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Can CO_2 molecule adsorb effectively on Al-doped boron nitride single walled nanotube?

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ABSTRACT

The adsorption of carbon dioxides (CO_2) is very important in environmental and industrial applications. The boron nitride nanotube (BNNT) with large surface and polarity may be a good candidate as CO_2 capture. Unfortunately, the pristine BNNT is almost inert to the highly stable CO_2. To renew technical applications of BNNT for CO_2 adsorption, we explore the possibility of CO_2 adsorption on various (n, 0) (n = 6, 8, 10, 12 and 14) Al-doped BNNT by density functional theory (DFT) calculations. The results show that the Al-doped BNNT could be a potential CO_2 adsorption material, and the CO_2 adsorption energies are independent of BNNT diameters. Furthermore, the interactions between CO_2 and exemplified (6, 0) Al-doped BNNT are investigated by density of states (DOS) and electron density. We found the interaction between CO_2 and Al_B-BNNT is stronger than that of CO_2 and Al_N-BNNT. The adsorption of CO_2 can induce new density of state, as well as a local charge fluctuation due to more electron density redistribution on the atoms near CO_2 molecule.

1. Introduction

Carbon dioxide (CO_2) is the focus of much research activity. On one hand, carbon-based fossil fuels increase carbon dioxide in the atmosphere. The increased CO_2 level is believed to enhance the greenhouse effect. There is a pressing need to reduce releases. While on the other hand, because CO_2 is the most easily available renewable, non-toxic, non-flammable and highly functional carbon resource [1]. Thus, the absorption and activation of CO_2 at a large scale is the most pressing issue to the manufacture of useful chemicals [2]. However, due to the carbon dioxide has highly stable nature, how to absorb and activate carbon dioxide effectively is one of the most immanent problems awaiting solutions.

It has been proposed that CO_2 reduction materials should possess some special properties such as large surface area, good thermal and chemical stability, good electrical conductivity as well as strong adsorption sites. Thus, the materials of nanostructured form incorporated above properties have been a main focus in carbon dioxide adsorption research. For example some CO_2 adsorbents [3–5] have been proposed previously including carbon nanotubes (CNT), silicon carbide nanotubes (SiCNT) and aluminum nitride (AlN) nanotubes, but their adsorbent interactions are too weak to suitable for ambient gas capture. Some researchers have proposed that the boron nitride nanotube (BNNT), which has large surface and polarity, may be a good candidate as CO_2 capture. However, the pristine BNNT with large band gap [6,7] is almost inert to the highly stable CO_2. Do it means that we have reached a dead end in utilizing BN nanotubes as CO_2 capture media? The answer is definitely no. Even though nanotubes themselves may not be able to adsorb CO_2 effectively, they may be served as supporting system for CO_2-absorbing metal. So in order to capture carbon dioxide, we expected to increase the BNNT chemical activity via modifying its nanostructures.

It is well known that the chemically active impurities can modify the structure of some interesting materials [8,9]. Early studies have demonstrated that the influence of atomic doping on the electronic and structural properties of BNNT is significant [10–12]. Especially, the boron nitride nanotubes with boron-rich [13] and boron vacancy [14] have been confirmed to adsorb CO_2 effectively. Al-doped and Ga-doped BN nanotubes [15] can detect CO molecule. Xie et al. have studied CO and NO adsorption on transition metals doped (8, 0) boron nitride nanotube. [16] The implication of these studies is that an improved BN material might potentially adsorb certain gas molecule. In this case, we are interested in investigating whether the Al-doped BNNT can be used as a promising CO_2 absorption material. As we know, the pauling electronegativity of the aluminum atom (1.61) is much smaller than that of boron (2.04) and nitrogen (3.04) [17]. In principle, no matter where we doped the aluminum atom, this will lead to a significant charge transfer from Al to B and N, respectively. Therefore, we guess that this doped structure could become a potential CO_2 selective binding material. To our best of knowledge, no prior theoretical

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investigations have been reported on this issue. However, this subject is an important issue for renewing technical applications for CO_2 adsorption of BNNT. Motivated by the absence of theoretical efforts, we first present an attempt of density functional theory (DFT) study for the adsorption of carbon dioxide gas molecule on various zigzag aluminum doped boron nitride nanotubes in the present work. Furthermore, in order to investigate the effect of nanotubes diameter on gas adsorption properties, a series of zigzag (n, 0) type single walled BN nanotubes with impurity are considered.

2. Computational methods

The density functional theory calculations of CO_2 gas adsorption on aluminum doped boron nitride nanotubes were performed using Dmol^3 program (Accelyrs Inc.) [18,19] to derive their equilibrium geometries, total energies, density of states and charge analysis. Electronic exchange correlation was treated using generalized gradient approximation (GGA) [20,21] with Perdew and Wang (PW91) functional [22]. The (6, 0) zigzag BN nanotube as a representative example was investigated using both functionals GGA with PW91 and local density approximation (LDA) [23] with the PWC [24]. The convergence criterion for energy change between optimization cycles, maximum force and displacement are set to 10^{-6} Ha, 0.002 Ha A^{-1}, and 0.005 Å, respectively. The self-consistent field computations criterion was chosen to be 10^{-5} Ha. The electronic wave functions were expanded in a double numerical basis set including d-polarization function (DND) [18,19] truncated at a real space cut-off of 4.8 Å. A $25 \times 25 \times 12.8$ Å^3 supercell that of the periodicity of doped BN nanotubes was set for all calculations. The minimum distance between the opposing sidewall of neighboring nanotubes is longer than 19.6 Å, which is sufficiently large to render interaction between the NT and its periodic images is negligible. For geometry optimization, the Brillouin zone is sampled by Γ point only, which yields $0.077 \times 0.077 \times 0.016$ Å^{-1} actual spacing. As for electronic structure calculations, the Brillouin zone for all doped BN nanotubes supercell models is sampled by $1 \times 1 \times 5$ special k-points using the Monkhorst–Pack scheme [25] in which a uniform grid of k points along the three axes in reciprocal space is produced. A 5×10^{-3} Ha smearing [26] and 6 pulay direct inversion of the iterative subspace (DIIS) [27] was applied to system to facilitate convergence of the electronic structures. In the present work, we have considered two type doped models of (n, 0) zigzag single walled BNNTs. These two models were noted using Al_B-BNNT (a B atom on the sidewall substituted by Al atom) and Al_N-BNNT (a N atom substituted by Al atom), respectively. For gas molecule absorption, two type different possible adsorption sites, outside and inside of nanotube are examined. No symmetric constraints are considered when carrying out calculations.

The adsorption energy of CO_2 molecule on Al–doped BNNT is defined as $E_{ad} = E_{sub+CO_2} - E_{sub} - E_{CO_2}$, where E_{sub+CO_2} is the total energy of the substrate (Al-doped boron nitride nanotube) after adsorbing CO_2, E_{sub} is the energy of pure substrate, and E_{CO_2} is the total energy of isolated CO_2 molecule. By definition, negative E_{ad} corresponds to favorable or exothermic adsorption of CO_2 on Al-doped BNNT.

3. Results and discussion

3.1. Aluminum atom doped boron nitride nanotubes (BNNTs)

For the convenience of presentation, we will not describe all the optimized structures of various sized Al-doped BNNTs. Instead, taking the (6, 0) BNNT as an example, we study the geometric structures of two forms BNNTs (Al_B-BNNT and Al_N-BNNT) in which a B or N atom is substituted by aluminum, respectively. The optimized results are displayed in Fig. 1a. As can be seen, the collective structural change is that the doped aluminum atom moves away from the pristine lattice site, leading to the local distortion of the tube. It is well known that pure boron nitride nanotube has two types B—N bonds: one is in parallel with the tube axis, and another is oblique to the tube axis. When a B atom of BNNT is substituted by Al atom (see Fig. 1a), the B—N bond in intrinsic boron nitride nanotube, which is in parallel with the tube axis, increases about 1.44 Å up to 1.68 Å. However, when an N atom is substituted by Al atom, the B—N bond

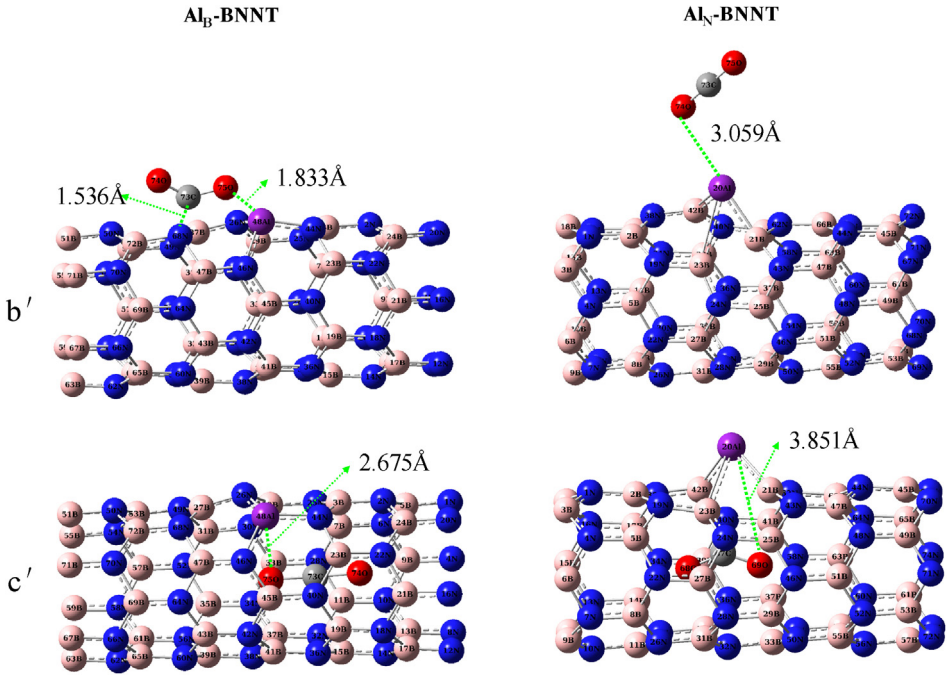

Fig. 1. Optimized geometry of both (6, 0) Al-doped BNNTs at GGA level (a) the Al-doped BNNTs without CO_2 molecule (b) the adsorption of CO_2 molecule in the outside of the tube (c) the adsorption of CO_2 in the inside of tube. The first column corresponds to Al_B-BNNT, while the second corresponds to Al_N-BNNT.