DFT Study on Optoelectronic Properties of Graphene Quantum Dots with Various Sulfur Doping Patterns

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ABSTRACT

This study explores the effects of sulfur doping on the electronic and optical properties of Graphene Quantum Dots (GQDs) using Density Functional Theory (DFT). Three sulfur doping configurations are analyzed: substitutional doping (S_g), where sulfur atoms replace carbon atoms in the graphene lattice, edge/terminal doping (S_h), where sulfur is added at the edges or terminals, and thiophene-like doping (S_p), where sulfur is incorporated into five-membered rings at the graphene edges. The results show that sulfur doping reduces the energy gap of GQDs, with values of 1.444 eV for S_g, 1.213 eV for S_h, and 1.487 eV for S_p, indicating enhanced electrical conductivity and electronic reactivity. Optical absorption spectra reveal a redshift in the sulfur-doped GQDs compared to pristine GQDs, with absorption peaks at 858.7 nm for S_g, 1022.2 nm for Sh, and 833.9 nm for S_p, demonstrating their potential for applications in optoelectronic devices such as sensors and photodetectors. These findings highlight the significant impact of sulfur doping on the properties of GQDs, making them promising candidates for use in various nanoelectronic and optoelectronic applications.

Keywords: Graphene Quantum Dots, Sulfur Doping, Density Functional Theory, Band Gap, Optoelectronic Properties.

INTRODUCTION

Graphene Quantum Dots (GQDs) are a special class of the nanomaterials with excellent structural, electronic, optical properties and hence they have drawn immense attention in energy storage, quantum computing, sensors and optoelectronic devices [1-4]. These properties mainly come from the special structure of carbon atom in 0D form and the quantum confining effect and esdge-state transition. These properties strongly impact the electronic structure, and in particular on the band gap, which is a parameter that controls their optical and electronic response [5, 6]. GQDs are therefore extensively investigated for their applications in light-emitting devices, photocatalysis, bioimaging and also in futuristic computing technologies [8 ,7]. However, despite their potential, GQDs still face significant challenges in terms of optimizing their properties for practical applications. The need for precise control over their electrical and optical characteristics remains a major hurdle. Specifically, the ability to tune the band gap, enhance charge transport, and improve optical absorption is critical for maximizing their performance in devices. This has led to considerable research efforts aimed at engineering the electronic structure of GQDs through various doping strategies [9, 10].

Doping is a well-established approach to modifying the electronic properties of semiconducting materials, and it is particularly effective for tuning the performance of GQDs [11-13]. Numerous studies have shown that introducing heteroatoms, such as nitrogen, boron, phosphorus, and sulfur, into the graphene lattice can significantly alter the band gap, improve charge transport, and influence optical properties [14-16]. Among these dopants, sulfur has attracted considerable attention due to its unique ability to modify both the electronic and optical characteristics of GQDs [17, 18]. Sulfur doping is known to increase the Fermi level, narrow the band gap, and introduce new charge carriers into the system, which improves charge transfer and enhances the material's optical absorption, particularly in the visible and near-infrared regions [19, 20].

Despite these promising findings, a comprehensive understanding of the full impact of sulfur doping on the properties of GQDs remains lacking. Specifically, the effects of sulfur doping in different configurations and its role in altering the electronic structure and performance of GQDs have not been fully explored. This gap in knowledge forms the foundation of the current study. The objective of this research is to utilize Density Functional Theory (DFT) to examine the effects of sulfur doping in three distinct patterns: substitutional doping, edge/terminal doping, and thiophene-like doping [21-24]. By investigating how these different doping configurations affect the electronic structure, band gap, and optical properties of GQDs, the study aims to provide deeper insights into the potential of sulfur-doped GQDs for various optoelectronic applications.

This study will not only contribute to the fundamental understanding of how sulfur modifies GQD properties, but it will also help guide the design of more efficient materials for use in advanced technological applications, including solar cells, light-emitting devices, photodetectors, and other nanoelectronic systems.

Computational Methods

The graphene quantum dot with a seven-benzene ring structure ($C_{24}H_{12}$) was optimized via DFT simulations using the Gaussian 09 software package, employing the B3LYP functional and the 6-31G basis set. GQDs have an energy gap (Eg), as well as key electronic properties such as the Fermi level (E_{FL}), the highest occupied molecular orbital (HOMO) energy (E_{HOMO}), the lowest unoccupied molecular orbital (LUMO) energy (E_{LUMO}), and electronic density of states (DOS) [25]. DFT also provides valuable chemical reactivity descriptors for investigating reactivity patterns, excited states, and toxicity. The characteristics include chemical hardness (η), chemical softness (S), chemical potential (μ), and electrophilicity index (ω). These metrics may be used to evaluate and predict the chemical behavior and stability of the system [25-27]:

$$\mu = -\frac{(IP + EA)}{2} \tag{1}$$

$$\eta = \frac{(IP - EA)}{2} \tag{2}$$

$$S = \frac{1}{\eta} \tag{3}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{4}$$

The ionization potential (IP) and electron affinity (EA) may both be successfully studied using Koopman's theorem, which produces the following formula [26, 28]:

$$IP = -E_{\mathrm{HOMO}} \tag{5}$$

$$EA = -E_{\mathrm{LUMO}} \tag{6}$$

Furthermore, we use the formula below to get both the electronic band gap and the energy associated with the Fermi level [28, 29]:

$$E_{\mathrm{g}} = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} \tag{7}$$

$$E_{\mathrm{FL}} = \frac{(E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}})}{2} \tag{8}$$

The structural integrity of GQDs doped with sulfur is assessed by estimating the formation energy per atom. This metric is produced by subtracting the total energy of each constituent atom from the average total energy of the whole system [4]. A larger negative formation energy indicates a more stable structure, indicating the system's tendency to achieve a lower-energy state when the atoms are chemically bound [27].

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RESULTS AND DISCUSSIONS

The effects of sulfur doping on the electronic and optical properties of graphene quantum dots have been systematically investigated through DFT simulations. The results indicate that the introduction of sulfur in various doping configurations substitutional (S_g), edge/terminal (S_h), and thiophene-like (S_p) leads to significant changes in both the electronic structure and optical behavior of the GQDs, enhancing their potential for use in optoelectronic devices such as photodetectors, sensors, and solar cells.

The pristine graphene quantum dot structure, shown in Fig. 1, consists of a seven-benzene ring configuration ($C_{24}H_{12}$), with uniform bond lengths and a specific electrostatic potential distribution across the molecule. The density of states (DOS) depicted in the figure demonstrates the electronic properties of the pristine GQD. The electrostatic potential plot for the gas phase reveals no significant electrostatic variations within the pristine structure. Figure 1 shows that the pure graphene quantum dots have a an average C-C bond length of 1.42 Å, which is comparable to earlier results [16, 30-32].

When sulfur is introduced in different doping configurations, the energy gap (E_g) of the GQDs significantly reduces. Specifically, the energy gaps for substitutional doping (S_g), edge/terminal doping (S_h), and thiophene-like doping (S_p) are 1.444 eV, 1.213 eV, and 1.487 eV, respectively, compared to the pristine GQD, which has a larger band gap. This reduction in the band gap enhances the electrical conductivity and electronic reactivity of the GQDs. As shown in Table 1, the energetic data for GQDs with and without sulfur clearly indicate significant changes in the HOMO and LUMO energies, thus reducing the HOMO-LUMO gap and improving the electronic conductivity.

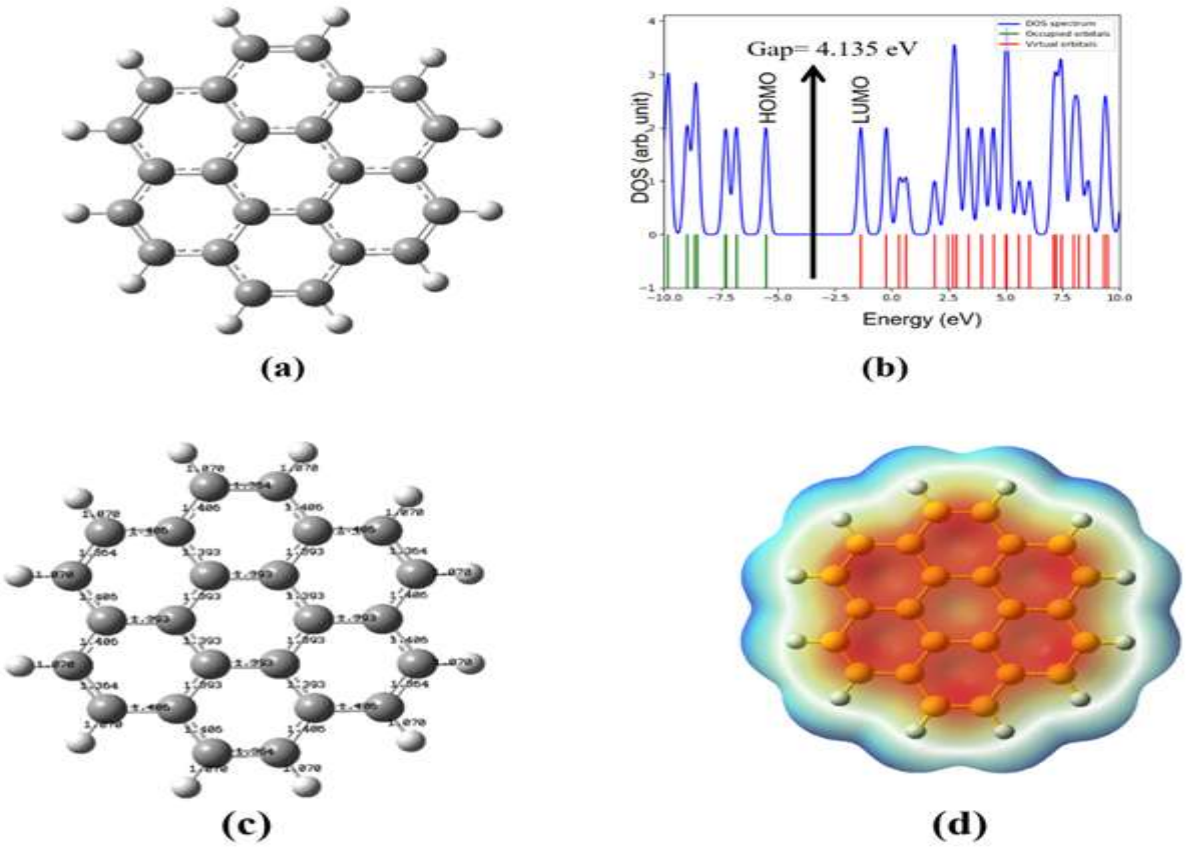

Figure 1: (a) Pristine graphene quantum dot structure, (b) density of state, (c) structured geometries and bond lengths, and **(d)** molecule electrostatic potential graphic for gas phase.

Table 1 shows the energetic data for graphene quantum dots with and without S, including HOMO energies (E_{HOMO}), Fermi level energy (E_{FL}), LUMO energies (E_{LUMO}), energy gap (E_g), change in E_g (ΔE_g), Formation energy (E_{FORM}) All energies are in eV units.

System	E_{HOMO}	E_{FL}	E_{LUMO}	E_g	ΔE_g%	E_{FORM}
GQD pristine	-5.403	-3.335	-1.268	4.135	-	-249.31
GQD-S_g	-3.076	-2.354	-1.632	1.444	-65.04%	-228.84
GQD-S_h	-2.951	-2.344	-1.738	1.213	-70.63%	-232.51
GQD-S_p	-3.025	-2.281	-1.538	1.487	-64.00%	-268.51

The formation energy calculations, presented in Table 1, reveal that all three doping configurations have negative formation energies, indicating that the sulfur-doped GQD structures are stable. Among these, the edge/terminal doping (S_h) configuration shows the lowest formation energy, suggesting that this doping configuration is the most stable and likely to occur in practical applications. The sulfur doping configuration further influences the electronic properties, as demonstrated in Fig. 2, which illustrates the density of states for each doping pattern (S_g, S_h, S_p). The doped GQDs exhibit smaller HOMO-LUMO gaps, suggesting that sulfur doping promotes favorable electron transfer characteristics, which are essential for efficient charge transport in electronic devices.

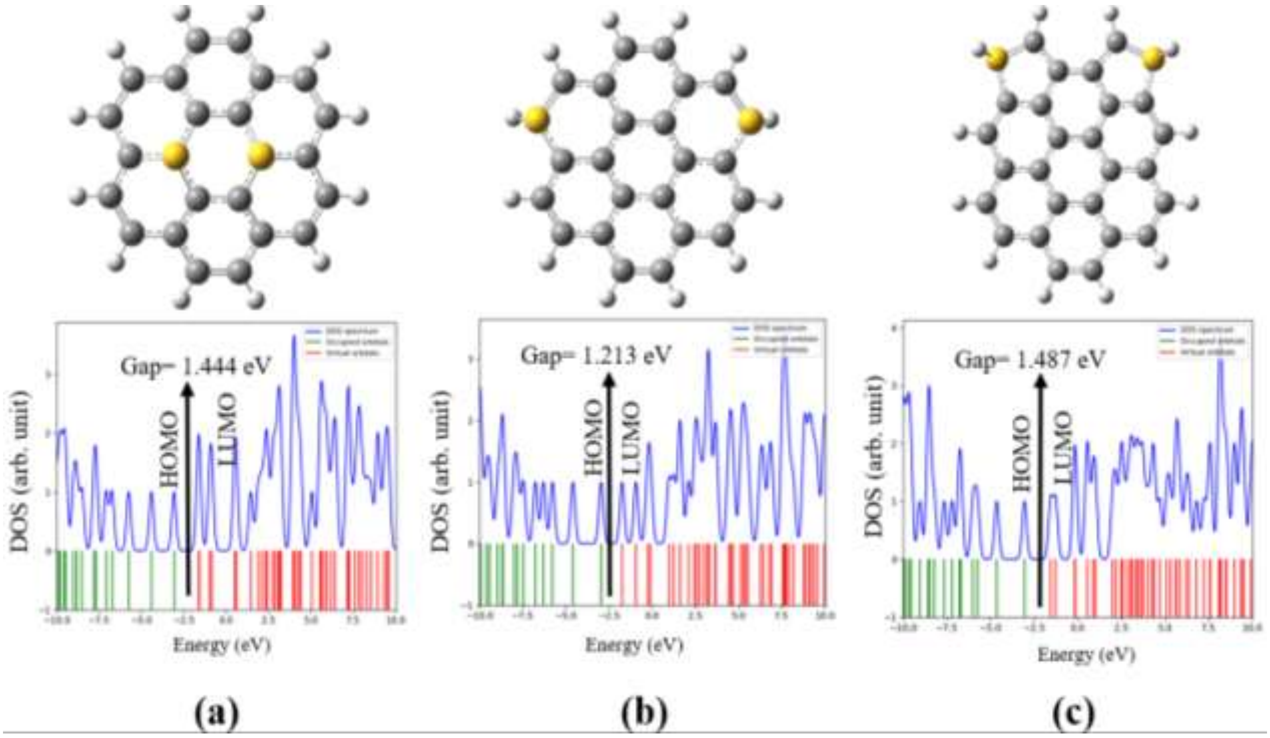

Figure 2: The density of states of graphene quantum dots doped with sulfur (S) atoms in three configurations: (a) substitutional S doping (S_g), (b) edge/terminal S doping (S_h), and (c) thiophene-like S doping (S_p). The sulfur atoms are represented in yellow colour.

The optimal geometries and bond lengths for each doping configuration are shown in Fig. 3, which clearly illustrates how the doping alters the structure of the quantum dots. Additionally, the molecular electrostatic potential (MEP) analysis, depicted in Fig. 4, reveals that sulfur doping alters the electrostatic distribution of the GQDs, enhancing their ability to interact with external stimuli. The electrostatic potential at the sulfur sites is more negative, suggesting increased reactivity at these sites.

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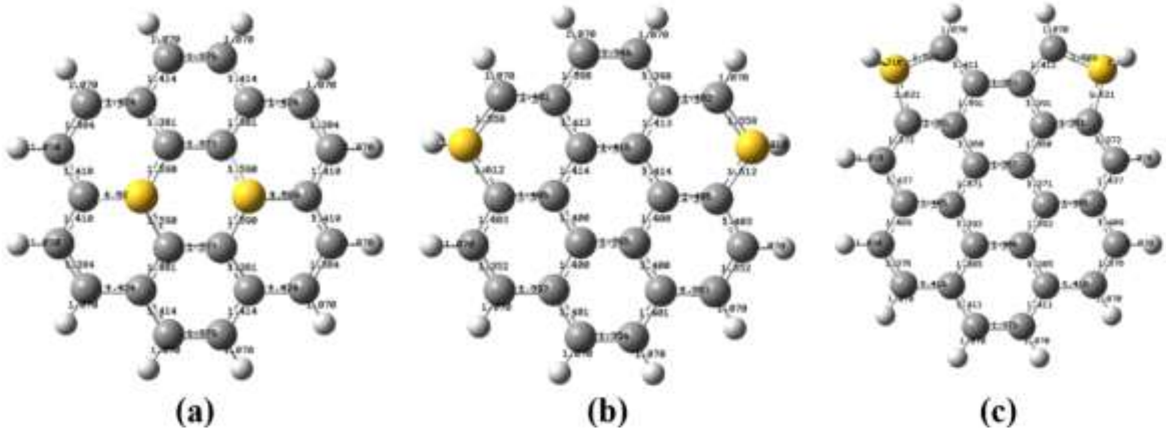

Figure 3 Shows the optimal geometries and bond lengths (in angstroms) of graphene quantum dots doped with sulfur atoms, resulting in (a) substitutional S doping (S_g), (b) edge/terminal S doping (S_h), and (c) thiophene-like S doping (S_p).

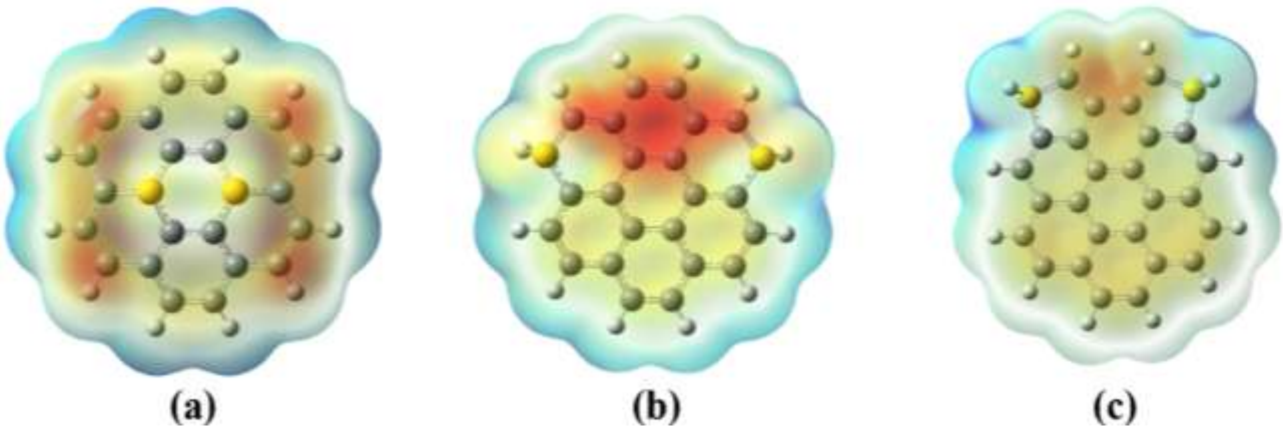

Figure 4 illustrates the molecular electrostatic potential (MEP) graphic obtained in the gas phase of graphene quantum dots functionalized with S atoms, resulting in three structures: **(a) S_g**, **(b) S_h**, and **(c) S_p**. A color spectrum is displayed, with red indicating the lowest electrostatic potential energy and blue representing the greatest.

The global chemical descriptors such as chemical hardness (*η*), chemical softness (*S*), ionization potential (*IP*), and electron affinity (*EA*) were also calculated to evaluate the reactivity and stability of the sulfur-doped GQDs. As shown in Table 2, the sulfur doping increases the chemical softness and decreases the chemical hardness, signaling enhanced chemical reactivity. Additionally, the improved electron affinity and ionization potential further suggest that sulfur doping enhances the charge transfer capacity, thereby improving the reactivity of the GQDs for catalytic and sensing applications.

Table 2: displays key global chemical descriptors, including ionization potential (*IP*), electron affinity (*EA)*, chemical potential (*μ*), chemical hardness (*η*), chemical softness (*S*), and electrophilicity index(*ω*). These parameters are crucial in defining the reactivity and electronic stability of the investigated systems.

System	*IP*	*EA*	*μ*	*η*	*S*	*ω*
GQD pristine	5.403	1.268	-3.3355	2.067	0.483	2.69
GQD-S_g	3.076	1.632	-2.354	0.722	1.385	3.837
GQD-S_h	2.951	1.738	-2.3445	0.606	1.649	4.531
GQD-S_p	3.025	1.538	-2.2815	0.743	1.344	3.5005

The optical properties of the sulfur-doped GQDs were evaluated through their absorption spectra, with a clear redshift observed in the absorption peaks compared to the pristine GQDs. The absorption maxima were observed at 858.7 nm for S_g, 1022.2 nm for S_h, and 833.9 nm for S_p, as compared to the pristine GQD, which exhibited an absorption peak in the ultraviolet region, see Table 3. This shift toward the near-infrared region indicates that sulfur doping significantly broadens the optical absorption spectrum of the GQDs, which is crucial for optoelectronic applications requiring light absorption in the visible to near-infrared range.

Table 3 presents the conductivity (σ), optical absorption threshold (λ_{abs}), and absorption regions of the graphene quantum dots with and without sulfur. The results indicate that the sulfur-doped GQDs exhibit an enhanced optical absorption, particularly in the near-infrared region, compared to the pristine GQDs. This is significant as the enhanced absorption makes sulfur-doped GQDs promising candidates for applications in photodetectors and photovoltaic devices, where light absorption in the near-infrared range is crucial. In terms of conductivity, Table 3 shows that the doping of sulfur improves the electrical conductivity of the GQDs, particularly in the edge/terminal (S_h) configuration. This is in line with the reduced band gap observed in the sulfur-doped structures, which facilitates better charge transport. The reduction in the band gap, which leads to increased electrical conductivity, is an essential factor for the potential application of these materials in electronic devices that require efficient charge transfer.

Table 3: shows the conductivity ***(σ)***, optical absorption threshold ***(λ_{abs})***, and absorption regions of graphene quantum dots with and without S**.**

Systems	σ (S/m)	λ_{abs} (nm)	Region
GQD pristine	8.1×10^{-31}	299.9	Ultraviolet (UV) region
GQD-S_g	7.42×10^{-9}	858.728	Near-Infrared (NIR)
GQD-S_h	6.47×10^{-7}	1022.259	Near-Infrared (NIR) region
GQD-S_p	3.23×10^{-9}	833.8937	Near-Infrared (NIR) region

Overall, the results demonstrate that sulfur doping significantly enhances the electrical, chemical, and optical properties of GQDs. Specifically, sulfur-doped GQDs exhibit a reduced energy gap, improved charge transfer properties, and a shift in optical absorption toward the near-infrared region, making them promising for a wide range of optoelectronic applications. Among the doping configurations, the edge/terminal sulfur doping (S_h) configuration exhibits the most favorable stability and reactivity, making it a preferred choice for future experimental investigations and device applications.

These computational findings contribute to a deeper understanding of the impact of sulfur doping on the properties of GQDs. Future experimental efforts should focus on synthesizing sulfur-doped GQDs with controlled doping configurations and investigating their performance in real-world applications, including sensors, photodetectors, and photovoltaic devices. These studies will be essential for confirming the theoretical predictions and unlocking the full potential of sulfur-doped GQDs in advanced electronic systems.

CONCLUSION

This theoretical study employed Density Functional Theory (DFT) to investigate the influence of sulfur functionalization on the electronic and optical properties of graphene quantum dots (GQDs). The introduction of sulfur atoms significantly reduced the band gap compared to pristine GQDs, indicating an enhancement in electrical conductivity and electronic activity. The analysis of molecular electrostatic potential and other chemical descriptors, such as ionization potential, electron affinity, chemical hardness, softness, and electrophilicity index, revealed an increase in charge transfer capabilities and electronic reactivity in sulfur-doped structures. The optical absorption spectra demonstrated a clear redshift, with absorption peaks shifting from the ultraviolet region in pristine GQDs to the near-infrared region in sulfur-doped GQDs. Specifically, the absorption peaks were observed at 858.7 nm for the Sg structure, 1022.2 nm for the Sh structure, and 833.9 nm for the Sp structure, showcasing their potential for optoelectronic applications such as sensors, photodetectors, and photovoltaic devices. These findings highlight the effectiveness of sulfur functionalization in modifying both the electronic and optical properties of GQDs, making them highly promising candidates for use in next-generation optoelectronic and nanoelectronic devices. Future experimental studies are encouraged to validate these theoretical predictions and explore the real-world applications of sulfur-functionalized GQDs in advanced electronic systems.

REFERENCES

1. S. A. Ansari, "Graphene quantum dots: novel properties and their applications for energy storage devices," *Nanomaterials,* vol. 12, no. 21, p. 3814, 2022.
2. Y. R. Kumar, K. Deshmukh, K. K. Sadasivuni, and S. K. Pasha, "Graphene quantum dot based materials for sensing, bio-imaging and energy storage applications: a review," *RSC advances,* vol. 10, no. 40, pp. 23861-23898, 2020.
3. S. T. Jalood, Z. A. A. Alhasani, and F. N. Ajeel, "Engineering the Electronic and Optical Properties of Graphene Quantum Dots via NiO Dimer: A DFT Investigation," *Transactions on Electrical and Electronic Materials,* pp. 1-11, 2025.
4. F. N. Ajeel, N. B. Shwayyea, M. K. Salman, A. M. Khudhair, and A. B. Ahmed, "Tuning the electronic and optical properties of graphene quantum dots by vacancy defect with Si-doping: DFT insights," *Applied Physics B,* vol. 131, no. 7, p. 143, 2025.
5. S.-Y. Li and L. He, "Recent progresses of quantum confinement in graphene quantum dots," *Frontiers of Physics,* vol. 17, no. 3, p. 33201, 2022.
6. N. Gupta *et al.*, "Large-scale efficient mid-wave infrared optoelectronics based on black phosphorus ink," *Science Advances,* vol. 9, no. 49, p. eadi9384, 2023.
7. H. Cho, G. Bae, and B. H. Hong, "Engineering functionalization and properties of graphene quantum dots (GQDs) with controllable synthesis for energy and display applications," *Nanoscale,* vol. 16, no. 7, pp. 3347-3378, 2024.
8. M. Kadhem, N. B. S. Ajeel, F. N. Ajeel, and A. M. Khudhair, "Investigating the Effects of TiO Impurities on the Electronic Properties of Graphene Nanoflakes Using DFT Method," *Sumer Journal for Pure Science,* 2024.
9. I. V. Ershov, A. A. Lavrentyev, D. L. Romanov, and O. M. Holodova, "Tuning Optical Excitations of Graphene Quantum Dots Through Selective Oxidation: Effect of Epoxy Groups," *C,* vol. 11, no. 3, p. 51, 2025.
10. W. Liu, Y. Han, M. Liu, L. Chen, and J. Xu, "Effect of defects on optical and electronic properties of graphene quantum dots: a density functional theory study," *RSC advances,* vol. 13, no. 24, pp. 16232-16240, 2023.
11. S. K. Khamees, F. N. Ajeel, K. H. Mohsin, and M. N. Mutier, "Influence of B, si, ge, and as impurities on the electronic properties of graphene quantum dot: A density functional theory study," *Nano Trends,* vol. 7, p. 100049, 2024.
12. F. Ajeel and K. T. Yalkhoum, "Tuning the Electronic Properties of Graphene through MgO Impurities: DFT Investigations," *Sumer journal for Pure Science,* 2024.
13. J. Feng, H. Dong, L. Yu, and L. Dong, "The optical and electronic properties of graphene quantum dots with oxygen-containing groups: a density functional theory study," *Journal of Materials Chemistry C,* vol. 5, no. 24, pp. 5984-5993, 2017.
14. S. Kaushal, M. Kaur, N. Kaur, V. Kumari, and P. P. Singh, "Heteroatom-doped graphene as sensing materials: A mini review," *RSC advances,* vol. 10, no. 48, pp. 28608-28629, 2020.
15. N. Sohal, B. Maity, and S. Basu, "Recent advances in heteroatom-doped graphene quantum dots for sensing applications," *RSC advances,* vol. 11, no. 41, pp. 25586-25615, 2021.
16. F. N. Ajeel, M. N. Mutier, K. H. Mohsin, S. K. Khamees, A. M. Khudhair, and A. B. Ahmed, "Theoretical study on electronic properties of BN dimers doped graphene quantum dots," *BioNanoScience,* vol. 14, no. 2, pp. 1110-1118, 2024.
17. R. Rabeya, S. Mahalingam, A. Manap, M. Satgunam, M. Akhtaruzzaman, and C. H. Chia, "Structural defects in graphene quantum dots: A review," *International Journal of Quantum Chemistry,* vol. 122, no. 12, p. e26900, 2022.

18. A. Kalluri, B. Dharmadhikari, D. Debnath, P. Patra, and C. V. Kumar, "Advances in structural modifications and properties of graphene quantum dots for biomedical applications," *ACS omega,* vol. 8, no. 24, pp. 21358-21376, 2023.
19. I. Shtepliuk and R. Yakimova, "Nature of photoexcited states in ZnO-embedded graphene quantum dots," *Physical Chemistry Chemical Physics,* vol. 25, no. 15, pp. 10525-10535, 2023.
20. P. Ramachandran *et al.*, "N-doped graphene quantum dots/titanium dioxide nanocomposites: A study of ROS-forming mechanisms, cytotoxicity and photodynamic therapy," *Biomedicines,* vol. 10, no. 2, p. 421, 2022.
21. J. Feng *et al.*, "Density functional theory study on optical and electronic properties of co-doped graphene quantum dots based on different nitrogen doping patterns," *Diamond and Related Materials,* vol. 113, p. 108264, 2021.
22. J. Feng *et al.*, "Theoretical study on the optical and electronic properties of graphene quantum dots doped with heteroatoms," *Physical Chemistry Chemical Physics,* vol. 20, no. 22, pp. 15244-15252, 2018.
23. J. Feng *et al.*, "Theoretical insights into tunable optical and electronic properties of graphene quantum dots through phosphorization," *Carbon,* vol. 155, pp. 491-498, 2019.
24. P. Rani, R. Dalal, and S. Srivastava, "Effect of surface modification on optical and electronic properties of graphene quantum dots," *Applied Surface Science,* vol. 609, p. 155379, 2023.
25. E. V. Gómez, N. A. Ramirez Guarnizo, J. D. Perea, A. S. López, and J. J. Prías-Barragán, "Exploring molecular and electronic property predictions of reduced graphene oxide nanoflakes via density functional theory," *ACS omega,* vol. 7, no. 5, pp. 3872-3880, 2022.
26. D. M. Mamand and H. M. Qadr, "Corrosion inhibition efficiency and quantum chemical studies of some organic compounds: theoretical evaluation," *Corrosion Reviews,* vol. 41, no. 4, pp. 427-441, 2023.
27. F. N. Ajeel, Y. W. Ouda, and S. A. Abdullah, "Graphene nanoflakes as a nanobiosensor for amino acid profiles of fish products: Density functional theory investigations," *Drug Invention Today,* vol. 12, no. 12, p. 9, 2019.
28. H.-g. Kim and H. J. Choi, "Thickness dependence of work function, ionization energy, and electron affinity of Mo and W dichalcogenides from DFT and GW calculations," *Physical review B,* vol. 103, no. 8, p. 085404, 2021.
29. Y. Oh, S. Song, and J. Bae, "A review of bandgap engineering and prediction in 2D material heterostructures: a DFT perspective," *International Journal of Molecular Sciences,* vol. 25, no. 23, p. 13104, 2024.
30. K. H. Bardan, F. N. Ajeel, M. H. Mohammed, A. M. Khudhair, and A. B. Ahmed, "DFT study of adsorption properties of the ammonia on both pristine and Si-doped graphene nanoflakes," *Chemical Physics Impact,* vol. 8, p. 100561, 2024.
31. F. N. Ajeel, S. K. Khamees, K. H. Mohsin, and M. N. Mutier, "Effect of AlN dimers on the electronic properties of graphene quantum dot: DFT investigations," *Chemical Physics Impact,* vol. 7, p. 100364, 2023.
32. F. N. Ajeel, K. H. Mohsin, H. G. Shakier, S. K. Khamees, and M. N. Mutier, "Theoretical insights into tunable electronic properties of graphene quantum dots through ZnO doping," *Chemical Physics Impact,* vol. 7, p. 100305, 2023.