Electronic Structure and Energetic Stability of Corner-Engineered Zigzag Graphene Nanoribbons Synthesized by a Bottom-Up Approach

Prabhat Ranjan[1], Dr. Uma Shankar Chaudhary[2]

[1]Research Scholar (PAT-2020), Enrollment No. Phy.08/20, Dated-10.04.2024 University Dept. of Physics BNMU Madhepura

[2]Professor & Head, University Dept. of Physics BNMU Madhepura

DOI: https://doi.org/10.51584/IJRIAS.2026.11100037

Received: 21 October 2026; Accepted: 26 October 2026; Published: 03 November 2026

ABSTRACT

Zigzag graphene nanoribbons have attracted considerable research interest because of their distinctive edge states, tunable electronic properties and potential applications in nanoscale electronic and spintronic devices. In this study, the electronic structure and energetic stability of corner-engineered zigzag graphene nanoribbons synthesized through a bottom-up approach are investigated. Particular emphasis is placed on understanding how nanometer-scale corners, edge configurations and atomic arrangements influence the electronic energy spectrum, density of states, band structure and structural stability. The bottom-up synthesis strategy offers opportunities for precise control over the atomic geometry and edge topology, enabling systematic investigation of structure–property relationships. The energetic stability of different corner configurations can be assessed by comparing their total energies and formation energies, while electronic characteristics can be evaluated using appropriate first-principles computational methods, such as density functional theory. The study also examines how variations in corner geometry affect the formation of localized electronic states, the tuning of the band gap and the emergence of potentially spin-polarized edge states. This investigation provides a theoretical framework for understanding the relationship between atomic-scale structural modifications and the resulting electronic behavior of zigzag graphene nanoribbons. The findings are expected to support the rational design of structurally stable, electronically tunable graphene nanostructures for future applications in nano electronics, quantum devices and advanced carbon-based functional materials.

Keywords: Zigzag Graphene Nanoribbons; Corner Engineering; Electronic Structure; Energetic Stability; Bottom-Up Synthesis; Edge States; Spin-Polarized States.

1. INTRODUCTION

Graphene nanoribbons have emerged as promising nanomaterials for next-generation electronic and spintronic applications because of their exceptional electrical properties, tunable band structures and atomic-scale dimensions [1]. Among different configurations, zigzag graphene nanoribbons exhibit distinctive edge-localized electronic states that strongly influence their magnetic behavior, energy gaps and overall electronic characteristics. Engineering the atomic geometry of these nanoribbons, particularly through the introduction of nanometer-scale corners, offers an effective strategy for modifying their electronic properties and controlling localized states. The bottom-up synthesis approach enables the fabrication of structurally precise graphene nanoribbons through the controlled assembly of molecular precursors [2]. Compared with conventional top-down fabrication methods, this approach provides improved control over ribbon width, edge topology and atomic arrangements. Corner engineering introduces additional opportunities to tailor the spatial distribution of electronic states and investigate the relationship between structural configurations and energetic stability [3]. Understanding these relationships requires systematic examination of the electronic band structure, density of states, total energy and

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume XI Issue X October 2026

formation energy using suitable computational techniques, particularly density functional theory. Despite significant progress in graphene nanoribbon research, the combined effects of atomic-scale corner geometry and structural stability require further investigation. Therefore, this study focuses on the electronic structure and energetic stability of corner-engineered zigzag graphene nanoribbons synthesized through a bottom-up approach, providing insights into their potential development for advanced nanoelectronic and quantum technologies.

2. SYNTHESIS

The synthesis of corner-engineered zigzag graphene nanoribbons through a bottom-up approach involves the controlled assembly of molecular precursors to achieve precise atomic structures and well-defined edge configurations [4]. This strategy typically consists of two principal stages surface-assisted polymerization and subsequent cyclodehydrogenation as shown in fig.-(2) and fig.-(3).

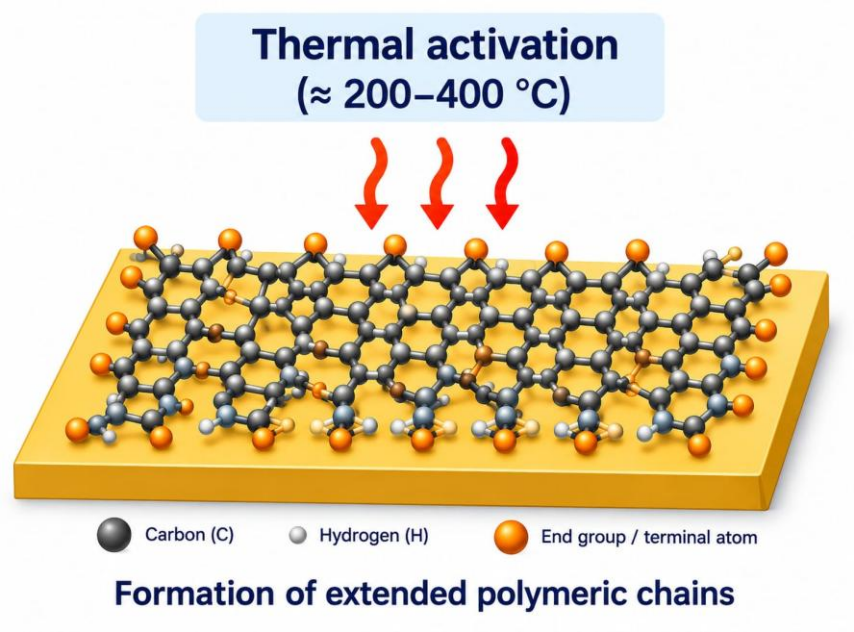
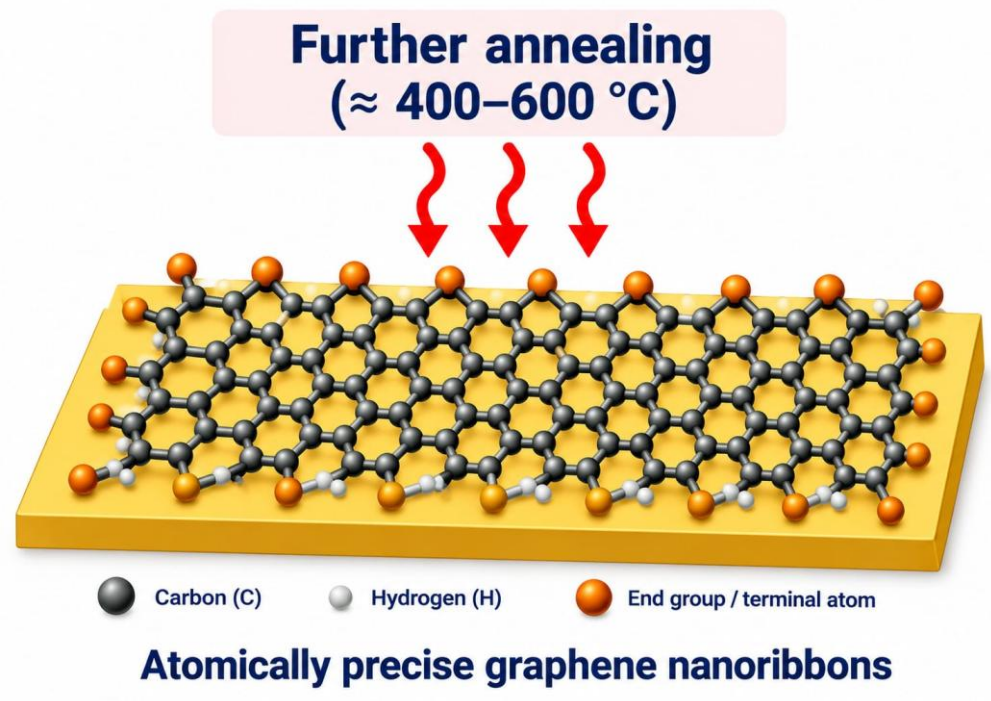


Fig.-(1) Surface-Assisted Polymerization



ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume XI Issue X October 2026

Fig.-(2) Cyclodehydrogenation

Initially, appropriately designed halogen-functionalized aromatic precursor molecules are deposited onto a suitable metallic substrate under controlled ultrahigh-vacuum conditions. Upon thermal activation, the precursor molecules undergo surface-assisted coupling, forming extended polymeric chains. Further annealing promotes intramolecular cyclodehydrogenation, leading to the formation of atomically precise graphene nanoribbons. Corner engineering can be introduced through the molecular design of precursor units containing specific geometric features, which determine the positions, angles and structural configurations of the resulting corners [5]. By adjusting precursor architecture and reaction conditions, different nanoribbon geometries can be investigated to establish relationships between atomic arrangement and electronic behavior. Appropriate substrate selection and temperature control are essential for facilitating molecular coupling, minimizing structural defects and promoting the formation of stable nanostructures.

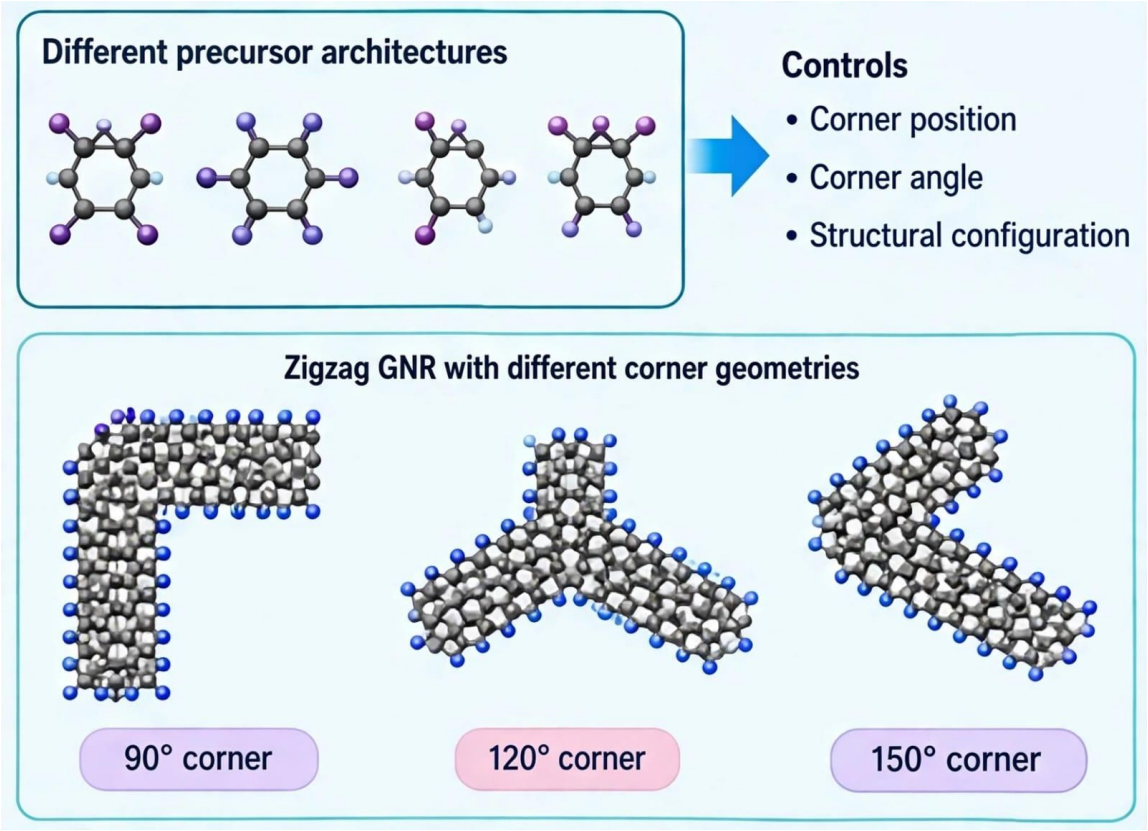


Fig.-(3) Corner Engineering

The synthesized nanoribbons can be characterized using scanning tunneling microscopy and spectroscopy, atomic force microscopy and complementary spectroscopic techniques to examine their morphology, atomic arrangement and electronic states [6]. Atomic structures reconstructed from experimental data can then be analyzed and validated through density functional theory (DFT) calculations. This integrated synthesis and characterization framework enables systematic investigation of corner-dependent electronic structures and energetic stability, supporting the development of precisely engineered graphene nanomaterials for advanced nanoscale applications.

3. TUNING THE ELECTRONIC PROPERTIES

The electronic properties of corner-engineered zigzag graphene nanoribbons (ZGNRs) can be tailored by controlling their atomic geometry, edge configuration, ribbon width and corner arrangement. Zigzag edges support localized electronic states near the Fermi level, which significantly influence the band structure, magnetic ordering and electrical conductivity of these nanostructures [7]. Introducing nanometer-scale corners provides an additional degree of freedom for modifying the spatial distribution of electronic wave functions and regulating interactions between neighboring edge states.

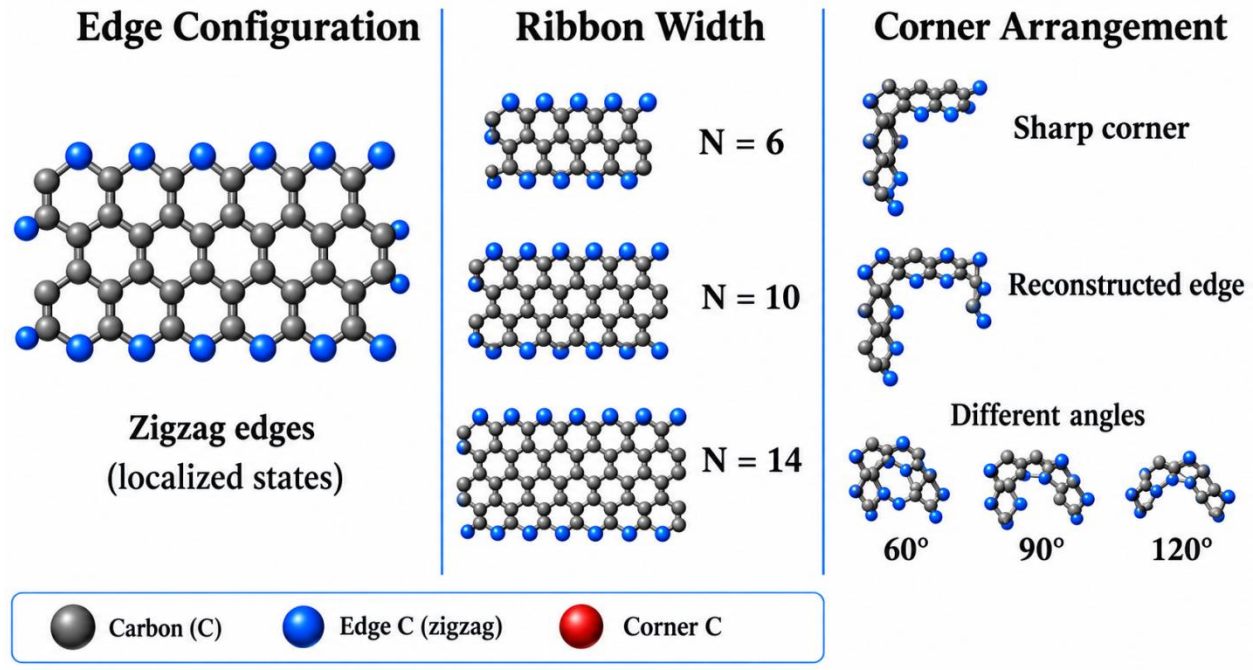


Fig.-(4) Structural Parameters for Tuning

The electronic behavior of a corner-engineered ZGNR can be described using the Hamiltonian

$$\hat{H}\Psi_n(r) = E_n\Psi_n(r) \cdots\cdots(1)$$

where $\hat{H}$ is the electronic Hamiltonian, $\Psi_n(r)$ is the n-th electronic wave function, and E_n is its corresponding energy eigenvalue. For a simplified tight-binding model of a graphene nanoribbon

$$\hat{H} = -\sum_{\langle i,j\rangle,\sigma} t_{ij}(R)\, c_{i\sigma}^{\dagger} c_{j\sigma} + h.c. \cdots\cdots(2)$$

where, t_{ij} represents the hopping energy between neighboring carbon atoms, while R denotes the atomic geometry, including ribbon width, edge orientation and corner arrangement. Corner geometry can affect the degree of electronic localization and alter the energy levels associated with specific atomic configurations [8]. Sharp corners, reconstructed edges and variations in corner angles may produce distinct electronic states, potentially resulting in changes in the band gap and density of states as shown in fig.-(5) and fig.-(6).

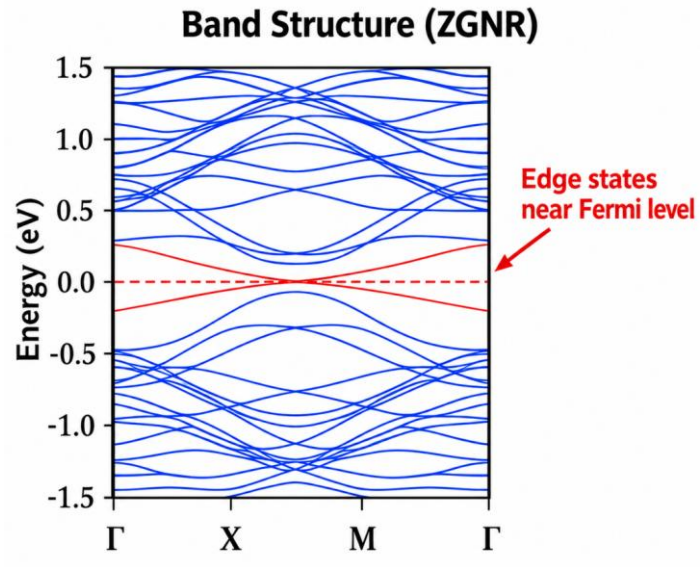


Fig.-(5) Effect on Electronic Structure

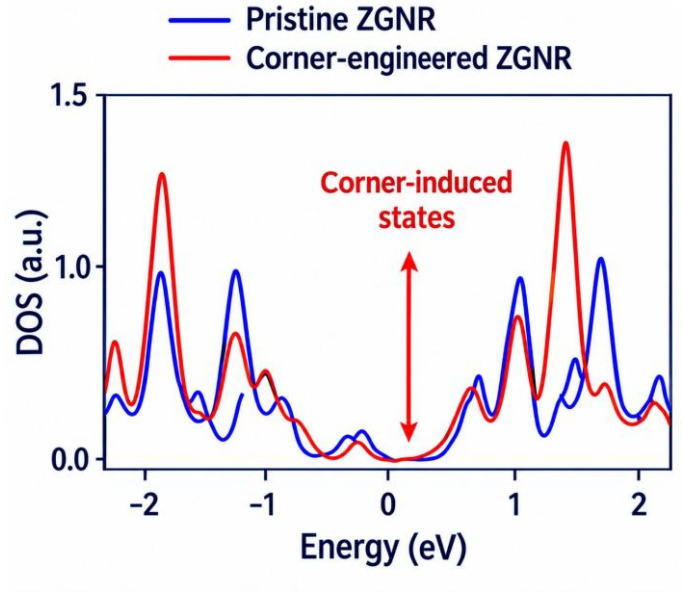


Fig.-(6) Graph Between Energy and Density of States (DOS)

The effect of corner engineering on electronic localization can be quantified using the inverse participation ratio (IPR)

$$IPR_n = \sum_i |\Psi_n(i)|^4 \quad \cdots\cdots(3)$$

For a normalized wave function, a larger IPR generally indicates stronger localization, whereas a smaller IPR indicates greater spatial delocalization. The electronic coupling between two localized corner states can be expressed as

$$t_{12} = \langle \Psi_1 | \hat{H} | \Psi_2 \rangle \quad \cdots\cdots(4)$$

where t_{12} represents the coupling strength between states localized at different corners. This coupling depends on their spatial separation, wave-function overlap, and local atomic structure. Furthermore, the coupling between localized states at different corners can influence the overall electronic response of the nanoribbon. These effects can be systematically investigated using density functional theory (DFT), which provides information about electronic band structures, projected density of states, charge distributions and spin-polarized configurations. The bottom-up synthesis approach offers opportunities to realize these structural modifications through rational molecular precursor design [9]. By correlating calculated electronic properties with atomic-scale structural parameters, the influence of corner engineering can be evaluated systematically. Such investigations can establish useful design principles for controlling electronic behavior in grapheme nanoribbons. Ultimately, corner-dependent electronic tuning may contribute to the development of nanoscale transistors, spintronic components and quantum devices with precisely controlled electronic characteristics. The electronic band gap is determined by the difference between the conduction-band minimum and the valence-band maximum

$$E_g = E_{CBM} - E_{VBM} \quad \cdots\cdots(5)$$

To evaluate the corner geometry modifies the band gap, one can compare different structural configurations

$$\Delta E_g = E_g(\theta_2) - E_g(\theta_1) \quad \cdots\cdots(6)$$

where, θ_1 and θ_2 represent two different corner angles or structural configurations. The equation quantifies the change in the calculated band gap between these configurations.

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume XI Issue X October 2026

4. TUNING THROUGH EDGE ORIENTATION

Edge orientation plays a crucial role in determining the electronic structure and energetic stability of corner-engineered zigzag graphene nanoribbons (ZGNRs). The arrangement of carbon atoms along the ribbon boundaries influences the distribution of electronic states, magnetic interactions and energy dispersion near the Fermi level. Zigzag-oriented edges are particularly significant because they support localized edge states that can strongly affect the magnetic and transport properties of graphene nanostructures [10]. Modifying edge orientation through atomic-scale corner design provides an opportunity to manipulate these characteristics. In corner-engineered nanoribbons, variations in edge direction, corner angle and atomic connectivity may influence the interaction between adjacent edge states. Such structural variations may modify the spatial distribution of electronic states, the band-gap properties and the density of available electronic states. In addition, alterations in edge configuration can influence the relative stability of different spin arrangements and determine the energetic favorability of competing atomic structures [11]. Therefore, understanding the relationship between edge orientation and electronic behavior is essential for developing structurally stable graphene nanoribbons with tailored functionalities. The bottom-up synthesis approach facilitates precise control over edge topology through the rational selection of molecular precursors. Computational methods, particularly density functional theory, can be employed to evaluate the electronic band structure, total energy and spin-polarized states associated with different edge configurations [12]. A comparative analysis of the findings helps clarify how variations in edge orientation influence structural stability and electronic properties. Such investigations can establish useful design principles for optimizing zigzag graphene nanoribbons for future nanoelectronic and spintronic applications.

5. TUNING THROUGH WIDTH CONTROL

Ribbon width is a fundamental structural parameter governing the electronic properties and energetic stability of corner-engineered zigzag graphene nanoribbons (ZGNRs). Changes in width modify quantum confinement, the interaction between opposing zigzag edges and the spatial distribution of electronic wave functions [13]. Consequently, width-dependent variations can influence the band structure, density of states, magnetic ordering and energy gap of these nanostructures. Investigating width control is therefore essential for understanding the relationship between atomic dimensions and electronic behavior [14]. In narrow ZGNRs, interactions between electronic states localized at opposite edges can significantly influence their energy levels and magnetic configurations. As the ribbon width increases, these interactions generally weaken, potentially changing the electronic spectrum and the stability of different spin arrangements. When nanometer-scale corners are introduced, their influence may also depend on ribbon width, as the spatial separation between corner-localized states and edge states can alter their coupling [15]. These effects provide additional opportunities to regulate electronic characteristics through combined width and corner engineering. The bottom-up synthesis approach enables systematic width control through the design of molecular precursors with predefined structural dimensions. Density functional theory (DFT) can be applied to evaluate and contrast the total energy, formation energy, electronic band structure and spin-dependent states of graphene nanoribbons with varying widths as shown in fig.-(7).

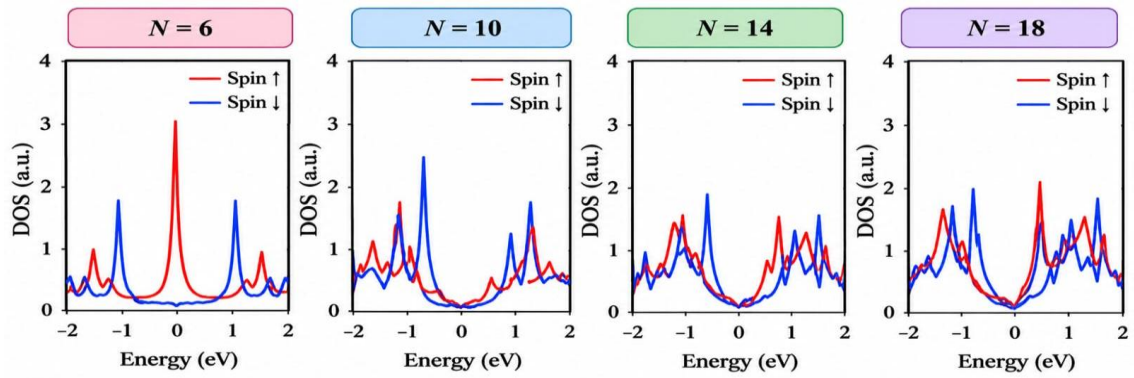


Fig.-(7) Density of States (DOS) versus Ribbon Width

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume XI Issue X October 2026

Examining these parameters helps determine the most stable atomic arrangements and elucidate the relationship between ribbon dimensions and their electronic characteristics. Understanding these width-dependent effects can support the rational design of graphene nanoribbons for nanoscale transistors, spintronic devices and other advanced electronic applications.

6. TUNING THROUGH DOPING

Doping represents an effective strategy for modifying the electronic structure and energetic stability of corner-engineered zigzag graphene nanoribbons (ZGNRs). Introducing selected heteroatoms, such as nitrogen, boron or sulfur, into the carbon framework can alter the local electronic environment, charge distribution and bonding characteristics as shown in fig.-(8). These modifications provide opportunities to control the Fermi level, density of states, band-gap characteristics and potential spin-dependent behavior of graphene nanostructures [16]. The resulting properties depend on the dopant species, concentration, substitutional position and local atomic configuration. In corner-engineered ZGNRs, the effects of doping may be particularly significant near corners and zigzag edges, where localized electronic states can strongly influence the overall electronic response. Dopant atoms introduced at these locations may modify local charge density, influence magnetic interactions and create additional electronic states within the energy gap. However, the energetic favorability of different doping configurations must be carefully evaluated because variations in local bonding and atomic coordination can affect structural stability.

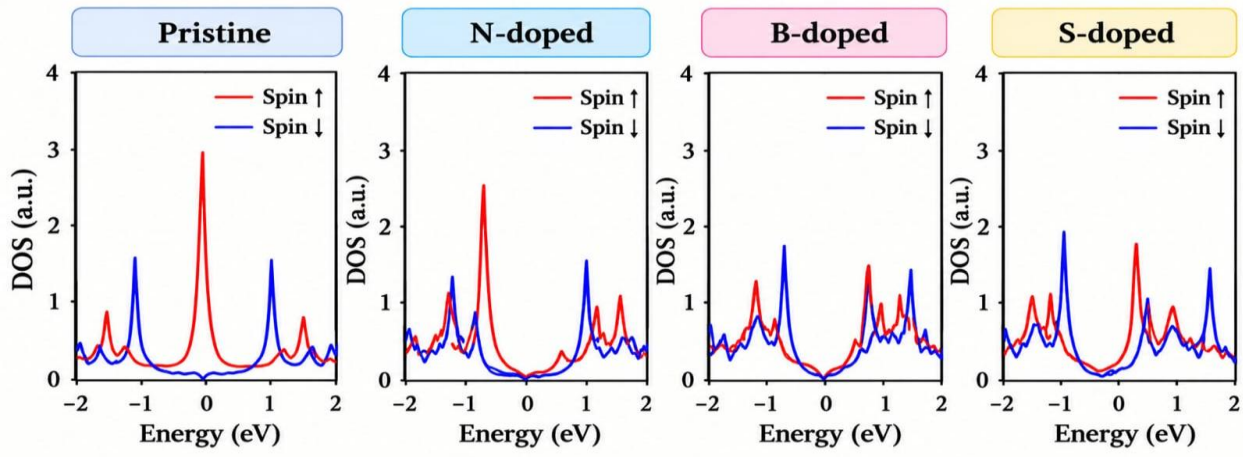


Fig.-(8) Tuning Through Doping From Different Materials

The bottom-up synthesis approach offers potential opportunities to incorporate selected heteroatoms through the rational design of molecular precursors [17]. Density functional theory calculations can be employed to investigate dopant formation energies, electronic band structures, charge transfer and spin-polarized states. Comparing different dopant positions and concentrations can identify configurations that provide favorable combinations of stability and electronic tenability [18]. Such investigations can contribute to the development of functional graphene nanoribbons for nanoelectronics, spintronics and emerging quantum technologies.

7. TUNING THROUGH STRAIN

Strain engineering provides an effective approach for controlling the electronic properties and energetic stability of corner-engineered zigzag graphene nanoribbons (ZGNRs). Applying mechanical deformation modifies carbon–carbon bond lengths, bond angles and orbital interactions, thereby influencing the electronic band structure and spatial distribution of electronic states [19]. Depending on its magnitude and direction, strain can alter the band gap, density of states, magnetic interactions and charge transport characteristics of these nanostructures. Consequently, strain offers an additional mechanism for tailoring their functional properties without necessarily introducing chemical impurities. In corner-engineered ZGNRs, the effects of strain may become particularly important near corners and zigzag edges, where localized electronic states are sensitive to changes in atomic geometry [20]. Tensile or compressive strain

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume XI Issue X October 2026

can modify the coupling between edge-localized states and corner-associated electronic states, potentially influencing their energy levels and spin configurations. Furthermore, strain-induced structural distortions may affect the relative energetic stability of different corner arrangements. Excessive deformation, however, can introduce unfavorable bonding configurations or promote structural reconstruction. The influence of strain can be investigated using density functional theory calculations by applying controlled uniaxial or biaxial deformation to optimized nanoribbon structures. Relevant parameters include strain-dependent total energy, band structure, density of states and spin polarization. Comparing these quantities enables the identification of mechanically stable configurations and reveals relationships between deformation and electronic behavior. Integrating strain engineering with bottom-up synthesis and atomic-scale corner design could provide valuable opportunities for developing adaptable graphene nanoribbons for advanced nanoelectronic and spintronic applications.

8. RESULTS AND DISCUSSION

The electronic structure and energetic stability of corner-engineered zigzag graphene nanoribbons (ZGNRs) can be understood by examining the relationships between atomic geometry, edge configuration and electronic-state distribution. Density functional theory (DFT) offers a reliable computational approach for analyzing relaxed atomic configurations, electronic band structures, density-of-states distributions, and formation energies to assess the stability and electronic behavior of nanostructures. These analyses help identify how nanometer-scale corners influence the structural and electronic characteristics of graphene nanoribbons. Corner geometry is expected to affect the localization and interaction of electronic states associated with zigzag edges. Variations in corner angles, atomic connectivity and ribbon width may modify the energy spectrum and alter the distribution of states near the Fermi level. Similarly, edge orientation and heteroatom doping can introduce additional changes in charge distribution and spin polarization. These effects highlight the importance of atomic-scale structural control in tailoring the electronic behavior of graphene nanostructures. Energetic stability can be assessed by comparing the total energies or formation energies of different corner configurations under consistent computational conditions. Structures exhibiting lower formation energies are generally more favorable relative to the chosen reference states, although kinetic factors and synthesis conditions may also influence experimental realizability. Furthermore, strain can modify both structural stability and electronic characteristics through changes in carbon–carbon bonding. Overall, combining bottom-up synthesis with computational analysis offers a promising framework for investigating structure–property relationships and guiding the design of stable, electronically tunable zigzag graphene nanoribbons for future nanoelectronic and spintronic applications.

9. CONCLUSIONS

This study highlights the significance of corner engineering in controlling the electronic structure and energetic stability of zigzag graphene nanoribbons (ZGNRs) synthesized through a bottom-up approach. Atomic-scale modifications in corner geometry, edge orientation, ribbon width, doping and strain provide valuable opportunities to regulate electronic states, band-gap characteristics, charge distribution and magnetic behavior. Density functional theory offers an effective computational framework for investigating these structural and electronic properties and comparing the relative stability of different nanoribbon configurations. Understanding the relationship between atomic arrangement and energetic stability is essential for identifying promising structures for practical applications. Integrating precise molecular synthesis with theoretical modeling can further improve the understanding of corner-dependent electronic behavior and support the rational design of functional graphene nanostructures. These insights may contribute to the development of advanced nanoelectronic, spintronic and quantum devices. Future investigations should emphasize experimental validation, synthesis reproducibility and the influence of environmental conditions on the stability and performance of corner-engineered graphene nanoribbons.

REFERENCES

1. J. Zhang, B. Ghawri, D. Dutta, R. Fasel, M. Calame, G. Borin Barin, and M. L. Perrin, "Bottom–Up-Synthesized Graphene Nanoribbons for Nanoelectronics," *Nature Reviews Materials*, vol. 11, pp. 194–212, 2026.
2. T.-J. Liu, F. M. Arnold, A. Ghasemifard, Q.-L. Liu, D. Golze, A. Kuc, and T. Heine, "Electronic Structure and Topology in Gulf-Edged Zigzag Graphene Nanoribbons," *Physical Review Materials*, vol. 9, Art. no. 014203, 2025.
3. W. Jiang, Z.-F. Liu, Q.-P. Wu, and X. Xiao, "Role of Edge Reconfiguration in Generating Corner States in Zigzag Graphene Nanoribbons," Physica E: Low-Dimensional Systems and Nanostructures, vol. 172, Art. no. 116260, 2025.
4. J. Min, X. Ou, X. Liu, W. Zou, Z. Li, L. Deng, and Y. Deng, "Edge Effect Induces Spin-Gapless Semiconducting and Half-Metallic Properties of N-Doped Zigzag Graphene Nanoribbons," Physica E: Low-Dimensional Systems and Nanostructures, vol. 167, Art. no. 116172, 2025.
5. F. R. E. Borges, J. A. Gonçalves, R. J. C. Batista, T. M. Manhabosco, and E. E. de Moraes, "Advancing Carbon Nanoribbons: Structural and Electronic Properties," Computational Condensed Matter, vol. 47, Art. no. e01293, 2026.
6. Y. Fu, H. Yang, Y. Gao, L. Huang, and co-authors, "On-Surface Synthesis of NBN-Doped Zigzag-Edged Graphene Nanoribbons," *Angewandte Chemie International Edition*, vol. 59, no. 23, pp. 8873–8879, 2020.
7. M. Pizzochero et al., "Edge Disorder in Bottom-Up Zigzag Graphene Nanoribbons: Implications for Magnetism and Quantum Electronic Transport," *The Journal of Physical Chemistry Letters*, vol. 12, no. 19, pp. 4692–4696, 2021.
8. P. P. Shinde, J. Liu, T. Dienel, O. Gröning, T. Dumslaff, M. Mühlinghaus, A. Narita, K. Müllen, C. A. Pignedoli, R. Fasel, P. Ruffieux, and D. Passerone, "Graphene Nanoribbons with Mixed Cove-Cape-Zigzag Edge Structure," *Carbon*, vol. 175, pp. 50–59, 2021.
9. N. T. Cuong, M. Otani, and S. Okada, "Absence of Edge States near the 120° Corners of Zigzag Graphene Nanoribbons," *Physical Review B*, vol. 87, Art. no. 045424, 2013.
10. P. Ruffieux, S. Wang, B. Yang, C. Sánchez-Sánchez, J. Liu, T. Dienel, L. Talirz, P. Shinde, C. A. Pignedoli, D. Passerone, T. Dumslaff, X. Feng, K. Müllen, and R. Fasel, "On-Surface Synthesis of Graphene Nanoribbons with Zigzag Edge Topology," *Nature*, vol. 531, pp. 489–492, 2016.
11. S. Wang, L. Talirz, C. A. Pignedoli, X. Feng, K. Müllen, R. Fasel, and P. Ruffieux, "Giant Edge State Splitting at Atomically Precise Graphene Zigzag Edges," *Nature Communications*, vol. 7, Art. no. 11507, 2016.

A. Yamanaka and S. Okada, "Energetics and Electronic Structure of Graphene Nanoribbons under a Lateral Electric Field," *Carbon*, vol. 96, pp. 351–361, 2016.

12. S. Okada, "Energetics of Nanoscale Graphene Ribbons: Edge Geometries and Electronic Structures," *Physical Review B*, vol. 77, Art. no. 041408(R), 2008.
13. K. Wakabayashi, K. Sasaki, T. Nakanishi, and T. Enoki, "Electronic States of Graphene Nanoribbons and Analytical Solutions," *Science and Technology of Advanced Materials*, vol. 11, no. 5, Art. no. 054504, 2010.
14. E. Louis, E. San-Fabián, G. Chiappe, and J. A. Vergés, "Electron Enrichment of Zigzag Edges in Armchair-Oriented Graphene Nanoribbons Increases Their Stability and Induces Pinning of the Fermi Level," *Carbon*, vol. 154, pp. 211–218, 2019.
15. T. Asano and J. Nakamura, "Edge-State-Induced Stacking of Zigzag Graphene Nanoribbons," ACS Omega, vol. 4, no. 26, pp. 22035–22040, 2019.
16. J. Cai et al., "Atomically Precise Bottom-Up Fabrication of Graphene Nanoribbons," *Nature*, vol. 466, pp. 470–473, 2010.
17. P. H. Jacobse, A. Kimouche, T. Gebraad, M. M. Ervasti, J. M. Thijssen, P. Liljeroth, and I. Swart, "Electronic Components Embedded in a Single Graphene Nanoribbon," Nature Communications, vol. 8, Art. no. 119, 2017.

18. J. Yamaguchi, H. Hayashi, H. Jippo, A. Shiotari, M. Ohtomo, M. Sakakura, N. Hieda, N. Aratani, M. Ohfuchi, Y. Sugimoto, H. Yamada, and S. Sato, "Small Bandgap in Atomically Precise 17-Atom-Wide Armchair-Edged Graphene Nanoribbons," Communications Materials, vol. 1, Art. no. 36, 2020.
19. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, "The Electronic Properties of Graphene," *Reviews of Modern Physics,* vol. 81, no. 1, pp. 109–162, 2009.