The electronic structure studies of hybrid $h$-BNC sheets based on a semi-empirical Hamiltonian

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**ABSTRACT**

The quest for modulating the wide bandgap of a pristine $h$-BN sheet for device-related applications has prompted the present study of ternary 2-dimensional sheets, $h$-BNC, that contain carbon domains of different shapes and sizes embedded in the $h$-BN network. The structural stability and electronic properties of hybrid $h$-BNC sheets containing rectangular-, circular-, hexagonal-, and triangular-shaped carbon domains are investigated using a real-space electronic structure method, where an environment-dependent semi-empirical Hamiltonian is used within a framework of a linear combination of atomic orbitals and self-consistent charge calculations. This method allows a study of larger carbon domains embedded in the $h$-BN matrix beyond what is possible via first-principles calculations, and thus serves to complement previous theoretical studies on hybrid $h$-BNC systems. The electronic density of states reveals mid-gap states for all $h$-BNC sheets, suggesting a narrowing of the energy gap compared to the pristine $h$-BN sheet. They arise from the breaking of the hexagonal symmetry due to bond distortions at the interface between the carbon domain and the $h$-BN network. The features of such mid-gap states strongly depend on the size and shape of carbon domains and the type of bonding (C-N, C-B, or a mixture of both) at the interface. The hybrid $h$-BNC sheet containing rectangular carbon domains switches from a semiconductor to a gapless semi-metal-like, and to a metal-like system as the size of the carbon domain increases. The energy gap of the $h$-BNC sheet containing hexagonal carbon domains exhibits a power-law decrease with the size of the carbon domains. On the other hand, the energy gap of the hybrid $h$-BN sheet containing circular carbon domains oscillates as the size of the carbon domain is increased. For electron-rich hybrid $h$-BNC sheets containing triangular graphene domains and C-N interfaces, a p-type-like behaviour is obtained. On the other hand, for electron-deficient hybrid $h$-BNC sheets, containing triangular graphene domains and C-B interfaces, the electronic behaviour switches from a p-type-like semiconductor to a metal-like behaviour as the number of carbon atoms increase. The top of the valence band was found to be half-filled for all triangular domains. The results obtained here may pave the way for novel device concepts based on $h$-BNC sheets.

1. Introduction

It is well-known that the properties of materials in reduced dimensions are different from their bulk counterparts because of effects arising from the quantum confinement of electrons, resulting in size-dependent electronic, transport, magnetic, and optical properties. The successful synthesis of few atoms’ thick graphitic materials and hexagonal-BN ($h$-BN) sheets via mechanical exfoliation [1,2] and chemical vapour deposition (CVD) techniques [3,4], and the desire to incorporate these materials in nanoscale devices, have led to a flurry of activities focusing on modulating the electronic structures of both graphene (a zero-bandgap semiconductor) and $h$-BN sheets (a wide bandgap insulator with a bandgap of $\sim 5.5\,\text{eV}$ [5]). It has been demonstrated by several theoretical studies that graphene domains embedded in an $h$-BN network result in reducing the energy gap of pristine $h$-BN sheet [6–9] and, similarly, $h$-BN domains embedded in graphene result in the opening of the bandgap of graphene [10–12]. Furthermore, the hybrid $h$-BN/graphene ($h$-BNC) system exhibits half-metallicity, magnetism, and interesting transport properties [13–18]. A crossover from a ballistic regime to the localized regime has been reported for boron domains embedded in graphene nanoribbons [13]. For superlattices of $h$-BN ribbons (BNNRs) and graphene nanoribbons (GNRs)

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with hydrogen passivated zigzag edges, the electronic structures could be tuned from semiconductor, half-metal, to a ferromagnetic metal [15–19]. Other electronic studies for BNNR/GNR superlattices with armchair edges have also been conducted [20]. Hybrid graphene/h-BN sheets with mono-vacancy, stone-wales, or line defects in graphene domains have been studied [21–24] to understand the role played by defects formed during growth processes. Other hybrid structures based on graphene/graphene [25,26] and graphene nano-roads in boron nitride sheets have [14] have also been studied for tailoring the energy gap.

The experimental realizations of 2D ternary BNC sheets [27–29], graphene/boron nitride lateral heterostructures [30–32], epitaxially grown graphene on h-BN [33], vertically aligned hexagonal boron nitride nanosheets hybridized with graphitic domains [34], etc. have provided further impetus to the bandgap engineering studies of composite 2D BNC systems. For a controlled fabrication of planar graphene domains of different shapes (triangular, rectangular, circular, and hexagonal) and sizes embedded in an h-BN network has been reported by Wei et al. [28]. Using a carbon-substitution reaction method [29], graphene sheets can be converted to boron nitride and boron nitride–carbon sheets in a chemical reaction involving B2O3 and graphene sheets in a nitrogen atmosphere and using molybdenum oxide as a promoter. A topological substitution reaction that converts graphene to h-BNC and h-BN layers has been used to create graphene/h-BNC/h-BN in-plane heterostructures [36].

A large-area atomic layer of h-BNC consisting of hybridized h-BN and carbon domains has been successfully synthesized by the thermal catalytic chemical vapour deposition (CVD) method with methane and ammonia-borane as precursors and copper foil as the catalyst [27]. This experiment allowed the carbon content in the hybrid structure to be controlled and thus allowed a study of the energy gap as a function of the atomic percent composition of carbon (e.g., 0%, 35%, 65%, 85%, etc.) in the hybrid structure. A variety of characterization tools (AFM, HRTEM, Raman, XPS, EELS, and UV–vis absorption spectroscopy, etc.) were used to determine the atomic structure and bonding of hybrid ternary BNC films. Based on the results of these characterizations, the authors argued that the observed structure was neither an alloy nor a stacked structure of h-BN and graphene, but a hybrid 2D structure composed of graphene and BN domains. Specifically, the absorption spectroscopy conducted on the synthesized samples revealed a second absorption peak corresponding to carbon domains in the hybrid h-BN sheet, and the position of this peak shifted to higher wavelengths as the carbon content in the hybrid structure increased. More specifically, the optical gap shifted from 1.62 eV to 1.51 eV, as the carbon content in the hybrid BN sheet increased from an atomic percentage of 65 %–85 %. This experiment demonstrated that by controlling the domain size of graphene domains, one can tune the energy gap in a hybrid sheet composed of the h-BN and graphene domains.

Motivated by the experimental results of Ref. [27], a comprehensive study of graphene domains of different shapes (triangular, rectangular, circular, and hexagonal) and sizes embedded in an h-BN network is conducted in this work, using an environment-dependent semi-empirical Hamiltonian within the framework of linear combination of atomic orbitals that allows charge calculations self-consistently [37–39]. The method allows simulations of larger graphene domains embedded in the h-BN matrix beyond what is possible via density functional theory (DFT), and thus serves to complement previous theoretical studies [6–9] on hybrid h-BNC systems. The present study uses a 15 × 10 supercell (37.52 Å × 43.42 Å) to allow size-dependent electronic structure studies of graphene domains in a h-BN network that are larger than those previously studied. The largest graphene domain structure studied here contains ~ 40 % carbon concentration. A previous theoretical study of circular graphene domains in h-BN network could only approach a carbon concentration of 11 % in a DFT-based calculation [6]. Bhomwick et al. [7] have calculated the formation energy of hexagonal graphene domains embedded in an h-BN network with either the armchair or the zigzag interface. Nurten Akman and Cem Özdogan [9] investigated triangular and hexagonal graphene islands in the h-BN hybrids, but the supercell chosen in their calculation (e.g., 22.2 Å × 22.6 Å) may not be large enough to avoid image interactions between the graphene domains for studies of their largest h-BNC sheets (e.g., 19 (H)(h-BN)) containing 54 carbon atoms. Since experiments usually contain graphene domains of random size and arbitrary shapes, a robust semi-empirical method is required to handle such situations. A comparison of results from previous studies [6–9] and the present work will be discussed in the appropriate sections corresponding to different types of graphene domains in h-BN networks.

The following sections present the methodology used here and the results for stable hybrid h-BNC sheets of different shapes and sizes that report the formation energy of the graphene island in h-BN networks, the energy gaps of h-BNC sheets vis-à-vis to the size and shape of graphene domains will also be discussed.

2. Methodology

2.1. The SCED-LCAO semi-empirical method

The structural stability and the electronic properties of h-BNC sheets are studied here using an environment-dependent (ED) semi-empirical Hamiltonian, developed using a linear combination of atomic orbitals (LCAO) framework, with its interactions captured through environment-dependent (ED) functions and charges calculated self-consistently (SC). Hereafter, this method will be referred using the acronym SCED-LCAO. A systematic study of graphene domains of different shapes and sizes, in particular, large graphene domains embedded in h-BNC sheets, requires a robust semi-empirical Hamiltonian that can efficiently simulate several structures at the same time and can reliably predict new structures. The SCED-LCAO method was designed to meet this need for efficient simulations of large nanostructures. This method has been successfully applied to study the bulk phases as well as low-dimensional structures of silicon-based, carbon-based, and boron-based systems [37–39].

The matrix element of the SCED-LCAO Hamiltonian is given as [37]:

\[
\tilde{H}_{n\alpha,\beta}(R_0) = \frac{1}{2} \left[ (\epsilon_{n\alpha} + \epsilon_{n\beta}) K(R_0) S_{n\alpha,\beta}(R_0) + \frac{1}{2} \sum_{ij} W_{n\alpha}(R_{ij}) + \frac{1}{2} \sum_{ij} W_{n\beta}(R_{ij}) \right] K(R_0) S_{n\alpha,\beta}(R_0) \\
+ \frac{1}{2} \left[ (N_{i} - Z) U_{i} + (N_{j} - Z) U_{j} \right] S_{n\alpha,\beta}(R_0) + \frac{1}{2} \sum_{ij} \left( N_{i} V_{i}(R_{ij}) - Z_{i} V_{i}(R_{ij}) \right) + \sum_{ij} \left( N_{j} V_{j}(R_{ij}) - Z_{j} V_{j}(R_{ij}) \right) \right] S_{n\alpha,\beta}(R_0)
\]
For a non-orthogonal basis set, the first term in the above expression represents the two-center interaction term. Here $\epsilon_{ij}$ and $\epsilon_{ij}^{\beta}$ represent the modified Hückel-like parameters, $S_{ij}^{\alpha\beta}(R_{ij})$ is the overlap matrix element, and $K(R_{ij})$ is a scaling function. Intuitively, it is apparent that when an atom is in aggregate, the on-site energies must deviate from their atomic orbital energies and the Hamiltonian must also allow for the occurrence of excited orbitals. The second term in Eq. (1) allows in a phenomenological way the occupation of excited orbitals through a function $W(R_{ij})$. The third term is the on-site electron correlation term, where $U_{i}$ is a Hubbard-like parameter, and $N_{i} - Z_{i}$ describes the deviation of the actual number of electrons ($N_{i}$) from the valence electron number ($Z_{i}$) of the atom at the site $i$. The last term contains the environment-dependent electron-electron and electron-ion interactions, which are represented through potential functions $V_{\alpha}(R_{ij})$ and $V_{\alpha}(z_i)$, respectively. The functional forms of $V_{\alpha}(R_{ij})$, $V_{\alpha}(R_{0})$, $W_{\alpha}(R_{ij})$, $K(R_{ij})$, $S_{ij}^{\alpha\beta}(R_{ij})$), and the parameters describing these functions are given in Refs. [37–39]. The semi-empirical functions describing the interaction terms of the SCED-LCAO Hamiltonian have been chosen carefully to capture the screening effects of electrons in a multi-atom environment, and the parameters of the semi-empirical functions are fitted to first-principles database of properties (see the Supplementary Information for detail discussion).

2.2. SCED-LCAO parameters for the nitrogen element

The structural and electronic structure studies of the hybrid h-BNC sheets require the development of SCED-LCAO Hamiltonian parameters for B, N, and C. We have previously developed these parameters for carbon and boron [38,39]. In this work, we, therefore, report only the SCED-LCAO parameters for the nitrogen element. Using a sp² basis set, the SCED-LCAO Hamiltonian parameters for the nitrogen element are determined by fitting the structural parameters and binding energies of selected clusters and bulk phases with the corresponding properties obtained using DFT based calculations. For example, to obtain the SCED-LCAO parameters for nitrogen, the cohesive energies and bond lengths of a series of B$_n$N$_m$ and C$_n$N$_m$ clusters were calculated using a DFT based method and fitted them to the corresponding SCED-LCAO calculated properties. Further details about the optimization of the SCED-LCAO Hamiltonian parameters are presented in the Supplementary Information. Table 1 lists the optimized SCED-LCAO Hamiltonian parameters for the nitrogen element.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Symbol</th>
<th>Value</th>
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<tr>
<td>$\epsilon_{i}(eV)$</td>
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<td>$B_{\sigma\sigma}(\AA^{-1})$</td>
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<td>$\epsilon_{i}(eV)$</td>
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<td>$\epsilon_{i}(eV)$</td>
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<tr>
<td>$\epsilon_{i}(eV)$</td>
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<tr>
<td>$W_{\alpha}(d^{-1})$</td>
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<td>$a_{\pi\pi}(\AA^{-1})$</td>
<td>$3.43835$</td>
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<tr>
<td>$W_{\alpha}(d^{-1})$</td>
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<td>$d_{\pi\pi}(\AA)$</td>
<td>$1.44240$</td>
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<tr>
<td>$\alpha_{\pi\pi}(d^{-1})$</td>
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<td>$B_{\pi\pi}(\AA^{-1})$</td>
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</tr>
<tr>
<td>$\alpha_{\pi\pi}(d^{-1})$</td>
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</tr>
<tr>
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<td>$d_{\pi\pi}(\AA)$</td>
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<tr>
<td>$U(eV)$</td>
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<td>$B_{\pi\pi}(\AA^{-1})$</td>
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<tr>
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<td>$A(eV)$</td>
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<td>$a_{\pi\sigma}(d^{-1})$</td>
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<tr>
<td>$d_{\sigma}(\AA)$</td>
<td>$0.61063$</td>
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The optimized SCED-LCAO parameters for the nitrogen element were further tested for their transferability [40] by comparing the calculated values of the structural properties and the energy gap of the h-BN sheet and the Wurtzite BN (w-BN) bulk with other reported results [41]. The optimized lattice constants for the w-BN structure and the h-BN sheet, as obtained from SCED-LCAO [40] were overestimated by a few percent (1%–2%) with respect to the values reported in Ref. [42] and Ref. [5,42], respectively. On the other hand, the SCED-LCAO energy gaps for the w-BN structure and the h-BN sheets were found to be 5.26 eV and 3.36 eV, respectively. The energy gap results reported for the w-BN structure are in the range 4.5–5.5 eV [41]. The experimental energy gap reported for the h-BN sheet is 5.56 eV [5] while the quasi-particle energy gap reported for the h-BN sheet in the GW approximation is 6.0 eV [43]. The DFT calculation usually underestimates the energy gap [44,45] compared to GW calculations [43]. Since the SCED-LCAO Hamiltonian parameters are fitted against the DFT database, the SCED-LCAO energy gap results reported here are expected to be similar to the DFT energy gaps. Despite this underestimation of the energy gap, one can glean useful information regarding the trend for the formation energy and the energy gap behavior vis-à-vis the size and shape of carbon domains, and role of the strain at the graphene-BN interface in inducing the impurity states and the Fermi level pinning. It is worth noticing that even for the bulk h-BN, the literature reports a wide-ranging experimental and theoretical values for the energy gap from 3.20 to 5.97 eV, and both direct and indirect energy gaps have been reported [44–46].

2.3. Computational details

A supercell of size $15 \times 10$ containing 600 atoms and a vacuum of 1000 Å was considered for optimizing the structure of the pristine h-BN sheet using the SCED-LCAO method. The simulations of the 2D hybrid h-BNC systems were then performed by considering graphene domains of different shapes (i.e., the triangular, the circular, the hexagonal, and the rectangular domains) and sizes with the goal of understanding their roles as well as that of the interface on the structural stability and the electronic structure of hybrid h-BNC sheets. In particular, the size- and shape-dependence of the formation energy, the electronic density of states, and the energy gap of hybrid h-BNC sheets will be discussed. Fig. 1 depicts the four different shapes of graphene domains considered in the present study of the hybrid h-BNC sheet.

Fig. 1. A schematic illustration of a $15 \times 10$ h-BNC sheet with the four types of graphene domains (the triangular, the circular, the hexagonal and the rectangular domains) embedded in the pristine h-BN sheet.
3. Results and discussions

3.1. Triangular graphene domains

In the case of triangular graphene domains embedded in the h-BN sheet, two distinct interfaces can be formed: (i) boron atoms replaced by carbon atoms along the perimeter of the triangular carbon domain (referred as T-B type triangular graphene domains), leading to electron-rich h-BNC sheet and (ii) nitrogen atoms replaced by carbon atoms along the perimeter of the triangular carbon domain (referred as T-N type triangular graphene domains), leading to electron-deficient h-BNC sheet. In the former case, the interface between the graphene domain and the h-BN sheet will have solely C—B bonds while in the second case, the interface between the graphene domain and the h-BN sheet will have solely C—B bonds. Since the C—B bond length is larger than the C—C and B—N bond lengths, the C—N bond length is smaller than both the C—B and B—N bond lengths, the respective strains at the interface in the two cases will lead to mid-gap states. Furthermore, because of excess electrons in h-BNC sheets with T-B-type triangular carbon domains compared to a pristine h-BN sheet, the Fermi level is expected to shift to higher energy level and, for h-BNC sheets with T-N type triangular carbon domains, the valence band edge will shift to lower energy level.

These two factors, namely, the interfacial strain and the location of the Fermi level control the electronic properties of h-BNC sheets with triangular carbon domains. Previous spin-polarized DFT studies in h-BN sheets have revealed metallic and half-metallic ground states [8-10]. There are subtle differences in the interfaces of triangular carbon domains studied here and the cases discussed in Ref. [9], with the latter having no incomplete hexagonal carbon ring even at the interface. Hence, the triangular domains in Ref. [9] will have less strain at the interface compared to the case discussed here and will also have different number of C—N (C—B) bond distributions at the interface, even for carbon domains of similar sizes, leading to different electronic structures and behaviors.

3.1.1. Triangular carbon domains with the C-N boundary

Four different cases of triangular carbon domains embedded in the h-BN sheet with progressively increasing number of carbon atoms 3, 21, 57, and 111 were considered. The first case labelled T-B1 has three carbon atoms in the triangular region, where three boron atoms of the pristine h-BN sheet were replaced by 3 carbon atoms. It is the smallest triangular carbon domain considered in this work. The initial structure of the second case labelled T-B2 was obtained by replacing both boron and nitrogen atoms in the interior of a triangular region by carbon atoms. The T-B2 structure has 21 carbon atoms in the triangular domain. But in the perimeter region, only the boron atoms were replaced by carbon, resulting in solely C—N bonded boundary. Two larger triangular carbon domains with 57 and 111 carbon atoms in h-BN sheets were also considered, respectively, with their initial structures constructed using similar procedures. However, these larger triangular domains were not stable upon relaxation. Fig. 2(a) shows the optimized and relaxed structures for T-B1 and T-B2 using SCED-LCAO. Fig. 2(b) shows the corresponding electronic density of states (DOS) for these two cases, which are compared with the DOS for a pristine h-BN sheet (top panel). It is evident from Fig. 2(b) that the pristine h-BN is a wide bandgap semiconductor, exhibiting a gap of 3.3 eV. For the case of the T-B1 structure with a 3-atom carbon domain, one notices an impurity state emerging above the top of the valence band edge (indicated by the dashed circle). Since the C—N bond lengths (~1.2 Å) in the triangular region are about 8% shorter than the B—N bond lengths (~1.5 Å) of a pristine h-BN sheet, this strain introduces the “impurity state” in the bandgap. More specifically, a calculation of the site-projected local density of states (LDOS) for the T-B1 structure reveals that this state is associated with nitrogen atoms at the interface between the triangular carbon domain and the h-BN sheet (see Fig. S5(a)). Since T-B1 hybrid sheets have excess electrons compared to a pristine h-BN sheet, the Fermi level will be shifted upwards, and, furthermore, since the topmost level is only half-occupied, this sheet hybrid will behave like a p-type semiconductor.

For the case of the T-B2 structure with 21 carbon atoms in the triangular domain, many more unoccupied impurity states in the bandgap region of the pristine h-BN sheet were found. The DOS associated with these impurity states are shown at the bottom panel of Fig. 2 (b). Based on the site-projected local density of states (red curve, denoted by T-B2 (G)), these states arise from carbon atoms in the triangular domain, and since there are only 21 carbon atoms in a supercell of 600 atoms, their contribution to the DOS appears as small features in the total DOS, but are sharp, suggesting these are localized states (which correspond to flat band structures). Since the total electrons in the T-B2 hybrid structure also has more electrons than the pristine h-BN sheet, the Fermi level is shifted upwards. The topmost level in this case is also half-filled, and so this hybrid sheet will also exhibit a p-type behaviour.

3.1.2. Triangular carbon domains with the C-B boundary

The relaxed structures corresponding to triangular carbon domains with 3, 12, 57, and 111 carbon atoms embedded in h-BN sheet (labelled T-N1, T-N2, T-N3, T-N4 respectively), and with C—B bonded interfaces are shown in Fig. 2(c). Compared to pristine h-BN sheet, these hybrid sheets have less total number of electrons, and hence these hybrid sheets are electron deficient. In contrast to the previous case, in these hybrid sheets the triangular graphene domain is obtained by replacing both boron and nitrogen atoms of a pristine h-BN sheet by carbon atoms, but the perimeter region is obtained by replacing nitrogen atoms with carbon, which results in a C—B bonded triangular graphene domain. The optimized structures and their corresponding DOS are shown in Fig. 2(c) and (d), respectively. Upon relaxation, there is a major re-arrangement of carbon atoms including the appearance of some 5-member carbon rings and carbon atoms bonding with 4 boron atoms and 3 nitrogen atoms near one of the vertices of the triangular region. The DOS of such hybrid sheets, when compared to a pristine h-BN sheet, reveals isolated impurity states both above the valence band (VB) and below the conduction band (CB) for the T-N1 case. This hybrid sheet, with half-occupancy of its valence band, exhibits a p-type semiconducting behaviour. As the size of the carbon domains increases from the T-N1 case to the T-N4 hybrid sheet, more impurity states appear in the bandgap region and are no longer isolated. Furthermore, the DOS corresponding to the VB and the CB states broaden considerably with their tails extending towards the gap, and the gap region getting filled with states. The electronic behaviour of these hybrid structures transition from a semiconducting to a metal-like behaviour as the number of carbon atoms in the domain increases. A calculation of the partial DOS reveals a strong hybridization of carbon, nitrogen, and boron orbitals for the impurity states in the gap region (see Fig. S5(b)). For such electron deficient hybrid sheets, the Fermi level shifts downward compared to the pristine h-BN.

3.2. Circular carbon domains

For the hybrid h-BN sheets with circular carbon domains, equal numbers of boron and nitrogen atoms were replaced within a circular region of a pristine h-BN sheet by carbon atoms. In these hybrid sheets, the total number of electrons remain the same as the pristine h-BN sheet. To investigate the size-effects of circular carbon domains in the hybrid h-BN sheets, six different sizes of C-1, C-2, C-3, C-4, C-5, and C-6, containing 6, 12, 42, 60, 114, and 144 carbon atoms embedded in the h-BN sheet, were considered. For a pristine h-BN sheet using a 15 × 10 supercell, the diameter of the largest possible circular carbon domain (C-6) that could be accommodated is 23.97 Å. For the initial structures considered in this case, the interface of graphene-like quantum dots and the h-BN sheet has equal numbers of C—N and C—B bonds along the boundary, with each carbon atom at the boundary bonded with either a
Fig. 2. (a) The relaxed hybrid h-BNC sheets for two different sizes of triangular carbon domains, labelled T-B$_1$ and T-B$_2$, respectively. The three panels in (b) correspond to the total DOS plotted versus $\epsilon - \epsilon_F$ for a pristine h-BN sheet and the hybrid h-BNC sheets labelled as T-B$_1$ and T-B$_2$, respectively with C-N interfaces. The dashed circle in (b) indicates the impurity states above the Fermi level. T-B$_2$ (G) (red curve) represents the LDOS from the carbon domains. The relaxed structures corresponding to T-N$_1$, T-N$_2$, T-N$_3$, and T-N$_4$ hybrid h-BNC sheets with triangular carbon domains and a C-B interface. The corresponding electronic DOS plotted versus $\epsilon - \epsilon_F$ are shown in (d). The location of the Fermi level is at zero for all hybrid h-BNC sheets.
pair of boron or a pair of nitrogen atoms. Upon relaxation, the hexagonal rings of graphene-like domains are practically intact in the interior region of the domain. But at the boundary, all hexagonal rings which contain either C–C bonds or a mixture of C–C and B–N bonds are distorted. The relaxed hybrid h-BN sheets embedded with carbon domains of different sizes are shown in Fig. 3 (a). The results for the total electronic DOS, corresponding to the six cases of the hybrid h-BN sheets with circular domains, are shown in Fig. 3 (b) and are compared with the DOS of a pristine h-BN sheet. The DOS calculation reveals new impurity states both above the VB and below the CB. The top of the valence band is filled unlike the case of triangular carbon domains. These impurity states arise mainly from the strain induced by the competitions among C–B, C–N, and C–C bonds. The energy gap of the hybrid h-BN sheet is reduced compared to the pristine h-BN sheet due to the impurity states appearing in the gap region. Fig. 3(b) compares the total density of states for h-BN sheets with circular carbon domains of increasing sizes with that of a pristine h-BN sheet. The band gap oscillates based on the strain at the interface of such circular domains. For the largest carbon domain with 144 carbon atoms, the DOS at the carbon site is also shown (red curve labelled C-6(G)) in Fig. 3(b). Clearly, most of the contributions to the impurity states come from the carbon atoms. The results of site-projected density of states from boron and nitrogen atoms are given in the supplementary section (Fig. S5(c)). While the contributions to the DOS from boron and nitrogen are much smaller compared to that of

![Fig. 3. (a) The relaxed structures of the hybrid h-BNC sheets containing six different sizes of embedded circular carbon domains. The seven panels in (b) correspond to the total DOS for a pristine h-BN sheet and the hybrid h-BNC sheets labelled C-1, C-2, C-3, C-4, C-5, and C-6, respectively. C-6 (G) (red curve) represents the total DOS projected on to the carbon sites. The Fermi energy for all hybrid sheets is located at 0 eV.](image)
carbon, a slight hybridization from B, C, N orbitals can be seen. As the size of the carbon domain increases, the impurity states are more pronounced and such states are seen above the VB edge and below the CB. This is due to the increased number $\mathrm{C-B}$ and $\mathrm{C-N}$ bonds at the interface that increases the strain. The energy gap behaviour of circular carbon domains is mainly dictated by the strain at the interface. The details of the energy gap behaviour are described in Section 3.5.

### 3.3. Hexagonal carbon domains

The optimized structures of the hybrid $\mathrm{h-BNC}$ sheets (H-1, H-2, H-3, and H-4) embedded with four hexagonal carbon domains are presented in Fig. 4(a). The hybrid sheet labelled H-1 was formed by assembling three nearest-neighbour hexagonal carbon rings at the centre of the $\mathrm{h-BN}$ sheet. This structure was formed by removing six boron and seven nitrogen atoms from the original $\mathrm{h-BN}$ network with 13 carbon atoms. The sheet labelled H-2 contains a carbon network of seven hexagonal rings with six of them around a central one (24 carbon atoms). The sheet labelled H-3 was formed by adding another twelve hexagonal carbon rings around H-2 (54 carbon atoms). The hybrid $\mathrm{h-BNC}$ sheet labelled H-4 contains 96 carbon atoms, and was constructed by adding 18 hexagonal carbon rings around the H-3 unit, where the distance between the opposite edges of the hexagonal carbon domain is 17.99 Å. This is the largest hexagonal carbon domain investigated in this work. At the boundary between the hexagonal carbon domain and the $\mathrm{h-BN}$ sheet, two types of bonding were found: (i) a carbon atom connected to a boron atom and two carbon atoms or (ii) a carbon atom connected to a nitrogen atom and two carbon atoms. These two types of bonding alternate along the edges of the hexagonal boundary. Upon relaxation, the interior region containing carbon atoms is practically intact and only a slight distortion of the hexagonal $\mathrm{h-BN}$ network is discernible (see, Fig. 4(a)).

As found in previous cases, the results for the DOS of the hybrid $\mathrm{h-BNC}$ with hexagonal carbon domains reveal new states above the VB and below the CB edge. For the H-1 hybrid sheet with the odd total number of electrons, the highest occupied state is only half-filled. However, for all the other hexagonal sheets (H-2, H-3, and H-4), the highest occupied state is filled. As the number of carbon atoms in the domain increases, many closely separated states appear above and below the Fermi level, making the tails of the VB and the CB extended into the gap region of the pristine $\mathrm{h-BN}$ sheet and resulting in a reduction in the energy gap. Fig. 4(b) shows the total DOS for hexagonal domain types of the hybrid $\mathrm{h-BNC}$ sheets (blue curve) and were compared with the DOS for a pristine $\mathrm{h-BN}$ sheet. The site projected DOS for carbon atoms in the domain are shown for the H-4 type hybrid sheet (red curve). The site projected DOS on carbon, boron, and nitrogen atoms for the H-3 type hybrid sheet also reveal that the new states arise mainly from carbon atoms (see Fig. S5(d) in Supplementary Information).

### 3.4. Rectangular carbon domains

As a final case study to understand the role of the size and the shape of carbon domains on the energy gap of the hybrid $\mathrm{h-BNC}$ sheets, seven rectangular carbon domains were embedded in the $\mathrm{h-BN}$ sheet, which
were labelled as R-1, R-2, R-3, R-4, R-5, R-6, and R-7, respectively. For the R-1 hybrid sheet, the initial structure was constructed by replacing 5 boron and 5 nitrogen atoms of the pristine sheet with 10 carbon atoms. Similarly, the other larger rectangular hybrid sheets (i.e., R-2, R-3, R-4, R-5, R-6, and R-7) were constructed that lead to 28, 54, 88, 130, 180, and 238 carbon atoms in the domains, respectively. The dimension of the largest rectangular domain considered was 29.97 Å × 21.00 Å. For all the cases considered here, equal numbers of boron and nitrogen atoms were replaced by carbon atoms in the domain region. Interestingly, for carbon atoms along the armchair boundary, C–B and C–N bonds alternate along this boundary. However, for the zigzag boundary, one side has C–B bonds, and the opposite side has C–B bonds. The competition between various types of bonding lengths introduces the local strain in the hybrid h-BN sheets. Fig. 5(a) shows the relaxed structures corresponding to these seven cases. Although the carbon domains in the interior region have nearly intact hexagonal carbon rings, the hexagonal rings containing boron, nitrogen, and carbon atoms at the boundary region were distorted. Fig. 5(b) shows results of the total DOS for these seven cases. It was found that for smaller rectangular carbon domains, a number of isolated states appear within the energy gap of the pristine h-BN sheet. As the size of the carbon domain increases, induced new states are no longer isolated. For larger carbon domains, the DOS at the top of the VB and the bottom of the CB states show considerable broadening. The site projected DOS on carbon, boron, and nitrogen atoms reveal that these new states arise mainly from carbon and nitrogen atoms for the R-7 sheet (see Fig. S5(e)). The partial DOS from carbon atoms (red curve) for the R-7 sheet was shown in Fig. 5(b).

Fig. 5. (a) The relaxed structures of the hybrid h-BNC sheets containing rectangular carbon domains of different sizes. The eight panels in (b) correspond to the total DOS for a pristine h-BN sheet and the hybrid h-BNC sheets labeled R-1, R-2, R-3, R-4, R-5, R-6, and R-7, respectively. R-7 (G) (red curve) represents the site-projected partial DOS from carbon domains. The Fermi energy for all hybrid sheets is located at 0 eV.
and the rectangular domains).

against the number of carbon atoms (see the formula in the inset).

of different shapes (Fig. 7. The formation energy per atom of such sheets are calculated using the formula:

\[ \varepsilon \approx \frac{1}{n^2} \]

where, \( E_{\text{tot}} \) denotes the total energy of the hybrid sheet, and \( N_{\text{total}} \) and \( N_{\text{domain}} \) denote the number of boron and nitrogen atoms in the pristine h-BN sheet. The results are shown in Fig. 7. It was found that the cohesive energy of the hybrid h-BN sheet decreases linearly with the size of the carbon domain, and irrespective of the shape of the domain.

The cohesive energy \( E_{\text{cohesive}} \) can be fitted by the linear formula:

\[ E_{\text{cohesive}} = -6.27 - 0.0168n, \]

where \( n \) is the number of atoms in the carbon domain. It is found that hybrid sheets with larger carbon domains are more stable than those with smaller carbon domains. For the same sized hybrid sheets, the T-N type triangular hybrid sheets with C-B boundaries are less stable than the other hybrid sheets.

3.7. The energy gap of the hybrid h-BN sheets

This section reports the energy gap of hybrid h-BNC sheets for carbon domains of different shapes and sizes, as obtained by the SCED-LCAO method. It should be noted that the SCED-LCAO calculations are performed in real-space, which are equivalent to a Gamma point calculation in the traditional k-space. Apparently, the real-space SCED-LCAO approach has the power in dealing with large-scale and complex systems having low symmetry, such as the hybrid h-BNC sheets with the 15 × 10 supercell studied in this work. The energy gap is determined by looking directly at the eigenvalue spectrum, and the Fermi Energy is identified from the topmost occupied energy level, corresponding to the total number of valence electrons in the system.

The SCED-LCAO calculations for the electronic structures of the hybrid h-BNC sheets have demonstrated that the energy gap depends on the shape of the carbon domains in the h-BNC sheet because the strains at the interfaces of triangular, circular, hexagonal, and rectangular carbon domains and the h-BN network are different, depending on the type, the number of carbon atoms, and the distribution of chemical bonds along the boundary.

In the case of T-B hybrid sheets, the interface contains C–N bonds (1.20 Å), while the interior region contains C–C bonds (1.46 Å), and the region exterior to the carbon domain contains B–N bonds (1.49 Å). This

<table>
<thead>
<tr>
<th>Graphene domains</th>
<th>( E_{\text{gap}} ) (eV)</th>
<th>Graphene domains</th>
<th>( E_{\text{gap}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-B</td>
<td>0.048</td>
<td>H-1</td>
<td>0.102</td>
</tr>
<tr>
<td>T-B</td>
<td>0.446</td>
<td>H-2</td>
<td>0.899</td>
</tr>
<tr>
<td>T-N</td>
<td>0.901</td>
<td>H-3</td>
<td>0.586</td>
</tr>
<tr>
<td>T-N</td>
<td>0.104</td>
<td>H-4</td>
<td>0.462</td>
</tr>
<tr>
<td>T-N</td>
<td>0.127</td>
<td>R-1</td>
<td>0.354</td>
</tr>
<tr>
<td>T-N</td>
<td>0.009</td>
<td>R-2</td>
<td>0.025</td>
</tr>
<tr>
<td>C-1</td>
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<td>R-3</td>
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</tr>
<tr>
<td>C-2</td>
<td>0.355</td>
<td>R-4</td>
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</tr>
<tr>
<td>C-3</td>
<td>0.566</td>
<td>R-5</td>
<td>0.005</td>
</tr>
<tr>
<td>C-4</td>
<td>0.661</td>
<td>R-6</td>
<td>0.034</td>
</tr>
<tr>
<td>C-5</td>
<td>0.158</td>
<td>R-7</td>
<td>0.037</td>
</tr>
<tr>
<td>C-6</td>
<td>0.579</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
mismatch among the three types of bond lengths in the vicinity of the circular carbon domains exhibits an oscillation behavior.

For the case of the hexagonal domains in the hybrid h-BNC sheets, the initial structure contains complete hexagonal carbon rings within the graphene-like domain, and the hexagonal perimeter contains C–B and C–N bonds alternating along each of its edges. Since the six-fold symmetry of hexagonal rings of the graphene-like domain is not broken upon relaxation, there are no symmetry-broken states within the gap. However, there are slight distortions along the domain boundary because of the presence of alternating C–B bonds and C–N bonds, which introduce mid-gap states above the VB and below the CB and reduce the gap of a pristine h-BN sheet. These hybrid sheets exhibit a semi-conducting behavior, which is similar to the DFT results reported in the literature [7]. The energy gap decreases in a power-law manner according to the formula $E_{gap} \approx \frac{n}{n_0}$, where $n$ is the number of atoms in the carbon domain (see the dashed curve in Fig. 8).

For the case of the rectangular graphene domains embedded in the hybrid h-BNC sheets, the armchair and the zigzag edges exhibit different types of bonding. Along the armchair boundary, the C–N and C–B bonds alternate with each other. But, along the zigzag boundary, one edge has only C–B bonds and the other edge exhibits only C–N bonds. The competition among these different bond lengths along the boundary and C–C bonds in the interior of the domain leads to different energy gap behavior as compared to that in the hybrid h-BNC with hexagonal domains (as shown in Fig. 8 with purple inverted triangles). The hybrid sheet R1 exhibits an energy gap of 0.35 eV, but all the other larger rectangular carbon domains embedded in the h-BN sheets are gapless, with the R7 hybrid sheets exhibiting metallic characteristics. Strong hybridizations of carbon and boron orbitals at the Fermi level, with lesser contributions from nitrogen orbitals can be seen for the R7 hybrid sheets (Fig. S5(e) in the Supplementary Information). The energy gap versus the number of carbon atoms ($n$) in the domain shows a power-law decrease governed by the expression $E_{gap} \approx \frac{c}{n^{1.4}}$ (dash-dotted curve in Fig. 8), with the exponent having a value of 0.4.

Table 2 summarizes the energy gaps for the hybrid h-BNC sheets of different sizes and shapes that were studied in this work using the SCED-LCAO method. Since the SCED-LCAO Hamiltonian parameters are fitted to the DFT, the energy gaps will be underestimated compared to GW or experimental gaps. But this work provides useful guidance regarding the energy gap behaviour of the hybrid h-BNC sheets and the relationship between the energy gap and the interface characteristics, as dictated by the shape and size of carbon domains.

4. Conclusions

The structural stability and the energy gap of hybrid h-BNC sheets are comprehensively studied for carbon domains of different shapes and sizes using an environment-dependent semi-empirical Hamiltonian developed within the LCAO framework (SCED-LCAO). This work demonstrates that the energy gap of the hybrid h-BNC sheet can be modulated by changing the size and shape of carbon domains. The thermodynamic feasibility and stability of these hybrid sheets are
examined through the calculations of formation energies and cohesive energies, respectively. Both the formation energies and the cohesive energies of hybrid h-BNC sheets decrease as the size of the carbon domains increases and are independent of the shape of the carbon domains. But the interface characteristics of hybrid h-BNC sheets have a profound influence on their energy gap behaviour. Depending on the type of bonds and how they are distributed at the interface of the h-BN network and carbon domains, the electronic behaviors of hybrid h-BNC sheets can be modulated. The strains at the interface of the hybrid h-BNC sheets with triangular carbon domains. The electronic behaviors of both hexagonal and circular carbon domains in h-BN networks are semiconducting, but the energy gap as a function of the number of carbon atoms exhibits a power-law decrease in the former case and an oscillatory behavior in the latter case. For the rectangular carbon domains, the electronic behaviour switches from a semi-conducting to a semi-metallic one, as the size of the carbon domains increases. Furthermore, for the hybrid h-BNC sheets with triangular domains and C-N interfaces, a p-type semiconducting behaviour was found. For hybrid h-BNC sheets with triangular domains and C-B interfaces, the electronic behaviour switched from p-type semiconductor to semi-metallic. The impurity states for T-N \(2p\) orbitals of carbon, boron, and nitrogen. On the other hand, the impurity states for the smallest T-B \(2p\) hybrid sheet arise mainly from the \(2p\) orbitals of the nitrogen atom.

It should be remarked that since the parameters of the SCED-LCAO Hamiltonian are fitted to the DFT database, the energy gap predicted here will be underestimated compared to GW calculations or experimental gaps, but, yet, the method can provide comparisons of the trends in the energy gap behaviours of different types of hybrid h-BNC sheets.

It is evident from this study that the electronic properties of hybrid sheets are sensitive to the nature of the interface between the carbon domain and the h-BN network, and a rich variety of electronic behaviors, from semiconducting, semi-metallic, to metallic, can be achieved by manipulating the interface and the size of the carbon domains. From the perspective of bandgap engineering applications, the hybrid h-BNC sheets with the hexagonal and the circular carbon domains have the potential to be realized as promising electronic materials.

Authors’ contribution

Dr. Cherno Kah performed the simulations reported here. Dr. Lyle Smith developed the initial set of nitrogen parameters for the SCED-LCAO method. Dr. Chakram Jayanthi contributed to the analysis and writing of this manuscript. Dr. Ming Yu contributed to all aspects of this project as outlined above.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References


