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The mechanism of spontaneous doping of boron atoms into graphene

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HIGHLIGHTS

- The mechanism of spontaneous doping of boron into graphene is investigated.
- Boron atom can substitute carbon atom in graphene without any energy barrier.
- The mechanism is reversible.

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ABSTRACT

The mechanism of spontaneous doping of boron atoms into graphene is proposed from *ab-initio* calculations. When boron and oxygen atoms are placed beside the graphene plane, boron can substitute spontaneously carbon atom in graphene without any energy barrier. More interestingly, the mechanism of spontaneous boron doping is reversible, i.e., the boron dopant also can be removed by the similar barrier-free process. Therefore, the mechanism of doping and contra-doping in this paper should be very useful to control boron doping of graphene.

1. Introduction

Graphene has attracted eyeballs of theoreticians and experimentalists due to its unique physical and chemical properties [1–8] since it was experimentally discovered in 2004 [9]. The carbon-based nanomaterials can be constructed from graphene by wrapping, rolling and stacking [10]. The study about fundamental physics of graphene may help us to understand the properties of all carbon-based materials. There are already lots of investigations on graphene, covering from electronic structures to transport properties. Graphene is a gapless material, although the mobility of the charge carrier in graphene is superior to conventional Si-based materials, which may limit the actual applications of graphene in electronics and optoelectronics, particularly in logic and switching. Therefore, in order for gating to apply graphene in these areas, one first modulate its electronic structure, especially around the K and K' points. It is known that doping is an effective method to open an energy gap or to control the type of carrier density in graphene.

A type of application of graphene and its derivatives is as gas sensors by adsorbing the gas molecules on their surfaces [11–15]. For example, by the density functional theory (DFT) calculations, Wehling et al. [16] found that the density of state of graphene was sensitive to the adsorbate NO_2, which successfully explained the experimental observation [17]. Other experimental and theoretical investigations confirmed that it was a physisorption behavior. The sensitivity of graphene to the adsorbates may be relative to the impurities effect [18–21].

Doping can tune the physical and chemical properties of graphene. Boron atoms are typical substitutional dopants. The local atomic structure does not distort and the B–C bond is covalent and quite strong, comparable to that of the host C–C bond, after boron doping into graphene. For electronic structure, boron doping makes the Dirac point move below the Fermi energy. Therefore, the boron atom acts as the hole doping [22]. However, doping is known to be a very difficult task due to the existing strong sp^2-bond in graphene. To modulate the doping type in atomic and molecular levels may be very important for the application of graphene. Oxidation is an important method in manipulating the massive production of graphene, furthermore, the oxygen-rich environment also is unavoidable for in future applications of graphene. Here, we propose a new controllable mechanism of boron doping into graphene with the help of oxygen atoms. The mechanism has two interesting features. First, the doping process is spontaneous without any energy barrier. Second, the mechanism is reversible, i.e., the boron dopant can be removed by a similar process.

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2. Computational details

A 50-atom supercell is used to simulate the 5×5 pristine graphene sheet. The periodical boundary conditions (PBC) are employed in parallel direction of the graphene plane. In vertical direction, the neighbor layers are separated by a vacuum region of 15 Å to avoid the interaction between layers. The calculations of forces, electronic and magnetic structures are performed by VASP code [23,24] using a pseudo-potential plane wave (PP-PW) method within the framework of the density functional theory [25]. We choose GGA-type PBE function as the exchange correlation function [26]. The projector-augmented wave (PAW) [27,28] is used to describe the interaction between ions and electrons for carbon, boron, and oxygen atoms. An equivalent cutoff energy of 500 eV for plane wave expansion of the PAW is used. The Brillouin Zone (BZ) is sampled using a $5\times5\times1$ Monkhorst–Pack grid [29] for the structure relaxation. The conjugate gradient minimization scheme [30] is used to perform atom position optimization until all the forces on every atom is less than 0.01 eV/Å. To obtain accurate total energy, charge density, and electronic density of state (DOS), the denser k-points of $15\times15\times1$ and the tetrahedron method [31] are chosen.

3. Results and discussion

First of all, we discuss the adsorption properties of single oxygen or boron atom adsorbed on the graphene plane. Three classical adsorption sites are considered: bridge site (B), top site (T), and hollow site (H), as shown in Fig. 1(a). The adsorption energy, defined as $E_a=E_{XG}-E_G-E_X$, is adopted to evaluate the ability of the adsorption of the oxygen (or boron) atoms on graphene, where E_{XG} is the total energy of oxygen(boron)–graphene system, E_G is the energy of graphene and E_X is the energy of the isolated oxygen (boron) atoms. After minimization of the forces on atoms, the analyses of total energy and structures are performed to understand the stability of the adsorption. The results are listed in Table 1. For oxygen adsorbed on graphene, the bridge site is the favorable adsorption site with the adsorption energy of -2.66 eV, judging from E_a. The distance between the graphene plane and oxygen atom (d_O) is 1.66 Å. Because of oxygen atom resting on graphene, two carbon atoms next to oxygen atom are pulled out of the plane by the same value of 0.41 Å. The T and H sites are the second and third favorable adsorption sites. d_O and E_a are 1.45 Å and -1.67 eV, respectively, for T site and d_O and E_a are 2.29 Å and -0.68 eV, respectively, for H site. Especially, carbon atom still remains in the plane almost in the H site case. The short distance between adsorbate and graphene and large adsorption energy gives us sufficient reasons to believe that oxygen atom can be chemisorbed on graphene. For boron adsorbed on graphene, the adsorption energy is relatively small, indicating the physisorption behavior. Like oxygen adsorption, the B site is the lowest-energy site with $E_a=-0.18$ eV, denoting that boron atom tends to be adsorbed in the B site of graphene. It is worthwhile to point out that the plane shape of graphene keeps unchanged almost after boron atom locating on its surface for three adsorption sites.

As discussed above, oxygen and boron atoms tend to locate in the bridge site. Therefore, we place a boron and an oxygen atom in the bridge site of both sides of graphene. The initial distances are 3.0 Å, as shown in Fig. 1(b). The conjugate gradient (CG) minimization scheme is used to minimize forces on atoms. Seen from the minimization process of forces, we find that: (1) the oxygen atom tends to pull one of the two adjacent carbons out of the graphene plane and (2) boron atom tends to bind with three adjacent carbon atoms around this center carbon because of the octet rule. Just for two reasons, the C–C bonds around the oxygen atom become weaker and weaker. A carbon atom is completely removed from its original spot and is replaced with boron atom at

Table 1
The distance between oxygen (boron) and graphene plane $d_O(d_B)$ (in Å), the distance of carbon displaced from the graphene plane d_C (in Å), and the adsorption energy E_a (in eV), for different sites of single oxygen or boron atom adsorbed on graphene. T, H, and B indicate top, hollow, and bridge adsorption sites.

Atoms	Sites	T	H	B
O	d_O	1.45	2.29	1.66
	d_C	0.3	0.0	0.41
	E_a	−1.67	−0.68	−2.66
B	d_B	1.77	2.74	1.87
	d_C	0.0	0.0	0.0
	E_a	−0.14	−0.04	−0.18

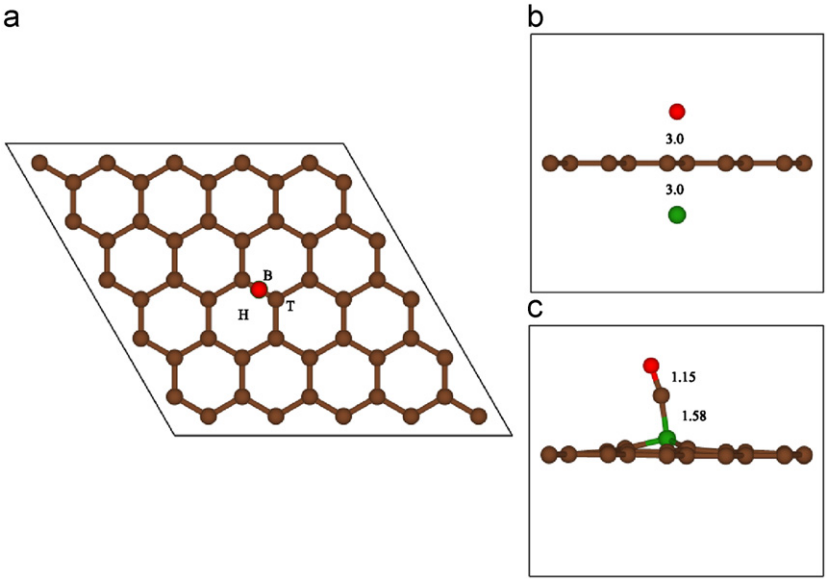

Fig. 1. Initial and relaxed structures for graphene with boron and oxygen atom placed beside the plane: (a) top view, (b) side view, and (c) the relaxed structure. Yellow ball expresses carbon atom, grey boron atom, and red oxygen atom. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)