Annals of Computing (2025), 1(4):9-18
https: doi.org /10.5281/zenodo.15235880

Research Article

Effect of Nitrogen Position in Tailoring the Electronic Properties of Graphene Quantum Dot: A DFT Investigation

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Received 13 March 2025; Acceptance 6 April 2025; Published 17 April 2025.

Abstract

Graphene quantum dots (GQDs) are nanoscale materials with tunable optical and electronic properties due to quantum confinement and edge effects. Nitrogen doping has proven especially effective in enhancing these properties, improving conductivity, reactivity, and fluorescence. Studying how nitrogen atoms, when doped at different sites in GQDs, affect their electronic structure is essential for advancing their use in applications like sensing, imaging, and energy storage. This study presented a comparative analysis of the electronic properties of pristine, edge-doped (GQD-N_e), and center-doped (GQD-N_c) nitrogen graphene quantum dots (GQDs), with a focus on their band structure and density of states (DOS) using density functional theory (DFT). The band structure of the pristine GQD reveals a direct band gap of approximately 2.18eV, indicative of its semiconducting behavior. Upon nitrogen doping, significant modifications in the electronic structure are observed. Edge doping introduces localized states near the Fermi level (E_F), resulting in a substantial narrowing of the band gap and enhanced electronic states in the mid-gap region. This is attributed to the higher electronegativity and lone pair electrons of nitrogen atoms at the edges, which distort the local electronic potential. In contrast, center doping yields a moderate increase in states near the E_F, maintaining a more ordered band structure and preserving much of the original semiconducting character. The DOS analysis supports these findings, showing a high density of electronic states around E_F in GQD-N_e and a moderate increase in GQD-N_c compared to the pristine system. These results demonstrate that nitrogen doping provides a tunable route to engineer the electronic properties of GQDs, with edge doping favoring enhanced conductivity and center doping offering balanced semiconducting behavior for potential nanoelectronic and optoelectronic applications.

Keyword: DFT, Graphene quantum dots, Edge-doped nitrogen, Center-doped nitrogen, Density of States.

Introduction

Nanotechnology is one of the hottest and interesting research frontiers today as materials tend to behave differently at nanoscale compared to bulk materials, it focuses on manipulating matter at the atomic and

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molecular scale (1-100 nanometers) to create novel materials, devices, and systems with unique properties and applications [1]. Hence in-depth understanding of the behavior of nanomaterials is crucial for designing their functional applications. Remarkable improvement in theoretical and computational methods makes computational science an alternative way to complement experimental investigation [2]. Density functional theory (DFT) simulation is one of the first principle computational approaches for atomistic modeling of nanomaterials systems. These approaches enable us to carry out "virtual experiments" for investigating physical properties and dynamics of material systems at the nanoscale. In the past decade, researchers have worked on the successful development of 0D graphene quantum dots (GQDs) in lines of the 2D graphene [3]. GQDs consist of a monolayer or a few monolayers of graphene-related to quantum confinement and edge effects [4]. These materials offer several superior qualities, including robust chemical inertness and fluorescence activity, photostability, low cytotoxicity, luminescence emission and excellent biocompatibility, high solubility, high surface area, long term opposition to photobleaching, and better surface grafting [5]. These properties, in turn, offer the opportunity to explore novel structural, optical and electrical phenomena that are unavailable in other materials. The adjustment of electron and quantum confinement behaviour of GQDs has become supremely attractive especially in comparison to graphene. These advanced properties make this material an encouraging candidate for several applications such as sensors, biosensors, bioimaging, photovoltaic and energy storage devices etc [6, 7].

Heteroatom doping of carbon quantum dots not only enables great improvement of fluorescence efficiency and tenability of fluorescence emission, but also provides active sites in carbon dots to broaden their applications. Nitrogen as a biocompatible element offers a promising direction for doping of carbon quantum dots [8].

Quantum dot is made up of finite number of atoms (from a few up to thousands) whose interaction is governed by laws of quantum mechanics in many body systems [9].

Based on very general argument, all physical characteristics of quantum dot, including the luminescence properties are completely determined once their ground state structures are total energies as a function of the system's parameters are known. Hence, the ability to perform reliable and accurate the ability to perform reliable and accurate calculation of the ground state total energy and structures, and how they vary with the system's parameters is vital in determining the electronic properties. This study aims to investigate the effect of nitrogen doping at two distinct sites—edge and center—on the electronic properties of graphene, with a focus on understanding how doping influences and potentially tailors these properties.

Research Method

In this work, DFT calculations were performed with the generalized gradient approximations of Perdew-Burke-Ernzerhof (GGA-PBE) exchange-correlation functional. Vanderbilt ultra-soft pseudo potentials and the plane wave basis sets are implemented in the Quantum ESPRESSO package of materials square [10].

These plane wave basis sets (PW) and ultra soft pseudo potentials represent the electron-ion interactions. The approach is based on an iterative solution of the Kohn-Sham equation of the density functional theory in a plane-wave set with the projector-augmented wave pseudopotentials [11]. The study adopted the Perdew-Burke-Ernzerhof (PBE) exchange-correlation (XC) functional of the generalized gradient approximation (GGA) in our calculations with the plane-wave cutoff energy was set to 40Ry and the Monkhorst-Pack scheme is used for sampling the Brillouin zone [12]. In the calculations, the structures were fully relaxed with a Gamma–centred 8 × 8 × 2 k-mesh. The partial occupancies were treated using the tetrahedron methodology with Blöchl corrections [13]. For geometry optimizations, all the internal coordinates were relaxed until the Hellmann-Feynman forces were less than 0.005 Å.

To calculate the electronic properties with emphasis on the density of states, band gaps and band structures of undoped GQD, edge-doped (GQD-N_e) and centered doped (GQD-N_c). We used DFT within the generalized gradient approximation (GGA) approach in which the local field effects are included at Hartree level only. Further, the density of states points to the availability of the number of states in a system which is important for determining the energy distribution of carrier and carrier concentration within a semiconductor [14]. Generally, in semiconductors, the motion of free electrons is limited with zero, one, and two spatial dimensions. Knowledge of the density of states of low dimensional nanostructures is required when applying semiconductor states to the systems of these dimensions.

The number of states achieved by a quantum system is the possible number of available states, mathematically expressed as

$$\phi(E) = \frac{V_{system}}{V_{single\ state}} \times N \tag{1}$$

$$E = \frac{\hbar^2}{2m}\left(\frac{n_x^2 x^2}{L_x^2} + \frac{n_y^2 x^2}{L_y^2} + \frac{n_z^2 x^2}{L_z^2}\right) \tag{2}$$

The density of states depends on the energy gained by an electron. It is the first derivative of the state with respect to energy. It is mathematically expressed,

$$g(E) = \frac{d\phi(E)}{dE} \tag{3}$$

$$g(E) = 2\sum_n \delta(E - E_n)^{1/2} \tag{4}$$

For a system such as GQD-N built out of two atom types, it is desirable to express the relative contribution of the atoms to the total DOS by calculating the projected or partial density of states for each atom. The projected DOS of the atom of type t is given by

$$g_i^t(E) = \frac{2}{V_{BZ}} \int Q_i^t \delta(E - E_n(k)) dk \tag{5}$$

A more detailed view of a material's electronic structure is often possible by examination of its band structure from which the band gap can be evaluated. The band structure represents the energy of the available electronic states along a series of lines in reciprocal space that typically forms a closed loop beginning and ending at the Γ-point. In this study, the electronic band structures and the corresponding density of states for GQD and GQD-N were computed at the equilibrium lattice constants.

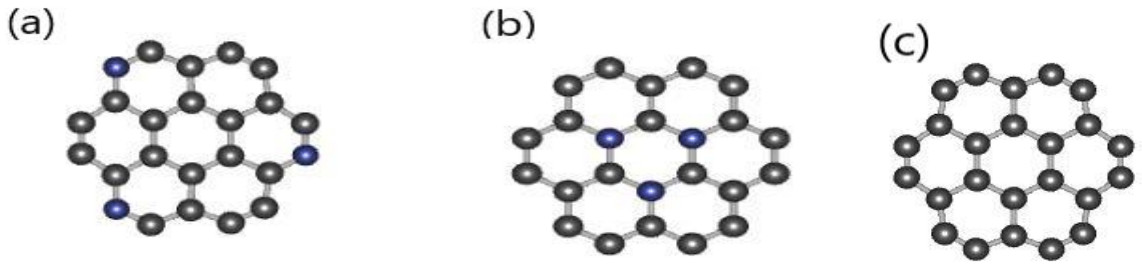


Figure 1. A ball and stick model of (a) GQD-N_e (b) GQD-N_c (c) Pristine GQD

Results and Discussion

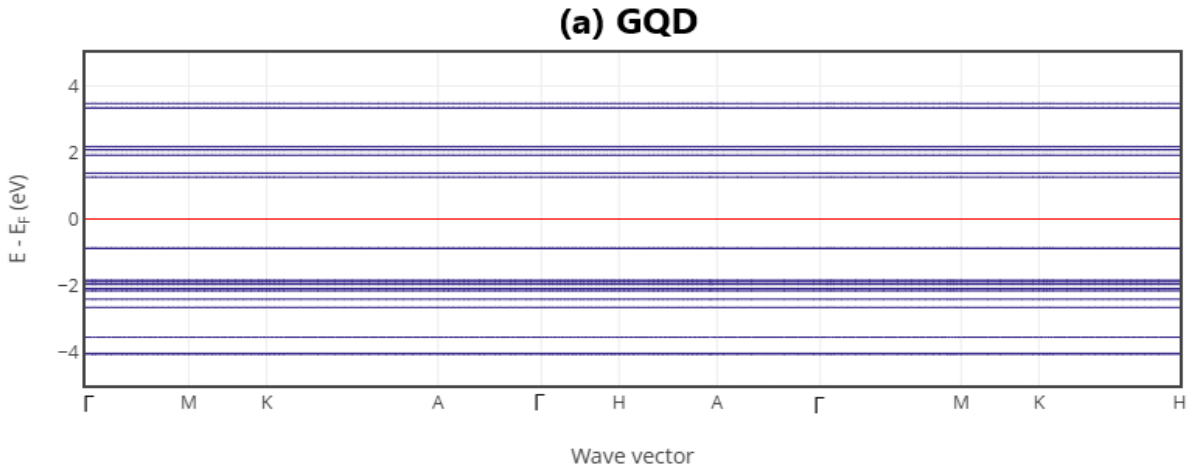
Band Structure

To comprehensively assess the impact of nitrogen doping on the electronic properties of graphene quantum dots (GQDs), the electronic band structures of the pristine GQD, edge-doped GQD (GQD-N_e), and center-doped GQD (GQD-N_c) were calculated and are presented in Fig.2. The corresponding band gaps are extracted and summarized in Table 1. The band structure of the pristine GQD (Fig. 2(a)) reveals a relatively wide and direct band gap, with both the valence band maximum (VBM) and conduction band minimum (CBM) clearly separated in energy. The calculated band gap for the pristine structure is approximately **2.18eV at** Γ-point, consistent with its semiconducting nature [15]. The band dispersion is minimal, reflecting the quantum confinement effects typical of small-scale graphene systems. The discrete and flat nature of the bands suggests strong electron localization and limited overlap of atomic orbitals, resulting in reduced charge carrier mobility. The electronic band structures of edge-doped (GQD-N_e) and center-doped (GQD-N_c) nitrogen-doped graphene quantum dots reveal distinct differences in energy dispersion and band gap characteristics. In both systems, flat bands dominate the energy range, indicative of the localized nature of states due to quantum confinement. However, closer inspection shows that GQD-N_e exhibits a greater density of nearly flat bands around the Fermi level compared to GQD-N_c. This feature in GQD-N_e can be attributed to the localized states introduced by nitrogen atoms at the edges of the quantum dot. These edge-doped N atoms introduce defect-like states due to their higher electronegativity and lone pair electrons, resulting in perturbed π-electron delocalization and creating mid-gap states or states close to the

conduction or valence bands. These features are consistent with prior observations that edge doping in GQDs tends to break sublattice symmetry and localize charge carriers [15, 16]. In contrast, GQD-N_c displays a relatively more ordered and symmetric band structure with slightly fewer mid-gap states. The bands are still relatively flat, consistent with the finite size of the quantum dot, but the impact of center doping on the electronic structure is more moderate. Nitrogen substitution at the center results in more delocalized interaction with the carbon π-network, contributing to the preservation of GQD's semiconducting behavior without introducing strongly localized edge-like states [17].

Table 1. Band gap calculation of the structures

System	Band Gap (eV)	Doping Site	Band Characteristics
Pristine GQD	2.18	None	Clear semiconducting gap visible, consistent with typical graphene quantum dots.
GQD-N_e	1.27	Edge	Band gap reduces, indicating localized states near the Fermi level due to edge doping.
GQD-N_c	1.64	Centre	Slightly reduced band gap compared to pristine, but larger than edge-doped.



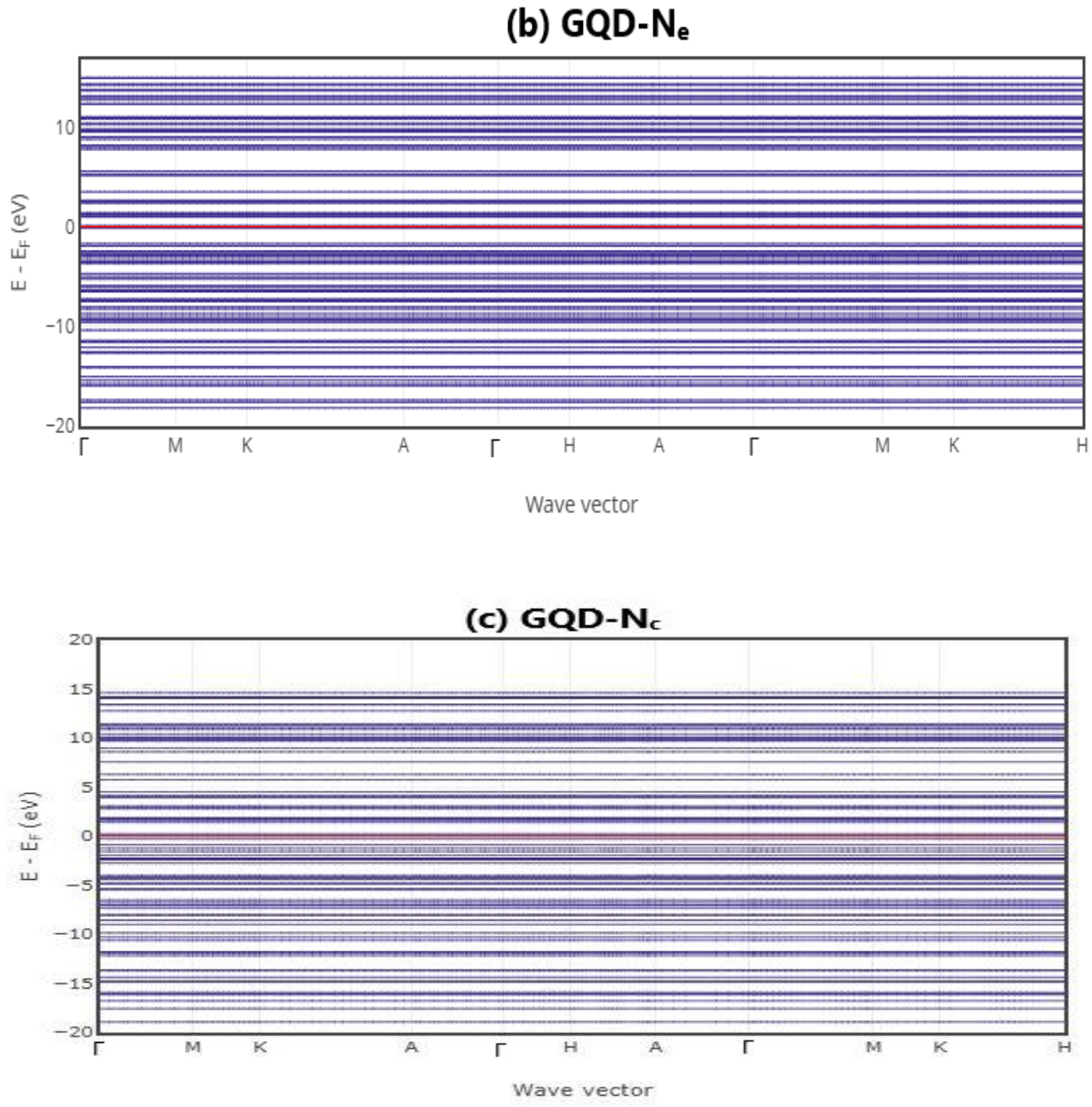


Figure 2. Energy band in the electronic structure calculations of (a) Pristine GQD (b) GQD-N_e (c) GQD-N_c

Density of States

The total density of states (TDOS) for the pristine graphene quantum dot (GQD), as illustrated in Figure 3(a), shows a series of sharp and well-defined peaks distributed within the energy window of approximately -20eV to -6eV. Notably, there is a distinct absence of electronic states near the Fermi level (E_F) which reflects the semiconducting nature of the undoped GQD. The presence of discrete energy levels is attributed to quantum confinement effects and the finite size of the GQD structure. These features indicate

that the electronic structure of the pristine GQD is dominated by the π and π* states arising from sp^2-hybridized carbon atoms. The DOS profile suggests a band gap of approximately 2.18eV, aligning with typical values reported in literature for similar carbon-based nanostructures [15]. Edge doping with nitrogen leads to significant changes in the DOS profile, as shown in Figure 3(b). Unlike the pristine structure, GQD-N_e exhibits a considerable number of states near the Fermi level. This results in a narrowing of the band gap, which corresponds to an increased density of mid-gap states. Furthermore, the peaks appear broader and more irregular, indicating the emergence of localized states and a perturbation of the original electronic structure. This distortion can be attributed to the electronegative nature of nitrogen atoms substituted at the edges. Nitrogen introduces lone pair electrons and modifies the local electronic potential, thereby creating localized defect states that interact with the π-system of the GQD. These findings are in agreement with theoretical and experimental studies that have shown edge doping to be a highly effective strategy for modulating the electronic properties of carbon nanostructures [18]. In contrast to edge doping, nitrogen doping at the center of the GQD results in a less pronounced but still notable alteration of the DOS, as presented in Figure 3(c). States are observed near the Fermi level, though with lower intensity compared to the edge-doped case. The overall distribution of DOS is more ordered and symmetric, suggesting a relatively minor disruption of the GQD's electronic structure. Center doping incorporates nitrogen atoms into the bulk of the GQD lattice, where they act as substitutional dopants within the hexagonal carbon framework. This configuration leads to the formation of donor-like states that slightly perturb the band structure without introducing substantial structural defects. As a result, the semiconducting nature is largely retained, albeit with a narrower band gap compared to the pristine system. Similar behavior has been reported in earlier density functional theory (DFT) investigations [15].

The partial density of states (PDOS) offers a deeper understanding of the atomic and orbital contributions of specific atomic species to the electronic states of a material. Figures 3(b) and 3(c) present the PDOS for GQD-N_e and GQD-N_c, respectively, decomposed into contributions from carbon and nitrogen atoms in each system. In the PDOS of GQD-N_e, the carbon atoms show strong and broad contributions across the entire energy window, particularly in the conduction band (above the Fermi level), which indicates their dominant role in the electronic states of the system. The nitrogen atoms, though significantly lower in intensity, exhibit noticeable peaks near the Fermi level and in both the valence and conduction bands. These contributions suggest that edge-positioned nitrogen atoms interact with the delocalized π-electron system, introducing localized states near the Fermi level, which may contribute to enhanced electronic reactivity or conductivity [19]. The modest overlap between the nitrogen and carbon states also implies a degree of hybridization, facilitating charge delocalization at the edge. In contrast, the PDOS of GQD-N_c reveals dominant carbon atom contributions throughout the valence and conduction bands. However, the nitrogen atoms, located at the center of the dot, exhibit significantly weaker and flatter PDOS features. Their minimal participation near the Fermi level suggests that the central nitrogen atoms are more electronically isolated compared to edge-

doped counterparts. This isolation may reduce the extent of orbital overlap and hybridization, limiting their influence on the electronic structure. Nonetheless, a minor presence of nitrogen states in the conduction band hints at a potential role in modulating higher-energy electronic transitions.

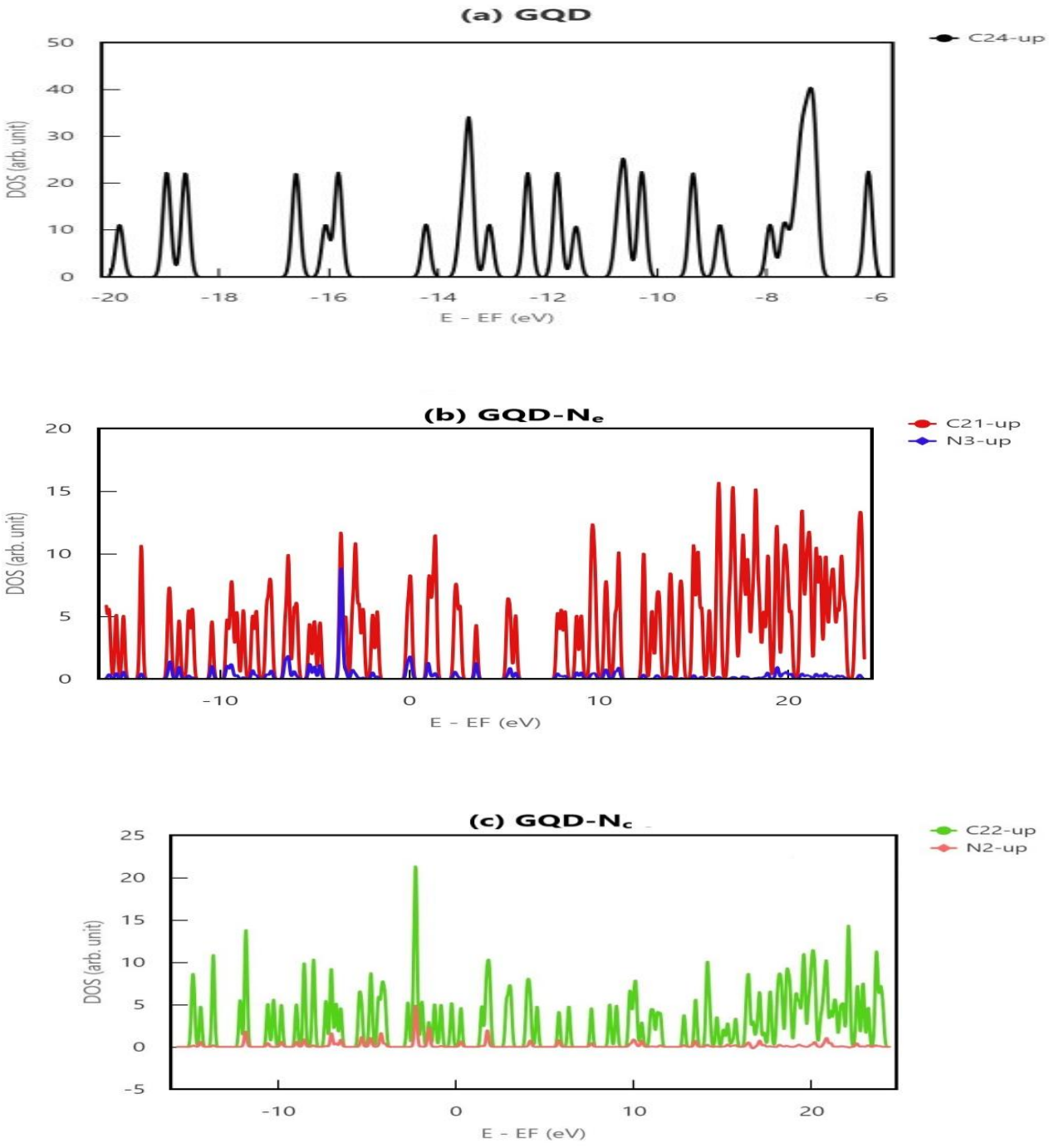


Figure 3. The calculated density of states for (a) Pristine GQD (b) GQD-N_e(c) GQD-N_c

Conclusion

In conclusion, based on DFT calculation, the effect of N-doping on different sites of GQDs has been investigated systematically. It was found that effective tailoring of electronic properties of GQDs depends on the position of the dopant. Substitutional doping on the edge introduces significant mid-gap states and center doping causing milder perturbations on the density of states. These modifications directly correlate with band structure changes and are critical for tuning the optical and electrical behavior of GQDs for applications in nanoelectronics, photocatalysis, and bioimaging.

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