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RESEARCH ARTICLE

Electronic Properties of Adsorption of CO, CO_2, OH, and B_2 on Nitrogen Doped Graphene Nanosheets as a Gas Sensor Application for Harmful Gases

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Abstract

In the present work, the sensitivity of hybrid nitrogen-graphene nanosheet (Ndoped graphene) toward a series of small gas molecules (CO, CO_2, OH, and B_2) has been calculated based on the first-principles calculations. The properties that have been investigated are the density of state, IR spectra, and the electronic and structural properties. Interestingly, we observed that the adsorptions of (CO, CO2, OH, and B2) on the N-doped graphene are small physisorption with adsorption energy (E_{ad}) between 0.75 to 1.15 eV, whereas the adsorption of CO on N doped graphene is high chemisorptions. The adsorption of CO and CO_2 on the electronic properties lead to a decreasing in the highest occupied molecular orbital (E_{HOMO}) and lowest unoccupied molecular orbital (E_{LUMO}) and Fermi energy (E_f), and increasing in the energy band gap (E_g). Our findings indicate the possibility of using this nanosheet as a gas sensor for harmful gases (CO, CO_2).

Keywords: *Electronic properties, Nitrogen- graphene nanosheet, Gas sensor, Harmful gases.*

Introduction

Graphite-have recently attracted attention as a viable and not expensive filler in composite materials [1], and can be used in many applications due to the excellent in plane mechanical, structural, electrical, and thermal properties [2]. One layer of graphite (graphene) has raised interest in a wide scientific community for its extraordinary thermal, electrical, electronic mechanical and other properties [3]. Graphene is a new carbon material and has two-dimensional crystal of honeycomb structure. In addition, it can be found in a freestanding state, and has extremely high electron mobility, thermal and electric conductivity, optical transparency, and mechanical toughness [4].

Graphene's many superior properties justify its nickname of a 'miracle material'. However, some of these characteristics have been achieved only for the highest-quality samples (mechanically exfoliated graphene) and for graphene deposited on special substrates like hexagonal boron nitride [5,6]. Also, has not only unusual properties regarding mechanical strength, 2-diemensional films and thermal conductivity, but peculiar electronic characteristics such as Dirac-particles with a linear dispersion, simply absorption coefficient of lights and transport energy gap [7, 8]. Investigations of the structural and electric properties of some graphene/metal interfaces, still not completely understood. Such studies required a careful review of the growth protocols reported in the literature to reproduce them and thereby fully control the features of the interfaces. The attention was devoted in particular to the electronic (filled and empty) states of graphene. However, the density functional theories (DFT) investigate the reaction barrier reduction for the adsorption of atomic hydrogen at linear bends in graphene.

It is found a significant barrier lowering (≈15%) for realistic radii of curvature (≈20 Å) and that adsorption along the linear bend leads to a stable linear kink. The calculated electronic properties of individual and multiple kink lines, and demonstrate how these act as effected barriers for electron transport [9]. On the other hand, DFT calculation are successful in the study the electronic properties of two-dimensional material and adsorption of NO, NO_2, NH_3,

and SO_2 on nitrogen doped graphene for gas sensor applications [10-14]. In addition, several aspects of graphene are studied using DFT calculations such as chemical and electronic properties of graphene-based structures of gas of adsorption graphene-silicene hybrid a gas sensor [15, 16].

Computational Methods

All the calculations are performed using DFT and the geometric structures were completely optimized using Gaussian 09 program package [17]. The system is simulated including 42 carbon atoms of N-graphene, and consisting of 30 carbon atoms and 12 nitrogen atoms as illustrated in Fig. 1. The adsorption energy (E_{ad}) is calculated as the difference between the total energy of molecules on the N-doped graphene ($E_{(gas+NG)}$) and the total energies of molecules and N-doped graphene E_{NG} [11],

Ead =E (gas+ N-graphene) – (ENG - Egas) …….. (1)

The diversity of relative energy of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbital of free N-graphene and adsorbed molecule on N-doped graphene gives the mechanism of interaction. The LUMO is lacking of electrons, thus, it has a power of accepting electrons, whereas HOMO can be defined as an electron donor owing to having excess of electrons. In present work, we will employ the DFT to investigate the influence of harmful gas (CO, CO_2, OH and B_2) on the electronic, structural, density of state (DOS) and spectroscopy properties.

Results and Discussion

Electronic Structure of N-doped Graphene

Fig. 1 illustrates the optimized structure of N-graphene, it found that the C–C bond length is be 1.31 Å, which is smaller than that of C–N (1.45 Å) in N-graphene. Our results are in good agreement with the previous work that confirmed planar structure of N-graphene [18]. Table I shows the calculated electronic and structural properties of N-graphene. The energy gap (E_g) and Fermi energy (E_f) are computed from the EHOMO and ELUMO, (Eg=(ELUMO-EHOMO)) and (Ef=(EHOMO +ELUMO)/2). Our result show that N-graphene is a semiconductor with energy band gap equal 1.16 eV and the Fermi energy equal 5.46 eV.

Clearly, Fig. 2 shows that the highest numbers of degenerate states in the conduction and valence bands are 3.78. In addition, it is evident that there are states available for the occupation at high DOS for a specific energy level and no states can be occupied at a zero-DOS for energy level.

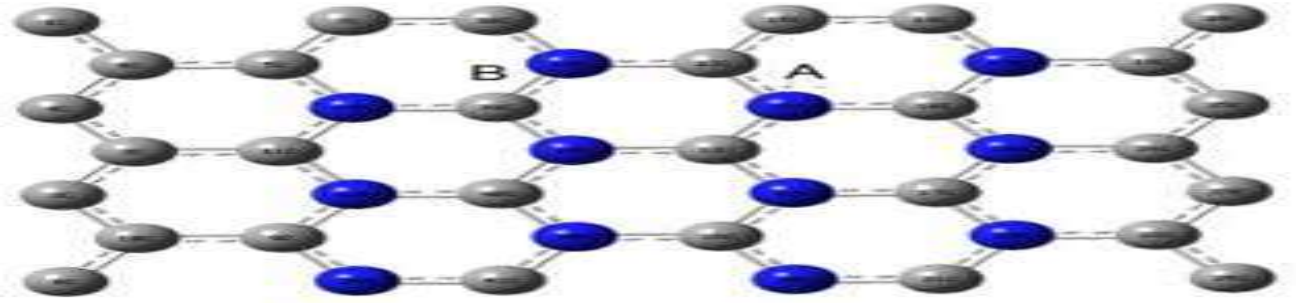

Fig. 1: the optimized structure of N-graphene

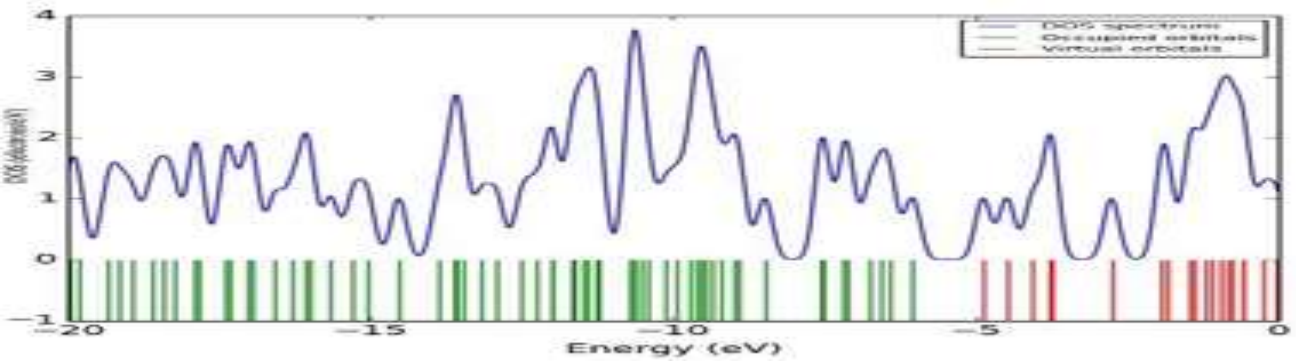

Fig. 2: The density of state of N-graphene

Adsorption of Gas Molecules on N-graphene

In this work, we have been studied the adsorption of gases on the structural and electronic properties of N-graphene at two sites, A-site above N-atom and B-site on C-atom as depicted in Fig. 3. It is well known that the CO molecule combines with blood hemoglobin that prevents the union of oxygen and hemoglobin. In addition, CO is known as colorless and a non-irritating gas [19]. The CO adsorbed on N-graphene is shown in Fig. 3. It is found from the figure that the bond lengths of N–C and C – O are 1.55 Å, and 3.11 Å, respectively, whereas the angles of N–C–O and C–C–O are 175° and 119.17° respectively. Clearly, Table I show that the values of E_{HOMO}, E_{LUMO} and E_f for N-graphene are higher than adsorbed N-graphene at site- A and site- B, conversely, the computed energy gap adsorbed on N-graphene at site- A is higher than pristine N-graphene, while at site-B is smaller than N-graphene. The adsorption energy for N-graphene at B site is smaller than at A site. On the other hand, the DOS for adsorbed N-graphene at the two sites A and B are closed (3.80 and 3.85), and higher than those in N-graphene. Thus, the CO adsorption leads to an increase in the DOS in the conduction and valence bands as observed in Fig. 4.

Table I: The electronic and structure properties of adsorption of CO, CO_2, OH and B_2 on N-graphene at sites A and B

Properties	CO		CO_2		OH		B_2	
	site A	site B	site A	site B	site A	site B	site A	site B
EHOMO	-6.04	-6.37	-6.27	-6.48	-6.38	-5.68	-4.46	-5.85
ELUMO	-4.88	-5.11	-5.34	-5.00	-5.21	-4.46	-4.46	-5.85
E_f	-5.46	-5.74	-5.80	-5.74	-5.80	-5.07	-5.25	-5.19
E_g	1.16	1.27	0.93	1.48	1.17	1.21	1.79	1.33
Ead	-1.49	-1.42	2.97	1.15	-0.75	-4.67	-6.68	-6.71

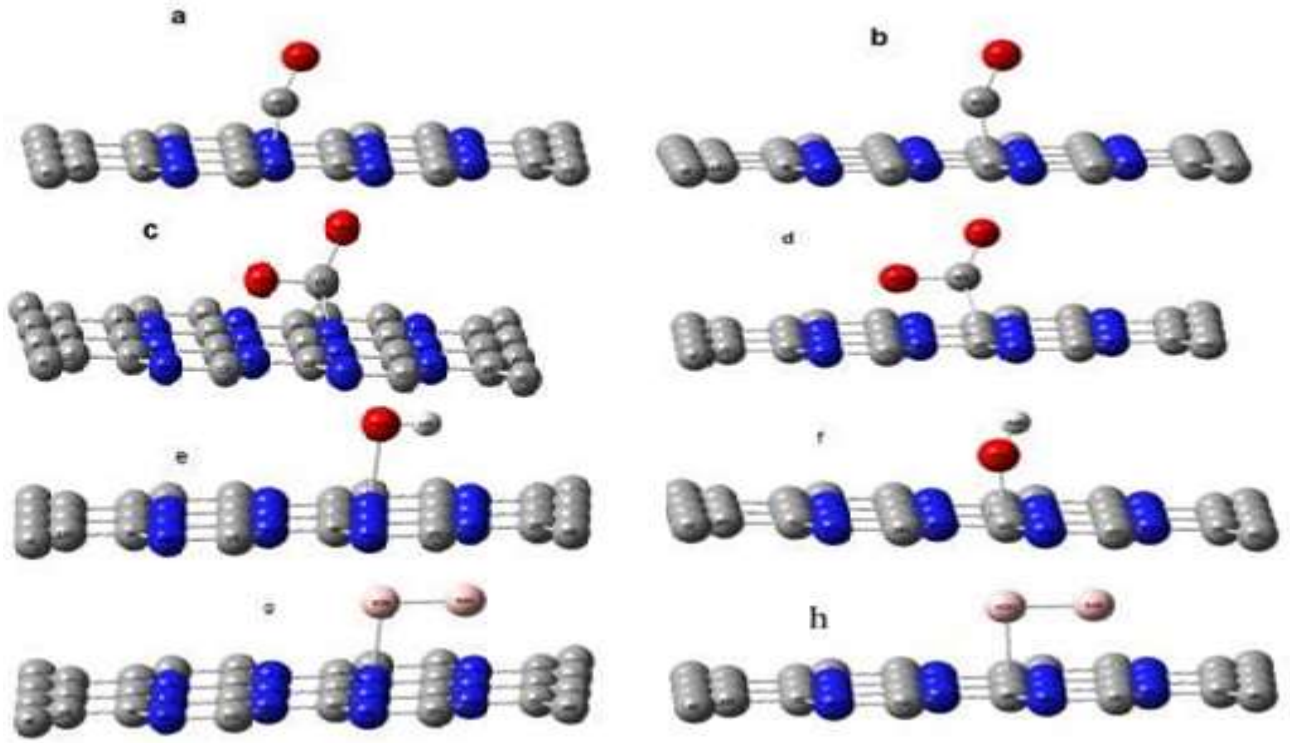

Fig. 3: The side view of the adsorption gas molecules of (a) and (b) CO, (c) and (d) CO_2, (e) and (f) OH, (g) and (h) B_2 on N-graphene

The reduction of CO_2 is considered as the most challenging issue in environmental protection. The search for suitable materials with optimum cost and efficiency, capable of detecting CO_2 in order to incorporate them in the fabrication of devices such as sensors [20].The effect of CO_2 adsorption on the electronic properties of N-graphene lead to a decreasing in the values of E_{HOMO}, E_{LUMO} and E_f and increasing in the E_g and E_{ad} values at sites A and B as listed in Table I. The values of E_{ad} at site- B are higher than at site A are shown the Table I, this indicate that this nanosheet can be used as a chemical sensor for CO_2. On the other hand, the effects of OH and B2 adsorption on the properties of N-graphene lead to an increasing in the values of E_{HOMO}, E_{LUMO}, E_g and E_f at site- A, while

the values at site- B are decreasing .The effect of CO_2 adsorbed on N-graphene as shown in Fig.3 (c and d). It was found that bond lengths of N–C and C –C are 1.309, and 1.5757 Å, respectively, and the angles of N–C–O and O–C–O are 71.209° and 125.1727°, respectively. It is noticed from Fig.4 (e and f) that the DOS of CO_2 adsorbed on N-graphene at site- A and B are respectively 3.73 and 3.67, this adsorption lead to decreases in comparison with the DOS of pristine N-graphene.

Hydroxide (OH) consists of an oxygen and hydrogen atom that held together by a covalent bond, and carries a negative electric charge. It is an important but usually minor constituent of water. It functions as a base, a ligand, a nucleophile, and a catalyst. The hydroxide ion forms salts, some of which dissociate in aqueous solution, liberating solvated hydroxide ions. Sodium hydroxide is a multimillion-ton per annum commodity chemical. In addition, the hydroxide ion is a natural part of water, because of the self-ionization reaction [21]. The effects of OH adsorbed on N-graphene are shown in Fig. 3(c and d), we find that bond lengths of N–C and C–C are 1.4401Å, and 1.4024 Å, respectively, and the angles of C–O-H and N-C-OH are 110.05°, 100.20°. On the other hand, Figure 4(e and f) illustrates the effect of OH adsorption on the DOS of adsorbed N-graphene at sites A and B are equal to 3.96 and 3.71, respectively. It is deduced from the figure that the adsorption leads to a decrease in comparison with the DOS of pristine N-graphene.

Boron is primarily used in chemical compounds; almost half of all boron consumed globally is an additive in fiberglass for insulation and structural materials. The next leading use is in polymers and ceramics in high-strength, lightweight structural and refractory materials. Borosilicate glass is desired for its greater strength and thermal shock resistance than ordinary soda lime glass. Boron as sodium perborate is used as a bleach [22].

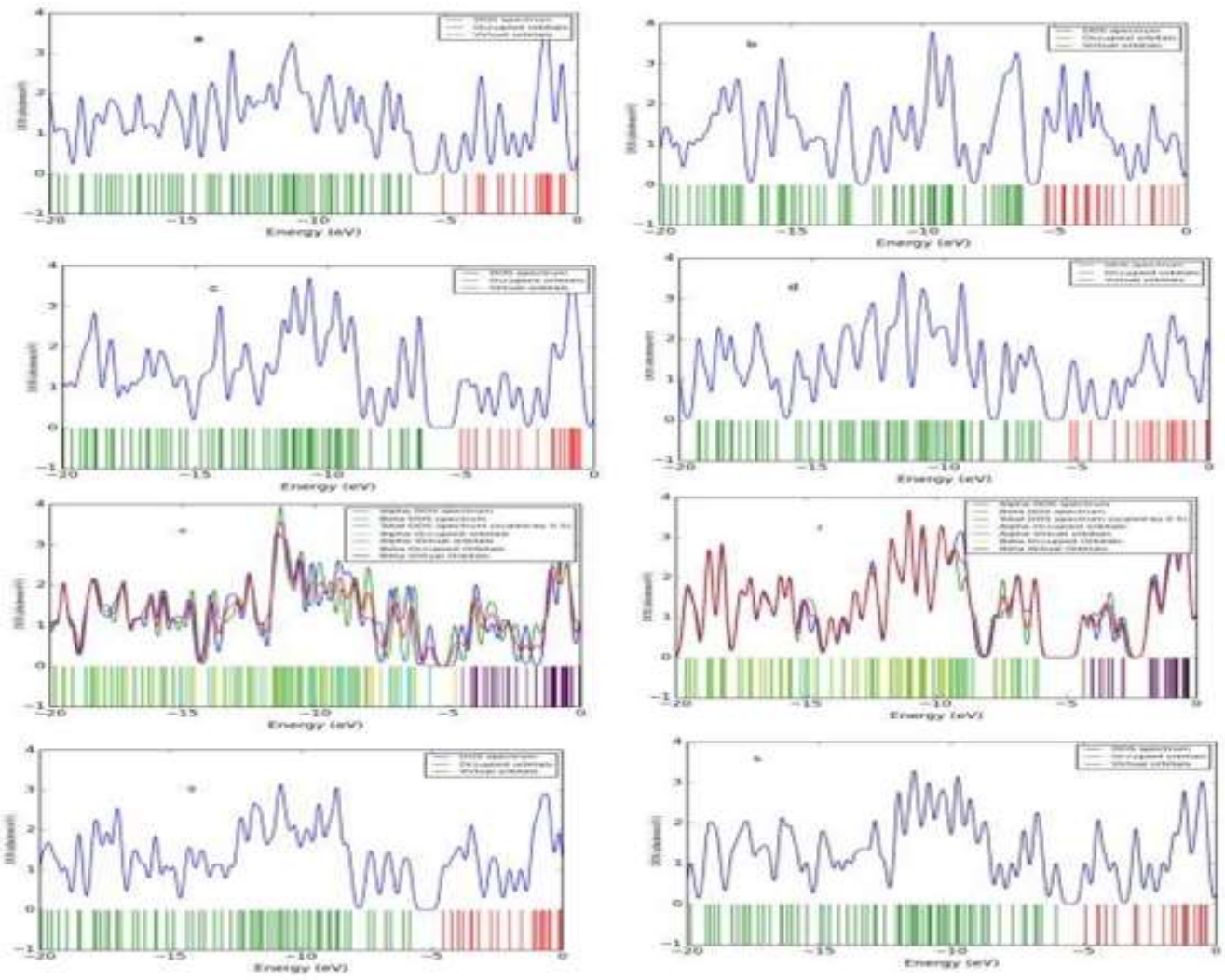

Fig. 4: The Density of states of adsorption gas molecules of (a) and (b) CO, (c) and (d) CO_2, (e) and (f) OH, (g) and (h) B_2 on N-graphene

The effects of B2 adsorbed on N-graphene are shown in Fig. 3 (g and h). Our result show that the bond lengths of N–C and C–C are 1.532 and 1.2257Å, respectively, and the angles of C–B–B and N-C-B are 114.84° and 113.80°. Fig. 4(g and h) shows the effect of B_2 adsorption on the DOS of adsorbed N-graphene at sites A and B equal to 3.17 and 3.30, respectively. This result indicates that there is a decrease in DOS in comparison with those of pristine N-graphene.

IR Spectra

Fig. 5 (1) shows the computed IR spectra of pristine N-graphene. The harmonic vibrational frequencies were calculated for the studied using 3-21G N-stretching at the 2101.48 and 1569.19 cm^{-1}.

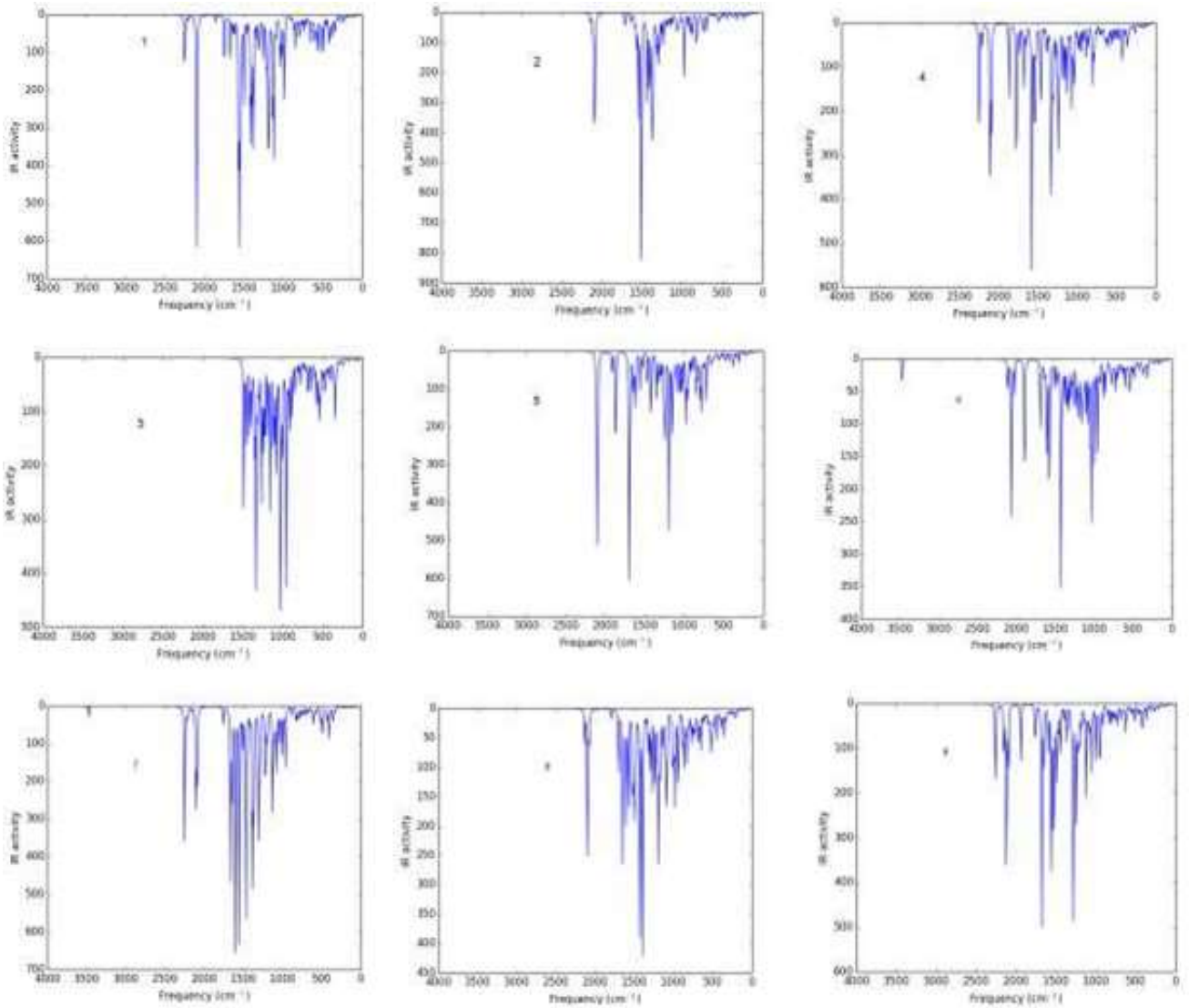

Fig. 5: IR spectra for (1) pristine N-graphene, and gas molecules of (2) and (3) CO, (4) and (5) CO_2, (6) and (7) OH, (8) and (9) B_2 on N-graphene

The effect of CO adsorbed on N-graphene is shown in Fig. 5 (2 and 3). It was found that the stretching vibration of C–C, N –C and C-O at, respectively, 1030.62, 1280.27 and 887.202 cm^{-1} at site A, and at 1366.50, 1504.85 and 2101.82 cm^{-1} at site B. On the other hand, the effect of CO_2 adsorbed on N-graphene is plotted in Fig. 5 (4 and 5).

It is clear that the stretching vibration of C–C, N –C and C-O at respectively, 1725.36, 1579.33 and 1827.94 cm^{-1} at site A, and at 1709.05, 1196.18 and 1872.35 cm^{-1} at site B. The effect of OH adsorbed on N-graphene is shown in Fig. 5(6, and 7), it is noticed that the stretching vibration of C–C, N –C, and C-OH, at 1617.86, 2259.25 and 1469.24 cm^{-1} respectively at site A. and at 1586.57, 2087.17, 1039.3 cm^{-1} at site B. Finally, the effect of B_2 adsorbed on N-graphene is shown in Fig. 5(8 and 9), It is found that the stretching vibration of C–C, N –C and C-B_2 at 1680.34, 2134.1 and 1289.33, and at 1656.97, 2110.64 and 984.82 (and N-C-B at 1406.66) cm^{-1}, respectively.

It is concluded from this figure that the effect of CO and CO_2 adsorbed on N-graphene lead

to a new vibrational frequencies mode such as C-O, C-OH, C-B_2, N-OH, and N-B_2, different change of vibrational frequencies.

Conclusions

In summary, DFT method have been used to investigates the electronic, structural, and vibrational properties of the effect of harmful gases on N-doped graphene at two different occupation sites (A and B). These gases included CO, CO_2, OH, and B_2. The result revealed that the effect of CO and CO_2 adsorption on the electronic properties of N-graphene lead to a decreasing in the values of E_{HOMO}, E_{LUMO} and E_f, and an increasing in the values of E_g and E_{ad} at sites A and B .

In addition, the effect of OH and B_2 adsorption on the electronic properties of N-graphene lead to the increasing the values of E_{HOMO}, E_{LUMO}, E_g and E_f at sites A, whereas the values at site B are decreasing.

In addition, it is observed that the effect of adsorbed CO, CO_2, OH, and B_2 on N-Graphene lead to new vibrational frequencies mode such as C-O, C-OH, N-OH, C-B_2, and N-B_2. Most importantly, our designed nanosheet can be used as a gas sensor for the harmful gases due to the values of adsorption energies.

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