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Gas adsorption, energetics and electronic properties of boron- and nitrogen-doped bilayer graphenes

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ABSTRACT

We study stabilities and electronic properties of several environmental polluting or toxic gas molecules (CO, CO_2, NO, and NO_2) adsorbed on B and N atoms in bilayer graphene using first-principles electronic-structure calculations. We find that NO and NO_2 molecules can be bound chemically on B-doped bilayer graphene with large adsorption energies, while CO and CO_2 molecules are not adsorbed chemically on B-doped one. In the case of the N-doped graphene, all four gases do not bind with chemical bonds but adsorb rather physically with small adsorption energies at long distances between gases and graphene. The adsorptions of NO and NO_2 molecules on B-doped bilayer graphene induce the acceptor states above the Fermi energy, and we also find that the charge transfer takes place when the NO and the NO_2 molecules are adsorbed. Thereby, the B-doped bilayer graphene is expected to be useful for NO and NO_2 gas sensor materials.

1. Introduction

Graphene, an atomic layer consisting of two-dimensional hexagonal carbon arrangement, shows various unique mechanical and electronic properties [1–5]. Among them, one of the remarkable properties is that graphene possesses extremely high carrier mobility [3]. Thereby, graphene is expected to be a potential device material for next-generation nanoelectronics. Furthermore, graphene as well as carbon nanotubes (CNTs) is reported to be sensitive to adsorbates [6–8]. For example, graphene is shown to be sensitive to NO_2 molecule [6]. Carbon nanotubes are demonstrated to detect NH_3 and NO_2 gases with fast response time and high sensitivity at room temperature [7,8]. Thus, graphene and CNTs are also good candidates for promising sensor applications due to the high carrier mobility as well as the high sensitivity to adsorbates. In this regard, doped graphene and CNTs are also important candidate materials for sensor applications since substitutional doping with a heteroatom can often enhance the reactivity of nanomaterials. There are so far a large number of reports on boron (B) and nitrogen (N) doped monolayer graphenes and nanotubes since B, C, and N elements have similar structural properties [9–16]. The electronic properties of graphene and CNTs doped with B and/or N atoms can be modified, and therefore chemically doped carbon nanomaterials are applied to developments of sensor applications [17–23]. Although there are several theoretical reports regarding gas adsorption on impurity-doped monolayer graphene and carbon nanotubes, our knowledge as to gas adsorption into bilayer graphene is still limited at present [19,23–25].

In this paper, we report polluting or toxic gas adsorption effects on energetics and electronic properties of B-doped and N-doped bilayer graphenes using first-principles electronic-structure calculations in the framework of the density-functional theory. We study CO, CO_2, NO and NO_2 gases as gas molecules. We find that the four kinds of molecules are not chemically bound to the N-doped bilayer graphene. We also find that NO and NO_2 molecules are adsorbed with chemical bonds on the B-doped bilayer graphene, while CO and CO_2 molecules are not adsorbed chemically. From the result of the energy-band structures, the NO and NO_2 molecules induce the acceptor states above the Fermi energy. At the same time, the charge transfer takes place between NO or NO_2 molecule and B-doped graphene layer: In the case the adsorption of the NO molecule on the B-doped bilayer graphene, electrons move from NO molecule to the B-doped graphene layer, while in the case of the NO_2 molecule they move from the B-doped graphene layer to the NO_2 molecule. We also exhibit scanning tunneling microscopy (STM) images of B-doped bilayer graphene before

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and after the adsorptions of NO and NO_2 molecules, and the NO and NO_2 molecules are detectable by using STM methods.

2. Methodology

We perform first-principles total-energy calculations within the framework of the density-functional theory (DFT) [26]. The interactions between the ions and the valence electrons are described by the norm-conserving Troullier-Martins pseudopotentials [27], and exchange–correlation effects are treated using the local density approximation (LDA) parameterized by Perdew and Zunger [28,29]. It is reported that the LDA calculations give comparable results with generalized gradient approximation (GGA) calculations including van der Waals (VDW) interactions for relative energetics and interlayer distances of the *h*-BN bulks, graphite, and the graphene/*h*-BN hybrid structures [30].

In this work, the *AB*-stacked bilayer graphene is used. As for the B(N)-doping site, there can be two different sites: One is that one C atom on top of C atom is replaced with a dopant (Fig. 1(a)) and the other is that one C atom on top of the center of a hexagon is replaced with a dopant (Fig. 1(b)). Here, the latter case is used because it is energetically more favorable than the former case for both B and N dopings, as already discussed in our previous literature [25].

To calculate energetics and electronic structures of B(N)-doped bilayer graphenes, we use a 4×4 supercell along the directions parallel to the graphene sheet. Wavefunctions in the Kohn–Sham equations are expanded in terms of the plane-wave basis set with the cutoff energy of 50 Ry. The supercell lattice constant along the direction perpendicular to bilayer graphene is set to be 20 Å. The Brillouin-zone integration (BZ) is performed with $6 \times 6 \times 1$ *k*-points sampling. Upon the geometry optimization, atomic configurations are updated until Hellmann–Feynman forces acting on all atoms are less than 0.05 eV/Å. Computations have been performed using Tokyo Ab-initio Program Package (TAPP) [31].

To discuss the energetics regarding gas adsorption on B- and N-doped bilayer graphenes, the adsorption energy is defined by

$$E_a = E_{\mathrm{tot}} - E_{\mathrm{gra}} - E_{\mathrm{mol}}, \tag{1}$$

where E_{tot} and E_{gra} are the total energies of B(N)-doped bilayer graphene with and without the adsorption of gas molecules, respectively, and E_{mol} is also total energy of an isolated gas molecule.

In order to discuss the charge transfer between the graphene sheets and adsorbed molecules, we calculate the spatial distribution of the total charge density difference which is given by

$$\rho_{\mathrm{dif}}(r) = \rho_{\mathrm{tot}}(r) - \rho_{\mathrm{gra}}(r) - \rho_{\mathrm{mol}}(r), \tag{2}$$

where $\rho_{\mathrm{tot}}(r), \rho_{\mathrm{gra}}(r)$, and $\rho_{\mathrm{mol}}(r)$ are total charge densities of the molecule-adsorbed doped bilayer graphene, the doped bilayer graphene without adsorbates, and the isolated gas molecule calculated at the same atomic positions, respectively, and r is a three-dimensional coordinate. It is noted that the atomic configurations used to calculate $\rho_{\mathrm{gra}}(r)$ for the doped bilayer graphene without adsorbates and to calculate $\rho_{\mathrm{mol}}(r)$ for the isolated gas molecule are the same as corresponding parts of the atomic configurations of the molecule-adsorbed doped bilayer graphene, and therefore the total charge densities of $\rho_{\mathrm{gra}}(r)$ and $\rho_{\mathrm{mol}}(r)$ have been calculated independently.

The STM images are calculated based on the Tersoff–Hamann approximation [32–35]. In this approach, the tunneling current $I(r)$ is assumed to be proportional to the local density of states $\rho(r, \epsilon)$ (LDOS) of the surface at the tip position integrated over a range of an energy ϵ restricted by the applied bias voltage V, i.e.,

$$I(r) \sim \int_{E_F}^{E_F+eV} \rho(r, \epsilon) d\epsilon, \tag{3}$$

where E_F is the Fermi energy. The negative and positive voltages reflect the occupied and unoccupied electronic states, respectively.

3. Results and discussion

3.1. Energetics and structures

We study atomic structure of pristine *AB* stacking bilayer graphene. The optimized interlayer distance of *AB* stacking is 3.33 Å and the bond length between adjacent two C atoms in a planar sheet of bilayer graphene is 1.41 Å [25].

We next show atomic structures of B- and N-doped bilayer graphenes. In the B-doped bilayer graphene, the bond length between B and C atoms is found to be 1.47 Å, while the bond length between N and C atoms is 1.40 Å in the case of the N-doped bilayer graphene [25]. The B–C bond length is much longer compared with C–C bond length in a pristine bilayer graphene, and it possesses a similar value to that of the B-doped monolayer graphene [19]. On the other hand, the C–N bond length is slightly shorter than C–C bond length in a pristine graphene and is almost the same as the C–N bond length in N-doped monolayer graphene [36]. It should be noted that the B atom as well as N atom resides in a planar sheet of bilayer graphene.

We study the adsorption of gas molecules on B- and N-doped bilayer graphenes. Table 1 shows the adsorption energies (E_a) and the distances (d) between molecule and dopant atom for the adsorption of CO, CO_2, NO, and NO_2 molecules on B-doped and N-doped bilayer graphenes. For the N-doped cases, one finds that all four molecules are not chemically adsorbed and the adsorption energies are relatively small as well as the distances between molecule and dopant atom are very long (d >2.6 Å). These features are similar to those of N-doped monolayer graphene [19]. For the B-doped cases, CO and CO_2 molecules are not adsorbed with

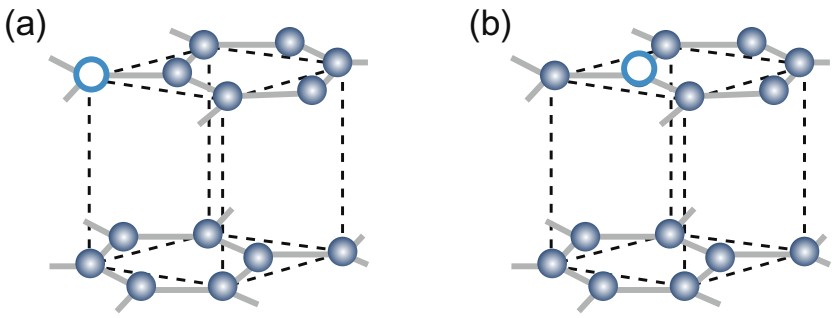

Fig. 1. Schematic view of boron and nitrogen-doped bilayer graphenes without adsorbates. One carbon atom at the upper layer is replaced by boron and nitrogen atoms. The open circles denote the substitution sites with boron and nitrogen atoms.