

Fig. 3 gives the projected density of states (PDOS) of the benzene molecule which adsorbed on the graphene surface with transition metal dopants. Electronic transport properties are determined by the electronic states near the Fermi energy, therefore it is important to investigate the spin splitting properties near the Fermi energy of the PDOS. It is clear that the PDOS of isolated benzene molecule is not spin polarized, which is shown in Fig. 3(f). However, obvious spin nondegeneracy appears around the Fermi level, as shown in Fig. 3(a) and (b), which means that the p-d orbital couplings between the 3d orbital of the doped atoms and the 2p orbital of the benzene molecule will generate new spin states, so obvious spin polarization of the benzene molecule appears when the dopants are Mn and Cr. In Fig. 3(c), there is no obvious spin splitting around the Fermi level compared with those in Fig. 3(a) and (b). And as shown in Fig. 3(d) and (e), only a shift of the PDOS appeared, and there is also no obvious spin splitting around the Fermi level. Thus, we can draw that benzene molecule adsorbed on Mn- and Cr-doped graphene surface will become spin polarized and there is no obvious spin splitting when it is adsorbed on Fe-,

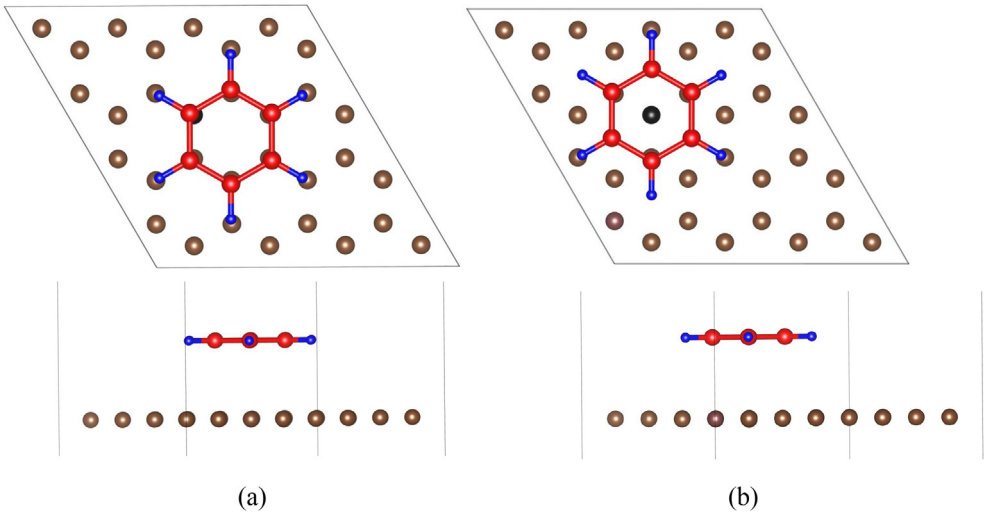

Fig. 1. Top and side views of the two different adsorption types of (a) hollow and (b) stack for benzene/graphene. The black atom in graphene corresponds to the position of the transition metal dopants.