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Boron and nitrogen doping in graphene: an experimental and density functional theory (DFT) study

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Abstract

Boron (B) and Nitrogen (N) doped few layer graphene (BNG) is directly synthesized via electric arc discharge (EAD) method. NH_3 and BCl_3 gas mixtures are used in the synthesis atmosphere. Raman spectroscopy is used to determine graphene's purity and number of layers. The investigation of structure and morphology of pristine graphene and BNG are carried out via Transmission Electron Microscopy (TEM). The presence of B and N in the structure of graphene is detected by Energy Dispersive X-ray Spectroscopy (EDS) analysis. Elemental mapping show that N and B are distributed homogeneously in the graphene structure. It is observed that doping process did not affect the positions of the D, G and 2D bands in the Raman spectroscopy. The effect of doping on the number of layers of graphene is found negligible. TEM results exhibit that pristine graphene and BNG have 5 to 6 layers. Besides, the theoretical calculations based on Density Functional Theory (DFT) are employed to support experimental studies. Theoretical results based on DFT showed that bonding of B and N is favorable.

1. Introduction

Graphene, consisting of carbon atoms having sp2 hybridization with hexagonal lattice structure, is an extraordinary two-dimensional (2D) material. Graphene has remarkable chemical, mechanical and physical properties. High tensile strength (130 GPa), outstanding elastic modulus (1 TPa), great surface area (2630 $m^2\ g^{-1}$) and high thermal conductivity (5000 $W\ m^{-1}\ K^{-1}$) are some of the outstanding features of graphene [1–5].

Synthesis of graphene can be classified into two different approaches: bottom-up and top-down. For top down, graphene is obtained directly from graphite. Arc discharge, solution-based exfoliation, micromechanical cleavage, electrochemical exfoliation, exfoliation of graphite intercalation compounds, exfoliation of graphite oxide, evaporation with laser and unzipping carbon nanotubes are some of the top down synthesis methods. On the other hand, in the bottom-up approach, small organic molecules are used to form graphene layers via catalytic processes. Chemical vapour deposition (CVD), epitaxial growth on SiC and SiC degradation on high temperature are the most commonly used bottom-up synthesis methods. The arc discharge method have some advantages comparing to other methods due to its low cost, high efficiency and no need for any catalyst. Also, graphene which is synthesized by arc discharge has good dispersibility in organic solvent and high thermal stability. In the EAD method, many parameters such as carbon sources, buffer gases, pressure,catalysts current/voltage, electrode morphologies /diameters affect the purity and number of layers of synthesized graphene [6–10].

Chemical doping is a commonly used method for modifying the properties of materials. The elemental composition, surface and electronic properties of the material can be altered by chemical doping process. For carbon based materials, chemical doping is aiming to increase electrical and thermal conductivity [11].

Generally, there are two techniques to dope graphene: (1) the adsorption of the selected materials to the graphene surface, (2) substitutional doping of specific atoms into the lattice structure of graphene [4].

Various elements such as Nitrogen (N), Sulfur (S), Boron (B), Phospor (P), Oxygen (O) and Fluorine (F) can be doped into graphene. B and N are mostly preferred chemical dopants for graphene since they have similar atomic dimensions with that of C and moreover they can form strong bonds with C. B and N doped graphene can be used in several applications area such as fuel cells, sensors, spin filter devices and lithium ion batteries [2, 3, 12].

There are many process used for the direct synthesis of B and N doped graphene such as EAD, CVD, solvothermal method, segregation growth. According to other methods, arc discharge is suitable for mass production. Also this method provides *in situ* substitution of atoms such as N and B. during graphene synthesis process. The disadvantages of the method are the high current/voltage requirement, low level of doping and mostly the multi-layered graphene production [13–15].

Zou *et al* synthesized N doped graphene nano flakes by arc discharge. Doping process is increasing the static magnetization property while decreasing the electrical conductivity. Also graphene lattices substantially reduce crystallization degree. Dey *et al* synthesized B and N doped graphene quantum dots by two-step chemical processes consisting of arc discharge and chemical scissoring. Li *et al* reported that synthesis of large scale N doped multilayer (2–6 layers) graphene via arc discharge in the He and NH_3 mixing atmosphere. Sedelnikova *et al* were synthesized carbon products by arc discharge method with the addition of B and/or N. Morphological and electrical properties of synthesized carbon products has been investigated. They observed that boron-nitrogen doped carbon products showed the highest electrical conductivity. Wu *et al* synthesized monolayer graphene doped with N and B via CVD technique by using solid precursors such as urea and boric acid. Synthesized graphene has better electrical and optical properties than plasma treated N and B doped graphene. Bepete *et al* reported basic methodology for growing large area graphene doped with small BN domains on copper foils using a one-step CVD technique with methane, boric acid powder and nitrogen gas as the C, B and N source. Wang *et al* developed a simple low-cost approach for mass production of B and N doped graphene with various N and B doping levels by thermal annealing graphene oxide with boric acid under ammonia atmosphere. The resultant samples were showed that good oxygen reduction reaction (ORR) for electrocatalytic activities. Guan *et al* synthesized few layer N doped graphene nanosheets (GNSs) by arc discharge method under N atmosphere at high temperature. The N doping graphene has been performed at 800 °C. They claimed that this method was cheaper and safer than other methods [3, 16–22].

In this study, BNG is synthesized directly by EAD. NH_3 and BCl_3 gas mixtures are used in the synthesis atmosphere. Raman spectroscopy results of pristine graphene indicates successful synthesis of high purity, 5 to 6 layers of graphene. According to Raman spectroscopy results of BNG, B and N atoms are entered to graphene lattice. The presence of B and N in the structure of graphene are also detected by EDS analysis. Furthermore the crumpled structure of graphene is observed by TEM. Moreover, DFT calculations with B3LYP method have been utilized on doping of B and N into graphene structure.

2. Material and methods

2.1. Experimental

BNG are synthesized using homemade stainless steel arc discharge reactor. High purity graphite rods (99,9%) are used as anode and cathode. Arc discharge reactor is kept under vacuum for 5 min. After the vacuum process, the reactor is filled with NH_3-BCl_3 gas mixtures and the arc current is kept constant at 150 A. According to the literature available, the key difference is the buffer gases we used in the synthesis of BNG. Formation of BNG occurs at the inner surface of the reactor (figure 1(b)). All the experimental parameters are given in table 1. BNG synthesis diagram are shown in figure 1(a). The synthesis of high purity and few layers graphene by EAD method are described in a previous study [6].

Raman spectroscopy (Renishaw in via reflex) are used to determine graphene's purity and number of layers. The Raman spectra is measured from 500 to 3000 cm^{-1} via an excitation wavelength of 532 nm. Structure and morphology investigations of the graphene and Selected Area Diffraction (SAED) are carried out via TEM (JEOL JEM 2100 UHR) at an accelerating voltage of 200 kV. The relative amount of N and B in the structure of synthesized graphene is determined by EDS (Bruker XFlash 6–100) systems. Elemental mapping is performed to determine the distribution of N and B in graphene.

2.2. Theoretical work

The theoretical calculations employed in this study have been based on DFT [23]. The software of Gaussian 09 [24] has been used with the B3LYP-Hybrid method [25, 26]. The basis set of 6–31G (d,p) has been utilized in calculations for all atoms.

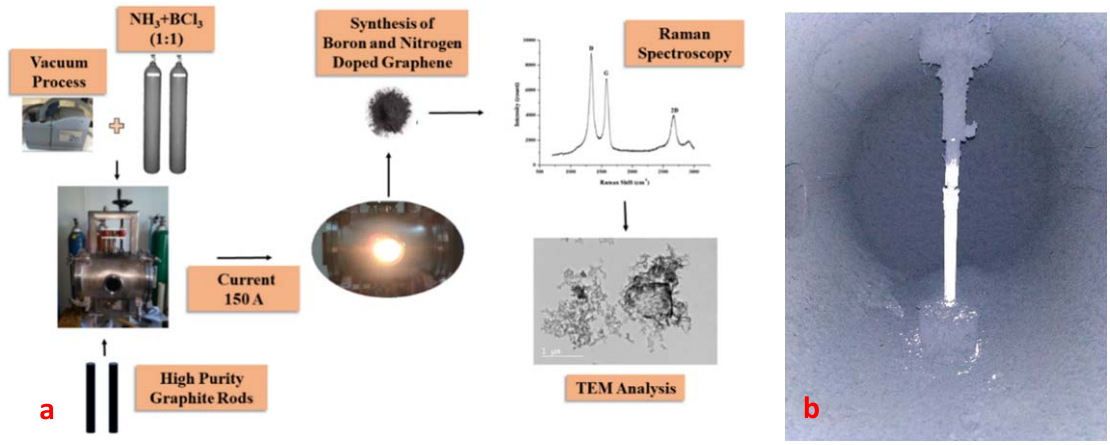

Figure 1. BNG synthesis diagram (a), inner surface of the reactor (b).

Table 1. Experimental parameters.

Gases and Ratio of Gas Mixtures	$NH_3 + BCl_3$, 50%–50%
Characteristics of Electrodes	99,9% purity, diameter: 12 mm, length: 10 cm
Pressure of Gas	0.1 bar
Vacuum Period Before the Synthesis	5 min
Arc Current During the Synthesis	150 A

The graphene cluster used for calculations has been modeled as two layers including 60 C atoms (30 C atoms in each layer). Dangling bonds of the C atoms have been saturated with H atoms in order to obtain neutral cluster. In this work, all atoms of the structures except H atoms were relaxed during all DFT calculations. The terminating H atoms have been kept fixed during the calculations. B and N atoms have been doped into each layer of the graphene structure.

Equilibrium geometry (EG) calculations are used to optimize geometries and obtain energies. In present study, energy difference values include zero point energy (ZPE) corrections. These energies are calculated using the frequency keyword (freq = raman) in Single Point Energy (SPE) calculations. In addition, Raman frequency and thermal energy are calculated by SPE calculations at 298 K in Gaussian software [27]. This energy value is computed as follows:

$$E = E_{\text{electronic}} + \text{ZPE} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}} \quad (1)$$

where E is the sum of the electronic, zero point and thermal energies. Additionally, the convergence criteria are 12×10^{-4} for gradients of root-mean-square (rms) displacement, 18×10^{-4} for max displacement, 3×10^{-4} for rms force and 45×10^{-5} for max force for theoretical calculations utilized in this study.

3. Results and discussions

3.1. Raman analysis

We employ Raman spectroscopy technique in order to detect the characteristic bands of synthesized pristine and BNG. D, G and 2D bands are located at 1335 cm^{-1}, 1573 cm^{-1} and 2670 cm^{-1}, respectively for pristine graphene as shown in figure 2(a). D band indicates defects in the structure of carbon based materials due to the lattice distortion introduced by impurity elements. The position and shape of the G band shows doping effect, defects, number of graphene layers and stress. The 2D band is the characteristic band of graphene and its shape is related to the number of layers.

L_G/L_{2D} ratio is calculated with Raman spectroscopy results in order to determine the total graphene layers while, L_D/L_G ratio is used to obtain information about graphene's purity. According to the literature, L_D/L_G ratio should be between 0 and 1. In a previous work [28], for a single graphene L_G/L_{2D} ratio was reported as 0.25.

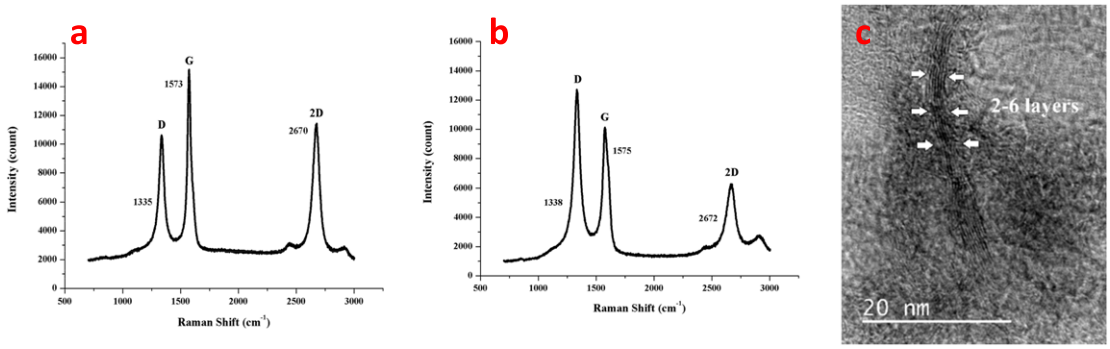

Figure 2. Raman spectroscopy results for pristine graphene (a), BNG (b) and TEM images of graphene layers for BNG (c).

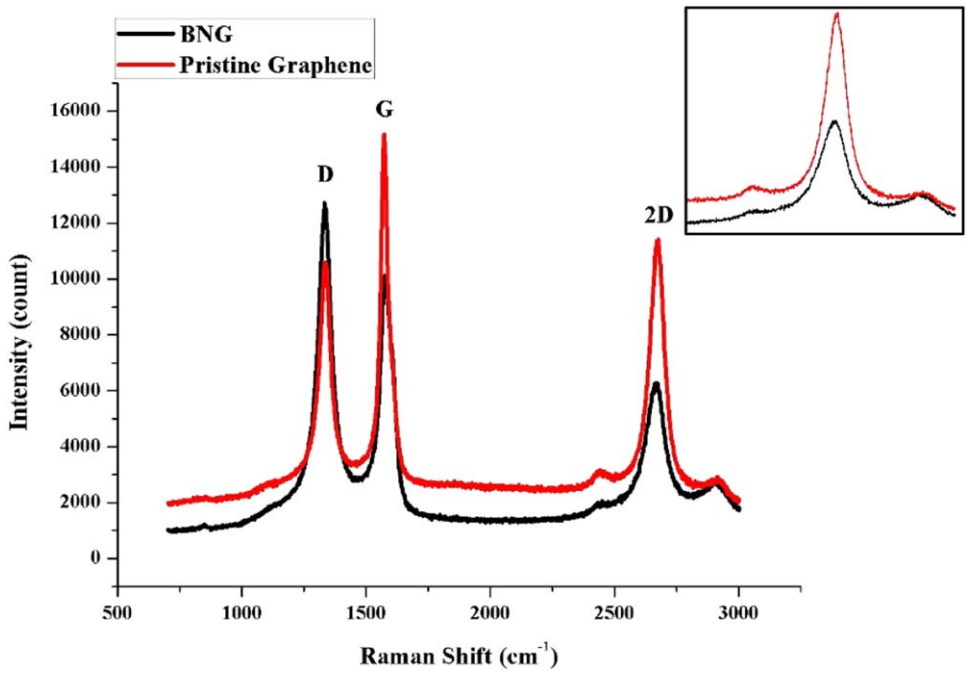

Figure 3. Comparative Raman Spectroscopy results for Pristine Graphene and BNG.

Table 2. Band ratios for pristine graphene and BNG.

Type of Graphene	D Band Intensity (L_D)	G Band Intensity (L_G)	2D Band Intensity (L_{2D})	L_D/L_G Ratio	L_G/L_{2D} Ratio
Pristine Graphene	10 588	15178	11360	0,70	1,34
BNG	12656	10129	6278	1,25	1,61

Table 2 shows L_D/L_G and L_G/L_{2D} ratios of pristine graphene and BNG. As seen from figure 2(b), doping process did not affect the positions of the D,G and 2D bands which is similar with previous findings [29].

Graphene layers have a more irregular structure than pristine graphene due to the doping process [30]. Besides, the number of layers of graphene has also increased after doping process. Comparative Raman spectroscopy results for pristine graphene and BNG are shown in figure 3.

An increase in the intensity of the D band of BNG is observed compared to that of pristine graphene (figure 3). This result indicates that B and N atoms are introduced into the lattice of graphene. On the other hand, B and N doping resulted with a downshift in the relative intensity of the G band. The 2D band is sensitive to doping process and defects. As shown in figure 3a decrease in the relative intensity and a broadening are observed in the 2D band of BNG.

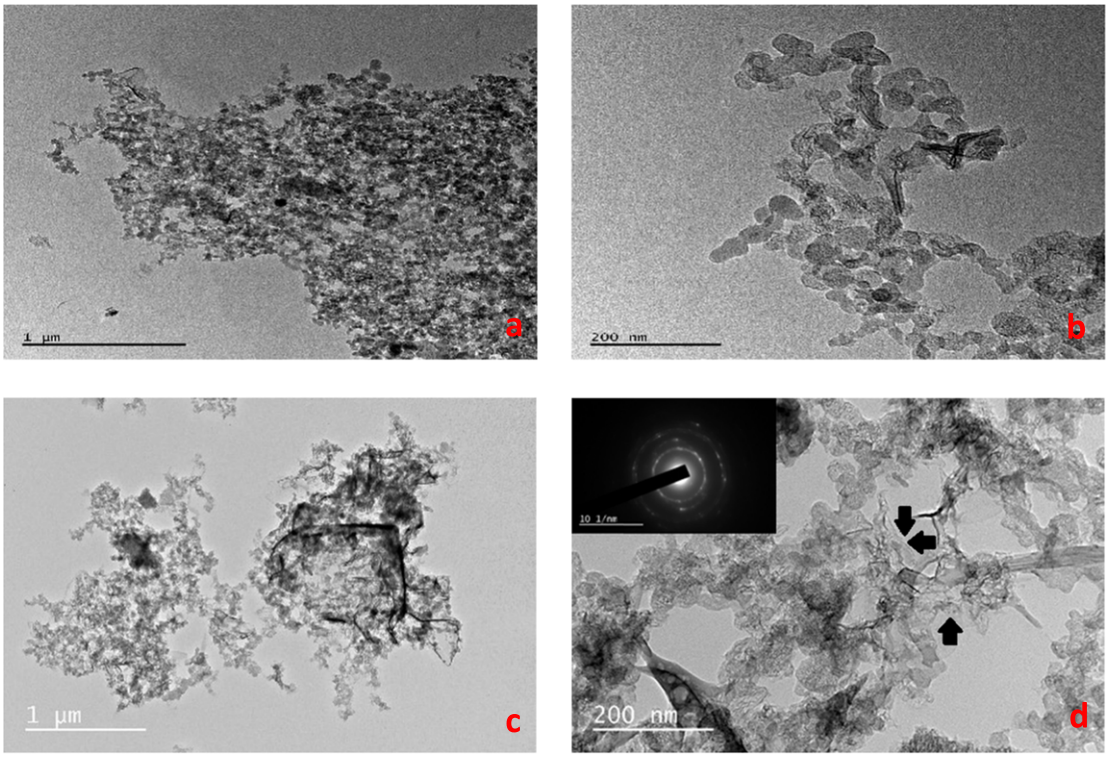

Figure 4. TEM images of the synthesized pristine graphene (a), (b) and BNG (c), (d). Inset shows the corresponding SAED pattern.

On the other hand, the relative ratio of L_D/L_G is increased from 0.70 to 1.25. According to the literature available, distortions occur in the graphene structure because of different bond distance in the BNG structure (C–C, C–B, C–N bonds). The L_G/L_{2D} ratio varies between 1.34 and 1.61 for pristine graphene and BNG, respectively. According to L_G/L_{2D} ratio, pristine graphene and BNG have 5 to 6 layers. The effect of doping on the number of layers of graphene is found negligible [30].

3.2. TEM

The morphological observations of pristine and doped graphene are performed via TEM. Figure 4 shows 2D planar-like structure for pristine graphene and BNG. The arrow marks in figure 2(c) also indicate the number of layers, which is in good agreement with our Raman results. Graphene has the 0.213 ∼ 0.215 nm spacing for the hexagonal diffraction pattern [31]. BNG has ∼0,248 nm spacing due to structures distortion caused by the intercalation of N and B atoms. Also, SAED pattern of BNG shows a ring like diffraction pattern with dispersed bright spots [32]. SAED pattern are consistent with previous studies [12, 33]. Elemental mapping is also performed in order to prove the existence of N and B as shown in figure 5. It is observed that both N and B are distributed homogenously on graphene layers [11, 34].

Elemental mapping results show that N and B are distributed homogeneously in the graphene structure. As a result of EDS analysis, 69,76% C, 10,14% N and 20,10% B are determined in the structure.

3.3. Theoretical calculations

Firstly pristine graphene cluster is optimized by EG calculation. The optimized structure of two layers graphene cluster is represented in figure 6. B and N atoms have been doped into the layers of the graphene structure. Two B atoms and two N atoms have been used for this purpose. In order to simplify the modelling studies have been performed based on the two layers graphene and two B and N atoms. B and N atoms have been doped on different seven positions in two layers graphene structure. These seven positions have been optimized by EG calculations. The optimized geometries for these positions have been presented in figure 7.

Table 3 shows energy values including ZPE and thermal corrections for these positions. As can be seen from the table 3, total energy values (including corrections) for position 1 have been calculated to be −2310.3090268 a.u., which designates that doping of B and N atoms into the graphene structure as position 1 (B-N) is most favorable. Moreover, for the position 1, total energies have been computed as 1.71 and 2.08, respectively based

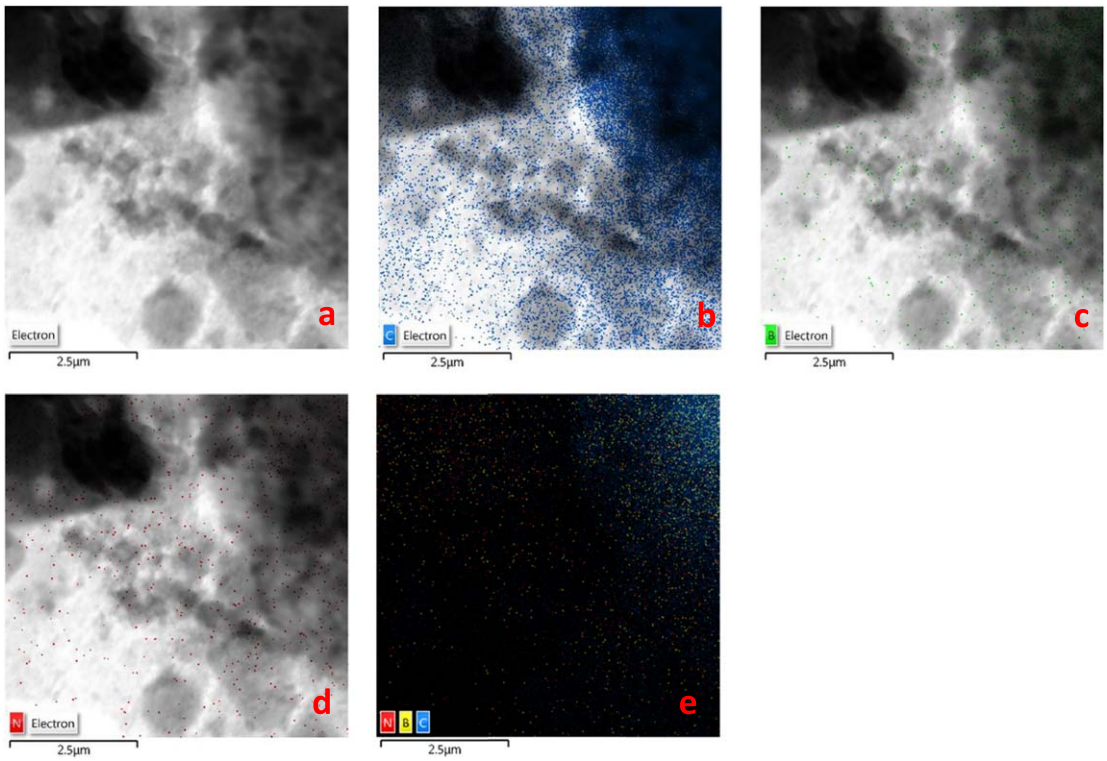

Figure 5. (a) TEM image for elemantel mapping region and results and (b) Carbon (c) Boron (d) Nitrogen (e) C, B and N element mapping images of BNG.

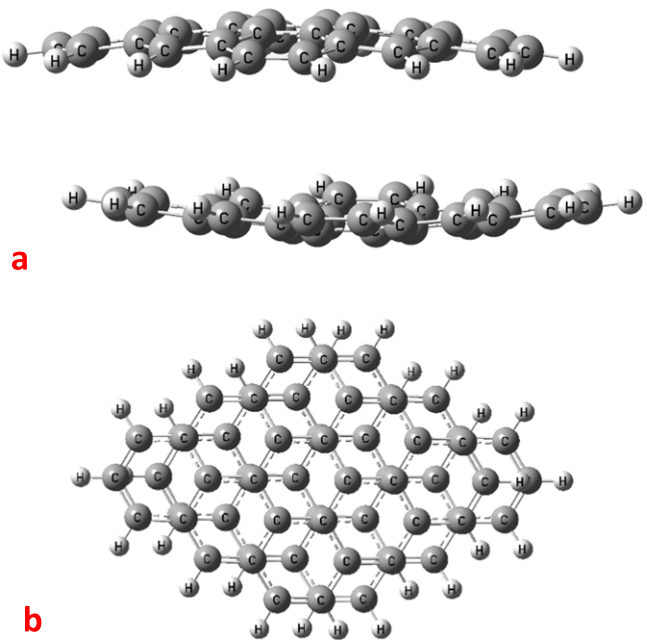

Figure 6. Optimized two layers graphene structure (a) Side view (b) Top view.

on the Raman frequency calculations (by SPE). On the other hand, L_D/L_G and L_G/L_{2D} ratios for synthesized BNG samples are calculated as 1.25 and 1.61, respectively. The theoretical calculations are performed based on two BNG layers however, the experimentally obtained BNG are 5 to 6 layers. The variation between theoretically

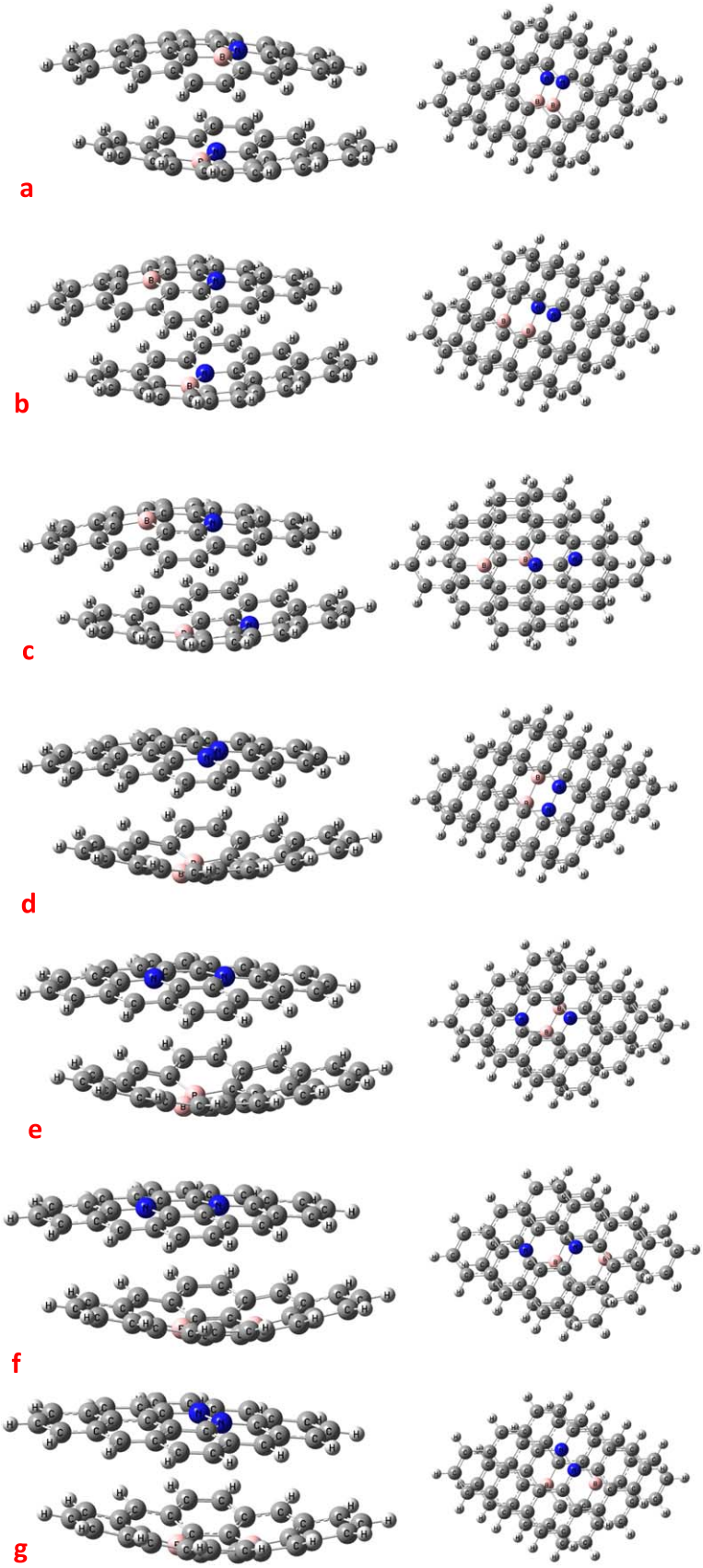

Figure 7. Optimized geometries (with top and side views) for positions of B and N atoms (a) Position 1 (b) Position 2 (c) Position 3 (d) Position 4 (e) Position 5 (f) Position 6 (g) Position 7.

calculates and experimentally obtains band ratios data can be result of number layer differences. Theoretical result (doping B and N atoms as B-N on each layer of the graphene structure) supports the experimental result that N and B are distributed homogeneously in the graphene structure.

Table 3. Total energies (including ZPE and thermal corrections) of optimized structures for positions.

Positions	Total Energy (a.u.)
1	−2310.3090268
2	−2310.2568475
3	−2310.2044684
4	−2310.0407781
5	−2310.0648080
6	−2310.0916711
7	−2310.0586882

4. Conclusions

The synthesis and characterization of BN doped graphene with DFT-B3LYP calculations for B-N doped graphene clusters were investigated in this study. The summary of results as follows:

1. B and N are successfully doped into the few layer graphene structures in EAD system designed and manufactured by our project team
2. L_D/L_G and L_G/L_{2D} ratios are calculated for both pristine and BNG based on Raman measurements. It is observed that L_D/L_G ratio increases from 0.70 to 1.25 while, L_G/L_{2D} ratio varied from 1.34 to 1.61. This increase showed that B and N were successfully introduced into the graphene lattice.
3. Theoretical calculations also confirm that B and N are homogenously distributed in graphene lattice. Different scenarios for the position of B and N atoms in the graphene lattice are examined. Among all these possibilities, the most favorable one is the bonding of B to N (B-N in each layer) as shown in position 1 (figure 7(a)).
4. The wrinkled nature of pristine graphene and BNG is detected by TEM. Besides the number of layers were also determined. The interplanar distance of BNG are calculated from SAED, the calculated value is compared with previous studies. This difference is the result of structural distortion due to the BN doping.

As a future study suggestion, electrical and thermal conductivity and energy storage capabilities of BNGs can be examined. It can be compared with BNG materials produced by different methods. Furthermore, different conditions can be tried for higher purity and low-layered graphene production.

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