Interaction of O_2, CO_2, NO_2 and SO_2 on Si- doped Carbon Nanotube

M. R. Sonawane, Darshan Habale, B. J. Nagare, and Rita Gharde

Abstract— **We report reactivity of silicon doped single walled carbon nanotube (Si–CNT) towards the small atmospheric gas molecules O_2, CO_2, SO_2 and NO_2 using density functional theory based on the numerical basis set method. The reactivity of gas molecules is explained with binding energy, band structure, charge density, and density of states. We found that the substitutional doping of silicon atom in CNT increases the binding energy as compared with pure CNT. The charge density analysis reveals the formation of sigma (σ) bonds between silicon and carbon atoms. Further, the band structure and density of states clearly illustrate the creation of extra state near the Fermi level and reduction in the band gap, which acts as a reactive center for adsorption of the molecules on Si–CNT. We have observed that the large value of adsorption energy shows the chemisorption between molecules and Si–CNT. Mulliken population analysis clearly reveals the charge-induced dipole interactions between the Si–CNT and molecules, which are responsible for chemisorption for gas molecules. The donor like impurity state generated in energy gap almost disappears after adsorption of all gas molecules excluding NO_2. We further note that molecules accept the electronic charge from nanotubes and have significant influence on electronic structure near the Fermi level and are responsible for the increase in the p-type conductivity of tubes.**

Index Terms—**Density Functional Theory, Gas Molecules, Interaction, Si–CNT.**

I. INTRODUCTION

Since last two decade, carbon nanotubes [1] have attracted many research scholars all over the world due to its exciting mechanical, electronic, magnetic, and thermodynamic properties in the various field namely; nanoelectronic devices, energy storage, chemical probes, biosensors, field emission displays and medical monitoring [2] – [4]. Because of high surface to volume ratio, the carbon nanotubes are suitable for adsorption of atmospheric gas molecules. The change in electronic and structural properties of carbon nanotubes and their exposure to environmental gases have been studied by experimental and theoretical methods [5] – [16].

Recently, Kong and Collins et al have studied physical and electronic properties and observed the change in the electrical resistance of single walled carbon nanotubes due to adsorption of the NO_2, NH_3 and O_2. They have also found that these molecules are adsorbed on pure CNT by weak van der Waal interactions and in some cases by strong van der Waal interactions [5], [6]. Now many research groups are studying the functionalization of the carbon nanotube using chemical doping, local defects, radial deformation and metal assistance [17], [18] to improve its adsorption properties. Among all, the metal assistance is an effective way to functionalize the carbon nanotubes which significantly improves the structural and electronic properties.

Further, it is observed that the element like Pd, Li, Ti are used as catalytic to increase weight percentage of H_2 on single wall carbon nanotubes [19], B–doped single wall carbon nanotube is reactive towards CO molecule [20] and Al_{13}–carbon nanotube system can adsorb NH_3 molecules [21]. The chemical reactivity and transport properties of carbon nanotubes are improved by the doping of silicon atom in the carbon nanotubes [22]. The substitutional doping of silicon atom prefers sp^3 hybridization instead of sp^2 hybridization and creates extra states near the Fermi level which act as catalytic center for the adsorption of the gas molecules [13], [22]. Guanlun Guo et al. [14] have also studied the interactions of small organic gas molecules such as Formaldehyde, Carbon Monoxide and hydrogen sulfide on Si–doped carbon nanotubes (Si–CNT). Haihui Jiang et al [23] have used density functional theory to study the interaction of the chemical pollutant polychlorinated dibenzo–p–dioxin and dibenzofurans and found that these organic molecules are chemically adsorbed on the Si–CNT.

However, to the best of our knowledge, there is no report on the interaction of O_2, CO_2, NO_2 and SO_2 on Si–CNT. In the following section, we study the adsorption of these molecules on the basis of geometrical and electronic properties such as structural stability, binding energy, band structure, charge density, Mulliken population analysis and density of states using density functional theory based on numerical basis set method. Now, we will see the computational details followed by the results and discussions.

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II. COMPUTATIONAL METHODS

The density functional theory (DFT) calculations were carried out using DMol^3 package [24], [25], [26] which is based on the linear combination of atomic orbitals. The geometry optimization of structures was performed using generalized gradient approximation (GGA) with Perdew-Burke Ernzerhof (PBE) functional [27]. All–electron

calculations were performed with the double numerical basis sets plus polarization function (DNP). All electron Kohn Sham wave functions expanded in the local atomic orbital basis set with orbital cutoff of 4.0 Å. and SCF convergence of 1×10^{-5} eV. 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 Brillouin zone sampling was approximated by 1 x 1 x 5 special k points Monkhorst-pack Scheme for geometry optimization and energy calculations. To get accurate band–structure and density of state, we have used maximum k-points of 9 x 9 x 21 in Brillouin zone sampling. The Mulliken population analysis was carried out to predict the charge transfer between molecules and Si–CNT.

In this study, we have chosen a Si–CNT (8, 0) of diameter 6.26Å as the model adsorbent whereas the gas molecules O_2, CO_2, SO_2 and NO_2 as adsorbates. We have examined four different possible adsorption sites such as 1) 'Si atom (Site–A)', 2) 'chiral bond (Site–CH)', 3) 'axial bond (Site–B)' and 4) 'centriod of hexagon (Site–H)' of Si–CNT are shown Fig. 1 (b).
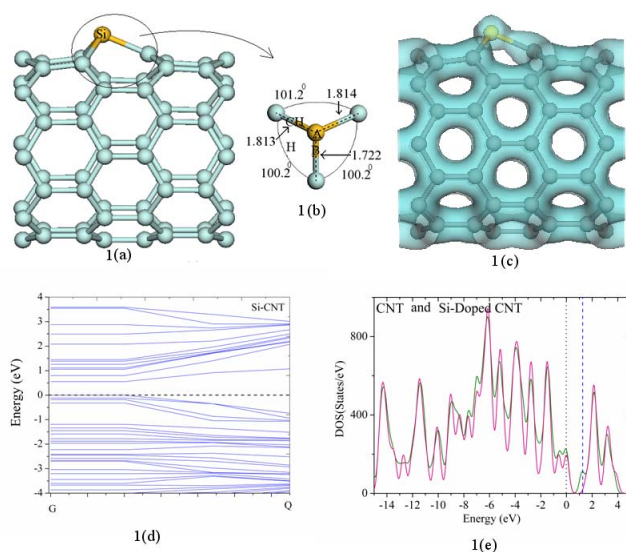

Fig. 1(a) The ground state structure of the Si–CNT. (b) The cross sectional view of Si–CNT with bond length (in angstrom) and bond angle (in degree) (c) Isosurface of the charge density of Si–CNT, (d) Band structure of Si–CNT. The Fermi level is indicated by black dotted line. (e) The density of state (DOS) of CNT and Si–CNT. (Dotted black line–Fermi level and dotted blue line to show extra unoccupied state)

In all calculations, the Si–CNT and isolated gas molecules O_2, CO_2, SO_2 and NO_2 were first optimized to minimize their total energies. Each of these individual gas molecules were kept at four different adsorption sites as mentioned above and optimized together to get lowest energy stable structure as shown in the figures. All the gas molecules other than NO_2 found most stable on axial bond (Si–C) (Site–B) where as NO_2 on silicon atom (Si) (site–A) of Si–CNT. The binding energy (E_b) of all stable configurations is calculated by

$$E_b = -[E_{T\,(Si–CNT + molecule)} - E_{T\,(Si–CNT)} - E_{T\,(molecule)}]$$

Here $E_{T\,(Si–CNT + molecule)}$ denotes the total energy of molecule and Si–CNT system, $E_{T\,(Si–CNT)}$ denotes the total energy of Si–CNT and $E_{T\,(molecule)}$ is the total energy of isolated gas molecule. To verify the computational accuracy of model, we have calculated the binding energy, band structure, density of states, and the energy band gap of Si–CNT which is comparable to the reported results [14], [23].

III. RESULTS AND DISCUSSION

A. Geometric properties of Si–CNT

First, we discuss the geometrical and electronic properties of Si–CNT. The ground state geometry of Si–CNT is shown in Fig. 1(a). we have observed that the silicon atom projects out of the tube wall and creates local deformation (radial bump) due to larger covalent radius of silicon atom (1.11 Å) as compared with carbon atom (0.77 Å). The deformation at silicon site shows both (Si–C) chiral bonds are of same length (1.814 Å) and axial bond (1.722 Å) of short length. The bond angles between C – Si –C bonds for all three combinations are in the range of 100.1^0 to 101.1^0, which indicates tetrahedral structure of bonding and prefers sp^3 hybridization. This structural deformation results into a significant change in electronic properties such as binding energy, band gap, density of states, charge density and charge transfer. The calculated structural parameters found to be in good agreement with the results reported by Guanlun Gua et al [14] and Haihui Jiang et al [23].

B. Electronic properties of Si–CNT

To understand the electronic structure of Si–CNT, we have calculated charge density, band structure and density of states. The Fig. 1(c, d, and e) shows isosurface of charge density, band structure and density of states of CNT (pink color line) and Si–CNT (green color line). The isosurface of charge density clearly indicates formation sigma bond between silicon and carbon atoms. Further, Mulliken Population analysis shows silicon atom acquires positive charge of magnitude 0.0815e. This clears that the charge is transferred from the silicon atom to the vicinity carbon atoms. Such charge polarization at dopant site (silicon atom) acts as an affinity center for chemisorption of the gas molecules. Thus doping of silicon atom creates an extra unoccupied energy state at 1.26 eV in the conduction band. This extra energy state is clearly observed in band structure of Si–CNT as shown Fig. 1(d). The additional state reduces the band gap of Si–CNT to 0.54 eV as compared to band gap of pure CNT (band gap of pure CNT is 0.607 eV). The DOS analysis also shows same unoccupied state [see Fig. 1(e), shown by doted blue line]. Such donor like impurity may act as a capturing center for atoms or molecules which cannot be trapped by the pristine CNT. Thus, the doping of the silicon atom increases the p–conductivity of the CNT which improves the reactivity of CNT.

To explain the interaction of gas molecules O_2, CO_2, SO_2 and NO_2 on Si–CNT, we have examined the details of adsorption configuration and change in structural and electronic properties of each gas molecule on Si–CNT. The most stable configurations for O_2, CO_2, SO_2 and NO_2

adsorption are shown in Fig. 2(a) – 5(a), corresponding - isosurface of charge density in Fig. 2(b) – 5(b), band structure in Fig. 2(c) – 5(c) and density of states in Fig. 2(d) – 5(d) respectively. The equilibrium distances, bond lengths, bond angles, binding energies, energy gaps and the net charge transferred from the Si–CNT to the respective gas molecules are summarized in table 1.

TABLE I: The Table Shows the Structural and Electronic Properties of Adsorption of the Gas molecules CO_2, NO_2, O_2 and SO_2 on (8, 0) Si–CNT with bond length (in Å), Bond Angle (degree), Binding energy E_B (in eV) and Charge Transfer (Q_T).

Gas Molecule	Bonds	Bond Length (Å)	Binding Energy (eV)	Charge transfer (e)	Energy Band Gap (eV)
O_2	d(Si-O) d(C-O) d(O-O)	1.699 1.488 1.560	−2.627	0.632	0.311
CO_2	d(Si-O) d(C-C) d(C-O) d(C-O)	1.724 1.577 1.402 1.198	−1.787	0.359	0.316
SO_2	d(Si-O) d(C-S) d(S-O) d(S-O)	1.683 2.006 1.489 1.779	−1.811	0.466	0.310
NO_2	d(Si-O) d(N-O) d(N-O)	1.680 1.160 1.581	−2.643	0.416	0.388

C. Interaction of O_2 molecule with Si–CNT

Oxygen is an electronegative and polar molecule having tendency to accept the charges. We have performed total energy calculations to observe the interaction of O_2 on Si–CNT and traced most stable configuration. Oxygen molecule is directly located above the axial bond (Si–C) of the nanotube. The oxygen molecule binds to the silicon and carbon atom by forming sigma (σ) bonds Si–O and C–O of lengths 1.698 Å and 1.488 Å respectively [see Fig. 2(a)]. Such chemical attachment of O_2 is known as cycloaddition [29]. The optimized bond length of free O_2 molecule is 1.226 Å which is very close to the reported value 1.21 Å. After adsorption of O_2 molecule on Si–CNT, the bond length between oxygen – oxygen atoms is increased from 1.226 Å to 1.516Å. We have found that oxygen atoms of O_2 molecule are not dissociated. The elongation in bond length indicates both oxygen atoms strongly interacting with silicon and carbon atoms. Due to such strong interaction the tube's geometry is deformed and Si–C bond is slightly pulled out of the sidewall of the nanotube. The bond lengths of carbon atoms of Si–C bond with their neighboring carbon atoms are also slightly increased from 1.432 Å to 1.501 Å. Thus, it is clear that sp^3-hybridization occurred between carbon and oxygen atom.

The binding energy of oxygen molecule on Si–CNT for most stable configuration is –2.627 eV and which is remarkably more than the value –0.25eV reported by Jhi et al [7] for interaction of O_2 with CNT and –1.02 eV reported by Fenglei Cao et al [29] with Si–CNT. The large value of binding energy indicates the interaction of oxygen molecule with Si–CNT is enhanced as compared to the CNT. The band structure and DOS [see Fig. 2(c, d)] shows that the two states in valance band near Fermi level merge into single highly occupied energy state at – 0.577 eV. The extra unoccupied state at 1.496 eV appeared in conduction band of Si–CNT shifts towards Fermi level and its unoccupied density of states is found to be enhanced. Due to adsorption of Oxygen molecule, highly occupied state in valance band and unoccupied states in conduction band near the Fermi level get broaden and they reduces the band gap to 0.31 eV of Si–CNT. Thus the conductivity of nanotube gets increased. The Mulliken population analysis also shows silicon atom occupies more positive charge of 1.483 e by donating electrons to oxygen molecule and to the neighboring carbon atoms. The positive charge acquired by silicon atom is increased from 0.0815 e to 1.483 e, clearly suggests an effective charge transfer –0.632 e from Si–CNT to the oxygen molecule, which is more than - 0.1 e charge transferred from CNT to oxygen molecule reported by P. Giannozzi et al [10]. The isosurface of charge density clearly shows formation of sigma (σ) bonds between oxygen and silicon [see Fig. 2(b)]. Thus we found that doping of silicon increases interactions between oxygen molecule and Si–CNT.
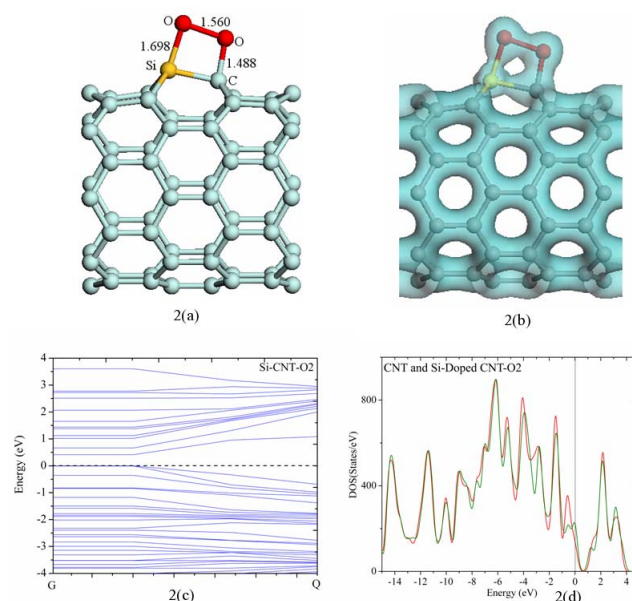

Fig. 2 (a) The ground state structure of the O_2 molecule adsorbed on Si–CNT. (b) Isosurface of the charge density of the Si–CNT with adsorbed O_2 molecule. (c) Band structure of the Si–CNT with adsorbed O_2 molecule (d) The density of state (DOS) of CNT and Si–CNT with adsorbed O_2 molecule. The Fermi level is indicated by dotted (black) line

D. Interaction of CO_2 molecule with Si–CNT

The geometry optimization of nanotube–gas molecule system shows that the CO_2 molecule is adsorbed on axial bond (Si–C) (site–B) of Si–CNT and forms most stable configuration of system. We have observed that CO_2 molecule is chemically attached by cycloaddition to Si–CNT forming sigma bonds Si–O of length 1.724 Å and C–C of length 1.577 Å with nanotube atoms [See Fig. 2(a)]. Further,

CO_2 adsorption produces local structural deformation at interaction site. The length of Si–C bond is increased from 1.722 Å to 1.772 Å and angle O–C–O is significantly decreased from 180^0 to 125.1^0. Such a structural deformation at adsorption site is attributed to modify the hybridization of carbon atom in axial bond (Si–C) from sp^2 to sp^3 in Si–CNT. The small values of chemical bonding indicate the strong interaction between the CO_2 molecule and Si-CNT.

The binding energy of most stable configuration system is found to be –1.787 eV. The large value of binding energy justifies the chemisorption of CO_2 molecule on Si–CNT. The DOS of nanotube–molecule system shows two occupied energy states are merged into single occupied energy state at energy level –0.470 eV but occupancy of this density of states is less as that of the state observed in interaction of O_2. Also the extra energy state in conduction band is slightly shifted towards Fermi level [See Fig. 3(d)). Thus significant change in the DOS at Fermi level of Si–CNT due to CO_2 adsorption reduces band gap from 0.549 eV to 0.316 eV. The reduction in band gap suggests the significant increase in conductivity of Si–CNT and it is turned out to be more p-type conducting.

The band structure of Si–CNT for CO_2 adsorption is also modified near the Fermi level. The partially filled states in valance band and conduction are slightly approached towards the Fermi level as shown in Fig. 3(c), which justifies the remarks about the change in band gap and subsequently conductivity of nanotube. The silicon atom is low electronegative than the oxygen atoms in CO_2 molecules. Thus silicon atom in Si-CNT donates charge to the CO_2 molecule and in the surrounding carbon atoms. So CO_2 molecule gets chemisorbed due to sharing lone pair of electrons of oxygen with silicon and carbon atoms in Si-CNT. The Mulliken population analysis shows silicon atom acquires more positive charge of magnitude –1.508 e and effective charge transfer –0.359 e from Si–CNT to CO_2 molecule. The isosurface charge density shown in Fig. 3(b) clearly visualizes the similar mechanism of chemisorption and formation of chemical bonds between Si-CNT and CO_2 molecule like O_2 molecule.
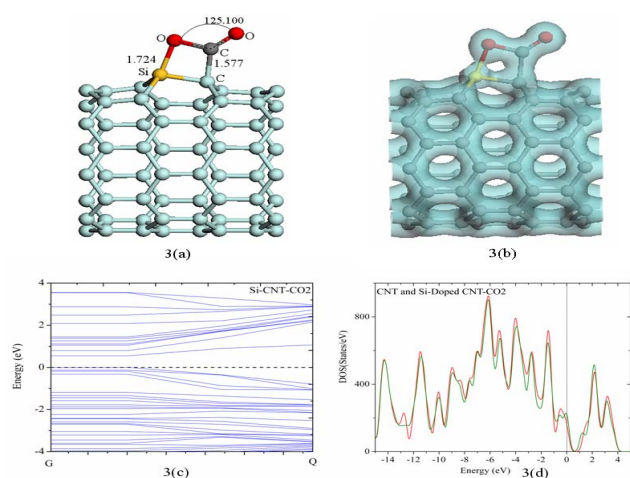
E. Interaction of SO_2 molecule with Si–CNT

The Sulfur dioxide is most hazardous pollutant in the Atmosphere which is emitted by volcanic eruptions, Combustion of coal and petroleum products.The oxidation of SO_2 in the presence of NO_2, forms H_2SO_4 and acid rain, this is one of the main causes of environmental pollution. SO_2 molecule is also adsorbed on axial bond (Si–C) of Si–CNT with most stable configuration. The sulfur and oxygen atom forms covalent bonds Si–O and C–S of length 1.683 Å and 2.000 Å respectively as shown in Fig. 4(a). The chemisorption modifies the angle geometry of SO_2 molecule. The bond angles of SO2 molecule are reduced from 120^0 to 108.9^0 preferring sp^3 hybridization.

The binding energy for stable configuration of SO_2 adsorption is - 1.811 eV. From the DOS of SO_2 adsorption on Si–CNT, we found that two partially occupied energy states are modified to single slightly more occupied state at energy level -0.536 eV near Fermi. The unoccupied energy state observed in DOS of Si–CNT also disappears and new unoccupied state at energy level 1.382 eV is observed, which is found to be broaden and shifted towards Fermi level as shown in Fig. 4(d), there by reducing band gap of Si–CNT to 0.310 eV. Thus the conductivity of Si-CNT is changed due to adsorption of SO_2 molecule. The change in conductivity is almost same as that of O_2 and CO_2 adsorption. The band-structure plot as shown in Fig. 4(c) do not show any substantial changes as compared with O_2 and CO_2 except increase in number of states inside of valance band near to Fermi level. The interaction of silicon atom shows that it donates the charge to gas molecule and also to the vicinity carbon atoms. Thus in SO_2 adsorption silicon atom acquires more positive charge of magnitude 1.544 e than 0.815 e in pure Si–CNT.
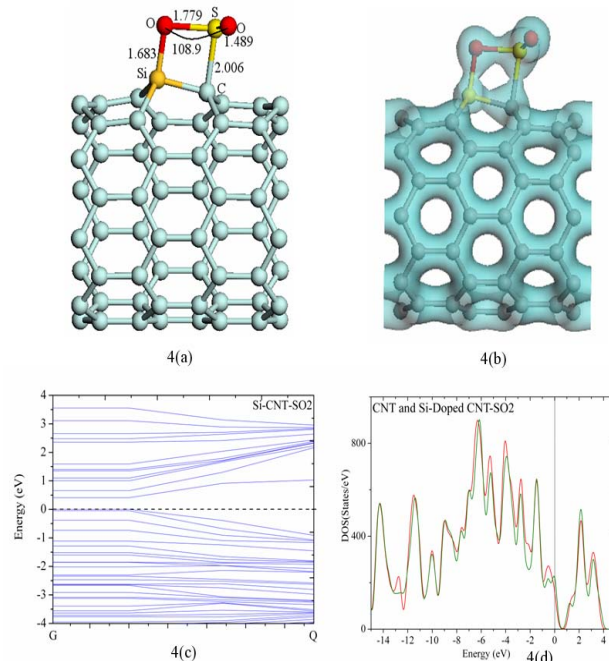

4(a)

4(b)

4(c)

4(d)

Fig. 4 (a).The ground state structure of the SO_2 molecule adsorbed on Si–CNT. (b). Isosurface of the charge density of the Si–CNT with adsorbed SO_2 molecule. (c) Band structure of the Si–CNT with adsorbed SO_2 molecule (d) The density of state (DOS) of CNT and Si–CNT with adsorbed SO_2 molecule. The Fermi level is indicated by dotted (black) line

3(a)

3(b)

3(c)

3(d)

Fig. 3 (a).The ground state structure of the CO_2 molecule adsorbed on Si–CNT. (b). Isosurface of the charge density of the Si–CNT with adsorbed CO_2 molecule. (c) Band structure of the Si–CNT with adsorbed CO_2 molecule (d) The density of state (DOS) of CNT and Si–CNT with adsorbed CO_2 molecule. The Fermi level is indicated by dotted (black) line.

Hence charge is transferred from Si–CNT to SO_2 molecule and the Mulliken population analysis shows effective charge transfer from Si–CNT to SO_2 of the order of –0.466 e. The isosurface as shown in Fig. 4(b) shows similar hybridization mechanism as mentioned in O_2 and CO_2 molecules.
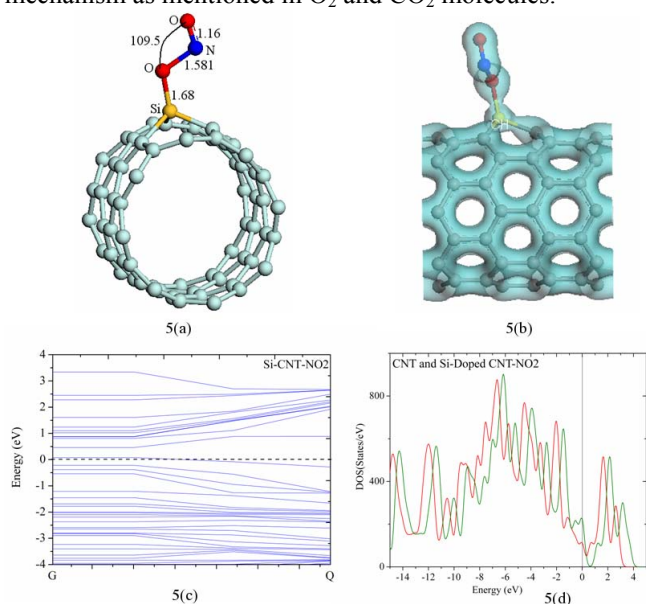

5(a)

5(b)

5(c)

5(d)

Fig. 5 (a).The ground state structure of the NO_2 molecule adsorbed on Si–CNT. (b). Isosurface of the charge density of the Si–CNT with adsorbed NO_2 molecule. (c) Band structure of the Si–CNT with adsorbed NO_2 molecule (d) The density of state (DOS) of CNT and Si–CNT with adsorbed NO_2 molecule. The Fermi level is indicated by dotted (black) line

F. Interaction of NO_2 molecule with Si–CNT

NO_2 is reactive with alkenes at room temperature producing very hazardous pollutant in atmosphere. Many research groups have aimed to develop sensor and scrubber for such hazardous pollutants. We have studied the change in geometrical and electronic properties of Si–CNT due to adsorption of NO_2. The most stable adsorption configuration is silicon atom Si (site–A) as shown in Fig. 5(a). The NO_2 adsorption is somewhat different than other gas molecules. It is chemisorbed on silicon atom with formation of Si–O bond of length 1.581 Å as shown in Fig. 5(a). The small value of bond length indicates NO_2 interaction via oxygen atom with Si–CNT is very strong. The bond angle of NO_2 molecule is significantly decreased from 133^0 to the 109.5^0. We have observed that the silicon atom is pulled outward by NO_2 adsorption and bond length of Si-C bond is increased from 1.732 Å to 1.778 Å.

The binding energy of most stable configuration of Si–CNT for NO_2 adsorption is –2.643 eV, which is much larger as compared to binding energy of -0.4 eV reported by Wai-Leung Yim. et al (12) for CNT. The band–structure and DOS of Si–CNT for NO_2 adsorption shown Fig. 5(c, d) indicates complete different features as compared to DOS of Si–CNT. More interestingly the two occupied states near the Fermi level of Si–CNT are modified and the new occupied states are generated at energy levels –1.140 eV and –0.0435 eV, which are spread over the wide range in valance band near Fermi level. The newly formed extra energy state at 1.244 eV located in the conduction band at 0.696 eV of

Si–CNT almost reduced and it is shifted towards the Fermi level. This results into reduction in energy band gap of Si–CNT due to NO_2 adsorption to 0.388 eV. The DOS of NO2 adsorption on Si–CNT as shown in Fig. 5(d) is continuous in nature which indicates that the conductivity of Si–CNT is completely changed and becomes semimetalic. It is completely different than other molecules as explained above. The charge is transferred from Si–CNT to NO_2 gas molecule due to high electronegativity. Thus silicon atom acquires positive charge of 1.452 e by donating charges to the NO_2 as well as to surrounding carbon atoms. The Mulliken population analysis shows effective charge transfer from Si–CNT to NO_2 molecule of the order of –0.416 e. The lone pair of electrons on oxygen atom is shared with silicon atom forming a covalent bond with oxygen. This mechanism of electron transfer helps to stabilize NO_2 chemically on Si–CNT. The isosurface charge density also demonstrate similar mechanism like charge analysis and formation of sigma bond between silicon and oxygen shown in Fig. 5(b).

IV. CONCLUSION

We have used density functional theory based on linear combination of atomic orbitals to study the adsorption of small atmospheric gas molecules namely; O_2, CO_2, SO_2 and NO_2. We found that silicon doping changes the hybridization of silicon atom from sp^2 to sp^3 and create extra states near the Fermi level. All the gas molecules are chemically adsorbed onto Si–CNT with significant increase in binding energy. We have also found that there is net electron transfer from Si–CNT to gas molecules due to more electronegative nature. The charge density shows clear overlapping of electronic orbitals between gas molecules and Si–CNT. The density of states for adsorption O_2, CO_2 and SO_2 shows extra state created near Fermi energy disappear, result into increase in P–type conductivity of the tube. In case of NO_2, the density of states near Fermi level is increased and become continuous and Si–CNT becomes semi–metallic.

The isosurfaces shows remarkable overlap between Si–CNT and molecules, demonstrating strong electronic (orbital) interaction and clear flow of the electronic charge between the Si–CNT and gas molecules. The charge density clearly shows the formation of sigma bonds between the Si–CNT and molecules. The all gas molecules accept the electronic charge from Si–CNT and have significant influence on electronic structure of Si–CNT at the Fermi level and are responsible for the increase in holes carriers in the tube. The donor like impurity state generated in band gap due to doping of silicon atom almost disappears for adsorption of all gas molecules excluding NO_2. Furthermore, electron charge transferred a semiconductor Si–CNT can be turned into p-type conductor after O_2, CO_2 and SO_2 adsorption. The DOS of NO_2 adsorption is continuous in nature which indicates that Si–CNT becomes semimetalic.

In general, we have observed that silicon doping in Si–CNT produces sp^3 hybridization and creates additional states near the Fermi level which result in the enhancement of the adsorption properties of carbon nanotube. The theoretical results further suggest that the gas–induced modification of the density of states close to the Fermi level might

significantlyaffect the transport properties of nanotubes

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