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Adsorption of NO$_2$, HCN, HCHO and CO on pristine and amine functionalized boron nitride nanotubes by self-consistent charge density functional tight-binding method

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Abstract

The adsorptions of toxic gases including NO$_2$, HCN, HCHO and CO molecules on the pristine and amine functionalized (5,0) single-wall boron nitride nanotubes (BNNTs) are investigated based on self-consistent charge density functional tight-binding (SCC-DFTB) method. The calculated results indicate that the pristine (5,0) BNNT exhibits weak adsorption for the gas molecules. Based on the calculated adsorption energy, interaction distances and charge transfer, amine functionalization at a boron atom of the pristine (5,0) BNNT enhances the sensitivity of the pristine (5,0) BNNT toward the gas molecules. The electronic densities of state results reveal that new local states in the vicinity of Fermi level for adsorption between amine functionalized BNNT and the gas molecules significantly appear. This confirms the improved sensitivity of the pristine (5,0) BNNT functionalized with amine for adsorption of the toxic gases. This study is expected to provide a useful guidance on gas sensing application of pristine and amine functionalized BNNTs for detection of the toxic gases at room temperature.

1. Introduction

Since boron nitride nanotubes (BNNTs) were first theoretically investigated in 1994 [1], they have attracted great attention both theoretical and experimental studies for different applications including gas sensors [2–6], drug delivery [7–9], gas storage [10–18] etc. The structures of BNNTs are similar to carbon nanotubes (CNTs) [2, 3] that exhibit remarkably electronic and mechanical properties, chemical stability [19, 20] and high thermal conductivity [21, 22]. The electronic properties of BNNTs are independent on their diameters and chirality [1, 2, 22]. Because of their uniquely electronic properties, BNNTs based gas sensors have been intensively theoretically studied for normal/toxic gas detection such as carbon monoxide (CO) [5, 23, 24], nitrogen dioxide (NO$_2$) [25, 26], hydrogen cyanide (HCN) [3, 4, 27], hydrogen gas (H$_2$) [28], oxygen (O$_2$) [29], and formaldehyde (HCHO) [2, 30]. Sensitivity and chemical reactivity of BNNTs to toxic gas molecules can be improved by doping metal atoms. For examples, Wang et al [2] studied the adsorption of formaldehyde molecule by pristine and silicon doped single-walled (8,0) BNNTs by performing density functional theory (DFT). The results showed that the silicon doped (8,0) BNNTs, regardless of boron or nitrogen atom doping of the BNNTs, exhibited higher sensitivity to formaldehyde than the pristine (8,0) BNNTs. Fan et al [19] reported that the adsorption of acetone on BNNTs was enhanced by doping transition metals (Al, Si, Cu, Co, Ni, Ga and Ge) on the BNNT surfaces. Zeng et al [4] investigated the performance of Al, Ni and Cu doped (8,0) BNNTs for adsorption of hydrogen cyanide using DFT. It was found that doping with these metals on the BNNTs can increase the adsorption of hydrogen cyanide. Xie Fan et al [5] studied adsorption of CO and NO gases on transition metals (V, Cr, Mn, Fe, Co, Ni) doped (8,0) boron nitride nanotube via PBE formulation. The transition metals could be used to tune magnetic moment and electronic structure of BNNT. Moreover, BNNTs with small diameters showed stronger interaction and higher sensitivity to toxic gases than those of BNNTs with bigger diameters.
Also, previous theoretical studies showed that the interaction between gas molecules and BNNTs doped with metals at boron atoms was stronger than N atom of the nanotubes [3, 32].

Covalent/noncovalent functionalization on BNNT surfaces can improve the electronic properties of BNNTs for gas sensor applications [22, 33–35]. The previous studies reported that the band structures of BNNTs may be changed by chemical functionalization [36, 37]. To the best of our knowledge, the reports about BNNTs functionalized with amine groups (NH₂) for adsorption of toxic gases are less available. Based on these motivations, we thus present the study of sensor performances of pristine (5,0) single-walled BNNT (pristine BNNT and amine functionalized (5,0) single-walled BNNT (NH₂-(5,0) BNNT) for adsorption of important dangerous NO₂, HCN, HCHO and CO gases using self-consistent charge density functional tight-binding (SCC-DFTB) method including van der Waals dispersion corrections. These gas molecules are chosen because they are the most common air pollutants that usually cause harm to human health and ecosystem. The air pollutions are generated from car engines, factories, power plants, human activity and natural processes [38, 39], i.e., typical internal car combustion engine produces high concentrations of CO when fuels burn incompletely. Internal combustion engines and the use of gas stoves for cooking also produce NO₂. The HCN is released from combustion of organic matter, building fires, cigarettes or car exhaust fumes while HCHO is found from furniture, cosmetics, cleaning products, glues, paints as well as contaminants in seafood [40]. Therefore, new sensing materials for detection of these air pollutions are still important. The results of this study are attributed to provide useful information and guidance for gas sensor designs in future experiments.

2. Calculation method

The SCC-DFTB method is based on a second-order expansion of the DFT total energy expression in term of charge density variation with respect to a reference density [41–45]. The total energy of SCC-DFTB based on the Kohn–Sham orbitals is given by following equation [44]:

\[
E_{\text{SCC–DFTB}} = \sum_i (\phi_i | H_0 | \phi_i) + \frac{1}{2} \sum_{\alpha, \beta} \gamma_{\alpha \beta} \Delta q_{\alpha} \Delta q_{\beta} + E_{\text{rep}}
\]

(1)

where \( \phi_i \) are the Kohn–Sham orbitals, \( H_0 \) is unperturbed Hamiltonian, \( \Delta q_{\alpha} \) and \( \Delta q_{\beta} \) indicate the induced charges of atoms A and B relative to the number of valence electrons, \( \gamma_{\alpha \beta} \) is the second derivative with respect to its total charges and \( E_{\text{rep}} \) denotes two-body repulsive potential.

It should be noted that the benchmark of the SCC-DFTB calculation was systematically investigated with first principles DFT methods such as local-spin density approximation (LSDA), PBE, and hybrid exchange B3LYP DFT flavors [46]. The SCC-DFTB provided the molecular structures, energies and electronic properties in excellent agreement with DFT methods but was ∼100–1000 times faster. The SCC-DFTB can also include reliable description of dispersions and weak interactions (Van der Waals and H-bonding) that are important roles for investigation of gas adsorption on a sensing material which is consistent with experimental observations [40, 45, 47, 48]. Moreover, the SCC-DFTB was proved to be effective in the simulation studies of boron nitride nanostructures systems [49–51].

In this study, structural optimizations and electronic properties of pristine and NH₂-(5,0) BNNTs with and without adsorption of NO₂, HCN, HCHO and CO gas molecules were investigated by using SCC-DFTB method. For amine functionalization on the surface of pristine (5,0) BNNT, the nitrogen atom of amine molecule was bonded with a boron atom of the pristine (5,0) BNNT. The pristine and NH₂-(5,0) BNNTs with length of 21.30 Å and diameter of 3.91 Å include 110 and 113 atoms, respectively. The BNNTs were saturated with hydrogen atoms at both ends to reduce boundary effects [19, 40, 52]. The matsci-0-3 parameter set for O-N-C-B-H system was employed for calculations. The parameter set supplies two center Hamiltonian matrix elements and two-body repulsive interactions [53]. It should be noted that the matsci-0-3 parameter set is well to describe BN interactions with small organic molecules containing oxygen, nitrogen, carbon and hydrogen [54–56]. The adsorption energy \( E_{\text{ad}} \) of pristine and NH₂-(5,0) BNNTs with gas molecules is calculated according to the equation:

\[
E_{\text{ad}} = E_{\text{tot}}(\text{BNNTs} + \text{gas molecules}) - E_{\text{tot}}(\text{BNNTs}) - E_{\text{tot}}(\text{gas molecules})
\]

(2)

where \( E_{\text{tot}}(\text{BNNTs} + \text{gas molecules}) \) is total energy of pristine or NH₂-(5,0) BNNTs with gas molecules, \( E_{\text{tot}}(\text{BNNTs}) \) and \( E_{\text{tot}}(\text{gas molecules}) \) are total energies of pristine or NH₂-(5,0) BNNTs and gas molecules, respectively.

To find the most favorable adsorption sites of pristine and NH₂-(5,0) BNNTs, gas molecules were placed at different distances and orientation configurations (vertical and parallel positions) above the BNNT surfaces. All atoms of each gas molecule were pointed out into the boron (B) or nitrogen (N) atoms of the BNNTs. The adsorption of gas molecules on pristine and NH₂-(5,0) BNNTs surfaces can be classified into physisorption/chemisorption via the calculated adsorption energy. It should be noted that physisorption is characterized by
weak physical interaction (~10–100 meV) such as Van der Waals forces and hydrogen bonding while chemisorption involves a chemical reaction between the surface and the adsorbate with much stronger bonding bonds such as covalent bonding, strong electrostatic, and ionic bonding (>200 meV) [57–60]. For study of electronic charge transfer, the net charge transfer (Q) is defined as the charge difference between gas molecules adsorbed on the BNNT surfaces and isolated gas molecules [2, 61] and can be obtained by equation (3):

\[ Q = Q(\text{BNNTs + gas molecules}) - Q(\text{gas molecules}) \]  

where \( Q(\text{BNNTs + gas molecules}) \) and \( Q(\text{gas molecules}) \) represent the charges of gas molecules adsorbed on the BNNT surfaces and isolated gas molecules, respectively.

The energy gap \( (E_g) \) of the BNNTs is calculated using \( E_g = |E_{\text{LUMO}} - E_{\text{HOMO}}| \), where \( E_{\text{LUMO}} \) and \( E_{\text{HOMO}} \) are the energy levels of the lowest unoccupied molecular orbital and the highest occupied molecular orbital, respectively.

3. Results and discussion

3.1. Structural and electronic properties of pristine and amine BNNTs

The pristine (5,0) BNNT was optimized to obtain the most stable structure as presented in figure 1(a). For the pristine (5,0) BNNT, bond lengths of a boron atom with its three neighboring nitrogen atoms; B-N1, B-N2 and B-N3 as shown in the inset of figure 1, were measured to be 1.536 Å, 1.537 Å and 1.537 Å, respectively. After amine functionalization at the boron atom, it was found that the local structure deformation at the boron atom functionalized with NH2 molecule occurred. The boron atom of BNNT was slightly pulled out of the BNNT surface and its bond lengths with three surrounding nitrogen atoms were changed. The B-N2 and B-N3 were slightly elongated and found to be 1.578 Å. The B-N1 was slightly shrunk with bond length of 1.487 Å. The bond lengths obtained in this study are in agreement with a previous study based on \textit{ab initio} DFT calculations [33].

The result suggests that the covalent bond between the boron atom of BNNT and nitrogen atom of NH2 molecule (bond length of 1.591 Å) is strong. This structural deformation is mainly due to the change in the local hybridization of the boron atom from sp2 to sp3 orbitals [22, 33, 62]. However, the overall structure of the nanotube after functionalization seems to be almost unchanged.

To study electronic properties, \( E_g \), Fermi energy \( (E_F) \), and electronic densities of state (DOSs) before and after functionalization were calculated as shown in table 1 and figure 1(b). After functionalization, a change in band structure was found. The energy gap increased from 1.37 eV to 1.65 eV. The increased energy gap indicates that \( \pi - \pi^* \) band crossing of the pristine (5,0) BNNT is disturbed by NH2 sidewall functionalization [34, 35]. The band gap slightly opens up between the conduction and valence bands. This effect is attributed to the breaking of the nanotube mirror symmetry due to the strong interaction between the BNNTs and NH2 molecule [20, 34, 35]. Figure 1(b) shows DOS of pristine and NH2-(5,0) BNNTs. By comparison with the DOS of the nanotubes before and after amine functionalization, it can be obviously seen that the increased DOS of NH2-(5,0) BNNT appears below the vicinity of the Fermi level from −2.4 eV to −0.3 eV. This is considered that NH2 moiety acts as acceptor impurity because of sp3 hybridization between NH2 molecule and the nanotube which induces an impurity state near the Fermi level [35]. In addition, DOS curve behavior of BNNT after amine functionalization is shifted to lower energies. It can indicate that the structure is more stable [63].

3.2. Adsorption of NO2, HCN, HCHO and CO on the pristine (5,0) BNNT

To analyze adsorption performance of the pristine (5,0) BNNT to toxic gases including NO2, HCN, HCHO and CO, the different adsorption structures were constructed and optimized. Some optimized structures for the most favorable adsorption sites are shown in figure 2. The typical calculated adsorption parameters are presented in table 2.

For NO2 adsorption, N and O atoms of NO2 molecule close to B or N atoms of the pristine (5,0) BNNT as displayed in figure 2(a). The calculated values of \( E_{\text{ad}} \) at N-N, N-O, B-N and B-O adsorption sites were −132.9, −77.7, −79.9 and −144.3 meV, respectively. The corresponding interaction distances were found to be 1.57, 2.11, 1.00 and 1.50 Å, respectively. Negative values of \( E_{\text{ad}} \) show that adsorption of NO2 molecule on the pristine (5,0) BNNT is exothermic [2, 3]. Charge transferred from the pristine (5,0) BNNT to NO2 molecule was only 0.0283 e, it indicates that NO2 molecule undergoes weakly physical adsorption on the pristine (5,0) BNNT due to weak van der Waals interaction [2, 3, 24, 25]. The corresponding energy gap was calculated to be 1.96 eV which increased 0.59 eV than that of the pristine (5,0) BNNT. This suggests that conductivity of the pristine (5,0) BNNT after NO2 adsorption decreases. Based on the results of table 2, the pristine (5,0) BNNT exhibits low sensitivity to NO2 molecule, regardless of B or N atoms of the pristine (5,0) BNNT.

In case of HCN adsorption as presented in figure 2(b), according to table 2, the lowest value of \( E_{\text{ad}} \) was −106.4 meV at N-N and B-C adsorption sites with interaction distances of 1.59 and 1.50 Å, respectively. Unlike
other gases, HCN molecule prefers to adsorb on the pristine BNNT surface with parallel position. However, the charge transfer from HCN molecule to pristine (5,0) BNNT is quite small (≈0.1 e). Interaction distances are smaller than 2.00 Å. The less negative \( E_{\text{ad}} \) value reveals a weak physical adsorption between HCN molecule and the pristine (5,0) BNNT [3, 4, 64]. This result is in agreement with [3, 4, 64, 65]. Looking at the calculated \( E_{\text{gap}} \), it was found that the \( E_{\text{gap}} \) values at N-N and B-C adsorption sites fell to 1.12 eV. It means that adsorption of HCN molecule on the pristine (5,0) BNNT can improve conductivity of the nanotube. According to the results, the pristine (5,0) BNNT is little sensitive to HCN molecule.

For HCHO adsorption as shown in figure 2(c), we considered all adsorption sites including H, O and C atoms of HCHO molecule being close to B or N atoms of the pristine (5,0) BNNT, in vertical axis of HCHO
molecule for H and O atoms and in parallel axis for C atom. The results showed that the most favorable adsorption site appeared at N-C adsorption site with the $E_{\text{ad}}$ value of $-180.2$ meV. This result is consistent with [66] which reported that the most favorable adsorption site between HCHO and boron nitride sheet was found at C atom of HCHO interacting with N atom of the sheet. The corresponding charge transfer was calculated to be

| System       | Adsorption Site | Distance (Å) | $E_{\text{ad}}$ (meV) | Q (e)  | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) | $E_{\text{g}}$ (eV) |
|--------------|----------------|--------------|------------------------|-------|------------------------|------------------------|----------------|
| (5–0)-BNNT-N/NO$_2$ | N–N  | 1.57         | $-132.9$               | $-0.1807$ | $-6.23$           | $-4.75$           | 1.48          |
|               | N–O  | 2.11         | $-77.7$                | $-0.0283$ | $-6.34$           | $-4.38$           | 1.96          |
| (5–0)-BNNT-B/NO$_2$ | B–N  | 1.00         | $-79.9$                | $-0.0019$ | $-5.95$           | $-4.69$           | 1.26          |
|               | B–O  | 1.50         | $-144.3$               | $-0.0723$ | $-6.12$           | $-4.71$           | 1.42          |
| (5,0)-BNNT-N/HCN     | N–N  | 1.59         | $-106.4$               | 0.1075  | $-6.06$           | $-4.94$           | 1.12          |
|               | N–C  | 1.53         | $-81.9$                | 0.0896  | $-6.38$           | $-4.51$           | 1.87          |
|               | N–H  | 2.00         | $-0.7$                 | 0.0003  | $-6.21$           | $-4.80$           | 1.41          |
| (5,0)-BNNT-B/HCN     | B–N  | 1.25         | $-9.8$                 | 0.0272  | $-6.04$           | $-4.60$           | 1.43          |
|               | B–C  | 1.50         | $-106.4$               | 0.1075  | $-6.06$           | $-4.94$           | 1.12          |
|               | B–H  | 3.25         | $-0.8$                 | 0.0001  | $-6.22$           | $-4.80$           | 1.42          |
| (5–0)-BNNT-N/HCHO     | N–O  | 1.06         | $-168.2$               | 0.0238  | $-6.26$           | $-4.4$            | 1.86          |
|               | N–C  | 2.00         | $-180.2$               | 0.0907  | $-6.04$           | $-4.97$           | 1.07          |
|               | N–H  | 2.24         | $-55.6$                | 0.0451  | $-6.08$           | $-4.97$           | 1.11          |
| (5–0)-BNNT-B/HCHO     | B–O  | 2.12         | $-52.7$                | 0.0430  | $-5.95$           | $-4.74$           | 1.21          |
|               | B–C  | 2.00         | $-3.4$                 | 0.0002  | $-6.23$           | $-4.85$           | 1.38          |
|               | B–H  | 2.53         | $-20.4$                | 0.0261  | $-6.10$           | $-4.67$           | 1.43          |
| (5–0)-BNNT-N/CO       | N–C  | 1.52         | $-101.7$               | 0.0516  | $-6.25$           | $-4.83$           | 1.42          |
|               | N–O  | 2.75         | $-1.6$                 | 0.0000  | $-6.19$           | $-4.81$           | 1.38          |
| (5–0)-BNNT-B/CO       | B–C  | 2.50         | $-58.8$                | 0.0495  | $-6.04$           | $-4.62$           | 1.42          |
|               | B–O  | 1.64         | $-15.5$                | 0.0392  | $-6.06$           | $-4.64$           | 1.42          |
0.0907 e from HCHO molecule to the nanotube. This result suggests that the adsorption between HCHO (C atom site) and the pristine (5,0) BNNT (N atom site) results from an ionic bond interaction [66]. The ionic bonding plays an important role for charge transfer between the gas molecule and the BNNT. In this case, the ionic bond interaction is quite weak because of less charge transfer. As the results, the pristine (5,0) BNNT is weakly sensitive to HCHO molecule.

For CO adsorption, the C and O atoms of CO molecule in the vertical axis of CO molecule close to B or N atoms of the pristine (5,0) BNNT at different distances. The previous studies reported that CO adsorption on BNNTs in the perpendicular position to the BNNT axis was more stable than the parallel position to the BNNT axis [23, 67]. Figure 2(d) displays some optimized structures of the pristine (5,0) BNNT for CO adsorption. It is observed that the adsorption between CO molecule and the pristine (5,0) BNNT at C atom side of CO molecule is stronger than its O atom side. The calculated $E_{\text{ad}}$ values at N-C and B-C adsorption sites were $-101.7$ and $-58.8$ meV, respectively. A change in energy gap of the nanotube by CO molecules was very less. Based on small $E_{\text{ad}}$ values, large interaction distances and very small amount of charge transfer due to weakly physical interaction [68, 69], the pristine (5,0) BNNT is not sensitive to CO molecule.

### 3.3. Adsorption of NO$_2$, HCN, HCHO and CO on the amine BNNT

Figure 3 shows some optimized structures for the most favorable adsorption between the NH$_2$-(5,0) BNNT and NO$_2$, HCN, HCHO and CO gas molecules at different distances. Table 3 presents typical adsorption parameters of the NH$_2$-(5,0) BNNT with these gas molecules.

For NO$_2$ adsorption, the possible adsorption sites like NO$_2$-the pristine (5,0) BNNT system were investigated as shown in figure 3(a). It was found that the properties of the NH$_2$-(5,0) BNNT were significantly changed. At all adsorption sites, the $E_{\text{ad}}$ values obviously increased in comparison with the pristine (5,0) BNNT. This demonstrates that the interaction between the NH$_2$-(5,0) BNNT with NO$_2$ molecule is stronger than the pristine (5,0) BNNT. The negative $E_{\text{ad}}$ value indicates exothermic process of nature. Charge transferred from the
pristine \(\text{NH}_2\) prefers N atom close to the \(\text{NH}_2\)-the nanotube and HCN molecule strongly overlap and charge clearly
sensitivity of the pristine interaction between HCN molecule and the nanotube and sensitivity of the nanotube to HCN molecule.

HCN adsorbed on the pristine
interaction between B atom of the nanotube and C atom of the gas molecule is enhanced which is consistent with
molecules. HCHO molecule prefers to adsorb on B or N atoms of the \(\text{NH}_2\)-adsorption site. The maximum value reached to 0.2241 e. The charge transfer and \(E_{\text{ad}}\) value of HCN absorbed
calculated charge transfer shows that charge mostly transferred from the HCN molecule to the nanotube at B-N
reported that adsorption of HCN molecule with its N atom site interacting with BNNTs showed a stronger
enhanced by amine functionalization.

From the results, functionalization of \(\text{NH}_2\) molecule on pristine
BNNT at either B or N atoms of the nanotube, it was found that energy gap increased. This demonstrates that the
chemisorption

\(\text{NH}_2\) to \(\text{NO}_2\) molecule found at N-N adsorption site was 0.3072 e, which is higher than that of the pristine (5,0) BNNT. In case of energy gap, it dropped to 1.46 eV compared with 1.65 eV of the \(\text{NH}_2\)-(5,0) BNNT without \(\text{NO}_2\) adsorption. This result reveals that the conductivity of the \(\text{NH}_2\)-(5,0) BNNT is improved by adsorption of \(\text{NO}_2\) molecule. As the results, the sensitivity of pristine (5,0) BNNT to \(\text{NO}_2\) molecule can be
enhanced by amine functionalization.

For HCN adsorption on the \(\text{NH}_2\)-(5,0) BNNT, some optimized structures for adsorption are shown in
figure 3(b). N and H atoms of HCN molecule were perpendicular to the nanotube surface and C atom was
parallel to the nanotube surface. Based on table 3, the \(E_{\text{ad}}\) values for all adsorption sites are higher than that of
HCN adsorbed on the pristine (5,0) BNNT. For example, the minimum \(E_{\text{ad}}\) value of the \(\text{NH}_2\)-(5,0) BNNT at
N-N sites was −220.1 meV, which is about two times that of the pristine (5,0) BNNT. The previous studies
reported that adsorption of HCN molecule with its N atom site interacting with BNNTs showed a stronger
interaction than those of H and C atom sites [3, 27, 64]. The interaction distances between the nanotube and
HCN molecule are also smaller than 2.00 Å. The previous studies calculated that the interaction distance
between HCN molecules and metal doped BNNTs was about 2.00 Å [4, 70] which corresponds to this study. The
calculated charge transfer shows that charge mostly transferred from the HCN molecule to the nanotube at B-N
adsorption site. The maximum value reached to 0.2241 e. The charge transfer and \(E_{\text{ad}}\) value of HCN absorbed
\(\text{NH}_2\)-(5,0) BNNT at B-N adsorption site are larger than that of the pristine BNNT, indicating that the orbitals of
the nanotube and HCN molecule strongly overlap and charge clearly flows. This reveals that HCN molecule
prefers N atom close to the \(\text{NH}_2\)-(5,0) BNNT at B atom. When HCN molecule interacted with the \(\text{NH}_2\)-(5,0)
BNNT at either B or N atoms of the nanotube, it was found that energy gap increased. This demonstrates that the
adsorption of HCN molecule changes band gap of the \(\text{NH}_2\)-(5,0) BNNT which belongs to chemisorption [4, 5].
From the results, functionalization of \(\text{NH}_2\) molecule on pristine (5,0) BNNT improves both the strength of the
interaction between HCN molecule and the nanotube and sensitivity of the nanotube to HCN molecule.

Figure 3(c) shows some optimized structures for adsorption between the \(\text{NH}_2\)-(5,0) BNNT and HCHO
molecules. HCHO molecule prefers to adsorb on B or N atoms of the \(\text{NH}_2\)-(5,0) BNNT similar to the case of the
pristine (5,0) BNNT. As listed in table 3, it was found that the trend of \(E_{\text{ad}}\) values of HCHO absorbed \(\text{NH}_2\)-(5,0)
BNNT increased with the same range of interaction distance which indicates that the interaction is
chemisorption [2, 69, 71]. The most charge transfer of HCHO absorbed pristine BNNT is positive which is
charge transfer from HCHO molecule to the pristine BNNT similar to the \(\text{NH}_2\)-(5,0) BNNT. It was found that the
charge transfer of HCHO absorbed \(\text{NH}_2\)-(5,0) BNNT was found at B-C adsorption site and reached to 0.1299 e. This result may be understood that \(\text{NH}_2\)-(5,0) BNNT is more accepting capability and ionic bond
interaction between B atom of the nanotube and C atom of the gas molecule is enhanced which is consistent with
a decrease in the \(E_g\) value from 1.65 eV to 1.14 eV. The results indicate that amine functionalization improves the
sensitivity of the pristine (5,0) BNNT to HCHO molecule. Also, the same information was obtained at B-O site.

| System               | Adsorption site | Distance (Å) | \(E_{\text{ad}}\) (meV) | \(Q\) (e) | \(E_{\text{HOMO}}\) (eV) | \(E_{\text{LUMO}}\) (eV) | \(E_g\) (eV) |
|----------------------|----------------|--------------|------------------------|--------|-------------------|-------------------|---------|
| \(\text{NH}_2\)-(5,0) BNNT/NO\(_2\) | N-N           | 4.11         | −202.2                 | −0.3072| −6.16             | −4.70             | 1.46    |
|                      | N-O           | 2.10         | −187.5                 | −0.2761| −6.15             | −5.28             | 0.86    |
|                      | B-N           | 3.05         | −248.9                 | −0.3248| −6.07             | −4.83             | 1.24    |
|                      | B-O           | 4.75         | −248.9                 | −0.3248| −6.07             | −4.83             | 1.24    |
| \(\text{NH}_2\)-(5,0) BNNT/HCN | N-N           | 1.25         | −220.1                 | 0.0825 | −6.18             | −4.32             | 1.86    |
|                      | N-C           | 1.56         | −196.1                 | 0.1624 | −6.26             | −4.40             | 1.86    |
|                      | N-H           | 2.00         | −3.9                   | 0.0378 | −6.43             | −4.68             | 1.75    |
|                      | B-N           | 2.50         | −30.7                  | 0.2241 | −6.37             | −4.62             | 1.75    |
|                      | B-C           | 1.73         | −180.7                 | 0.0352 | −6.27             | −4.45             | 1.81    |
|                      | B-H           | 3.71         | −3.9                   | 0.0387 | −6.43             | −4.68             | 1.75    |
| \(\text{NH}_2\)-(5,0) BNNT/HCHO | N-O           | 2.15         | −230.7                 | 0.0302 | −6.52             | −4.44             | 2.12    |
|                      | N-C           | 1.91         | −188.9                 | 0.2702 | −6.24             | −4.39             | 1.85    |
|                      | N-H           | 1.59         | −50.4                  | 0.0683 | −5.34             | −4.64             | 0.70    |
|                      | B-O           | 1.27         | −217.6                 | 0.0883 | −6.14             | −4.40             | 1.74    |
|                      | B-C           | 1.25         | −113.5                 | 0.1299 | −6.02             | −4.88             | 1.14    |
|                      | B-H           | 2.80         | −59.2                  | 0.1977 | −6.02             | −5.25             | 0.77    |
| \(\text{NH}_2\)-(5,0) BNNT/CO | N-C           | 1.15         | −123.6                 | 0.1185 | −6.21             | −4.72             | 1.49    |
|                      | N-O           | 1.50         | −77.0                  | 0.1216 | −6.22             | −4.50             | 1.72    |
|                      | B-C           | 1.83         | −56.8                  | 0.4986 | −6.08             | −4.48             | 1.60    |
|                      | B-O           | 3.12         | −2.2                   | −0.0001| −6.30             | −4.64             | 1.66    |

Table 3. Calculated adsorption parameters of target gas molecules absorbed on the amine BNNT.
which confirms the improved sensitivity of the pristine (5,0) BNNT functionalized with NH2 molecule to HCHO molecule. In addition, the results show a good agreement with previous studies [2, 66].

In case of CO adsorption on the NH2-(5,0) BNNT, we also investigated the same adsorption sites with the pristine (5,0) BNNT and some optimized structures for adsorption between the NH2-(5,0) BNNT and CO molecule are displayed in figure 3(d). After optimization, it was found that the Ead values of CO absorbed NH2-(5,0) BNNT at N-O and N-C adsorption sites obviously increased reaching to $-77.0$ meV and $-123.6$ meV, respectively. A decrease in interaction distances of the adsorption sites was found to be 1.50 Å and 1.15 Å, respectively. In case of pristine BNNT, charge transferred from CO molecule to the pristine BNNT at all adsorption sites. For NH2-(5,0) BNNT, the most charge transfer from the CO molecule to NH2-(5,0) BNNT was found to be at N-C adsorption site with value of 0.4986 e. As the results, it can conclude that amine functionalization on the pristine (5,0) BNNT enhances adsorption between CO molecule and the NH2-(5,0) BNNT.

3.4. Electronic densities of state
To better understand the adsorptions between pristine, NH2-(5,0) BNNTs and target gas molecules, electronic densities of state for these systems were calculated. Figure 4 shows the calculated DOSs of the most stable adsorption sites between the pristine, NH2-(5,0) BNNTs and target gas molecules. It should be noted that the changes in DOSs in the area around Fermi level are expected that significant changes in electronic properties of the pristine and NH2-(5,0) BNNTs for adsorption of target gas molecules are found. In figure 4(a), it can be seen that a new local state appears near the conduction band edge for NO2/NH2-(5,0) BNNT. This indicates that the NH2-(5,0) BNNT exhibits a n-type semiconductor with donor impurity states for NO2 adsorption [2]. This confirms the improved sensitivity of the NH2-(5,0) BNNT to NO2 molecule. In case of HCN adsorption with DOSs plot as shown in figure 4(b), a significant change in calculated DOSs for HCN/NH2-(5,0) BNNT was observed. Two new local states appear near the Fermi level. One occurs on the top of valence band and the other one appears near edge of the conduction band compared with HCN/(5,0) BNNT. This suggests the existence of
a new hybrid orbital between HCN molecule and NH$_2$-(5,0) BNNT [4] confirming higher sensitivity than HCN/ (5,0) BNNT and the improved reactivity of the nanotube. For the calculated DOSs of HCHO adsorbed on the pristine and NH$_2$-(5,0) BNNTs as presented in figure 4(c), a new local state of the HCHO/NH$_2$-(5,0) BNNT occurs below Fermi level at $-0.3$ eV which corresponds to figure 1(b). This indicates that the NH$_2$-(5,0) BNNT is more sensitive to HCHO molecule than the pristine (5,0) BNNT. While calculated DOSs for the adsorption of the pristine and NH$_2$-(5,0) BNNTs with CO molecule are shown in figure 4(d). It was found that a new local state of CO/NH$_2$-(5,0) BNNT appears above the valence band compared with DOS of the CO/(5,0) BNNT. The DOS change suggests that the NH$_2$-(5,0) BNNT is more active toward CO molecule than the pristine (5,0) BNNT.

Figure 5. The relation between recovery time and desorption energy of target gases absorbed on (a) pristine and (b) amine BNNTs.
3.5. Recovery time and desorption energy

In this section, the relation between recovery time and desorption energy of pristine and NH$_2$-BNNTs was investigated at room temperature for its possibility as a gas sensor of target gas molecules. The strong interaction results in a long recovery time which suggests that the desorption process is difficult. The recovery time can be theoretically calculated based on transition state theory as the following equation [72, 73]:

$$\tau = \frac{\nu_0}{kT} \exp\left(\frac{-E_{ad}}{kT}\right)$$

where $\nu_0$ is the attempt frequency (\(\sim 10^{12} \text{s}^{-1}\) [72, 74]), T is temperature (300 K), and k is the Boltzmann’s constant. As the equation, it is expected that more negative values of $E_{ad}$ prolong the recovery time. To calculate desorption energy, $E_{ad}$ value is equal to activation energy ($E_a$) which must be overcome in desorption process [74]. The desorption energy ($E_a$) can be predicted by assuming to be $-E_g$ [75]. This indicates that more negative $E_{ad}$ values require higher desorption energy and long recovery times in desorption process. Figure 5 shows the relation between recovery time and desorption energies calculated from the most favorable adsorption sites of target gases absorbed on the pristine (5,0) and amine BNNTs. For the pristine (5,0) BNNT as presented in figure 5(a), the recovery time of NO$_2$, HCN, HCHO and CO molecules was found to be $2.64 \times 10^{-10}$, $6.11 \times 10^{-11}$, $1.05 \times 10^{-9}$, and $5.10 \times 10^{-11}$ s with the desorption energies of 144.3, 106.4, 180.2 and 101.7 meV, respectively. In case of the amine BNNT as shown in figure 5(b), the recovery time of NO$_2$, HCN, HCHO and CO molecules was calculated to be $1.51 \times 10^{-8}$, $4.95 \times 10^{-9}$, $7.46 \times 10^{-9}$ and $1.19 \times 10^{-10}$ s with the desorption energies of 248.9, 220.1, 230.7 and 123.6 meV, respectively. To compare results with other popular sensing materials, the recovery time of NO$_2$ desorption from the surface of carbon nanotube based gas sensors was found to be in the range of 5 μs to 16 s with corresponding to the adsorption energy range of $-0.34$ to $-0.79$ eV at room temperature [76]. Yong et al studied that the recovery times of NO and NO$_2$ on the graphitic GaN sheets were 1.1 μs and 0.16 ms, respectively [77]. Li et al reported that the recovery time of SnO$_2$ microspheres for a HCHO sensor was 25 s [78]. Therefore, it suggests that the NH$_2$-(5,0) BNNT has the good potential to act as a room temperature gas sensor with relative short recovery time.

4. Conclusion

In summary, we have studied the structural and electronic properties of the pristine and amine functionalized (5,0) BNNTs for adsorption of NO$_2$, HCN, HCHO and CO gas molecules using SCC-DFTB method. After amine functionalization, the structural and electronic properties of the pristine (5,0) BNNT were changed due to structural deformation from the change in local hybridization of the boron atom from sp$^2$ to sp$^3$ orbital. The calculated DOS of the NH$_2$-(5,0) BNNT below Fermi level increased. According to the adsorption results, the NH$_2$-(5,0) BNNT exhibits higher sensitivity to these gas molecules than that of the pristine (5,0) BNNT due to significant changes in band structure. For the adsorption of NO$_2$, HCN and CO molecules, it was found that new local states appear on and above the top of valence band in which a new local state of HCHO adsorbed on the NH$_2$-(5,0) BNNT occurs below Fermi level with increasing DOS. From the obtained results of recovery time and desorption energy, amine functionalized (5,0) BNNT at B atom of the nanotube can be used as reusable gas sensors for NO$_2$, HCN, HCHO and CO molecules at room temperature. The number of gas molecules adsorbed on pristine and amine functionalized BNNTs as well as dynamic properties will be deeply studied for future work. The results in this study are expected to be useful guidance for applications in gas sensor devices for detection of toxic gases.

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