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Computational studies of carbon decorated boron nitride nanocones

A. Nouri[1], M. Mirzaei[2*] and M. Yousefi[3]

[1] Department of Chemistry, Shahre-Qods Branch, Islamic Azad University, Shahre-Qods, Iran
[2] Young Researchers Club, Pharmaceutical Sciences Branch, Islamic Azad University, Tehran, Iran
[3] Department of Chemistry, Shahre-Rey Branch, Islamic Azad University, Tehran, Iran

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ABSTRACT

Density functional theory (DFT) calculations have been performed to investigate the properties of carbon decorated (C-decorated) models of boron nitride (BN) nanocones. To this aim, the apex and tip of nanocone have been substituted by the carbon atoms to represent the C-decorated models. The results indicated that dipole moments and energy gaps could reveal the effects of C-decorations on the properties of BN nanocones. Computations of quadrupole coupling constants (Qcc) for boron-11 and nitrogen-14 of the optimized structures have indicated that those boron and nitrogen atoms close to the C-decorated regions detect the most significant effects of C-decorations. Moreover, these atoms could play dominant role in determining the properties of the C-decorated BN nanocones.

Keywords: Carbon decoration; Boron nitride; Nanocone; Density functional theory

INTRODUCTION

The conical structures, which are called nanocones, have been found to be the caps at the ends of nanotubes very soon after the discovery of carbon nanotubes (CNTs) [1, 2]. Some times later, they have been also synthesized as free standing structures [3, 4]. Besides the carbon nanostructures including nanotube, nanocone, and etc., further studies have indicated that boron nitride (BN) nanostructures could be considered as proper candidates for substituting the carbon nanostructures [5]. In contrast with the carbon nanostructures, which are metal or semiconductor depending on their structural topologies, the BN nanostructures have been found to be always semiconductors [6, 7]. During the constructions of BN nanostructures, the impurities such as carbon atoms could participate in the process to yield carbon decorated BN nanostructures [8]. Therefore, the structural properties of the original BN nanostructures could detect the effects of the impurities and the resulted impure nanostructures might yield new properties. Previous studies have indicated that the effects of carbon impurities on the properties of BN nanotubes could be well detected by computing quadrupole coupling constants (Qcc) for boron-11 (^{11}B) and nitrogen-14 (^{14}N) atoms [8, 9].

In this work, we would investigate the effects of carbon decorations on the properties of BN nanocones by means of density functional theory (DFT) calculations. To this aim, we have chosen the models of BN nanocones with 240° declination angles to represent the original

* Corresponding author: mdmirzaei@iaups.ac.ir

and carbon decorated (C-decorated) models of BN nanocones (Figs. 1 – 4). To make the C-decorated models, the boron and nitrogen atoms of the apexes and tips of nanocones have been substituted by carbon atoms in different ways. The geometries of nanocones have been firstly optimized and the Qcc parameters have been subsequently computed for the ^{11}B and ^{14}N atoms of the optimized structures. Since both of the apex and tip of BN nanocones are open ended, individual decorations of apex and tip of nanocones have been investigated separately. The boron and nitrogen atoms of the apex of nanocone are substituted by the carbon atoms in the C_{Apex} model (Fig. 2). The boron and nitrogen atoms of the tip of nanocone are substituted by the carbon atoms in the C_{Tip} model (Fig. 3). The boron and nitrogen atoms of the apex and tip of nanocone are substituted by the carbon atoms in the $C_{Apex\text{-}Tip}$ model (Fig. 4). It is noted that the atoms at the apexes and tips of our investigated original and C-decorated BN nanocones are saturated by hydrogen atoms to avoid the dangling effects [10]. The optimized properties and the computed values of Qcc are tabulated in Tables 1 – 3.

METHOD

DFT calculations based on the B3LYP exchange-correlation functional and the 6-31G* standard basis set have been performed by the Gaussian 98 package [11]. According to our earlier studies, the considered level of calculations is proper for determining the properties of BN nanostructures [9]. At the first step, the investigated structures of the original model: $B_{35}N_{35}H_{14}$ (Fig. 1), the C_{Apex} model: $B_{34}N_{34}C_2H_{14}$ (Fig. 2), the C_{Tip} model: $B_{29}N_{29}C_{12}H_{14}$ (Fig. 3), and the $C_{Apex\text{-}Tip}$ model: $B_{28}N_{28}C_{14}H_{14}$ (Fig. 4) have been relaxed during the all-atomic optimization processes. Subsequently, the optimized properties (Table 1) and the values of Qcc for ^{11}B and ^{14}N atoms (Tables 2 and 3) have been evaluated in the optimized structures of the investigated original and C-decorated BN nanocones. To evaluate the values of Qcc, electric field gradient (EFG) tensors (q_{ii}: $|q_{zz}| > |q_{yy}| > |q_{xx}|$) have been firstly calculated in the optimized structures. Subsequently, the calculated EFG tensors (q_{zz}) have been converted to the values of Qcc by the equation of Qcc (MHz) = $e^2Qq_{zz}h^{-1}$; in which the standard values of Q are used [12]: $Q(^{11}B) = 40.59$ mb and $Q(^{14}N) = 20.44$ mb.

RESULTS AND DISCUSSION

We have investigated the effects of different C-decorations on the properties of original BN nanocones through performing DFT calculations for four considered models of BN nanocones. The original model (Fig. 1) only includes the boron and nitrogen atoms, in which the atoms at the apex and tip are saturated by the hydrogen atoms. In the C_{Apex} model (Fig. 2), one boron atom and one nitrogen atom at the apex of BN nanocone are substituted by two carbon atoms, in which the atoms at the apex and tip are still saturated by the hydrogen atoms. In the C_{Tip} model (Fig. 3), six boron atoms and six nitrogen atoms at the tip of BN nanocone are substituted by twelve carbon atoms, in which the atoms at the apex and tip of nanocone are saturated by the hydrogen atoms. In the $C_{Apex\text{-}Tip}$ model (Fig. 4), one boron atom and one nitrogen atom at the apex of nanocone and six boron atoms and six nitrogen atoms at the tip of nanocone are substituted by fourteen carbon atoms, in which the existence of hydrogen atoms is due to saturations of atoms at the apex and tip of nanocone. Our results by the optimization processes (Table 1) have indicated that the C-decorations significantly increase the values of dipole moments with respect to the original model. The most significant effects of C-decorations on the

dipole moments have been observed for the C_{Tip} model, in which the boron and nitrogen atoms at the tip of BN nanocone are substituted by the carbon atoms. The effects of C-decorations on the values of dipole moments of the C_{Apex} model, in which the boron and nitrogen atoms at the apex of BN nanocone are substituted by the carbon atoms, are the least significant observations of the effects among the C-decorated models. The values of energy gaps also detect the effects of C-decorations in the models of the investigated BN nanocones. Parallel to the results of dipole moments, the effects of C-decorations on the energy gap of the C_{Tip} model are the most significant observations of the effects among other nanocones. Moreover, the change of the value of energy gap for the C_{Apex} model is the least significant observation with respect to the original BN nanocone. Interestingly, the value of energy gap is increased for the C_{Apex} model with respect to the original model whereas the values for the C_{Tip} and $C_{Apex\text{-}Tip}$ models are significantly decreased. Since the natures of covalent bonds are changed in the C-decorated models, it is reasonable to observe that different values of total energies are calculated for the original and C-decorated models.

The values of Qcc for ^{11}B and ^{14}N atoms of the optimized structures of the investigated original and C-decorated BN nanocones are tabulated in Tables 2 and 3. The values of Qcc indicate that the atoms could be divided into layers based on the similarities of the magnitude of the values of Qcc for the atoms of each layer. Since the values of Qcc are proportional to the electronic densities at the atomic sites, these parameters could reveal insightful trends about the electronic properties of the investigated structures [8, 9, and 13]. For the original model (Fig. 1), the value of Qcc for boron atom of layer one, which is located at the apex of nanocone, is the smallest one among the boron atoms. The largest value of Qcc for boron atoms of the original model belongs to the boron atoms of layer ten, which construct the tip of nanocone. Furthermore, slight changes are also observed for the values of Qcc for boron atoms of other layers, which mean that the electronic properties of boron atoms of the original BN nanocone are slightly changed in the body of nanocone. For nitrogen atoms, the values of Qcc for nitrogen atoms of layers one and ten, apex and tip, are larger than all other atoms of the original BN nanocone. In contrast with the boron atoms, similar magnitudes of values of Qcc are observed for nitrogen atoms at the apex and tip of the original BN nanocone. However, the changes of values of Qcc for nitrogen atoms of other layers, which make the body of nanocone, are much more notable than the changes of values of Qcc for boron atoms of the body of nanocone. It is important to note that the natures of boron and nitrogen atoms are initially different, in which the boron atom has lack of electrons in the valence shell whereas the nitrogen atom has lone pair of electrons in the valence shell. Therefore, the behaviors of these atoms are expected to be different in comparison with each other.

In the C_{Apex} model (Fig. 2), in which one boron atom and one nitrogen atom at the apex of nanocone are substituted by two carbon atoms, the values of Qcc for boron atoms of layer two only detect the effects of C-decorations whereas the values of Qcc for other boron atoms are remained unchanged. Due to the C-decorations, the magnitude of Qcc for the boron atoms of layer two are significantly increased with respect to the original model, in which the new magnitude is close to the magnitude of Qcc for boron atoms at the tip of nanocone in layer ten. The trend means that the C-decorations could duplicate some electronic properties of boron atoms. For the nitrogen atoms, the most significant changes are observed for the values of Qcc for the nitrogen atoms of

layer two among the available nitrogen atoms. It is important to note that, in the C_{Apex} model, the boron and nitrogen atoms of layer two are in covalent bonding with the carbon atoms; therefore, their electronic properties are significantly changed with respect to the original BN nanocone. Moreover, the values of Qcc for other nitrogen atoms in the body of the C_{Apex} model also detect slight effects of C-decorations.

In the C_{Tip} model (Fig. 3), in which the boron and nitrogen atoms at the tip of BN nanocone (layer ten) are substituted by the carbon atoms, the values of Qcc are also divided into atomic layers based on similarities of the electronic properties for atoms of each layer. For the boron atoms, the most significant effects of C-decorations are observed for the atoms of layers eight and nine. Furthermore, the values of Qcc for other boron atoms also detect slight effects of C-decorations with respect to the original BN nanocone. For the nitrogen atoms, the values of Qcc for the nitrogen atoms of layer nine only detect the most significant effects of C-decorations whereas slight changes are observed for other nitrogen atoms.

In the $C_{Apex-Tip}$ model (Fig. 4), in which the boron and nitrogen atoms at the apex and tip of BN nanocone (layers one and ten) are substituted by the carbon atoms, the values of Qcc for boron and nitrogen atoms are divided into atomic layers. The results indicate that the electronic properties for those atoms close to the apex of nanocone are similar to the C_{Apex} model and the electronic properties for those atoms close to the tip of nanocone are similar to the CTip model. Interestingly, the electronic properties for boron and nitrogen atoms of the $C_{Apex-Tip}$ model are mixtures of the electronic properties for boron and nitrogen atoms of the C_{Apex} and C_{Tip} models. The values of Qcc for boron and nitrogen atoms indicate that the most significant effects of C-decorations are observed for the atoms of layers two and nine whereas slight changes are only observed for the atoms of other layers.

CONCLUSIONS

We have performed DFT calculations to investigate the properties of C-decorated BN nanocones by evaluating the values of Qcc for boron and nitrogen atoms in the optimized structures of the considered models. By the calculated results, some trends could be highlighted as the concluding remarks. First, the values of dipole moments detect the effects of C-decorations, in which the most significant effects are observed for the C_{Tip} model. Second, the values of energy gaps also detect the effects of C-decorations, in which the most significant effect is still observed for the C_{Tip} model. Third, since the natures of covalent bonds are changed in the C-decorated BN nanocones, the values of total energies are changed for the C-decorated models with respect to the original model. Fourth, in the C_{Apex} model, the most significant effects are only observed for the values of Qcc for those atoms close to the apex of nanocone. Fifth, in the C_{Tip} model, the most significant effects are only observed for the values of Qcc for those atoms close to the tip of nanocone. Sixth, in the $C_{Apex-Tip}$ model, mixtures of properties of C_{Apex} and C_{Tip} models are observed for the atoms of the $C_{Apex-Tip}$ model. And finally, the electronic properties of BN nanocones are changed due to C-decorations, in which the changes of properties for the atoms close to the C-decorated regions could play dominant roles in determining the properties of the C-decorated BN nanocones.

Table 1. Optimized properties*

Property	Original Model	C_{Apex} Model	C_{Tip} Model	$C_{Apex-Tip}$ Model
Stochiometry	$B_{35}N_{35}H_{14}$	$B_{34}N_{34}C_2H_{14}$	$B_{29}N_{29}C_{12}H_{14}$	$B_{28}N_{28}C_{14}H_{14}$
Dipole Moment /Debye	5.55	6.98	15.32	13.59
Energy Gap /eV	5.27	5.31	1.12	1.13
Total Energy /keV	-76.15	-76.05	-75.56	-75.46

* See Figs. 1 - 4 for the atomic numbers

Table 2. Quadrupole coupling constants (Qcc) /MHz for boron atoms*

Atom	Original Model	C_{Apex} Model	C_{Tip} Model	$C_{Apex-Tip}$ Model
Layer 1	1.87	—	1.90	—
Layer 2	2.79	3.34	2.78	3.38
Layer 3	3.09	3.05	3.09	3.03
Layer 4	2.86	2.86	2.83	2.85
Layer 5	2.96	2.96	2.93	2.96
Layer 6	2.86	2.86	2.77	2.77
Layer 7	2.86	2.86	2.86	2.77
Layer 8	2.87	2.87	2.48	2.48
Layer 9	2.68	2.68	2.75	2.74
Layer 10	3.53	3.53	—	—

* See Figs. 1 - 4 for the atomic numbers. Layers are indicated by L in the figures.

Table 3. Quadrupole coupling constants (Qcc) /MHz for nitrogen atoms*

Atom	Original Model	C_{Apex} Model	C_{Tip} Model	$C_{Apex-Tip}$ Model
Layer 1	2.19	—	2.19	—
Layer 2	0.57	2.35	0.57	2.37
Layer 3	1.76	1.83	1.77	1.84
Layer 4	1.03	1.10	1.00	1.01
Layer 5	1.02	1.01	1.02	1.05
Layer 6	0.76	0.77	0.63	0.64
Layer 7	0.77	0.75	0.59	0.59
Layer 8	0.67	0.69	0.61	0.60
Layer 9	0.44	0.44	1.96	1.96
Layer 10	2.21	2.22	—	—

* See Figs. 1 - 4 for the atomic numbers. Layers are indicated by L in the figures

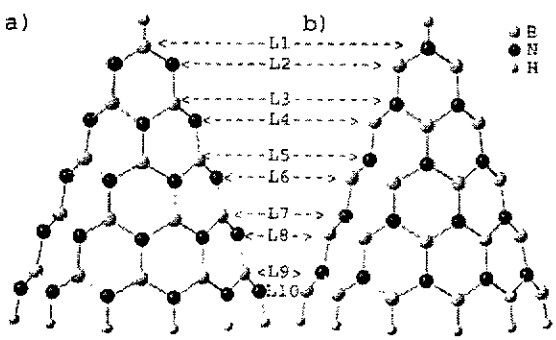

Fig. 1. The original model of BN nanocone. The 2D views of front and back sides of nanocone are shown in panels a and b. The atomic layers are designated by L.

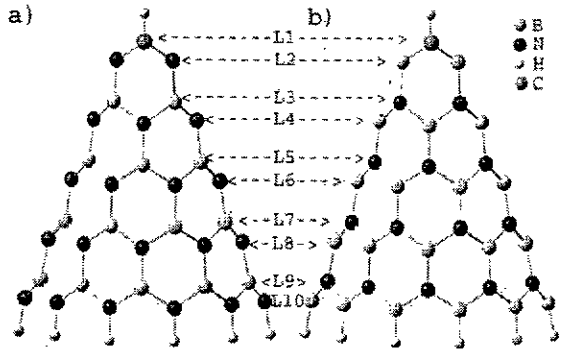

Fig. 2. The C_{Apex} model of BN nanocone. The 2D views of front and back sides of nanocone are shown in panels a and b. The atomic layers are designated by L.

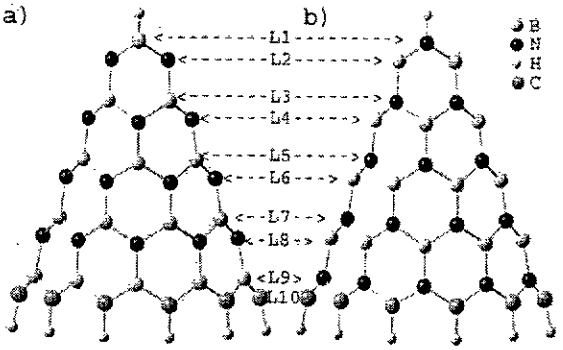

Fig. 3. The C_{Tip} model of BN nanocone. The 2D views of front and back sides of nanocone are shown in panels a and b. The atomic layers are designated by L.

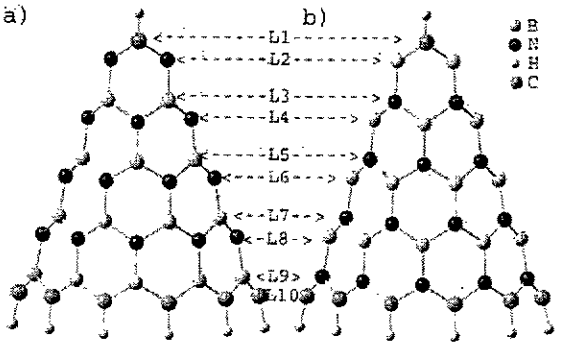

Fig. 4. The $C_{Apex\text{-}Tip}$ model of BN nanocone. The 2D views of front and back sides of nanocone are shown in panels a and b. The atomic layers are designated by L.

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