

Determination of Ru and Ni-Doped Carbon Nanotube as Sensor Identifying CHCl_3 Molecular using DFT Method

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Key words: Chloroform, electronic results, adsorption process, energy, dipole moments

Abstract: First-principles computations have been applied to scrutinize the adsorption behavior of Chloroform CHCl_3 molecule on the external surface of Ruthenium (Ru) and Nickel (Ni) -doped (8,0) zigzag single-walled carbon nanotubes (SWCNTs) with 10 and 12Å length. Binding energy corresponding to the most stable configuration of CHCl_3 on the Ru-doped CNT at the length 10Å is found to be -9.080 eV which is high typical sensitivity to CHCl_3 molecule. In this study, two sensitive nanotube is configured of the CHCl_3 molecule by replacing one carbon atom of the SWCNT with Ru and Ni atom. Our results indicate that the adsorption of CHCl_3 molecular on pristine carbon nanotube is weak because there is no marked change in the energy gap but Ru- and Ni-doping CNT can lowering the energy gap of $\text{CHCl}_3/\text{CNTs}$ complexes. Our electronic results reveal that there is a notable orbital hybridization among two species in adsorption process being an evidence of strong interaction. For the $\text{CHCl}_3/\text{CNTs}$ complexes, the energy gaps, dipole moments, natural atomic orbital occupancies and global indices are computed. Finally, we reported a novel type of Chloroform sensor that can be used for detecting the presence of CHCl_3 molecule.

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INTRODUCTION

Since, the discovery of Carbon Nanotubes (CNTs) through 1991 via. Iijima, Carbon Nanotubes (CNTs) the promise is pretty much substance it can revolutionize the electronics and nanoelectronics technologies. Along with that unusual electronic characteristics (Rahmanifar *et al.*, 2016; Boroznina and Zaporotskova, 2018; Amorim *et al.*, 2013). CNT are so, interesting systems from both, the physical and the technological, viewpoint further to their prominent mechanical properties such as high stiffness and an formidable young's modulus of almost 1 TPa

(Wagner *et al.*, 2012). Carbon nanotubes based gas sensors due to their exquisitely sensing capability, like high sensitivity, speedy reaction, small size and occasional running temperature (Cui *et al.*, 2018). (CNT) can be either Single-Walled [SW] with discrete fragment of curved carbon sheet or Multi-Walled [MW] (Rahmanifar *et al.*, 2016). Single-wall CNTs are perfect applicants to study general transport properties of quasi-one-dimensional systems (Latessa *et al.*, 2007).

Every SWCNT can be indicated with a pair of integers $[n, m]$ and categorized to 3 types, particularly, armchair nanotubes $[n, n]$, zigzag nanotubes $[n, 0]$ and

chiral nanotubes [n, m] with n m. These residences have made probable the application of CNTs in lots of areas including electronic devices, fuel cell, hydrogen storage, electrode catalysis, gas sensing, etc., (Kanchanatip *et al.*, 2018; Correa *et al.*, 2016).

Chloroform (trichloro-methane) CHCl_3 is an organic compound, colorless, sweet smelling, dense liquid and is considered somewhat carcinogenic, toxic and hazardous, several million tons are produced annually as a precursor to industry as poly-tetrafluoroethylene and refrigerants, but its use for refrigerants is being phased out, it was once a widely used anesthetic and used as a solvent in the pharmaceutical industry and for producing dyes and pesticides (Flanagan and Pounder, 2010; Leikin and Paloucek, 2008). Chloroform vapors depress the central nervous system of human beings and animal. It is immediately treacherous and perfidious to life and health. Breathing about 1000 ppm for a short time can cause dizziness, fatigue, eyesight disturbance, headache, lung congestion, kidney damage, cancer and even death. Chronic chloroform exposure can damage the liver and the kidneys (where chloroform is metabolized to phosgene) and some people develop sores when the skin is immersed in chloroform (Perillo and Rodriguez, 2013). The national institute for occupational safety and health set two limits for chloroform, recommended exposure limit of 2 ppm [for 60 min] based on risk evaluations using human or animal health effects data and permissible exposure limit of 50 ppm as carcinogen substance with targeted organs such liver, kidneys and central nervous system (Zhang *et al.*, 2013; Liu *et al.*, 2013).

They reported that the interaction of CHCl_3 on Ru and Ni-doped carbon nanotubes surface are weak, while the Ru- and Ni-doped on the (8,0) CNT at the length 10 Å can slightly enhance adsorption capability of the CHCl_3 molecule in comparison with pristine CNT and other nanotubes (Kanchanatip *et al.*, 2018). In this study, the adsorption of CHCl_3 molecule on the Ru- and Ni-doped CNT at the length 10 and 12 Å has been investigated. The analyses considered the CHCl_3 adsorption capability and examined the effect of Ru- and Ni-doped on the electronic and structural properties, potential applications as nanosensor and adsorption capability of CNT through DFT calculations. The optimized geometries, electronegativity, electronic chemical potential, global softness, global hardness, electrophilicity index, were calculated and compared with the Ru- and Ni-doped (8, 0) zigzag SWCNTs at the length 10 and 12 Å. We hope our results can provide experiments with useful information on designing sensors employing the carbon nano-materials.

MATERIALS AND METHODS

Computational methods: In this research, we examined the adsorption behavior of the CHCl_3 molecule on zigzag

single wall Ru and Ni-doped (8, 0) CNT. All atoms, the optimizations and energy calculations are performed using Gaussian 09 program package at the level of Density Functional Theory (DFT) with B3LYP/6-31G. The Ru-doped and Ni-doped (8,0) zigzag CNTs at the length 10 and 12 Å. The binding energy (E_{ad}) of a CHCl_3 on the CNT is determined through the following equation (Ghalib, 2014):

$$E_{ad} = E_{\text{Ru-CNT-CHCl}_3} - (E_{\text{Ru-CNT}} + E_{\text{CHCl}_3}) \quad (1)$$

$$E_{ad} = E_{\text{Ni-CNT-CHCl}_3} - (E_{\text{Ni-CNT}} + E_{\text{CHCl}_3}) \quad (2)$$

where, $E_{\text{Ru-CNT-CHCl}_3}$ and $E_{\text{Ni-CNT-CHCl}_3}$ are the total energy of the Ru doped and Ni-doped interacting with the CHCl_3 . $E_{\text{Ru-CNT}}$ and $E_{\text{Ni-CNT}}$ are the total energy of Ru and Ni-doped on the CNT and is the total energy of an isolated CHCl_3 molecule. The electrophilicity index which calculates the stabilization in energy when the system obtains an additional electronic charge. Thus, μ is defined according to the following equation:

$$\mu = \frac{I.P + E.A}{2} \quad (3)$$

$$I.P = -E_{\text{HOMO}} \quad (4)$$

$$E.A = -E_{\text{LUMO}} \quad (5)$$

where, E_{HOMO} is the energy of highest occupied molecular orbital and E_{LUMO} is the energy of lowest unoccupied molecular orbital. X is defined as the negative of μ , as follows: $X = -\mu$. Furthermore, η can be determined as: $\eta = (E_{\text{LUMO}} - E_{\text{HOMO}})/2$. S and ω are specified as the following equations, respectively:

$$S = \frac{1}{2\eta} \quad (6)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (7)$$

RESULTS AND DISCUSSION

The CHCl_3 adsorbed on the Ru and Ni-doped CNT: Considering the detailed properties and behavior of transitional metal doping on the adsorption of CHCl_3 molecule on the (8, 0) CNTs at the different length systems for most stable configurations, we substitute a carbon atom in the middle of CNT at length 10 Å by one Ru and Ni atoms Fig. 1 indicates the schematic of the possible adsorption sites of a CHCl_3 molecule adsorbed on the Ru and Ni-doped (8,0) CNT surface.

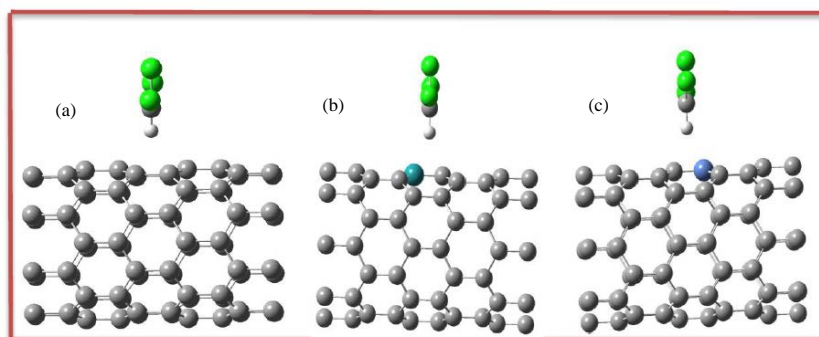


Fig. 1(a-c): The optimized structure for the most stable configuration of CHCl_3 molecule on Ru- and Ni-doped CNTs/ at length 10 \AA systems: (a) CNT- CHCl_3 , (b) CNT-Ru- CHCl_3 and (c) CNT-Ni- CHCl_3

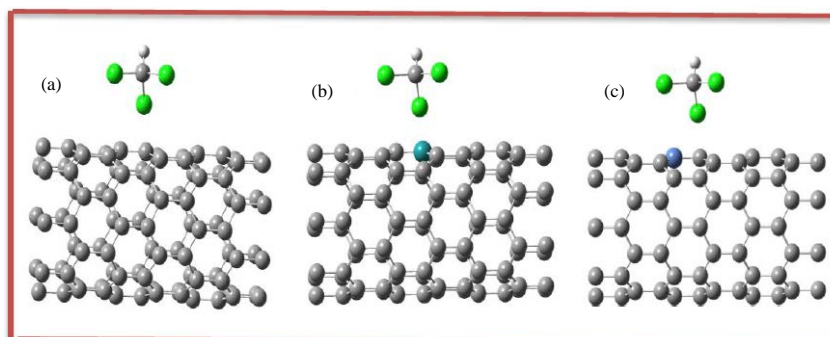


Fig. 2(a-c): The optimized structure for the most stable configuration of CHCl_3 molecule on Ru- and Ni-doped CNTs at length 12 \AA systems: (a) CNT- CHCl_3 , (b) CNT-Ru- CHCl_3 and (c) CNT-Ni- CHCl_3

The binding energy for CHCl_3 adsorption on the Ruthenium and Nickel-doped CNT are with a well maximum about -9.080 eV and -12.425 eV , respectively. In contrast, the adsorption of CHCl_3 molecule on the Ru-doped CNT can be attributed to the strong hybridization between the Ruthenium orbitals and carbon orbitals. In this case, the binding energy for CHCl_3 on the Ru site is more than the Ni site with a similar configuration. The average Ru C and Ni C bond lengths are about 1.414 \AA and 1.421 \AA , respectively. While with the CHCl_3 adsorption on Ru and Ni-doped CNT at length 10 \AA due to increase of the average Ru C and Ni C bond lengths are about 1.422 \AA and 1.422 \AA , respectively. We believe that the doping of Ru atom on the CNT is slightly eligible than the Ni-doped CNT. The current calculations show that the adsorption energy of CHCl_3 on the Ru-doped and Ni-doped CNT with an equilibrium distances Fig. 1. The computations indicate that the adsorption of CHCl_3 molecule on surfaces of Ru and Ni-doped (8, 0) CNT at length 12 \AA are about -8.364 and -45.693 eV with distances of 2.194 and 2.428 \AA , respectively (Fig. 2). Our calculations result show that the interaction between CHCl_3 and zigzag CNT at length

12 \AA are slightly stronger than zigzag CNT at length 10 \AA . Recently, these computations indicate that the Ru and Ni atoms play a significant role in enhancing the CHCl_3 adsorption on the CNT in comparison with pristine CNT.

Electric dipole moment: When a chloroform is adsorbed on such systems, the charge distribution would be scrutinized by the dipole moment vector of species which prominently the size and direction of the dipole moment vector are changed when a CHCl_3 approaches to the surface of Ru and Ni-doped carbon nanotubes have dependence on the adsorption configurations. The results of the electric dipole moment for CHCl_3 and sites show that the adsorption energy is the highest in the equilibrium distances which are listed (Table 1 and 2). The result demonstrates that during CHCl_3 adsorption for all systems the total dipole moment increases. We consider that dipole moment for Ru and Ni-doped CNTs at length 10 and 12 \AA are about 0.727 , 0.623 , 0.412 and 1.332 Debye, respectively. In the case of the CHCl_3 adsorption on the Ru and Ni-doped CNTs at length 10 and 12 \AA are about 10.100 , 8.039 , 9.140 and 3.934 Debye,

Table 1: HOMO (eV), LUMO (eV), bond Gap (eV) and dipole moment (Debye) for CHCl₃ adsorptions on the Ru and Ni-doped CNT/at length 10 Å surfaces at the B3LYP/6-31G level

Property	E _{HOMO} (eV)	E _{LUMO} (eV)	Energy gap (eV)	Binding energy (eV)	Dipole moment (Debye)
CNT	-6.347	-5.505	0.842	-	0.000
CNT-Ru	-6.230	-5.642	0.588	-	0.727
CNT-Ni	-6.231	-5.687	0.544	-	0.623
CNT-CHCl ₃	-5.893	-5.264	0.629	-9.327	8.080
CNT-Ru-CHCl ₃	-5.884	-5.346	0.538	-9.080	10.100
CNT-Ni-CHCl ₃	-5.911	-5.395	0.516	-12.425	8.039

Table 2: HOMO (eV), LUMO (eV), bond Gap (eV) and dipole moment (Debye) for CHCl₃ adsorptions on the Ru and Ni-doped CNT/ at length 12 Å surfaces at the B3LYP/6-31G level

Property	E _{HOMO} (eV)	E _{LUMO} (eV)	Energy gap (eV)	Binding energy (eV)	Dipole moment (Debye)
CNT	-6.089	-5.570	0.519	-	0.000
CNT-Ru	-6.056	-5.487	0.569	-	0.412
CNT-Ni	-5.942	-5.404	0.538	-	0.324
CNT-CHCl ₃	-5.994	-5.496	0.498	-7.851	2.980
CNT-Ru-CHCl ₃	-5.726	-5.283	0.443	-8.364	9.140
CNT-Ni-CHCl ₃	-5.878	-5.415	0.463	-45.693	3.934

Table 3: Chemical potential (μ), hardness (η), Softness (S) and electrophilicity (ω), of CHCl₃ molecule adsorptions on the Ru and Ni-doped CNTs at the length 10 Å surfaces at the B3LYP/6-31G level. All parameters are in units of eV

Property	I.P (eV)	E.A (eV)	Chemical potential (eV)	Hardness (eV)	Softness (eV)	Electrophilicity (eV)
CNT	6.347	5.505	-5.926	0.421	1.187	41.706
CNT-Ru	6.230	5.642	-5.936	0.294	1.700	59.925
CNT-Ni	6.231	5.687	-5.959	0.272	1.838	65.273
CNT-CHCl ₃	5.893	5.264	-5.578	0.314	1.592	49.544
CNT-Ru-CHCl ₃	5.884	5.346	-5.615	0.269	1.858	58.662
CNT-Ni-CHCl ₃	5.911	5.395	-5.653	0.258	1.937	61.930

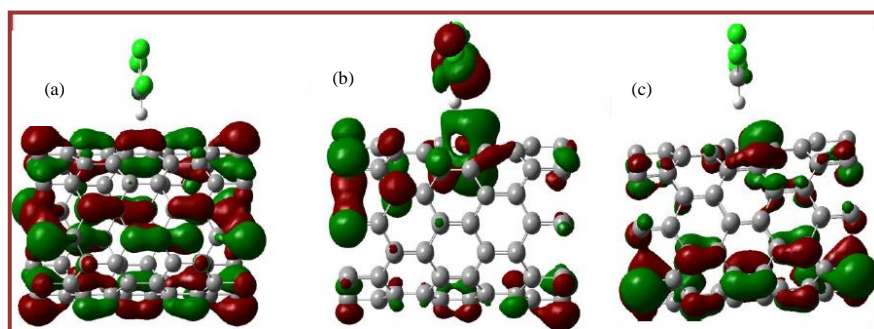


Fig. 3(a-c): Charge distribution of HOMO and LUMO orbitals on the Ru- and Ni-doped CNTs at length 10 Å loaded with one CHCl₃ molecule at the B3LYP/6-31G method

respectively. Substantially, both electron transfers and dipole moment imply this concept that Ru and Ni-doped CNT with absorption of the CHCl₃ are caused to increase the polarization and change dipole moments (Fig. 3-6).

Global indices: The global hardness of types is specified as its endurance toward deformation in the presence of an electric field. Increasing in global hardness leads to increase in stability and diminish in reactivity of the species (Soltani *et al.*, 2012). The global indices of reactivity in the basis of the DFT for CHCl₃ adsorption on the Ru and Ni-doped zigzag CNTs at the length 10 Å are presented in Table 3. When CHCl₃ adsorbs on the Ru and Ni-doped, hardness, electrophilicity and electronic

chemical potentials of CNTs will be reduced, also softness will be increased. The results also indicate that when CHCl₃ is chemisorbed on the exterior surface of the Ru and Ni-doped/CNTs, a fairly large charge transfer to the CHCl₃ could occur which suggests that their electronic transport properties could be notably changed upon chemisorptions of CHCl₃. The direction of electron flow will be characterized via. electronegativity or chemical potential. When CHCl₃ is added to Ru- and Ni-doped/CNTs electrons are transferred from the higher chemical potential to the lower chemical potential, in order to the electronic chemical potentials become identical. As a result, electrons will flow from a definite occupied orbital in a Ru and Ni-doped/CNTs and will go into a definite empty orbital in a CHCl₃.

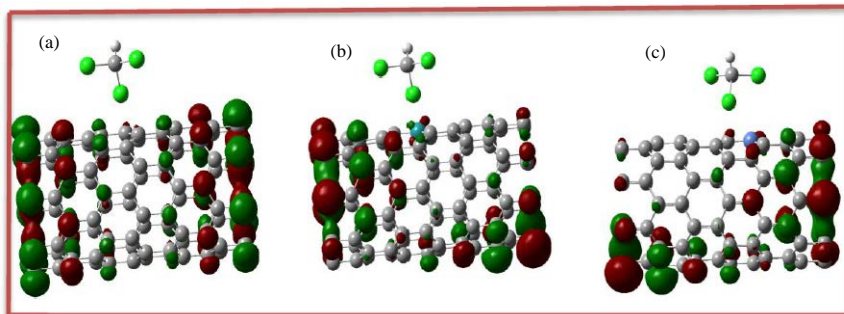


Fig. 4(a-c): Charge distribution of HOMO and LUMO orbitals on the Ru- and Ni-doped CNTs at length 12 Å loaded with one CHCl₃ molecule at the B3LYP/6-31G method

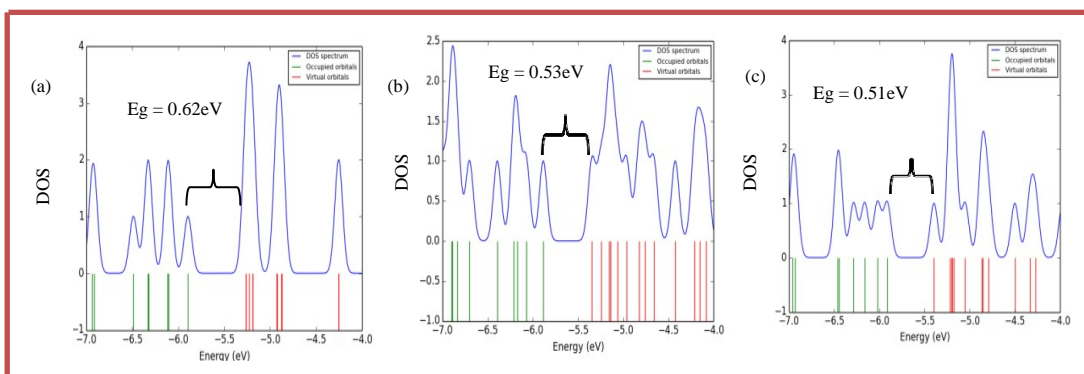


Fig. 5: Total Density of States (DOS) for CHCl₃ molecule on Ru- and Ni-doped CNT at length 10 Å (a) CNT-CHCl₃, (b) CNT-Ru-CHCl₃ and (c) CNT-Ni-CHCl₃

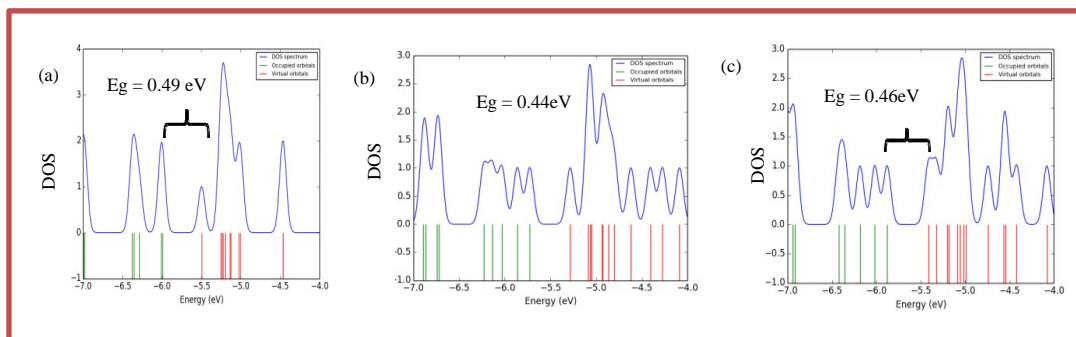


Fig. 6: Total Density of States (DOS) for CHCl₃ molecule on Ru- and Ni-doped CNT at length 12 Å (a) CNT-CHCl₃, (b) CNT-Ru-CHCl₃ and (c) CNT-Ni-CHCl₃

Table 3 consists of variable information regarding the quantum molecular descriptor which could be explained as follows: Considering the amount of chemical potential the table shows that, there is downward trend for Ru and Ni-doped CNT at the length 10 Å from -5.936, -5.959 eV to -5.615, 5.53 eV CNT/CHCl₃. Hardness is also scrutinize and it is decreased in

Ru-doped (10, 0) CNT from 0.294 to 0.269 eV, while the mode is reverse for Ni-doped CNT at the length 10 Å of reduction. It is extracted from the data that there is a reverse result for doping of Ru and Ni atoms. And, no noticeable changes have been found to happen as result of the increasing of length CNT (Table 4).

Table 4: Chemical potential (μ), hardness (η), Softness (S) and electrophilicity (ω), of CHCl₃ molecule adsorptions on the Ru and Ni-doped CNTs at the length 12 Å surfaces at the B3LYP/6-31G level. All parameters are in units of eV

Property	I.P (eV)	E.A (eV)	Chemical potential (eV)	Hardness (eV)	Softness (eV)	Electrophilicity (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-Ni	5.942	5.404	-5.673	0.269	1.858	59.817
CNT-CHCl ₃	5.994	5.496	-5.745	0.249	2.008	68.538
CNT-Ru-CHCl ₃	5.726	5.283	-5.504	0.221	2.262	68.997
CNT-Ni-CHCl ₃	5.878	5.415	-5.646	0.231	2.164	8.218

CONCLUSION

The adsorption behavior and electronic properties of CHCl₃ adsorption on transitional metal doping of Ru and Ni atoms on outer surface of (8, 0) single walled carbon nanotube at the length 10 and 12 Å were studied through DFT calculations. For CHCl₃ adsorption on the Ru- and Ni-doped- CNTs, electronic properties of the tubes will be changed. Our results indicated that the transfer of charge from CHCl₃ to doping atoms (Ru and Ni atoms) is a remarkable factor in the change of the electrical conductance of the carbon nanotubes. On the basis of our calculations, it seems that doping effect on CNTs can detect CHCl₃ molecule. Diminish in HOMO–LUMO energy gaps, ionization potential, and global hardness with the adsorption of CHCl₃ on the transitional metal doped in CNT surface due to increase of the chemical reactivity and also lead to the lowering of stability in the complexes.

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