

A review of the types and properties of B and N co-doped graphene

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ABSTRACT

This paper discusses the different types of B/N co-doped graphene, such as neighborhood, intercalation, para-doping on the carbon six-membered ring of monolayer graphene, and monolayer and stacked doping of h-BN with graphene. The structure and characterization of each type are examined. Additionally, the impacts of B/N co-doping on the optical properties, O₂ adsorption, and chemical properties of graphene are explored. Finally, the future challenges in boron and nitrogen co-doped graphene research are outlined.

KEYWORDS

Graphene; Doping; Type; Property

1. INTRODUCTION

Since its discovery through mechanical exfoliation in 2004, great efforts and resources have been devoted by the scientific fraternity to explore the extraordinary physical and chemical properties of graphene [1, 2]. Two-dimensional graphene consists of a solitary layer of carbon atoms organized in a honeycomb pattern. Every carbon atom employs three of its four valence electrons to create robust σ -bonds via sp^2 hybridization with adjacent carbon atoms. The remaining electron in the perpendicular σ_z orbital forms a delocalized Π bond above and below the carbon plane. This distinctive electron-valence bond configuration underpins the diverse and remarkable characteristics of graphene [3].

Graphite exhibits strong electrical conductivity due to the intersection of its valence band and conduction band at the Dirac point, leading to a nought band gap. In contrast, graphene possesses exceptionally high electron mobility, reaching values of $140,000 \text{ cm}^2/(\text{V} * \text{S})$ and $4000 \text{ cm}^2/(\text{V} * \text{S})$ at moderate carrier concentrations [4]. This remarkable electrical characteristic enables graphene to serve as an effective conductor of electricity, leading to its utilization in applications such as supercapacitors and micro-nano-electromechanical devices. However, the absence of a band gap in graphene limits its potential in electronic devices, causing issues like excessive current leakage and low switching ratios [5]. To leverage graphene's capabilities in electronics, the need to introduce a band gap becomes imperative. Current research explores various methods to create a band gap, including quantum confinement, doping, and symmetry-breaking techniques [6]. Both doping and symmetry-breaking methods induce specific defects in graphene, emphasizing the importance of studying stable defect formation methods to facilitate the opening of band gaps in graphene.

In previous studies focusing on graphene doping, researchers explored doping with metal atoms like Au, Co, and Mn [7]. Chen Qingling's team investigated the impact of active metal atom doping, specifically Li, Na, and K atoms, observing that the structural size of graphene significantly increased

post-doping, creating practical application limitations [8]. Laref conducted first-principle studies to assess the alterations in energy band structures, density of states, and optical absorption of graphene following boron and nitrogen doping [9]. The results indicated that boron-doped monolayer graphene exhibited energy band distribution closer to the Fermi energy level compared to nitrogen-doped graphene. Ji-Sun Han's team synthesized graphene co-doped with boron and nitrogen at varying temperatures and utilized it as an electrocatalyst for redox reactions, highlighting the pivotal role of boron and nitrogen in catalyzing the redox process through synergistic effects [10]. Additionally, the doping of hexagonal boron nitride (h-BN) with graphene showcased numerous outstanding properties. h-BN emerged as an excellent substrate for graphene preparation due to its flat surface and absence of dangling bonds and charge impurities. Overall, B\N co-doped graphene exhibits diverse and exceptional properties, offering promising applications. This study aims to summarize and conclude the plethora of types and properties associated with graphene co-doped with boron and nitrogen.

2. TYPES OF BORON AND NITROGEN CO-DOPING AND THEIR CHARACTERIZATION

2.1. B/N-neighbor, Inter, Pair Co-Doped Graphene

2.1.1. Characterization of graphene with B\N neighborhood co-doped

Ren Fucheng's research team employed density functional theory for determining the state density and band structure of boron and nitrogen co-doped graphene. Their findings revealed a 25% doping ratio of B and N atoms in the graphene structure. In the Brillouin region, at the point of high symmetry G, a division was observed at the valence band's peak and the conduction band's base, resulting in a band gap value of 2.406 eV. This band gap value places boron and nitrogen co-doped graphene outside the typical semiconductor span of 0-3 eV, eliminating its semi-metallic conductivity properties [11].

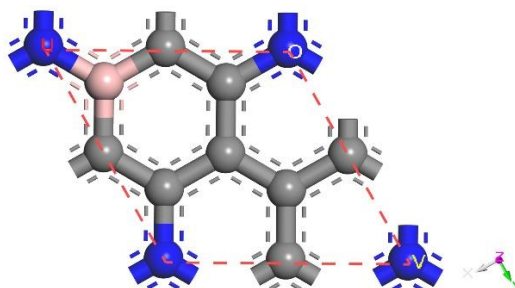


Figure 1. The structure of B\N neighborhood co-doped graphene

(The blue corresponds to nitrogen, pink indicates boron, and black denotes carbon)

2.1.2. Characterization of graphene with B\N interstitial co-doped

The band structure and state density of this graphene type significantly deviate from that of intrinsic graphene. In B and N interstitial doped graphene, the energy bands undergo a split. In contrast to neighboring doped graphene, the division between the valence's peak and the conduction bands' base happens in the Brillouin zone's highly symmetrical H-K, leading to a distinct band gap. The measurement of the band gap stands at 1.296 eV, which is roughly half of the gap value noted in the adjacent doped graphene formation [11].

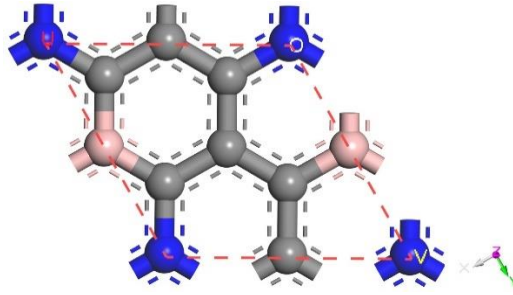


Figure 2. The structure of B\N interstitial co-doped graphene

(The blue represents nitrogen, pink denotes boron, and black signifies carbon)

2.1.3. Characterization of graphene with B and N para-doped

The energy band structure and density of states of the doped graphene are akin to those observed in neighboring and interstitial doping scenarios, with boron and nitrogen atoms doped in a 25% para-doping ratio for substituting carbon atoms within the graphene framework. The top of the valence band and bottom of the conduction band in the doped graphene undergo a split, observed in the Brillouin zone at the high G-point, leading to a band gap value of 2.572 eV. Notably, the energy band of the neighboring co-doped graphene also aligns with the G-point in the Brillouin zone, with a band gap value of 2.406 eV, closely resembling the para-doped co-doped configuration [11].

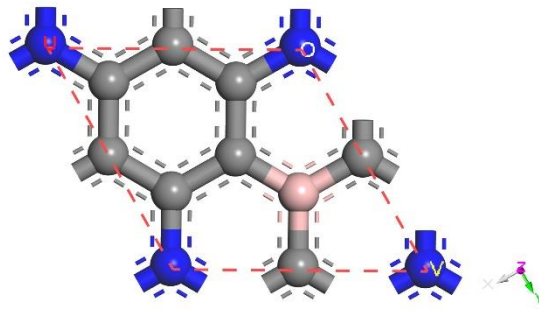


Figure 3. The structure of B\N para-doped graphene

(The blue signifies nitrogen, pink indicates boron, and black represents carbon)

2.2. Hexagonal Boron Nitride Doped Graphene

2.2.1. Co-planar doping of hexagonal boron nitride with graphene

By employing atmospheres like $\text{NH}_3\text{-BH}_3$ to provide both B and N sources simultaneously, it becomes easier to form h-BNC mixed two-dimensional compounds [5]. The binding energy of intrinsic graphene is measured at 7.95 eV/atom, while h-BN has a binding energy of 7.12 eV/atom, indicating the stability of their structures [12, 13]. The B-N bond length is calculated to be 1.45 Å, and the C-C bond length is 1.42 Å, with a minimal difference between the two bond lengths [14, 15]. The band gap of h-BN is 5.97 eV, whereas intrinsic graphene is devoid of a band gap [16]. The compatibility between h-BN and graphene is evident, with h-BN doping promoting the band gap opening in graphene. Prashant P. Shinde's team conducted calculations on the band gap of h-BN doped graphene with various doping concentrations and types, comparing them to intrinsic graphene [17]. The band gap is determined by the narrowest region of graphene and remains consistent regardless of the concentration and shape of boron nitride patches. In graphene's thinnest area, characterized by two to five zigzag-c chains, the band gap maintains a relative stability near the GGA figure of about 0.75 eV.

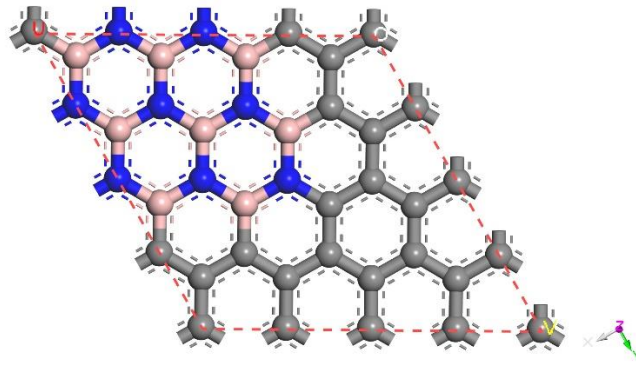


Figure 4. The structure of Co-planar doping of hexagonal boron nitride with graphene
(The blue represents nitrogen, pink indicates boron, and black signifies carbon)

2.2.2. Hexagonal boron nitride and graphene stacked doping

Matching the h-BN and graphene lattices vertically in a stack allows for more controlled doping modulation. Hexagonal boron nitride (h-BN) exhibits a planar hexagonal structure akin to graphene, possesses high insulating properties, and offers excellent lattice matching with graphene [18]. Hence, h-BN can be utilized as a substrate for graphene to modulate the energy bands effectively. In a typical scenario, one or more layers of h-BN are initially grown on a copper sheet via chemical vapor deposition (CVD), typically utilizing reaction sources like $B_3N_3H_6$ or NH_3-BH_3 . Subsequently, the cultivation of graphene occurs atop the h-BN layer using CVD, resulting in a vertical multilayer structure comprising "graphene/h-BN/copper" [19].

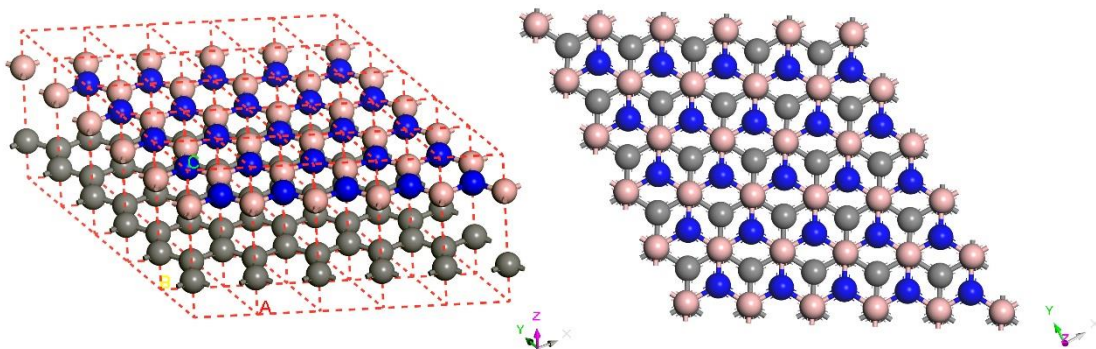


Figure 5. The structure of Hexagonal boron nitride and graphene stacked doping
(The blue signifies nitrogen, pink represents boron, and black denotes carbon)

3. PROPERTIES OF B\N CO-DOPED GRAPHENE

3.1. Optical Properties Of B\N Co-Doped Graphene

Graphene undergoes significant changes in its optical properties when subjected to an elevated concentration of B\N co-doping. As the concentration increases, the primary absorption peak of graphene co-doped with B\N consistently shifts towards longer wavelengths, starting from the initial position at 4 eV. At a doping concentration of 75%, the peak fully transitions into the visible region, approximately around 652.5 nm. Reflectance and absorption coefficients in boron and nitrogen co-doped graphene demonstrate a similar trend in accordance with these findings [20].

3.2. Adsorption Of O₂ By Graphene With B\N Co-Doped

Within graphene co-doped with B\N, the dopant boron serves as the active site for oxygen (O_2) adsorption. Studies have revealed that oxygen molecules exhibit a preference for adsorbing on the

hollow sites of graphene co-doped with B\N, either bonding with active site atoms to form triangular configurations or attaching to individual active site atoms as O- O-entities [21]. The calculated adsorption energy of O₂ on graphene with B\N co-doped stands at -1.11 eV [22]. This favorable adsorption characteristic towards O₂ establishes a solid groundwork for utilizing B/N co-doped graphene as a catalyst for redox reactions.

3.3. Chemical Properties Of Graphene With BN Co-Doped

The B\N co-doping of graphene enhances its surface reactivity owing to the significant phenomenon of electronegativity contrast between the boron and nitrogen atoms. Mehdi D. Esrafil's team delved into the catalytic impacts of B/N co-doped graphene on CO oxidation, revealing that the Langmuir-Hinshelwood (LH) mechanism prevails over the Eley-Rideal (ER) mechanism for CO oxidation on B/N co-doped graphene due to its lower reaction activation energy [22]. Additionally, Han's team highlighted the substantial catalytic activity of graphene with B/N co-doped attributed to the high density of states (DOS) near the Fermi energy level, facilitating efficient electron transfer from O₂'s highest occupied molecular orbital [21].

4. SUMMARY

B and N co-doped graphene plays a pivotal role in bandgap control engineering and catalysis, advancing its application potential toward real-world utility. Various forms of B and N arrangements on graphene, such as neighborhood, interstitial, para-doping on the carbon six-membered ring of monolayer graphene, and monolayer and stacked layer doping of h-BN with graphene, contribute to the diversity in properties. The doping concentration and spatial arrangement of boron and nitrogen atoms significantly impact the physical and chemical attributes of graphene. While numerous theoretical simulations have elucidated the characterization and properties of B/N co-doped graphene, further exploration is warranted to enhance the preparation and characterization of this material for its widespread applicability.

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