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# First-principles calculations of a doped graphene system for the adsorption of harmful gases in sensing applications

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#### Abstract

This study investigates the effects of carbon monoxide (CO) and nitric oxide (NO) on the structural characteristics of pristine and doped graphene using density functional theory (DFT) calculations based on the Perdew-Burke-Ernzerh (PBE) approach within the generalized gradient approximation (GGA). Various calculations were performed to assess adsorption energies, ideal positions, charge transfer, band structures, density of states, and electronic properties. For CO, the adsorption energies on pristine and nitrogen (N)-doped graphene were found to be -0.01 eV and -0.03 eV, respectively, while the adsorption energy on aluminium (Al)-doped graphene was significantly higher at -3.07 eV. Regarding NO, the pristine and Aldoped graphene displayed adsorption energies of -0.01 eV and -2.24 eV, respectively, whereas N-doped graphene showed a much stronger adsorption energy of -3.65 eV. The results indicate substantial charge transfer between CO and the graphene lattice during adsorption, suggesting that Al-doped graphene is more sensitive to CO compared to pristine and N-doped graphene. In contrast, for NO adsorption, pristine and N-doped graphene demonstrated greater sensitivity than Al-doped graphene.

**Keywords**: Quantum Espresso, Electronic properties, pristine graphene, adsorption energy, gas sensors.

# 1. Introduction

Common air pollutants like CO and NO are primary produced by internal combustion engine emissions and incomplete fuel combustion (1), (2). Due to the high toxicity of CO and NO and facile and facile binding to haemoglobin in the human body, which inhibits haemoglobin from

mixing with oxygen, hypoxia and poisoning may result(3),(4) . In addition to being an extremely dangerous flammable gas, CO and NO are also odourless and colourless. Gas sensors are essential for detecting the presence of CO and NO gases and providing an early warning to prevent dangerous events like poisoning, fires, and explosions. Improved gas sensor performance is becoming more and more necessary as environmental protection gains importance. Because graphene is composed of carbon atoms rather than the typical metal-oxide semiconductor materials, it has excellent physical and chemical properties that can help increase sensitivity to gas molecules. Additionally, graphene has a unique two-dimensional structure, an exceptionally large specific surface area, high carrier mobility, and low electrical noise (5,6).

Graphene has been suggested that such a device could be used as a highly sensitive gas sensor (7). The experiments by Panteleimonov et al. (8) have shown that the H2O, NH3, CO and NO2 molecules can be detected using graphene devices at relatively low molecular concentrations by monitoring the variation of carrier densities upon adsorption of these molecules onto graphene. Theoretical studies have been conducted to maximize the potential of graphene sensors. For example, Leenaerts et al.(9,10) studied the adsorption of H2O, NH3, CO, NO2, and NO on graphene substrates by first-principles calculations.

Previous studies (11) found that boron doping in graphene improves interactions with small gas molecules such as CO, NO, NO2 and NH3. Their results suggest that CO undergoes only weak physisorption with B-doped graphene, while the B dopant serves as a strong chemisorption site for NO, NO2, and NH3. Dai et al.(10) (1)suggested that boron-doped graphene could serve as an effective sensor for detecting major pollutants such as NO and NO2. This is based on a theoretical study investigating the adsorption capacity of graphene doped with boron, nitrogen, aluminium and Sulphur for various gases including H2, H2O, O2, CO2, CO, NO2, NO, SO2, NH3 and N2. Graphene doped with aluminium was also mentioned.

The selected gas molecules are of significant practical importance for industrial, ecological and medical applications. Furthermore, NO and CO serve as representative electron acceptors and donors, respectively, capable of forming charge transfer interaction with graphene. The aim of this work is to gain a fundamental understanding of how different adsorbed small gas molecules CO and NO influence the electronic properties of pristine and N-doped graphene or Al-doped graphene and to investigate their effects. Additionally, investigate how applying Van der Waals affected the adsorption energy values for various substrates and how it enhanced the results.

# 2. Computational details

The first-principle DFT implemented in Quantum Espresso (12),(13)was the framework within which all computations were performed using a soft pseudopotential. The exchange correlation function used in this investigation was the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerh function (PBE) (14). Previous studies have also shown that this functional, particularly when combined into an empirical dispersion term, can verify experimental bond distances and activation energies(15,16). However, a series of theoretical

studies have shown that PBE is able to accurately predict the sensing feature of these materials when they adsorb small gas molecules(17,18).

Van der Waals interactions (vdw), which are generated by dynamic correlations between fluctuating charge distributions, are not clearly defined by GGA or local density approximation (LDA) with DFT calculations. GGA underestimates the relatively low binding energies, while LDA overestimates them (19,20). The DFT-D2 approach provides a useful solution to this challenge by adding a dispersive force correction based on interatomic potentials of the  $C^6R^{-6}$  form to a standard DFT exchange-correlation function, thus enabling simple energy decomposition into vdw and electronic components. Van der Waals forces were considered in all calculations using the DFT+D2 method within the framework of the Grimme scheme and nonlocal vdw-DF(21,22).

In Quantum Espresso, the default algorithm for atomic position optimization is the BFGS algorithm(9,23) which is one of the most powerful methods for solving unconstrained optimization problems. In the geometry optimization, a cutoff energy of 450 eV is chosen for the propagation of fundamental plane waves. All atom positions are completely relaxed until the electronic self-consistency energy reaches less than  $10^{-5}$  eV and the force acting on each atom between two ion steps is less than 0.0001 eV/ °A (24).

A Fermi smearing parameter of 0.2 eV was used in the calculations. The Brillouin zone integration was calculated using the  $4 \times 4 \times 1$  k-points. For the calculation of the total and partial density of states (TDOS/PDOS), k-points of  $6 \times 6 \times 1$  were selected to obtain precise band structures.

In this article, we describe the adsorption studies of small gas molecules (CO and NO) on pristine graphene, N-doped graphene, and Al-doped graphene using first-principles density functional theory (DFT) calculations.

We constructed the hexagonal unit cell of graphene with the two carbon atoms (C) of different sublattices using the Winmostar computing environment(19), where a=b=2.46 °A, c=10 Å, and  $\alpha=\beta=90^{\circ}$  and  $x=120^{\circ}$ . The supercell is stretched in the z-direction from the graphene surface with a lattice parameter of 10 °A along the z-axis to prevent image interactions between neighbouring graphene layers.

In earlier research, different molecular adsorption sites were typically considered for the adsorption of the molecules CO and NO (24). As shown in Fig. (1a), the top position (T), which is directly above a single carbon atom, the bridge position (B) is in the middle of a carbon-carbon bond, and the hollow position (H) is in the centre of a hexagon represent the three different locations(25). Only the top position was utilised in this paper, and on the graphene sheet, the CO and NO are perpendicular.

We begin by building pristine graphene by repeating the unit cell into hexagonal supercell configurations of  $(4 \times 4 \times 1)$  and  $(3 \times 3 \times 1)$  with 32 and 18 carbon atoms (C), respectively. (32 and 18 carbon atoms) represents an isolated graphene layer in each simulated system, for which different doping configurations and concentrations are considered. In a singly doped graphene layer, a nitrogen atom or an aluminium atom has taken the place of a carbon atom at the centre of the pristine graphene, forming N-doped graphene and Al-doped graphene. In previous supercell configurations, we can achieve dopant concentrations of 3.125% to 5.55%.

In our study, a single gas molecule vertically adsorbed on layer of pristine, N-doped graphene and Al-doped graphene at the top position of the replaced carbon atom. The distance between the graphene layer and the bottom atom of the gas molecule is set to 1.5 A. The most stable energy of the previous structure is obtained before and after the adsorption of CO and NO gas molecules

We construct a cubic cell with a single adsorbed CO or NO molecule 5 °A long (21). Atomic structure optimizations of the isolated CO and NO gas molecules were then performed to obtain the most stable average energy of the isolated gas molecule.

The adsorption energy  $E_{ads}$  of gas molecule on graphene, was calculated using eq. (1) under the most stable adsorption configuration with the lowest total energy and the highest adsorption energy.

$$E_{ads} = E_{gas+graphene} - E_{graphene} - E_{gas}$$
(1)

where  $E_{gas+graphene}$ ,  $E_{graphene}$  and  $E_{gas}$  are the total energies of the adsorbed system, isolated graphene, and gas molecules, respectively. Adsorption energy is typically negative, indicating an exothermic interaction, whereas positive values suggest unstable adsorption. Systems with larger absolute adsorption energies are more stable. Conversely, lower absolute adsorption energies suggest instability. The charge transfer coefficient  $\Delta Q$ between graphene and a gas, based on Löwdin charge analysis, is calculated using equation (2)(26,27).

$$Q_{\text{transfer}} = Q_{\text{gas after adsorption}} - Q_{\text{gas before adsorption}}$$
 (2)

where  $Q_{gas after adsorption}$  and  $Q_{gas before adsorption}$  are the Lowdin charges on the gas molecule after and before adsorption on the CO-doped graphene surface (23). Negative charges suggest a donor role for the gas molecule, while positive charges suggest an acceptor role. The suggested method computes both individual atom and total system charges within a simulation framework.

To assess how well the six substrates adsorbed CO and NO molecules, we next calculated and analysed the adsorption energy, final adsorption distance, charge density, band structure, and density of states. These computational methods and techniques allow for a detailed understanding of the interactions between CO and NO molecules and doped graphene, providing valuable insights for applications in gas sensing and other fields.

# 3. Results and discussions

After performing geometrical atomic relaxation, both the N-doped graphene and Al-doped graphene retained the planar form of pristine graphene within the doped layer. Figure 1 illustrates the respective models. The measured value of 1.421Å(10,28) is also near when compared to the carbon-carbon bond length of 1.42Å(29) in pristine graphene.



Fig. 1. Top views and side views of different graphene models after full relaxation: (a) pristine graphene, which has three different adsorption sites: T, B, and H representing positions above the carbon atom, above the carbon-carbon bond, and above the centre of the hexagonal ring of graphene, respectively; (b) nitrogen-doped graphene; (c) aluminium-doped graphene.

In accordance with earlier theoretical research on Al-doped SWCNTs and Al-doped graphene, the carbon-nitrogen atom distance for N-doped graphene was discovered to be 1.41 Å, and the carbon-aluminum atom distance for Al-doped graphene was discovered to be 1.67 Å. Al-doped graphene exhibits higher adsorption energy and more energy loss than N-doped graphene (27). The optimized graphene lattice constant acquired from the optimization process corresponds to the experimentally observed value of 2.46 °A (20).

#### 3.1. The adsorption of CO

Figure 2 shows the most stable configurations of pristine, N-doped graphene, and Al-doped graphene after complete geometrical relaxation of CO adsorption. The atoms C, O, Al, and N are represented by gray, red, pink, and blue spheres, respectively. The adsorption results indicate that both the N-doped and pristine graphene remained essentially unchanged, as illustrated in Figures 2(a) and 2(b). The structural modification of Al-doped graphene occurs due to CO adsorption, as illustrated in Fig. 2(c), where Al atoms protrude from the graphene plane to an elevation of about 1.86Å(30). The neighboring carbon atoms project to varying degrees, yet this projection is consistent among them.



Fig. 2. Top views and side views of most stable configurations of (a) pristine graphene, (b) nitrogen-doped graphene and (c)aluminium-doped graphene after the adsorption of a CO molecule on the top site of C (N or Al) atom with the oxygen atom facing upwards, are presented.

Based on the graphene supercell  $3 \times 3 \times 1$ , we computed table 1 shows the equilibrium distance D for the most stable adsorption system between graphene and CO. CO was adsorbed on both pristine and N-doped graphene, with different adsorption energies of -0.02 eV(11,32) and -0.03 eV and distances from the CO to graphene surface 3.7 and 3.21 Å. On the other hand, the charge transfer quantities with negative charge (a negative charge indicates that the gas molecule functions as a donor) were significantly different, at |0.001|e and |0.01|e. With a CO adsorption energy of -3.07 eV and bond length of 2.02 Å, AL-doped graphene demonstrated considerable CO sensitivity(19). These investigations confirm that there is a positive charge transfer of about 0.15e from the CO molecule to the AL-doped graphene, increasing the CO molecule's bond length from 1.14 Å to 1.15 Å upon adsorption while leaving pristine and N-doped graphene unchanged.

We utilized PBE-D2 and vdw-DF methods to improve the adsorption energy. These techniques resulted in the following adsorption energies: -0.13 eV (32) and -0.15 eV for pristine graphene, -0.11eV (20) and -0.18 eV for N-doped graphene, and -3.54 eV and -3.43 eV for Al-doped graphene, as indicated in Table I.

The band structures, charge density differences, and electronic densities of states (DOS) for systems with and without adsorption were calculated to explore the impact of CO molecule adsorption on the electronic properties of graphene by using graphene super cell  $4 \times 4 \times 1$ . Figure 3 illustrates the energy band diagrams and densities of states for these systems, respectively. The corresponding high-symmetry k-points in the Brillouin zone for the systems are labeled as  $\Gamma$ , M, K, and  $\Gamma$ .

Adsorption system	Ead (eV)	Method	D	$\triangle Q(e)$
	Our study		(Å)	
CO on pristine	-0.02	GGA-		
graphene		PBE		
	-0.13	PBE-D2		
			3.7	-0.001
	-0.15	Vdw-DF		
CO on N-doped	-0.03	GGA-		
graphene		PBE		
	-0.11	PBE-D2		
			3.21	-0.01
	-0.18	Vdw-DF		
	1			

Table I. Calculation results of the most stable adsorption configurations.

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CO on Al-doped	-3.07	GGA-		
graphene		PBE		
	-3.54	PBE-D2	2.02	0.15
	-3.43	Vdw-DF		

The negligible bandgap observed in Fig. 3(a) suggests that the algorithm employed in this study for analyzing the graphene adsorption system is appropriate, as referenced in (33). After CO adsorption, the band structure depicted in Fig. 3(b) closely resembles that of pristine graphene, with no significant variation in the density of states (DOS) between the CO adsorption system on pristine graphene in Fig. 3(b) and pristine graphene in Fig. 3(a) around the Fermi level. Although a large peak follows CO adsorption at 2.1 eV, it is far from the Fermi level. These results suggest that CO molecules have no effect on pristine graphene. As a result, pristine graphene electrical characteristics remain unchanged upon CO adsorption. The N-doped graphene opened a band gap from zero to 0.21eV, as shown in Fig. 3(c), indicating the suitability of the algorithm used in this study. Because a nitrogen atom has one extra electron than a carbon atom, alternate doping of the nitrogen atom causes the Fermi level to rise to the conduction band, as seen in Fig. 3(d).

As a result, the nitrogen atom functions as an n-type dopant. The band structure around the Fermi level is virtually unchanged, despite the appearance of a flat band around the Fermi level and a large peak at 1.2eV in the DOS graph as shown in figure 3(d). There are still no discernible differences between Figs. 3(d) and 3(c) regarding the fermi level to the DOS curves.

The AL-doped graphene opened a band gap from zero to 0.4eV, as shown in Fig. 3(e), that is larger than that of the N-doped, because the valence electrons of the added Al atom are one fewer than those of the C atom. Fig. 3(f) demonstrates that the Fermi level migrated into the valence band, suggesting that the Al atom can function as a p-type dopant. Doping an Al atom introduces impurity into the graphene band, improving the graphene-to-CO contact. This can be confirmed by looking at Fig. 3(f), which shows that a flat band start appearing close to the Fermi level and a large peak at 0.2 eV in the DOS figure and the big change of the band structure is an evidence that the AL doped is the best sensor for CO molecule

In figure 4 (a), the total dos of pristine graphene with and without CO adsorption is comparable with only a significant peak present at a 2.1 eV distance from the Fermi level upon CO adsorption. Figure 4(b) shows the total density of states of N-doped graphene with and without CO, except for the peak at 1.2 eV. Figure 4(c) reveals that AL-doped graphene, with and without CO, exhibited a large peak close to the fermi level at 0.2 eV, which is evidence of its high sensitivity to CO molecule.



Fig. 3. Electronic structures and DOS of (a) Pristine graphene; (b) System of CO adsorbed on pristine graphene; (c) N-doped graphene; (d) System of CO adsorbed on N-doped graphene; (e) Al-doped graphene; (f) System of CO adsorbed on Al-doped graphene.



Fig. 4. Total density of state profiles before and after CO adsorption for (a) pristine graphene (b)N-doped Graphene (c) Al-doped Graphene

#### **3.2 Adsorption of NO**

The configuration of NO on graphene is like that of CO on graphene systems. On N-graphene, the CO molecule aligns with its C atom adjacent to the N atom, while the O atom of NO is closer to the N atom. The adsorption energies and closest distances for NO adsorbate on pristine, N-doped, and AL-doped graphene are given as -0.02 eV, -3.65 eV(34) and -2.24 eV with the closest distances of 3.4 °A, 3.17 °A and 1.98 °A respectively, as shown in table II.

The use of PBE-D2 and the non-local exchange correlation function (vdw-DF) significantly improved the results for pristine graphene (-0.09 eV, -0.16 eV), N-doped (-3.88 eV, -4.01 eV), and for AL-doped (-3.68 eV, -3.97 eV) graphene, with AL-doped graphene showing greater sensitivity due to chemical adsorption.

Figure (5b) indicates the emergence of a flat band adjacent to the fermi level, whereas in figure (5c), the band gap widened, and the fermi level shifted toward the valence band, transforming the N-doped graphene into an n-type semiconductor upon NO adsorption. In figure (5d), the charge transfer is |0.33|e to the positive side, while figure (5e) indicates an increase in the band gap of the AL-doped graphene accompanied by a shift of the fermi level toward the conduction band, making it a p-type semiconductor. Upon adsorption of NO, the charge transfer amounts to |0.31|e, resulting in a flat band above the fermi level.

Figure 5 presents the overall DOS curves for each system. The analysis results confirmed the band structures shown in figure 5 from the DOS closing to the fermi level. The DOS of the NO adsorption system on pristine graphene in Figure 5(a) is almost the same as that of pristine graphene in Figure 5(b) near the Fermi level. At 0.2eV no adsorption, but a significant peak occurs near the Fermi level. Pristine graphene retains its electronic properties unaltered in the absence of NO molecule. The discovery implies graphene's resistance to NO molecule. According to figure 5(c), the fermi level in the conduction band substantially increased. Despite a significant peak at 0.1 eV, no noticeable distinctions can be discerned in the DOS curve's fermi levels between figures (5d) and (5c). Figure (5e) reveals a band gap agreement with band structure studies, where the fermi level shifts into the valence band. Figure (5f)'s peak around the fermi level rose due to NO adsorption on the AL-doped graphene surface.

Figure 6 illustrates the total dos of pristine, N-doped, and AL-doped graphene before and after NO adsorption, revealing the differences close to the fermi level for all.





Fig. 5. Energy band diagrams of different systems, (a) Pristine graphene; (b) System of NO adsorbed on pristine graphene; (c) N-doped graphene; (d) System of NO adsorbed-on N-doped graphene; (e) Al-doped graphene; (f) System of NO adsorbed-on Al-doped graphene.



Fig. 6. Total density of state profiles before and after NO adsorption for (a) Pristine Graphene (b)N-doped Graphene (c) Al-doped Graphene.

Table II. Calculation results of the most stable adsorption configurations.

Adsorption system	Ead (eV)	Method	D	$\triangle Q(e)$
	Our study		(Å)	
NO on pristine	-0.02	GGA-		
graphene		PBE		
	-0.09	PBE-D2		
			3.4	0.05
	-0.16	Vdw-DF		

NO on N-doped	-3.65	GGA-		
graphene		PBE		
	-3.88	PBE-D2		
			3.17	0.33
	-4.01	Vdw-DF		
NO on Al-doped	-2.24	GGA-		
graphene		PBE		
	-3.68	PBE-D2	1.98	-0.11
	-3.97	Vdw-DF		

#### 4. Conclusion

The N-doped semiconductor's Fermi level shifts toward the conduction band. It was possible to determine the ideal arrangement, adsorption energies, charge transfer, and electronic characteristics, such as band structures, density of states, and partial density of states. Using the dispersion of GGA + PBE, the adsorption energies of CO and NO molecules on pristine graphene and N-doped graphene were - 0.02 eV, -0.09 eV, -0.02 eV, and -0.03 eV, respectively. The adsorption energies of NO and CO on Al-doped graphene, in contrast, were significantly higher at -2.24eV and -3.07 eV, respectively and these results improved by using non-local vdw-DF and PBE-D2. Our results also show that during adsorption, charge transfer takes place between the graphene sheet and the CO or NO molecules. This suggests that Al-doped graphene has a higher affinity for CO, while N-doped graphene is more prone to adsorb NO compared to pristine graphene. The shift to the fermi level toward the conduction band in N-doped graphene and shifted toward the valence band in AL- doped graphene makes them n-type and p-type semiconductors, respectively.

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