Structure and stability of hydrogen atom adsorbed on nitrogen-doped carbon nanotubes

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Abstract. The adsorption process of hydrogen atom on nitrogen-doped carbon nanotube (CNT) and its effects on the electronic properties are investigated using the first-principles density-functional methods. As possible hydrogen adsorption sites, three different positions are considered to discuss adsorption energies of the hydrogen atom on N-doped (10,0) CNTs. It is found that the favorable hydrogen adsorption site on N-doped (10,0) CNT is not on top of the nitrogen atom but on top of carbon atoms next to the nitrogen atom. Interestingly, it is found that the impurity state induced by doping with nitrogen atom is shifted from conduction-band minimum to valence-band maximum by the adsorption of the hydrogen atom.

1. Introduction
Carbon nanotube (CNT) has been widely investigated since it possesses unique structural and electronic properties such as quasi-one-dimensional form and high electron mobility [1, 2]. The chemical functionalization of CNTs by doping and adsorption of impurity atoms and molecules is of great importance for a realization of nanotube-based nanoelectronics devices. It is well-known that the doping is a practical way to modify electronic structures of CNTs [3]. Nitrogen is a good dopant for carbon-based materials, and nitrogen-doped CNTs have been synthesized experimentally and studied theoretically [4, 5].

The adsorption of hydrogen atoms and molecules on pristine CNTs has been also studied for developments of future nanoelectronics applications such as hydrogen storages and gas sensors [6, 7]. The N-doped CNT adsorbed by the hydrogen atom is expected to exhibit the novel electronic property since impurity defect often serves as a reactive site and the adsorption of the impurity on nanotubes might lead to dramatic changes in their electronic properties [8]. However, the knowledge of hydrogen adsorption effects on N-doped CNT is still limited so far. In order to tailor the desired electronic properties of N-doped CNTs, it is of high importance to understand interactions of hydrogen atom with N-doped CNT and the differences between the electronic structure of N-doped CNTs and that with the adsorbed H atom.

In this work, we report adsorption effects of hydrogen atom upon nitrogen-doped (10,0) CNT using the first-principles total-energy calculations in the framework of the density-functional theory. The adsorption energies of hydrogen atom at several different sites in N-doped CNT are calculated, and it is found that the adsorption of H atom on C atoms next to N atom is energetically favored rather than that on the N atom. The effects of hydrogen-atom adsorption on electronic structures of N-doped CNT are also discussed.
Figure 1. Optimized atomic structures of N-doped (10,0) carbon nanotubes: (a) top view with three possible hydrogen adsorption sites labeled as A, B, and C, and (b) its side view, and (c) N-doped (10,0) nanotube with hydrogen atom adsorbed on the C site. θ₁ and θ₂ denote bond angles around carbon atom labeled as C.

2. Computational Methods

The model system considered here consists of two unit cells for a zigzag (10,0) CNT, and therefore the N-doped (10,0) CNT contains 79 C atoms and one N atom. In Fig. 1(a), the atomic structure of N-doped (10,0) CNT is illustrated, together with three different hydrogen adsorption sites labeled as A, B, and C. Figures 1(b) and (c) show side views of the optimized geometries of N-doped (10,0) CNT without and with H atom, respectively.

Our calculations are carried out using the first-principles total-energy methods within the density-functional theory [9]. The interactions between the ions and the valence electrons are described by the norm-conserving Troullier-Martins pseudopotentials [10], and exchange-correlation effects are treated using the local density approximation (LDA) parameterized by Perdew and Zunger [11, 12]. The wave functions are expanded in a plane-wave basis and the kinetic-energy cutoff is taken to be 50 Ry [13]. The atomic positions are optimized until the Hellmann-Feynman force on each atom becomes less than 0.05 eV/Å. One-dimensional Brillouin-zone integration is performed with four k-point sampling.

3. Results and Discussion

3.1. Energetics and geometry

To discuss the stability of hydrogen atom adsorbed on the N-doped (10,0) CNT, we calculate the adsorption energies $E_{\text{ad}}$ defined as

$$E_{\text{ad}} = E_{\text{tot}} - E_{\text{N-CNT}} - E_{\text{H}},$$

where $E_{\text{tot}}$ and $E_{\text{N-CNT}}$ are total energies of N-doped (10,0) CNT with and without hydrogen atom, respectively, and $E_{\text{H}}$ is the total energy per atom of the H₂ molecule.

In Table 1, we list the adsorption energy of hydrogen atom at three sites in N-doped CNT. The adsorption of H atom on the N atom (site A) is energetically unfavorable since the positive adsorption energy corresponds to endothermic adsorption ($E_{\text{ad}} > 0$), whereas each H atom adsorbed on two different C atoms next to the N atom (sites B and C) is expected to be both stable due to their exothermic behavior ($E_{\text{ad}} < 0$). The adsorption energy at site C is somewhat lower than that at site B, which should be the curvature effect of N-doped CNT. We thus find that the adsorption of H atom upon N-doped CNT is energetically favored when H atom is adsorbed on the C atom rather than on the N atom.

We next study the atomic geometries of N-doped (10,0) CNT without and with H atoms, as shown in Figs. 1(b) and (c), respectively. The bond angles θ₁ and θ₂ of N-doped CNT without H atom are 114.2° and 119.2°, respectively, and the N atom resides in the $sp^2$-bonding configuration.
Table 1. Calculated adsorption energies ($E_{ad}$) for N-doped (10,0) CNT with hydrogen atom at three different sites. Three sites A, B, and C are shown in Fig. 1.

| Position | A    | B    | C    |
|----------|------|------|------|
| Adsorption energy $E_{ad}$ (eV) | 0.96 | -0.28 | -0.29 |

[Fig. 1(b)]. After H atom is adsorbed on N-doped CNT, the C–H bond with the length of 1.11 Å is formed, and the bond angles $\theta_1$ and $\theta_2$ change into 106.4° and 112.3°, respectively. It can be seen that the C atom bonded with H atom protrudes from the original surface of the nanotube and the C–H pair forms a covalent bond [see Fig. 1(c)]. By the adsorption of H atom, the configuration of the C atom in N-doped CNT transforms from $sp^2$ into $sp^3$-hybridized configurations.

3.2. Electronic structure

We have studied the effect of hydrogen-atom adsorption on the electronic structures of N-doped (10,0) CNT. Figures 2 (a), (b), and (c) show the calculated energy-band structures of pristine (10,0) CNT, N-doped (10,0) CNT, and N-doped (10,0) CNT with H atom, respectively. The pristine (10,0) CNT exhibits semiconducting properties with a band gap of $\sim$ 0.72 eV, as shown in Fig. 2(a) [5]. When carbon atom in pristine (10,0) CNT is substituted by nitrogen atom, the impurity state associated with the N atom appears below conduction-band minimum and would act as a donor state [Fig. 2(b)]. This is because N atom possesses extra one electron compared with C atom. When H atom is adsorbed on the C site in N-doped (10,0) CNT, the originally partially-filled impurity state is completely filled with electrons and the donor state induced by nitrogen doping disappears [Fig. 2(c)]. Thus, the adsorption of H atom causes dramatic changes in the electronic structure of N-doped CNT.

4. Summary

The adsorption effects of hydrogen atom on geometry, energetics, and electronic structure of nitrogen-doped (10,0) carbon nanotube have been investigated using the first-principles density-functional study. Adsorption energies of hydrogen atom at three different adsorption sites are

![Figure 2. Energy bands of (a) pristine (10,0) CNT, (b) N-doped (10,0) CNT, and (c) N-doped (10,0) CNT with hydrogen atom. The H atom is adsorbed at C site of N-doped (10,0) CNT in Fig. 1(a). The pristine (10,0) CNT considered here consists of 40 carbon atoms. The Fermi level is set to be zero.](image_url)
calculated and the adsorption energy is found to be much lower when H atom is adsorbed on
top of C atoms next to the N atom than when it is on top of the N atom. The energy bands of
N-doped (10,0) CNT and that with H atom are also obtained. By adsorption of H atom upon
N-doped CNT, the originally half-filled impurity level is to be filled with the electrons, leading
to the Fermi-level shift into valence-band maximum.

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