Physica B 405 (2010) 3337–3341

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Density functional calculation of transition metal adatom adsorption on graphene

Leibo Hu, Xianru Hu, Xuebin Wu, Chenlei Du, Yunchuan Dai, Jianbo Deng *

Institute of Theoretical Physics, Lanzhou University, Lanzhou 730000, PR China

ARTICLE INFO

Article history:
Received 25 July 2009
Received in revised form
7 March 2010
Accepted 3 May 2010

Keywords:
Adsorption on graphene
Density-functional theory
Metal–nonmetal contacts
Electron density of states

ABSTRACT

The adsorption of 15 different transition metal adatoms on graphene is studied using first-principles density-functional theory with the generalized gradient approximation. The adsorption energy, stable geometry, density of state, and magnetic moment of each adatom–graphene system are calculated. For the adatoms studied from Sc to Zn of the Periodic Table, and noble metals, the distortion of the graphene layer on B of T sites is quite significant in some cases, and the adsorption is characterized by strong hybridization between adatom and graphene electronic states. The favored adsorption site indicates the main chemical bond between adsorbate and graphene. Half filled d shell TM atoms and Au, Ag, Zn have small adsorption energy. The reduction in magnetic moment from the isolated to the adsorbed atom is explained by the perspective of charge transfer, and electron shift between different orbit states of the adatom.

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1. Introduction

Graphene is a two-dimensional (2D) honeycomb-structured lattice of carbon atoms. The bonding is very strong and thus graphene is highly stable. Several experimental groups have successfully produced isolated, and room-temperature stable graphene [1–3]. Since electronic transport measurements through a graphene sheet require contacts to metal electrodes, it is of importance to understand the interactions between graphene and metal. The adsorption of graphene on a series of metal substrates has attracted many attentions recently [4–6]. Metals adsorbed on nanoscale carbon surfaces have been shown experimentally to form a variety of structures [7], and these structures can be manipulated to give rise to interesting new phenomena. Understanding the metallic structures that form and their interface with the carbon surface is essential to fabricate electronic devices for applications and transport experiments [8,9].

Several previous theoretical studies have been performed in order to provide an atomic-level understanding of the interactions between adatoms and graphene. These investigations focused on the stable configurations of alkali adatoms on graphene [10,11], embedding transition-metal (TM) atoms in graphene [12], charge transfer between graphene and metal adatoms [5], and magnetism [13]. One of the avenues of research being pursued in the materials science of graphene is the tailoring of its electronic properties by chemical adsorption of transition metal atoms [14].

In this paper, the adsorption of 15 different TM adatoms on graphene is studied, and details of our method are described in Section 2. We provided a comprehensive comparison based on previous work for Fe, Mn, Co atoms deposited on top of a flat graphene sheet [14]. TM atoms from Sc to Zn are studied, we further included noble metals and Mo, as they have a filled or half filled d shell. The adsorption energy, geometry, density of states (DOS), and magnetic moment are calculated. Our purpose is to reveal the features of surface functionalization of mono- and bi-layer graphene, and we hope our results can be applied to the substrate-based graphene systems.

Single wall carbon nanotube (CNT), which is an unique material for nanotechnology, is graphene sheet rolled up into a compact tube of finite diameter. It is interesting to discuss adsorption on both sides of the CNT. Experiments have demonstrated the ability to control metal adatom diffusion between metal clusters on CNT surfaces [15]. The interaction between TM atoms on the inner side and the outer side can also be expected. For such purpose, adsorption on CNT wall should be investigated in detail. Rojas has used the graphene sheet as a prototype for CNT to lower computational requirements [16,17]. We expect to be able to apply the result for graphene for selection of target adsorbate atomic species or molecular species for nano-structure on CNT. As the strong curvature of small-radius CNT leads to rehybridization of the sp^2 C–C bond and can result in adsorption behavior that is different from graphene [18], further investigation of this issue is necessary.

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* Corresponding author.
E-mail address: dengjb@lzu.edu.cn (J. Deng).

0921-4526/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2010.05.001

2. Methods

Our calculations were performed using spin-polarized density-functional theory (DFT) implemented in the quantum-ESPRESSO package [19], which is based on the plane-wave pseudopotential method. DFT, in spite of not taking van der Waals part of the interlayer interaction into account, has been proved to give the correct equilibrium structure and to be accurate enough to tackle the complex band structure of 3D graphite and CNT in the vicinity of the Fermi energy (E_f) [20–24].

In our calculation, a plane-wave basis set with a maximum plane-wave energy of 400 eV cutoff is used in combination with Vanderbilt ultrasoft potential and Perdew–Burke–Ernserhof (PBE) [25] exchange-correlation functional within the generalized gradient approximation (GGA). All parameters in the calculation are chosen to converge the total energy of 0.001 meV. The occupation state is 'smearing', and the value of Gaussian spreading for Brillouin-zone (BZ) integration is 0.05 eV, K-points are generated automatically with the size of 3 × 3 × 1 for the graphene sheet.

The graphene sheet was represented by a basis of 24 carbon atoms, distributed in a honeycomb arrangement. We use our calculated graphene lattice constant of 2.46 Å, which is identical to the experimental value. We let the x and y directions be parallel and the z direction perpendicular to the graphene plane. The supercell is tetragonal $8.52 \times 7.38 \times 15$ Å^3 with periodic boundary conditions in x, y, z in order to represent an infinite sheet. A distance of 15 Å along the z-axis is large enough that the overlap of the electronic states of neighboring adatoms is small, and the adatom–adatom and graphene–graphene interaction can be ignored (several test calculations for a basis of 96 carbon atoms and 25 Å along the z-axis gave essentially the same results). The configurations of the adatom–graphene system are shown in Fig. 1. The supercell dimensions are kept fixed for all calculations.

We consider the binding of the adatom on three sites of high symmetry: the hollow (H) site at the center of a hexagon, the bridge (B) site at the midpoint of a carbon–carbon bond, and the top (T) site at directly above a carbon atom (Fig. 2). The structures are considered to be in equilibrium when the force acting on the atoms drops below 0.001 eV/Å.

First, a series of static calculations are performed. In this process, we put the adatoms at high-symmetry positions (B, H and T sites) with three distances of 1.5, 2.5 and 3.5 Å, respectively, along a line perpendicular to the graphene layer to determine the interaction potential of adatoms with graphene, and we fix the position of adatoms at x, y-axes, then relax the distance at z-axis. After the locally stable configurations have been found in the high-symmetry positions, we re-relax the adatoms at all possible directions to have locally more stable positions. It is common for the ground-state structure to distort from such high-symmetry positions, lowering the overall symmetry of the system [14]. After relaxation, the adsorption geometry is obtained from the positions of the atoms.

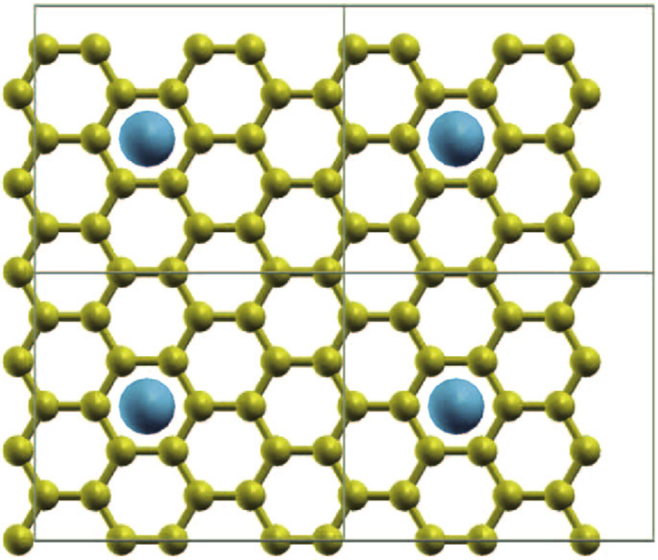

Fig. 1. (Color online) Adatom on the hollow site in a graphene sheet which was represented by a basis of 24 carbon atoms.

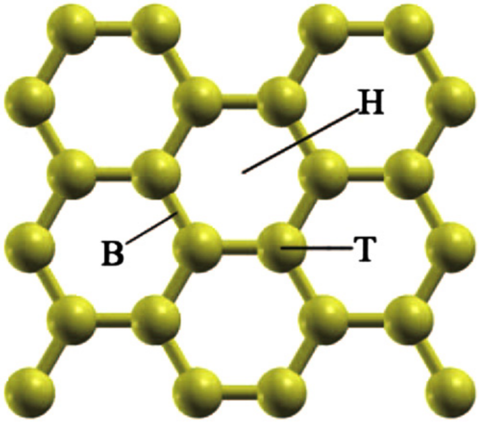

Fig. 2. (Color online) The three adsorption sites considered: hollow (H), bridge (B), and top (T).

To calculate adsorption energies, we also require the total energy of an isolated atom, which is approximated by the calculation with a single atom in a cubic supercell of length 15 Å. Only the gamma point of the BZ is sampled in this case.

3. Result and discussion

3.1. Adsorption energy and geometry

In this work, the adsorption energy is defined as

$$\Delta E = E_{ag} - E_g - E_a \quad (1)$$

where E_{ag} is the spin-polarized total energy for the optimized equilibrium configuration of the graphene and the adatom. E_g is the total energy of the isolated graphene per tetragonal supercell (containing 24C atoms), and E_a is the spin-polarized total energy of the corresponding adsorption adatom in its ground state. Adsorption energies and structural properties for the three sites considered are summarized in Table 1.

Of the three above adsorption sites considered, the site with the minimum total energy is referred to as the favored site. The height (h) of adatom is defined as the difference in z coordinate of the adatom and the average of the z coordinates of the C atoms in the graphene layer. The distortion of graphene layer is quantified by computing the maximum deviation of the C atoms from the average of their positions in the z direction. The distance between the adatom and its nearest carbon atom (d_{AC}) is also calculated. We also calculated the magnetic moment of the each isolated atom and the per corresponding adatom of the adatom–graphene system.

We find that the H site is the most stable site for the TM atoms with partially filled d shell, while the adsorption energy is the largest and height is the smallest. H site is the most optimal one, as it has the largest number of neighboring C atoms for lowering the adsorption energy. For an ionically bonded adatom, the

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