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Fundamental Insights into Ionic Conductivity and Structural Orientation in Single and Holey Multilayer Graphene: A Density Functional Theory Simulation Approach

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ABSTRACT

The recent advancements of graphene in industry and research have garnered considerable attention from researchers due to its perceived benefits across various fields. However, graphene in a single or pure structure has several issues, notably its low conductivity and fewer atoms. Thus, the objective of this study is to comprehend its functionality as a catalyst support material, particularly in applications related to fuel cells. This investigation examines the electronic properties of single-layer, holey graphene and multilayer holey, specifically in terms of surface area and conductivity, utilizing the Density Functional Theory (DFT) Method. The software employed for this purpose is Materials Studio 2016, which is used to develop chosen graphene structures then geometry optimization simulation and analyses electronic properties. The study's outcomes encompass the determination of energy band structure is 0.0 eV for all structures, higher density of states level for holey multilayer graphene (~8.0 electrons/eV at 0.0 eV), Higher Mulliken charge distribution among atoms at -0.103e around the pore, and HOMO-LUMO energy gap (0.30 eV for Graphene, 0.29 eV for holey Graphene, and 0.13 eV for holey multilayer graphene) for all examined structures. The findings reveal that holey multilayer graphene with multiple layers exhibits superior electronic properties and attains a notably high conductivity value. Consequently, this research makes a substantial contribution, particularly in advancing the development of structures for better electronic conductivity.

Keywords: Graphene; Electronic properties; Band Structure; Density of States; Mulliken Charge

INTRODUCTION

Graphene, a two-dimensional wonder material made of a single sheet of carbon atoms structured in a honeycomb lattice, has captured the attention of scholars since its discovery (Dwivedi 2022; Peng et al. 2020; Rajput et al. 2021; Su & Hu 2021), high electron mobility (Chu n.d.; Gracia-Espino et al. 2016; Hassan & Ali 2021), high conductivity (Osman et al. 2022, 2023; Shaari et al. 2018, 2021), and distinctive quantum effects (Peng et al. 2020) are only two of its outstanding electrical characteristics that have stimulated many studies and opened up a wide

range of potential for upcoming technological improvements (Cea & Guinea 2020). Graphene has also achieved excellent physical properties, such as high Young's modulus (1 TPa), excellent fracture strength (125 GPa), super thermal conductivity (5000 W m− 1 K− 1), and high charge-carrier (electron) mobility of 200,000 cm2 V−1 s−1 (Yu et al. 2021). Due to these properties, graphene has various applications, including fuel cell electrodes (Dwivedi 2022; Su & Hu 2021; Yue et al. 2015), optical purposes (Akram et al. 2022; Leng n.d.; Nadeem et al. 2022), and energy storage (Anikina et al. 2022; Umar et al. 2023).

The structure of graphene using DFT has been extensively studied by many researchers, including Hu et al., who have studied the electronic structure of graphene using first principles in Materials Studio® software by analysing band structure and density of states. They found that the energy gap of graphene is zero (0.0 eV) (Hu et al. 2021). In addition, Pakhira et al. (2016) also studied the electronic properties of monolayer graphene and bilayer graphene. By studying the band structure and density of states, they also found that the band gap is zero (0.0 eV). Birowska et al. (Birowska et al. 2011) studied graphene and graphite layers with the density functional theory approach. They also found zero values in the energy gap for graphene and graphite. The holey structure of graphene was studied by Abdelati et al. (Abdelati et al. 2021) by changing the size of the holes in the structure. By analysing the density of states and HOMO-LUMO analysis, they found that new density of states peaks in the absorption spectra of graphene quantum dots appear due to pore formation (approaching the fermi level). Pore passivation seems to impact holey Graphene quantum dot absorption spectra most, although their termination causes marginal peak changes. The study of holey graphene was continued by Barkov et al. by controlling the size of the graphene pores (Barkov & Glukhova 2021). In general, they found the possibility to control the electron conductivity of holey graphene by changing its neck width (the lowest HOMO-LUMO energy gap was recorded at 0.62 eV with a pore size of 7.75 Å).

A study also made by AlZahrani et al. (AlZahrani & Srivastava 2009) for DFT in graphene exhibits that the band structure for graphene is gapless. No band gap was detected as graphene has an overlapping π orbital in its 2p hybridisation (Liu et al. 2010; Tiwari et al. 2020; Tyagi et al. 2019; White et al. 2020). As there was no band gap, the mobility of the electron would be higher (Basri et al. 2022). Additionally, the DOS/PDOS structure of graphene has been demonstrated by Liang et al. and Majidi et al. (Liang et al. 2019a; Majidi et al. 2018) to have a very unusual value of p-orbital at a specific energy level, with the lack of d-orbital since it only possesses the 's' and 'p' orbitals in its electronic configuration (Anikina et al. 2022; Gao et al. 2021), which means that these structures can interact well with the other elements/compounds as a dopant or adsorbent (Arabha & Rajabpour 2021). Kadhim et al. (Kadhim et al. 2023) also experimented on the molecular orbital of this structure. The findings have made graphene a potential structure for upcoming energy research, as the molecular orbital (HOMO-LUMO) gap decreased, indicating a sign of conductivity and selectivity of analytes (Yar et al. 2019).

Usually, graphene exists as a single layer (Gao et al. 2021; Hu et al. 2021; Su & Hu 2021; Tyagi et al. 2019). The active surface area and number of graphene atoms are limited, affecting the conductivity of graphene in terms of energy gap and band structure as it is a charge carrier (Jafri et al. 2010; Kane & Mele 2005). To overcome this problem, theoretically, graphene layers will be added and stacked (either A-A stacking or A-B stacking). The A-B stacking has the lowest ground state energy (Pakhira et al. 2016) because the hollow multilayer graphene has a higher number of atoms and apparent layers. Further studies to explore multilayer porous graphene are essential to prove that porous multilayer graphene has more conductivity, supported by research that states the performance of graphene can be increased by adding more layers to it. Thus, this work investigates the characteristics, band structure, and distribution of density of states (DOS), charge distribution, and orbitals of graphene and hollow multilayer graphene. This study can provide a deeper understanding of the electronic fundamentals of graphene when reducing atoms or adding layers.

METHODOLOGY

Computes of density functional theory (DFT) were completed utilizing the Materials Studio® software package (version 8.0 BIOVIA Inc.) and the CASTEP module. The experiment's work is depicted in Figure 1.

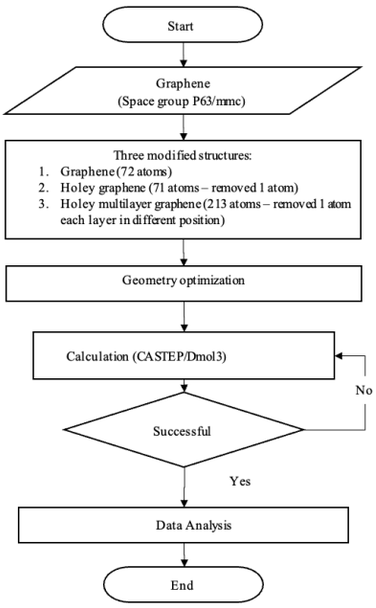


FIGURE 1. Flow chart for the procedure of this simulation study.

The most stable electronic state was identified by geometry optimisation. With a space group of P63/MMC, lattice parameters of a = 2.470 Å, b = 2.470 Å, c = 1.930 Å, and lattice angles of α = 90º, β = 90º, and γ = 120º, the graphene lattice structure was taken from the current model. A 3 x 3 x 1 supercell was used to enlarge the structure for single-layer graphene, and a 3 x 3 x 3 supercell was used for holey multilayer graphene. Graphene and holey multilayer graphene band configurations were first estimated. Using the PBE function in the GGA scheme with a Fermi smearing value of 0.01 Ha (1 Ha = 27.2114 eV) to optimise the structure, DOS and PDOS graphs were constructed for each graphene and its holey multilayer structure. A DN basis set with basis file 4.4 and a fine k-point set (2 x 2 x 1) was also created. The findings section includes a comparison of the data. The Mulliken charge was used to determine the charge population analysis. By creating nonperiodic models and determining the structure's gamma k-point, the highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO-LUMO) energies were determined and diagrammed for each structure.

The essential concepts of molecular structure stability and reactivity are elucidated and rendered universally applicable by the Density Functional Theory (DFT) method (Basri et al. 2022). To establish the interrelations among energy, structure, and reactivity attributes of complexes, pertinent data on chemical potential, electrophilicity index, electronegativity, softness, and hardness have been compiled utilizing the energies associated with the Frontier Molecular Orbitals (FMOs), namely the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO). These parameters play a crucial role in quantum chemical computations. The subsequent equation employs Koopman's theorem, demonstrating how the global reactivity can be deduced from the HOMO-LUMO data value (Equation 1-5).

The chemical potential;

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

where IP = $-E_{HOMO}$ and EA = $-E_{LUMO}$

The hardness;

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

RESULTS AND DISCUSSIONS

GRAPHENE AND HOLEY MULTILAYER GRAPHENE STRUCTURE

After geometry optimization, the Graphene, Holey graphene, and Holey multilayer graphene structures are shown in Fig.2. With a honeycomb-like shape atom, Graphene has a sp2 hybridization along the atomic bonds. The holey multilayer graphene has a weak Van Der Waals force attached to it. In Figure 2, different hole positions from each layer were detected.

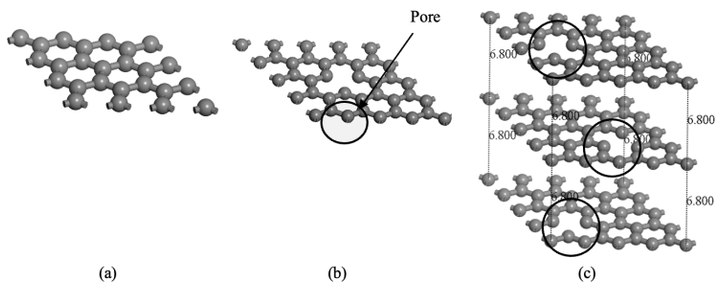


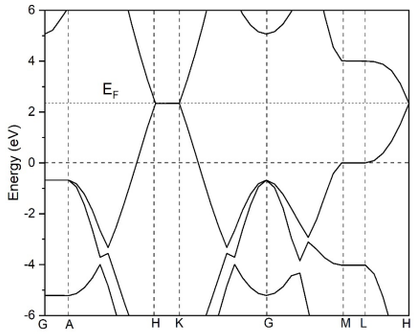
FIGURE 2. (a) Graphene, (b) holey graphene, and (c) holey multilayer graphene structure after geometry optimization

BAND STRUCTURE

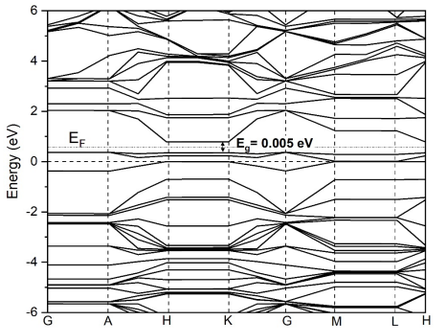
To liberate the electrons from a gap between the low-energy valence and high-energy conduction bands, energy must be applied. The energy level of the valence band is low; if there is a gap between these two levels, the valence band's energy level is lower (Koshino 2019). It is possible to identify between conductors, semiconductors, and insulators using the presence and amplitude of this band gap (Koshino 2019).

In Figure 3(a), the graphene structure exhibits no band gap, consisting of G, A, H, K, G, M, and L critical points (except for holey multilayer graphene, which consists of G-F-Z-Q-G critical points). More bands detected at positive energy value (conductor region). The electrons are more likely to be in a conductive phase, with a Fermi level of 2.25 eV. The results of this study show that graphene has a high concentration of electronic states that are good for energy applications and can be used as an electrode once the energy level reaches a specific threshold. Conductivity is a crucial characteristic for efficient charge transfer in energy electrode materials, such as those employed in batteries or electrochemical cells, during electrochemical operations. The material's conductivity is enhanced due to several bands at positive energy levels, suggesting the availability of a wide range of electronic states that are available for charge carriers to traverse.

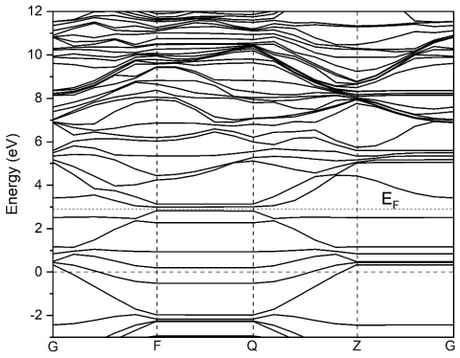
The holey and multilayer graphene in Figure 3(b) and Figure 3(c) are more likely to exhibit the same situation as the graphene structure (band gap of 0.005 eV in Figure 3(b) and zero band gap in Figure 3(c)) with Fermi levels of 0.05 eV and 2.8 eV, respectively. However, many bands were detected at both regions (positive and negative energy values) compared to Figure 3 (a), with the positive energy region having more bands, indicating that the electrons are more in the conducting region than the insulating region. The argument that holey and multilayer graphene will likely have band structures similar to single-layer graphene but with small Fermi level and band gap alterations highlights how structural changes affect electrical properties. Because it has nanoscale gaps or vacancies in the graphene lattice, holey graphene can disturb the electrical band structure locally. Multilayer graphene's interlayer interactions change its electrical properties compared to pure single-layer graphene. Despite expected similarities, the finding of multiple bands in the positive and negative energy regions of holey and multilayer graphene, with a focus on the positive energy region, is an interesting variation from the pristine graphene structure. This suggests that structural alterations create a more diverse electronic environment with more conductivity-friendly electronic states. More bands are found in the positive energy region, implying greater conductivity than single-layer graphene due to electron mobility and metallic behavior. Single-layer, multilayer, and holey graphene have different Fermi levels, demonstrating the intricate relationship between electrical structure and structural morphology. Fermi level is a reference energy level for occupied and unoccupied electronic states at zero temperature. The Fermi level shifts in holey and multilayer graphene show how structural changes affect electronic properties. Charge carrier concentration, band dispersion, and doping may cause these changes. Clarifying these complex electrical characteristics may affect the customization of graphene-based materials for materials engineering and design applications. Holey and multilayer graphene have more bands in the positive energy area, which may boost conductivity and make them promising electrodes for supercapacitors and lithium-ion batteries or any other energy storage devices. The tunability of electronic properties through structural modifications allows graphene-based materials to be optimized for semiconductor and optoelectronic applications, where band structure and carrier transport are crucial.



(a)



(b)



(c)

FIGURE 3. *Ab initio* band structure of (a) graphene, (b) holey graphene, and (c) holey multilayer graphene

Graphene, as a distinctive semiconductor, constitutes a single-layer graphite sheet. Analogous to graphite, graphene exhibits unique characteristics arising from its orthogonal π and π* orbitals, which do not undergo overlap but rather intersect solely at six specific points known as Dirac Points (Wang et al. 2018). Consequently, graphene functions as a semimetal with a zero-band gap (Duan et al. 2015). This can support the evidence of the zero-band gap for graphene, holey graphene, and holey multilayer graphene. Unfortunately, the band gap value of holey graphene is 0.005 eV most probably because of the more accurate GGA-PBE functional calculation applied.

A crucial component of graphene's electrical characteristics, the band gap varies with the number of layers, providing tunability that can be used in a variety of ways. The band gap can be altered by many techniques, including chemical and electric fields, when the number of graphene layers rises. This is important for applications in electronics and optoelectronics. In theory, the band gap should vary with the number of layers. Because of its negligible band gap, single-layer graphene is not widely used in semiconductor applications. However, because to variations in the charge distribution between layers, bilayer graphene can display a tunable band gap up to 0.29 eV when exposed to an electric field (Witjaksono & Junaid 2018).

A vertical electric field or surface adsorption can be used to induce and adjust a band gap in few-layer graphene, especially in ABC-stacked arrangements. The band gap varies in size depending on the metal used for adsorption, and it is directly related to the charge transfer density (Quhe et al. 2013). Furthermore, top and back gates can be used to adjust the band gap in multilayer graphene. The gap size is determined by the number of layers and stacking symmetry (Avetisyan et al. 2009b).

Band gap engineering techniques include electric field application. By varying the gate voltage, a band gap that is induced in multilayer graphene by applying a perpendicular electric field can be adjusted. The circular asymmetry of the band structure affects the gap size, and this approach works for both even and odd numbers of layers (Avetisyan et al. 2009a). Additionally, chemical functionalisation is a different technique that can change the optical band gap in graphene by attaching chemical groups like epoxy, hydroxyl, and carboxyl, as shown by both theoretical and experimental research (Bhatnagar et al. 2017). Surface adsorption and superstrate interactions, on the other hand, allow metals to be adsorbed on graphene surfaces and interact with polarisable superstrates to greatly increase the band gap, which is advantageous for optoelectronic devices and digital applications (Hague 2011; Quhe et al. 2013).

DENSITY OF STATES

The Density of States structures for Graphene, holey graphene, and holey multilayer graphene were plotted (Figure 4). Holey Graphene possessed a higher DOS value than holey multilayer graphene and Graphene. Comparing holey multilayer graphene and Graphene, the holey multilayer structure had a higher DOS value than the single Graphene at -5 eV and -10 eV. The higher DOS value is due to the many atoms captured in that structure. However, at 12.5~18.0 eV, there is an additional DOS value for Holey graphene and Holey multilayer graphene. Some researchers found zero DOS at the fermi level (Nurhafizah et al. 2022).

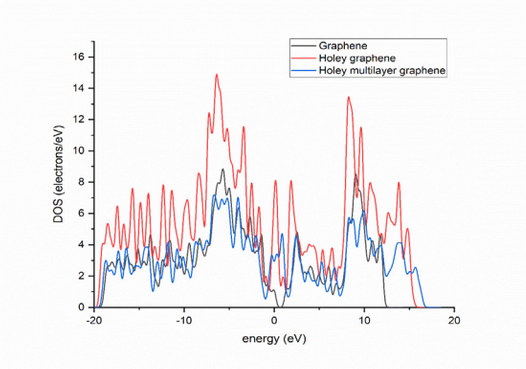


FIGURE 4. Density of states for graphene, holey graphene, and holey multilayer graphene

The elevated DOS value seen in holey graphene indicates a greater abundance of electronic states within the material in comparison to holey multilayer graphene and pristine graphene. The enhanced accessibility of electronic states can influence the electronic characteristics of the material. The existence of voids or imperfections in holey graphene is likely responsible for the observed augmentation in the density of electronic states. Defects can create extra energy levels within the band structure, which might impact the density of states (DOS). Introducing flaws into holey graphene can be helpful for some applications since it allows for the fine-tuning of its electrical characteristics. It enables the alteration of the electronic structure of the material, potentially customising it for specific electrical or optoelectronic functions. In addition, a greater DOS value indicates a greater abundance of accessible electronic states, which might affect the electrical conductivity of the material. Materials with a higher density of states (DOS) may display distinct electrical characteristics, which can be significant in applications such as sensors or electronic devices. The comparison of density of states (DOS) values offers a quantitative assessment of the variations in electronic structure across the three materials. This analysis provides valuable insights into how the presence of defects affects the density of electronic states.

The partial Density of States (DOS) data for all structures (Figure 5) were graphically represented to examine the individual atom contributions within the structure. The colours employed in the plot denote distinct orbitals, where black corresponds to s-orbitals, red represents p-orbitals, and blue signifies d-orbitals in the Partial DOS (PDOS). The PDOS displays the various energy and PDOS levels. Holey multilayer graphene in Figure 5(c) exhibits a greater PDOS level of p-orbital than Graphene in a range of -5.0 to -10.0 eV, about 25.0 electrons/eV. Consequently, there is an increased concentration of electronic states linked to p-orbitals in holey multilayer graphene within this particular range of energy. The more considerable s-orbital PDOS value of 15.0 electrons/eV at a range of -15.0 to -17.5 eV is also present in holey multilayer graphene. In specific energy ranges, holey Graphene exhibits comparatively larger PDOS values for both the s and p orbitals (highest s orbital at -20 to 10 eV, highest p orbital at -8.5 eV). All structures lack any noticeable d-orbital curve value. Large electrical conductivity is also provided by the high DOS close to Fermi energy (Singh et al. 2020).

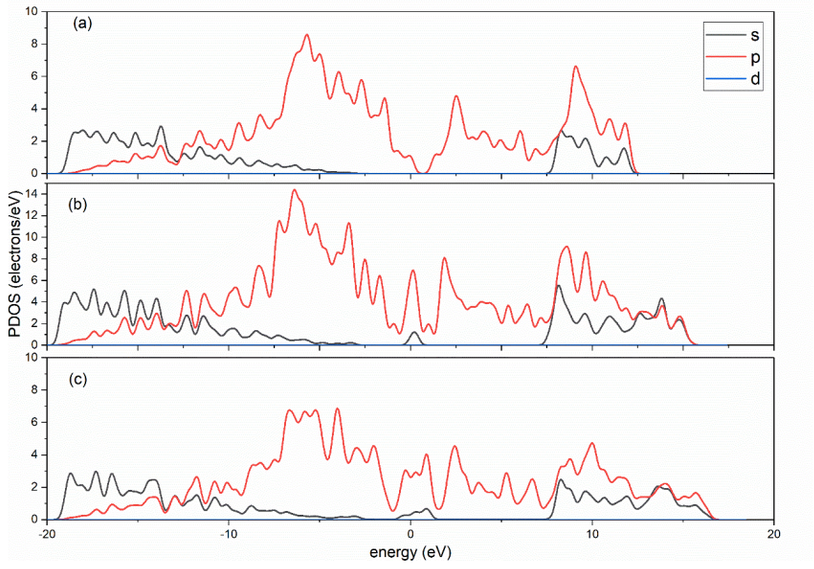


FIGURE 5. Partial density of states of (a) graphene, (b) holey graphene, and (c) holey multilayer graphene

The DOS plot can be used to visually represent the range of energy levels that are allowed for transitions, such as thermal excitation. An occupied band refers to an electron that is present in the valence band. By absorbing energy and momentum, it has the ability to transition into a conduction band characterised by a Fermi energy of 0 eV. The energy absorbed is equivalent to the energy discrepancy between the final and initial states in the conduction band. The probability of this occurrence increases with higher initial and ultimate energies, yet this condition remains valid regardless of energy.

MULLIKEN CHARGE

The application of Mulliken charge analysis to these structures allowed for the investigation of electron transfer. Figure 6 depicts the movement of electrons by analysing the Mulliken Charge distribution in each atom. The findings indicate that regular Graphene exhibits a neutral electron flow, with a net charge of 0.00e. This suggests that neutral Graphene lacks the ability to transport electrons. In a study conducted by Marahatta (2019), the neutral graphene Mulliken charge was observed to vary between -0.004 and +0.004 e, indicating distinct atomic charge values (Marahatta & Marahatta 2019). This is primarily attributed to the influence of the symmetrical lattice structure employed. In comparison to non-perforated Graphene, the perforated section (located closest to the deleted carbon atom) had a greater charge distribution of -0.103e, suggesting that these atoms were prepared to acquire electrons from another atom. Nevertheless, electron transmission is unattainable near the periphery of holey Graphene (Figure 6(b)). In Figure 6(c), the holey multilayer graphene exhibits a charge of around -0.10e, which is consistent with the charge seen in each layer of holey graphene.

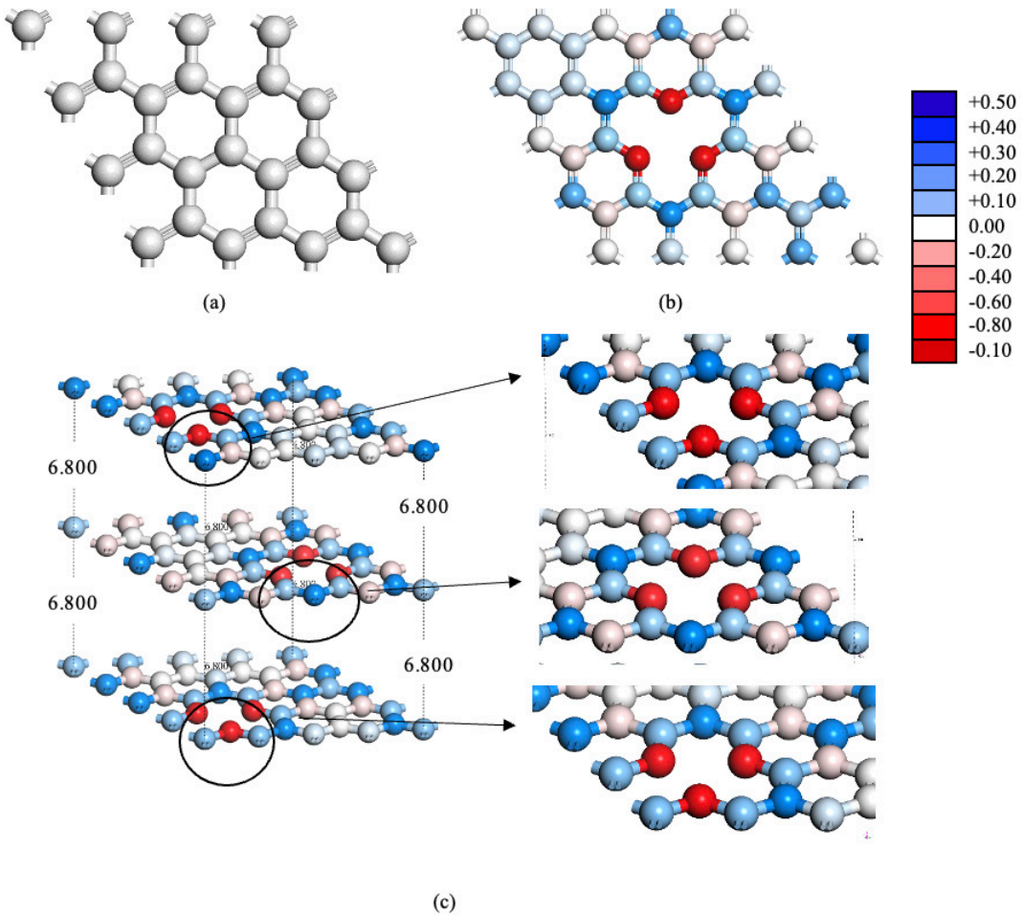


FIGURE 6. Mulliken charge distribution of (a) graphene, (b) holey graphene, and (c) holey multilayer graphene. The +ve sign indicates losing electrons, while the -ve sign indicates gaining electrons. A -0.103e charge was detected around the holey part.

According to the findings presented in Figure 6, it is proposed that the porous component plays a vital role in facilitating electron transport by including dopant atoms, such as P and N, in addition to the commonly researched C atoms. An investigation conducted by Liang et al. in 2019 examined the utilisation of graphene structures doped with phosphorus (P) and nitrogen (N) for the purpose of oxygen reduction reaction (ORR) (Liang et al. 2019). They found out that there is about 0.746 charge transferred from the structure (Graphene-P, N) to the chemisorbed O_2 molecule. Transferred electrons from the substrate to O_2 can extend the O-O bond and partially occupy the $2\pi^*$ anti-bonding orbital, which lowers the bond order and encourages the $4e^-$ pathway (Liang et al. 2019). For further studies, this structure can be added with another catalyst (especially a transition element combined with Oxygen such as MnO_2).

The Mulliken charge distribution patterns that have been found provide useful insights into the electrical interactions occurring within holey and multilayer graphene arrangements. These insights are particularly relevant in understanding the impact of structural alterations on the localization and transmission of charges. The utilisation of a symmetrical lattice structure in these materials is of utmost importance in determining the occurrence of charge redistribution events. This structure dictates the spatial organisation of electronic states and impacts the likelihood of electron transfer activities at locations.

The investigation shows that the perforated regions of holey graphene have different charge distribution features compared to non-perforated graphene, especially near the removed carbon atoms. The higher charge distribution of -0.103e indicates that these atoms are more likely to accept electrons from nearby species. The presence of defect sites in the holey graphene lattice highlights the possibility of catalytic activity. These sites, characterised by localised charge imbalances, play a crucial role in facilitating electron transfer processes that are necessary for catalytic reactions.

Nevertheless, although there is an improved distribution of charges near defect sites, the research also suggests that electron transmission is not possible towards the outer edges of holey graphene. This observation implies that there may be constraints in electron transport processes near structural defects, indicating the need for careful placement of catalysts to enhance catalytic efficiency and electron transfer kinetics.

The identified Mulliken charge distribution patterns offer valuable insights into the electrical interactions taking place in holey and multilayer graphene structures. Specifically, these findings provide insights into the impact of structural alterations on the localization and propagation of electric charges. The symmetric lattice structure of these materials plays a critical role in governing charge redistribution processes as it dictates the spatial arrangement of electronic states and influences the probability of electron transfer activities at certain sites.

The study reveals distinct characteristics of charge distribution within the perforated regions of holey graphene in comparison to non-perforated graphene, particularly in close proximity to carbon atoms that have been removed. The charge distribution of -0.103e seen in this case suggests that these atoms have a higher propensity to accept electrons from neighbouring species. This event emphasises the potential for defect spots inside the holey graphene lattice to serve as catalytic sites, where localised charge imbalances boost electron transfer processes required for catalytic reactions.

Additionally, the research findings indicate that electron transmission is not viable in proximity to the periphery of holey graphene, despite the enhanced charge distribution observed at defect sites. The presence of structural faults may impose limitations on electron transport processes, necessitating the strategic placement of catalysts to optimise catalytic efficiency and electron transfer kinetics.

Furthermore, the charge distribution patterns observed in holey multilayer graphene exhibit a consistent trend with those observed in individual layers of holey graphene, characterised by an average charge of approximately -0.10e per layer. This consistency highlights the ability to duplicate charge redistribution events over multiple graphene layers and demonstrates how multilayer designs might enhance catalytic activity by promoting advantageous electronic interactions between adjacent layers.

The findings underscore the importance of strategic positioning to enhance catalytic performance on graphene substrates, while simultaneously mitigating potential limitations associated with electron transport in the vicinity of defects. Optimal catalyst placement would involve focusing on regions with enhanced charge distribution, such as defect sites in holey graphene, as this would expedite the electron transfer mechanisms required for catalytic reactions. Furthermore, the potential for optimising catalytic performance can be realised through the utilisation of interlayer electronic interactions and tailored charge redistribution events in multilayer graphene frameworks.

In conclusion, the analysis of Mulliken charge results provides valuable insights into the electrical properties and catalytic phenomena exhibited by both holey and multilayer graphene structures. The identified charge distribution patterns demonstrate the influence of structural symmetry on electron transfer pathways and underscore the potential for strategically positioning catalysts to optimise catalytic

performance. These findings enhance our foundational understanding of catalysts based on graphene and provide opportunities for the careful development and design of catalyst-support systems for various energy conversion and environmental remediation purposes.

HOMO-LUMO ANALYSIS

The energy, Highest Occupied Molecular Orbital (HOMO), and Lowest Unoccupied Molecular Orbital (LUMO), and other characteristics of a molecule must be understood to calculate its chemical reactivity (Basri et al. 2022). The concepts of HOMO and LUMO are valuable tools for comprehending the electronic arrangement and chemical responsiveness of molecules, especially within the realm of molecular orbital theory and organic chemistry. The energy of the LUMO that accepts electrons is equivalent to the electron affinity (EA) when molecules interact. The ionisation potential (IP) is directly connected to the energy of the electron-donating HOMO. The HOMO-LUMO energy gap, which refers to the difference in energy levels between the HOMO and the LUMO, is crucial in evaluating the electrical conductivity of molecules. Furthermore, it clarifies the specific characteristics of the ultimate charge transfer interaction that occurs within a molecule. The disparity in energy levels between the HOMO and LUMO directly impacts the level of ease at which a reaction can take place. Reduced energy gaps typically suggest more advantageous interactions and decreased activation energies for reactions.

The correlation between the HOMO and LUMO is crucial for comprehending molecular reactivity and chemical bonding. Molecular orbital interactions can occur when the HOMO of one molecule interacts with LUMO of another molecule during a chemical reaction. The intersection of the HOMO and LUMO results in the creation of novel molecular orbitals, which have an impact on the overall electronic configuration of the system. Molecules with substantial HOMO-LUMO energy gaps have limited chemical reactivity and excellent kinetic stability (Basri et al. 2022). Electrons may only be taken out of the HOMO level (below) by adding an electron to the LUMO level (above). Therefore, adding an electron to the high-lying LUMO to remove electrons from the low-lying HOMO is energetically unfavourable (Basri et al. 2022). For example, compared to molecules with a tiny HOMO-LUMO energy gap, those with a big gap are more likely to remain stable and show more chemical stiffness (Basri et al. 2022). The HOMO and LUMO energy levels diverge significantly when the HOMO-LUMO energy gap is substantial.

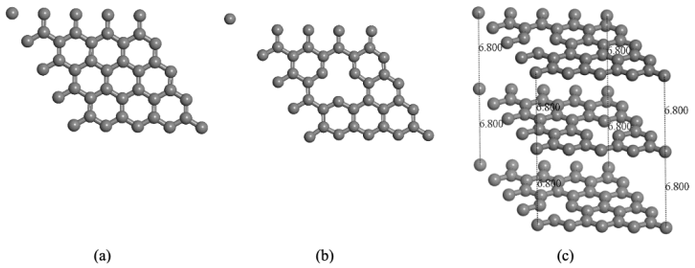


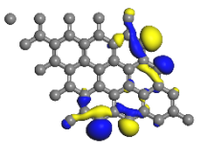
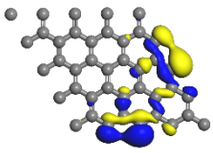
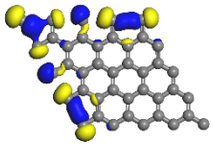
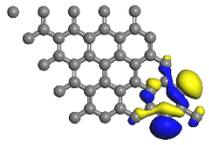
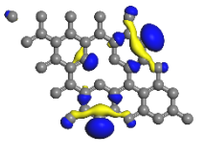
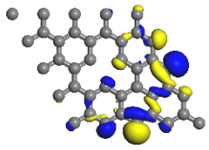
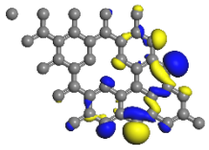
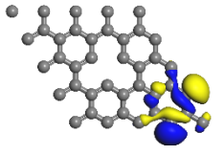
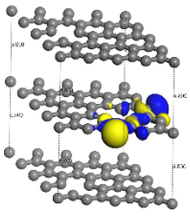
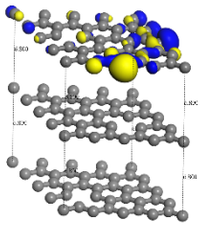
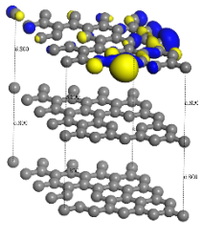
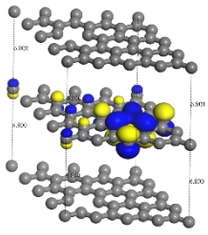
FIGURE 7. Nonperiodic structure for (a) graphene, (b) holey graphene and (c) holey multilayer graphene

In this part, the analysis of HOMO-LUMO requires a nonperiodic structure to obtain the orbitals accurately. Figure 7 shows the nonperiodic structure of both Graphene by removing their brilluion zones. In Figure 7(a), figure 7(b), and Figure 7(c), holey multilayer graphene exhibits some shape defects compared to the previous structure. The HOMO-LUMO energy and its diagram are shown in Table 1. The finding indicates that the HOMO-LUMO energy gap for holey multilayer graphene is the lowest (0.13 eV) compared to holey Graphene (0.29 eV) and Graphene (0.30 eV). A smaller HOMO-LUMO energy gap is associated with materials that have enhanced electrical conductivity and a higher likelihood of participating in electronic transitions.

The term "holey" denotes the presence of flaws or perforations inside the structure of graphene. These flaws can have a substantial effect on the electrical characteristics of the material. Holes or flaws in graphene create localised states within its band structure, which impact the energy levels of the HOMO and the LUMO. The presence of a narrow HOMO-LUMO energy gap (0.13 eV) in holey multilayer graphene indicates a significant level of electron delocalization and a relatively low energy barrier for the movement of charge carriers between the HOMO and LUMO states. This attribute is advantageous for electronic applications as it signifies enhanced conductivity and potential utilisation in devices where electrical transport is vital.

Holey graphene has a greater disparity in energy levels between its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), with a gap of 0.29 eV, in contrast to holey multilayer graphene. This indicates that there is a greater resistance for the movement of charge carriers and potentially reduced ability to conduct electricity as compared to holey multilayer graphene. The energy difference between the HOMO and LUMO in pristine graphene is significantly greater, measuring 0.30 eV. Compared to holey graphene and holey multilayer graphene, pure graphene may have lower electronic conductivity because it lacks imperfections that might create extra electronic states.

TABLE 1. HOMO-LUMO energy value for all structures

Structure	Energy (eV)				
	HOMO-1	HOMO	LUMO	LUMO+1	E_{LUMO}-E_{HOMO}
Graphene					0.30
	-6.03	-5.74	-5.44	-5.38	
Holey Graphene					0.29
	-6.86	-6.84	-6.55	-6.56	
Holey multilayer graphene					0.13
	-6.41	-6.39	-6.26	-6.21	

Data from HOMO and LUMO values are used to calculate the global reactivity parameter value, which is shown in Table 2, calculated by using equation 1-5. The findings data indicates that graphene and modified holey structures' chemical potential values differ significantly. Graphene has a lower chemical potential than holey Graphene (-6.70 eV) and holey multilayer graphene (-5.88 eV) at -5.59 eV. The chemical potential (μ) is a thermodynamic parameter that quantifies the energy needed to introduce an additional particle into a system, while keeping the volume and entropy unchanged. Within the realm of electronic systems, it is commonly linked to the energy threshold at which electrons are introduced or eliminated. A decreased chemical potential at a particular energy level signifies a reduced energy demand for introducing an electron into the system. This research indicates that the existence of defects in holey graphene and holey multilayer graphene is likely to affect the chemical potential. Defects can introduce supplementary electronic states inside the band structure, so influencing the distribution of electrons and the material's overall chemical potential. In addition, a reduced chemical potential indicates that, at the specified energy level, graphene has a higher electron concentration or electron density in comparison to holey graphene and holey multilayer graphene. These changes can affect the electrical characteristics and chemical responsiveness of the materials. Comparing the chemical potentials quantitatively allows us to understand how the electronic structure and electron distribution change among the three materials at the given energy level.

The electrophilicity, electronegativity, and value softness indices all show a pattern that is quite similar to this one. Graphene, as a pure substance, possesses a highly organised and uniform arrangement, leading to reduced electrophilicity and electronegativity. Graphene is renowned for its exceptional electrical conductivity and comparatively low reactivity. The softness index of graphene can be affected by its regular structure, indicating a certain degree of stability. Introducing flaws, or gaps, in holey graphene can enhance its electrophilicity. Defects can function as sites that take electrons, resulting in an increased electrophilic nature. Defects in a material can augment its electron-attracting capacity, hence potentially increasing its electronegativity. Defects inside the material might lead to local fluctuations in electron density, hence increasing the softness index and rendering the material more susceptible to deformation. Introducing flaws in multilayer graphene can enhance its electrophilicity and electronegativity, similar to holey graphene. The softness index may see a comparable rise as a result of the existence of flaws in the multilayer configuration.

Compared to graphene and holey graphene (0.15 eV), holey multilayer graphene has a lower chemical hardness (0.05 eV) calculated using equation (2), suggesting an increased ability for charge transfer. The reduced hardness in holey multilayer graphene is primarily attributed to the introduction of pores, which create localized energy states, leading to a smaller HOMO-LUMO gap and enhanced electron delocalization (Papageorgiou et al. 2017). Moreover, the multilayer structure facilitates additional interlayer interactions that reduce confinement effects and further lower η (Yu et al. 2020). These structural modifications result in increased electrical conductivity and chemical reactivity, making holey multilayer graphene a promising candidate for applications in energy storage, catalysis, and electronic devices (Lokhande et al. 2020).

TABLE 2. Chemical potential, hardness, softness, and electronegativity value list for graphene, holey graphene and holey multilayer graphene

Global Reactivity	Graphene	Holey graphene	Holey multilayer graphene
Chemical potential (μ/eV)	-5.59	-6.70	-6.33
Chemical Hardness (η/eV)	0.15	0.15	0.07
Chemical Softness (σ/eV^{-1})	3.33	3.45	7.69
Electronegativity (χ/eV)	5.59	6.70	6.33
Electrophilicity index (ω/eV)	104.16	154.56	307.74

CONCLUSIONS

This paper highlights the electronic characteristics of graphene and how adding layers and holes affected those characteristics. Graphene's molecular characteristics play a significant role in enhancing its functionality for a wide range of applications, particularly in energy (as a fuel cell material). The absence of a band gap in the holey multilayer graphene band structure was found through investigation, suggesting that this element conducts electricity. Furthermore, 2.5 eV is the Fermi level. The holey multilayer structure has a high curvature and strong electron mobility, according to curvature testing. Our findings shows that the atom closest to the holey section experiences a stronger negative Mulliken charge distribution of -0.103e, according to the Mulliken charge of those structures (tendency to gain electron). Comparing holey multilayer graphene to graphene and holey graphene, DOS research revealed that the former had a greater density of states value and the latter its partial density of states. The Holey multilayer graphene contains a tiny gap of 0.13 eV, according to the HOMO-LUMO study. For instance, this improves the structure's conductivity better compared to the conventional graphene.

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DECLARATION OF GENERATIVE AI AND AI-ASSISTED TECHNOLOGIES IN THE WRITING PROCESS

During the preparation of this work, the authors used QuillBot in order to improve language and readability. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

DECLARATION OF COMPETING INTEREST

None.

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