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Ab initio investigation of pristine and doped single-walled boron nitride nanotubes as acetone sensor

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ABSTRACT

The sensor properties of single-walled boron nitride nanotubes (BNNTs) towards acetone are studied by investigating the intermolecular interactions of acetone with a serials of pristine and doped BNNTs. Density-functional theory (DFT) with empirical dispersion corrected is adopted to explore the adsorption properties of acetone on the surface of BNNT. Results show that acetone binds strong to the surface of pristine BNNTs with small diameter and the adsorption energy decreases significantly as the tube diameter increases. The adsorption of acetone on serials of doped BNNTs (Al, Si, Cu, Co, Ni, Ga, and Ge) shows that the adsorption of acetone on BNNT can be strengthened by the doped impurity. With the analysis of charge density, density of states, molecular orbitals, and the noncovalent interaction index (NCI), the study shows that the sensitivity of BNNT-based chemical gas sensor towards acetone can be remarkable improved by introducing appropriate dopant. The study also reveals the potential application of BNNT as sensor for the detection of acetone molecule.

1. Introduction

Carbon nanotubes (CNTs) which were first discovered in 1991 by Iijima [1] are explored by researchers extensively in a wide range of applications [2–8]. BNNTs which possess a similar structure with CNTs have been the focus of research area in recent years [9–19]. Due to the outstanding mechanical properties, high thermal conductivity, and superior chemical stability [20], BNNTs have become promising potentials in applications of nano-electronic devices and nanomedicine [21–23]. The properties of BNNTs can be tuned by functional groups wrap around with covalent or non-covalent interactions to produce special functions of BNNTs [24,25]. BNNTs are promising candidates in diverse therapeutic and nanomedicine application fields due to the noncytotoxic and biocompatible characteristics of these materials [6,11,26–34]. Compared with CNTs, BNNTs are more attractive since they are less toxic and their electronic properties are independent on the diameter and chirality of the tube. Semiconducting BNNTs are high sensitive due to their great surface to volume ratios and the high chemical stability especially under oxidative, hazardous, and high-temperature environments. The BNNTs are polar and are expected to be more superior to CNTs due to the electrophilic boron and nucleophilic nitrogen atoms [13,35–37]. Gas sensors based on BNNTs have attracted lots of attention due to their excellent sensing capabilities [35–39].

The acetone is a polar organic solvent and a major chemical commodity which is reported to be the main non-methane organic pollutant in atmosphere. In the human body acetone is produced and disposed of through normal metabolic processes [40,41]. It is usually present in the human blood and urine. Diabetes patients produce a larger amount of acetone which can be an indicator of the disease [40,41]. In recent years, there has been increasing interest in research and development activities related to acetone detection [42–47]. Temperature-programmed desorption experiments show that acetone is chemisorbed on nanotubes [42,43]. Theoretical studies on the adsorption of acetone on single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) show large desorption energies [44]. Results also reveal that defects of the tube have large effect on the binding of acetone to CNTs [47]. Since the discovery of BNNTs, a large amount of theoretical and experimental studies are performed to explore the capability of BNNT as sensors [13,35–39,48]. BNNTs doped with atoms especially metals are found to improve the conductivity and chemical reactivity of the tube [12,49–51]. Researches by Baierle et al. found that carbon doped BNNTs showed improved sensor properties compared with non-defective BNNTs [52]. Wu et al. found that the adsorption property of BNNT towards hydrogen can be enhanced by doped platinum atoms [53]. Studies by Wang et al. revealed that the adsorption reactivity of BNNTs

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towards HCOH can be improved by Si doping [54]. The adsorption of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) on the pristine and Ni-doped BNNTs showed that the Ni-doped BNNTs presented much higher reactivity toward TCDD than the pristine BNNTs [55]. All of the above studies reveal that BNNTs especially doped BNNTs can be developed as gas sensors with high sensitivity, shorter response time and low cost. The unique sensor properties of BNNTs inspire us to investigate the sensor properties of BNNTs towards acetone.

In this work, we presented a systematical study at the DFT level to investigate the interactions of acetone with the pristine and doped single-walled BNNTs. The aim of the study is to explore the promising materials for detecting the acetone molecule. This study also hopes to provide useful information to reveal the chemical and biological activities of BNNTs when they are adsorbed by acetone. The paper is organized in the following parts: in the computational method section we describe briefly the methods and scheme we used in the study. In the results and discussion section, the stability and interaction of the acetone with pristine and doped BNNTs are analyzed by optimized geometry structures and binding energies. With the analysis of charge density, density of states, molecular orbitals, and the noncovalent interaction index (NCI), the potential sensor application of BNNT in detecting of the acetone molecules is revealed. Conclusions are made in last section.

2. Computational method

For studying the properties of nano system with large size, the dispersion incorporated self-consistent density functional tight-binding (SCC-DFTB-D) method is attracting attentions from researchers more than ever since it can give reasonable accuracy results at a remarkably reduced computational cost [56–59]. The SCC-DFTB method is extended to the time-dependent density functional tight-binding case (SCC-DFTB-TD) to treat the excited state [60,61]. The SCC-DFTB and the time-dependent case SCC-DFTB-TD method are used widely to study the properties of nano-sized systems, including both the ground states and excited states [61,62]. In this study, the geometry structures are firstly optimized by SCC-DFTB-D method and then refined by the DFT method. DFT calculations are performed by the orca program [63] with the Perdew-Burke-Ernzerhof (PBE) functional [64] incorporated by dispersive interactions developed by Grimme [65]. It is revealed by previous studies that the dispersion corrected DFT with PBE functional can well describe the weak interaction to study systems with noncovalent interactions [66,67]. The SCC-DFTB calculations are performed by the DFTB+ 1.3.1 program [68]. The matsci-0-3 parameter set was used for the O–N–C–B–H system which provides the two center Hamiltonian matrix elements and two-body repulsive interactions [69]. The adsorption energy of the adsorbate molecules with the BNNTs is calculated according to the formula:

$$\Delta E_{ads} = E_{mol+BNNT} - (E_{mol} + E_{BNNT}) + E_{BSSE} \quad (1)$$

where $E_{mol+BNNT}$ is the optimized energy of the molecule (acetone) adsorbed over the BNNT system, E_{BNNT} and E_{mol} are the optimized energies of the BNNT and the molecule, and the E_{BSSE} is the basis set superposition error correction to eliminate the effect for basis set incompleteness by adopting the counterpoise correction method [70].

The zigzag BNNT clusters (type (5, 0), (8, 0) (9, 0) (10, 0)) with diameter range from 3.9 Å to 8.0 Å were used in this study. The BNNTs were saturated by hydrogen atoms at both ends to account for periodic boundary effect. To find the possible absorption sites of the BNNTs with lowest energy, the acetone is placed on top of the BNNT surface with the closest distance of about 3.4 Å, which is a typical distance of dispersion interaction. A serials of initial positions with different orientation on the BNNT surface are tried. There are mainly two different types of initial positions for the interacting system. The first type is with the methyl group interacting with the BNNT surface. The second type is with the active carbonyl (C═O) site interacting with the BNNT surface. The angles between main backbone of the acetone molecule and BNNT are rotated from 0° to 180°. The acetone molecule is initially placed on top of the hollow site at the center of the hexagon ring, above the B—N bond bridge, and on top of the nitrogen atom or boron atom. The initial trial structures ensure that all parts of acetone can well interact with the BNNT surface. For studying the doping effect on the sensor properties of the BNNT towards acetone, the nitrogen atom or boron atom are replaced by Al, Co, Cu, Ga, Ge, or Ni atom. We have optimized all sensible conformers of the structures, and the adsorption properties of the most stable complex were present below.

3. Results and discussion

For studying the sensor properties of the pristine BNNTs, the acetone was firstly placed on different initial positions of the BNNT surface, with the methyl group or the carbonyl (C═O) active site interacting with the BNNT surface. It is placed on top of the hollow site at the center of the hexagon ring, above the B—N bond bridge, and on top of the nitrogen atom or boron atom. Four types of BNNTs, zigzag (5, 0) types with diameter of 3.91 Å, (8, 0) with diameter 6.26 Å, (9, 0) with diameter 7.05 Å, and (10, 0) with diameter 7.83 Å, are selected to study effect of tube size on the sensor properties of BNNTs. Optimized acetone molecules and BNNTs are used to investigate the adsorption between the two complexes. Results of the lowest energy structures are shown in Fig. 1. In the figures it is shown that the most favorable adsorption site of acetone on BNNTs is the top site directly on top of the boron atom with the oxygen atom of the carbonyl (C═O) interacting with the born atom of the BNNTs. The corresponding detailed information of adsorption energy, the closest contact between the acetone and tube, C—O bond length of the acetone molecule, and the Mulliken charge transferred from BNNT to acetone molecule are presented in Table 1. For the (5, 0) tube, a closest contact between acetone and BNNTs is the O—B bond with the bond length of 1.68 Å, which is in the range of a typical chemical adsorption distance. The acetone binds strongly with the BNNTs by strong O—B chemical interaction and the acetone molecule is tilted to allow the methyl group to interact with BNNT surface. Two hydrogen atoms of the methyl group interact with the nitrogen atom on the tube with closest contacts of 2.37 Å and 2.67 Å respectively. This bond distance show that the interaction between the methyl group and BNNT surface is a weak interaction. With the three interactions the acetone molecule binds strongly to the BNNT surface. The adsorption energy calculated by Eq. (1) is 77.2 kcal/mol. The C—O bond length of acetone when adsorbed on the tube is 1.25 Å. The bond length is lengthened compared with the C—O bond length of the isolated acetone molecule (1.22 Å). The closest contact of 1.68 Å between the two complexes and the lengthening of the C—O bond both indicate that a strong interaction exists between the two complexes. The adsorption energy of about 77.2 kcal/mol shows that the adsorption is in the strong chemisorption range.

We have also analyzed the size effect on the adsorption properties of BNNTs towards acetone. The most stable adsorption structure of acetone on the Zigzag type BNNTs (8, 0) with diameter 6.26 Å is shown in Fig. 1b. For the (8, 0) tube which has a larger diameter, the most favorable structure is similar to case of the (5, 0) tube. The closest interaction distance is also between the oxygen of carbonyl (C═O) and the boron atom on the tube, but