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Formation energy investigation of monovacancy defects for CBNNTs

A.A.El-Barbary[1,2]*, Kh.M.Eid[1], M.A.Kamel[1], M.M.Hassan[1]
[1]Physics Department, Faculty of Education, Ain Shams University, Cairo, (EGYPT)
[2]Physics Department, Faculty of Science, Jazan University, Jazan, (KINGDOM OF SAUDI ARABIA)
E-mail : ahla_eg@yahoo.co.uk

ABSTRACT

We present a theoretical study of the formation energies of monovacancy defects of CBNNTs(1:5) (BN/C with ratio 1/5). We have considered a range of different nanotube diameters and chiralities, as well as different arrangements of C and BN. Applying B3LYP/6-31g(d,p) with using density functional theory (DFT), three distinct structural combinations of carbon nanotubes (CNTs) and boron-nitride nanotubes (BNNTs) have been investigated in order to model carbon boron nanotubes (CBNNTs): BN-random distribution, BN-row distribution, and BN-zigzag distribution. We have shown for first time a detailed study of formation energies of the monovacancy defects in CBNNTs can be altered depending on the position of the removing carbon atom rather than their diameters and chiralities. The smallest formation energies are obtained when the carbon atom is removed close to a nitrogen atom, however the highest formation energies are obtained when the carbon atom is removed close to a carbon atom. This work may allow the fundamental control needed for designing next-generation electronic components of CBNNTs.

KEYWORDS

Formation energy;
Heterojunctions;
CBNNTs;
Monovacancy defect;
DFT.

INTRODUCTION

Carbon nanotubes (CNTs) and Boron-nitride nanotubes (BNNTs) possess different electrical behaviors. Therefore, the heterogeneous CBNNTs may allow the fundamental control needed for designing next-generation electronic components, sensors, and structural composites[1-8]. With the development of fabrication technology in nanometer materials, heterojunctions formed between nanotubes have recently been synthesized[9-15]. However, the behaviors of the resulting heterojunctions as growth, defects and stability are still unknown. This information is necessary when designing optimal synthesis procedures for these structures and for understanding their resulting properties, which may be tuned for specific applications. Monovacancy defects can be created during the growth, therefore it is considered to be the most common defect. In this article we provide a detailed theoretical study of the formation energies of monovacancies of short heterogenous C/BN nanotube segments, applying density functional theory (DFT) calculations and using G03W package. Most of the previous works have been studied the pristine short heterogeneous nanotube segments. Previous

DFT studies have shown that the electronic structure of hybrid CBNNTs depends on the pattern and the composition of C and BN within the tube lattice[2-8]. In our calculations, the short CNT and BNNT segments corresponding to zigzag (5,0), (7,0) and (9,0) and armchair (4,4), (6,6) and (7,7) structures, were chosen to model the general features of these hybrid materials, see Figure 1. Here, we define three distinct structural combinations of short CNT with BNNT segments to be used in our modeling investigations: (1) alternating segments of CNT and BNNT (BN-random distribution), (2) continuous segments of CNT and BNNT through the radial tube (BN-row distribution), and (3) continuous segments of CNT and BNT through the tube axis (BN-zigzag distribution). While many other arrangements can be imagined, we focus on these three well-defined geometric linkages, in order to establish well-characterized formation energies of monovacancies of short heterogeneous CBNNT segments. Also, the modifications of formation energies due to effects of various ratios of number of BN atoms to number of C atoms within short CBNNT segments have been investigated. However, the monovacancy defects are created at different three positions: by removing a carbon atom close to a carbon atom (v_1), or close to a boron atom (v_2) or close to a nitrogen atom (v_3).

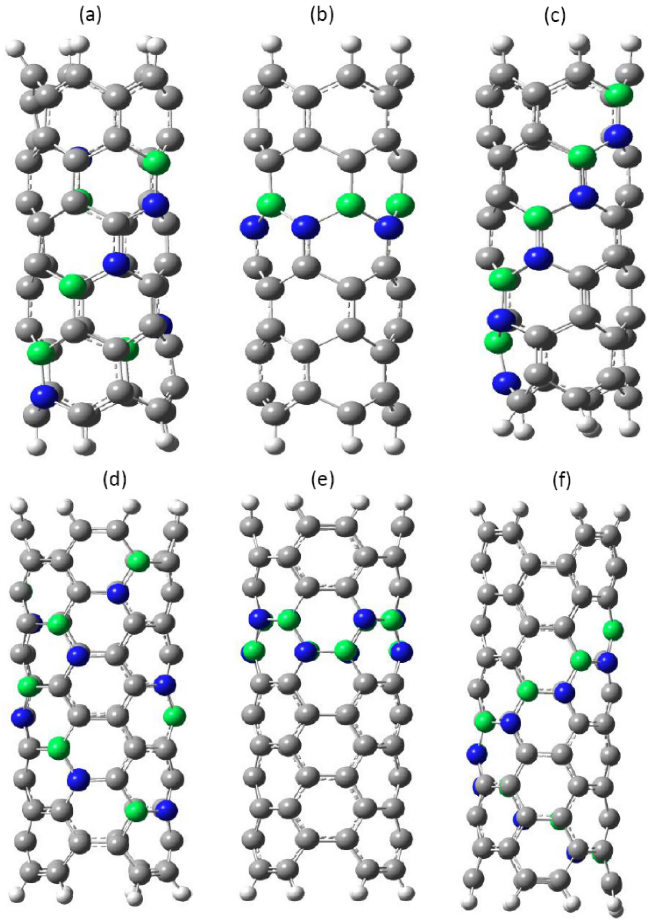

Figure 1 : Fully optimized geometries of a) BN-random b) BN-row c) BN-zigzag of (5,0) CBNNTS(1:5), d) BN-random, e) BN-row, and f) BN-zigzag of (4,4) CBNNTS (1:5). Carbon atom (gray), nitrogen atom (blue) and boron atom (green).

COMPUTATIONAL METHODS

All calculations were performed with the DFT as implemented within G03W package[16-18], using B3LYP exchange-functional and applying basis set 6-31g(d,p). All obtained structures are fully optimized with spin average. Eighteen structures of pristine short heterogeneous CBNNT segments with ratio 1/5 of BN atoms to C atoms, have been investigated. The BN atoms are distributed through the CNT by three ways as explained before: BN-row distribution, BN-random distribution and BN-zigzag distribution. Every distribution is applied on six short CBNNT segments; (5,0)CBNNT, (7,0)CBNNT, (9,0)CBNNT, (4,4)CBNNT, (6,6)CBNNT and (7,7)CBNNT. For monovacancy defects in short CBNNT segments, fifty-four structures with ratio CBNNTs(1:5) are studied. The monovacancy defects are applied at different three positions (v_1, v_2, v_3), as explained before, for each structure of the eighteen different configurations of short CBNNT segments. The formation energies of monovacancy defects (E_f)[19] are calculated using the following formula:

$$E_f = E_p - E_d - E_c \quad (1)$$

where E_p is the total energy of pristine nanotube, E_d is the total energy of the defected nanotube, and E_c is the chemical potential of carbon atoms.

RESULTS

By employing ab initio simulations, Berseneva *et.al*[20] have been studied the C doping of h-BN systems. They found that although radiation damage should definitely play a role in the substitution process, the main driving force for the substitution is the energetics of the system, as it costs less energy to substitute a B-atom than N-atom, especially when the system is positively

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charged. In this paper we have studied the formation energies of monovacancy defects in BN doping in CNTs. Figure 1 shows the three different ways of distributing BN atoms in zig-zag and arm-chair carbon nanotubes, BN-random distribution, BN-row distribution and BN-zigzag distribution.

Vacancy migration in hexagonal boron nitride Boron vacancies have been studied by Zobelli et.al.[21], they have found that boron first thermally activated and can migrate to form more stable BN divacancies whoever, in the contrary, nitrogen vacancy migration is energetically unfavorable within all the temperature range below the melting point of h-BN. For each structure of the Eighteen different configurations of undefected CBNNTs, the mono-vacancy defects are created by three ways: removing a carbon atom close to a carbon atom (v_1), or removing a carbon atom close to a boron atom (v_2) or removing a carbon atom close to a nitrogen atom (v_3), see Figures 2,3. Hence, in this work,

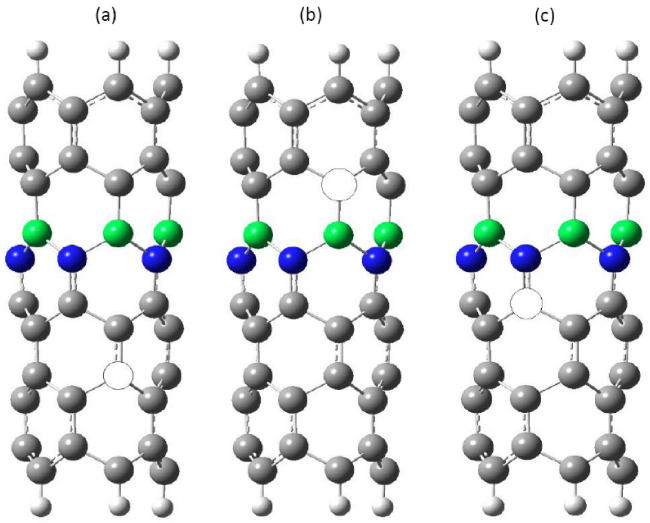

Figure 2 : Positions of monovacncy defects a) v_1 b) v_2 and c) v_3 for BN-row (5,0)CBNNTS (1:5). The big circles refere to positions of the mono-vacancy defects.

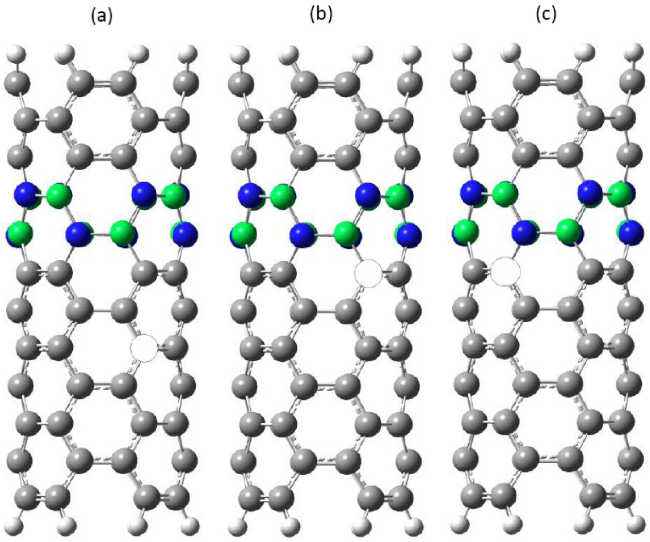

Figure 3 : Positions of monovacncy defects a) v_1 b) v_2 and c) v_3 for BN-row (4,4)CBNNTS (1:5). The big circles refere to positions of the mono-vacancy defects.

fifty-four monovacancy defect structures of heterogeneous CBNNTs(1:5) are investigated.

From TABLE 1, for (5,0) CBNNTs the heighest and the lowest calculated formation energies for monovacancy defects are 9.91 eV and 7.12 eV when the carbon atom is removed close to carbon atom and nitrogen atom, respectively, comparing with 7.82 eV for the monovacancy defect in pristine (5,0)CNT. For (7,0) CBNNTs, the heighest and the lowest calculated formation energies for mono-vacancy defects are 9.73 eV and 7.31 eV when the carbon atom is removed close to carbon atom and nitrogen atom, respectively, comparing with 9.53 eV for the monovacancy defect in pristine (7,0)CNT. For (9,0) CBNNTs, the heighest and the lowest calculated formation energies for mono-vacancy defects are 10.24 eV and 8.23 eV when the carbon atom is removed close to carbon atom and nitrogen atom, respectively, comparing with 9.80 eV for

TABLE 1 : Calculated formation energies for mono-vacancy defects in CNTs , $E_f(v)$, and zig-zag CBNNTs(1:5), $E_f(v_1)$, $E_f(v_2)$ and $E_f(v_3)$. Energy is given in eV.

	CNTs	CBNNTs(1:5)								
		BN-random			BN-row			BN-zigzag		
	$E_f(v)$	$E_f(v_1)$	$E_f(v_2)$	$E_f(v_3)$	$E_f(v_1)$	$E_f(v_2)$	$E_f(v_3)$	$E_f(v_1)$	$E_f(v_2)$	$E_f(v_3)$
(5,0)	7.82	9.91	8.67	8.34	7.98	7.44	7.12	9.72	8.20	7.76
(7,0)	9.53	9.14	8.99	8.87	9.08	8.37	7.31	9.73	8.62	8.00
(9,0)	9.80	9.71	8.62	8.67	10.24	9.23	8.23	10.21	8.11	9.15

v_1 refers to remove a carbon atom close to another carbon atom; v_2 refers to remove a carbon atom close to a boron atom; v_3 refers to remove a carbon atom close to a nitrogen atom

the monovacancy defect in pristine (9,0)CNT. For all zig-zag CBNNTs(1:5), it is noticed that the formation energies are increased with increasing the stability/diameters of CBNNTs(1:5). Accroding to different ways of BN-distribution, the formation energies are for BN-raw distribution < BN-zigzag distribution < BN-random distribution.

From TABLE 2, For (4,4) CBNNTs, the heighest and the lowest calculated formation energies for mono-vacancy defects are 9.89 eV and 7.43 eV when the carbon atom is removed close to carbon atom and nitrogen atom, respectively, comparing with 10.18 eV for the monovacancy defect in pristine (4,4)CNT. For (6,6) CBNNTs, the heighest and the lowest calculated formation energies for mono-vacancy defects are 10.31 eV and 8.17 eV when the carbon atom is removed close to carbon atom and nitrogen atom, respectively, comparing with 10.28 eV for the monovacancy defect in pristine (6,6)CNT. For (7,7) CBNNTs, the heighest and the lowest calculated formation energies for mono-vacancy defects are 10.72 eV and 7.88 eV when the carbon atom is removed close to carbon atom and nitrogen atom, respectively, comparing with 10.63 eV for the monovacancy defect in pristine (7,7)CNT. For all arm-chair CBNNTs(1:5), it is noticed that the formation energies are increased with increasing the stability/diameters of CBNNTs(1:5). Accroding to different ways of BN-distribution, the formation energies are for BN-random distribution < BN-raw distribution < BN-zigzag distribution.

TABLE 2 : Calculated formation energies for mono-vacancy defects in CNTs , $E_f(v)$, and arm-chair CBNNTs(1:5), $E_f(v_1)$, $E_f(v_2)$ and $E_f(v_3)$. Energy is given in eV.

	CNTs	CBNNTs(1:5)								
		BN-random			BN-row			BN-zigzag		
	$E_f(v)$	$E_f(v_1)$	$E_f(v_2)$	$E_f(v_3)$	$E_f(v_1)$	$E_f(v_2)$	$E_f(v_3)$	$E_f(v_1)$	$E_f(v_2)$	$E_f(v_3)$
(4,4)	10.18	9.60	8.30	7.43	9.20	8.77	8.54	9.89	7.40	7.90
(6,6)	10.28	9.91	8.86	8.17	10.02	9.42	9.48	10.31	8.30	8.55
(7,7)	10.63	9.38	8.62	7.88	10.27	9.66	9.71	10.72	8.44	8.61

CONCLUSION

A complete set of formation energies calculations, considering a range of different nanotube diameters and chiralities, as well as different arrangements of C and BN is reported. Eighteen structures of short heterogeneous CBNNT segments, and fifty four structures for monovacancy defected of short heterogeneous CBNNT segments are studied using B3LYP/6-31g(d,p). There are three distinct structural combinations of CNTs with BNNTs have been used in our modeling investigations: BN-random distribution, BN-row distribution and BN-zigzag distribution. For all zig-zag and arm-chair CBNNTs(1:5), it is noticed that the formation energies are increased with increasing the stability/diameters of CBNNTs(1:5). It is easier to create the monovacancy defect on CBNNTs when the carbon atom is close to a nitrogen atom. Also, it is found that the formation energy of monovacancy defect on CBNNTs is always less the formation energy of monovacancy defect on CNTs. Accroding to different ways of BN-distribution, the lowest formation energies are to be BN-raw distribution and BN- radom distribution for zig-zg and arm-chair CBNNT(1:5), respectively.

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