New active sensor of gas toxic CO, NaCN and ClCN by using doped carbon nanotube (8,0) with Fe, Ni and Ru single atome :DFT study

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Abstract

Using Gaussian 09 software, we studied the toxicity of CO and ClCN on the surface of (8,0) single-walled carbon nanotubes (SWCNT) doped with transitional metal TM= (Fe, Ni, and Ru) using density functional theory (DFT) computation. There were other studies of the adsorption energy as well as equilibrium distances, gaps in energy, total energy, and density of states (DOS). According to the considerable energy gap fluctuation during gas molecule adsorption, TM=(Fe, Ru, and Ni)-doped gas senses adequately, according to the findings. Tests revealed softer and more reactive doped SWCNT systems had lower band gaps but higher ionization energies and electronegativity. Doping modified carbon nanotubes as a novel means of manipulating their electrical characteristics may be concluded, and the best sensor for both CO and ClCN is found to be CNT-Ni.

Keywords : Carbon nanotube , DFT, Senser,
DOI Number: 10.14704/nq.2022.20.3.NQ22341 NeuroQuantology 2022; 20(3):509-519

1. Introduction

Since the 1991 Iijima discovery of carbon nanotubes "Rashmanifre, Yoosefian, and K-Maleh (2016). In the field of electronics and nanoelectronics, carbon nanotubes are "a mainly promising material that can transform." Other than that, it has certain peculiar electrical features [Boroznina, Zaporotskova 2017, and Amorim et al. 2013]. "From both a physical and technical standpoint, [CNTs] are fascinating systems. "Their mechanical qualities, including as high rigidity and an impressive Young's modulus of roughly 1 TPa, are also notable. As a result of their exceptional detecting abilities, "Carbon nanotubes-based gas sensors" have been developed. These sensors have features like high sensitivity, quick response, compact size, and low operating temperature. Cuia, Zhanga, Chen, and Tangc (2019) [Cuia]. It is possible to get (CNT) in two different configurations: as a single-walled "multi-walled [MW] or with a distinct carbon sheet fragment. The general transport features of quasi-one-dimensional systems are best studied using single-wall CNTs." For further information, please refer to [Latessa, Pecchia, and Di Carlo, 2007].

n, m may be used to designate any SWCNT and they can be divided into three types: armchair nanotubes (n, n), zigzag nanotubes (n, 0), and chiral nanotubes (n, m). For example, CNTs may now be used in a wide

range of applications ranging from electrical devices to fuel cells to hydrogen storage to electrode catalysis to gas sensing owing to the properties of CNTs' homes.There are several sectors in which gas sensing methods are critical, including medicine [Sharafeldina and Allam, 2017]. For real-time and leakage detections of dangerous gases, gas sensors with high sensitivity and selectivity are essential [Kanchanatip, Tulaphol, Den, Grisdanurak, Miao, and Yang, 2018]. Improved gas sensing properties may be achieved by doping the carbon nanotubes with additional atoms [Arasteh and Naseh, 2018]. Single-walled carbon nanotubes (SWCNTs) can also be used to locate gasoline molecules, organic chemicals, and biological substances, because the adsorption function of SWCNTs can be optimized by adding heteroatom impurities (along with germanium, nicole, lron, paiiadium, and ruthenium) and forming active sites in the tube walls. It has been shown that carbon nanotubes (CNTs) with low measurement and an excessive surface to volume ratio may be used as gas chemical sensors to detect several chemicals, including CO and ClCN.

As a result of photochemical reactions in the troposphere and other factors such as volcanoes, forest fires, iron smelting and routine human activities, Carbon monoxide is a colorless and odorless gas "metabolism of animals.Through the combination of hemoglobin and the production of carboxylic acid, carbon monoxide may reduce the flow of oxygen to the body's organs "hemoglobin is the chemical name for red blood cells. At a blood sugar level of seven hundred, around half of a person's hemoglobin may be changed to carboxy hemoglobin "Carbon dioxide (CO) concentrations of ppm can lead to unconsciousness, seizure, and death [Zahedi, Yari and Bahmanpour, 2016; Fadradi, Movlarooy, 2018]. Despite extensive research, the adsorption of CO on carbon nanotubes has been shown to be poor. In spite of extensive attempts to increase the CO bonding energy on carbon nanotubes, the sensors described non [Fadradi, Movlarooy, 2018] are inapplicable.

As the name suggests, CK is a colorless and very poisonous gasoline.

Three atoms make up the molecule of this gas "C, N, and Cl may be linearly connected to the covalent triple bond (C, N) and the unmarried covalent bond (Cl, C). Flammable and hazardous gases may be produced when dry air or water come into contact. Cyanogen Chloride is used in this process ""and is particularly harmful to the blood"" in chemical war plans" As a result, the human body suffers from "breathing failure and metabolic blockage." "Animals are also included. Toxic and rapidly decomposing, CK is harmful to eyes and respiratory organs once it comes into contact [Zhang, Quan and Yang in 2018, Movlarooy and Fadradi in 2018, as well as Ahn and Hahn in 2018].

Here, one can see how the interaction between molecules (CO, NaCN, and ClCN) and carbon nanotubes (CNTs) is examined utilizing the DFT approach to a great extent. In this work, we want to get a basic understanding of the molecular interactions between the gaseous adsorbates (Ru-CNT, Fe-CNT, and Ni-CNT models) and the adsorbates themselves. There are calculations done for adsorption electricity (Eadvert), binding distance, and electronic form of gasoline molecule species. The molecular design of new adsorbents and sensing compounds is dependent on this information. Calculations based on the fundamental principles suggest that the proposed models of (Ru-CNT, Fe-CNT, and Ni-CNT) have been chosen.

2. Computational Methods

These open-edged (8,0) zigzag single-walled nanotubes (SWNTs) with optimal chemical orientations were used to investigate the adsorption behavior of gas molecules. 96 carbon atoms in an 8-CNT with a length of 12.140 A(°) were selected for the experiment. In terms of diameter, it measures 6.267 A°, while the average bond length between C and C is 1.421 A°. Doping the (8,0) SWCNT with transition metals was done by substituting one carbon atome of the SWCNT

with a transition metal atome. The adsorption of CO, NaCN, and ClCN on pristine, TM-doped, and defected (8,0) single-walled carbonAnanotubes was studied in terms of structure, electrical characteristics, charge transfer, and adsorption energy. The GaussSum 09 software was used to compare the electronic density of state (DOS) of the arsine adsorbed on the CNTs with each other. Arsine was inserted in the same input file as nanotubes to be optimized jointly. The B3LYP level and 6-31G basis were used to finish the computations with the Gaussian 09 program under the auspices of density functional theory (DFT). Energy gaps between the highest occupied molecular orbital (HOMO) and its lowest unoccupied orbital (LUMO) were estimated, as well as the energy gap, lionization potential, and electron affinity (E.A).

I.P = -E_{HOMO} (1)

E.A = - E_{LUMO} (2)

The Koopmans' theorem [19] may be used to compute several physical qualities such as hardness (η).

$\eta = \frac{I.P-E.A}{2}$ (3)

Additionally, the following equation serves as a definition for chemical potential (μ);

= -μ =$\frac{E_{HOMO} + E_{LUMO}}{2}$ (4)

where $E_{HOMO}$and $E_{HOMO}$are both the energy of the lowest unoccupied molecular orbital, which is ELUMO.

Softness (S) and electrophilicity (ω) are described as the subsequent equations, respectively

$S = \frac{1}{2\eta}$ (5)

$\omega = \frac{\mu^2}{S}$ (6)

The adsorption energy Ead is calculated according to the expression (7) as follows:

Ead = $(E_{tube} + E_{gas}) - E_{tube-gas}$ (7)

Table 1. As well as the orbital parameters: HOMO and LUMO energies, Eg and D.M. of distinct systems. Adsorption energy and the orbital parameters

system	E_{HOMO}(eV)	E_{LUMO}(eV)	E_g(eV)	E_{ad}(eV)	D.M(Debye)
CNT	-6.089	-5.570	0.519	....	0.000
CNT-Ru	-6.056	-5.487	0.569	....	0.412
CNT-Fe	-6.087	-5.518	0.569	....	1.332
CNT-Ni	-5.942	-5.404	0.538	....	1.518
CNT-ClCN	-6.068	-5.553	0.515	-0.980	0.945
CNT-Fe-ClCN	-5.925	-5.464	0.461	-8.544	3.208
CNT-Ni-ClCN	-5.922	-5.504	0.462	-36.355	1.342
CNT-CO	-6.099	-5.579	0.520	-1.855	0.492
CNT-Ru-CO	-5.903	-5.464	0.439	-1.127	3.069
CNT-Ni-CO	-6.091	-5.592	0.499	-34.437	1.998

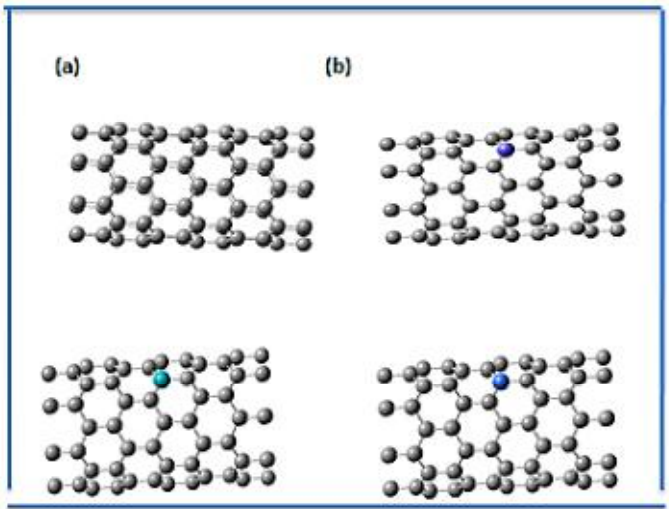

Fig. 1. solitary, clean geometries TM-doped CNT and CNT CNT pure, CNT-Fe, CNT-Ru, and CNT-Ni are all types of CNT.

3. Results and discussion

3.1. Optimization of the geometry

Fig. 1 shows how doping carbon nanotubes with Ru, Fe, and Ni atoms greatly alters the geometric structure of the doped carbon nanotubes, whereas Table 1. shows the geometric structure of isolated PSWCNT and TM-doped CNT after relaxing. Bond lengths for CCC at PSWCNT decreased from 1.43 nm to 1.80 nm for Ni–C, 1.41 nm for Fe–C and 1.41 nm for Ru TM-CNT, as reported in Table 2. Carbon nanotubes' hexagonal structure is distorted as a result of this. The adsorption of various gas molecules may be influenced by the carbon nanotube's curvature. Adsorption-induced curvature changes in virgin and doped carbon nanotubes are shown in Table 2. Because various adsorbates modify the bond lengths in certain areas of carbon nanotubes, the curvature of a CNT may vary depending on the adsorbate.

There are a variety of ways in which the CO and ClCN may be oriented with regard to the PSWCNT's surface. The adsorption energies of these compounds on PSWCNT may be inferred from the findings of several works on the subject. Adsorption values in the case of TM-doped -CNT, on the other hand, do not need the consideration of alternative orientations for these structures "interactions of various sorts. Thereby "towards adsorption of CO and ClCN on PSWCNT," among all conceivable combinations. The following orientations may be used as a guide "They might be optimized with a specified basis set thanks to input file one. Figure 2 shows the structures with these weak connections completely relaxed. Table 2 lists the appropriate structural properties of the most stable PSWCNT-adsorbed configurations of CO and ClCN, whereas Table 1 lists the adsorption energies. CO adsorption on the C C bond site of the carbon ring is the most stable configuration for PSWCNT–CO, with Eads =-1.855 eV and molecular distance of 2.060 nm, as shown in the figure below. ClCN adsorbed on a hollow site with Eads = -0.980 eV and d = 2.396 is the most stable configuration in the PSWCNT–ClCN system. The poor adsorption energies of PSWCNT–CO and PSWCNT–ClCN show us that PSWCNT is not suited for adsorption of the above-mentioned spices, as shown by the low adsorption energies.

The DFT may be used to discover the most stable configurations of the molecules indicated above on TM-CNT. If you'd want to optimize structures using the information provided in this article, you may create input files for TM doped CNT systems based on that knowledge. The TM-doped _CNT undergoes structural changes as a result of the adsorption of CO and ClCN. Table2 lists the equivalent findings for all TM-doped _CNT systems. Adsorption energies of all systems

are much higher than those for PSWCNT systems, suggesting that the presence of TM-doped. improves the carbon nanotube's capacity to adsorb these gas molecules. Figure 2 shows the situation.

Table 2. Relaxed PCNT and TM-doped CNT structural characteristics before and after analyte adsorption.

System	Bond	Bond length(Aº)	Distance(Aº)
CNT	C1-C2	1.42	
	C1-C3	1.42	
	C1-C4	1.42	
CNT-Ru	Ru1-C2	1.42	
	Ru1-C3	1.41	
	Ru1-C4	1.41	
CNT-Fe	Fe1-C2	1.41	
	Fe1-C3	1.42	
	Fe1-C4	1.41	
CNT-Ni	Ni1-C2	1.78	
	Ni1-C3	1.80	
	Ni1-C4	1.80	
CNT-ClCN	C1-C2	1.41	2.795
	C1-C3	1.42	
	C1-C4	1.41	
CNT-Fe-ClCN	Fe1-C2	1.42	1.687
	Fe1-C3	1.41	
	Fe1-C4	1.41	
CNT-Ni-ClCN	Ni1-C2	1.41	2.394
	Ni1-C3	1.41	
	Ni1-C4	1.42	
CNT-CO	C1-C2	1.41	2.060
	C1-C3	1.42	
	C1-C4	1.41	
CNT-Ru-CO	Ru1-C2	1.41	1.974
	Ru1-C3	1.42	
	Ru1-C4	1.41	
CNT-Ni-CO	Ni1-C2	1.41	1.866
	Ni1-C3	1.41	
	Ni1-C4	1.42	

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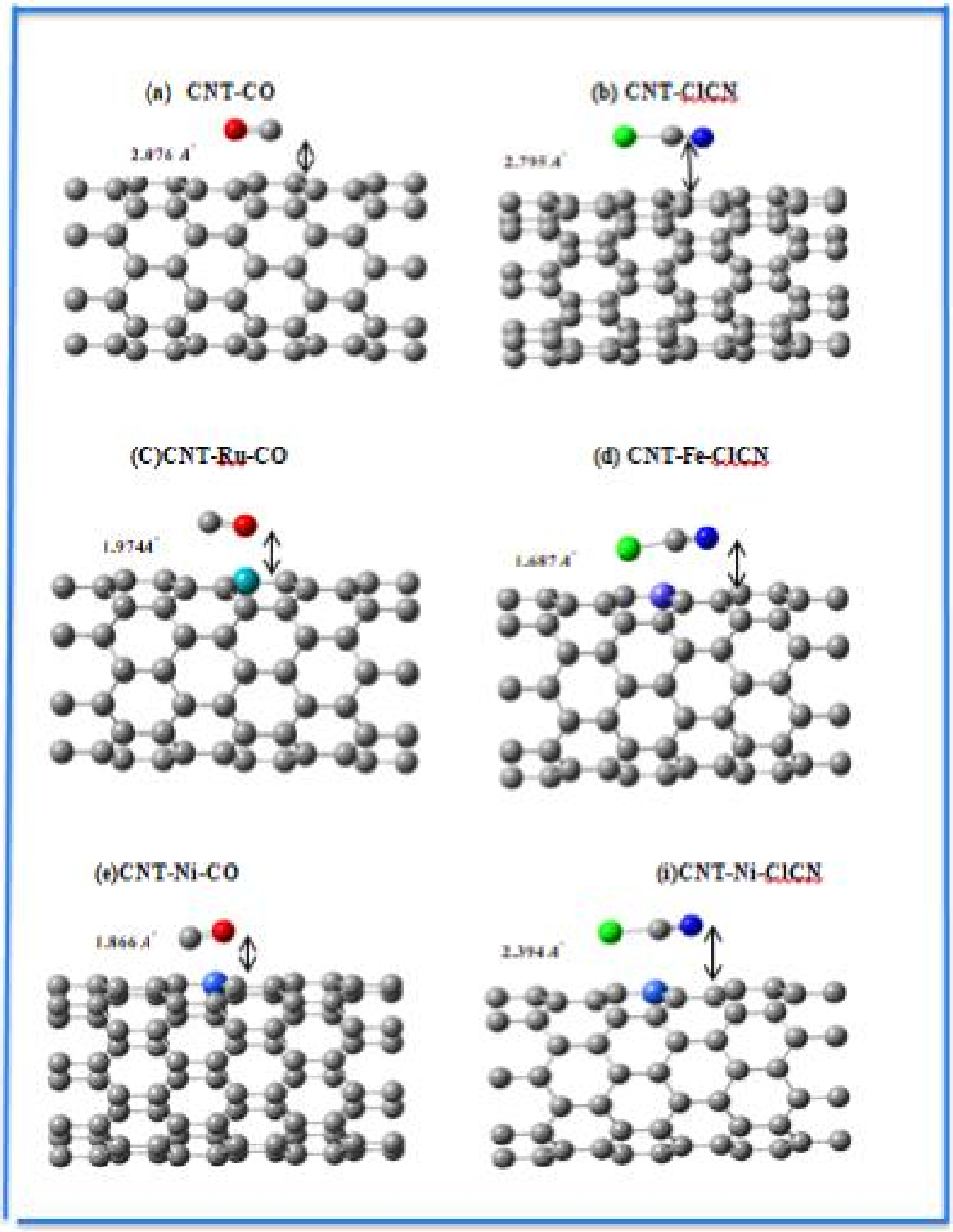

Fig. 2. Structure of TM-doped CNT complexes with CO and ClCN transitional metals.

3.2. Orbital analysis

To further investigate the adsorption of CO and ClCN on PSWCNT and TM-CNT, we looked at the electrical properties of these materials.

Table 3. CO, NaCN, and ClCN adsorption on PCNT or TM-doped CNT has a chemical potential (μ), hardness (η), softness (S), and electrophilicity (ω). The eV unit is used to measure all parameters.

System	I.P (eV)	E.A(eV)	$\mu\ (eV)$	η (eV)	S (eV)	$\omega\ (eV)$
CNT	6.089	5.570	-5.829	0.259	1.930	65.593
CNT-Ru	6.056	5.487	-5.771	0.284	1.760	58.633
CNT-Fe	6.087	5.518	-5.802	0.284	1.760	59.265
CNT-Ni	5.942	5.404	-5.673	0.269	1.858	59.817
CNT-ClCN	6.068	5.553	-5.810	0.257	1.945	65.673
CNT-Fe-ClCN	5.925	5.464	-5.694	0.230	2.173	70.480
CNT-Ni-ClCN	5.922	5.504	-5.735	0.231	2.164	71.190
CNT-CO	6.099	5.579	-5.839	0.262	1.923	65.563
CNT-Ru-CO	5.903	5.464	-5.683	0.219	2.283	73.735
CNT-Ni-CO	6.091	5.592	-5.841	0.249	2.008	68.508

TM-doped CNT, PSWCNT–CO, PSWCNT–ClCN, and TM-CNT–CO and TM-CNT–ClCN systems' energies. These systems were analyzed, and in Table 1, the highest and lowest occupied molecular orbitals (HOMO and LUMO) for each are shown in Fig. 3 and the data is stated. Figure 3 shows the HOMO–LUMO shifts on Fe, Ru, and Ni atoms following TM doping on carbon nanotubes, which is consistent with a smaller energy gap (Eg), as reported in Table 1. TM-doped CNT is more reactive than PSWCNT as a result of this reduction in Eg. Figs. 3 and 4 show that adsorption of CO and ClCN on the surface of PG does not result in a significant shift in complexes other than isolated PSWCNT, showing that no hybridization has occurred and that there is only a weak contact.

TM-doped CNT compared to PSWCNT for CO and ClCN adsorption. As a consequence, the TM-CNT–CO and TM-CNT–ClCN complexes are more conductive and reactive than the TM-CNT alone.

The electric dipole moment of complexes is one of the most important indicators of gas charge distribution following adsorption. The dimensions and directions of the electric dipole moment vector change depending on the adsorption location configurations as CO and ClCN travel towards PSWCNT and TM-doped-CNT surfaces. Isolated CO and ClCN as well as PSWCNT and TM-CNT, and the most stable complexes of these compounds are shown in Table 1 (electric dipole moment data). Isolated PSWCNT had a dipole moment of 0.00 Debey, whereas CO and ClCN had a dipole value of 3.118 Debey, while PSWCNT alone had a dipole moment of 0.945 Debey. Adsorption of the analytes on PSWCNT resulted in marginally altered dipole moments. In the presence of CO and ClCN, the TM-CNT dipole moment rose and decreased, respectively. The dipole moments of all adsorbent–adsorbate systems were significantly bigger in the case of TM-CNT compared to PSWCNT.

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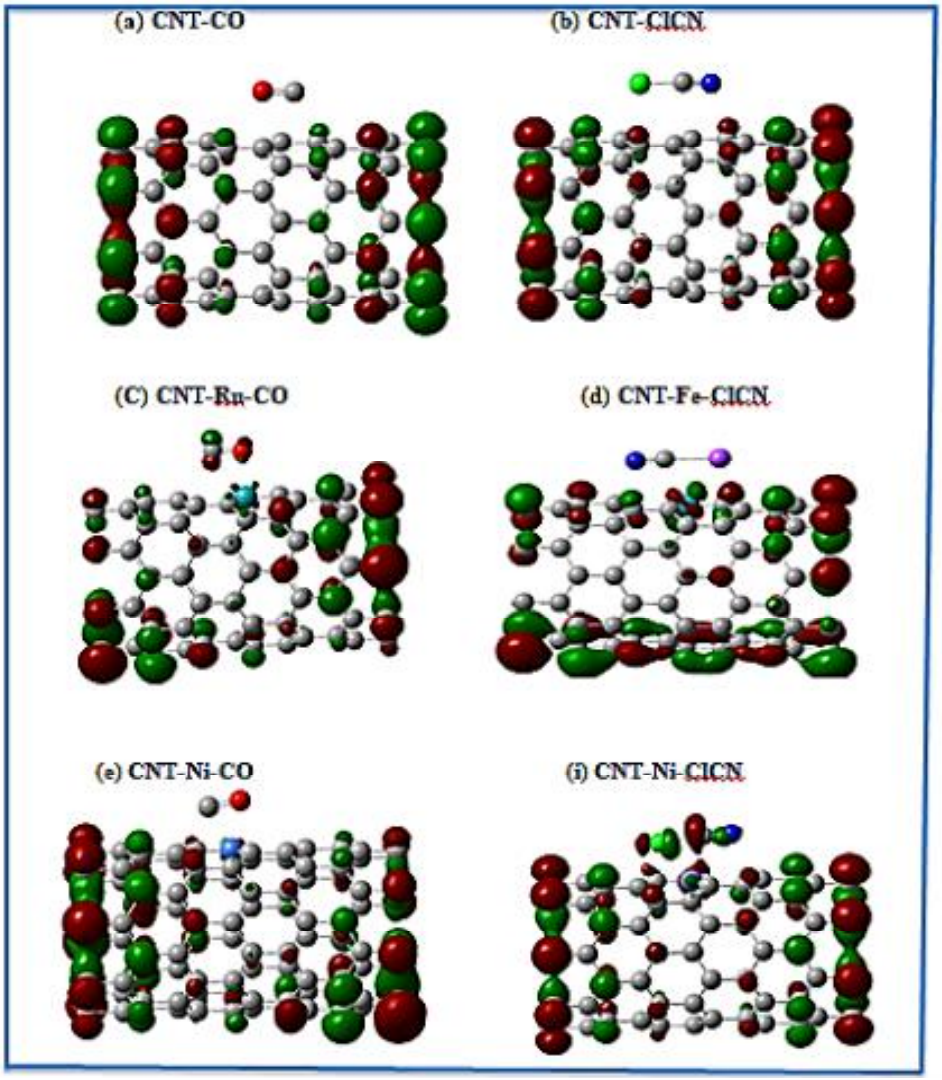

Fig. 4. The electron density in HOMO–LUMO for all the systems under investigation

3.3. Global indices

Table 3 shows the global reactivity indices in the DFT framework for CO and ClCN adsorption on PSWCNT and TM-CNT. Global hardness is defined as the resistance of a system to deformation in the presence of an electric field. Global hardness and global softness are linked in a different way here. Stability decreases and reactivity rises as a consequence of an increase in the softness of materials. The hardness, chemical potentials, electrophilicity, and softness of complexes do not change considerably after adsorption of CO and ClCN on PSWCNT. CO and ClCN adsorption on TM-CNT results in drastic changes in the structure under study's mechanical and chemical properties, as well as its softness and electrophilicity.

3.4. Density of states study

The density of states (DOSs) for PSWCNT and TM-doped CNT systems with and without adsorption were computed to further investigate the electronic characteristics following CO and ClCN adsorption; the findings are displayed in Fig. 4 When comparing the DOS of an isolated PSWCNT to that of PSWCNT–CO and PSWCNT–ClCN complexes, we detect no evidence of hybridization. For the adsorption of the above-mentioned compounds, PSWCNT would not be an ideal adsorbent When TM-CNT and the above-mentioned molecules are adsorbed, one may notice significant changes in the hybridization of these molecules with the TM-CNT. It is shown in Figure 4 that the TM doping in carbon nanotubes allows it to

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increase its electrical conductivity by moving the Homo and LUMO peak to the lower value, which reduces the electrical conductivity of the nanotube. The presence of CO and ClCN may be detected with high sensitivity by comparing the changes in TM-CNT system conductivity before and after adsorption. As a result, TM-CNT may be a viable sensor material for the detection of CO and ClCN.

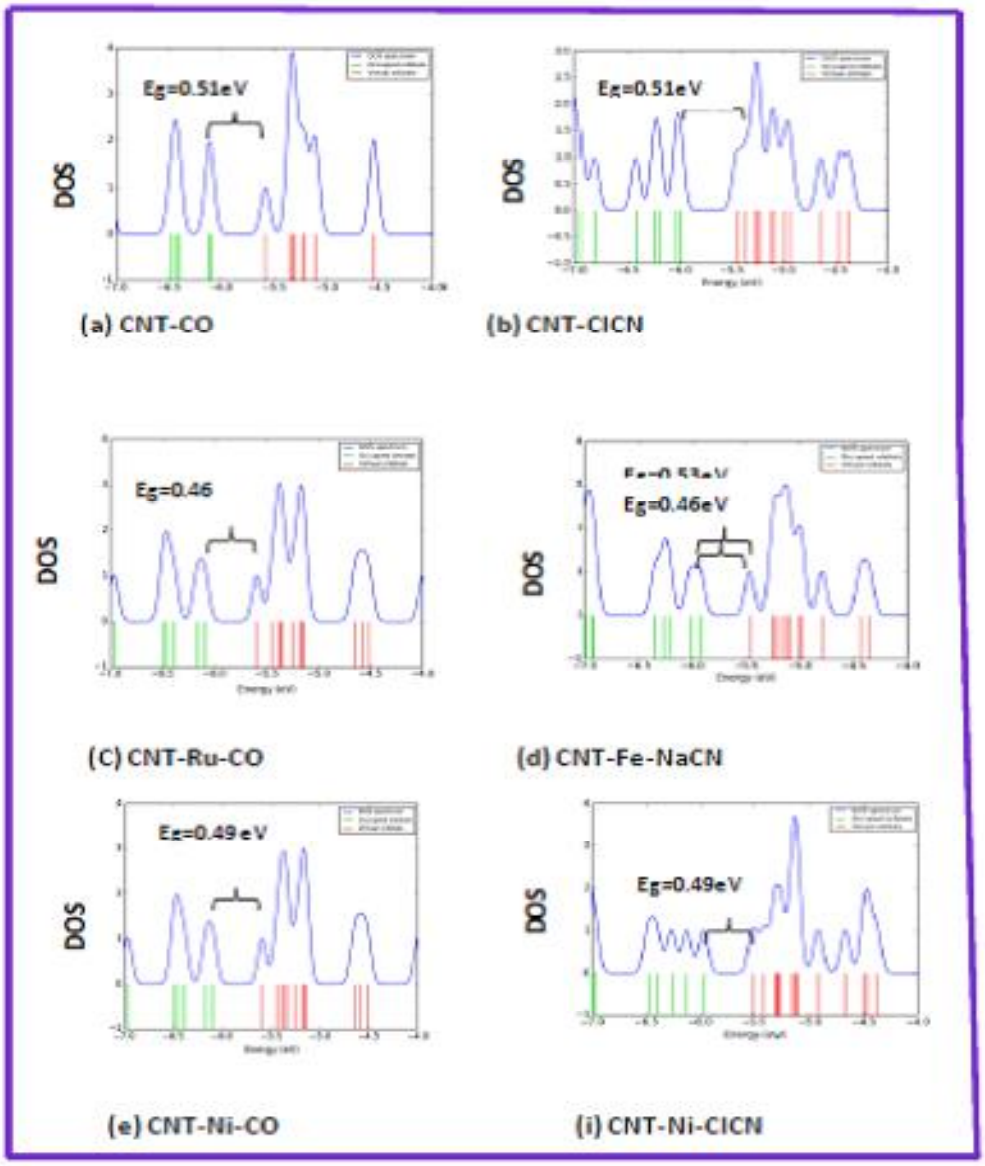

Fig. 5. The DOS for PCNT, PCNT–CO, PCNT–NaCN, PCNT–ClCN, and PCNT–TM-doped CNT CO and ClCN that are all segregated from one other.

4. Conclusions

In order to compare the adsorption of CO and ClCN on the pure and TM-doped single-walled carbon nanotubes, One may establish a theory of CO and ClCN adsorption enhancement theoretically utilizing DFT. It is proven that the poor physisorption of these gas molecules on pure SWCNT could be greatly increased to the hazardous gas by doping TM into structure of SWCNT. A change in SWCNT's electronic structure is induced by the doped TM, which subsequently results in an extremely high adsorption of the molecules being adsorbed. Different analyses, such as differential optical spectroscopy (DOM), have successfully demonstrated the

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moderate adsorption of these gas molecules by pure carbon nanotubes and the strong adsorption by TM-SWCNT. A modest energy gap seems to be the determining factor in the TM-doped SWCNT's improved CO and ClCN sensitivity, as shown by the Global indices. Due to the fact that virgin SWCNT does not adsorb well to these gas molecules, we present the TM-doped SWCNT as a more effective adsorbent/sensor. We discover that the best sensor for CO and ClCN is CNT-Ni.

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