



# Stone-Wales defects in graphene-like boron nitride-carbon heterostructures: Formation energies, structural properties, and reactivity



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## ABSTRACT

The geometries, formation energies, and reactivities of Stone-Wales (SW) defects in a series of graphene-like boron nitride-carbon (GBNC) heterostructures were studied using density functional theory. The data obtained were compared with those on pristine graphene and hexagonal boron nitride (h-BN) sheets. SW defects strongly deform GBNC structures that results in local distortions at defect sites. The energies of defect formation increase on going from narrow to wide models, and they depend on the orientations of the SW defect. Additionally, the local chemical reactivities of pristine as well as SW defected GBNC sheets were probed with carbene (CH<sub>2</sub>) addition reactions. It was established that pristine GBNC sheets exhibit enhanced reactivity in comparison with graphene and h-BN counterparts. Moreover, independent of the orientations of the SW defect, the reactivity of the bonds inside the SW defects of GBNC heterostructures increased considerably. The SW defects create active sites on the surface of GBNC sheets and can promote their further derivatization.

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## 1. Introduction

The discoveries of single-walled carbon nanotubes (SWCNTs) and graphene resulted in a new era in nanotechnologies [1,2]. Their unique mechanical, physical, chemical, thermal, and electronic properties were studied in detail [3–15]. The fruitful efforts of scientific community give rise a wide range of interesting applications, which in many cases are more fascinating than those stemming from graphite, a bulky counterpart. These findings stimulated both theorists and experimentalists to study other useful nanostructures based on a six-membered honeycomb network, namely hexagonal boron nitride (h-BN) and boron nitride nanotubes (BNNTs) [16,17]. They are structural analogues of graphene and SWCNTs, respectively, and can be imagined as a flat or rolled graphene sheet, where carbon atoms are fully substituted by boron and nitrogen atoms in an alternate manner.

Boron nitride (BN) nanomaterials have distinct differences from their two-dimensional carbon analogues, for instance, they have a wide band gap, high thermal and chemical stabilities. Besides this, they possess almost equal mechanical robustness in comparison with graphene and SWCNTs. However, the synthesis of BN

structures is a much more difficult task than design of graphene sheets and SWCNTs. The detailed data on BN and carbon nanostructures may be found elsewhere [12,14,16–18].

In order to provide additional diversity of properties, the heterostructures composed of graphene and h-BN are hotly pursued. The aforementioned similarities and dissimilarities have stimulated considerable interest in graphene-like boron nitride-carbon (GBNC) heterostructures since the close geometries guarantee a good match in the lattice and bond lengths, while the differences in properties provide a high degree of the tunability of the functions and performance [19,20]. Very recently, novel electronic switches, spin filters, and electromechanic sensors based on GBNC sheets have been studied computationally [21–26]. Mechanical studies have shown that GBNC sheets display strong plastic deformations, and the failure mechanism is governed by the boundaries between two regions [27–29]. Electronic properties of such sheets depend on few factors such as the distance between boron nitride and carbon domains, the shape of domains, the concentration of different components in the GBNC sheet, and the defects [19].

Moreover, GBNC sheets as two-dimensional materials with tunable optical properties and high carrier mobility offer vast opportunities for thin-film excitonic solar cells (XSC) production. To tune electronic band gap, optical absorption, and exciton binding energy

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of a GBNC monolayer one should vary the carbon domain size and shape [19,30]. Thus, Bernardi et al. presented the XSC model based on semiconducting GBNC material with the potential to achieve tunable 10–20% power conversion efficiency [30]. Recently, Zhang et al. have theoretically studied electronic properties of GBNC heterostructures by systematically considering possible interface configurations [31]. Electronic properties of such structures, depending on the type of the interface, show half-metallic or semi-conducting character. The authors have emphasized the novelty and diversity of the potential applications of GBNC heterostructures, and proposed them as a practical alternative to graphene and graphene nanoribbons [31].

Using tight-binding simulations, Tran et al. showed that the band gap of the GBNC nanoribbons could be strongly suppressed with the increase of the transverse electric field [32]. Furthermore, they have achieved an on/off ratio higher than  $10^4$  at room temperature owing to the electric field effects. This high on/off ratio indicates that such GBNC structures are good candidates for electronic switches.

It is worth mentioning, however, that the experimentally available GBNC materials are not structurally perfect. A series of defects, such as vacancies, dopants, and Stone-Wales (SW) defects, may crucially alter their electronic and mechanical properties. A decade ago, chemical reactivities near the SW defect on the sidewall of SWCNTs were studied [33]. In turn, the comprehensive works of Li et al. and An et al., using periodic and cluster calculations, respectively, investigated the influence of SW defects on electronic properties and reactivities of BNNTs [34,35]. They followed by a number of papers on defective graphene, silicene, h-BN, and other two-dimensional materials [19,36–38]. Very recently, Wang et al. have studied the formation, structural, and electronic properties of Stone-Wales defects in h-BN [39].

However, defects in GBNC heterostructures receive little attention. By analogue with their counterparts, one may conclude that the effects of defects on electronic, gas adsorption, and mechanical properties as well as chemical reactivity are of importance. In spite of the significant interest in such materials, the detailed studies of SW defects in heterostructures are rather scarce. Many questions are far from being answered.

For these reasons, a theoretical study on the SW defects influence on reactivity and structural properties of GBNC sheets is certainly in need. Quantum chemistry calculations in the framework of density functional theory (DFT) were carried out aiming to answer the following questions: (i) are the small GBNC sheets more favorable for SW defect formation; (ii) how does the SW defect affect the reactivity of a GBNC monolayer; (iii) what is the comparative behavior of graphene, h-BN, and GBNC sheets; (iv) what is the most reactive site at boron nitride/carbon interface in a GBNC sheet? We expect that the present work can answer these questions thus clarifying the interface effects and stimulating new experimental and theoretical investigations on hybrid nanomaterials.

## 2. Computational methods

DFT calculations were carried out using Orca 3.0.3. program package [40]. The GGA PBE functional [41,42] together with the SVP basis set [43] were employed to optimize the geometrical structures of all studied models. In SVP, the inner shell atomic orbitals are described by a single basis function, two basis functions are provided for each valence shell atomic orbital, augmented by a set of polarization functions. The PBE has been demonstrated to be a reliable and commonly used level of theory in the study of different nanostructures [38,39,44]. For all calculations, the convergences in energy and force were set to  $5 \times 10^{-6}$  e<sub>h</sub> and  $3 \times 10^{-4}$  e<sub>h</sub>/Bohr.

Three types of finite-size nanostructures, graphene, h-BN, and GBNC sheets, were considered to represent defective and defect-free materials. Although coronene (C<sub>24</sub>H<sub>12</sub>) can be regarded as the smallest molecule that resembles properties of graphene [14,45,46], we employ larger models to study defect formation and surface reactivity. Heidari et al. considered h-BN models consisting of 28 hexagons as appropriate to study their sensing properties [47]. Besides this, previous papers of Pan et al. and Li et al. reported that the formation energies of SW defects in SWCNTs and BNNTs depend not only on the defects orientation, but also on NTs radii [35,48]. Thus, to address this issue as well as exclude influence of a size of our models, we employ into consideration five GBNC sheets of various widths as well as five graphene and h-BN models for the sake of comparison. The following structures C<sub>72</sub>H<sub>24</sub>, C<sub>88</sub>H<sub>26</sub>, C<sub>104</sub>H<sub>28</sub>, C<sub>120</sub>H<sub>30</sub>, C<sub>136</sub>H<sub>32</sub>; B<sub>36</sub>N<sub>36</sub>H<sub>24</sub>, B<sub>44</sub>N<sub>44</sub>H<sub>26</sub>, B<sub>52</sub>N<sub>52</sub>H<sub>28</sub>, B<sub>60</sub>N<sub>60</sub>H<sub>30</sub>, B<sub>68</sub>N<sub>68</sub>H<sub>32</sub>; C<sub>36</sub>B<sub>18</sub>N<sub>18</sub>H<sub>24</sub>, C<sub>44</sub>B<sub>22</sub>N<sub>22</sub>H<sub>26</sub>, C<sub>52</sub>B<sub>26</sub>N<sub>26</sub>H<sub>28</sub>, C<sub>60</sub>B<sub>30</sub>N<sub>30</sub>H<sub>30</sub>, C<sub>68</sub>B<sub>34</sub>N<sub>34</sub>H<sub>32</sub> were used to represent graphene, h-BN, and GBNC sheets, respectively (Figs. S1–S3 (Supporting Information)). All edges of studied models are saturated with hydrogen atoms to avoid the dangling.

The SW defect was made by rotating a C–C or B–N bond, depending on the studied model, by 90° with four adjacent hexagons fused into two pentagon-heptagon pairs. Defect formation energies (E<sub>r</sub>) are defined as:

$$E_r = E_{SW} - E_{pristine},$$

where E<sub>pristine</sub> and E<sub>SW</sub> denote the total energy of the pristine sheet and that containing SW defect, respectively.

Because of the considerable reactivity, carbene (CH<sub>2</sub>) was used as a probe to study the reactivity of SW defect sites in GBNC sheets. The reaction energy (E<sub>r</sub>) is defined as:

$$E_r = E_{total}(CH_2/NS) - E_{total}(CH_2) - E_{total}(NS),$$

where E<sub>total</sub>(CH<sub>2</sub>/NS) denotes total energy of the CH<sub>2</sub>-attached nanostructure, E<sub>total</sub>(CH<sub>2</sub>) is the total energy of carbene, and E<sub>total</sub>(NS), is the total energy of a studied nanostructure. Thus, a negative E<sub>r</sub> denotes exothermic reaction.

## 3. Results and discussions

### 3.1. Geometry structures of SW defects in graphene, h-BN, and GBNC sheets

It was established earlier that there are two kinds of C–C and B–N bonds in SWCNTs and graphene as well as in BNNTs and h-BN, respectively [35,49,50]. One of them is ‘parallel’ to the axis of the nanotube (or the direction of the sheet elongation), and the other is ‘slanted’ (Fig. 1); they are denoted by ‘1’ and ‘2’, respectively. Thus, two types of SW defects in graphene and h-BN are possible. By analogue, we will consider two types of bonds in the GBNC sheets (Fig. 1). Fig. 2 shows the optimized structures of C<sub>68</sub>B<sub>34</sub>N<sub>34</sub>H<sub>32</sub> GBNC sheets containing SW defects. It is noteworthy that we consider two Stone-Wales defects, namely straight (SWI) and slanted (SWII), depending on the rotation of a B–C or B–N bond, respectively (Fig. 2).

For graphene sheets, the obtained data on d<sub>C–C</sub> are consistent with the previous studies. The lengths of the bonds at the 7-7 ring fusions of SWI (1.36 Å) and SWII (1.35 Å) defects also correlate well with previous findings [51,52]. The B–N bond lengths in the h-BN sheet are 1.46 and 1.45 Å. The abridgement of the bonds at the 7-7 ring fusions is 0.8–0.9 Å irrespective of the type of SW defect.

The new B–B and N–N bonds appear in the defective h-BN sheets. The length of the B–B bond (1.68 Å) is independent of the type of the SW defect, while the N–N bond in the case of SWII (1.43 Å) is somewhat longer than that in h-BN with SWI (1.42 Å).

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