JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

DFT study of nitrogen-doped armchair Graphenenanoribbons for sensing dimethyl disulphide: Bulk and Electronic Properties

Harmandar Kaur[1], Sukhdeep Kaur[2], Rupendeep Kaur[2], and Deep Kamal Kaur Randhawa[1]
[1] Department of Engineering and Technology, GNDU Regional Campus, Jalandhar,India
{harmandar.ecejal,rupendeep.elec, sukhdeep.elec}@gndu.ac.in, [2] Department of Electronics Technology, GNDU, Amritsar, India

Abstract

Sulfur derivatives such as dimethyl disulfide (DMDS), a key semiochemical, play a significant role in plant growth by enhancing enzyme activity, nitrogen metabolism, and protein synthesis. Multiple studies have identified DMDS as an important bio-fertilizer that supports the development of various plant species. Monitoring sulfur-based volatile organic compounds (VOCs) like DMDS in agricultural environments is crucial, as it allows for more efficient and eco-friendly nutrient management practices. The availability of DMDS can directly influence the vitality and longevity of plant species.

In this study, we investigate the adsorption behavior of the DMDS molecule on a nitrogen-doped armchair graphenenanoribbon (AGNR) using density functional theory (DFT). A first-principles DFT analysis is carried out on a monoatomic nitrogen-doped AGNR to detect the interaction with DMDS and evaluate its potential as a sensor for plant-related VOCs. The analysis of bulk, electronic, and transport properties indicates the suitability of the doped nanoribbon for sensing applications. The results confirm the occurrence of an adsorption process, and the electronic characterization reveals that the DMDS-adsorbed nitrogen-doped AGNR exhibits n-type semiconducting behavior, highlighting its potential for VOC detection in agricultural settings.

Keywords: adsorption,DFT,armchair graphenenanoribbon, sensing,plant VOC

1 Introduction

Recent studies have highlighted the crucial role of semiochemicals in facilitating both intra- and inter-kingdom interactions among plants. These volatile organic compounds (VOCs), which are small and aromatic, influence plant behavior and can either stimulate or inhibit the growth of neighboring species. Acting as primary agents of plant communication, these molecules influence phenotypic plasticity and support key ecological functions such as growth regulation, tolerance to abiotic stress, disease resistance, and defense against herbivores and pathogens.VOCs serve as long-distance chemical messengers capable of diffusing through the air to influence the behavior of nearby plants or microbial species. In the plant kingdom, they function not only as signaling molecules but also as fumigants that activate plant defense systems. These VOCs are often emitted by plant growth-promoting rhizobacteria (PGPR), which act as symbionts, enhancing crop yield, weight, stress tolerance, and disease resistance. Their potential applications in agriculture are increasingly recognized [1]. A notable example is dimethyl disulfide (DMDS), a sulfur-based VOC produced by *Pantoeaagglomerans*, which plays a pivotal role in maintaining rhizospheric health by improving sulfur nutrition [2].

Given this context, it is evident that VOC-based chemical signaling is a natural mechanism plants use to regulate growth and cope with stress [3]. In this study, we focus on the nanoscale detection of DMDS—a key semiochemical involved in these vital plant processes. The aim is to enable the development of a nanosensor that could detect DMDS levels and facilitate external supplementation in case of deficiency, potentially through an advanced olfactometer system [4].

Graphene, the first two-dimensional nanomaterial discovered, has led to the exploration of numerous other 2D materials due to its exceptional properties [5]. These properties can be tuned through various techniques [6]. Graphenenanoribbons (GNRs), which are narrow strips derived from monolayer graphene, exhibit remarkable characteristics such as high carrier mobility, tunable bandgaps, semiconducting behavior, and strong mechanical strength [7-10]. These attributes make GNRs highly promising candidates for sensing applications. Existing literature reports the successful use of GNRs in detecting a variety of gases and VOC biomarkers [11-13].

Specifically, GNRs have shown excellent potential for building ultra-sensitive chemical sensors due to their high sensitivity, selectivity, quick response and recovery times, compact size, and low power consumption [14-17]. In this context, our work represents the first known effort to employ doped armchair graphenenanoribbons (AGNRs) for nanosensing the plant growth-promoting molecule DMDS using density functional theory (DFT). The AGNRs are doped with nitrogen to enhance their sensing capabilities. Figure 1 illustrates the adsorption of the DMDS molecule on nitrogen-doped AGNR.

This research contributes to the field of smart agriculture by providing a framework for improved field practices through the detection and management of plant semiochemicals. The rest of this paper is structured as follows: Section 2 outlines the computational methods used to analyze the bulk and electronic properties of the DMDS-adsorbed AGNR complex, while Section 3 presents the results and discussion related to its nanosensing application, followed by the conclusion.

2 Computational Method

The sensing capabilities of nitrogen-doped armchair graphenenanoribbons (AGNRs) for detecting the plant growth-promoting compound dimethyl disulfide (DMDS) were investigated using the Virtual NanoLabAtomistix Toolkit [18]. This study involves an in-depth analysis of the bulk and electronic properties of the DMDS-AGNR complex to evaluate its potential as a sensor. First-principles calculations were employed using density functional theory (DFT) in conjunction with the non-equilibrium Green's function (NEGF) approach.

The exchange-correlation effects were treated using the Perdew-Burke-Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) [19], combined with a double-zeta polarized (DZP) basis set [20]. Nitrogen doping in the AGNR was implemented via single-atom substitution [21].

All calculations were carried out on fully relaxed geometries, ensuring structural optimization with self-consistent field (SCF) convergence. A density mesh cutoff of 75 Hartree and an electronic temperature of 300 K were used. The force and stress tolerances were set to 0.05 eV/Å and 0.05 eV/Å^3, respectively. Prior to analyzing the electronic and transport properties, the systems underwent complete geometric relaxation.For k-point sampling, a Monkhorst-Pack grid of 1×1×12 was used for geometry optimization, while a denser grid of 1×1×100 was applied for electronic transport calculations [22].

3 Results and Discussion

3.1 Geometric Structure Analysis

Armchair graphenenanoribbons (AGNRs) used in this study are constructed with six atoms across their width (w = 6). To reduce reactivity at the edges, they are passivated with hydrogen atoms, as the edges of graphene are typically more chemically active than the surfaces. Literature has shown that the sensing capabilities of graphene-based materials can be significantly altered through selective doping or the introduction of structural defects [17]. Doping is commonly employed to enhance the electronic and sensing properties of graphenenanoribbons (GNRs) [21,23].

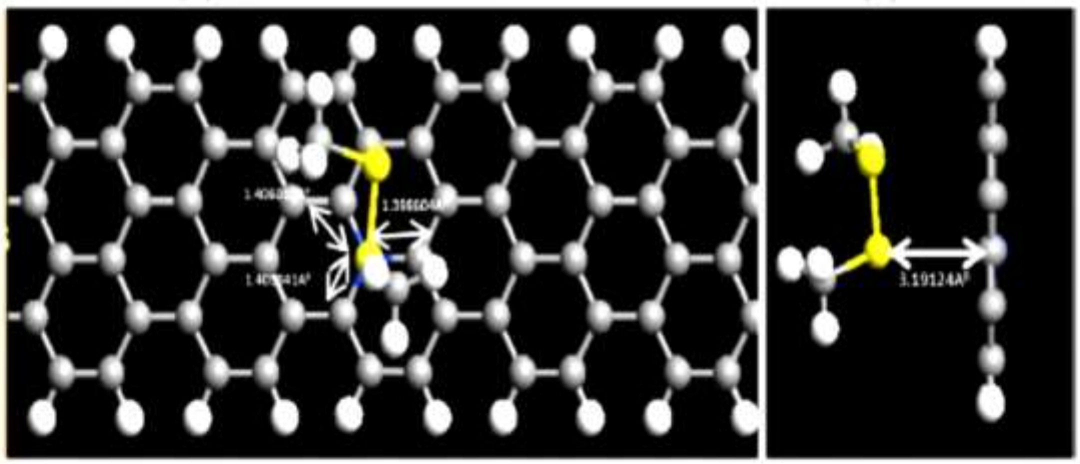

Fig.1. Optimized AGNR with DMDS having (a) nitrogen-doped top view (b) nitrogen-doped side view

For nitrogen-doped AGNR with DMDS, both C–N and C–C bond lengths begin at 1.42 Å. Upon optimization, the C–N bond reduces to 1.36 Å, while the C–C bond shortens slightly to 1.40 Å, as shown in Figures 2(a) and 2(b).

The changes observed in the bulk properties arise due to the interaction between the adsorbate (DMDS) and the adsorbent (doped AGNR) during the adsorption process. These structural and electronic variations indicate that the presence of the adsorbed molecule significantly alters the properties of the doped nanoribbon complex. Notably, the influence of VOC molecules on electronic properties is more pronounced in nanoribbons with a finite bandgap compared to those without. This characteristic is crucial for nanosensing applications. Therefore, the adsorption behavior and its impact on both bulk and electronic properties are analyzed using the relaxed structures obtained.

3.2 Adsorption of DMDS on Doped Nitrogen AGNR

To investigate the adsorption behavior of dimethyl disulfide (DMDS) on various nitrogen-doped armchair graphenenanoribbon (AGNR) geometries, a first-principles approach based on density functional theory (DFT) is employed. The analysis is conducted on optimized complex structures to evaluate the effect of DMDS adsorption on the bulk properties of the doped AGNR. The adsorption energy is calculated using the following formula:

$$E_{ad}= E_{D-AGNR+DMDS} - E_{D-AGNR} - E_{DMDS} \quad (1)$$

where $E_{D\text{-}AGNR+DMDS}$, $E_{D\text{-}AGNR}$ and E_{DMDS} denote the total energies of the doped (nitrogen) AGNR molecule complex, doped (nitrogen) AGNR, and the isolated DMDS VOC molecule, respectively. A comprehensive analysis of the adsorption behavior between the DMDS molecule and nitrogen-doped AGNR involves calculating key parameters, including the relaxed distance after structural optimization D (in Å), the energy gap Eg, and the adsorption energy Ead . Table 1 summarizes the computed values of these parameters for DMDS complexes with AGNR doped with nitrogen.

Table 1. The calculated band gap energy (Eg), the adsorption energy (Eads), the interaction distance of DMDS molecule with doped nitrogen AGNR for relaxed structure

Configuration	$E_g(eV)$	$E_{ad}(eV)$	D(Å)
Nitrogen-AGNR	0.823	−0.308	3.191

To study the adsorption behavior of dimethyl disulfide (DMDS) on nitrogen-doped AGNR, the DMDS molecule was initially positioned at a distance from the doped AGNR structure prior to optimization. Following structural relaxation, the optimized distance between the DMDS molecule and the nitrogen-doped AGNR was found to be 2.95241 Å, as shown in Fig. 2. The corresponding adsorption energy was calculated to be −0.34467 eV, confirming that adsorption occurs.
For the nitrogen-doped AGNR, the optimized DMDS distance was found to be 3.19 Å, as illustrated in Fig. 2, with an adsorption energy of −1.31 eV. This negative value confirms the occurrence of adsorption, suggesting the suitability of this complex for further electronic analysis aimed at VOC detection.

3.3 Band Structure Analysis

The band gap is calculated to assess the changes in the electronic properties of nitrogen-doped AGNRs before and after adsorption of dimethyl disulfide (DMDS). The band structure illustrates the energy levels of available electronic states along specific paths in reciprocal space, highlighting the band gaps—or forbidden energy regions—within the material. Table 1 summarizes the band gap values and binding distances for nitrogen-doped AGNRs following DMDS adsorption.

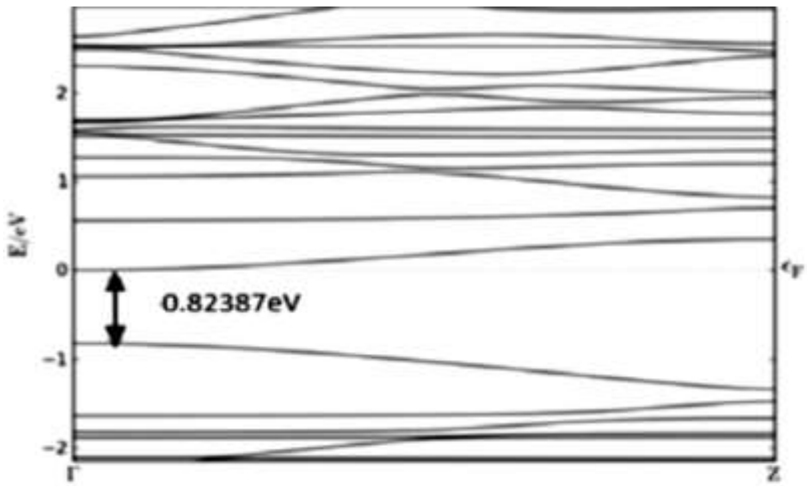

Fig. 2. Band structure of nitrogen doped AGNR adsorbed dimethyl disulphide

For nitrogen-doped AGNR, the band gap is 0.823 eV post-adsorption (Fig. 2). The band structure analysis indicates notable modifications in the electronic properties of the doped AGNRs upon interaction with DMDS.The nitrogen doped AGNR with dimethyl disulphide complex shows n-type semiconductor behaviour. This is a useful finding that can be utilised in creating various electronic devices at nanoscale level.

3.4 Density of States Analysis

To investigate the interaction of dimethyl disulfide (DMDS) with nitrogen-doped AGNRs, the density of states (DOS) of the resulting complex is analyzed. The DOS plot illustrates the energetically favorable electronic states that can be occupied, representing the number of available electron or hole states per unit volume at a specific energy level. These plots provide insight into carrier concentrations and the energy distribution of charge carriers.

Figure 3 presents the DOS profiles for nitrogen-doped AGNR following DMDS adsorption. DOS of nitrogen-doped AGNR complex reveals an increased number of peaks with higher DOS values in both the valence and conduction bands after DMDS adsorption, indicating enhanced electronic activity.

The DOS result is in agreement with the band structure analyses shown in Figure 3. For nitrogen-doped AGNR, the DOS plot shows significant variation within the conduction band (0–2 eV), with particularly high DOS values between 1 and 2 eV. Additionally, a gap appears in the valence band from −1 eV to −0.2 eV, indicating a region devoid of electronic states, as illustrated in Fig. 3.

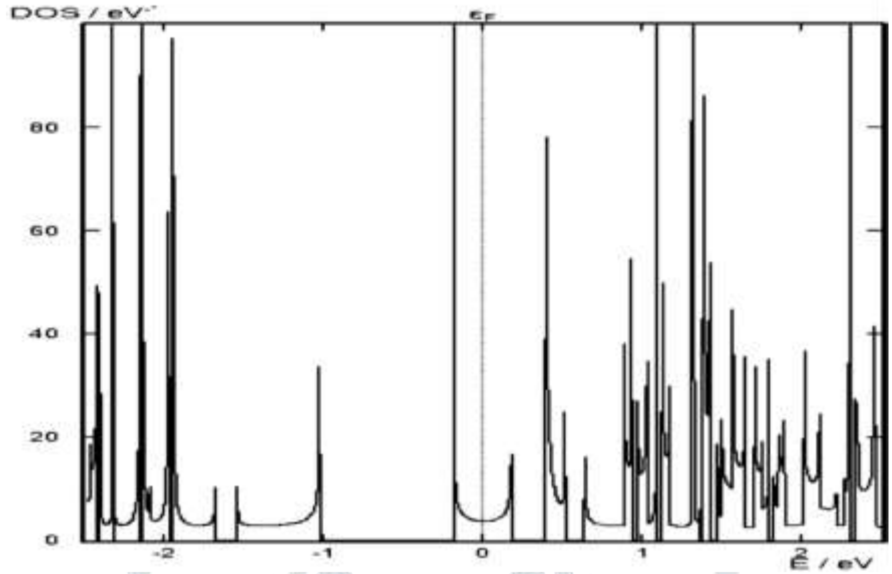

Fig.3. DOS of nitrogen doped AGNR with dimethyl disulphide complex

3.5 Transmission Spectrum Analysis

The transmission spectrum represents the sum of available transport modes from the band structure at each energy level. The transmission spectra for nitrogen-doped AGNR interacting with dimethyl disulfide (DMDS) are shown in Fig.4. These spectra reflect the combined effects of the electronic band structure and the density of states, as previously illustrated in Figures 2 and 3, respectively.

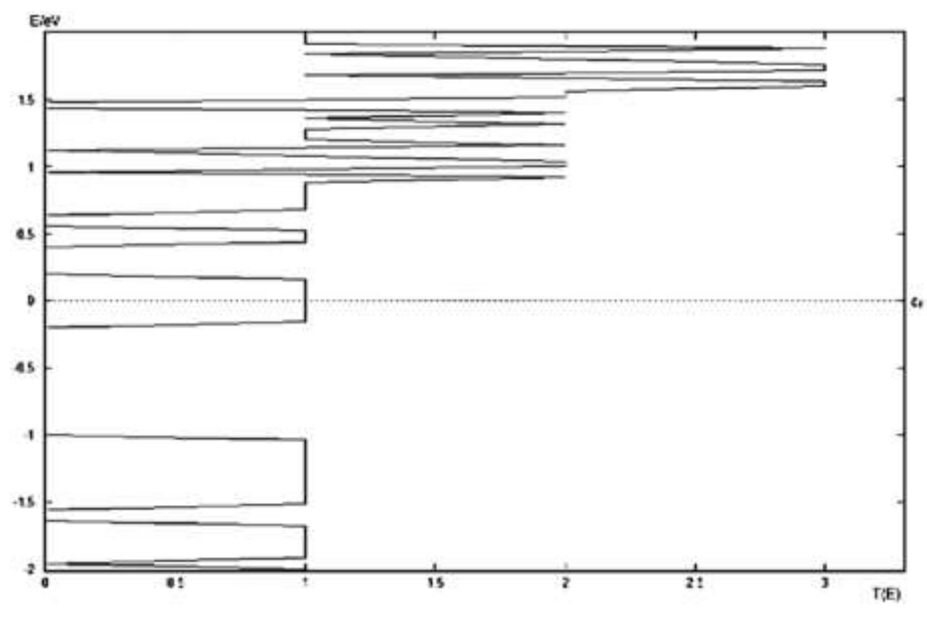

Fig.4. Transmission spectrum of nitrogen doped AGNR adsorbed dimethyl disulphide complex.

For the nitrogen-doped AGNR–DMDS complex, the zero transmission window spans from 0 to –1 eV, as seen in Figure4. These results are consistent with earlier band structure and DOS analyses and further confirm the semiconducting behavior of the complexes: nitrogen-doped AGNR shows n-type behavior.

4 Conclusion

Dimethyl disulfide (DMDS) plays a crucial role in promoting plant growth and enhancing resistance to diseases. However, reduced or depleted levels of this essential volatile organic compound (VOC) can hinder plant development. In such cases, external supplementation—for example, through fertilizers—may be necessary. To address the need for monitoring DMDS levels, this study investigates the sensing capabilities of doped armchair graphenenanoribbons (AGNRs), using nitrogen as dopants. The analysis is conducted by examining the bulk and electronic properties of the relaxed AGNR–DMDS complexes.

The bulk property analysis includes calculations of the relaxed binding distance, adsorption energy, and energy bandgap. The obtained values confirm the occurrence of adsorption and indicate strong interactions between DMDS and the doped AGNRs. Electronic properties are further evaluated through band structure analysis, density of states (DOS), and transmission spectrum analysis.

The results reveal that nitrogen-doped AGNRs display n-type semiconducting characteristics. These findings highlight the potential of doped AGNRs as effective nanoscale sensors for detecting dimethyl disulfide. Moreover, the results can contribute to the development of advanced nanoelectronic devices for smart agriculture and environmental monitoring applications.

References

1. Vasseur-Coronado, M., et al.: Ecological role of volatile organic compounds emitted by pantoeaagglomerans as interspecies and interkingdom signals. Microorganisms 9(6), 1186 (2021)
2. Aziz,M., et al.: Augmenting sulfur metabolism and herbivore defense in Arabidopsis by bacterial volatile signaling. Front. Plant Sci. 7, 458 (2016)
3. Meldau, D.G., Meldau, S., Hoang, L.H., Underberg, S., Wünsche, H., Baldwin, I.T.: Dimethyl disulfide produced by the naturally associated bacterium bacillus sp b55 promotes nicotianaattenuata growth by enhancing sulfur nutrition. Plant Cell 25(7), 2731–2747 (2013)
4. Farag El-Shafie, H.A., Faleiro, J.R.: Semiochemicals and their potential use in pest management. Biological control of pest and vector insects, pp. 10–5772 (2017)
5. Novoselov, K.S., et al.: Electric field effect in atomically thin carbon films. Science 306(5696), 666–669 (2004)
6. Nayak, L., Rahaman, M., Giri, R.: Surface modification/functionalization of carbon materials by different techniques: an overview. Carbon-containing polymer composites, pp. 65–98 (2019)
7. Seitsonen, A.P., Marco Saitta, A., Wassmann, T., Lazzeri, M., Mauri, F.: Structure and stability of graphenenanoribbons in oxygen, carbon dioxide, water, and ammonia. Phys. Rev. B 82(11), 115425 (2010)
8. Ge, H., Wang, G., Liao, Y.: Theoretical investigation on armchair grapheme nanoribbons with oxygen-terminated edges. arXiv preprint arXiv:1411.1526 (2014)
9. Kostya S Novoselov, K.S., et al.: Two-dimensional gas of massless dirac fermions in graphene. Nature 438(7065), 197–200 (2005)
10. Zhang, Y., Tan, Y.-W., Stormer, H.L., Kim, P.: Experimental observation of the quantum hall effect and berry's phase in graphene. Nature 438(7065), 201–204 (2005)
11. Leenaerts, O., Partoens, B., Peeters, F.M.: Adsorption of h 2 o, n h 3, co, n o 2, and no on graphene: a first-principles study. Phys. Rev. B 77(12), 125416 (2008)
12. Lin, X., Ni, J., Fang, C.: Adsorption capacity of h2o, nh3, co, and no2 on the pristine graphene. J. Appl. Phys. 113(3), 034306 (2013)
13. Zhang, Z., et al.: Study on adsorption and desorption of ammonia on grapheneNanoscale Res. Lett. 10(1), 1–8 (2015)
14. Tarun, T., Singh, P., Kaur, H., Walia, G.K., Randhawa, D.K.K., Choudhary, B.C.: Defective gaasnanoribbon-based biosensor for lung cancer biomarkers: a DFT study. J. Mol. Modeling 27(9), 270 (2021)
15. Walia, G.K., Randhawa, D.K.K., Singh, K., Singh, P., Kaur, H.: detection of nitrous oxide gas using silicenenanoribbons. Intelligent Circuits and Systems, p.147 (2021)
16. Kaur, H., Randhawa, D.K.K., Khosla, M., Sarin, R.K.: First principles study of sarin nerve gas adsorption on graphenenanoribbon with single molecule resolution. Mater. Today Proc. 28, 1985–1989 (2020)
17. Aghaei, S.M., Monshi, M.M., Calizo, I.: Highly sensitive gas sensors based on silicenenanoribbons. arXiv preprint arXiv:1608.07508 (2016)
18. Quantum wise, copenhagen, denmark: Atomistix toolkit version2015.0 (2016). https://www.quantumwise.com. Accessed Jan-June 2019
19. Perdew, J.P., Burke, K., Wang, Y.: Erratum: generalized gradient approximation for the exchange-correlation hole of a many-electron system [phys. rev. b 54, 16 533 (1996)]. Phys. Rev. B 57(23), 14999 (1998)
20. Abadir, G.B., Walus, K., Pulfrey, D.L.: Basis-set choice for DFT/NEGF simulations of carbon nanotubes. J. Comput. Electron. 8, 1–9 (2009)
21. Deji, R., Choudhary, B.C., Sharma, R.K.: Novel hydrogen cyanide gas sensor: a simulation study of graphenenanoribbon doped with boron and phosphorus. Physica E: Low-dimensional Syst. Nanostructures 134, 114844 (2021)
22. Monkhorst, H.J., Pack, J.D.: Special points for brillouin-zone integrations. Phys.Rev. B 13(12), 5188 (1976)
23. Seenithurai, S., Pandyan, R.K., Kumar, S.V., Manickam, M.: Electronic properties of boron and nitrogen doped graphene. Nano Hybrids 5, 65–83 (2013)