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Sensitivity and Adsorption Energy Analysis of B and Ga Doped Graphene/Silicene for HCl Gas Sensing

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ABSTRACT

Detecting highly toxic HCl fumes conveniently, quickly, and reliably is essential due to its potential human health hazards. Therefore, it is important to track trace amounts of HCl using sensors. Sensors based on the two-dimensional materials graphene and graphene-like materials have attracted widespread attention due to their sensitivity, especially when grafting them with other molecules or atoms to alter the electronic and structural properties. This work used DFT to investigate the adsorption mechanism of pure and (B, Ga) doped graphene/silicene on the hazardous gas HCl. Adsorption energy, charge transfer, sensitivity, and density of state were Calculated. The adsorption energy of pure Graphene/silicene are (-0.1306, -0.2857) with sensitivity (1.132, 5.311) respectively. Doping graphene and graphene-like structures with (B, Ga) atoms significantly enhances the adsorption energy of graphene. This suggests that doped graphene performs better than pure graphene in applications involving HCl gas adsorption and sensors. GNR_DopB has a (19.41eV) adsorption energy and (51.58%) sensitivity to HCl gas, while the adsorption energy of GNR_DopGa is (-0.958eV), and it has the highest sensitivity to gas among the calculated models (195.03%). The results showed that graphene doped with Ga atoms has high sensitivity to HCl gas. In contrast, graphene doped with B atoms has high adsorption energy and High sensitivity, indicating that it can be used as suitable equipment for high-efficiency sensing HCl gas.

1. INTRODUCTION

Colorless, toxic, and corrosive hydrogen chloride (HCl) is used extensively in scientific research and industrial processes [1]. The primary source of HCl, an air pollution gas, in the environment, is waste emissions from chemical and incinerator industries [2]. A continual release of HCl gas into the atmosphere will harm human health [3, 4], when it has been shown that excess hydrogen chloride is corrosive to the skin, eyes, nose, mucous membranes, and respiratory and digestive systems [5]. The possible health risks to humans make it imperative to detect highly hazardous HCl vapors conveniently, rapidly, and reliably [6].

Since the successful fabrication of monolayer graphene through mechanical exfoliation in 2004, there has been a significant focus on emerging two-dimensional (2D) materials in experimental and theoretical research. Other well-known group-IV monolayers besides graphene are silicene, germanene, tinene, plumbene, and its hydrogenated systems. These layered systems have rich and distinct intrinsic atomic interactions and geometric symmetries, making them excellent for researching a wide range of physical, chemical, and material phenomena [7].

Carbon-based materials are utilized in gas sorption, storage, and separation processes because of their abundant supply, strong pore structure, low weight, and exceptional chemical and thermal durability. According to recent research, graphene's superior sensitivity, linked to its high electron mobility, makes it an attractive prospect for use as a gas sensor [8].

One effective technique to change graphene's structure and electrical properties is to dope it with additional atoms or molecules [9].

The capacity of graphene to adsorb single molecules is one of its most unexpected properties. This suggests that 2D materials, with their vast area and active surface, are viable platforms to detect harmful gas molecules [10]. The first graphene-based gas sensor was reported by Novoselov et al. in 2007 and demonstrated that gas molecules could be detected at room temperature by adsorption or desorption from the graphene surface [11]. Through subsequent theoretical calculations, it was found that graphene is not ideal for absorbing gas, which greatly limits its ability to absorb gas in gas sensors [12, 13]. It may be possible to improve graphene's sensing ability by combining it with other atoms, Similarly, this applies to silicene as well. The adsorption of gaseous substances, including H_2O, NH_3, CO, NO_2, and NO, on graphene and graphene doped with Ga atoms was investigated by Liang et al. The findings indicate that the adsorption energy of all gas molecules on graphene is enhanced with the

introduction of Ga doping [14]. Deji et al. [15] investigion the adsorption of NO and NO_2 gases onto graphene doped with B and P atoms co-doping, increase in donor impurity(P) in co-doped system greatly enhances adsorption energies of NO and NO_2. Several research teams have considered monolayer silicene as a gas sensor thus far. For instance, Feng et al. [16] have utilized calculations from fundamental principles to study gas adsorption on silicene. The outcomes verified an excellent ability to sense NO_2, O_2, SO_2, NO, and NH_2 gases. Adsorption of NO_2 results in a half-metallic nature, while adsorption of the remaining gases opens the silicene band gap. Hu et al. [17] used first-principles calculations to show the silicene monolayer's strong reactivity towards nitrogen-based (NH_3, NO, and NO_2).

In this study, we investigate doped graphene/silicene with (B,Ga) atom using density function theory (DFT) and explore employing it as a HCl gas sensor and which ones give better sensing results.

2. MODELS AND COMPUTATIONAL METHODS

DFT computations were conducted using the Gaussian 09W software program [18]. With hybrid function B3YLP at basis set 6-31G at Ground state method, The Gausssum software tool was also used to visualize the density of states (DOS) to investigate (B, Ga) doping on the adsorption effect of gas molecules HCl on the electronic structure of Graphene/silicene. We used graphene/silicene nanoribbons (see Figure 1) the observed C-C bond length of graphene is 1.44 Å and the observed Si-Si bond length of silicene is 2.28 Å with a doped atom substituting a C/Si atom and a single HCl molecule adsorbed onto it. The corresponding dopant concentration is about 2.17%.

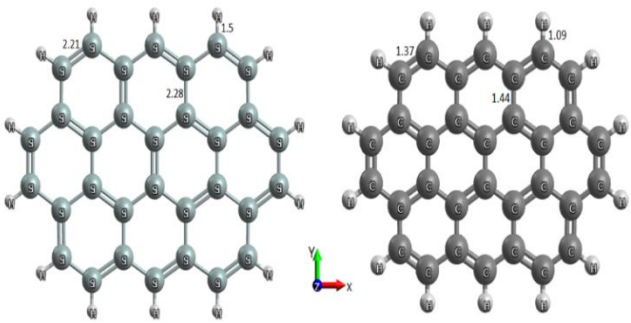


Figure 1. Armchair's geometric construction (Left) Silicene (Right) Graphene nanoribbon

Eq. (1) is used to compute the energy gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital in order to investigate further the conductivity and chemical stability of (B, Ga) doped graphene/silicene and adsorption system.

$$E_g = E_{LUMO} - E_{HOMO} \quad (1)$$

where, the lowest unoccupied molecular orbit (E_{LUMO}) and the highest occupied molecular orbit (E_{HOMO}), respectively, are represented [19].

Eqs. (2) and (3) estimate the IE (ionization potential) and EA (electron affinity) by Koopmans' theorem [20, 21]:

$$IP = -E_{HOMO} \quad (2)$$

$$EA = -E_{LUMO} \quad (3)$$

Eq. (4) is used to get the adsorption energy (E_a), which is the difference between the system's total energy (gas plus Ribbon) and the sum of the energies of the molecule (gas) and pristine doped graphene/silicene Ribbons [17].

$$E_a = E_{total} - (E_{Ribbon} + E_{gas}) \quad (4)$$

Adsorption energy is a physical term representing adsorption strength; it is typically negative, and adsorption becomes unstable when it reaches positive values. The system will be more stable the higher the absolute value of adsorption energy. Smaller ones can typically attest to the adsorption's instability.

The charge transfer (Q) between the gas molecules and the HCl- Nanoribbon is computed using Hirshfeld charge analysis.

$$Q = Q_{absorbed} - Q_{isolated} \quad (5)$$

In this case, $Q_{absorbed}$ indicates the charge of the gas molecules upon adsorption, and $Q_{isolated}$ means the charge of the gas molecules after isolation. The transport of electrons from gas molecules to the adsorbent surface and vice versa is indicated by positive Q [1]. The sensor's sensitivity (S) can be determined using Eq. 6:

$$S = \left(\frac{|E_g(1) - E_g(0)|}{E_g(0)}\right) * 100\% \quad (6)$$

where, $E_g(1)$ is the energy gap when gas is present, $E_g(0)$ is when gas is absent, and S is sensitivity.

3. RESULTS AND DISCUSSION

3.1 Doped ribbons and gas molecules' geometric structures

The molecular composition of HCl has been determined. Then, the structure of the gas molecule was improved, and its lowest formation energy was calculated. Figure 2 depicts the most stable structure, The Bond Length of the HCl molecule is 1.321 Å.

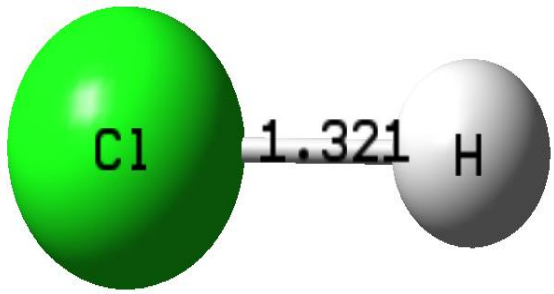


Figure 2. Molecular structure of optimized HCL

The Graphene/Silicene nanoribbon (GNR/SNR) was doped by a substituent atom(B/Ga); Figure 3 shows the grafting models (Dop_GNR/Dop_SNR), The Bond Length between C-B and C-Ga atoms are (1.51 and 1.87) respectively, and The Bond Length Between Si-B and Si-Ga atoms is (1.79 and 2.32).

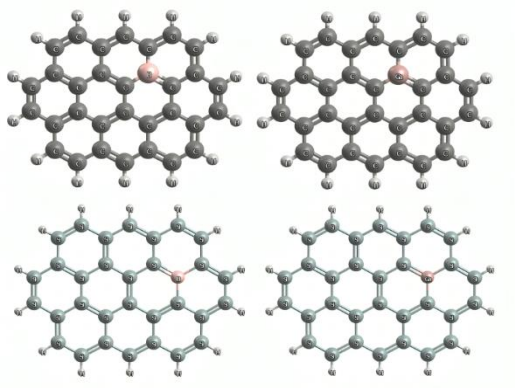


Figure 3. Structure of doped GNR/SNR with (B, Ga) atoms

The electronic properties of Pure and doped GNR/SNR were calculated. The following Table 1 summarizes the following: total energy, ionization potential, energy gap, molecular orbitals (HOMO and LUMO), and electron affinity. Total energy is a stability of the system, the more energy increases by negative value, the system becomes more stable. Results indicate that total energy was increase and became more stable, molecular orbitals increased, and the energy gap was reduced, resulting from doping; this result of the energy gap let the energy band become closed compared with pure GNR, while Ionization potential and electron affinity were increased.

Table 1. Represents the electronic properties of doped graphene/silicene with (B, Ga) compared with pure graphene/silicene

Structure	GNR			SNR		
	Pure	DopB	DopGa	Pure	DopB	DopGa
E_T(a.u.)	-1227.728	-1214.442	-3112.326	-9271.547	-9006.289	-10904.344
HOMO(eV)	-4.9681	-5.0832	-4.9898	-4.8655	-5.0666	-4.9026
LUMO(eV)	-2.0130	-2.9042	-2.7245	-3.4002	-4.3156	-4.3586
E_g(eV)	2.9551	2.1790	2.2653	1.4653	0.7510	0.5439
IP(eV)	4.9681	5.0832	4.9898	4.8655	5.0666	4.9026
EA(eV)	2.0130	2.9042	2.7245	3.4002	4.3156	4.3586

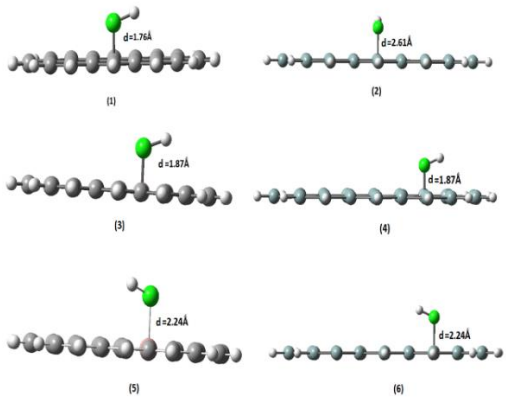
3.2 Adsorption energies of studied structures for HCl gas molecule

The variation in the distance between the hydrochloric acid and the different nanoribbons is calculated. After applying the optimization to the pure and doped GNR /SNR, the hydrochloric acid gas molecules are placed at a distance from the surface of the pure and doped graphene/silicene layers as shown in Figure 4(a). After optimization, we notice a change in the structure. For different nanoribbons and a change in the distance between the gas molecules and the nanoribbons, and as shown in Figure 4(b), the GNR doped with Ga atoms interacts with the gas significantly compared to the other models studied.

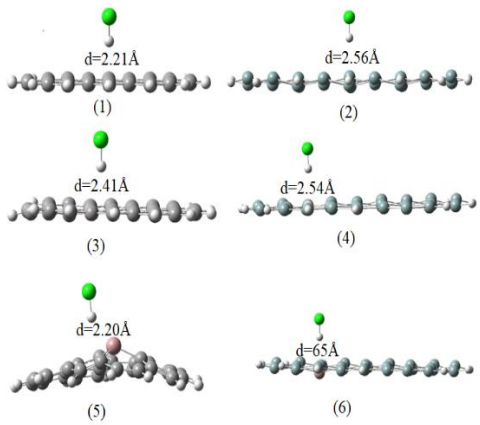
As shown in Table 2 Adsorption energy studies showed that the adsorption energy of hydrochloric acid gas on GNR and SNR is minimal, indicating weak physical adsorption, regardless of the composition of hydrochloric acid. Achieving the gas adsorption criteria was challenging due to the low adsorption energy. Next, we used hydrochloric acid gas adsorption on the models grafted with (Ga, B) atoms. The calculated results of the adsorption energy showed that the B atoms enhanced the absorption capacity of graphene by a large percentage. In contrast, the adsorption energy remained low for SNR doped with (Ga, B) atoms. The adsorption energy of GNR_DopB is 19.4eV, which is the best in this group.

Table 2. Distance between structures and HCl gas before and after optimization and the Adsorption energies

Structure	Distance (Å) (Before Optimization)	Distance (Å) (After Optimization)	E_a(eV)
GNR_Pure	1.67	2.21	-0.1306
SNR_Pure	2.61	2.56	-0.2857
GNR_DopB	1.87	2.41	19.4096
SNR_DopB	1.87	2.54	-0.2040
GNR_DopGa	2.24	2.20	-0.9578
SNR_DopGa	2.24	2.65	-0.6776



(a) Before optimization



(b) After optimization

Figure 4. Adsorption of HCl Gas Molecule by GNR/SNR pure and Dop (B, Ga) Ball-And-Stick Model (1) GNR_Pure (2) SNR_Pure (3) GNR_DopB (4) SNR_DopB (5) GNR_DopGa (6) SNR_DopGa

GNR and SNR in Pure condition have allowed sensitivity to HCl gas—the sensitivity to the gas increases for the (B, Ga) Doped GNR and SNR. Also, sensitivity to dope GNR shows better results than dope SNR; the highest value of sensitivity is 195.039 for GNR DopGa atom, which offers better sensitivity compared to the sensitivity of the GNR doped with transition metal atoms (Ti, V, Cr, Mn, Fe, Co) that were calculated by Tang et al. [1].

Table 3's charge transfer supports this conclusion as well. The transference between GNR/SNR and HCl is relatively modest by charge population analysis, only -0.063414e/-0.063414. Negative charge transfer, on the other hand, denotes the transfer of electrons from the Nanoribbon surface to the gas molecule. The degree of charge transfer changes somewhat upon grafting.

Table 3. The sensitivity and charge transfer for studied Ribbons

Nanoribbon	S%	Q(e)
GNR_Pure	1.13259669	-0.063414
SNR_Pure	5.311049211	-0.056414
GNR-DopB	51.5859141	-0.071071
SNR_DopB	0.217391304	-0.054227
GNR_DopGa	195.039039	-0.071071
SNR_DopGa	32.016008	-0.084182

3.3 Density of states (DOS)

The DOS spectrum helps illustrate molecular orbitals and their significance in chemical bonding [22]. Figure 5 presents the DOS distribution for GNR/SNR and gas-absorbed GNR/SNR to compare their electron characteristics. The curves overlap at the Fermi level, as seen in Figure 5 (1), suggesting that the conductivity change following HCl adsorption is not immediately apparent. In contrast to Figure 5 (1), SNR Pure has superior properties for detecting HCl gas compared to GNR Pure. In Figure 5 (2), however, the DOS change emerges at (-8.7 to -8 eV), and the slight change around the Fermi level indicates a little change in conductivity after absorbing HCl gas. Figure 5 (3) also shows an apparent change in DOS at (-8 eV), indicating a small amount of orbital hybridization. There is also a slight change in Conductivity after absorbing HCl gas. In Figure 5 (4), the change in DOS appears between (-8.6 to -8 eV), while the DOS peak increases significantly at (-11.6 eV) in Figure 5 (5), which means that the total charge density has grown considerably. There is a minimal change in the conductivity. On the other hand, Figure 5 (6) shows a significant rise in DOS at (-8.4) while overlapping at the Fermi level. This suggests there is unclear orbital hybridization between SNR DopGa and HCl and, thus, no discernible change in conductivity.

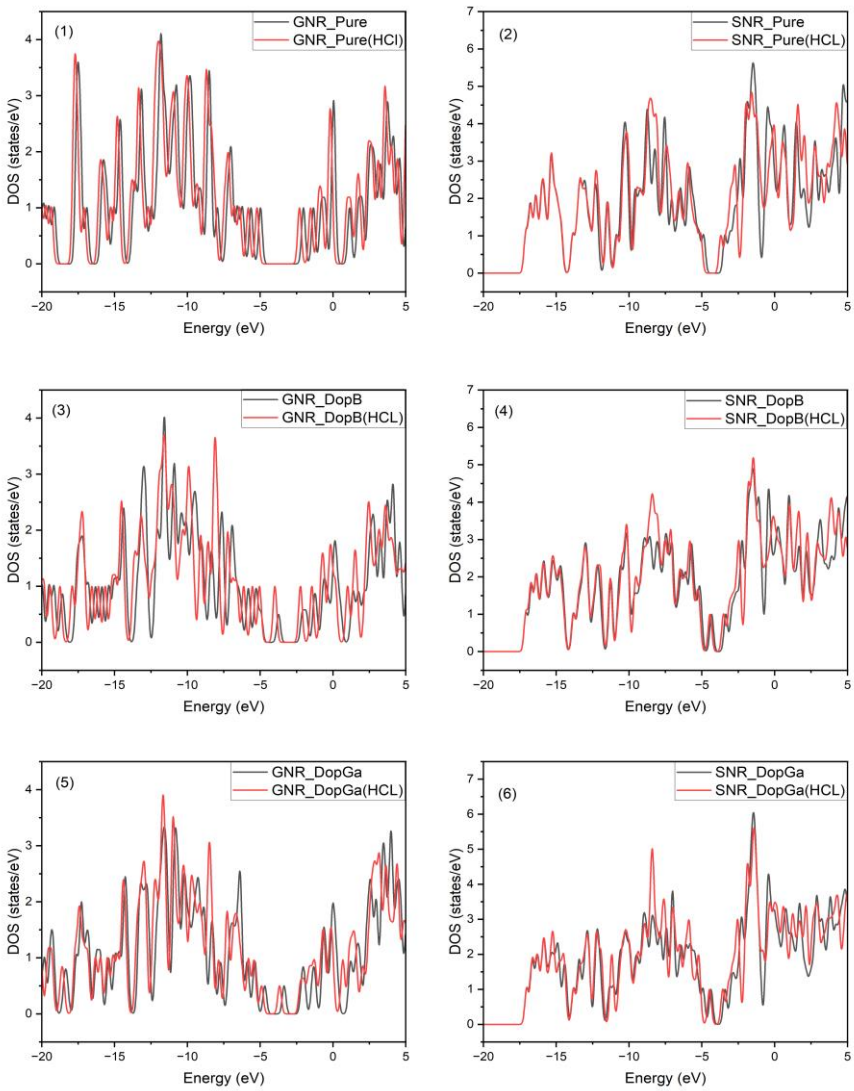


Figure 5. Compares the density of state (DOS) for studied structures without/with HCl

4. CONCLUSIONS

In this study, pure GNR and SNR materials were tested as HCl gas sensors, and the sensing process was improved by dopping with (B, Ga) atoms.

Density functional theory was used to study the adsorption mechanism of pure and doped GNR/SNR on the hazardous gas HCl. The results show that the adsorption energy of silicene is -0.2857 eV, and that of graphene is -0.1306 eV, indicating weak physical adsorption.it is show that pure GNR/SNR not suitable for sensing HCl gas. Doping GNR and SNR structures with (B, Ga) atoms significantly enhances the adsorption energy of GNR. This suggests that doped GNR performs better than pure GNR in applications involving HCl gas adsorption and sensors.

Among the models studied, GNR DopB and GNR DopGa are the optimal materials for detecting HCl gas.

REFERENCES

[1] Tang, H., Xiang, Y., Zhan, H., Zhou, Y., Kang, J. (2023). DFT investigation of transition metal-doped graphene for the adsorption of HCl gas. Diamond and Related Materials, 136: 109995. https://doi.org/10.1016/j.diamond.2023.109995

[2] Qiao, S., Sampaolo, A., Patimisco, P., Spagnolo, V., Ma, Y. (2022). Ultra-highly sensitive HCl-LITES sensor based on a low-frequency quartz tuning fork and a fiber-coupled multi-pass cell. Photoacoustics, 27: 100381. https://doi.org/10.1016/j.pacs.2022.100381

[3] Xie, Y.Z., Shan, G.G., Zhou, Z.Y., Su, Z.M. (2013). Schiff-base as highly sensitive and reversible chemosensors for HCl gas. Sensors and Actuators B: Chemical, 177: 41-49. https://doi.org/10.1016/j.snb.2012.10.046

[4] Matsuguchi, M., Takaoka, K., Kai, H. (2015). HCl gas adsorption/desorption properties of poly (N-isopropylacrylamide) brushes grafted onto quartz resonator for gas-sensing applications. Sensors and Actuators B: Chemical, 208: 106-111. https://doi.org/10.1016/j.snb.2014.10.137

[5] Boulet, L.P. (1988). Increases in airway responsiveness following acute exposure to respiratory irritants: Reactive airway dysfunction syndrome or occupational asthma? Chest, 94(3): 476-481. https://doi.org/10.1378/chest.94.3.476

[6] Mergu, N., Kim, H., Heo, G., Son, Y.A. (2020). Fabrication and topochemically controlled diacetylene-based polymer and its colorimetric application toward HCl detection. Dyes and Pigments, 174: 108061. https://doi.org/10.1016/j.dyepig.2019.108061

[7] Dien, V.K., Li, W.B., Lin, K.I., Han, N.T., Lin, M.F. (2022). Electronic and optical properties of graphene, silicene, germanene, and their semi-hydrogenated systems. RSC Advances, 12(54): 34851-34865. https://doi.org/10.1039/D2RA06722F

[8] Habeeb, M.A., Jappor, H.R., Al-Nesrawy, S.H.H. (2016). Adsorption of CO and CO2 molecules on nitrogen-doped armchair silicene/graphene nanoribbons as a gas sensor. International Journal of ChemTech Research, 9(7): 378-386. https://cdnx.uobabylon.edu.iq/research/zw4hls6V0m3XBSSNrfpw.pdf

[9] Khudair, S., Jappor, H. (2020). Adsorption of gas molecules on graphene doped with mono and dual boron as highly sensitive sensors and catalysts. Journal of Nanostructures, 10(2): 217-229. https://doi.org/10.22052/JNS.2020.02.003

[10] Nguyen, D.K., Hoang, D.Q., Hoat, D.M. (2022). Exploring a silicene monolayer as a promising sensor platform to detect and capture NO and CO gas. RSC Advances, 12(16): 9828-9835. https://doi.org/10.1039/D2RA00442A

[11] Schedin, F., Geim, A.K., Morozov, S.V., Hill, E.W., Blake, P., Katsnelson, M.I., Novoselov, K.S. (2007). Detection of individual gas molecules adsorbed on graphene. Nature Materials, 6(9): 652-655. https://doi.org/10.1038/nmat1967

[12] Zhang, T., Sun, H., Wang, F., Zhang, W., Tang, S., Ma, J., Gong, H., Zhang, J. (2017). Adsorption of phosgene molecule on the transition metal-doped graphene: First principles calculations. Applied Surface Science, 425: 340–350. https://doi.org/10.1016/j.apsusc.2017.06.229

[13] Zhang, Z., Liang, B., Chi, Y., Jiang, Y., Song, J., Guo, Y. (2021). Adsorption mechanism of SO2 on vacancy-defected graphene and Ti doped graphene: A DFT study. Superlattices and Microstructures, 159: 107036. https://doi.org/10.1016/j.spmi.2021.107036

[14] Liang, X.Y., Ding, N., Ng, S.P., Wu, C.M.L. (2017). Adsorption of gas molecules on Ga-doped graphene and effect of applied electric field: A DFT study. Applied Surface Science, 411: 11-17. https://doi.org/10.1016/j.apsusc.2017.03.178

[15] Deji, R., Jyoti, R., Choudhary, B.C., Singh, R., Sharma, R.K. (2021). Enhanced sensitivity of graphene nanoribbon gas sensor for detection of oxides of nitrogen using boron and phosphorus co-doped system: A first principles study. Sensors and Actuators A: Physical, 331: 112897. https://doi.org/10.1016/j.sna.2021.112897

[16] Feng, J., Liu, Y., Wang, H., Zhao, J., Cai, Q., Wang, X. (2014). Gas adsorption on silicene: A theoretical study. Computational Materials Science, 87: 218-226. https://doi.org/10.1016/j.commatsci.2014.02.025

[17] Hu, W., Xia, N., Wu, X., Li, Z., Yang, J. (2014). Silicene as a highly sensitive molecule sensor for NH3, NO and NO2. Physical Chemistry Chemical Physics, 16(15): 6957-6962.

[18] Frisch, M., Trucks, G., Schlegel, H.B., Scuseria, G., Robb, M., Cheeseman, J., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. (2009). Gaussian 09, Revision a. 02, 200, gaussian. Inc., Wallingford, CT, 271.

[19] Peng, X., Liu, D., Zhao, F., Tang, C. (2022). Gas sensing properties of Mg-doped graphene for H2S, SO2, SOF2, and SO2F2 based on DFT. International Journal of Quantum Chemistry, 122(22): e26989. https://doi.org/10.1002/qua.26989

[20] Naghavi, S.S. (2010). Theoretical study of correlated systems using hybrid functionals. Doctoral dissertation, Mainz, Univ., Diss. http://doi.org/10.25358/openscience-3284

[21] Riahi, S., Eynollahi, S., Ganjali, M.R. (2009). Calculation of standard electrode potential and study of solvent effect on electronic parameters of anthraquinone-1-carboxylic acid. International Journal of Electrochemical Science, 4(8): 1128-1137. https://doi.org/10.1016/S1452-3981(23)15212-6

[22] Babu, N.S. (2021). Donor− acceptor− donor (DAD) structural monomers as donor materials in polymer solar cells: A DFT/TDDFT approach. Designed Monomers and Polymers, 24(1): 330-342. https://doi.org/10.1080/15685551.2021.1997178