 Egypt. J. Chem. **Vol. 65**, No. 6. pp. 89 - 98 (2022)

Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

Investigation Ability of Single Walled Carbon Nanotubes to Detection Toxic Gases Utilizing DFT Calculations

Rajaa K. Mohammad[a], Shaymaa Hussein Nowfal[b], Mohammed A. Al-Seady[c]* and Hayder M. Abduljalil[4]

[1]*Department of Physics, College of Science, University of Karbala, Karbala, Iraq.*
[2]*University of Warith Al-Anbiyaa, College of Engineering, Department of Biomedical Engineering, Karbala, Iraq*
[3]*University of Babylon-Environmental Research and Studied Centre-Babylon-Iraq.*
[4]*University of Babylon-College of Science-Physics Department-Babylon-Iraq.*

Abstract

The interaction between poisonous gases and the surface of a single-walled carbon nanotube (SWCNT) is investigated using density function theory (DFT) in this work. Fluorine (F2), carbon monoxide (CO), and carbon dioxide (CO2) are the toxic gases used in this investigation (CO2). F_2 and CO have strong reactivity with the surface of SWCNT, according to adsorption calculations. They are chemical interactions as well. Because of its physical adsorption, the CO2 gas molecule does not interact with the current system. The current nanosystem can detect F_2 and CO gas molecules, according to the sensitivity calculation. Only chemical adsorption changed the UV-visible spectrum, and this was visible in F_2 and CO interactions. The optical response result describes how to develop and use an optical sensor for CO gas molecule detection in an environmental situation.F_2 and CO are acceptors, while CO_2 is a donor, according to charge transfer calculations.

Keywords: DFT, Adsorption energy, Chemical adsorption, Graphene, Two-dimensional materials

1- Introduction

Carbon nanotubes have been studied by scientists in recent years due to their unique features. Its unusual geometry and carbon allotrope qualities make it ideal for a variety of applications, including electronic devices, energy storage, chemical props, and biosensors[1–4]. Nanomaterials are good for gas chemical and physical adsorption due to their high surface to volume ratio and hollow form. One-dimensional materials such as nanowires, carbon nanotubes, and nanofibers are used to create gas sensors. Graphene is a two-dimensional substance that is derivative[5]. Lijima was the first to discover carbon nanotubes in 1991[6]. Researchers have been studying the thermal, electrical, electron transport, mechanical, and structural properties of nanotubes significantly in recent years[7]. gle walled carbon nanotubes (SWCNT) and multi walled carbon nanotubes (MWCN) are the two forms of carbon nanotubes (MWCNT). SWCNT has a diameter of approximately 1 nm, while MWCNT has a diameter of 5-100 nm[8]. The structural and electronic properties of gas molecules that adsorb on the surface of carbon nanotubes are altered[9, 10]. Carbon nanotubes respond faster, have a higher sensitivity, are smaller, and operate at a lower temperature[11, 12]. Carbon nanotubes are more suited for environmental, pharmacological, and biomedical applications because of certain

*Corresponding author e-mail: wellmsc@gmail.com (Mohammed A. Al-Seady)
Receive Date: 27 July 2021, Revise Date: 27 November 2021, Accept Date: 07 December 2021
DOI: 10.21608/EJCHEM.2021.87777.4232

characteristics [13-16]. The goal of this study was to calculate the interaction between gas molecules and the surface of SWCNT, as well as to point out the nature of the adsorption process. Fluorine (F2), carbon dioxide (CO2), and carbon mono-oxide (CO) were the gases studied.

2- Adsorption process across surface

A number of processes, including heterogeneous catalysis [17], contact formation in molecular electronics[18], and anchoring of biomolecules to solids for sensors and other biomedical applications[19], depend on the development of a bond between a molecule and a metal surface. The adsorption energy is a fundamental number that describes the strength of a molecule's interaction with a surface. Advanced surface science approaches can be used to determine the adsorption energy[20]. Alternatively, adsorption energies can be calculated with reasonable accuracy using density functional theory (DFT)[21]. [22] is the theoretical model that describes adsorption energy: $E_{Ad}=E_{(Gas+Rib.)}-(E_{(Gas)}+E_{(Rib.)})$ (1)

Where E_{Ad} represents the adsorption energy, $E(_{Gas+Rib}.)$, $E(_{Gas})$ and $E(_{Rib.})$ are the total energy for mixture adsorption, gas molecule and isolated nano-ribbon, respectively.

From equation (1) can be classify type of interaction depending on energy of adsorption formed. If E_{ad} varies in range (0.01-0.4) eV is physical interaction, greater than 0.4 eV is chemical[23].

3- Theoretical Background

Density functional theory (DFT), which is widely used in quantum mechanical methods in physics and chemistry, is used to analyze electronic systems and electronic structure. DFT has been most frequently used to evaluate the ground-state characteristics of metals, semiconductors, and insulators. DFT also is an useful strategy in computational physics and chemistry[24]. The Thomas-Fermi model was the historical starting point for the theory of density in 1927. They expressed an atom's kinetic energy as a function of electron number to determine its energy. Density, as well as the typical formulations for nuclear-electron and electron-electron interactions, which can also be represented in terms of electron density[25]. The DFT focuses on the much less convoluted electron density (r). The fundamental notions of DFT are based on ground state energy. The density of electrons determines all other electronic properties in the ground state[26]. However, the electronic density for minimal total energy corresponds with the exact ground conditions of the system.

4- Computational details

n this study, nano tube modular is utilized to create a graphene nano-ribbon structure with n=m=4 and a tube length of 1 nm. For the display system, export the structure to the Gaussian 5.0 version. The input data is then exported to Gaussian 09, which is used to calculate geometrical and electrical parameters, as well as adsorption energy. The ground state parameters were computed using the DFT approach, which was dependent on electron density. Higher Occupied Molecular Orbitals (HOMO) and Lower Unoccupied Molecular Orbitals (LUMO) are produced by molecular orbital energy, and the energy gap and relaxation structure are estimated using the DFT method. The time-dependent-density function theory is used to calculate UV-Visible characteristics. In this investigation, the basis set was 6-31G, and the hybrid function was B3LYP[27].

5- Result and discussions: Geometrical properties.

The geometrical properties of SWCNT at ground state are evaluated using DFT calculations in this study. Figure 1 depicts the geometrical structure of SWCNT, which includes bond length and angle between atoms that produced it. The outcome of the figure reveals that there are four types of bonds between atoms that are related to SWCNT. The lengths of their (C-C, C=C, C—-C, C-H) bonds are (1.4566-1.4801, 1.3546, 1.1413-1.4421, and 1.0853), respectively. The lengths of the C=C and C-H bonds are symmetric in values, according to the results. The angles between atoms (C-C-C, C-C—-C, and C-H=C) are (119.1111-119.1280, 115.5075-120.5344, and 121.8984-121.9001). All of the bond length and angle results correspond with those found in an earlier study[28].

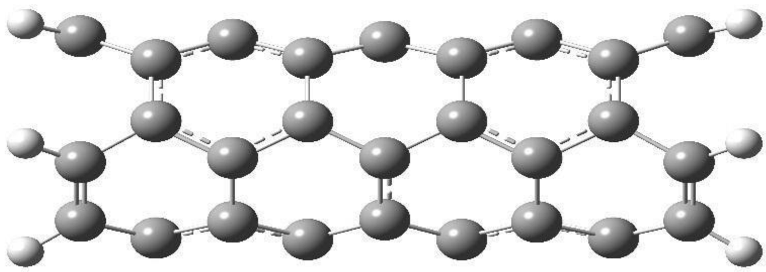


Figure (1): represent geometrical structure of SWCNT, the white and gray balls are H and C atoms, respectively.

6- Adsorption energy.

The term "adsorption energy" was used to characterize the interaction between a gas molecule and the surface of a SWCNT. Determine whether the interaction is chemical or physical. The value of adsorption energy measured in eV is listed in Table 2. In general, an adsorption process system with a high negative energy is considered to be more stable. According to computer simulations, the F2 gas molecule has After it CO, it has a strong reactivity with the surface of SWCNT. Chemical interactions between F2 and CO were also observed. The CO2 gas molecule interacts poorly with the surface of SWCNT, thus the amount of energy released during physical adsorption is minimal. During the adsorption phase, positive energy values appear, indicating that the system is unstable. Figure (2) depicts the molecular orientation of gases surrounding the surface of SWCNT[29].

Table (1): represent values of adsorption energy measured in eV unit and types of interaction

System	**Adsorption energy (eV)**	**Types of interaction**
SWCNT-F_2	-4.1964	Chemical
SWCNT-CO	-1.5337	Chemical
SWCNT-CO_2	0.00325	Physical

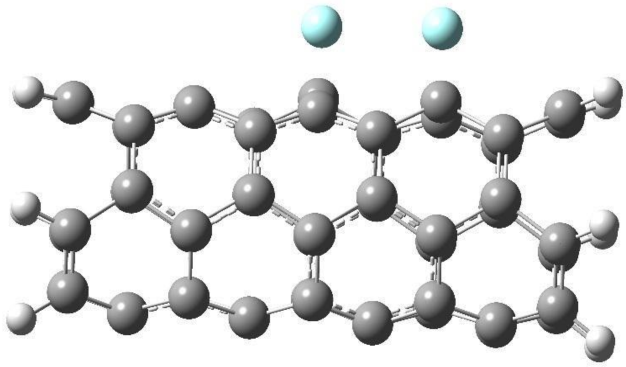
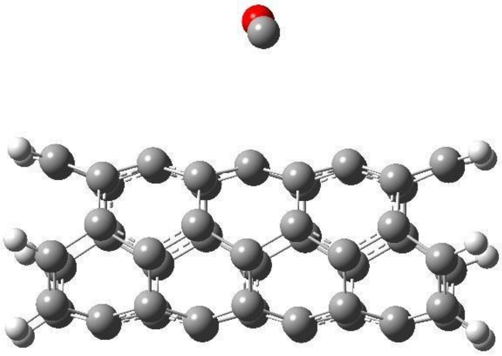
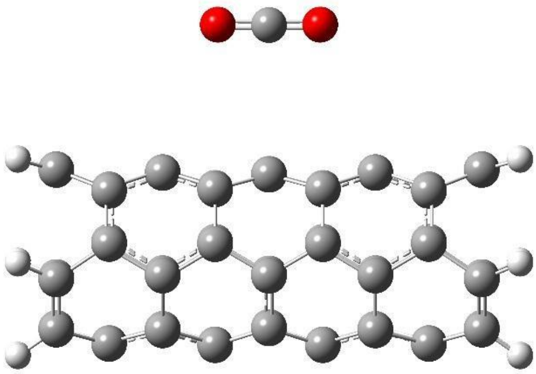
System	Geometrical orientation
SWCNT-F_2	
SWCNT-CO	
SWCNT-CO_2	

Figure (2): represent geometrical orientation of gases molecular around surface of SWCNT.

7-Electronic states and Energy gap.

The energy gap and molecular orbitals are effective tools for characterizing the amount of charge transportation between band energies. DFT simulations are used to investigate the properties in question 1. Table 2 shows the electronic states (HOMO and LUMO) as well as the energy gap in eV units. The results demonstrate that the molecular orbitals and energy gap were modified as a result of the high chemical adsorption between CO and F2 gas molecules. There was no change in CO2 adsorption because the coupled system was unstable. When F2 and CO gas molecules interact with the surface of SWCNT, the band energy narrows, but valance electrons travel freely from HOMO to LUMO through the energy gap .Reversely, CO_2 interaction process doesn't effect on energy gap because physical adsorption condition[30]. Table 3 represent values of sensitivity calculations. Results of the sensitivity shows that SWCNT more sensitive for F_2 and CO gases molecule.

Table (2): represent values of electronic states (HOMO and LUMO) and energy gap measured in eV unit

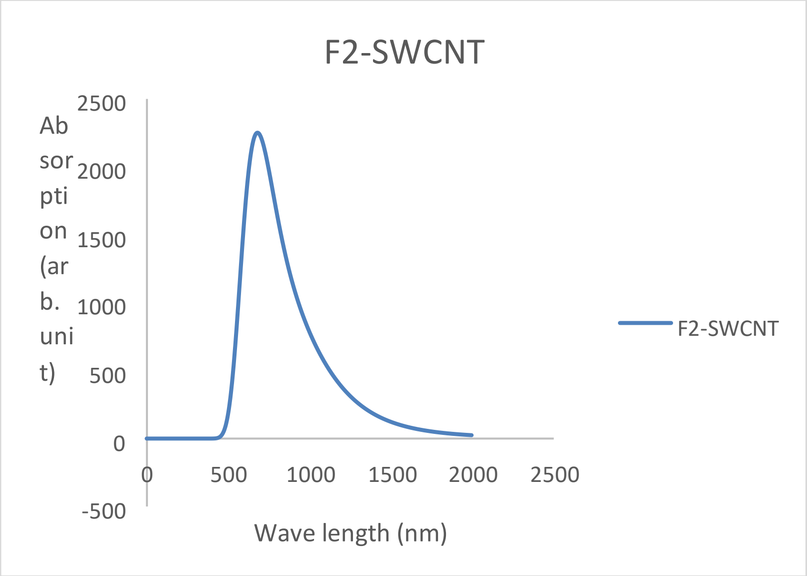
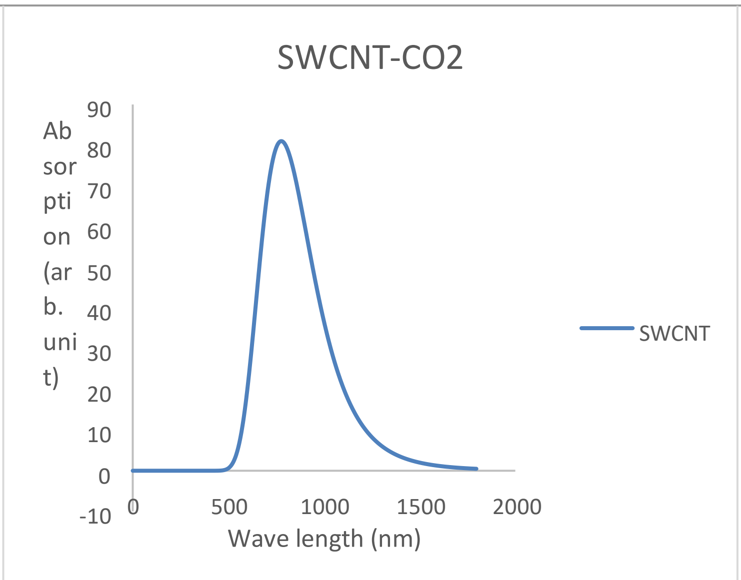
System	HOMO	LUMO	Eg
SWCNT-F2	-4.66641	-2.7445	1.921913
SWCNT-CO2	-4.57172	-2.32328	2.248445
SWCNT-CO	-4.30723	-2.323	1.984226
SWCNT	-4.55948	-2.30069	2.258785

Table (3): represent values of sensitivity for interaction systems.

System	Sensitivity *100%
SWCNT-F_2	0.15
SWCNT-CO	0.12
SWCNT-CO_2	0

8-UV-Visible properties.

The UV-Visible spectrum for the systems under examination was computed through using TD-DFT technique. UV-Visible spectra for SWCNT in pure and contact phases are shown in Figure (3). The maximum absorption wavelength for SWCNT was 812 nm. The result shows that a nanosystem in its pure state received electromagnetic radiation in the red region. Following the adsorption procedure, chemical exchanges between F2 and CO gas molecules had to have an immediate impact on the UV-Visible spectra, shifting it to the blue area of electromagnetic radiation. During the adsorption process, the maximum wave lengths of F2 and CO were 712 and 752 nm, respectively. Because of the low physical adsorption and absorption wave length, the CO2 gas molecule has no effect on the optical absorption of SEWNT in its pure state[31]. When compared to F2, optical response calculations show that SWCNT has a strong reactivity with CO gases. As a result of this finding, we can conclude that we have the ability to develop an optical sensor that can detect the F2 gas molecule. Table 3 shows the optical response values for the system under investigation.

System	UV -Visible
SWCNT -F2	
SWCNT -CO 2	

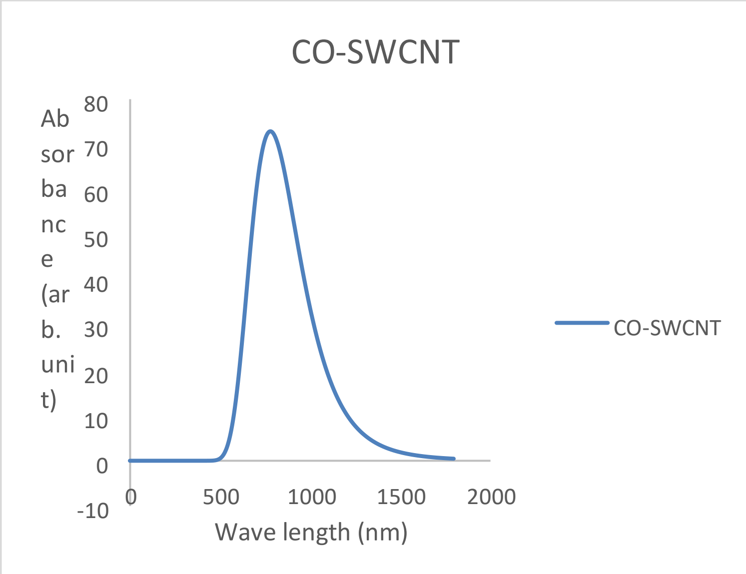
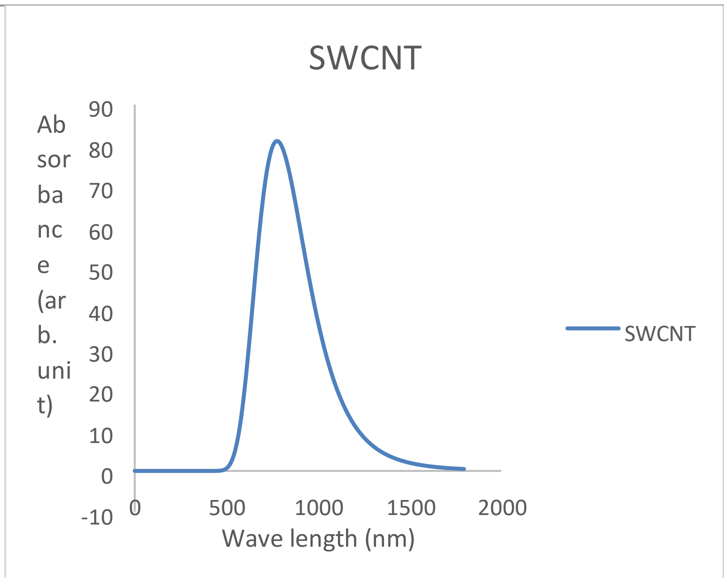
SWCNT -CO	
SWCNT	

Figure (3) represent UV-Visible spectra for SWCNT in pure and interaction phase

Table (4): represent optical response for adsorption gases molecule with surface of SWCNT.

System	Sensitivity *100%
SWCNT-F2	0.16
SWCNT-CO2	0.60
SWCNT-CO	0

9- Charge transfer analysis.

Charge transfer (CT) calculation consider important tool to determine amount of charge that transfer between reactors systems (gas molecules+ carbon nanotube). This method can be used to track the transfer of charge between gas molecules and carbon nanotubes[22]. If CT is positive, it indicates that charge is being moved from a gas molecule to a carbon nanotube, and vice versa[32]. CT values in electron units are presented in Tables (5). (e). The results show a clear trail of charge transfer from SWCNT to gas particles in the interaction of F2 and CO. In addition, due of the high chemical adsorption, the F2 interaction delivers a large quantity of charge as compared to CO. The charge transfer from the gas molecule to the SWCNT is visible in the CO2 interaction, but only in a small amount due to low physical adsorption[33]. The final results demonstrate that F2 and CO are acceptors, while CO2 is a donors..

Table (5) represent values of CT measured in electron unit (e).

System	CT (e) unit
SWCNT-F_2	-0.6489
SWCNT-CO	-0.3571
SWCNT-CO_2	0.0921

10-Conclusions

1- Geometrical structure calculations show that all bond length for system under study are agreements with experimental measurement.
2- Adsorption calculations show that F2 and CO gases molecule have chemical reaction with surface of SWCNT.
3- Sensitivity calculation shows that SWCNT sensitive F2 gases molecule greater from others.
4- Band gap energy changes only in a chemical interaction between two reactors.
5- Optical response calculations show that ability to design optical sensor for CO gas molecule

11- References

[1] N. Martin and J.-F. Nierengarten, *Supramolecular chemistry of fullerenes and carbon nanotubes*. John Wiley & Sons, 2012.

[2] A. Kumar, V. Kumar, and K. Awasthi, “Polyaniline–carbon nanotube composites: preparation methods, properties, and applications,” *Polym. Plast. Technol. Eng.*, vol. 57, no. 2, pp. 70–97, 2018.

[3] J. M. Marulanda, *Carbon nanotubes*. 2010.

[4] J. Zhao, A. Buldum, J. Han, and J. P. Lu, “Gas Molecules Adsorption on Carbon Nanotubes,” *MRS Online Proc. Libr. Arch.*, vol. 633, 2000.

[5] R. Srivastava, H. Suman, S. Shrivastava, and A. Srivastava, “DFT analysis of pristine and functionalized Zigzag CNT: a case of H2S sensing,” *Chem. Phys. Lett.*, vol. 731, p. 136575, 2019.

[6] E. Munoz-Sandoval, “Trends in nanoscience, nanotechnology, and carbon nanotubes: a bibliometric approach,” *J. nanoparticle Res.*, vol. 16, no. 1, pp. 1–22, 2014.

[7] M. A. Hobosyan, P. M. Martinez, A. A. Zakhidov, C. S. Haines, R. H. Baughman, and K. S. Martirosyan, “Laminar composite structures for high power actuators,” *Appl. Phys. Lett.*, vol. 110, no. 20, p. 203101, 2017.

[8] N. Sinha, J. Ma, and J. T. W. Yeow, “Carbon nanotube-based sensors,” *J. Nanosci. Nanotechnol.*, vol. 6, no. 3, pp. 573–590, 2006.

[9] X. Zhang, W. Liu, J. Tang, and P.

Xiao, "Study on PD detection in SF 6 using multi-wall carbon nanotube films sensor," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 17, no. 3, pp. 833–838, 2010.

[10] J. Kong *et al.*, "Nanotube molecular wires as chemical sensors," *Science (80-.).*, vol. 287, no. 5453, pp. 622–625, 2000.

[11] X. Zhang, B. Yang, X. Wang, and C. Luo, "Effect of plasma treatment on multi-walled carbon nanotubes for the detection of H2S and SO2," *Sensors*, vol. 12, no. 7, pp. 9375–9385, 2012.

[12] X. Zhang, B. Yang, Z. Dai, and C. Luo, "The gas response of hydroxyl modified SWCNTs and carboxyl modified SWCNTs to H2S and SO2," *Prz. Elektrotechniczny*, vol. 88, no. 7B, pp. 311–314, 2012.

[13] W.-C. Tian, C.-Y. Kuo, C.-J. Hsieh, H.-L. Lu, and C.-J. Lu, "A carbon nanotube gas sensor using CMOS-based platform," in *SENSORS, 2011 IEEE*, 2011, pp. 1036–1039.

[14] Y. Hizhnyi, S. G. Nedilko, V. Borysiuk, and V. A. Gubanov, "Computational studies of boron-and nitrogen-doped single-walled carbon nanotubes as potential sensor materials of hydrogen halide molecules HX (X= F, C l, B r)," *Int. J. Quantum Chem.*, vol. 115, no. 20, pp. 1475–1482, 2015.

[15] M. Noei, "C4H6 Adsorption on the Surface of a BN Nanotube: DFT Studies," *Int. J. Chem. Mol. Eng.*, vol. 9, no. 2, pp. 270–273, 2015.

[16] F. Mofidi and A. Reisi-Vanani, "Investigation of the electronic and structural properties of graphyne oxide toward CO, CO2 and NH3 adsorption: A DFT and MD study," *Appl. Surf. Sci.*, vol. 507, p. 145134, 2020.

[17] P. E. Turner and S. Duffy, "Evolutionary ecology of multiple phage adsorption and infection," *Bacteriophage Ecol. Popul. growth, Evol. impact Bact. viruses. Cambridge Univ. Press. Cambridge*, 2008.

[18] D. M. Ruthven, "Fundamentals of adsorption equilibrium and kinetics in microporous solids," in *Adsorption and diffusion*, Springer, 2006, pp. 1–43.

[19] J. Rouquerol, F. Rouquerol, P. Llewellyn, G. Maurin, and K. S. W. Sing, *Adsorption by powders and porous solids: principles, methodology and applications*. Academic press, 2013.

[20] V. A. Lavrenko, I. A. Podchernyaeva, D. V Shchur, A. D. Zolotarenko, and A. D. Zolotarenko, "Features of physical and chemical adsorption during interaction of polycrystalline and nanocrystalline materials with gases," *Powder Metall. Met. Ceram.*, vol. 56, no. 9, pp. 504–511, 2018.

[21] G. Crini and P.-M. Badot, "Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature," *Prog. Polym. Sci.*, vol. 33, no. 4, pp. 399–447, 2008.

[22] M. A. Al-Seady, E. Ahmed, H. M. Abduljalil, and A. A. Kahewish, "Studying the adsorption energy of CO gas molecule in different nano-systems using density function theory," *Egypt. J. Chem.*, vol. 64, no. 5, pp. 2607–2612, 2021.

[23] J. Li, Y. Lu, Q. Ye, M. Cinke, J. Han, and M. Meyyappan, "Carbon nanotube sensors for gas and organic vapor detection," *Nano Lett.*, vol. 3, no. 7, pp. 929–933, 2003.

[24] D. Young, *Computational chemistry: a practical guide for applying techniques to real world problems*. John Wiley & Sons, 2004.

[25] Y. Wang, "Theoretical Studies on Water Splitting Using Transition Metal Complexes." KTH Royal Institute of Technology, 2014.

[26] F. H. Hanoon, "Investigation Of The Electronic Structure For Rhenium Oxide Tetra Chloride By B3lyp Density Functional Theory," *J. Univ. Babylon*, vol. 21, no. 5, 2013.

[27] S. M. Nemaa, M. A. Mejbel, and H. M. Abduljalil, "The Defects Effect on Electronic and Structural Properties for

Boron–Nitride Sulfide Ribbons as a Gas Sensor Using DFT," in *Journal of Physics: Conference Series*, 2019, vol. 1234, no. 1, p. 12057.

[28] M. A. Al-Seady, R. A. Grmasha, N. A.-H. Al-Aaraji, and H. M. Abduljalil, "Investigation Adsorption Mechanism of Methane Gas in Graphene and Copper Doped Nano-ribbon Using Density Function Theory," in *Journal of Physics: Conference Series*, 2021, vol. 1879, no. 3, p. 32099.

[29] M. Yoosefian, "A high efficient nanostructured filter based on functionalized carbon nanotube to reduce the tobacco-specific nitrosamines, NNK," *Appl. Surf. Sci.*, vol. 434, pp. 134–141, 2018.

[30] A. S. Rad, "First principles study of Al-doped graphene as nanostructure adsorbent for NO2 and N2O: DFT calculations," *Appl. Surf. Sci.*, vol. 357, pp. 1217–1224, 2015.

[31] S. M. Aghaei, M. M. Monshi, I. Torres, S. M. J. Zeidi, and I. Calizo, "DFT study of adsorption behavior of NO, CO, NO2, and NH3 molecules on graphene-like BC3: a search for highly sensitive molecular sensor," *Appl. Surf. Sci.*, vol. 427, pp. 326–333, 2018.

[32] R. Chandiramouli, A. Srivastava, and V. Nagarajan, "NO adsorption studies on silicene nanosheet: DFT investigation," *Appl. Surf. Sci.*, vol. 351, pp. 662–672, 2015.

[33] S. H. Sakina, Z. Johari, Z. Auzar, N. E. Alias, M. S. Z. Abidin, and M. F. M. Yusoff, "Improving graphene nanoribbon gas sensing behavior through warping," *Mater. Res. Express*, vol. 4, no. 1, p. 15003, 2017.

.