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ORIGINAL RESEARCH ARTICLE

Electronic properties for interaction of explosive organic molecule (RDX) with pristine and Pd-Doped nanoflakes structures: A density functional theory study

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ABSTRACT

Graphene Nanoflakes (GNF) has used widely in the nanoelectronic and materials science field due to due to their mechanical and physical properties. The combination of the Density Functional Theory (DFT) computational method with the B3LYP functional and the 6-31G basis set, executed via the Gaussian 09 program, was used in this study to investigate the nanosensor's role in detecting the explosive organic molecule (RDX). This was achieved by determining the change in the band gap energy of the sensor, which influences its conductivity. The graphene sensor was modified by the addition of a substitutional palladium (Pd) atom. The results demonstrate an enhancement in device performance, evidenced by the change in the energy gap for all molecules studied. The better addition for the RDX sensor was found Pd atom due to improved electronic properties such as optimized structure, dipole moment, a decrease in the HOMO-LUMO energy gap, total energy, and density of states.

Keywords: DFT; nanosensor; nanoflakes; explosive; organic

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1. Introduction

Graphene is a universal material have honeycomb lattice structure with sp2-hybridized carbon atoms and two-dimensional monolayer (**Figure 1**)[1-4]. Graphene Nanoflakes (GNFs) are polycyclic aromatic hydrocarbon (PAH) molecules and represent the smallest fragment of graphene, with the chemical formula $C_{24}H_{12}$, comprising seven perifused benzene rings[5-8]. Therefore, GNFs are considered a model system for graphite. The structural characteristics of Polycyclic Aromatic Hydrocarbons (PAHs) are simply that they are carbon-hydrogen molecules made of multiple benzene rings fused together, with hydrogen atoms attached to their outer edges of these rings[9]. It is well known that Nanoflakes are a basic component of electronic materials[10].

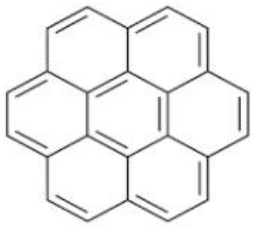

Figure 1. Graphene Nanoflakes (GNF) structure[11].

A sensor characterized by one of the following properties is labeled as a nanosensor: the sensor's size is in the nanoscale, or the sensor's sensitivity is in the nanoscale[12]. Since 2004, the technology has developed rapidly due to the realization that nanosensors are instrumental for monitoring physical and chemical phenomena[13-15]. The utilization of graphene in nanosensor systems was first reported in 2011[16]. Although these carbon materials still face crucial challenges in fabrication and optimization, continued progress in this field may lead to sensors with superior sensitivity[15,17].

Aromatic explosive molecules can be potentially detected using Graphene materials, which is important for safety applications[18,19]. Our studies focused upon the more common nitro-based explosive, such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). RDX is a synthetic product that does not occur naturally but is produced synthetically. It is a white, crystalline, explosive substance. It is often mixed with other explosives for military and civilian applications such as fireworks, demolition blocks, and rodenticide. RDX is commonly found at grenade and missile ranges, and munitions testing sites[20,21]. The adsorption of small organic molecules onto graphene is weak, but it can be enhanced by decorating or doping with different heteroatoms[3,22]. Improved electronic properties, conductivity, mobility, and chemical reactivity of the graphene surface are achieved by doping its surface with heteroatoms or transition metals[4].

This study involves an investigation of the detection of Explosive Organic Molecule (RDX), optimized structure, dipole moment, the HOMO-LUMO energy gap (highest- lowest unoccupied molecular orbital), total energy, and density of states. These analyses are conducted using first-principles Density Functional Theory (DFT) calculations.

2. Computational methodology

The Gaussian 09 program package was used for the first-principles calculations of electronic properties and structural optimization, which were carried out using DFT[23-25]. All calculations in this study were performed using the B3LYP functional (Becke's three-parameter functional and Lee-Yang-Parr functional) with the 6-31G basis set[26]. All electronic properties such as HOMO-LUMO orbital distribution, the energy gap ($E_{gap} = E_{LUMO} - E_{HOMO}$), the total energy ($E_{total}$),the density of states (DOSs), and dipole moment (μ) of structures studied have been calculated to find the change in their electronic properties upon adsorption of organic molecules. Relation between conductivity and E_{gap}could be presented by[27,28]:

$$\sigma \alpha \exp\left(-\frac{E_{gap}}{KT}\right)$$

Where k is the Boltzmann's constant (1.380649×10^{-23} J/k) and σ is the electrical conductivity. To obtain a higher electrical conductivity, energy gap (E_{gap}) at a given temperature must be smaller. Thus, the energy gap of the sensor [E_{gap}(GNF)], and the energy gap of a molecule RDX adsorbed on the sensor [E_{gap}(Molecule/GNF)] are studied. Moreover, the total energy (E_{total}) is an actual parameter for estimating the stability of materials structures. So, an increase in (E_{total})indicates a more stable and less reactive system.

3. Results and discussion

In this discussion, we focus on the important properties of organic molecule sensors. Graphene nanoflakes (GNFs) are not effective sensors for many organic molecules, such as RDX. Therefore, we study the interaction of organic molecules on the surface of doped GNFs. By substituting a carbon atom with a palladium (Pd) atom, we aim to improve various properties of GNF sensors. The calculated total energy values of the GNF-doped sensor are significantly higher compared to those of pristine GNF. An increase in total energy is an important parameter for estimating the stability of the structures. **Figure 2** shows the

geometry optimizations of the sensors and the organic molecule (RDX), completed using DFT with the B3LYP functional and the 6-31G basis set.

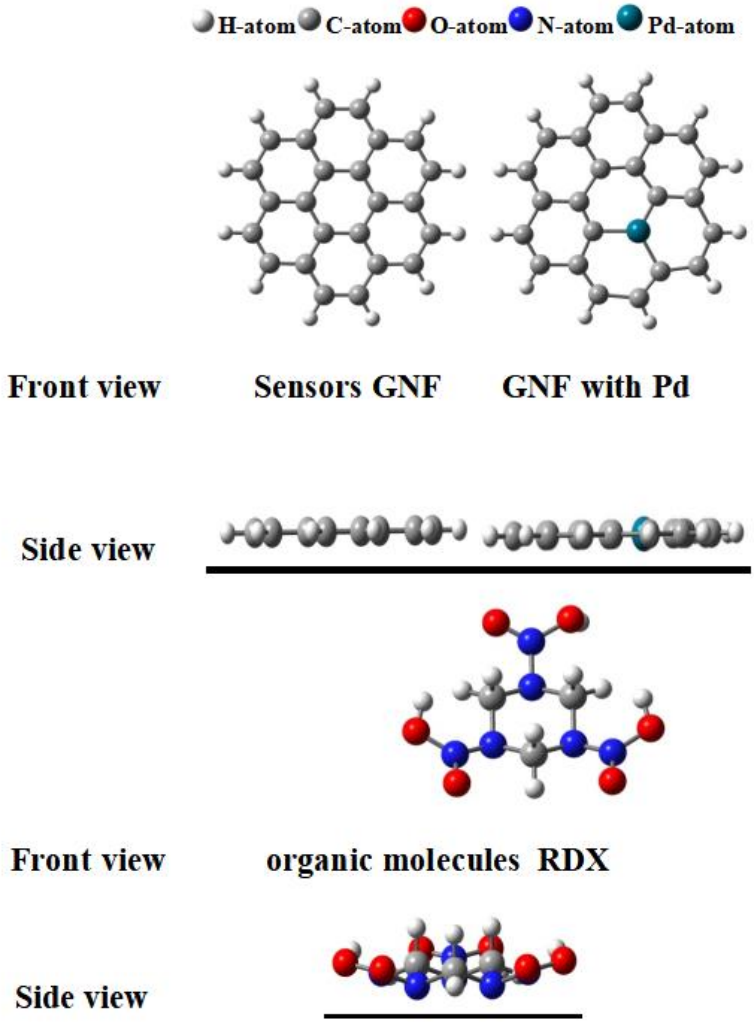

Figure 2. Optimized geometry of sensors and organic molecules (RDX) front view and side view, respectively, at B3LYP functional / 6-31G basis set.

The DFT calculations of the nanosensors show different energy gap values (E_{gap}). The energy gap decreases in the GNF-doped sensor compared to the pristine GNF, indicating an increase in the sensor's sensitivity. When the doped sensor interacts with the organic molecule (RDX), the energy gap further decreases compared to the interaction between the pristine sensor and the molecule.

Generally, the energy gap (ΔE) follows the sequence: GNF with Pd + RDX < GNF with Pd< GNF + RDX < GNF. These results indicate that the GNF-doped sensor is effective for detecting RDX, and DFT is a suitable approximation method for evaluating sensing performance.

Figure 3 represents the optimized geometries of the explosive molecule interacting with the sensor devices (obtained using DFT with the B3LYP functional and the 6-31G basis set). The HOMO and LUMO localized on RDX molecule and on the sensors for all structures under study is shown in **Figure 4** and results are listed in **Table 1.**

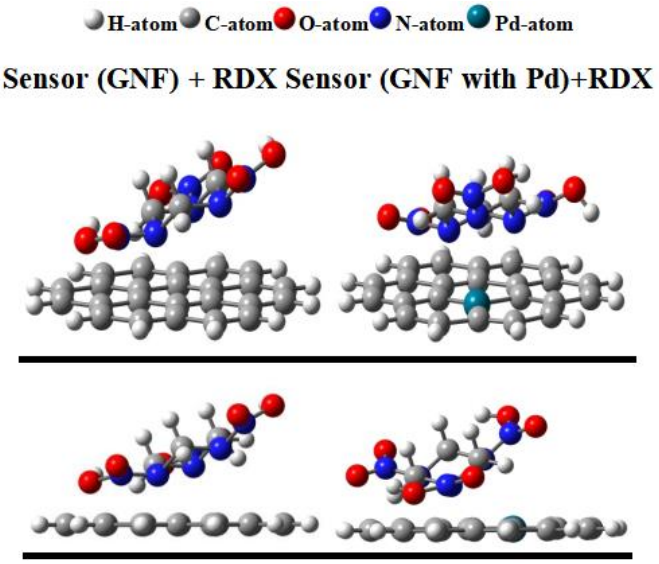

Figure 3. Optimized geometry of sensors with organic molecules (RDX) at B3LYP functional / 6-31G basis set.

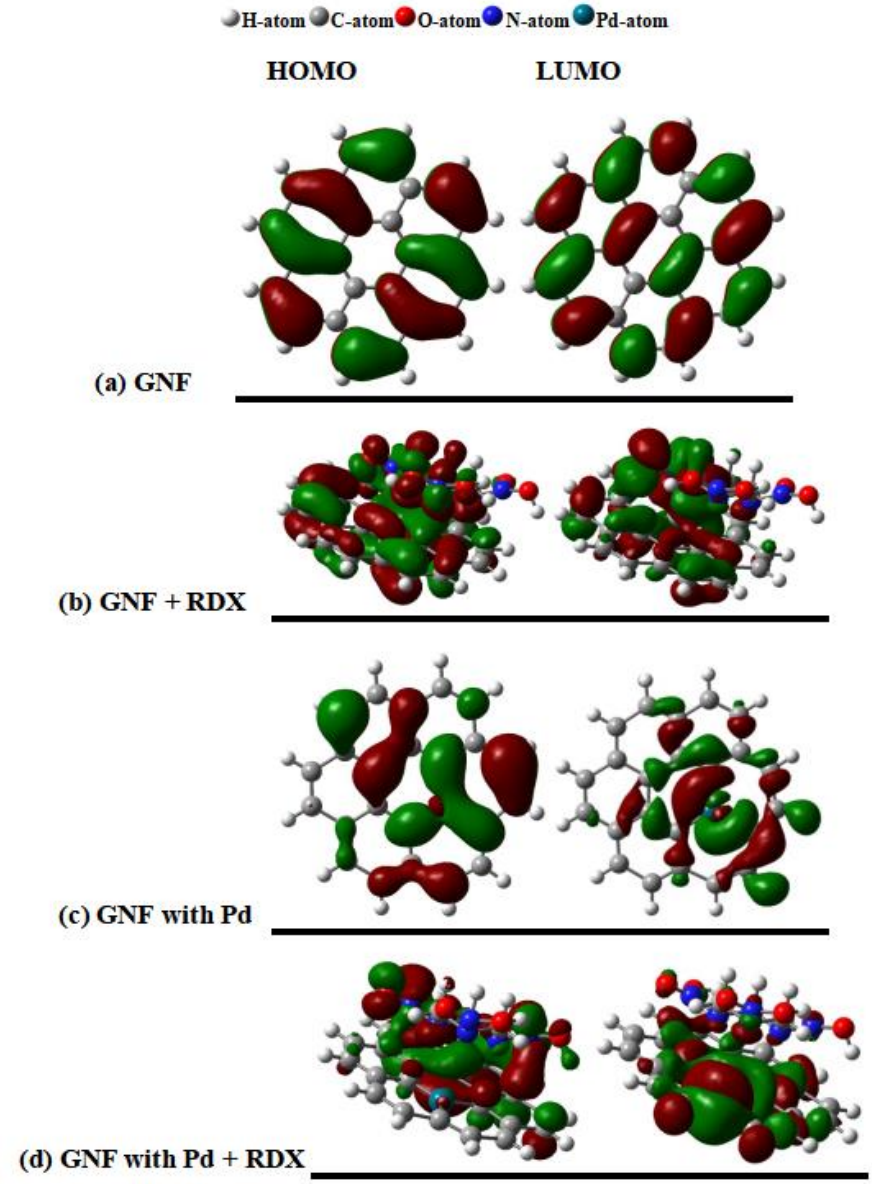

Figure 4. The localization of HOMO (left) and LUMO (right) for all structures under study.

Table 1. The structure name, the energy gap ($E_{gap} = E_{LUMO} - E_{HOMO}$), the dipole moment (μ), the total energy (E_{total}),and HOMO, LUMO energies of investigated sensors.

Structure	E_{gap} **(eV)**	μ **(Debye)**	E_{total} **(eV)**	E_{HOMO} **(eV)**	E_{LUMO} **(eV)**
RDX	…	6.760	- 24323.6	…	…
GNF	4.132	0	- 24946.3	- 5.614	- 1.481
GNF+ RDX	1.684	6.885	- 49251.8	- 4.001	- 2.316
GNF with Pd	1.578	1.274	- 157709.0	- 4.510	- 2.931
GNF with Pd + RDX	**1.266**	7.175	**- 182010.4**	- 3.569	- 2.303

Figure 5 shows the DOS the distance between green and red lines gives the E_{gap}. The height of the density of states in both HOMO and LUMO are the same approximately and so this refers to the possibility of the electronic transition between them so one expect that the electronic transition may occurs between many states in HOMO and LUMO but with different probability.

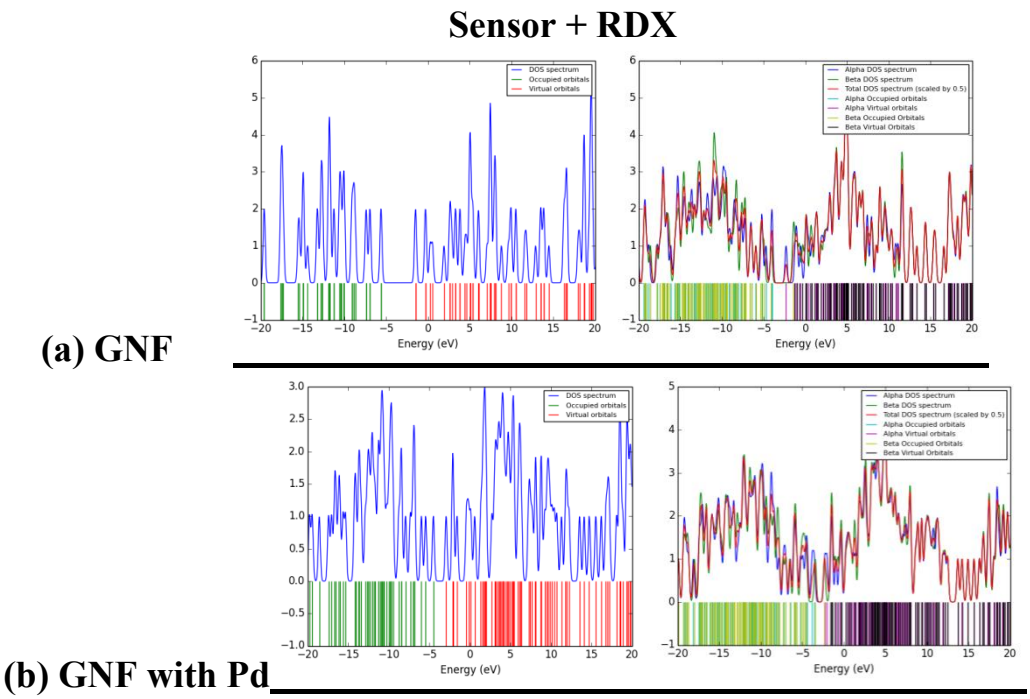

Figure 5. Calculated density of states (DOS) for all structures under study.

4. Conclusion

This study utilized density functional theory (DFT) calculations to examine how the adsorption of the organic molecule RDX impacts the electronic properties of both pristine and modified GNF structures. The results demonstrate that apparent sensitivity toward the organic molecule (RDX). Depending on the (E_{gap}) value, the ranking of the sensors is (GNF with Pd + RDX), (GNF + RDX) for RDX molecule. The Pd enhanced the sensing for RDX detecting. The total energy (E_{total}) values calculated of GNF-doped are higher compared to those of pristine GNF, this refers to high stable. The possibility of electron transfer across the energy gap is shown in the density of states (DOS). This study expect that its results will prompt further experimental research into the synthesis and modification of graphene Nanoflakes, aiming to achieve many diverse applications.

Declaration of competing interest

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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References

1. Ali, M. D., Starczewska, A., Das, T. K., &Jesionek, M. (2025). Exploration of Sp-Sp2 Carbon Networks: Advances in Graphyne Research and Its Role in Next-Generation Technologies. International Journal of Molecular Sciences, 26(11), 5140.
2. Abbas, R. F., Hassan, M. J., &Rheima, A. M. (2024). A Sustainable Modified Hummers Method for Synthesizing Graphene Oxide Nanosheets. Iraqi Journal of Applied Physics, 20(2A), 317-320.
3. Ray, S. C. (2024). Possible Magnetic Behaviors of 2D-Graphene (: H/N/Si) Materials: A Brief Review. e-Journal of Surface Science and Nanotechnology, 22(4), 296-315.
4. Haider, A., Rasheed, M. F., Abrar, A., Mumtaz, A., Zeb, A., Rehman, M. U., ...& Ashraf, S. (2025). THE CHEMISTRY OF 2D MATERIALS FROM GRAPHENE TO BEYOND. Kashf Journal of Multidisciplinary Research, 2(01), 197-221.
5. Jeong, J., & Lee, W. (2024). Calculation of Electronic Structures of Graphene Nanoflakes by Hückel Molecular Orbital Method: Exploration of the Shape, Size, and Edge Effects. Korean Journal of Materials Research, 34(12), 620-632.
6. Nasir, M. (2024). Exploration of Diradical Graphene Nanoflakes (GNFs) as NLO based Sensors for NOx (Doctoral dissertation, Chemistry Department COMSATS university Islamabad Lahore Campus).
7. Lee, Y. H., Kang, H., Kim, S., Yang, G., Yang, S., Oh, J. H., & Choi, S. (2025). Structural transformation of solid carbons produced from the methane pyrolysis process for turquoise hydrogen production. International Journal of Hydrogen Energy.
8. Kadhem, M., Ajeel, N. B. S., Ajeel, F. N., &Khudhair, A. M. (2024). Investigating the Effects of TiO Impurities on the Electronic Properties of Graphene Nanoflakes Using DFT Method. Sumer Journal for Pure Science.
9. Chen, G., Koide, T., Nakamura, J., &Ariga, K. (2025). Nanoarchitectonics for Pentagon Defects in Carbon: Properties and Catalytic Role in Oxygen Reduction Reaction. Small Methods, 2500069.
10. Soave, R., Cargnoni, F., &Trioni, M. I. (2024). Thermodynamic Stability and Electronic Properties of Graphene Nanoflakes. C, 10(1), 5.
11. Tran-Van, A. F., & Wegner, H. A. (2014). Strategies in organic synthesis for condensed arenes, coronene, and graphene. Polyarenes I, 121-157.
12. Dai, C., Chen, M., Lin, Y., Qi, R., Luo, C., Peng, H., & Lin, H. (2022). High performance gas sensors based on layered cobaltite nanoflakes with moisture resistance. Applied Surface Science, 604, 154487.
13. Dai, C., Chen, M., Lin, Y., Qi, R., Luo, C., Peng, H., & Lin, H. (2022). High performance gas sensors based on layered cobaltite nanoflakes with moisture resistance. Applied Surface Science, 604, 154487.
14. Nasir, M. (2024). Exploration of Diradical Graphene Nanoflakes (GNFs) as NLO based Sensors for NOx (Doctoral dissertation, Chemistry Department COMSATS University Islamabad Lahore Campus).
15. Darwish, M. A., Abd-Elaziem, W., Elsheikh, A., &Zayed, A. A. (2024). Advancements in nanomaterials for nanosensors: a comprehensive review. Nanoscale Advances.
16. Sorkin, V., & Zhang, Y. W. (2011). Graphene-based pressure nano-sensors. Journal of molecular modeling, 17, 2825-2830.
17. Deji, R., Verma, A., Choudhary, B. C., & Sharma, R. K. (2022). New insights into NO adsorption on alkali metal and transition metal doped graphene nanoribbon surface: a DFT approach. Journal of Molecular Graphics and Modelling, 111, 108109.
18. Dhahi, H. A., Ghorbani, S. R., Arabi, H., &Algharagholy, L. A. (2025). Graphene-Based Selective Detection of Explosive Molecules. Journal of Electronic Materials, 54(3), 1653-1663.
19. Abbas, R. F., Hassan, M. J. M., &Rheima, A. M. (2024). Adsorption of fast green dye onto Fe3O4 MNPs and GO/Fe3O4 MNPs synthesized by photo-irradiation method: Isotherms, thermodynamics, kinetics, and reuse studies. Sustainable Chemistry for the Environment, 6, 100104.
20. Chatterjee, S., Deb, U., Datta, S., Walther, C., & Gupta, D. K. (2017). Common explosives (TNT, RDX, HMX) and their fate in the environment: Emphasizing bioremediation. Chemosphere, 184, 438-451.
21. Doshi, M. (2021). Computational Design of Carbon Nanotube Sensors for Gas Phase Explosives Detection. The University of Texas at Austin.
22. Bhattacharyya, S., & Singh, A. K. (2016). Lifshitz transition and modulation of electronic and transport properties of bilayer graphene by sliding and applied normal compressive strain. Carbon, 99, 432-438.

23. Hohenberg, P., & Kohn, W. (1964). Inhomogeneous electron gas. Physical review, 136(3B), B864.
24. Kohn, W., & Sham, L. J. (1965). Self-consistent equations including exchange and correlation effects. Physical review, 140(4A), A1133.
25. Abbas, M., Ali, U., Faizan, M., & Siddique, M. B. A. (2021). Spirofluorene based small molecules as an alternative to traditional non-fullerene acceptors for organic solar cells. Optical and Quantum Electronics, 53(5), 246.
26. Nenadis, N., &Tsimidou, M. Z. (2024). Metrological aspects of a gas-phase DFT/B3LYP quantum-chemical approach to prioritize radical scavenging activity among a group of olive oil phenols. Exploration of Foods and Foodomics, 2(4), 326-338.
27. Mohamed, A., Visco Jr, D. P., Breimaier, K., &Bastidas, D. M. (2025). Effect of Molecular Structure on the B3LYP-Computed HOMO–LUMO Gap: A Structure− Property Relationship Using Atomic Signatures. ACS omega.
28. Moeini, V., &Gazi, A. H. M. (2024). Doped BC2NNTs with gallium: A new sensor to detect the presence of ozone gas in the gaseous environment. Computational and Theoretical Chemistry, 1235, 114578.