

# COMPARATIVE STUDY OF ADSORPTION OF OZONE MOLECULE ON PRISTINE AND SI DOPED SINGLE WALL CARBON NANOTUBE BY DENSITY FUNCTIONAL THEORY

R.G. Atram, M.R. Sonawane\*

<sup>1</sup>Government Institute of Science, Nagpur 440001, India

\*e-mail: smahadev123@gmail.com

**Abstract.** We report comparative study of ozone adsorption on pristine Single Walled Carbon Nanotube (SWCNT) (8, 0) and Silicon doped Single walled Carbon Nanotube (Si – SWCNT) by density functional theory calculations based on DeMol3 code. Importance is given to the effects of silicon doping in carbon nanotube for comparative study of adsorption of ozone. The results show that silicon doping keeps the semiconducting character of pure carbon nanotubes with reduction in band gap from 0.71 eV to 0.54 eV. The ozone gas molecule is physisorbed with binding energy 0.431eV and minute charge transfer of 0.013 e from pure carbon nanotube, consistent with the strong oxidizing nature of ozone. The binding energy and charge transfer indicate that the ozone adsorption on pure carbon nanotube is gentle and reversible. However, when ozone adsorbs on silicon doped carbon nanotube, a strong chemisorption occurs, leading to relevant structural relaxations and to the formation of a Si-O  $\sigma$  bond with binding energy 3.902 eV and charge transfer of 0.252 e. The band structure and density of states shows that the occupancy state in valence band near Fermi energy is completely altered due to ozone adsorption. The charge density analysis also shows formation of sigma bond between silicon and oxygen atoms. The charge density iso-surface shows the oxidation of silicon atom and dissociation of ozone molecule into silicon - oxide and releasing of oxygen molecule.

**Keywords:** CNT, Si-CNT, DFT, ozone, adsorption

## 1. Introduction

Carbon nanotubes (CNT) [1] have been intensively studied due to their unique geometrical, mechanical [2], chemical [3] and electrical [4] properties. Their electronic properties can vary from semiconducting to metallic depending on its molecular structure. The latest research efforts have aimed to improve both efficiency and selectivity of nanotube. More attention has been given, experimentally as well as theoretically to study electronic, thermal properties and their chemical reactivity [5–7]. These outstanding properties exhibited by carbon nanotubes have been made it suitable for applications in nanoelectronics [8], catalysis [9,10], sensors [11,12], energy capacitors and hydrogen storage devices [13].

To achieve the enviable results, many research works have been done on the characterization of nanotube, for example, the modification for the properties of nanotube by adsorption of atoms, molecules or clusters on the exterior walls of carbon nanotubes or by insertion of these species into their hollow interior. This offers a promising way in the design of new nanomaterials [14–16]. Furthermore, carbon nanotubes were exposed to several different gas molecules such as NO<sub>2</sub>, O<sub>2</sub>, and NH<sub>3</sub> [17,18] and observed the change in the electrical resistance. They have also shown that these molecules are weakly adsorbed on pure CNT due

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to van der Waal interactions. To improve the functionalization, many research groups are now using chemical doping, local defects, radial deformation and metal assistance [19,20]. The metal assistance is an effective way to functionalize the carbon nanotubes which significantly improves the structural and electronic properties.

Ozone interaction with carbon nanotubes has been studied experimentally [21-23] and theoretically [24,25]. More recently, it has been observed that ozone can react with the surface at defect sites [26]. It can also attack the more reactive end cap, opening it up and making it possible for the physical adsorption of other gases [27]. Ozonolysis can oxidize carbon-carbon double bonds of CNT. It is also observed that ozone exposure induces p-type doping and correspondingly reduces resistance in CNTs. [22,23]. Theoretical studies have shown that the binding energy of ozone on CNT is near about 0.3 eV depending on geometrical variation [22-25]. Since the binding energy was too small to explain ozone exposure effect on the CNT resistance. It was shown that some defects sites would be responsible for the ozone adsorption and the corresponding resistance change [22]. However, side wall defects are generally hard to detect experimentally. It was noticed that carbon nanotubes becoming gradually thicker could be attributed to a large number of defects accidentally, thus resulting in a diameter increase [28]. All above literature survey indicates that the understanding on the ozone interaction with CNT is not well established till today. Latest theoretical investigation shows that the Ozone can react chemically on (6, 6) and (8, 8) carbon nanotube but with less binding energy [29].

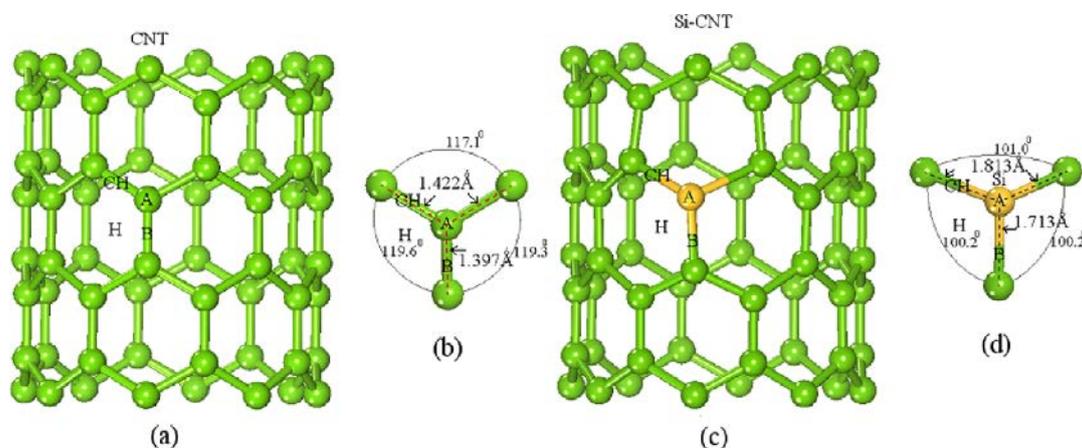
Despite these important contributions, the detailed adsorption mechanism of ozone on the CNTs is still less known and to the best of our knowledge; there is no report on the interaction of ozone molecules on Silicon doped carbon nanotube (Si-CNT). Here we performed extensive DFT calculations and studied the interactions of ozone with the semiconducting CNT and Si-CNT using electronic properties like binding energy, band structure, density of states and population analysis and compared adsorption nature on CNT and Si-CNT.

## 2. Computational Details

Calculations were performed using an all-electron linear combination of atomic orbital density functional theory (DFT) approach, implemented in DMol<sup>3</sup> [30,31] code within the generalized gradient approximation (GGA) and with the Perdew, Burke and Ernzerhof (PBE) correlation functional [32]. The chosen basis set was double numerical plus polarization (DNP), where each basis function was restricted to a global cut-off radius of 4.0 Å. The chosen cut-off value leads to atomic energies with an accuracy of 0.1 eV/atom, allowing calculations without significant loss of accuracy. The Brillouin zone k-point sampling was performed in a 1 x 1 x 2 Monkhorst–Pack mesh [33]. The all calculations were performed using periodic boundary conditions with 64-atoms within the supercell. The tetragonal unit cell of 20 x 20 x 8.4 Å dimension with lateral separation of 13.7 Å between tubes was used. This separation is sufficiently large to avoid interaction between the neighboring cells. The Mulliken population analysis was carried out to predict the charge transfer between molecule and nanotubes.

In this study, we used an (8, 0) zigzag CNT and Si-CNT of diameter 6.26 Å as a model to study the adsorption of ozone molecule. We have examined four different possible adsorption sites such as 'target C atom \ Si atom', 'chiral bond', 'axial bond' and 'centroid of hexagon' of CNTs. In all calculations, the nanotubes and isolated ozone molecule were first optimized to minimize their total energies. Further, ozone molecule is kept at four different adsorption sites as mentioned above on each of these individual nanotubes and optimized together to get lowest energy stable structure. The binding energy ( $E_b$ ) of all ground state structures are calculated by  $E_b = - [E_T (\text{adsorbent} + \text{adsorbate}) - E_T (\text{adsorbent}) - E_T (\text{adsorbate})]$ , where

$E_{T(\text{adsorbent} + \text{adsorbate})}$  denotes the total energy of molecule and CNT system,  $E_{T(\text{adsorbent})}$  denotes the total energy of CNT and  $E_{T(\text{adsorbate})}$  is the total energy of isolated gas molecule. To verify the computational accuracy of the model, we have calculated the binding energy of CNTs, density of states and the band gap which are comparable to reported results [34,35].

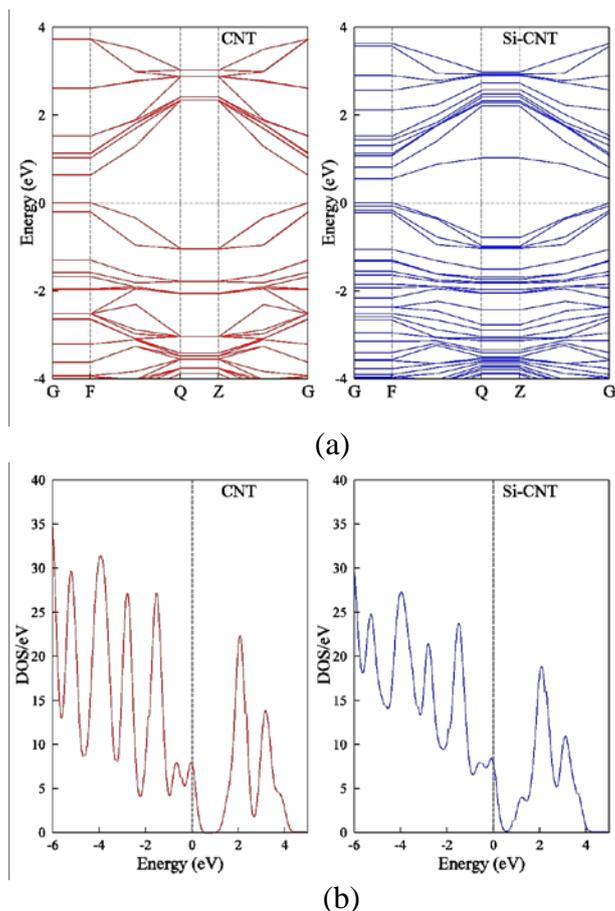


**Fig. 1.** (a) Ground state geometry of (8, 0) CNT. (b) Structural parameters at target atom. (c) Ground state geometry of (8, 0) Si-CNT. (d) Structural parameters at dopant. The green and yellow color represent carbon and silicon atom

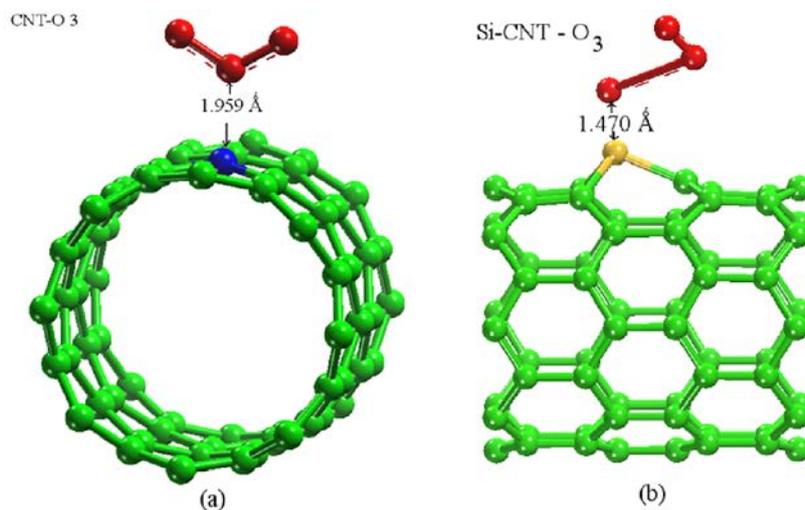
### 3. Results and Discussion

**Structural Properties of CNT and Si-CNT.** The optimized ground state geometry of pure CNT is shown in Fig. 1 (a) along with geometrical parameters in Fig. 1 (b). The bond angles between C–C bonds are found to be less than  $120^\circ$  which indicates trigonal structure of bonding and prefers  $sp^2$  hybridization. The stable structure of Si-CNT is shown in Fig. 1 (c) whereas change structural parameter due to doping of silicon atom is shown in Fig. 1 (d). The bond angles between (C-Si-C) bonds for all three combinations are less than  $109^\circ$ , which indicate tetrahedral structure of bonding and prefer  $sp^3$  hybridization. All structural parameters of our result for CNT and Si-CNT are reported in our previous work found to be in good agreement with reported results [34,35]. The structural deformation produced by silicon doping results into a significant change in electronic properties like binding energy, band gap, density of states, charge density and charge transfer.

**Electronic Properties of CNT and Si-CNT.** The band structure of CNT and Si-CNT are shown in Fig. 2 (a). The doping of silicon atom creates an extra unoccupied energy state at 1.26 eV in the conduction band as observed in plot of band-structure. The additional state reduces the band gap of Si-CNT to 0.54 eV as compared to band gap of pure CNT. The DOS of CNT and Si-CNT are shown in Fig. 2 (b). The DOS analysis also shows same unoccupied state below the conduction band. Such an unoccupied state act as donor like impurity and which plays significant role of capturing center for atoms or molecules. Further, Mulliken Population analysis shows silicon atom acquires positive charge of magnitude 0.0815 e. This clears that the charge is transferred from the silicon to the vicinity carbon atoms. Such charge polarization at dopant site (silicon atom) acts as an affinity center for chemisorption of the molecules or atom. Thus, the doping of the silicon atom increases the p-type conductivity of the CNT and which improves the reactivity of CNT.



**Fig. 2.** (a) Band structure plot of CNT and Si-CNT. (b) Density of state of CNT and Si-CNT. The Fermi level is indicated by dotted black line

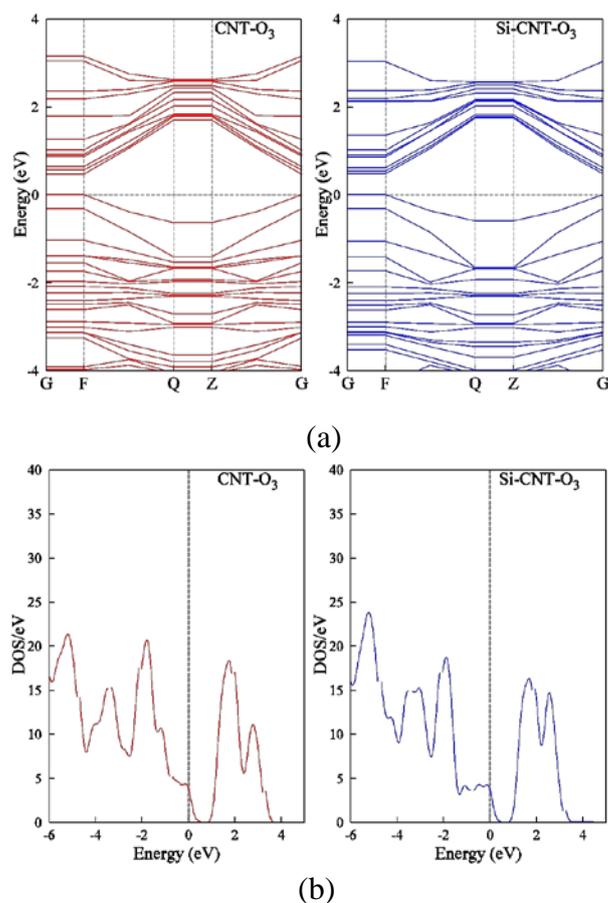


**Fig. 3.** Ground state geometries of  $O_3$  molecule adsorbed on (a) CNT and (b) Si-CNT. The target carbon atom is shown by blue colour

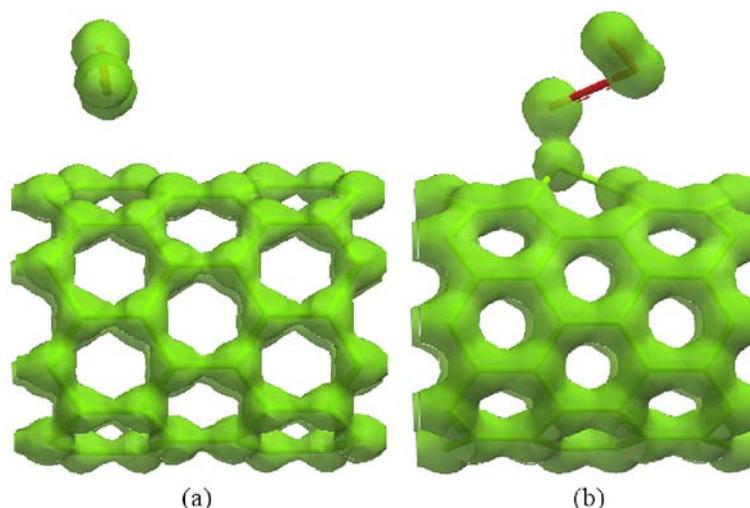
**Structural properties for adsorption of ozone molecule.** To understand the mechanisms of ozone interaction with CNT and Si-CNT, we have calculated structural and electronic properties. Ozone molecule is directly located above the target carbon atom (site-A) of CNT as shown in Fig. 3 (a). The ozone molecule is found physisorbed at distance of  $1.959 \text{ \AA}$ . The binding distance also indicates strong physisorption of ozone on CNT. The bond

angle between O-O-O oxygen atoms of ozone is decreased from  $118^\circ$  to  $116^\circ$ . The bond distances between O-O are also decreased from  $1.279 \text{ \AA}$  to  $1.251 \text{ \AA}$ . In Si-CNT, ozone molecule is chemisorbed on silicon atom (site A) (see Fig. 3 (b)). The ozone molecule binds to the silicon atom with formation of  $\sigma$  (Si-O) bond and its bond length found to be  $1.470 \text{ \AA}$ . In this case ozone molecule gets dissociated and single oxygen atom gets attached to silicon by  $\sigma$  bond whereas oxygen molecule is liberated from ozone. The bond lengths between oxygen atoms are  $1.089 \text{ \AA}$  and  $2.871 \text{ \AA}$ , whereas bond angle between O-O-O oxygen atoms of ozone is significantly decreased to  $96.90^\circ$ . As shown in Fig. 3 (b), the extended bond length between oxygen atoms of ozone confirms dissociation of ozone molecule.

**Electronic properties for adsorption of ozone molecule.** The band structure of CNT-O<sub>3</sub> molecule system is shown in Fig. 4 (a). The band structure of O<sub>3</sub> adsorption shows that the energy states in valence band near Fermi level are slightly separated as compared to band structure of CNT. Therefore, band gap of CNT-O<sub>3</sub> system is marginally more ( $0.63 \text{ eV}$ ) than the band gap ( $0.607 \text{ eV}$ ) of pure CNT. In DOS of CNT-O<sub>3</sub> system the occupancy of partially filled states is slightly increased at Fermi level as shown in Fig. 4 (b). Further, Mulliken Population analysis shows negligible charge  $0.013 \text{ e}$  transferred from CNT to O<sub>3</sub> molecule. The isosurface shown in Fig. 5 of CNT did not show overlapping of charge density between the O<sub>3</sub> molecule and CNT. Thus, ozone gas molecule is physisorbed with binding energy  $-0.43 \text{ eV}$  and small quantity of charge transfer from carbon nanotube, consistent with the strong oxidizing nature of ozone.



**Fig. 4.** (a) Band structure plot and (b) Density of state of O<sub>3</sub> molecule adsorbed on CNT and Si-CNT. The Fermi level is indicated by dotted black line



**Fig. 5.** Isosurface of the charge density of systems for  $O_3$  molecule adsorption on (a) CNT and (b) Si-CNT

The binding energy, charge transfer and isosurface of ozone adsorption on CNT clearly show the character of the interaction can still be classified as physisorption. The adsorption of  $O_3$  on Si-CNT is more pronounced as compared with CNT. However, when ozone adsorbs on Si-CNT, a strong chemisorption occurs, leading to relevant structural relaxations and to the formation of a Si-O  $\sigma$  bond with binding energy - 3.90 eV and charge transfer of 0.252 e. The band structure as shown in Fig. 7 is completely different than band structure of pure Si-CNT. The extra state observed in conduction band of Si-CNT is disappeared and some additional states are observed near Fermi level in valence band. These numbers of states are also clearly observed in DOS as shown in Fig. 8. These additional states reduce band gap of Si-CNT- $O_3$  system to 0.46 eV from 0.54 eV of Si-CNT. The occupancy of valence band at Fermi energy is completely altered due to ozone adsorption. The charge density analysis shows formation of sigma bond between oxygen and silicon atom. Contradictorily the isosurface of charge density shown in Fig. 5 visualize the dissociation of  $O_3$  molecule and formation of silicon-oxide with Si-CNT, where oxygen molecule is liberated from ozone molecule. Thus, chemisorption of ozone molecule shows oxidization of silicon atom doped in CNT and releasing of oxygen molecule. This result is very important to construct sensors with silicon doped carbon nanotube to capture hazardous pollutant like ozone.

## 6. Conclusions

Density functional simulations study has been performed for adsorption of ozone gas molecule on pure carbon nanotube and silicon doped carbon nanotube. Our study has been focused on effect of silicon doping for adsorption of ozone molecule on carbon nanotube. Silicon doping creates extra unoccupied state in conduction band which plays important role in adsorption of ozone molecule silicon doped CNT. The ozone adsorption on pure CNTs shows a small binding energy (-0.43 eV) and charge transfer (0.0815 e) indicates the process is most likely of physisorption kind. The extra states in band structure and DOS of Si-CNT plays significant role in ozone adsorption. The large values of binding energy (- 3.90 eV) and charge transfer (0.252 e) shows ozone adsorbs on the Si-CNT is more pronounced as compared to CNT. The bond length between two oxygen atoms in ozone molecule has been increased due to adsorption on Si-CNT. It is observed that ozone molecule gets dissociated and one oxygen atom gets attached to silicon by forming  $\sigma$  bond whereas oxygen molecule is liberated from ozone. The isosurface of charge density visualize the clear dissociation of  $O_3$  molecule and formation of silicon-oxide with Si-CNT and liberation of oxygen molecule

from ozone molecule. Thus Si-CNT captures ozone molecule forming silicon oxide and releasing oxygen molecule. The result gives grate potential to construct sensor which can capture hazardous ozone molecule. This can be an effective strategy to help in the reduction of the concentration of these harmful pollutants in the environment.

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