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Tuning the Electronic and Chemical Properties of Graphene Quantum Dots via CO_2 Adsorption: Insights from DFT Calculations

Diyaa Y. Hussein [1a], Fouad N. Ajeel [1b*] and Ali Ben Ahmed [2c]

[1]Department of Physics, College of Science, University of Sumer, Al-Rifai, Iraq.
[2]Department of Biomedical, Higher Institute of Biotechnology of Sfax, University of Sfax, Tunisia.

[a] E-mail: physicsdisr@gmail.com , [b*]Corresponding author: fouadnimr2@gmail.com, [c]E-mail: ali.benahmed@isbs.usf.tn

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***Abstract*— This study focuses on CO_2 edge adsorption mechanism, in which the CO_2 molecules interact at the edge sites of the graphene quantum dots (GQDs), leading to significant electronic and chemical modifications analyzed using the density functional theory (DFT). Edge adsorption plays a dominant role in governing the electronic characteristics and chemical reactivity of GQDs. The energetic and chemical properties were studied for the pristine GQDs and those functionalized with one to four CO_2 molecules at their edges. The results reveal that the CO_2 edge adsorption causes a substantial reduction in the energy gap up to 91.2% for GQDs modified with four CO_2 molecules. This adsorption also influences the Fermi level, HOMO–LUMO energies, and global chemical descriptors, including the ionization potential, electron affinity, chemical hardness, and electrophilicity. Furthermore, a saturation state is observed upon adsorption of four CO_2 molecules, beyond which additional adsorption produces negligible changes in electronic properties. These findings demonstrate that the CO_2 edge adsorption provides an effective and environmentally friendly strategy for tailoring the electronic and chemical behavior of GQDs, making them promising candidates for nanoelectronic, sensing, and energy-related applications.**

***Keywords*— Quantum dots; Carbon dioxide; Bandgap; Edge modification; DFT.**

I. INTRODUCTION

Nanomaterials have, in recent years, been one of the key areas of modern technology, especially in relation to electronics and energy applications [1-3]. One of these nanomaterials, graphene, is of interest thanks to its many properties, including high electrical conductivity, mechanical strength, and optical transparency [4-6]. Graphene Quantum Dots (GQDs) are nanostructures formed from sheets of graphene where, unlike bulk graphene, electrons are confined in all three dimensions of space to give a zero-dimensional structure [7, 8]. Because GQDs are zero-dimensional nanostructures, they possess different electronic and optical properties relative to bulk graphene, making them interesting for a range of applications such as sensors, optoelectronics, and biomedical imaging [9-11]. One promising approach to tune the properties of GQDs is chemical functionalization, especially at edges. Functionalization makes it possible to directly tailor the bandgap, ionization potential, electron affinity and chemical reactivity, hence has a potential to enhance the performance of GQDs in nanoelectronic and sensing applications [12-19]. Of the adjuvants available, the carbon dioxide molecule (CO_2) has been identified as an appealing modular agent on account of its abundance, environmental friendliness and high affinity to surface chemistries of carbon-based materials [20, 21]. CO_2 adsorption modifies the charge distribution and energy levels of GQDs, leading to modulation in their energy gap and reactivity.

In order to understand and predict these effects, DFT is an accurate tool for investigating molecular interactions and electronic structures [22-28]. It has been previously reported that the CO_2 functionalization can modulate the ionization energy, electron affinity and electrophilicity of GQDs and improves their sensing properties as well as charge transfer features [29-33]. Besides, the decrease of chemical hardness and enhancement of electron-accepting capacity have been associated with enhancement of reactivity/response characteristics in sensing application [31, 32]. The CO_2-modified GQDs have exhibited the improved mechanical stability and the tunable energy levels, which are promising candidates for flexible and energy-related devices [32, 33].

In the present work, we studied electronic and chemical properties of pristine and CO_2-adsorbed edge functionalized graphene quantum dots by CO_2 adsorption using density functional theory. In this study, the effect of the number of adsorbed CO_2 molecules (from 1 up to 4) is investigated on bandgap, charge distribution and the global chemical descriptors. The findings may shed light on the fact that edge adsorption is an efficient strategy to modulate the optoelectronic and chemical features of GQDs towards possible nanoelectronics and sensing applications.

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II. COMPUTATIONAL DETAILS

The electronic and chemical properties of pure GQDs and those modified with CO_2 molecules using density functional theory are explored with the Gaussian 09 software package [34]. For this, we applied the B3LYP exchange-correlation functional along with the 6-31G (d) basis set for all the atoms involved [35, 36]. This basis set is part of the well-known Pople-style basis sets, which are widely used in quantum chemistry calculations with the Gaussian program [37]. The model we used featured a hexagonal-shaped GQDs composed of a specific number of carbon atoms, with the chemical formula $C_{24}H_{12}$. After constructing the basic structure, we gradually added CO_2 molecules to the edge of the GQDs, starting with one and going up to four, to examine how increasing CO_2 coverage affected the system. The energy gap was then calculated by finding the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels [38-40]. The formation energy was calculated by the following equation to ensure the structural stability of the system modified by carbon dioxide [41]:

$$E_F = E_{GQD_S\,edge\,modification} - E_{GQD_S} - (2E_O + E_C + E_H) \quad (1)$$

where E_F is formation energy of the CO_2-functionalized GQD system, $E_{GQD_S\,edge\,modification}$ represents the total energy of the GQD after edge adsorption of CO_2, E_{GQD_S} is total energy of the pristine GQD, and $E_c + 2E_o$ denote energies of isolated carbon, oxygen, respectively.

In addition to the electronic structure, several chemical reactivity parameters were evaluated for both the pristine and CO_2-modified GQDs [42]. These included ionization potential (IP) [43-45], electron affinity (EA) [46], chemical potential (μ), chemical hardness (η) [47] , and electrophilicity index (ω) [23, 48]. Here, the chemical properties of the system were evaluated using the following equations:

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

This energy is required by the system to remove an electron from the HOMO orbital. According to Koopmans' theorem, the ionization energy can be approximated as the negative of the HOMO energy, which corresponds to the difference in total energy between the neutral system and the resulting cation (positively charged system) [49, 50]. This energy represents approximately the negative energy of the LUMO orbit according to Koopmans Theorem, so the equation becomes as follows [51]:

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

According to density functional theory, the average of the electron affinity and ionization potential can be used to estimate the chemical potential. It is calculated that the chemical hardness is half of the difference between these two values [52, 53]:

$$\mu = \frac{IP + EA}{2} \quad (4)$$

$$\eta = \frac{IP - EA}{2} \quad (5)$$

The tendency of a nanosystem to accept electrons is represented by the electrophilicity index, and as its value increases, the ability of a single molecule to accept electrons increases [54, 55], it is given by the following relationship:

$$\omega = \frac{\mu^2}{2\eta} \quad (6)$$

These parameters help describe how the material might behave in different chemical environments and provide insight into its potential use in sensing or electronic applications.

III. RESULTS AND DISCUSSIONS

The results imply that the fundamental properties of graphene quantum dots can be fine-tuned by introducing specific molecules like CO_2, which opens up exciting new avenues for their application in nanoelectronics devices. In the following, we discuss the properties of both the pristine (unmodified) and the CO_2-modified GQDs systems.

A. Pristine GQDs

The structure of the pure GQDs, which has a hexagonal arrangement of carbon atoms bonded together, is shown in Fig. 1a. To stabilize its structure and avoid the presence of more free valence bonds, hydrogen atoms are added to the edges carbon atoms. The distance between two carbon atoms (C–C bond) equals approximately 1.4 Å, in line with that typically observed for graphene [13, 14, 56]. The C–H bond distance is 1.08 Å or so, indicating strong chemical bond of the C–H as covalent character. Fig. 1b shows the density of states (DOS) of pristine GQDs. It exhibits distinct energy gap of ~ 4.101 eV between HOMO and LUMO levels. Such a large gap value suggests that the pure GQDs are insulating. By definition, insulators' energy gaps are larger than 3 eV and the determined gap of 4.1 eV in this work implies that pure GQDs demonstrably possess negligible electrical conductivity within our present methodology. This insulating behavior is significant in that it demonstrates how the following CO_2 functionalization can efficiently modify the material band structure and gradually reduce the gap, with semiconductor type of behaviors appropriate for nanoelectronic and sensing applications. Figure 1c shows optimized structure of the GQDs along with the distances between atoms. This gives a clear picture of the original shape and size, that will be used as a reference when studying how CO_2 affects the electronic properties.

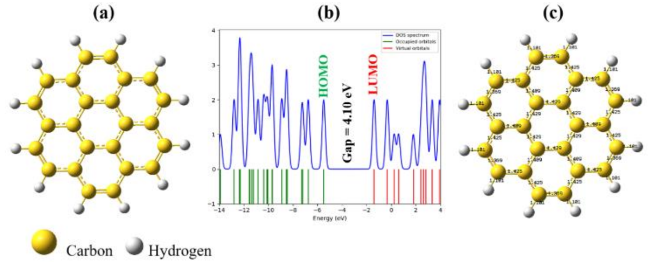

Figure 1: (a) Geometric structure of pristine GQDs, and their (b) DOS, (c) bond lengths.

B. *GQDs modification with CO_2 molecules*

In the present arrangement, the CO_2 molecules are adsorbed at the edge sites of the GQDs such that charge redistribution is changed due to local interactions as demonstrated in Fig. 2a because it locally redistributes electric charges in the system. This happens because the CO_2 molecule attaches to a specific site on the hexagonal lattice through one of its free ends. A key factor influencing this interaction is the electronic structure of the nanomaterial itself. When a single CO_2 molecule is added at one edge of the hexagonal ring, the energy gap decreases significantly, from 4.101 eV in the pristine state to approximately 1.779 eV after modification, as seen in Table 1. This reduction in the energy gap means that the material changes from being a semi-insulator to a semiconductor. As the LUMO levels move closer to the Fermi level and the HOMO levels shift to higher energies, the covalent bonds become stronger, which increases the overall stability of the system. This can be clearly seen in the DOS spectrum, Fig. 2b.

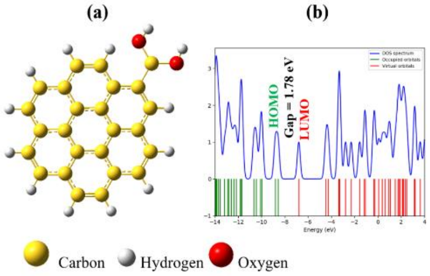

Figure 2: (a) Pure GQDs structure with one CO2 molecule, and their (b) DOS, (c) bond lengths.

Additionally, the data indicate that the CO_2 molecule fundamentally acts to draw electrons towards it resulting in increasing the ionization potential by three-fold as well as decreasing the HOMO energy level to -8.571 eV. In addition, the chemical potential drops to -7.681 eV, defined in Table 2, which is significant for those studies investigating electronegative behaviors. We note from structural analysis that there are minimal differences in the overall shape, illustrated in Fig 2c. Although there is a clear difference of bond lengths induced by charge redistribution when CO_2 interacts with the quantum dot edge, it is equally important to examine the electronic and chemical changes associated with edge modification.

An analysis of the bond length diagrams (Figs. 2c–5c) demonstrate that CO_2 adsorption has a profound impact on the structural conformation of the GQDs. Adsorption of CO_2 molecules induces significant changes in the C–C and C–O bond lengths at the edge sites (generally varying between 1.35 and 1.45 Å) when compared to pristine GQDs (average bond length: ∼1.40 Å). These changes reveal that the electron charge redistribution, induced by CO_2 adsorption across the QD film lattice, triggers a local strain and structural relaxation. In addition, the elongation of some C–C bonds around adsorption sites is consistent with the downward shift of LUMO levels, meaning better electron delocalization. Also, the nearby C–O bonds are squeezed slightly weaker, indicating the enhancement of local π–π association between CO_2 and graphene structure. The bond stretching and compression patterns further demonstrate that CO_2 adsorption not only changes the electronic structure but results in local mechanical distortion, which has the potential to promote surface reaction dynamics and increase sensing activity.

At this stage, once the system has two CO_2 molecules, we see significant differences from having only one molecule. Figure 3a illustrates that the second CO_2 molecule binds to a novel location on the edge of quantum dot than the first molecule. As a result, this leads to a simultaneous change in the electronic and chemical properties of the system. The DOS spectrum in Fig. 3b reveals that the energy gap between the HOMO and LUMO is still decreasing, and is now approximately 0.360 eV, which is lower than the pure or one molecule states. The energy gap is decreasing due to both the HOMO and LUMO levels of molecular orbitals moving closer to the Fermi level at the same time. In general, the modification of the electronic structure allows for increased mobility and conductivity of the electrons.

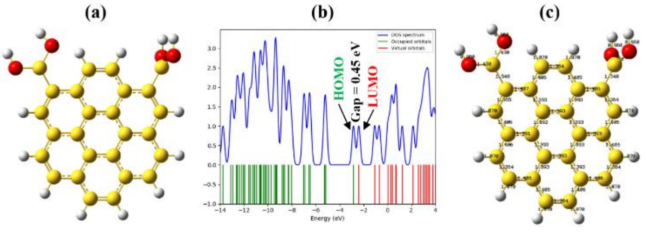

Figure 3: (a) Pure graphene quantum dot structure with two CO_2 molecules, and their (b) DOS, (c) bond lengths.

The electrical properties of the system show a substantial increase in electron transport in this state. For example, the ionization potential increases to 2.837 eV, and the chemical potential increases to -2.615 eV, indicating increased electrons. Structurally, as shown in Fig. 3c, the modification results in changes to bond lengths and bond angles - particularly for the region where the CO_2 molecules were bonded- which indicate that not only does the modification alter the electronic behavior, provide real modification forces, and shifts general stability and the systems interactions with the surroundings [57, 58].

Increasing the number of CO_2 molecules in the system by three, again represented in Fig. 4a, further enhances the effect. By attaching to new areas on the surface of the quantum dot that were not previously exposed to the gas, these CO_2 molecules also occupy active or "green" sites for a chemical reaction. In this way, the system is highly tunable and changes dramatically its electronic properties from a semi-insulating material to a conductor. A large gap, as indicated by the DOS spectrum at 0.395 eV in Fig. 4b reveals the change. In the present case, the HOMO level increases and LUMO level decreases at almost same time leading to large change in electronic structure. A likely reason for this phenomenon is the promotion of electron transfer in CO_2 system through the CO_2 adsorbed sites.

One of the most important parameters for quantifying this mechanism is electrophilicity index that reaches at maximum value of 88.078 eV with inclusion of three CO_2 molecules. This means that the system has been greatly enhanced in its capacity for electron acceptance. The electrophilicity index value was low (2.885 eV) and negligible when CO_2 molecules were not added to the pristine graphene quantum dot, confirming that an electron accepted by the original graphene quantum could hardly be a poor-quality because of the lower energy HOMO level. If one CO_2 molecule was further added, the electrophilicity index value increased remarkably (33.185 eV). When two CO_2 are adsorbed the electrophilicity index is (15.336 eV). The electrophilicity index was further found to decrease to 12.820 eV with the addition of four CO_2 molecules.

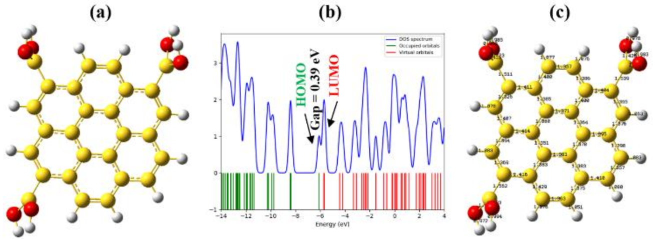

Figure 4: (a) Pure graphene quantum dot structure with three CO_2 molecules, and their (b) DOS, (c) bond lengths.

This non-linear trend shows that the changes are not a straightforward process and instead depend on how the molecules interact with the edge of GQDs. To explain these fluctuations, we can look at the bonding mechanism. In the first two cases, new bonds are formed between CO_2 and the quantum dot surface, changing the energy levels of the HOMO and LUMO levels. Thus, electrophilicity increases with the addition of one molecule and then decreases with two. Electrophilicity is the ability of the system to attract electrons. In the second case, the Fermi energy level is -2.615 eV or higher than the pure state, meaning that the electrons have a weaker binding energy. In the third instance, three CO_2 molecules are present, and new energy levels appear resulting in better orbital matching between the CO molecules and the quantum dot. Thus, the system becomes more unstable and accepts electrons even better. The chemical potential drops to -5.895 eV while the ionization potential soars to 6.092 eV. The large decrease in energy gap from 0.446 eV to 0.395 eV is responsible for the abrupt increase in electrophilicity, suggesting that the system can now attract electrons quite well (Table 2).

These observations suggest that the system is chemically dynamic and stable, which is encouraging for the applications of gas sensing and electrochemical catalysis. Analysis of the structure demonstrated unequivocal changes in bond lengths and angles around the CO_2 binding sites, as displayed in Fig. 4c. This illustrates that the CO_2 modifications are not just electronic and indicate structural changes in the system. Thus, this level of modification is a key point to control the electronic and chemical properties of the quantum dots.

In the case of three CO_2 molecules, as shown in Fig. 5, the electrophilicity changes abruptly from 88.07 eV to 12.82 eV, and simultaneously the chemical potential drops to -2.148 eV and the ionization potential drops to 2.327 eV. This drop is likely due to electron congestion in the quantum dot as it becomes saturated with CO_2 molecules and, therefore, the efficiency of accepting electrons dropped. In summary, we can have different reasons for the electrophilicity increase and drop. The increases may be due to how electrons are interacting collectively, while the decrease in electrophilicity is likely was caused by orbital saturation between the CO_2 and the quantum dot orbitals. The changing of the Fermi level energy in all cases and as it related to the number of CO_2 molecules (as shown in Table 1) can be attributed to differences in charge distribution and free electron balance between the orbitals.

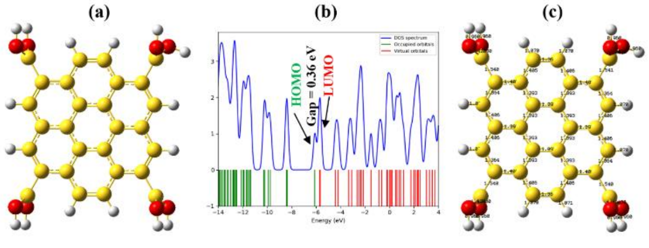

Figure 5: (a) Pure graphene quantum dot structure with four CO_2 molecules, and their (b) DOS, (c) bond lengths.

After modifying the system with four CO_2 molecules, the effects on both the electronic and chemical properties were observable. The four CO_2 molecules did not cover the surface of the quantum dot uniformly. Rather, they attached to different sites on the quantum dot surface, and in an asymmetric manner. This resulted in substantial changes to the organization of charges and electrons within the system. The CO_2 molecules configuration also led to significant modifications of the chemical bonds at the adsorption sites, which are shown in Fig. 5c. These observations essentially point to the significant structural rearrangement at the QD surface arising from likely local charge redistribution. From an electronic point of view, the DOS profile in Fig 5b describes a significant decrease in the energy gap to a very small energy gap (0.36 eV). So that, the CO_2 doping changes electronic character of the system significantly.

The energy levels of the HOMO and LUMO have shifted to -1.968 eV and -2.327 eV, respectively, and are very close to the Fermi level (see Table 1). This suggests this system is now more predisposed to transfer electrons which is favorable for many electronic applications. Interestingly, the difference in the energy gap between the third and fourth modified structures is quite small at only about 0.849%. This suggests that the system has reached a saturation point, where adding more CO_2 molecules doesn't significantly change the electronic properties. In terms of electron affinity (EA), the value dropped to (1.968 eV) in the final case, while it increased to (6.792 eV) in the first modification. This shows that the system was better at capturing electrons in the early stages of modification.

Table 1: The energetic data: the HOMO energies (E_{HOMO}), Fermi level energy (E_{FL}), LUMO energies (E_{LUMO}), energy gap (E_g), change E_g (ΔE_g) and formation energies (E_F) for graphene quantum dot with and without CO_2 molecules. All energies are in eV unit.

System	E_{HOMO}	E_{FL}	E_{LUMO}	E_g	ΔE_g (%)	E_F
Pristine GQDs	-5.490	-3.440	-1.389	4.10	-	-11.391
GQDs with one CO_2 molecule	-8.571	-7.681	-6.792	1.78	-56.6	-11.032
GQDs with two CO_2 molecules	-2.837	-2.615	-2.392	0.45	-89.1	-10.967
GQDs with three CO_2 molecules	-6.092	-5.895	-5.698	0.39	-90.4	-10.680
GQDs with four CO_2 molecules	-2.327	-2.148	-1.968	0.36	-91.2	-10.663

Table 2: The global chemical indexes: the ionization potential (IP), the electron affinity (EA), the chemical potential (μ), the chemical hardness (η), and electrophilicity (ω) calculated for graphene quantum dot with and without CO_2 molecules.

System	I_P	E_A	μ	η	ω
Pristine GQDs	5.490	1.389	-3.440	2.050	2.885
GQDs with one CO_2 molecule	8.571	6.792	-7.681	0.890	33.158
GQDs with two CO_2 molecules	2.837	2.392	-2.615	0.223	15.336
GQDs with three CO_2 molecules	6.092	5.698	-5.895	0.197	88.078
GQDs with four CO_2 molecules	2.327	1.968	-2.148	0.180	12.820

The chemical hardness values also support this observation. As more CO_2 molecules are added, the chemical hardness gradually decreases, as seen in Table 2. This means new energy levels are forming close to the Fermi level, making the system more reactive. At the beginning of the modification, the system shows high chemical reactivity. However, as more molecules are added, signs of saturation appear, and the chemical hardness starts to drop slowly. The progressive modification of the system leads to improved chemical reactivity, greater susceptibility to electric fields, and increased responsiveness to chemical reagents [59, 60].

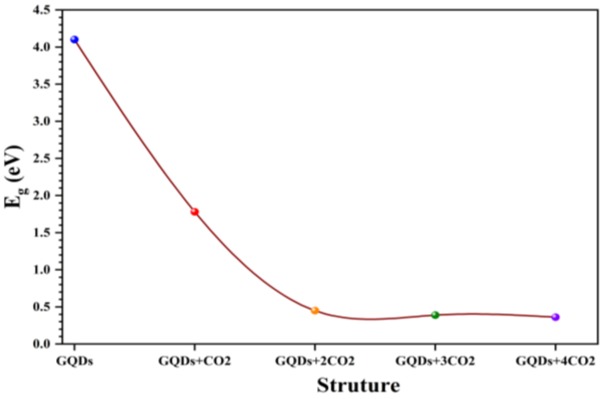

Figure 6: The energy gap of pristine GQDs, GQDs with one CO2, two CO_2, three CO_2, and four CO_2 molecules, respectively.

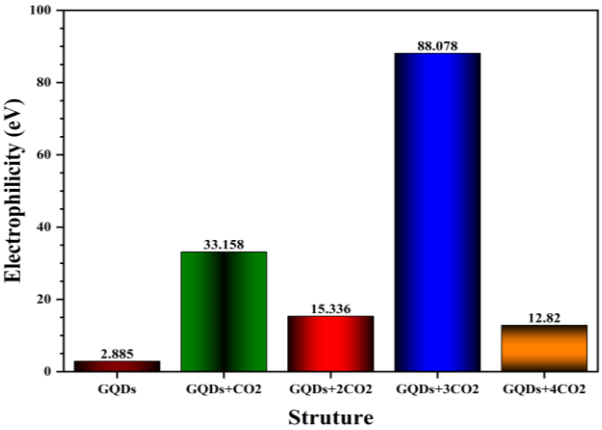

Figure 7: The electrophilicity of pristine GQDs, GQDs with one CO_2, two CO_2, three CO_2, and four CO_2 molecules, respectively.

Fig. 6 and 7 provide a graphical summary of how the energy gap and electrophilicity change continuously as more CO_2 molecules are added. This trend indicates a real modification in the electronic structure of the quantum dots. As a result, the material moves from being a semi-insulator to a weak semiconductor, and finally becomes a strong semiconductor with an energy gap comparable to that of germanium, a well-known semiconductor material.

Also, Fig.8 shows how the formation energy changes with each modification. In the first step, when one CO_2 molecule binds to the surface of the graphene quantum dot, a lot of energy is released. This causes the formation energy to drop sharply from 0 eV to -11.032 eV, which indicates a strong chemical bond between CO_2 and the edge of GQD, see Table 1. In the second and third modifications, the system remains stable, and the formation energy decreases slightly, suggesting that the system continues to accept additional CO_2 molecules without much resistance. However, in the fourth case, once the surface becomes nearly saturated with CO_2 molecules, some repulsion between molecules starts to occur and leads to a small increase in the formation energy. This small increase is when the GQD becomes saturated, and the stability of the modified system begins to decrease.

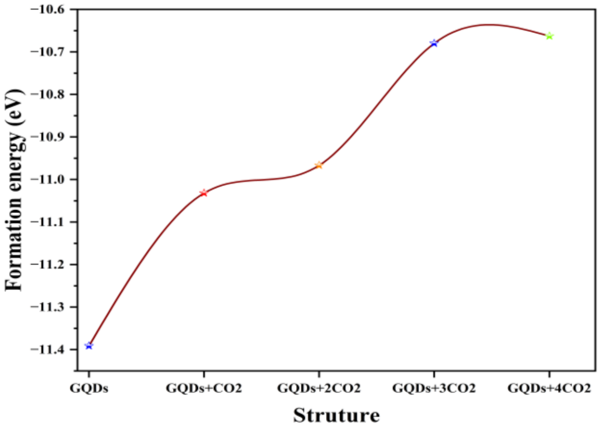

Figure 8: The formation energy of pristine GQDs, GQDs with one CO_2, two CO_2, three CO_2, and four CO_2 molecules, respectively.

IV.CONNLUSION

We performed a DFT-based study to investigate how edge adsorption of the CO_2 molecules modifies electronic and chemical properties of the graphene quantum dots. The results show that this edge adsorption significantly decreases the energy gap by up to 91.2% and alters HOMO and LUMO levels, Fermi energy, and related global chemical descriptors such as the ionization potential, electron affinity, chemical hardness, and electrophilicity. The findings confirm that the CO_2 adsorption occurs primarily at the edges of GQDs, where it drives the most pronounced changes in their electronic behavior. Moreover, a saturation state is reached after adsorption of four CO_2 molecules, beyond which additional adsorption has little influence on band structure or reactivity. This study demonstrates that the CO_2 edge adsorption offers an effective route to manipulate the electronic and chemical properties of the GQDs, paving the way for their future use in nanoelectronics, sensing, and energy devices.

CONFLICT OF INTEREST

Authors declare that they have no conflict of interest.

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