



# Pt-doped armchair graphene nanoribbon as a promising gas sensor for CO and CO<sub>2</sub>: DFT study

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## ABSTRACT

In this work, four armchair graphene nanoribbon (AGNR) based sensor materials were built using Atomistic ToolKit Virtual NanoLab (ATK-VNL) and utilized to detect carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) gases. First, the effect of passivating AGNR on the sensing performance toward CO and CO<sub>2</sub> gases has been investigated, where AGNR was passivated with hydrogen (H-AGNR) and nitrogen (N-AGNR). The obtained results reflected no significant changes in the adsorption parameters of CO and CO<sub>2</sub> molecules on H-AGNR and N-AGNR. Particularly, the adsorption energies between H-AGNR and N-AGNR systems and CO were found to be  $-0.446$  and  $-0.436$  eV, while for the case of CO<sub>2</sub>, the adsorption energies were found to be  $-0.426$  and  $-0.432$  eV, respectively. To enhance the sensing performance, both H-AGNR and N-AGNR systems were doped with platinum (Pt) forming another two systems: Pt-H-AGNR, and Pt-N-AGNR. After doping, the results revealed a significant increase in the adsorption energy to almost 9 times than the non-doped systems for the cases of CO on Pt-N-AGNR as well as CO<sub>2</sub> on both Pt-H-AGNR and Pt-N-AGNR. Moreover, an increase of almost 13 times was observed in the adsorption energy for the case of CO on Pt-H-AGNR. Besides to the adsorption energy ( $E_{ads}$ ), the adsorption distance ( $D$ ), charge transfer ( $\Delta Q$ ), the density of states (DOS), as well as the band structure have been examined to confirm the adsorption of CO and CO<sub>2</sub> on the four systems.

## 1. Introduction

Over the last couple of years, there has been an increasing interest to develop highly sensitive sensors for the detection of highly toxic gases [1]. Among these gases, the atmospheric pollutants CO and CO<sub>2</sub> are mostly produced as a result of continuous growth of industries and automobiles, and they negatively affect our health and lifestyle. CO, for instance, is a toxic, colorless, tasteless, and odorless gas [2]. Exposure to CO at a low concentration of  $\sim 35$  ppm may results in headache and dizziness, while exposure to concentrations higher than 150 ppm of CO would even lead to death [3,4]. Moreover, CO<sub>2</sub> is associated with the high global warming potential, and it becomes one of the major concerns worldwide due to its serious effects on humans [5]. The high, unacceptable, level of CO<sub>2</sub> in the air is produced mainly by the act of some of the human works in industrial applications as well as deforestation [6, 7]. Therefore, the exploration of highly effective gas sensors for detection of CO and CO<sub>2</sub> is a critical task [8].

Despite the significant properties and widespread usage of graphene in different applications [9–14], it has limitations in its selectivity as a

gas sensor while detecting some kinds of gas molecules, for example, CO, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub> [15–19]. It has been reported that, modifying the surface of graphene or generating graphene based materials with a controllable band gap, called graphene nanoribbons (GNR) [20], would help to overcome the limitations of graphene utilization as a gas sensor [21–24]. Due to the long and reactive edges, the huge surface area, and the high electron and hole mobility, GNR reflected promising results in the field of gas sensors [25–30].

Very recently, different studies have been published on the detection of CO and CO<sub>2</sub> gases using graphene based materials. For example, pristine, defective, In-doped and Sb-doped graphene have been used to detect CO [31]. The defective graphene was found to exhibit a high affinity to the CO molecule with high adsorption energy as compared with pristine and doped-graphene. This adsorption energy was found to be significantly enhanced upon applying negative electric field [31]. In another study, Fe-doped penta graphene was used to detect CO and CO<sub>2</sub> gases [32]. The results of this study reflected an improvement in the adsorption parameters of penta graphene upon doping with Fe. Moreover, graphyne oxide was used in a recent study to detect both CO and

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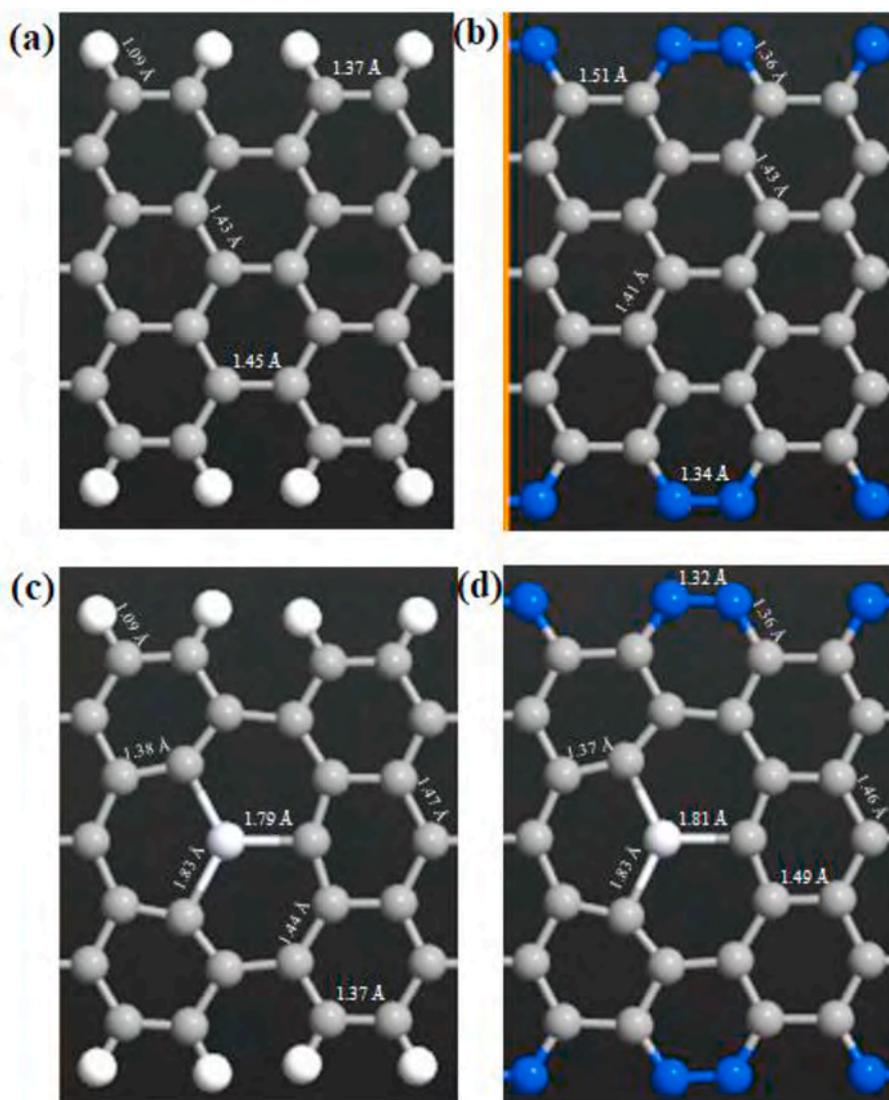


Fig. 1. Top views of the optimized structures of a) H-AGNR, b) N-AGNR, c) Pt-H-AGNR, and d) Pt-N-AGNR.

CO<sub>2</sub> as well as NH<sub>3</sub> gases [33]. The results of this study showed that the adsorption parameters were enhanced by functionalizing the surface of graphyne with oxygen atoms.

Platinum (Pt) metal exhibits distinguished properties in chemical and electrochemical reactions and known for its novel catalyst properties [34]. Doping graphene with Pt allows its utilization for selective and sensitive gas sensors, since doping modifies the electronic properties of graphene that control its semiconducting characteristics [35]. Such doping of AGNR with Pt allows taking advantage of the high electron affinity of Pt towards specific gases.

In the current study, four different graphene based gas sensitive materials were established based on density functional theory (DFT) integrated within Atomistic ToolKit Virtual NanoLab (ATK-VNL) package. The effect of passivation on the adsorption capacity of AGNR toward the detection of CO and CO<sub>2</sub> gases was first studied. Thus, AGNR was passivated with hydrogen (H-AGNR) and nitrogen (N-AGNR) and compared with the non-passivated system. Then, to enhance the sensing performance, the passivated AGNR was doped with Pt. Interestingly, the adsorption energies were found to be considerably enhanced upon doping H-AGNR and N-AGNR with Pt.

## 2. Computational methods

Adsorption of CO and CO<sub>2</sub> gases on the surface of H-AGNR, N-AGNR, Pt-H-AGNR, and Pt-N-AGNR systems have been investigated by DFT calculations using ATK-VNL (version 2018.06) package. The generalized gradient approximation, known as GGA, was adopted as the exchange correlation functional with the Perdew-Burke-Ernzerhof (PBE) as the processing method [36,37]. Although, GGA-PBE method has been reported to underestimate the binding energy [38], this issue was solved by implementing DFT-D2 of Grimme to correct the effect of Van der Waals interactions [37]. All the systems have been fully relaxed and optimized until a maximum force on each atom of 0.05 eV/Å was achieved. The linear combination of atomic orbitals (LCAO) basis set with medium accuracy and Fermi-Dirac occupation method as well as the fast Fourier transform (FFT) Poisson solver were used for all the structures. The Limited-memory Broyden-Fletcher-Goldfarb-Shanno (LBFGS) optimizer was used during the geometry optimization of all the systems [39]. A density mesh cutoff of 125 Hartree, and stress error tolerance of 0.01 GPa were chosen within the calculations for the four systems. In all calculations, a Monkhorst-Pack k point sampling of  $4 \times 4 \times 1$  for integration of Brillouin-zone was used. The adsorption of CO and CO<sub>2</sub> gas molecules were confirmed by investigating the adsorption energy ( $E_{ads}$ ), charge transfer ( $\Delta Q$ ), adsorption distance (D) (i.e. the smallest

**Table 1**  
Parameters of H-AGNR, N-AGNR, Pt-H-AGNR, Pt-N-AGNR.

System	Bond length (Å)			System	Bond length (Å)			
	C-C	C-H	C-Pt		C-C	C-N	N-N	C-Pt
H-AGNR	1.42	1.09	–	N-AGNR	1.45	1.36	1.34	–
Pt-H-AGNR	1.38 <sup>a</sup>	1.09	1.81	Pt-N-AGNR	1.37 <sup>a</sup>	1.36	1.34	1.82

<sup>a</sup> Around the position of the Pt atom.

distance among the gas molecule and graphene system), band structure, as well as density of states (DOS). The adsorption energy between the H-AGNR, N-AGNR, Pt-H-AGNR, and Pt-N-AGNR systems and the gas molecules has been calculated by the following formula [40–43]:

$$E_{ads} = E_{AGNR+gas} - (E_{AGNR} + E_{gas})$$

Where  $E_{AGNR+gas}$  is the total energy of CO or CO<sub>2</sub> adsorbed on either H-AGNR, N-AGNR, Pt-H-AGNR, or Pt-N-AGNR system.  $E_{AGNR}$  is the total energy of either H-AGNR, N-AGNR, Pt-H-AGNR, or Pt-N-AGNR system, and  $E_{gas}$  is the total energy of any of the optimized CO and CO<sub>2</sub> gases. A negative value of  $E_{ads}$  corresponds to steady adsorption structure [44–46].

Furthermore, to evaluate the charge transfer of the gas molecules, the Mulliken population method was used based on the following formula [47,48]:

$$\Delta Q = Q_i - Q_o$$

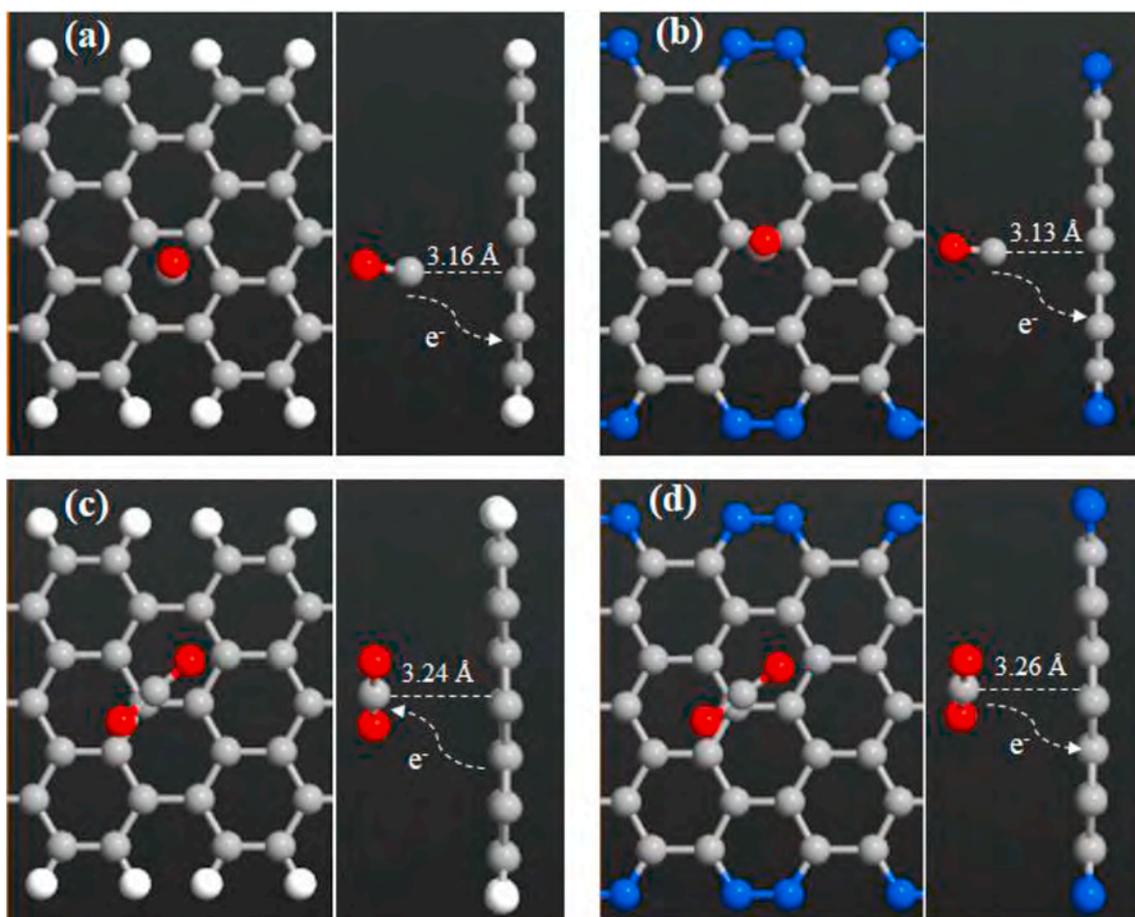
Where,  $\Delta Q$  is the charge transfer of the gas,  $Q_i$  and  $Q_o$  are the Mulliken charges of the CO or CO<sub>2</sub> gas molecules after and prior the adsorption,

respectively.

### 3. Results and discussion

#### 3.1. Optimization of systems

DFT calculations integrated within ATK-VNL is used to build four different AGNR based gas sensors [49] to detect CO, and CO<sub>2</sub>. AGNR is firstly passivated with H and N to form H-AGNR and N-AGNR systems. The two systems are then doped with Pt to form two new systems: Pt-H-AGNR and Pt-N-AGNR in order to enhance their sensing performance. These systems are optimized to reach the most stable configurations. The optimized structures of H-AGNR, N-AGNR, Pt-H-AGNR, and Pt-N-AGNR are shown in Fig. 1(a) – 1(d). Furthermore, the geometrical parameters of these systems are listed in Table 1. The obtained results show that the average C–C and C–H bond lengths of H-AGNR are 1.42 Å and 1.09 Å, respectively. For the case of N-AGNR, the average C–C bond length is 1.45 Å, the C–N bond is 1.36 Å, and the N–N bond is 1.34 Å as shown in Table 1. As clearly indicated in Fig. 1(c) – 1(d), the stable configurations of Pt-H-AGNR and Pt-N-AGNR are different from H-AGNR and N-AGNR. The positions of three C atoms around the Pt atom are changed to release the stress in the system [33]. Consequently, the average C–Pt bond length increases to 1.81 Å for the case of Pt-H-AGNR and 1.82 Å for the case of Pt-N-AGNR. Moreover, the C–C bond length around the position of Pt decreases to 1.38 and 1.37 Å for the cases of Pt-H-AGNR and Pt-N-AGNR, respectively. Fig. 2(a) – 2(d) show the optimized structures of CO and CO<sub>2</sub> adsorbed on H-AGNR, and N-AGNR systems. After optimization, the CO and CO<sub>2</sub> molecules reorient themselves in which the C atom of CO face the plane of both H-AGNR and N-AGNR systems as shown in Fig. 2(a) – 2(b). While for the



**Fig. 2.** Top and side views of the optimized structures of a) CO on H-AGNR, b) CO on N-AGNR, c) CO<sub>2</sub> on H-AGNR, and d) CO<sub>2</sub> on N-AGNR.

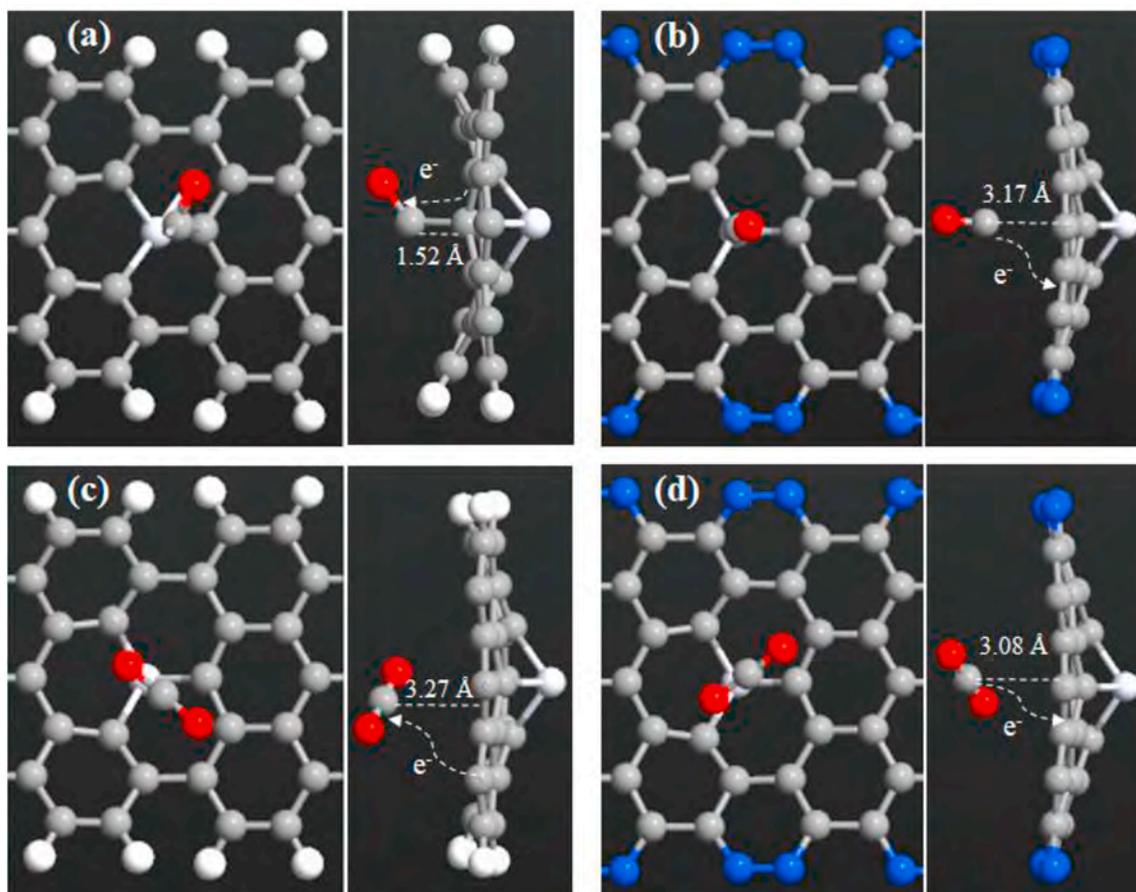


Fig. 3. Top and side views of the optimized structures of a) CO on Pt-H-AGNR, b) CO on Pt-N-AGNR, c) CO<sub>2</sub> on Pt-H-AGNR, and d) CO<sub>2</sub> on Pt-N-AGNR.

Table 2

Adsorption energy ( $E_{ads}$ ), adsorption distance ( $D$ ), band gap ( $E_g$ ), and charge transfer ( $\Delta Q$ ) of CO and CO<sub>2</sub> adsorbed on H-AGNR, N-AGNR, Pt-H-AGNR, and Pt-N-AGNR.

System	$E_{ads}$ (eV)	$D$ (Å)	$E_g$ (eV)	$\Delta Q$ (e)
H-AGNR	–	–	1.642	–
H-AGNR-CO	–0.446	3.16	1.646	–0.013
H-AGNR-CO <sub>2</sub>	–0.426	3.24	1.645	0.006
N-AGNR	–	–	0.413	–
N-AGNR-CO	–0.436	3.13	0.423	–0.027
N-AGNR-CO <sub>2</sub>	–0.432	3.26	0.407	–0.003
Pt-H-AGNR	–	–	0.722	–
Pt-H-AGNR-CO	–5.967	1.52	1.554	0.305
Pt-H-AGNR-CO <sub>2</sub>	–3.961	3.27	0.694	0.008
Pt-N-AGNR	–	–	0.772	–
Pt-N-AGNR-CO	–4.040	3.17	0.708	–0.031
Pt-N-AGNR-CO <sub>2</sub>	–4.014	3.08	0.708	–0.010

case of CO<sub>2</sub>, it is clearly demonstrated that CO<sub>2</sub> almost adopts a parallel configuration above the H-AGNR and N-AGNR systems (Fig. 2(c) - 2(d)) with the smallest adsorption distance detected between the C atom of CO<sub>2</sub> and another C atom from the system. The optimized structures of CO and CO<sub>2</sub> adsorbed on Pt-H-AGNR, and Pt-N-AGNR systems are shown in Fig. 3(a) - 3(d). For the case of CO on Pt-H-AGNR in Fig. 3(a), a chemical bond with length of 1.52 Å occurs between the C atom of CO and another C atom from the Pt-H-AGNR system. Moreover, the average C-Pt bond length increases to 2.0 Å. In contrast, no chemical reaction appears between CO and Pt-N-AGNR as shown in Fig. 3(b) with the average C-Pt bond length increases to 1.96 Å. As indicated by the figure, the Pt atom moves away and stays below the system's plane after the adsorption of CO gas. The same behavior is also observed for the cases of

CO<sub>2</sub> on Pt-H-AGNR, and Pt-N-AGNR systems without noticing any chemical reactions between the gas and the systems.

### 3.2. Adsorption parameters

To confirm the successful adsorption of CO and CO<sub>2</sub> gases on the surface of H-AGNR, N-AGNR, Pt-H-AGNR, and Pt-N-AGNR systems, the adsorption energies, adsorption distance, band gap, and charge transfer are calculated and listed in Table 2. The results show that the adsorption energies between H-AGNR and N-AGNR systems and CO are –0.446 and –0.436 eV, while for the case of CO<sub>2</sub>, the adsorption energies are –0.426 and –0.432 eV, respectively. In addition, the smallest distance between the gases and the systems is 3.13 Å for the case of CO adsorbed on N-AGNR. Moreover the charge transfer between H-AGNR and N-AGNR systems and CO are –0.013 and –0.027 e, while for the case of CO<sub>2</sub> the charge transfer are 0.006 and –0.003 e, respectively. The negative value of the charge transfer specifies that electrons transfer from the gas to the system. Which means that in the current case, electrons transfer from CO to both H-AGNR and N-AGNR systems, while for the case of CO<sub>2</sub>, electrons transfer to the gas in case of H-AGNR and from the gas in case of N-AGNR as demonstrated in Fig. 2.

Upon doping H-AGNR and N-AGNR with Pt, the adsorption energies between both Pt-H-AGNR and Pt-N-AGNR systems and the toxic CO gas increase significantly to –5.967 and –4.040 eV, while for the case of CO<sub>2</sub>, the adsorption energies increase to –3.961 and –4.014 eV, respectively. These values are within the acceptable range according to some of the recently published articles [50–53]. The remarkable improvement of the adsorption energies are mostly attributed to the increase of the specific surface area of the developed systems upon doping with Pt which facilitates the adsorption of the target gas on their surface [50]. In addition, the Mulliken population analysis demonstrate

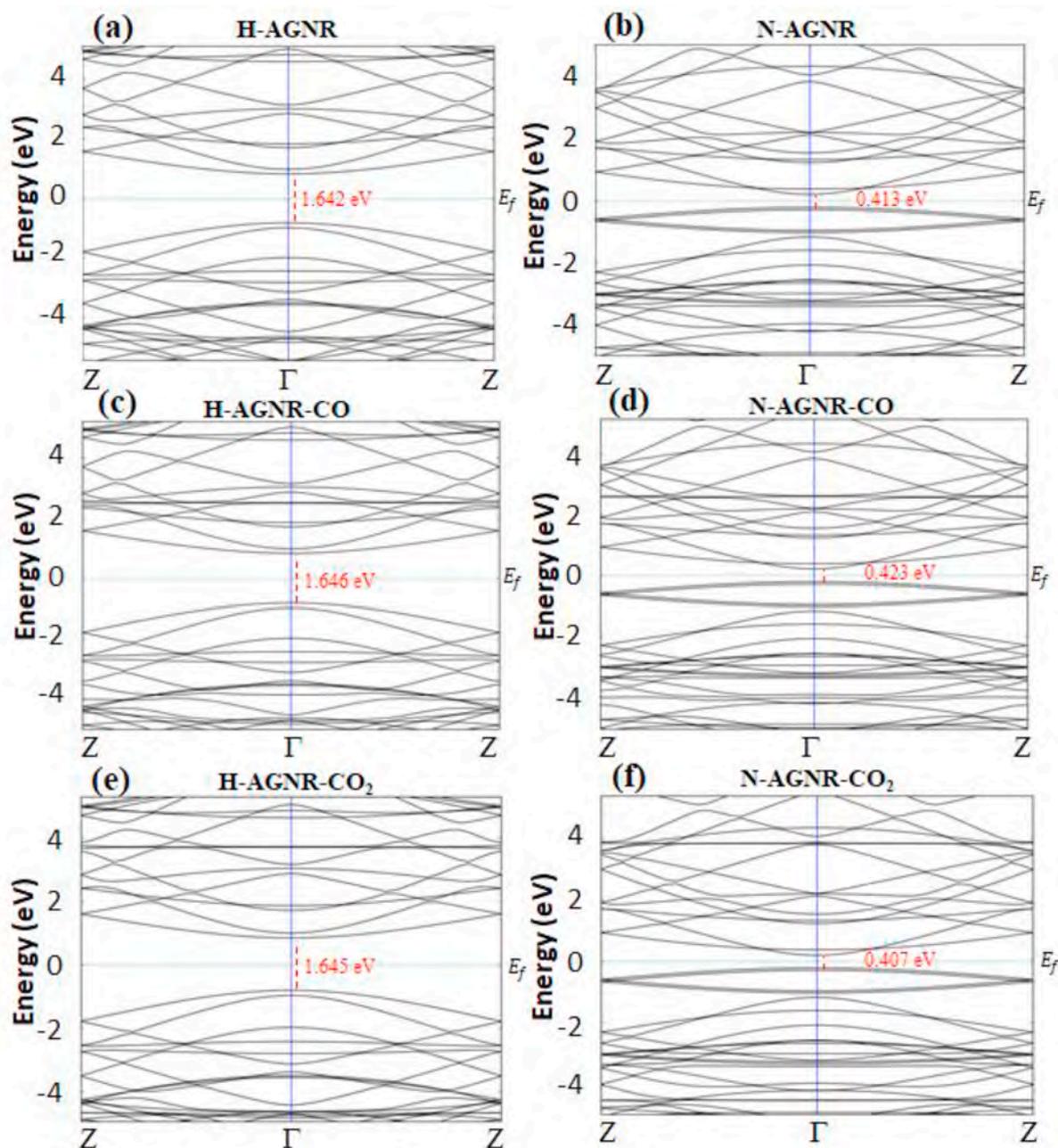


Fig. 4. Band structures of a) H-AGNR, b) N-AGNR, c) CO on H-AGNR, d) CO on N-AGNR, e) CO<sub>2</sub> on H-AGNR, and f) CO<sub>2</sub> on N-AGNR.

that 0.305 e transfer from the Pt-H-AGNR system to CO, while 0.031 e transfer from CO to Pt-N-AGNR. For the case of CO<sub>2</sub>, 0.008 e transfer from Pt-H-AGNR to the gas molecule and 0.010 e transfer from the gas to Pt-N-AGNR system. Moreover, the least adsorption distance between the gas molecules and the systems is observed between CO and Pt-H-AGNR as shown in Fig. 3(a) with 1.52 Å due to the formation of chemical bond among the C atom of CO and another C atom from the system. The results also show that the adsorption distance between CO and Pt-N-AGNR is 3.17 Å, while for the case of CO<sub>2</sub> the adsorption distances are 3.27, 3.08 Å for the cases of Pt-H-AGNR, and Pt-N-AGNR, respectively.

Finally, the results show no significant change in the adsorption parameters of CO and CO<sub>2</sub> adsorbed on both H-AGNR and N-AGNR. Indicating that, before doping, either passivating AGNR with H or N have the same impact on the sensing performance. In spite of that, the adsorption energies obtained in the current study are more than double

of those for CO and CO<sub>2</sub> adsorbed on pure AGNR (non-passivated) recently reported [54]. After doping with Pt, the same behavior is also observed for the case of CO<sub>2</sub>. However, the adsorption energy significantly increases to almost 9 times, larger than that of H-AGNR and N-AGNR due to the presence of the Pt atom. Meanwhile, for the case of CO on Pt-H-AGNR, the adsorption energy, and charge transfer are remarkably higher than that of Pt-N-AGNR system. The high adsorption energy (almost 13 times larger than the pristine case) and small adsorption distance as well as the noticeable charge transfer between CO and Pt-H-AGNR system are attributed to the chemical reaction that occurs between CO and the system. These results indicate that doping the H-AGNR system with Pt can be considered as a promising method to enhance its sensitivity as a gas sensor to detect the toxic CO and CO<sub>2</sub> gases.

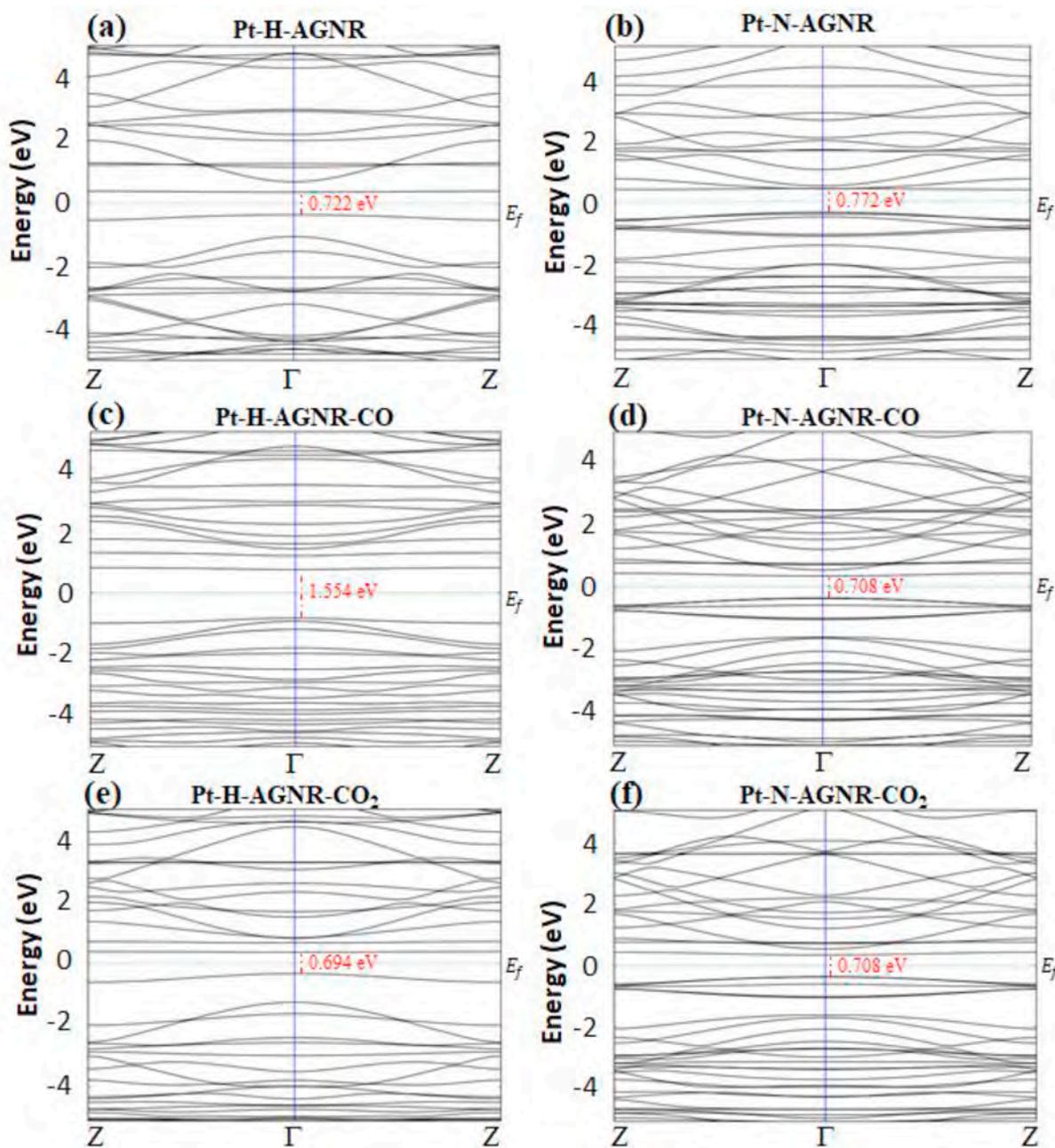


Fig. 5. Band structures of a) Pt-H-AGNR, b) Pt-N-AGNR, c) CO on Pt-H-AGNR, d) CO on Pt-N-AGNR, e) CO<sub>2</sub> on Pt-H-AGNR, and f) CO<sub>2</sub> on Pt-N-AGNR.

### 3.3. Band structure

To understand the effect of passivation and doping with Pt on the electronic properties of AGNR, the band structures of H-AGNR, N-AGNR, Pt-H-AGNR, and Pt-N-AGNR systems are investigated prior and after the adsorption of both CO and CO<sub>2</sub> gases. As demonstrated by Fig. 4, the band structure of AGNR has a parabolic style around the  $\Gamma$  point. A direct band gap of 1.642 eV appears at  $\Gamma$  point of the band structure of H-AGNR (Fig. 4(a)), while the band gap is 0.431 eV for the case N-AGNR (Fig. 4(b)). Those values are different from the recently reported value of 0.844 eV for the non-passivated AGNR [54], and they demonstrate the semiconducting nature of AGNR. Herein, introducing H or N at the edges of AGNR significantly affect the band gap. Upon the adsorption of CO and CO<sub>2</sub> on the surface of H-AGNR (Fig. 4(c) and (e)), the band gap increases slightly to 1.646 and 1.645 eV, respectively. In addition, some changes and new bands appear below and above Fermi level. For the

case of N-AGNR, the band gap increases to 0.423 eV after the adsorption of CO as shown in Fig. 4(d). In contrast, the band gap of N-AGNR decreases to 0.407 eV after the adsorption of CO<sub>2</sub> (Fig. 4(f)). Fig. 5 shows the band structures of Pt-H-AGNR, and Pt-N-AGNR before and after the adsorption of CO and CO<sub>2</sub> gases. As shown in Fig. 5(a), two flat bands appear near the Fermi level in the valence and the conduction bands, which result in decreasing the direct band gap to 0.722 eV after doping the H-AGNR with Pt. On the other hand, after doping N-AGNR with Pt, the valence and the conduction bands move away from the Fermi level and the direct band gap increases to 0.772 eV as shown in Fig. 5(b). For the case of CO adsorbed on Pt-H-AGNR in Fig. 5(c), the valence and the conduction bands move away from the Fermi level increasing the band gap remarkably to 1.554 eV. Moreover, the bands between  $-2.0$  and  $-5.0$  eV become almost flat. The noticeable changes of the band structure of CO adsorbed on Pt-H-AGNR is mainly attributed to the change in the Pt-H-AGNR structure upon chemical reaction with CO as

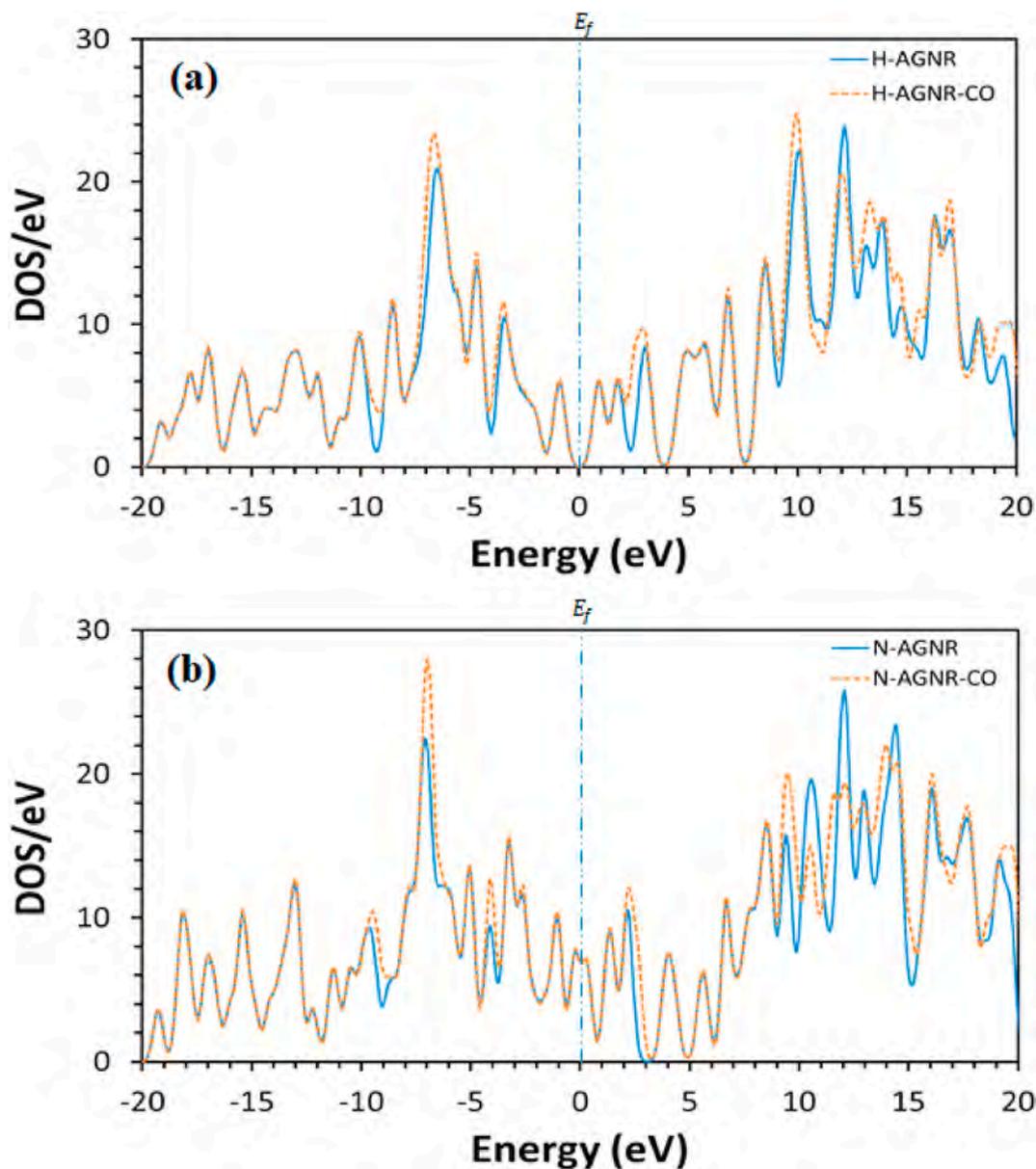


Fig. 6. Density of states of a) H-AGNR, and b) N-AGNR before and after the adsorption of CO.

demonstrated in Fig. 3(a). After the adsorption of CO<sub>2</sub> on the surface of Pt-H-AGNR (Fig. 5(e)), the band gap decreases to 0.694 eV. For the case of Pt-N-AGNR system, the band gap decreases to 0.708 eV upon the adsorption of both CO and CO<sub>2</sub> gases as shown in Fig. 5(d) and (f). The decrease of the bandgap is likely to be attributed to the hybridization and orbital overlapping. Finally, it is obvious from the band structure results that passivating AGNR with H and N as well as the doping with Pt considerably affects its electronic structure. Moreover, all the changes and the new bands that appear below and above Fermi level as well as the changes of the band gap after the adsorption of both CO and CO<sub>2</sub> gases indicate that the band structure results can be used to confirm the sensing of CO and CO<sub>2</sub>.

### 3.4. Density of states

To further confirm the interaction between the toxic CO and CO<sub>2</sub> gases and the built systems, the density of states for the H-AGNR, N-AGNR, Pt-H-AGNR, and Pt-N-AGNR systems before and after the adsorption of CO and CO<sub>2</sub> gases are investigated and shown in Figs. 6–9. For the case of CO adsorbed on H-AGNR system in Fig. 6(a), the DOS

around  $-6.4$  eV in the valence band and  $3.0$ ,  $10.1$ ,  $13.0$ ,  $17.0$  and  $19.4$  eV in the conduction band increase after the adsorption of CO. While for the case of CO on N-AGNR (Fig. 6(b)), noticeable variations in the DOS occur around  $-9.6$ ,  $-4.0$  eV in the valence bands and  $9.5$ ,  $10.5$  and  $12.1$  eV in the conduction bands. On the other hand, a noteworthy increase in the DOS around  $-8.5$ ,  $-4.7$ ,  $8.6$ ,  $13.3$ , and  $18.0$  eV is observed upon the adsorption of CO<sub>2</sub> on H-AGNR as shown in Fig. 7(a). Furthermore, for the case of CO<sub>2</sub> on N-AGNR (Fig. 7(b)), remarkable changes appear around  $-8.1$ ,  $-4.2$ ,  $4.0$ ,  $6.7$ ,  $8.7$ ,  $9.5$ ,  $10.6$ ,  $12.1$ ,  $17.7$ , and  $19.2$  eV.

After doping the H-AGNR system with Pt, the adsorption of CO show a significant impact on the DOS of Pt-H-AGNR system as compared with the non-doped system. As shown in Fig. 8(a), the whole DOS shifts to higher energy level with a considerably higher intensity around  $-6.5$ ,  $-0.8$ ,  $1.6$ ,  $5.8$ , and  $8.9$  eV upon the adsorption of CO on Pt-H-AGNR system. Furthermore, the adsorption of CO on Pt-N-AGNR (Fig. 8(b)) mainly affects the DOS around  $-7.2$  eV in the valence band and in the range of  $0.7$ – $17.3$  eV in the conduction band. For the case of CO<sub>2</sub> on Pt-H-AGNR in Fig. 9(a), a remarkable change appear in the DOS located at the range of  $-9.9$  to  $-2.7$  eV in the valence band and in the range of  $0.8$ – $16.1$  eV in the conduction band. Moreover, once CO<sub>2</sub> molecule is

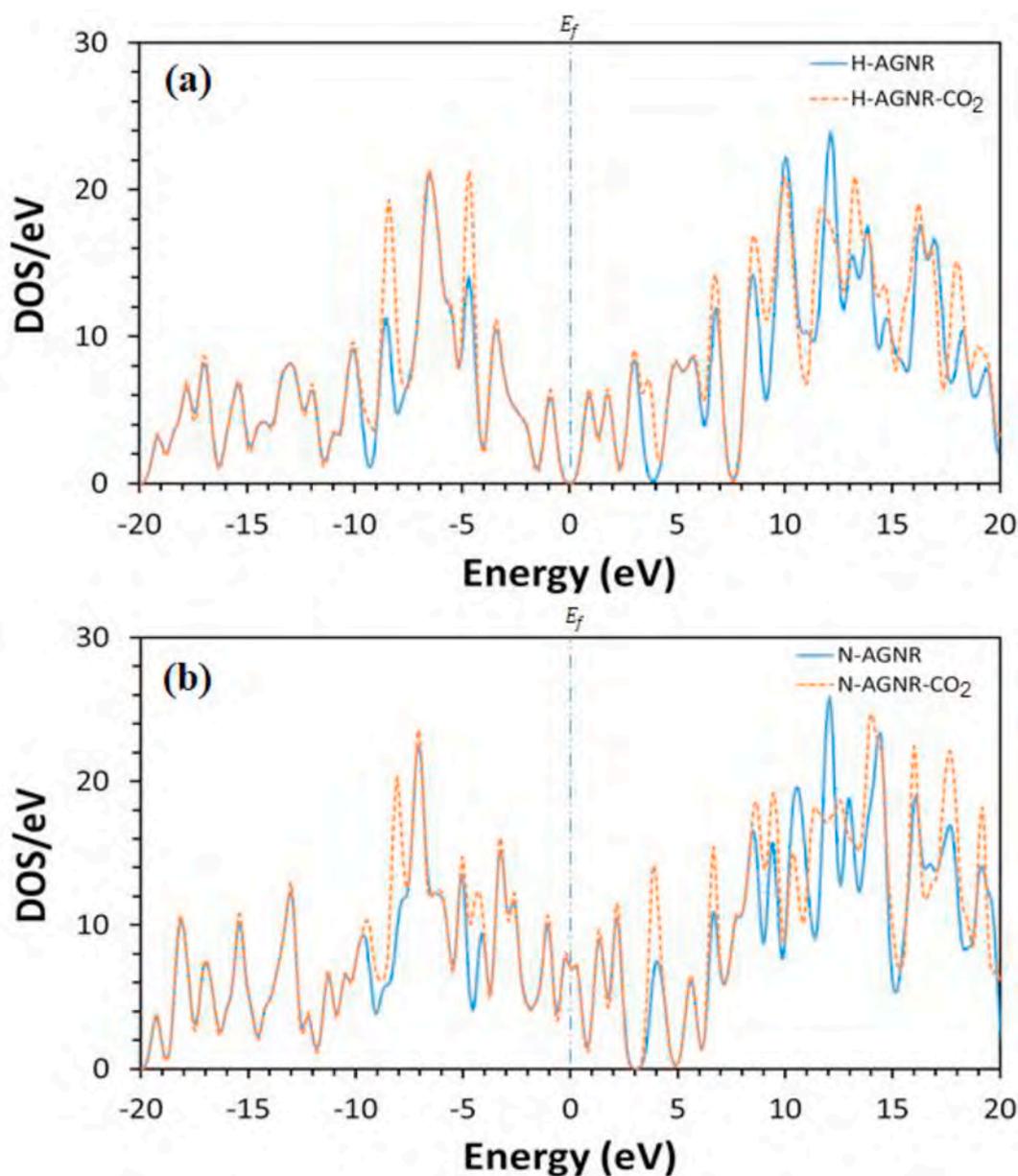


Fig. 7. Density of states of a) H-AGNR, and b) N-AGNR before and after the adsorption of  $\text{CO}_2$ .

adsorbed on the surface of Pt-N-AGNR, a considerable shift to high energy level is noticed for almost the entire DOS as shown in Fig. 9(b). At the end, it is clearly demonstrated by the DOS results that no remarkable variations are observed at Fermi level upon the gas adsorption. Nevertheless, the remarkable increase in the DOS below and above Fermi level of H-AGNR, N-AGNR, Pt-H-AGNR, and Pt-N-AGNR systems after the adsorption of CO and  $\text{CO}_2$  gases specifies that more states become available to be occupied which further indicates that both CO and  $\text{CO}_2$  gases are successfully adsorbed on the surface of the built systems [55].

Different studies have been reported in the recent years on the detection of CO and  $\text{CO}_2$  gases using graphene based materials. For instance, different doping elements of graphene have been investigated as gas sensors for  $\text{CO}_2$  detection [56]. The researchers used mono-vacancy graphene doped with B, N, P, and Al to enhance the sensing performance. They came to a conclusion that Al-doped graphene exhibited the highest adsorption energy of  $-1.38$  eV as it included a chemical reaction with  $\text{CO}_2$  gas molecule [56]. Very recently, functionalized AGNR has been used to detect CO,  $\text{CO}_2$ , and  $\text{SO}_2$  gases using a first principles study [54]. In the investigation, pure AGNR was used

firstly to detect the gases, then, the surface of AGNR was functionalized with epoxy and hydroxyl groups to improve the adsorption parameters. The determined adsorption energies between pure AGNR and CO and  $\text{CO}_2$  gases have been found to be  $-0.260$ , and  $-0.145$  eV, respectively [54]. These values have been considerably enhanced as a result of functionalizing the surface of AGNR. In the current study, upon passivating AGNR with H and N, the adsorption energies increase to  $-0.446$ , and  $-0.436$  eV for the case of CO, while for the case of  $\text{CO}_2$  the adsorption energies increase to  $-0.426$  and  $-0.432$  eV, respectively, as compared with the pure AGNR. These values further increased significantly to almost 9 times in some cases and nearly 13 times with  $-5.967$  eV for the case of CO adsorbed on the Pt-H-AGNR as a result of doping H-AGNR with Pt. This value is high and promising as compared with most of the recently reported CO gas sensors [31–33,54,57]. Therefore, the Pt-H-AGNR system is highly sensitive and selective towards detecting CO gas molecules, as it includes “chemisorption” occurrence. The chemisorption process have major influence on the electronic structure as well as bandgap widening. Therefore, the chemisorption of CO on Pt-H-AGNR system is predicted to exhibit distinct influence on

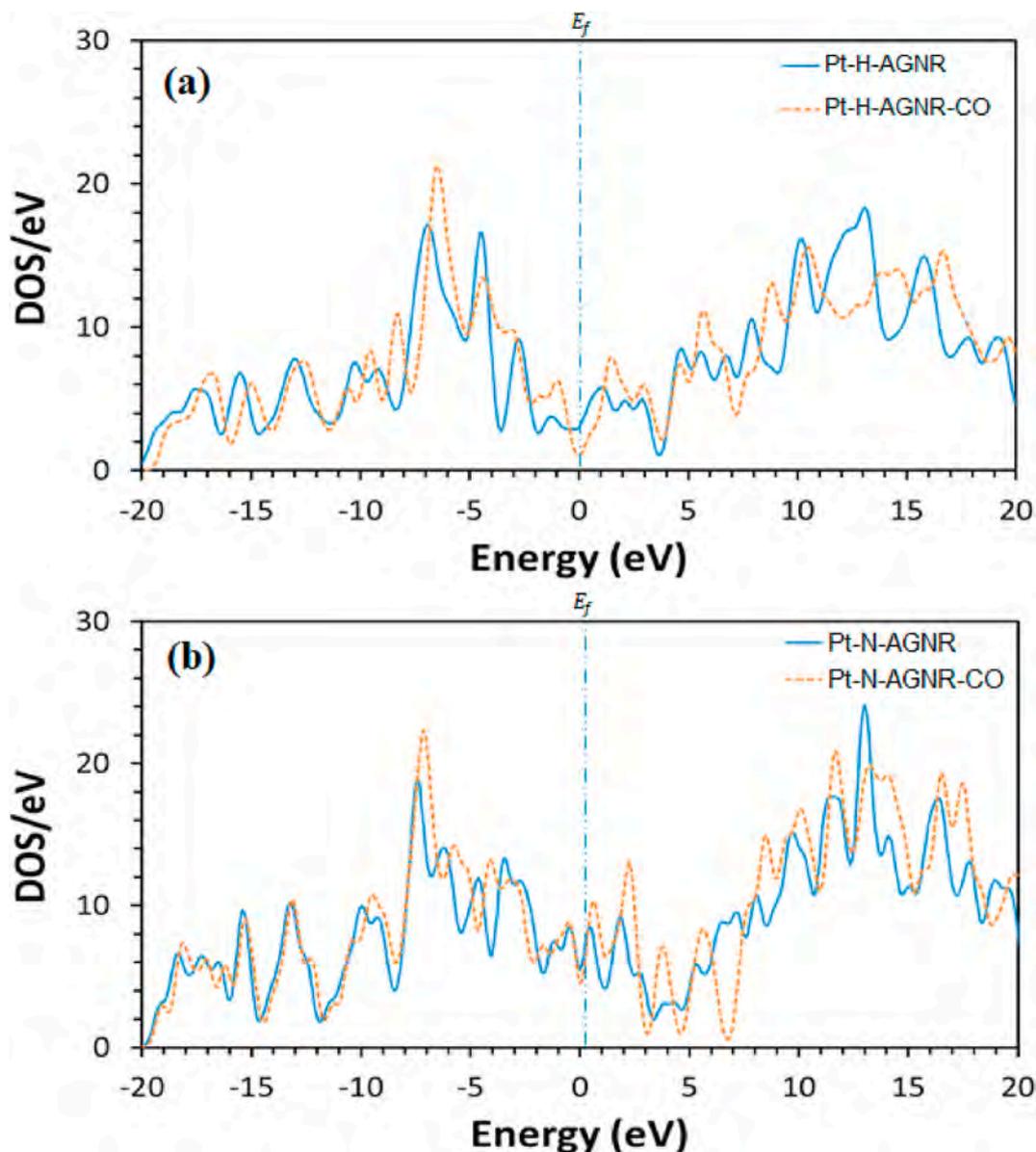


Fig. 8. Density of states of a) Pt-H-AGNR, and b) Pt-N-AGNR before and after the adsorption of CO.

the charge transport properties as well as sensor response.

#### 4. Conclusion

The effects of passivation and doping armchair graphene nanoribbon (AGNR) on the sensing performance to detect the toxic CO and CO<sub>2</sub> gases have been investigated in this work. To achieve the goal of this study, four systems that are passivated with hydrogen and nitrogen as well as doped with platinum were built: H-AGNR, N-AGNR, Pt-H-AGNR, and Pt-N-AGNR. The systems were generated based on Quantumwise Atomistix Toolkit package of Virtual Nanolab (ATK-VNL) and then used to adsorb CO and CO<sub>2</sub>. The results revealed that the two non-doped systems exhibit almost similar adsorption parameters, indicating that either passivating AGNR with H or N have the same impact when it comes to the adsorption of CO and CO<sub>2</sub>. Upon doping the H-AGNR and N-AGNR systems with Pt, the adsorption energy increased to almost 9 times for the case of CO<sub>2</sub> with no remarkable difference between H and N passivation. Furthermore, the adsorption energy increased to almost 9 times for the case of CO adsorbed on Pt-N-AGNR and nearly 13 times for the case of CO on Pt-H-AGNR, as compared with the non-doped systems.

Specifically, for the case of CO adsorbed on Pt-H-AGNR the adsorption energy and charge transfer increased significantly to  $-5.967$  eV and  $0.305$  e, respectively, and the adsorption distance decreased to  $1.52$  Å. Hence, the Pt-H-AGNR system is highly sensitive and selective to CO gas. This work indicates that doping the H-AGNR or N-AGNR with Pt may be considered as a promising technique to enhance their sensitivity and selectivity as gas sensors.

#### CRediT authorship contribution statement

**Ehab Salih:** Conceptualization, Data curation, Investigation, Writing - original draft. **Ahmad I. Ayesh:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing - review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

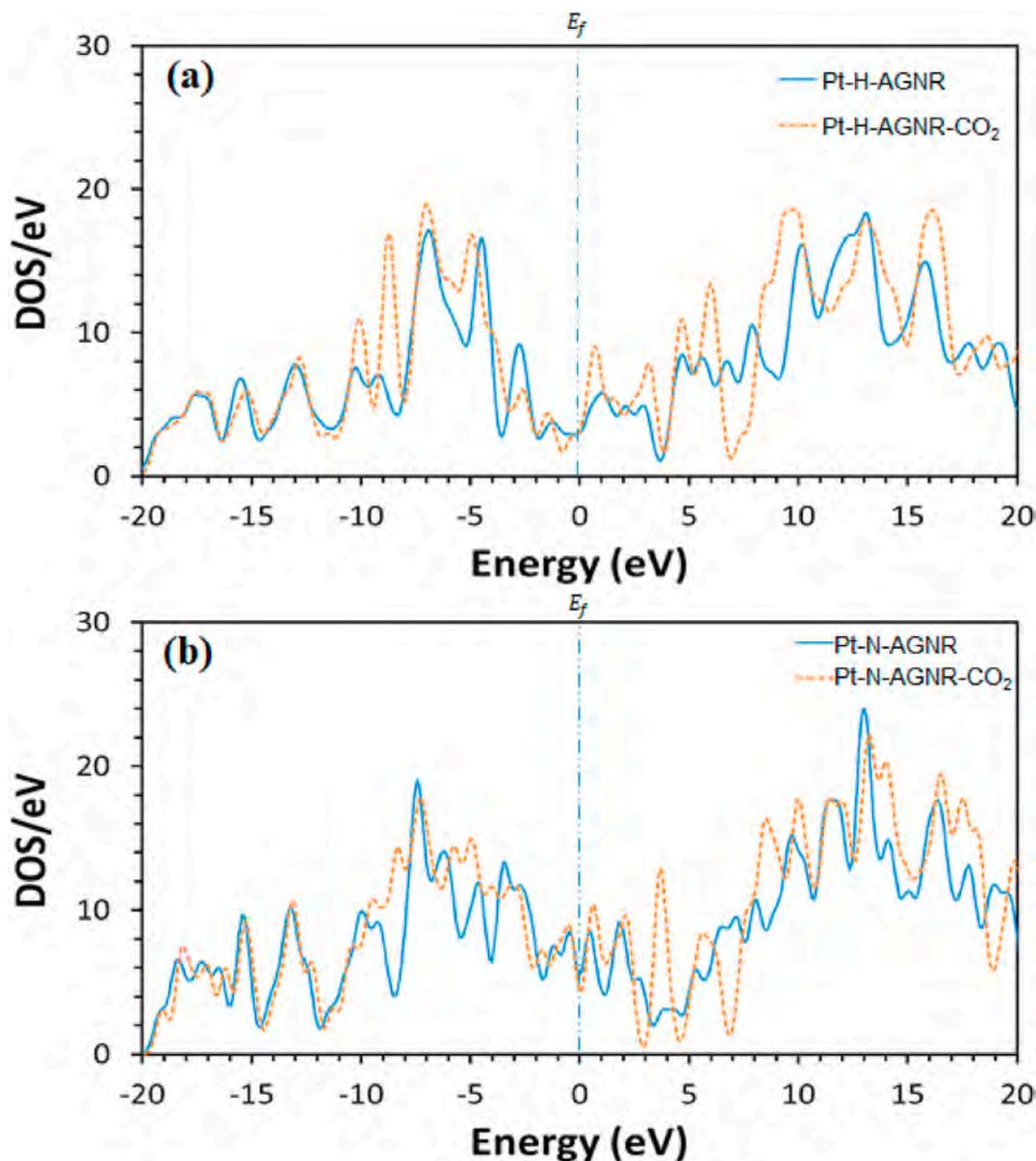


Fig. 9. Density of states of a) Pt-H-AGNR, and b) Pt-N-AGNR before and after the adsorption of CO<sub>2</sub>.

the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.physe.2020.114418>.

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