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First-principles study of O_3 molecule adsorption on pristine, N, Ga-doped and -Ga-N- co-doped graphene

Abstract. The adsorption of O_3 molecules (ozone) on graphene, N-doped graphene, Ga-doped graphene, and -Ga-N- co-doped graphene with an emphasis on O_3 detection was examined in this work. The physical characteristics of -Ga-N-co-doped graphene are significantly altered upon O_3 adsorption, which makes it a suitable choice for O_3 detection molecular sensors. The interaction between the O_3 molecule and the adsorbent is explained on the basis of their adsorption energy, adsorption distance and charge transfer. It was found that the adsorption of ozone molecules on the -Ga-N- co-doped graphene was more favorable in energy than that on the pristine one, representing the superior sensing performance of -Ga-N- co-doped system. In our work, we estimated the charge transfer between the O_3 molecule and doped graphene nanostructures based on Mulliken population analysis. The calculated adsorption energy value shows the ozone molecule more firmly adsorbs on the surface of -Ga-N- co-doped graphene nanostructures (E_{ads} = –1.74 eV) than that of pristine graphene (E_{ads} = –0.41 eV), deriving from a stronger covalent bond between the ozone molecule and the -Ga-N- co-doped graphene nanostructures. Our findings thus suggest that -Ga-N- co-doped graphene could be a highly efficient gas sensor device for O_3 detection in the environment.

Keywords: graphene, O_3 adsorption, density functional theory, N-doped graphene, Ga-doped graphene, -Ga-N- co-doped graphene, gas sensor, graphene-based sensors.

Introduction

Environmental pollution is a major concern today due to the increasing number of industrial processes, vehicle exhaust, electronic devices, and human activity, which has led to an urgent need for sensors that are sensitive, responsive, selective, and easy to recover. Sensing gases involving O_3 is crucial for improving home security and keeping the environment healthy, as well as for regulating emissions from vehicles and industries.

Ozone (O_3) is a molecule made up of three oxygen atoms [1], the color is colorless to pale blue. The odor of ozone is pungent and highly flammable. Ozone is found in different layers of the Earth's atmosphere. The majority of ozone resides in the stratosphere. Ozone is a protective layer that shields against harmful ultraviolet radiation hitting the earth. However, the ozone layer we breathe at ground level is dangerous. It forms through chemical reactions between oxides of nitrogen (NO_x) and volatile organic compounds (VOC) in the presence of sunlight [2]. It can have harmful effects on human health, causing respiratory problems. It also has detrimental impacts on vegetation and ecosystems. Therefore, various types of sensors, including graphene-based sensors, are used to measurement of a sensor response to ozone [3, 4].

Graphene-based sensors operate on the principle that the electrical conductivity of graphene can be influenced by the presence of certain gases, including ozone. When ozone molecules come into contact with graphene, they can either donate or accept electrons, leading to changes in the electrical properties of the graphene. This change in conductivity can be measured and correlated with the concentration of ozone in the surrounding environment [5].

Since the graphene discovered by brilliant and curious scientists as Andre Geim and Konstantin Novoselov, the area of two-dimensional (2D) nanomaterials have undergone rapid development, owing to their potential applications in various fields. Applications covered include: electronics [6], optoelectronics [7] and sensors [8], coatings [9], adhesives [10], lubricants [11], energy storage [12] and energy generation [13, 14] composites [15] and plastics [16], membranes [17] and filtration [18], life science [19] and biomedicine [20], construction materials [21], 3D printing/additive manufacturing [22] and much more.

Graphene nanostructures are very sensitive to many surface atoms because their two-dimensional structure means the entire material volume acts as a sensor surface. This makes them sensitive to external environments, such as temperature, electrical signals, chemicals, magnetism and biological agents [23–27]. Besides, to its sensitivity, graphene provides excellent mechanical strength, flexibility, thermal and electrical

conductivity, and compactness. Properties that make graphene attractive for sensor applications: ultra-high charge mobility, transparency, non-toxicity, high-tensile strength, high thermal conductivity, multi-functionality. The technique that graphene devices function as gas sensors is based on how surface adsorbates, which have specific adsorption sites and a chemical structure that makes them either donors or acceptors, change the electrical conductivity of the device [28, 29].

Graphene, graphene oxide (GO) and their related modified nanomaterials exhibit superior performances in the adsorption of environmental pollutants [30]. Despite its remarkable properties, graphene does have some drawbacks, and doping can address these limitations. Pristine graphene lacks a band gap, which can limit its use in certain electronic applications. Doping can be employed to open a band gap and make it more suitable for electronic devices, such as sensors. Also, doped graphene can exhibit enhanced sensitivity in gas sensing applications. Presently, a large number of studies reported on graphene doping to enhance electronic properties, where researchers introduce foreign atoms into the graphene lattice by replacing carbon atoms [31–34]. The toxic gases were often found to have adsorbed more strongly on doped graphene than on pristine graphene, based on the adsorption energies of the gases. This suggests that doped graphene sheets would make effective toxic gas sensors [35]. We choose nitrogen as a representative dopant in graphene depending on the dominant type of nitrogen functional group in which the planar nature of graphene is not disturbed. In comparison to a carbon atom, a nitrogen atom contains one additional electron and is similar in size [36], which is close to that of the carbon atom. Additionally, atoms of nitrogen and carbon can combine to create strong bonds [37]. A more stable structure may emerge in this way. We have also considered gallium (from group IIIA) atom. It is known that replacing a carbon atom in graphene with gallium is a useful way to improve the electronic properties sensing ability [38]. The advantage of choosing gallium as a potential dopant metal is its weak chemical interaction with graphene, which preserves the integrity of the graphene lattice. Multiple heteroatom co-doping has gained popularity recently because it gives an original, synergistically connected electronic structure. In an interesting study conducted by [39] the electronic properties of graphene has been tuned by nitrogen and sulfur co-doping with appropriate doping atom concentration. In another study by X. Yan and co-authors [40] have been investigated multiple transition metal atoms co-doped with graphene in different doping ways to study the effect on SO_2 gas. The results indicate that both Ti-doped as well as Co and Ti co-doped graphene are ideal for SO_2 sensors. Recently, our study [41] have examined that the addition of gallium and nitrogen atoms drastically changes the electronic structure of graphene and may be a good candidate for sensing this toxic gas SO_2. However, only a few reports about the -Ga-N- co-doping effect on the electronic properties of graphene. Therefore, in this paper, we also suggest to evaluate the adsorption behavior of -Ga-N- co-doped graphene.

It is thought that atomic-level awareness of condensed matter characteristics may be achieved by cutting-edge computer simulations. In the simulation, a real system has been created and its attributes are explored by the simulator. Research using simulations is analogous to experiments in numerous ways. On the other hand, full control over the experimental configurations and detailed access to findings are made possible because of simulations. These advantages make it possible to calculate first-principles material properties in light of the fundamental physics outlined in the Schrödinger equation without free parameters [29].

In materials science, density functional theory (DFT) has become a powerful tool for tackling a variety of issues [42]. DFT is today the most widely used method to study interacting electrons, and its applicability ranges from atoms to solid systems, from nuclei to quantum fluids. In the literature on DFT, the importance of computational approaches for 2D materials research is studied [43]. When it comes to doping graphene, density functional theory calculations play an increasingly important role in predicting and explaining the effects of doping on the electronic and structural properties of graphene-based materials. DFT calculations can be used to determine the binding energies between graphene and dopant atoms. This information is valuable for assessing the strength of the interaction and stability of the doped graphene system. DFT predictions guide experimentalists and researchers in designing and synthesizing doped graphene materials with desired electronic properties. This helps to save time and resources by narrowing down the search for optimal doping strategies.

For literature review, we reviewed different works related to adsorption of ozone molecule. Almost 20 years ago, researchers (2004) reported the feasibility of CNT film as an ozone sensor through first-principles calculations, centred around the interaction of O_3 with carbon nanotubes (CNTs) [44]. Moreover, in another research, ozone (O_3) adsorption on pristine Stone–Wales (SW) defective BC3 graphene-like sheets was investigated using density functional calculations and it was found that O_3 is weakly adsorbed on the pristine sheet [45]. The study of M. Vahdat and co-workers [46] reported about mechanistic insights on functionali-

zation of graphene with ozone. Their calculations highlights that O_3 is extremely attractive to functionalize graphene even at room temperature.

However, as far as we know, Ga-doped graphene and co-doped graphene by gallium and nitrogen atoms have not been reported for adsorption of O_3 molecule. In this work, the adsorption of O_3 molecule on the surface of pristine, N- and Ga- and co-doped by -Ga-N- graphene has been calculated using the state-of-the-art DFT simulation. The charge transfer between them and the density of states of the systems were studied in order to determine their interactions. This study is our starting point for future theoretical and experimental studies. We hope that it would be helpful for the both experimental and theoretical research groups that have been working on the development of graphene based sensors.

Computational details

All calculations have been carried out using spin unrestricted DFT framework as implemented in Dmol^3 module [47] to study the interactions between the O_3 molecules and pristine, N-doped graphene, Ga-doped graphene and -Ga-N- co-doped graphene. It is widely recognized that simulations limited to the local density approximation (LDA) underestimate equilibrium distances and overestimate bond energy E_b [48]. Therefore, we used the generalized gradient approximation (GGA) for improving the total energy, atomization energy and energy barrier. The Perdew-Burke-Ernzerhof (PBE) functional within GGA was taken to describe the exchange–correlation interaction [43, 49]. The DFT semi-core pseudopotential (DSPP) for core treatment with double numerical basis set plus polarization (DNP) basis set have been employed [50]. To ensure that the results of the calculations were comparable, identical conditions had been employed for graphene, the nitrogen doped graphene, the gallium doped graphene and also graphene co-doped by gallium and nitrogen system. The energy tolerance, maximum force and displacement convergence were set at 2×10^{-5} Ha, 0.004 Ha/Å and 0.005 Å respectively. The smearing technique was applied to the occupied orbitals with a smearing value of 0.005 Ha (1 Ha = 27.2114 eV). And a real space global cut off radius of 4.5 Å was employed. The Mulliken charge analysis computing procedure is used to find out the charge transfer values between the substrate and adsorbate.

To understand the interaction between the O_3 molecule and four systems, the adsorption energy was calculated by equation

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

where $E_{graphene+gas}$ is the total energy of graphene with adsorbed molecule, $E_{graphene}$ is the total energy of graphene, E_{gas} is the total energy of the molecule.

Results and Discussion

Properties of the Structure: We start first calculating with the geometric structure of O_3 was optimized to their steadiest configuration before studying their adsorption. Figure 1 displays the structure, and the information of bond lengths and angles are shown in Table 1.

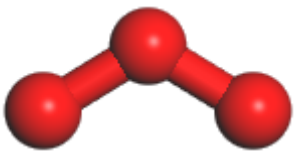

Figure 1. Structures of molecule O_3

Table 1

Structural parameters of structure

Gas molecule	Bond	Length (Å)	Angle (˚)
O_3	O-O	1.27	116.8

Geometry of Pristine Graphene and Doped Graphene: The optimized structure of graphene consists of 50 C atoms. The final configuration is shown in Figure 2. The C–C bond length calculated after optimization is found to be 1.42 Å, which agrees well with previous reports [51, 52].

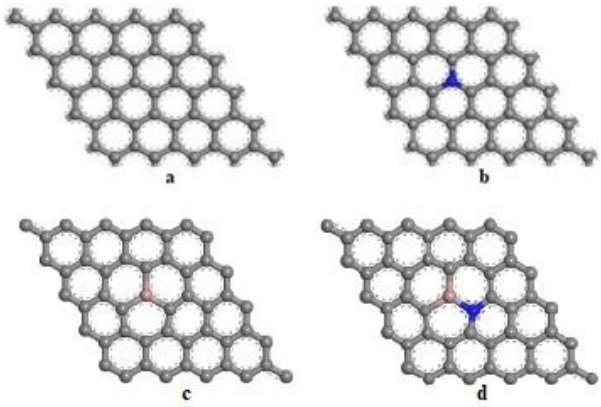

Figure 2. Relaxed geometries of 5×5 supercell of pristine graphene (*a*), where the carbon atoms are shown in grey and nitrogen-doped graphene (*b*), where the nitrogen atom is shown in blue; gallium-doped graphene (*c*), where the gallium atom is shown in pink; graphene co-doped by gallium and nitrogen atoms (*d*)

Adsorption of O_3 on Pristine Graphene: After that, we investigated the configuration of the O_3 molecule adsorbed on pristine graphene. The optimized structure for the adsorption of the O_3 molecule on pristine is shown in Figure 3. After optimization, the ozone molecule is positioned parallel above the graphene plane. The corresponding geometrical parameters, the adsorption parameters, and the charge transfer of the graphene + gas system are listed in Table 2.

In fact, the O-O distance (=1.27 Å) increases upon adsorption. Meanwhile, it should be noted that the optimized geometry of O_3 molecules on pristine graphene and found physisorption of the molecules due to the inert graphene surface. The results from other authors [46] agree with our results. This indicates that the pristine graphene is insensitive to O_3 molecules.

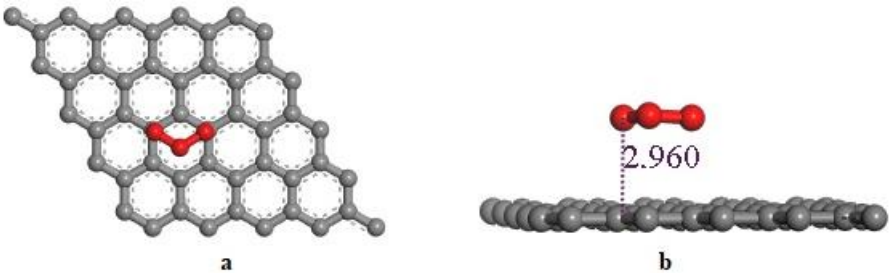

Figure 3. The top view (*a*) and side view (*b*) of graphene + O_3 system

Table 2

The detailed parameters of graphene+ gas system

System	Adsorption Distance (Å)	Bond Length (Å)	Bond Angle (˚)	E_{ads} (eV)	Q_T(e)
Graphene +O_3	2.96	1.31 (O_1-O_2) 1.31 (O_2-O_3)	116.8	–0.41	–0.259

Adsorption of O_3 on N-Doped Graphene: The carbon atom of graphene was replaced with the nitrogen atom to find a highly sensitive nanostructure, and the new structure was optimized. The adsorption of the O_3 molecule on N-doped graphene was studied, and the optimized geometry of the N-doped graphene+O_3 system is displayed in Figure 4. After optimization, the ozone molecule is positioned with a titled ∧ orientation above the graphene plane. The adsorption of the O_3 molecule on N-doped graphene is weak, so the interaction was not affected by the doped nitrogen atom. The ozone molecule is found physisorbed at a distance of 3.07 Å. Surprisingly, the energy adsorption between ozone molecules and nitrogen-doped graphene had a higher value.

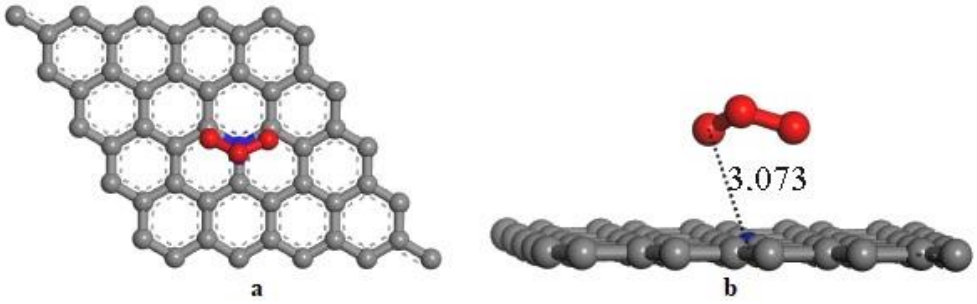

Figure 4. The top view (*a*) and side view (*b*) of nitrogen-doped graphene + O_3 system

Table 3

The detailed parameters of nitrogen-doped graphene+ gas system

System	Adsorption Distance (Å)	Bond Length (Å)	Bond Angle (˚)	E_{ads} (eV)	Q_T(e)
Nitrogen-doped graphene + O_3	3.07	1.32 (O_1-O_2) 1.32(O_2-O_3)	116.4	–0.73	–0.404

Adsorption of O_3 on Ga-Doped Graphene: The optimized geometry for the Ga-doped graphene + O_3 system is displayed in Figure 5. In this case, the larger atomic radius of the Ga atom results in a bond length value of 1.86 Å, which is longer than the C–C bond length in pristine graphene. The data conforms properly with the earlier report [53]. The corresponding distance between the O_3 molecule and Ga atom in the Ga-doped graphene is shorter than in the pristine graphene system. Moreover, the adsorption energy of the O_3 molecule in the Ga-doped graphene system is slightly larger than that of the O_3 molecule in the pristine graphene system. Furthermore, to investigate the changes in electronic structures in graphene caused by the physical or chemisorption of O_3 molecules, the net electron transfer (Q_T) from either the pristine or the Ga-doped graphene to the O_3 molecules was by Mulliken analysis, where Q_T is defined as the charge variation caused by the O_3 absorption. The Mulliken atomic charge analysis of the structure shows that charge transfers from doped graphene sheets to O_3 molecules. The electron transfer in the Ga-doped graphene is slightly larger than in the pristine graphene. The results, as shown in Table 4, indicate that graphene doped with gallium atom is much more sensitive to adsorption of molecule. This supports the notion that Ga doping influences the electronic properties of graphene substantially.

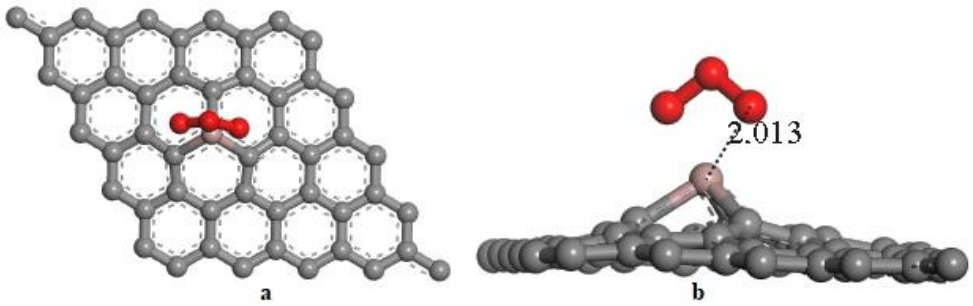

Figure 5. The top view (*a*) and side view (*b*) of gallium-doped graphene + O_3 system

Table 4

The detailed parameters of the Ga-doped graphene+ gas system

System	Adsorption Distance (Å)	Bond Length (Å)	Bond Angle (˚)	E_{ads} (eV)	Q_T(e)
Ga-doped graphene +O_3	2.01	1.36 (O_1-O_2) 1.38 (O_2-O_3)	107.5	-0.54	-0.48

Adsorption of O_3 on -Ga-N- co-doped graphene: Three different positions of the O_3 molecule on the -Ga-N- co-doped graphene were taken into consideration to investigate the adsorption behavior of the O_3 molecule and find the most favorable position: the bond-bridge (B-site), the center of the hollow (H-site),

and the center of the top (T-site). The optimized geometries with adsorption distance of all configurations were illustrated in Figure 6. For all configurations, the negative adsorption energies were found which indicate an attractive interaction between the ozone molecule and graphene co-doped by gallium and nitrogen. All adsorption sites of the O_3 molecule are preferred to adsorb with −1.46 eV, −1.74 eV and −1.49 eV at a distance 1.84 Å, 1.95 Å and 1.86 Å from the -Ga-N- co-doped graphene, respectively. The adsorption energies depend on the interaction distance. The adsorption energy is greatly increased with the reduced of interaction distance between the O_3 molecule and -Ga-N- co-doped graphene. This indicates that the adsorption site (H-site) shown in Figure 6 (*c*–*d*) is the most stable position with the strongest interaction between the O_3 molecule and graphene co-doped by gallium and nitrogen. The ozone molecule is positioned with a titled ∧ orientation above the graphene co-doped by gallium and nitrogen. Based on adsorption energy values in Table 5, the ozone molecule has more interaction with co-doped graphene by gallium and nitrogen atoms.

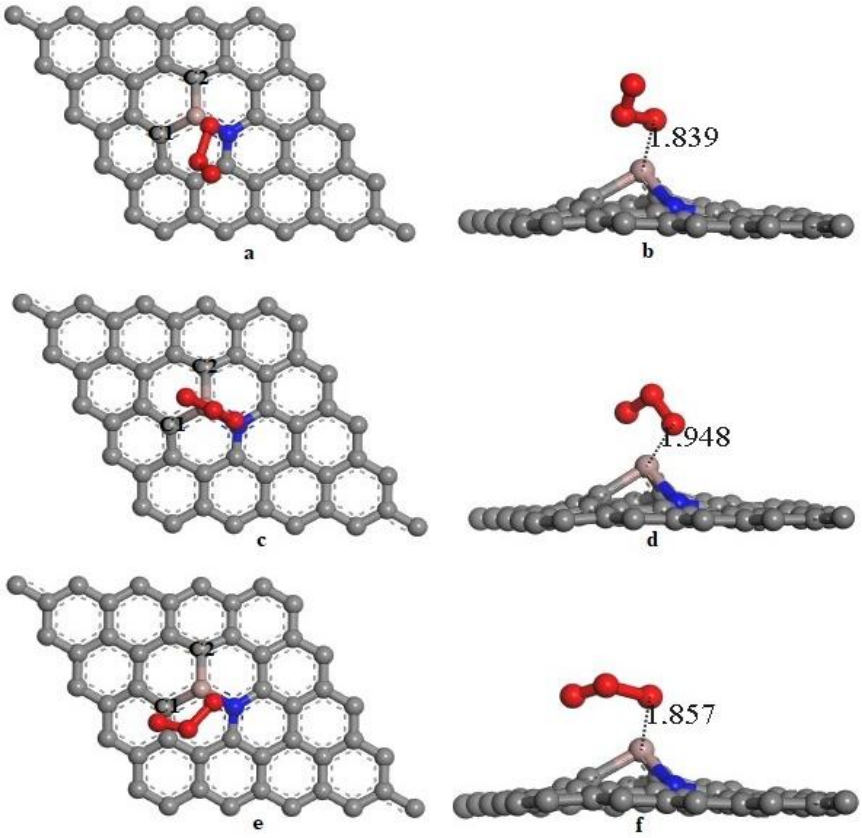

Figure 6. The top view (*a*) and side view (*b*) of -Ga-N- co-doped graphene+O_3 system in the B site; the top view (*c*) and side view (*d*) of -Ga-N- co-doped graphene+O_3 system in the H site; the top view (*e*) and side view (*f*) of -Ga-N- co-doped graphene+O_3 system in the T site.

Table 5

The detailed parameters of the -Ga-N- co-doped graphene + gas system

System	Adsorption Site	Adsorption Distance (Å)	Bond Types (Å)	Bond Length (Å)	Bond Angle (˚)	E_{ads} (eV)	Q_T(e)
-Ga-N- co-doped graphene +O_3	B	1.84	1.96 (Ga-N)	1.24 (O_1-O_2) 1.61 (O_2-O_3)	111.6	–1.46	–0.468
	H	1.95	2.03 (Ga-N)	1.36 (O_1-O_2) 1.41 (O_2-O_3)	107.2	–1.74	–0.53
	T	1.86	1.95 (Ga-N)	1.27 (O_1-O_2) 1.56 (O_2-O_3)	113.6	–1.49	–0.504

Before optimization, the bond length between gallium and nitrogen atoms was 1.420Å. Meanwhile, due to the co-doping of the Ga and N atoms, the stress of the two C atoms around it in the system changed, caus-

ing them to move away from their original positions. For instance, B site: C_1-Ga = 1.892 Å, C_2-Ga = 1.891 Å. We found that the bond length of Ga-N was 1.967 Å, while the angles of C_1-Ga-C_2, C_2-Ga-N, and C_1-Ga-N were 96.8°, 92.3° and 91.8°, respectively. H-site: C_1-Ga = 1.911 Å, C_2-Ga = 1.911 Å. We observed that the bond length of Ga-N was 2.027 Å, while the angles of C_1-Ga-C_2, C_2-Ga-N, and C_1-Ga-N were 99.6°, 88.8° and 88.7°, respectively. T-site: C_1-Ga = 1.885 Å, C_2-Ga = 1.887 Å. In this position, we found that the bond length of Ga-N was 1.956 Å, while the angles of C_1-Ga-C_2, C_2-Ga-N, and C_1-Ga-N were 94.6°, 92.9° and 92.5°, respectively. As seen in Table 5, we found that all initial B, H, and T configurations are almost changed. After optimization, the configurations do not keep their original adsorption site. The results of the adsorption energy indicate that the absorption on the H site is the most stable configuration, and the stability order is H > T > B.

Summary and Conclusions

In summary, in this work, we conducted a study based on density functional theory (DFT) calculations to investigate of adsorption ozone molecule on pristine, N-, Ga-doped graphene, and -Ga-N- co-doped graphene. The adsorption geometries, adsorption energies, and charge transfer analysis are obtained. The O_3 molecule showed physisorption on pristine graphene with low adsorption energies and little charge transfer, which suggests that the unmodified graphene material. The adsorption of O_3 on the N-doped graphene was slightly stronger, which had an adsorption energy of (−0.73 eV) and little charge transfer. The adsorption energy of O_3 on the Ga-doped graphene (−0.54 eV) was much lower than on N-doped graphene. The N doping improved the interactions between the gas, while the Ga doping had no significant effect on the interactions. In particular, the Ga doping of graphene significantly enhanced the adsorption of ozone molecules relative to pristine graphene. However, -Ga-N- co-doped graphene demonstrates high adsorption energy to ozone molecules (adsorption energy of −1.74 eV) that corresponds to the chemisorption. Thus, -Ga-N- co-doped graphene is of great interest for gas sensing applications since it has stronger interactions with the O_3 molecules than other structures discussed in the paper.

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Таза графенде, N, Ga және -Ga-N- қоса легирленген графенде O_3 молекуласының адсорбциясының алғашқы принциптерін зерттеу

Мақалада O_3 молекуласының (озон) графенге, азотпен легирленген графенге, галлиймен легирленген графенге және -Ga-N- қоса легирленген графенге адсорбциясы зерттелген. Графенге, азотпен легирленген графенге, галлиймен легирленген графенге және -Ga-N- қоса легирленген графенге O_3 адсорбциясы физикалық қасиеттердің айтарлықтай өзгеруіне әкеледі, бұл оны O_3 молекуласын анықтау мақсатында молекулалық сенсорлар үшін перспективті үміткер етеді. O_3 молекуласы мен адсорбент арасындағы өзара әрекеттесу олардың адсорбциялық энергиясы, адсорбция қашықтығы және зарядтың тасымалдануы негізінде түсіндіріледі. Озон молекуласының -Ga-N- қоса легирленген

графенге адсорбциясы таза графенге қарағанда энергия бойынша қолайлы екені анықталды, бұл -Ga-N- қоса легирленген жүйенің жоғары сенсорлық сипаттамаларын білдіреді. Осы жұмыста Малликен популяциясының талдауына негізделген O_3 молекуласы мен легирленген графен нанокұрылымдары арасындағы зарядты тасымалдау бағаланған. Озон молекуласы мен -Ga-N- графен нанокұрылымдары арасындағы күшті коваленттік байланыстан туындайтын адсорбция энергиясының есептелген мәні таза графенге (E_{ads} = –1,74 eV) қарағанда -Ga-N- қоса легирленген графен нанокұрылымдарының (E_{ads} = –0,41 eV) бетінде күштірек адсорбцияланатынын көрсетеді. Осылайша, біздің нәтижелеріміз -Ga-N- қоса легирленген графенмен қоршаған ортадағы O_3 анықтау үшін жоғары тиімді газ сенсоры құрылғысы болуы мүмкін екенін көрсетеді.

Кілт сөздер: графен, O_3 адсорбциясы, тығыздықтың функционалдық теориясы, азотпен легирленген графен, галлиймен легирленген графен, -Ga-N- қоса легирленген графен, газ сенсоры, графен негізіндегі газ сенсоры.

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Исследование первых принципов адсорбции молекулы O_3 на чистом графене, легированном N, Ga, и -Ga-N- со-легированном графене

В статье исследована адсорбция молекулы O_3 (озона) на графене, легированном графене с азотом, на легированном графене с галлием и -Ga-N- со-легированном графене с акцентом на обнаружение O_3. Адсорбция O_3 на графене, легированном графене с азотом, на легированном графене с галлием и -Ga-N- со-легированном графене приводит к значительному изменению физических свойств, что делает его перспективным кандидатом для молекулярных датчиков для обнаружения O_3. Взаимодействие между молекулой O_3 и адсорбентом объясняется на основе их энергии адсорбции, расстояния адсорбции и переноса заряда. Было обнаружено, что адсорбция молекулы озона на -Ga-N- со-легированном графене была более благоприятной по энергии, чем на чистом, что представляет собой превосходные сенсорные характеристики -Ga-N- со-легированной системы. В настоящей работе был оценен перенос заряда между молекулой O_3 и легированными наноструктурами графена на основе анализа популяции Малликена. Рассчитанное значение энергии адсорбции показывает, что молекула озона более прочно адсорбируется на поверхности наноструктур графена, со-легированных -Ga-N- (E_{ads} = –1,74 eV), чем на чистом графене (E_{ads} = –0,41 eV), вытекая из более сильной ковалентной связи между молекулой озона и -Ga-N- со-легированного графена. Таким образом, наши результаты показывают, что -Ga-N- со-легированный графен может быть высокоэффективным устройством датчика газа для обнаружения O_3 в окружающей среде.

Ключевые слова: графен, адсорбция O_3, теория функционала плотности, легированный азотом графен, легированный галлием графен, -Ga-N- со-легированный графен, газовый сенсор, сенсоры на основе графена.

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