

ADSORPTION OF DIBENZOXAZEPINE GAS ON TRANSITION METAL-DOPED SILICON CARBIDE NANOTUBES: A THEORETICAL INVESTIGATION

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Abstract

Dibenzoxazepine (CR) molecule is highly toxic gas, therefore, the development of highly sensitive materials for their adsorption and detection is desirable. Density functional theory (DFT) calculation was performed to study the adsorption behavior of CR gas on the pristine and transition metal (TM=Sc, Ti, Y, Zr, La, and Hf) -doped silicon carbide nanotubes (SiCNT) at both Si and C sites. The most stable adsorption configurations, adsorption distances, adsorption energies, charge transfers, energy gaps, orbital distributions, and density of states are obtained to understand the impacts of CR gas on the adsorption abilities and electronic properties of the pristine and TM-doped SiCNT surfaces. The results show that the pristine SiCNT exhibits low adsorption ability to CR gas. Conversely, the SiCNT doping with TM atom at Si and C sites enhances adsorption ability to CR gas. The strong adsorption of CR gas on TM-doped SiCNT surface is due to more favorable orbital interaction as well as shorter adsorption distance and larger charge transfer than pristine SiCNT. Moreover, the results reveal that the adsorption of CR gas significant changes in the electronic properties of TM-doped SiCNT. Therefore, the doping of TM atoms on SiCNT at both Si and C sites could enhance the adsorption ability and suitable for use as sensors for detecting CR gas.

Keywords: CR gas, Dibenzoxazepine, DFT, Silicon carbide nanotube, Sensor

Introduction

Dibenzoxazepine (dibenz oxazepine) or CR gas is an incapacitating agent and a lachrymatory agent. It is one of the chemical agents for use in war. Considering the toxicity that the CR gas causes intense skin irritation, in particular around moist areas; blepharospasm, causing temporary blindness and coughing, and gasping for breath and panic

(Aleksandrov and Emelyanov, 1990; Wright, 1998; Olajos and Salem, 2001). Therefore, the protection and detection of CR gas release to environmental is needed for controlling and monitoring.

Nanostructures have drawn the undivided attention of researchers as chemical sensors for

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various chemical agents (Gogotsi, 2006). When transition metal is doped on the surfaces of nanostructure, the physical, chemical, and electrical properties of nanostructure will be changed, thus the adsorption ability and sensitivity of nanostructure to gas molecules is increased. For example, the adsorption ability and sensitivity of carbon nanotube (CNT) to CO molecule are increased by Fe doping (Liu *et al.*, 2019). Our study suggests that a highly sensitive and selective gas detection based on TM-doped CNT (Tabtimsai *et al.*, 2019; Tabtimsai *et al.*, 2020). Pd-doped CNT show good performance for detecting H₂CO molecule as sensor (Zhou *et al.*, 2020). Pt-doped CNT could act as a promising adsorbing and sensing for COS gas detection (González F   *et al.*, 2020). Zhao *et al.* found that Sc, Ti, and Mn-doped graphenes show an excellent for NO sensing (Zhao *et al.*, 2018). Theoretical calculation has already found that Fe-doped silicon carbide nanotube (SiCNT) can intrinsically be excellent sensors for detecting O₃, SO₂, and NO₂ gases (Farmanzadeh and Ardehjani, 2018). Therefore, SiCNT is one of the commonly used nanostructures, employed as electronic sensors (Wu *et al.*, 2008; Mahdavi  ar and Abbasi, 2014). It can be potentially applied as a chemical gas sensor due to the significant charge separation between the Si (electron deficient, Lewis acid) and C (electron rich, Lewis base) atoms (Esrafil   and Behzadi, 2013). However, pristine SiCNT has a low sensitivity to chemical agents, which makes it impossible to be used as an appropriate sensor. Therefore, researchers have adopted various different techniques for resolving this problem, such as producing structural defects, functionalizing with chemical groups, and doping or decorating with impurity atoms on the surface of SiCNT for improving the interaction and sensitivity to gas molecule (Gueriba *et al.*, 2017; Ghiassi and Raissi, 2017; Lin *et al.*, 2020; Lin *et al.*, 2021). Various theoretical investigations have been reported about using SiCNT as a gas sensor. For example, Chen and co-workers studied NO₂ adsorbed on Pd-doped SiCNT, the results show that the NO₂ gas can be adsorbed on the surface or inside SiCNT. The Pd-doped SiCNT shows the superior sensing performance in detecting NO₂ (Lin *et al.*, 2021). Ghiassi and Raissi report that the CS₂ gas Pd- and Ni-doped SiCNTs and the electronic properties of Pd- and Ni-doped SiCNTs are changed upon exposure to the CS₂ molecule (Ghiassi and Raissi, 2017). Gueriba *et al.*, show that the Ca decorated SiCNT can hold up to 7 hydrogen molecules and can be a promising candidate for a hydrogen storage material (Gueriba *et al.*, 2017). Lin and co-workers

studied the adsorption of SO₂ gas on the pristine and P-doped SiCNTs, the obtained results indicate that SO₂ gas display physisorbed and chemisorbed on pristine and P-doped SiCNTs, respectively (Lin *et al.*, 2020). However, there is still no studied on the sensing properties of SiCNT doping with Sc, Ti, Y, Zr, La, or Hf atom to CR gas. Therefore, the doping of a TM atom is an efficient way to improve significantly their chemical stability and sensitivity of SiCNT to CR gas by using the density functional theory (DFT) calculation on structural property, adsorption energy, and electronic property.

Computational Details

The simulation processes of all calculations were performed using GAUSSIAN 09 program (Frisch *et al.*, 2009). The hybrid density functional theory (DFT) with Becke's three parameter exchange functional with the Lee-Yang-Parr correlation functional (B3LYP) (Becke, 1993; Becke, 1998), and the LanL2DZ (Los Alamos National Laboratory 2-Double-Zeta) split- valence basis set (Hay and Wadt, 1985; Wadt and Hay, 1985) were used in calculations. This basis set is used for atoms having large nuclei and where electrons around the nucleus are approximated via effective core potentials. Based on previous studies, LanL2DZ is used for nanostructures and it exhibits high performance in the field (Demir and Fellah, 2020; Gecim and Ozekmekci, 2021; Verma and Jaggi, 2022). The SiCNT model consisting of 39 Si, 39 C and 20 H atoms was modeled and used. Both ends of the tube were saturated by H atoms to avoid the boundary effects. The Si (TM_{Si}-SiCNT) and C (TM_C-SiCNT) atoms of pristine SiCNTs were replaced with Sc, Ti, Y, Zr, La, and Hf atoms (Figure 1. shows top and side views of Ti_{Si}- and Ti_C-SiCNT). Therefore, the adsorption of CR gas was expected to be the doping or active site. Two difference orientations N (CR(N)/SiCNT) and O (CR(O)/SiCNT) atoms of CR gas pointing to tube surface were considered. The change of energy gap (ΔE_{gap}), plot of HOMO, plot of LUMO, partial charge transfers (PCT), and density of states (DOS) were investigated and reported. Adsorption energy (E_{ads}) is defined as:

$$E_{\text{ads}} = E_{\text{CR/SiCNT}} - (E_{\text{SiCNT}} + E_{\text{CR}}) \quad (1)$$

where $E_{\text{CR/SiCNT}}$, E_{SiCNT} and E_{CR} are the total energy of the CR gas adsorbed on SiCNT, the total energy of SiCNTs and the total energy of isolated CR molecule.

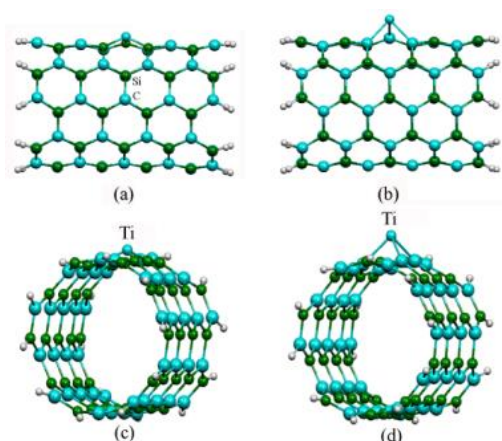


Figure 1. Optimization structures of (a) and (c) Tis-SiCNT and (b) and (d) Tic-SiCNT.

Results and Discussion

Geometrical structures

The optimization structures of CR gas adsorption on pristine and TM-doped SiCNTs are displayed in Figures 2-4, respectively. The averages Si-C bond lengths nearly the adsorption site of CR(N)/SiCNT and CR(O)/SiCNT are 1.852 and 1.804 Å, respectively. These values indicate that the bond length of bare SiCNT (1.806-1.807 Å) is slightly changed. The TM-Si (TM-C) bond lengths of all CR/TM-SiCNTs are elongated to 1.965 - 2.551 Å during the adsorption process. The value is larger than that of bare TM-doped SiCNT and the results are in good agreement with toluene adsorbed on TM-doped SiCNT (Sangnikul, 2020). Thus, the adsorption of TM-doped SiCNT to CR gas shows stronger interaction than pristine SiCNT.

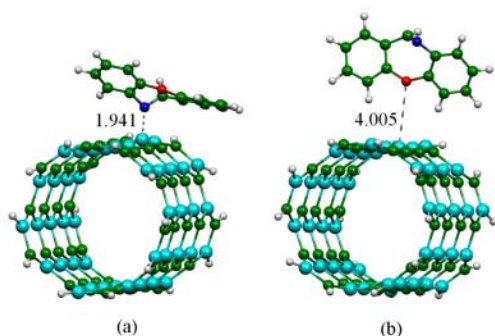


Figure 2. Optimized structures of (a) CR(N)/ SiCNT and (b) CR(O)/SiCNT.

The adsorption distances (AD) are defined as the nearest atom of CR gas and the SiCNT surfaces (see Figures 2-4). The adsorption distance of CR(N)/SiCNT (1.941 Å) is clearly shorter than CR(O)/SiCNT (4.005 Å). For TM_{Si}-SiCNT systems, the adsorption distances of CR(N)/TM_{Si}-SiCNT (1.949-2.768 Å) are shorter than CR(O)/SiCNT (2.193-2.807 Å). Whereas TM_C-SiCNT systems, the adsorption distances of CR(N)/TM_C-SiCNT (1.878-2.514 Å) are also shorter than CR(O)/TM_C-SiCNT (2.099-2.715 Å), suggest that when N atom of CR gas pointing to SiCNT surfaces, the adsorption strength is larger than that of O atom.

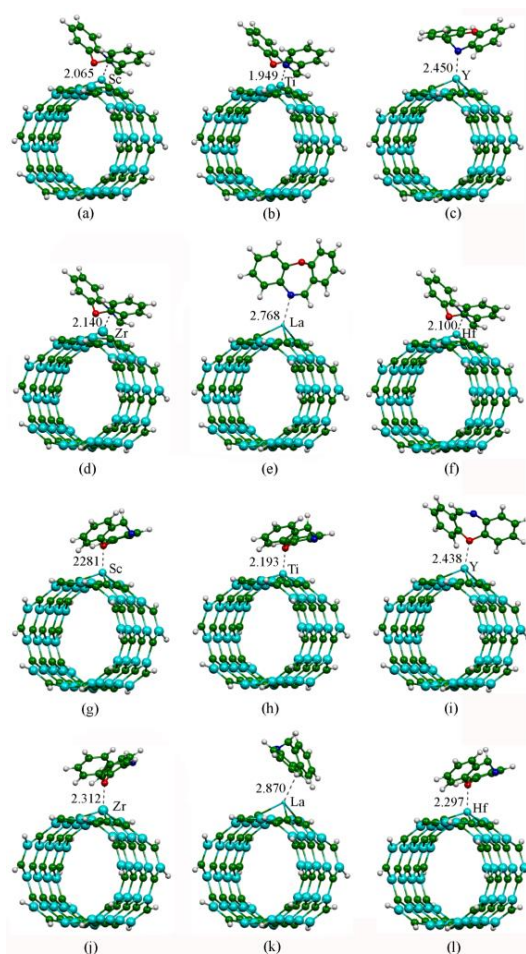


Figure 3. Optimized structures of (a) - (f) CR(N)/TM_{Si}-SiCNTs and (g) - (l) CR(O)/TM_{Si}-SiCNTs.

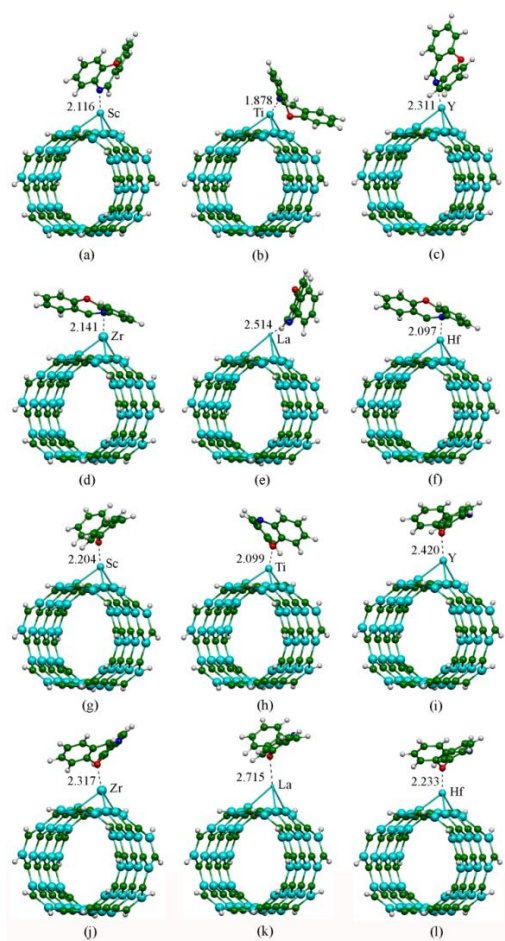


Figure 4. Optimized structures of (a) - (f) CR(N)/TM_C-SiCNTs and (g) - (l) CR(O)/TM_C-SiCNTs.

Adsorption energies

To enhance the adsorption ability of SiCNTs for CR gas, the performance of pristine and TM-doped SiCNTs was thoroughly investigated by taking advantage of DFT calculations. The adsorption energies (E_{ads}) of the CR gas adsorbed on pristine and TM-doped SiCNTs are listed in Table 1. The adsorption energies of CR(N)/SiCNT and CR(O)/SiCNT are -20.27 and -1.25 kcal/mol, respectively. For the CR/TM_{Si}-SiCNT systems, the adsorption energy values of CR(N)/TM_{Si}-SiCNTs are larger than CR(O)/TM_{Si}-SiCNTs (except for Y_{Si}- and Zr_{Si}-SiCNTs) which the adsorption abilities of TM_{Si}-SiCNT to CR gas are in order CR(N)/Ti_{Si}-SiCNT > CR(N)/Hf_{Si}-SiCNT > CR(N)/Sc_{Si}-SiCNT > CR(N)/La_{Si}-SiCNT and CR(O)/Ti_{Si}-SiCNT > CR(O)/Hf_{Si}-SiCNT > CR(O)/Sc_{Si}-SiCNT > CR(O)/Zr_{Si}-SiCNT > CR(O)/Y_{Si}-SiCNT > CR(O)/La_{Si}-SiCNT. Whereas, the adsorption energy values of CR(N)/TM_C-SiCNTs are also larger than

CR(O)/TM_C-SiCNTs which the adsorption abilities of TM_C-SiCNTs to CR gas are in order CR(N)/Ti_{Si}-SiCNT > CR(N)/Hf_{Si}-SiCNT > CR(N)/Zr_{Si}-SiCNT > CR(N)/Sc_{Si}-SiCNT > CR(N)/Y_{Si}-SiCNT > CR(N)/La_{Si}-SiCNT and CR(O)/Ti_{Si}-SiCNT > CR(O)/Hf_{Si}-SiCNT > CR(O)/Sc_{Si}-SiCNT > CR(O)/Zr_{Si}-SiCNT > CR(O)/Y_{Si}-SiCNT > CR(O)/La_{Si}-SiCNT. These confirm that the TM doping could improve the adsorption ability of SiCNT to CR gas which is in good accordance with previous theoretical calculation result for NO₂/Pd-SiCNT (Lin *et al.*, 2021), CS₂/Ni-SiCNT (Ghiassi and Raissi, 2017), CS₂/Pd-SiCNT (Ghiassi and Raissi, 2017), H₂CO/Fe-SiCNT (Roohi and Ardehijani, 2021), H₂CO/Ni-SiCNT (Roohi and Ardehijani, 2021), H₂CO/Cr-SiCNT (Roohi and Ardehijani, 2021), and H₂CO/Zn-SiCNT (Roohi and Ardehijani, 2021). The Ti-doped SiCNT displays the strongest interaction with CR gas, which is consistent with Ti-doped single wall carbon nanotube (SWCNT) exhibited the higher stability and sensitivity to NO₂ gas than Cu- and Pt-SWCNTs (Sharafeldin and Allam, 2017). The protruding on the TM-doped SiCNT surface can reduce steric effect of the tube surface, resulting in the increasing of adsorption ability. The shorter adsorption distances and higher charge transfer (excepting the CR(N)/SiCNT), all emphasize the stronger interaction strength between CR gas and TM-doped SiCNTs compared with pristine SiCNT. The adsorption abilities of TM_C-SiCNTs to CR gas are more stable than TM_{Si}-SiCNTs maybe due to TM_{Si}-SiCNTs are more stable than TM_C-SiCNTs (Roohi and Ardehijani, 2021). The adsorption ability of SiCNT to CR(N) is larger than CR(O) maybe the steric of O site is more than N site.

Moreover, the results indicate that when N atom of CR gas was closed to tube surface, the absolute adsorption energy values have higher than O atom. Base on the Pearson hard-soft acid-base (HSAB) concept, TM atom is soft atoms, in which C atom is soft atom whereas O atom is hard atom. Then TM atoms are more favorite C atom than that of O atom (Pearson, 1963). The TM_C-doped SiCNTs display stronger interaction with CR gas than the TM_{Si}-doped SiCNTs. This may be due to TM_{Si}-doped SiCNT displays higher stable than TM_C-SiCNT. The result good agrees with NO₂ adsorbed on P-doped SiCNT of previously theoretical calculation (Lin *et al.*, 2021).

Electronic property

To explore the effect of CR adsorption on the electronic properties of SiCNTs, the ΔE_g , PCTs, and plots of HOMO-LUMO distributions were analyzed. The results show that when CR gas

adsorbed on SiCNT, the energy gap of pristine (2.775 eV), Sc_{Si}- (0.762 eV), Ti_{Si}- (2.531 eV), Y_{Si}- (0.789 eV), Zr_{Si}- (2.531 eV), La_{Si}- (0.735 eV), Hf_{Si}- (2.395 eV), Sc_C- (1.170 eV), Ti_C- (1.605 eV), Y_C- (1.034 eV), Zr_C- (1.361 eV), La_C- (1.061 eV), and Hf_C-SiCNTs (1.524 eV) is changed to 1.197 (N) or 2.748 (O), 0.789 (N) or 0.870 (O), 2.667 (N) or 2.313 (O), 0.925 (O and N), 2.612 (N) or 2.068 (O), 0.598 (N) or 0.925 (O), 2.612 (N) or 1.687 (O), 1.143 (O and N), 1.987 (N) or 1.551 (O), 0.082 (N) or 0.980 (O), 1.850 (O) or 1.415 (O), 0.980 (N) or 0.979 (O), and 1.878 (N) or 1.415 (O) eV, respectively and the changes of energy gap (ΔE_g) due to CR adsorption are listed in Table 1. In comparison the energy gap of SiCNTs with and without CR adsorption, the energy gap is changed due to CR adsorption and electrical conductance is also changed. Herein, CR gas modifies the electronic energy levels of SiCNT and improves the interaction with CR gas near to the doping site. Therefore, it is possible to assume that the SiCNTs will have a considerable sensitivity toward CR gas. Roohi and Ardehjani reported that when comparison with bare SiCNT, the energy gap and electrical conductance changes due to H₂CO adsorption (Roohi and Ardehjani, 2021). The change in the energy gap of pristine SiCNT is predicted similarly to TM-doped SiCNT in which the Hf_{Si}-SiCNT displays the largest change ($\Delta E_g = 0.708$ eV). Therefore, the Hf_{Si}-SiCNT is predicted to be more sensitive than other systems.

The PCTs analyzed from natural bond orbital calculation were defined as the change of total charge of CR molecule after adsorption on SiCNT as shown in Table 1. The charges are transferred between CR gas and SiCNT in which larger charge between CR gas and TM-doped SiCNT than pristine SiCNT. In addition, for CR(O)/TM_{Si}-SiCNT, CR(N)/TM_{Si}-SiCNT, and CR(O)/TM_C-SiCNT, charges are transferred from CR gas to tube, which may account for the positive charge of TM atom. Whereas CR(N)/TM_C-SiCNT system, charges are transfer from tube to CR molecule. Therefore, CR(N)/TM_C-SiCNT system has isolated electron depletion at Si and TM atoms indicating their electron-donating behaviors. Moreover, PCT values between CR gas and TM-SiCNT are higher than pristine SiCNT, there is TM atom induced the interaction between them. Therefore, large charge transfer proves the strong interaction between CR and TM-SiCNT.

The HOMO and LUMO orbital distributions of CR gas adsorbed on pristine and Ti_C-doped SiCNTs are shown in Figure 5. The HOMO of

pristine and Ti_C-doped SiCNTs are located in tube surface. The LUMO orbitals of pristine SiCNT are located in CR gas whereas the LUMO orbitals of Ti_C-doped SiCNT are evenly located in the doping site indicating the electron redistribution and interaction of TM atom and CR gas are occurred. These results confirm that the CR gas is successfully adsorbed on SiCNT.

Table 1. Adsorption energies (E_{ads}), change of energy gap (ΔE_g) and partial charge transfer (PCT) of CR gas adsorbed on SiCNT.

Systems	E_{ads} (kcal/mol)	ΔE_g (eV) ^a	PCT (e) ^b
CR(N)	-20.27	1.578	0.131
CR(O)	-1.25	0.027	0.003
CR(N)/Sc _{Si}	-72.04	0.027	1.427
CR(O)/Sc _{Si}	-20.90	0.108	1.338
CR(N)/Ti _{Si}	-79.07	0.136	0.874
CR(O)/Ti _{Si}	-21.33	0.218	0.848
CR(N)/Y _{Si}	-31.85	0.136	1.869
CR(O)/Y _{Si}	-66.99	0.136	1.872
CR(N)/Zr _{Si}	-70.54	0.081	1.707
CR(O)/Zr _{Si}	-71.74	0.463	1.556
CR(N)/La _{Si}	-63.85	0.137	-
CR(O)/La _{Si}	-14.39	0.190	-
CR(N)/Hf _{Si}	-77.02	0.217	1.905
CR(O)/Hf _{Si}	-26.79	0.708	1.762
CR(N)/Sc _C	-84.88	0.027	-0.222
CR(O)/Sc _C	-73.93	0.027	0.480
CR(N)/Ti _C	-98.54	0.382	-0.412
CR(O)/Ti _C	-76.80	0.054	0.171
CR(N)/Y _C	-79.54	0.381	-0.404
CR(O)/Y _C	-68.45	0.054	0.110
CR(N)/Zr _C	-88.57	0.489	-0.392
CR(O)/Zr _C	-70.26	0.054	0.426
CR(N)/La _C	-72.44	0.081	-
CR(O)/La _C	-60.27	0.082	-
CR(N)/Hf _C	-94.84	0.345	-0.482
CR(O)/Hf _C	-75.68	0.109	0.146

^a ΔE_g is defined as $E_{g(CR/SiCNT)} - E_{g(SiCNT)}$.

^b PCT is defined as $Q_{CR/SiCNT} - Q_{freeCR}$.

^c Unconvergence.

Finally, the DOSs of CR/Ti-SiCNTs were calculated and displayed in Figure 6. The results show that the DOSs of Ti-SiCNT are significant changed after CR adsorption. It can be seen that new peaks appear at -3.5 to -2.5 eV of energy level for Ti_C-doped SiCNT system. These may be due to the hybridization between 3d-orbitals of the TM atoms and p-orbitals of N or O atom of CR gas. The results confirm that CR gas shows more clearly sensible effect to electronic properties of TM-doped SiCNT which were beneficial for sensing applications.

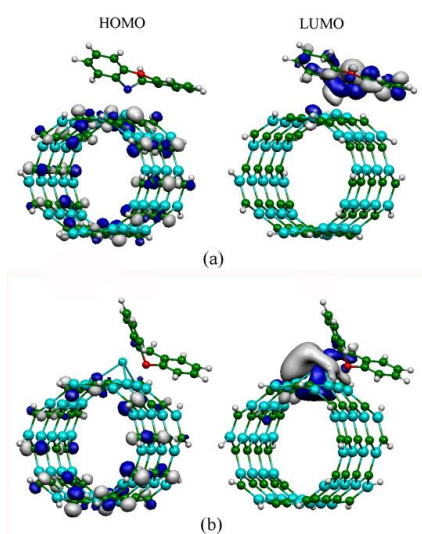


Figure 5. Plots of HOMO-LUMO of (a) CR(N)/SiCNT and (b) CR(N)/TiC-SiCNT.

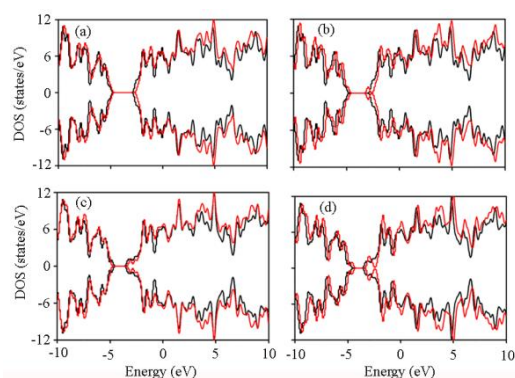


Figure 6. Plots of DOS of (a) CR(N)/TiSi-SiCNT, (b) CR(O)/TiSi-SiCNT, (c) CR(N)/TiC-SiCNT, and (d) CR(O)/TiC-SiCNT, respectively. Black and red lines are before and after CR adsorption, respectively.

Conclusions

Due to dibenzoxazepine molecule is highly toxic gas, thus, the development of highly sensitive materials for its adsorption and detection is desirable. The adsorption behaviors of CR gas on the pristine and transition metal (TM=Sc, Ti, Y, Zr, La, and Hf) -doped silicon carbide nanotubes at both Si and C sites were investigated theoretically based on density functional theory. The most stable adsorption configurations, adsorption distances, adsorption energies, charge transfers, energy gaps, orbital distribution, and density of states are obtained to understand the impacts of CR gas on

the adsorption abilities and electronic properties of the pristine and TM-doped SiCNT surfaces. The results show that the pristine SiCNT exhibits low adsorption ability to CR gas. However, it is found that the SiCNT doping with TM atom at Si and C sites enhance adsorption ability to CR gas which CR gas displays the strongest interaction with TiC-doped SiCNT. The N atom of CR gas closed to tube surface shows more adsorption ability than O atom. The TM_C-doped SiCNTs display stronger interaction with CR gas than the TM_{Si}-doped SiCNTs. The strong adsorption of CR gas on TM-doped SiCNT surfaces is due to more favorable orbital interaction as well as larger charge transfer than pristine SiCNT. Moreover, the results reveal that the adsorption of CR gas significant changes in the energy gaps and density of states of TM-doped SiCNT. Therefore, the doping of TM atoms on SiCNT at Si and C sites could enhance the adsorption ability and suitable for use as CR gas sensors.

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References

- Aleksandrov V.N., and Emelyanov V.I. (1990). Poisonous Substances. G.A. Sokolskiy, ed. Moscow.
- Becke, A.D. (1993). Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.*, 98:5,648-5,652. <https://doi.org/10.1063/1.464913>
- Becke, A.D. (1998). Density-functional exchange-energy approximation with correct a asymptotic behavior. *Phys. Rev. A*, 38:3,098-3,100.
- Demir, S., and Fellah M.F. (2020). A DFT study on Pt doped (4,0) SWCNT: CO adsorption and sensing. *Appl. Surf. Sci.*, 504:144,141. <https://doi.org/10.1016/j.apsusc.2019.144141>
- Esfarili, M.D., and Behzadi, H. (2013). A comparative study on carbon, boron-nitride, boron-phosphide and silicon-carbide nanotubes based on surface electrostatic potentials and average local ionization energies. *J. Mol. Model.*, 19: 2,375-2,382. <https://doi.org/10.1007/s00894-013-1787-y>
- Farmanzadeh, D., and Ardehjani, N.A. (2018). Adsorption of O₃, SO₂ and NO₂ molecules on the surface of pure and Fe-doped silicon carbide nanosheets: A computational study, *Appl. Surf. Sci.*, 462:685-692. <https://doi.org/10.1016/j.apsusc.2018.08.150>

- Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V.; Mennucci, B., Petersson, G.A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H.P., Izmaylov, A.F., Bloino, J., Zheng, G., Sonnenberg, J.L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A., Peralta, Jr., J.E., Ogliaro, F., Bearpark, M., Heyd, J.J., Brothers, E., Kudin, K.N., Staroverov, V.N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Rega, N., Millam, J.M., Klene, M., Knox, J.E., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Martin, R.L., Morokuma, K., Zakrzewski, V.G., GVoith, A., Salvador, P., Dannenberg, J.J., Dapprich, S., Daniels, A.D., Farkas, Ö., Foresman, J.B., Ortiz, J.V., Cioslowski, J., and Fox, D.J. (2009). GAUSSIAN 09, Revision A.02, GaussianInc, Wallingford CT.
- Gecim, G., and Ozekmekci, M. (2021). A density functional theory study of molecular H₂S adsorption on (4,0) SWCNT doped with Ge, Ga and B. *Surf. Sci.*, 711:121876. <https://doi.org/10.1016/j.susc.2021.121876>
- Ghiassi, H., and Raissi, H. (2017). Doped-SiCNT as a promising sensor for detection of CS₂ molecule. *J. Sulphur Chem.*, 38:372-383. <https://doi.org/10.1080/17415993.2017.1302449>
- Gogotsi, Y. (Ed.). (2006). *Nanomaterials Handbook* (1st ed.). CRC Press, 776. <https://doi.org/10.1201/9781420004014>
- González FÁ, A.J., Orazi, V., Jasen, P., Marchetti, J.M. and López-Corral, I. (2020). Adsorption of carbonyl sulfide on Pt-doped vacancy-defected SWCNT: A DFT study, *Appl. Surf. Sci.*, 525:146,331. <https://doi.org/10.1016/j.apsusc.2020.146331>
- Hay, P.J., and Wadt, W.R. (1985). Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J. Chem. Phys.*, 82:270-283. <https://doi.org/10.1063/1.448799>
- Gueriba, J.S., Padama, A.A.B., Villagracia, A.R., David, M., Arboleda Jr. N., and Kasai, H. (2017). Ab initio study on hydrogen interaction with calcium decorated silicon carbide nanotube. *Int. J. Hydrog. Energy*, 42:11,452-11,460. <https://doi.org/10.1016/j.ijhydene.2017.03.057>
- Lin, W.Q., Li, F., Chen, G.H., Xiao, S.T., Wang, L.Y., and Wang, Q. (2020). A study on the adsorptions of SO₂ on pristine and phosphorus-doped silicon carbide nanotubes as potential gas sensors. *Ceram. Int.*, 46:25,171-25,188. <https://doi.org/10.1016/j.ceramint.2020.06.307>
- Lin, W.Q., Xiao, S.T., Li, H.B., Ouyang, Y.G., Wang, L.Y., Wang, Q., and Chen, G.H. (2021). Theoretical study of NO₂ adsorption on SiCNT and P-doped SiCNT, *Physica E Low Dimens. Syst. Nanostruct.*, 127:114519. <https://doi.org/10.1016/j.physe.2020.114519>
- Liu, Y., Zhang, H., Zhang, Z., Jia, X., An, L. (2019). CO adsorption on Fe-doped vacancy-defected CNTs-A DFT study. *Chem. Phys. Lett.*, 730:316-320. <https://doi.org/10.1016/j.cplett.2019.06.013>
- MahdaviFar, Z., and Abbasi, N. (2014). The influence of Cu-doping on aluminum nitride, silicon carbide and boron nitride nanotubes' ability to detect carbon dioxide; DFT study. *Physica E Low Dimens. Syst. Nanostruct.*, 56:268-276. <https://doi.org/10.1016/j.physe.2013.09.008>
- Olajos, E.J., and Salem, H. (2001). Riot control agents: Pharmacology, toxicology, biochemistry and chemistry. *J. Appl. Toxicol.*, 21:355-391. <https://doi.org/10.1002/jat.767>
- Pearson, R.G. (1963). Hard and soft acids and bases. *J. Am. Chem. Soc.*, 85(22):3,533-3,539. <https://doi.org/10.1021/ja00905a001>
- Roohi, H., and Ardehjani, N.A. (2021). Adsorption performance of TM doped (TM = Fe, Ni, Cr and Zn) silicon carbide nanotubes towards formaldehyde: a DFT-M06-L study. *Mol. Phys.*, 120. <https://doi.org/10.1080/00268976.2021.2006351>
- Sangnikul, P., Tabtimsai, C., Rakrai, W., and Wanno, B. (2020). DFT investigation of toluene adsorption on silicon carbide nanosheet doping with transition metal for storage and sensor application. *Suan Sunandha Sci. Tech.*, 7:14-21.
- Sharafeldin, I.M., and Allam, N.K. (2017). DFT insights into the electronic properties and adsorption of NO₂ on metal-doped carbon nanotubes for gas sensing applications, *New J. Chem.*, 41:14,936-14,944. <https://doi.org/10.1039/C7NJ03109B>
- Tabtimsai, C., Wanno, B., Utairueng, A., Promchamorn, P., and Kumsuwan, U. (2019). First principles investigation of NH₃ and NO₂ adsorption on transition metal-doped single-walled carbon nanotubes. *J. Electron. Mater.*, 48:7,226-7,238. <https://doi.org/10.1007/s11664-019-07537-4>
- Tabtimsai, C., Rakrai, W., Phalinyot, S., Wanno, B. (2020). Interaction investigation of single and multiple carbon monoxide molecules with Fe-, Ru-, and Os-doped single-walled carbon nanotubes by DFT study: applications to gas adsorption and detection nanomaterials. *J. Mol. Model.*, 26:186. <https://doi.org/10.1007/s00894-020-04457-7>
- Verma, R., and Jaggi, N. (2022) Hydrogen adsorption on osmium and boron co-doped single walled carbon nanotubes for energy storage: A DFT study. *Diam. Relat. Mater.*, 130:109,452. <https://doi.org/10.1016/j.diamond.2022.109452>
- Wadt, W.R., and Hay, P.J. (1985). Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi, *J. Chem. Phys.*, 82:284-298. <https://doi.org/10.1063/1.448800>
- Wright, S. (1998). An appraisal of technologies of political control. The STOA Programme, Directorate General for Research, European Parliament, Luxembourg.
- Wu, R.Q., Yang, M., Lu, H.Y., Feng, Y.P., Huang, Z.G., and Wu, Q.Y. (2008). Silicon carbide nanotubes as potential gas sensors for CO and HCN detection. *J. Phys. Chem. C*, 112:15,985-15,989. <https://doi.org/10.1021/jp804727c>
- Zhao, D., Fan, X., Luo, Z., An, Y., and Hu, Y. (2018). Enhanced gas-sensing performance of graphene by doping transition metal atoms: A first-principles study. *Phys. Lett. A*, 382:2,965-2,973. <https://doi.org/10.1016/j.physleta.2018.06.046>
- Zhou, X., Zhao, C., Chen, C., Chen, J., and Li, Y. (2020). DFT study on adsorption of formaldehyde on pure, Pd-doped, Si-doped single-walled carbon nanotube. *Appl. Surf. Sci.*, 525:146,595. <https://doi.org/10.1016/j.apsusc.2020.146595>