



Received 04th October 2020,
Revised 10th January 2021,
Accepted 19th February 2021

DOI: [10.14456/past.2021.4](https://doi.org/10.14456/past.2021.4)

Theoretical Investigation of NO₂ Adsorption on C-, Si-, and Ge-doped Boron Nitride Nanomaterials

Wandee Rakrai¹, Chanukorn Tabtimsai¹, and Banchob Wann^{2*}

¹ Department of Chemistry, Computational Chemistry Center for Nanotechnology (CCCN), Faculty of Science and Technology, Rajabhat Maha Sarakham University, Maha Sarakham, 44000, Thailand

² Center of Excellence for Innovation in Chemistry (PERCH-CIC) and Supramolecular Chemistry Research Unit, Department of Chemistry, Faculty of Science, Mahasarakham University, Maha Sarakham, 44150, Thailand

*E-mail: banchobw@gmail.com

Abstract

The adsorption abilities, structural and electronic properties of nitrogen dioxide (NO₂) molecule adsorbed on pristine, and C-, Si-, and Ge-doped boron nitride nanosheets (BNNS) and nanotubes (BNNT) were investigated using the density functional theory method. The binding energies of doping reveal that the C atom doping exhibits the strongest binding ability with both BNNS and BNNT. In addition, the NO₂ molecule weakly interacts with the pristine BNNS and BNNT, whereas it has a strong adsorption ability with C-, Si-, and Ge-doped BNNSs and BNNTs. The electronic properties such as the energy gap and partial charge transfer of all atomic doped-BNNSs and BNNTs are significantly modified after NO₂ adsorptions. Thus, the C-, Si-, and Ge-doped BNNSs and BNNTs can be used as NO₂ gas storage and sensing.

Keywords: Adsorption, Boron nitride, DFT, Nanosheet, Nanotube, Nitrogen dioxide

1. Introduction

Boron nitride (BN) nanomaterials included nanotubes and nanosheets are chemical compound, consisting of equal numbers of boron (B) and nitrogen (N) atoms, which are not found in nature and is therefore produced synthetically. One-dimensional (1D) boron nitride nanotube (BNNT) was successfully synthesized in 1995 (1) and two-dimensional (2D) hexagonal boron nitride sheet (BNNS) was peeled off from a boron nitride crystal in 2005 (2). These nanomaterials are electrically insulator with a wide band gap, high thermal conductivity and interesting magnetic features (3). These properties cause that the boron nitride nanomaterials display great potential in many fields, such as nanodevices especially the chemical sensors. However, it was found that the modified BN is more sensitive sensing than that of pristine BN, therefore the defects in BN behave some interesting characteristics. In the process of preparations or modifications, various types of defects on BN can be formed, such as adatoms (4), vacancies or doping (5). The atom (AT) doped BNNTs and BNNSs further enlarge the application in gas chemical sensor, such as NO (6, 7), CO (7), O₂ (8), H₂ (9), NH₃ (10), SO₂ (11-13) and NO₂ (13).

Nitrogen dioxide (NO₂) is one of the toxic gases with pungent smell. It can be produced during combustion in factories and thermal power plants (14). The NO₂ gas displays highly toxic to nervous system and respiratory organs of human, consequently the detection of NO₂ plays a significant role, therefore the sensitive sensor design for NO₂ detection is essential (15, 16).

In the present work, group IV atoms (C, Si, Ge) have been selected for doping due to they have nearly the same atomic radius of B and N atoms and place between group III of B and group V of N. The geometrical structures, adsorption energies, and electronic properties of NO₂ adsorption on the pristine and AT-doped BNNSs and BNNTs have been investigated.

2. Computational details

The adsorptions of NO₂ on pristine BNNS, pristine (5,5) armchair BNNT and their doping with C, Si, or Ge atom were investigated in terms of geometric and electronic properties in which both ends of all nanomaterials were saturated by hydrogen atoms to avoid the boundary effects. Then the doping of C, Si, or Ge atom onto the BNNS and BNNT was modeled so that one of boron or nitrogen atom at the

middle site of the BNNS and BNNT was replaced by the C, Si, or Ge atom. In this work, replacing of B or N atom of the BNNS and BNNT with C, Si, or Ge atom was referred to be the B (C_B -BNNS, Si_B -BNNS, Ge_B -BNNS, C_B -BNNT, Si_B -BNNT, Ge_B -BNNT) or N (C_N -BNNS, Si_N -BNNS, Ge_N -BNNS, C_N -BNNT, Si_N -BNNT, Ge_N -BNNT) sites, respectively. The adsorbed NO_2 gas was set by placing this molecule over the C, Si, or Ge atom. All calculations were performed using the GAUSSIAN 09 software package (17) at the DFT level with the Lee–Yang–Parr correlation functional (B3LYP) (18–20) and the intensive Los Alamos LanL2DZ split–valence basis set (21–23). The intensive B3LYP/LanL2DZ theoretical method was used because this method was successfully utilized for many works (6, 8, 10, 24–26).

Electronic properties, including the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), the HOMO and LUMO energy gap (E_g), and the partial charge transfer (PCT) upon pristine and C–, Si–, or Ge–doped BNNS and BNNT and their NO_2 adsorptions were also studied at the same theoretical level. The energy gap was obtained from the difference between HOMO and LUMO energies. The partial charge transfer (PCT) during gas adsorptions was defined as a change in gas charge between the adsorption processes using the natural bond orbital (NBO) analysis (27). The molecular graphics of all optimized structures were generated using the MOLEKEL 4.3 program (28). The binding energies (E_b) of C–, Si–, and Ge–doped BNNS and BNNT were calculated by the following equation:

$$E_b = E_{AT-BNNS} - (E_{BNNS} + E_{AT})$$

$$E_b = E_{AT-BNNT} - (E_{BNNT} + E_{AT})$$

where $E_{AT-BNNS}$ and $E_{AT-BNNT}$ were the total energies of C–, Si–, or Ge–doped BNNS and BNNT. The E_{BNNS} and E_{BNNT} were the total energy of monovacant BNNS and BNNT, and E_{AT} was the total energy of free C, Si, or Ge atom.

The adsorption energies (E_{ads}) of NO_2 on the pristine and C–, Si–, or Ge–doped BNNS and BNNT were determined through the following equation:

$$E_{ads} = E_{gas/BNNS} - (E_{BNNS} + E_{gas})$$

$$E_{ads} = E_{gas/BNNT} - (E_{BNNT} + E_{gas})$$

where $E_{gas/BNNS}$ and $E_{gas/BNNT}$ were the total energy of NO_2 adsorbed on pristine or C–, Si–, or Ge–doped BNNS and BNNT. The E_{BNNS} and E_{BNNT} were the total energy of the pristine or C–, Si–, or Ge–doped BNNS and BNNT, and the E_{gas} was the total energy of the isolated NO_2 molecule. A negative value of E_{ads} referred to exothermic process.

3. Results and Discussion

3.1 Geometrical structures of pristine, C–, Si–, and Ge–doped BNNSs and BNNTs and their NO_2 adsorptions

The B3LYP/LanL2DZ optimized structure of pristine BNNS is displayed in Figure 1(a). The B1–N1, B1–N2, and B1–N3 bond lengths are estimated to be 1.454, 1.452, and 1.452 Å, respectively. These data

are in good agreement with the previous experiment (29) and theoretical results (30), which support the validity of this model and method. While the N1–B1–N2, N2–B1–N3, and N3–B1–N1 bond angles are estimated to be 119.7, 120.5, and 119.7°, respectively. The geometrical structure of BNNT is displayed in Figure 1(b). The B1–N1, B1–N2, and B1–N3 bond lengths are estimated to be 1.453, 1.454, and 1.454 Å, respectively, which are consistent with theoretical (31, 32) and experimental values (33). While the N1–B1–N2, N2–B1–N3, and N3–B1–N1 bond angles are estimated to be 119.2, 119.8, and 119.2°, respectively. The optimized structures of the doping of C, Si, or Ge atom onto the BNNS and BNNT are displayed in Figures 2 and 3, respectively. After replacing of B or N atom on the BNNS and BNNT with C, Si, or Ge atom, it is found that these atoms form three bonds with the nearest B or N atom. The bond lengths between the replacing atom and its neighboring three N or B atom of BNNS and BNNT are found in the range of 1.435–2.020 and 1.443–2.079 Å, respectively. Furthermore, the bond angles of all BNNS and BNNT replacing B or N atom with C, Si, or Ge atom are narrower than those of the N–B–N or B–N–B of pristine BNNS and BNNT.

The binding energies (E_b) of AT and BNNS and BNNT are displayed Table 1. The E_b values of AT–doped BNNSs and BNNTs are found in the range of –103.50 to –332.63 and –118.67 to –320.44 kcal/mol, respectively. The negative values of E_b imply that the interaction for doping atoms with BNNS and BNNT surfaces corresponds to the exothermic reaction. Furthermore, the BNNS and BNNT doping with C, Si, or Ge atom on B site shows strong interaction in comparison with the doping on N site, which is the result of having the larger E_b value. In addition, the C atom doping exhibits the strongest binding ability with both BNNS and BNNT. This may be due to atomic radius of C is nearly the same size atomic radius of B and N atoms and placed between them while atomic radius of Si and G atoms is bigger than those of atomic radius of Si and G atoms.

The optimized structures of the NO_2 adsorbed on pristine and C–, Si–, and Ge–doped BNNSs and BNNTs are displayed in Figures 4 and 5, respectively. The computed BDs between the adsorbed NO_2 and pristine BNNS and BNNT are 3.110 and 3.027 Å, respectively. The BDs between the adsorbed NO_2 and AT–doped BNNS and BNNT are found in the range of 1.581–2.296 and 2.514–2.921 Å, respectively. The short BDs confirm that the NO_2 molecule shows stronger adsorption with AT–doped BNNS and BNNT than that of pristine BNNS and BNNT.

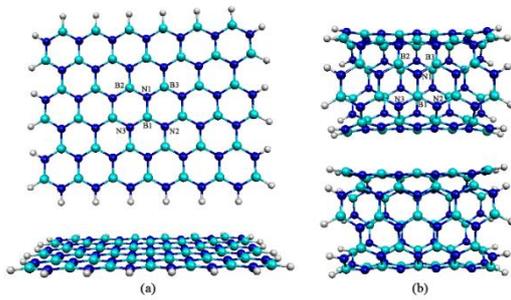


Figure 1 The B3LYP/LanL2DZ optimized structures of pristine (a) BNNS and (b) BNNT.

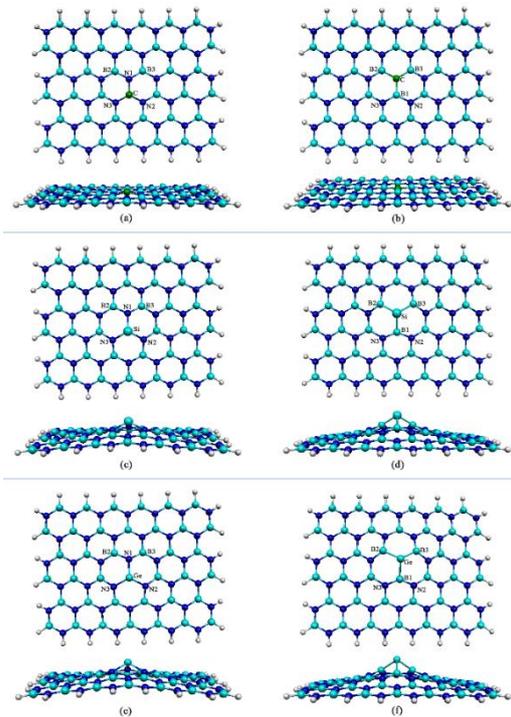


Figure 2 The B3LYP/LanL2DZ optimized structures of (a) C_B-BNNS, (b) C_N-BNNS, (c) Si_B-BNNS, (d) Si_N-BNNS, (e) Ge_B-BNNS, and (f) Ge_N-BNNS.

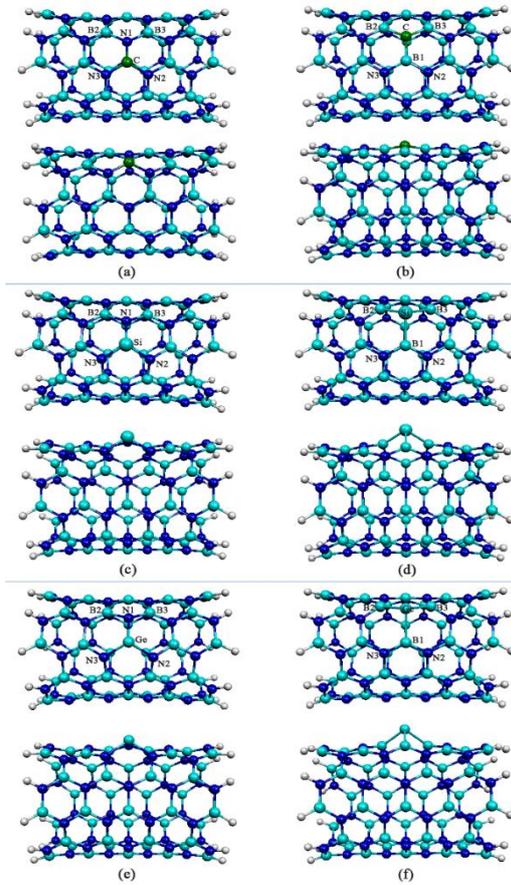


Figure 3 The B3LYP/LanL2DZ optimized structures of (a) C_B-BNNT, (b) C_N-BNNT, (c) Si_B-BNNT, (d) Si_N-BNNT, (e) Ge_B-BNNT, and (f) Ge_N-BNNT.

Table 1 The binding energies (E_b) of AT and BNNS and BNNT

Species	E_b^a
C _B + BNNS → C _B -BNNS	-332.63
C _N + BNNS → C _N -BNNS	-295.99
Si _B + BNNS → Si _B -BNNS	-270.73
Si _N + BNNS → Si _N -BNNS	-132.88
Ge _B + BNNS → Ge _B -BNNS	-235.67
Ge _N + BNNS → Ge _N -BNNS	-103.50
C _B + BNNT → C _B -BNNT	-320.44
C _N + BNNT → C _N -BNNT	-283.54
Si _B + BNNT → Si _B -BNNT	-274.64
Si _N + BNNT → Si _N -BNNT	-146.19
Ge _B + BNNT → Ge _B -BNNT	-243.14
Ge _N + BNNT → Ge _N -BNNT	-118.67

^a In kilocalories/mol (kcal/mol)

3.2 Adsorption energies of NO₂ molecule adsorbed on pristine, C-, Si-, and Ge-doped BNNSs and BNNTs

The adsorption energies of the NO₂ adsorbed on the pristine, C-, Si-, and Ge-doped BNNSs and BNNTs are listed in Table 3. The adsorption energies of the NO₂ adsorbed on the pristine BNNS and BNNT are -2.31 and -3.52 kcal/mol, respectively. These indicate that the pristine BNNS and BNNT display a weak sensitivity to the adsorption. The adsorption abilities of the NO₂ adsorbed on the AT doped-BNNSs are in the order: NO₂/Si_B-BNNS (-78.62 kcal/mol) > NO₂/Ge_B-BNNS (-67.17 kcal/mol) > NO₂/Si_N-BNNS (-63.48 kcal/mol) > NO₂/Ge_N-BNNS (-58.51 kcal/mol) > NO₂/C_B-BNNS (-48.57 kcal/mol) > NO₂/C_N-BNNS (-33.88 kcal/mol). The adsorption abilities of the NO₂ adsorbed on the AT doped-BNNTs are in the order: NO₂/Si_B-BNNT (-69.38 kcal/mol) > NO₂/Si_N-BNNT (-64.33 kcal/mol) > NO₂/Ge_N-BNNT (-57.90 kcal/mol) > NO₂/C_B-BNNT (-52.30 kcal/mol) > NO₂/Ge_B-BNNT (-47.45 kcal/mol) > NO₂/C_N-BNNT (-46.95 kcal/mol). The results show that the NO₂ adsorptions on the C-, Si-, and Ge-doped BNNSs and BNNTs are stronger than the pristine BNNS and BNNT in which replacing of B atom of the BNNS and BNNT with Si atom displays the strongest interaction with the NO₂ molecule.

3.3 Electronic properties of pristine, C-, Si-, and Ge-doped BNNS and BNNT and their NO₂ adsorptions

For the most stable configuration of pristine, C-, Si-, and Ge-doped BNNSs and BNNTs, we examined the highest occupied molecular orbital energies (E_{HOMO}), the lowest unoccupied molecular orbital energies (E_{LUMO}), and the energy gaps (E_g). The results of which are listed in Table 2. It is found that the calculated E_g for AT-doped BNNSs and BNNTs are found in the range of 2.449–3.973 and 2.585–3.619 eV, respectively. Which are significant smaller than the E_g of pristine BNNS (5.823 eV) and BNNT (6.014). Thus, the C, Si, and Ge atom doping can induce dramatically decrease in the E_g of BNNS and BNNT, in which the chemical reactivities of C-, Si-, and Ge-doped BNNSs and BNNTs are also increased.

The electronic properties of NO₂ adsorbed on pristine, C-, Si-, and Ge-doped BNNSs and BNNTs in terms of energy gap and partial charge transfers computed at B3LYP/LanL2DZ theoretical level are listed in Table 3. When NO₂ adsorbed on the pristine BNNS and BNNT, the energy gaps of BNNS and BNNT are changed. The energy gaps of the NO₂ adsorbed on the AT doped-BNNSs and BNNTs are found in the range of 3.37–3.81 and 2.78–3.92 eV, respectively. That means, after NO₂ adsorptions, the energy gaps of all AT doped-BNNSs and BNNTs are significant changed. These results indicate that electronic properties of C-, Si-, and Ge-doped BNNSs and BNNTs are modified by NO₂ adsorptions.

This means that the sensitivity of BNNS and BNNT based gas sensor for NO₂ could be improved by introducing appropriate atomic doping.

Table 2 The highest occupied molecular orbitals (E_{HOMO}), the lowest unoccupied molecular orbitals (E_{LUMO}), and energy gaps (E_g) of pristine, C-, Si-, and Ge-doped BNNS and BNNT

Species ^a	E_{HOMO} ^b	E_{LUMO} ^b	E_{gap} ^b
BNNS (1)	-6.504	-0.680	5.823
C _B -BNNS (2)	-3.265	-0.680	2.585
C _N -BNNS (2)	-6.585	-3.891	2.694
Si _B -BNNS (2)	-6.531	-2.558	3.973
Si _N -BNNS (2)	-6.259	-3.537	2.721
Ge _B -BNNS (2)	-6.504	-3.265	3.238
Ge _N -BNNS (2)	-5.987	-3.537	2.449
BNNT (1)	-6.612	-0.599	6.014
C _B -BNNT (2)	-4.163	-0.599	3.565
C _N -BNNT (2)	-6.721	-3.946	2.776
Si _B -BNNT (2)	-6.612	-2.993	3.619
Si _N -BNNT (2)	-6.422	-3.565	2.857
Ge _B -BNNT (2)	-6.585	-3.619	2.966
Ge _N -BNNT (2)	-6.150	-3.565	2.585

^a Spin multiplicities are in parenthesis.

^b In eV.

N Natural bond orbital (NBO) analysis was performed to evaluate electron transfer before and after NO₂ adsorption. The partial charge transfer (PCTs) was defined as $Q_{gas/BNNS} - Q_{gas}$, and $Q_{gas/BNNT} - Q_{gas}$ for BNNS and BNNT systems, respectively, where $Q_{gas/BNNS}$ and $Q_{gas/BNNT}$ were the total charge of NO₂ adsorbed on pristine or AT doped-BNNS and BNNT, respectively, and the Q_{gas} was the total charge of NO₂ in free case.

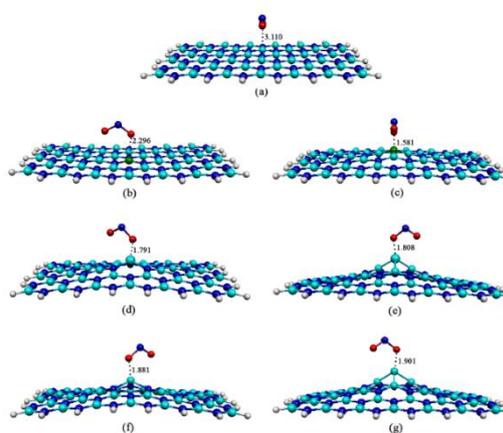


Figure 4 The B3LYP/LanL2DZ optimized structures of (a) NO₂/BNNS, (b) NO₂/C_B-BNNS, (c) NO₂/C_N-BNNS, (d) NO₂/Si_B-BNNS, (e) NO₂/Si_N-BNNS, (f) NO₂/Ge_B-BNNS and (g) NO₂/Ge_N-BNNS.

The adsorption distances are in Å.

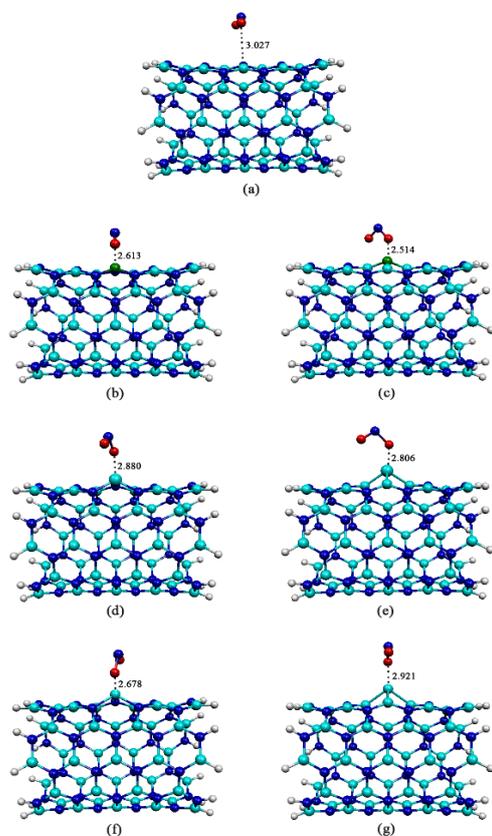


Figure 5 The B3LYP/LanL2DZ optimized structures of (a) NO₂/BNNT, (b) NO₂/C_B-BNNT, (c) NO₂/C_N-BNNT, (d) NO₂/Si_B-BNNT, (e) NO₂/Si_N-BNNT, (f) NO₂/Ge_B-BNNT and (g) NO₂/Ge_N-BNNT. The adsorption distances are in Å.

Table 3 Adsorption energies (E_{ads}), adsorption distances (ADs), energy gaps (E_g), and partial charge transfers (PCT) of NO₂ adsorbed on pristine, C-, Si-, and Ge-doped BNNS and BNNT

Species	E_{ads}^a	AD ^b	E_g^c	PCT ^d
NO ₂ /BNNS (2)	-2.31	3.110	1.85	0.024
NO ₂ /C _B -BNNS (1)	-48.57	2.296	3.37	-0.726
NO ₂ /C _N -BNNS (1)	-33.88	1.581	3.70	-0.270
NO ₂ /Si _B -BNNS (1)	-78.62	1.791	3.59	-0.606
NO ₂ /Si _N -BNNS (1)	-63.48	1.808	3.81	-0.548
NO ₂ /Ge _B -BNNS (1)	-67.17	1.881	3.54	-0.594
NO ₂ /Ge _N -BNNS (1)	-58.51	1.901	3.76	-0.545
NO ₂ /BNNT (2)	-3.52	3.027	1.28	0.022
NO ₂ /C _B -BNNT (1)	-52.30	2.613	3.92	-0.357
NO ₂ /C _N -BNNT (1)	-46.95	2.514	3.73	-0.251
NO ₂ /Si _B -BNNT (1)	-69.38	2.880	3.59	-0.563
NO ₂ /Si _N -BNNT (1)	-64.33	2.806	3.86	-0.545
NO ₂ /Ge _B -BNNT (1)	-47.45	2.678	2.78	-0.522
NO ₂ /Ge _N -BNNT (1)	-57.90	2.921	3.81	-0.544

^a Spin multiplicities are in parenthesis.

^b In kcal/mol.

^c In Å.

^d In eV.

^e In e.

The PCTs between NO₂ molecule with pristine BNNS and BNNT are 0.024 and 0.022 e, respectively. The small PCT values occurred during NO₂ adsorption on pristine BNNS and BNNT confirm a weak interaction between the BNNS and BNNT with NO₂ molecule. The PCTs between the NO₂ and AT doped-BNNS and BNNT are found in the range of -0.726 to -0.270 and -0.565 to -0.251 e, respectively. The PCT analysis indicates that partial charges are transferred from C-, Si-, or Ge-doped BNNS and BNNT to the NO₂ molecule. In addition, the PCTs of NO₂ adsorption on AT doped-BNNS and BNNT are found to be larger than that of the pristine BNNS and BNNT. This supports that the doping of C, Si, and Ge atom on BNNS and BNNT affects in the electronic properties of the pristine BNNS and BNNT after adsorption.

4. Conclusions

The adsorption of NO₂ molecule adsorbed on the pristine and C-, Si-, and Ge-doped BNNSs and BNNTs at B or N sites were investigated using the DFT method. The binding energies of doped-BNNSs and BNNTs are found in the range of -103.50 to -332.63 and -118.67 to -320.44 kcal/mol, respectively. The binding energies reveal that the C atom doping exhibits the strongest binding ability with BNNS and BNNT. The AT doped-BNNSs and BNNTs display higher adsorption strength to NO₂ molecule than the pristine BNNS and BNNT. The significant increase in adsorption energy and charge transfer is probable to induce significant changes in the electrical conductivity of the AT doped-BNNS and BNNT. Therefore, C-, Si-, and Ge-doped BNNS and BNNT can be used as advancing material for reliable and efficient NO₂ storage and sensing.

Acknowledgements

The financial support (2562A14702007) by Research and Development Institute, Rajabhat Maha Sarakham University is gratefully acknowledged. We also thank the Computational Chemistry Center for Nanotechnology (CCCN), Department of Chemistry, Faculty of Science and Technology, Rajabhat Maha Sarakham University, and Center of Excellence for Innovation in Chemistry (PERCH-CIC), Department of Chemistry, Faculty of Science, Mahasarakham University for the facilities provided.

Declaration of conflicting interests

The authors declared that they have no conflicts of interest in the research, authorship, and this article's publication.

References

- Chopra N.G., Luyken R.J., Cherrey K., Crespi V.H., Cohen M.L., Louie S.G., and Zettl A. Boron nitride nanotubes. *Science*. 1995. 269 : 966-967.

2. Novoselov K.S., Jiang D., Schedin F., Booth T.J., Khotkevich V.V., Morozov S.V., and Geim A.K. Two-dimensional atomic crystals. *P Natl Acad Sci USA*. 2005. 102 : 10451–10453
3. Golberg D., Bando Y., Huang Y., Terao T., Mitome M., Tang C., and Zhi C. Boron Nitride Nanotubes and Nanosheets. *Acs Nano*. 2010. 4 : 2979–2993.
4. Yazyev O.V. and Pasquarello A. Metal adatoms on graphene and hexagonal boron nitride: towards rational design of self-assembly templates. *Phys Rev. B*. 2010. 82 : 045407 – 045412.
5. Noorizadeh S. and Shakerzadeh E. Formaldehyde adsorption on pristine, Al-doped and mono-vacancy defected boron nitride nanosheets: A first principles study. *Comp Mater Sci*. 2012. 56 : 122–130.
6. Phalinyot S., Tabtimsai C., and Wannoo B. Nitrogen monoxide storage and sensing applications of transition metal-doped boron nitride nanotubes: a DFT investigation. *Struct Chem*. 2019. 30 : 2135–2149.
7. Xie Y., Huo Y-P., and Zhang J-M. First-principles study of CO and NO adsorption on transition metals doped (8,0) boron nitride nanotube. *Appl Surf Sci*. 2012. 258 : 6391–6397.
8. Sripadung P., Nunthaboot N., and Wannoo B. DFT investigation of O₂ and PH₃ adsorptions on group 8B metal-doped boron nitride nanotubes. *Sci. & Tech. RMUTT J*. 2018. 8(2) : 53–64.
9. Venkataramanan N.S., Khazaei M., Sahara R., Mizuseki H., and Kawazoe Y. First-principles study of hydrogen storage over Ni and Rh doped BN sheets. *Chem Phys*. 2009. 359 : 173–178.
10. Sripadung P., Nunthaboot N., and Wannoo B. Group 8B transition metal-doped (5,5) boron nitride nanotubes for NH₃ storage and sensing: a theoretical investigation. *Monatsh Chem*. 2019. 150 : 1011–1018.
11. Behmagham F., Vessally E., Massoumi B., Hosseini A., and Edjlali L. A computational study on the SO₂ adsorption by the pristine, Al, and Si doped BN nanosheets. *Superlattice Microst*. 2016. 100 : 350–357.
12. Deng Z-Y., Zhang J-M., and Xu K-W. First-principles study of SO₂ molecule adsorption on the pristine and Mn-doped boron nitride nanotubes. *Appl Surf Sci*. 2015. 347 : 485–490.
13. Al-Sunaidi A. Adsorption of SO₂ and NO₂ on metal-doped boron nitride nanotubes: A computational study. *Comput Theor Chem*. 2016. 1092 : 108–113.
14. Vanalakar S.A., Patil V.L., Harale N.S., Vanalakar S.A., Gang M.G., Kim J.Y., Patil P.S., and Kim J.H. Controlled growth of ZnO nanorod arrays via wet chemical route for NO₂ gas sensor applications, *Sensor Actuat B-Chem*. 2015. 221 : 1195–1201.
15. Lamsal L.N., Martin R.V., van Donkelaar A., Steinbacher M., Celarier E.A., Bucsele E., Dunlea E.J., and Pinto J. P. Ground-level nitrogen dioxide concentrations inferred from the satellite-borne ozone monitoring instrument. *J Geophys Res*. 2008. D16308. 113 : 1–15.
16. Kim J.S., Yoon J.W., Hong Y.J., Kang Y.C., Abdel-Hady F., Wazzan A.A., and Lee J.H. Highly sensitive and selective detection of ppb-level NO₂ using multi-shelled WO₃ yolk-shell spheres. *Sensor Actuat B-Chem*. 2016. 229 : 561–569.
17. Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Montgomery J.A., Vreven T., Kudin K.N., Burant J.C., Millam J.M., Lyengar S. S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G.A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J.E., Hratchian H.P., Cross J. B., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A., Cammi R., Pomell C., Ochterski J. W., Ayala P.Y., Morokuma K., Voth G.A., Salvador P., Dannenberg J.J., Zakrzewski V G., Dapprich S., Daniels A. D., Strain M.C., Farkas O., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Ortiz J., Cui Q., Baboul A.G., Clifford S., Cioslowski J., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R.L., Fox D.J., Keith T., Laham M.A., Peng C.Y., Nanayakkara A., Challacombe M., Gill P.M., Johnson B., Chen W., Wong M.W., Gonzalez C., and Pople J.A, GAUSSIAN 09. Revision A.02, Gaussian Inc., Wallingford, CT, 2009.
18. Lee C., Yang W., and Parr R.G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev. B*. 1988. 37 : 785–789.
19. Becke A.D. Density-functional thermochemistry. III The role of exact exchange. *J Chem Phys*. 1993. 98 : 5648–5652.
20. Becke A.D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys Rev. A*. 1988. 38 : 3098–3100.
21. Hay P.J. and Wadt W.R. *Ab initio* effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J Chem Phys*. 1985. 82 : 270–283.
22. Hay P.J. and Wadt W.R. *Ab initio* effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. *J Chem Phys*. 1985. 82 : 284–298.
23. Hay P.J. and Wadt W.R. *Ab initio* effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbital. *J Chem Phys*. 1985. 82 : 299–310.
24. Bai M.T., Bagheri Z., and Peyghan A.A. Transition metal atom adsorptions on a boron nitride nanocage. *Struct Chem*. 2013. 24 : 1039–1044.

25. Kaewruksa B. and Ruangpornvisuti V. Theoretical study on the adsorption behaviors of H₂O and NH₃ on hydrogen-terminated ZnO nanoclusters and ZnO graphene-like nanosheets. *J Mol Struct.* 2011. 994 : 276–282.
26. Vessally E., Dehbandi B., and Edjlali L. DFT study on the structural and electronic properties of Pt-doped boron nitride nanotubes. *Russ. J Phys Chem A.* 2016. 90 : 1217– 1223.
27. Foster J.P. and Weinhold F. Natural hybrid orbitals natural hybrid orbitals. *J Am Chem Soc.* 1980. 102(24) : 7211–7218.
28. Flükiger P., Lüthi H.P., and Portmann S. MOLEKEL 4.3. Swiss Center for Scientific Computing, Manno, Switzerland, 2000.
29. Almen N., Erni R., Kisielowski C., Rossell M.D., Gannett W., and Zettl A. Atomically thin hexagonal boron nitride probed by ultrahigh-resolution transmission electron microscopy. *Phys Rev. B.* 2009. 80 : 155425–155431.
30. Noorizadeh S. and Shakerzadeh E. Formaldehyde adsorption on pristine, Al-doped and mono-vacancy defected boron nitride nanosheets: A first principles study. *Comp Mater Sci.* 2012. 56 : 122–130.
31. Tabtimsai C., Nonsri A., Grattoo N., Massiri N., Suvanvapee P., and Wannoo B. Carbon monoxide adsorption on carbon atom doped perfect and Stone–Wales defect single-walled boron nitride nanotubes: A DFT investigation. *Monatsh Chem.* 2014. 145 : 725–735.
32. Peyghan A.A., Baei M.T., Moghimi M., and Hashemian S. Phenol adsorption study on pristine, Ga-, and In-doped (4,4) armchair single-walled boron nitride nanotubes. *Comput Theor Chem.* 2012. 997 : 63–69.
33. Oku T. and Narita I. Atomic structures and stabilities of zigzag and armchair-type boron nitride nanotubes studied by high-resolution electron microscopy and molecular mechanics calculation. *Diamond Relat. Mater.* 2004. 13:1254–1260.