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Sulfur doping at the tips of (6,0) boron nitride nanotube: A DFT study

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ABSTRACT

We have investigated sulfur (S) doping at the tips of (6,0) boron nitride nanotube (BNNT) by density functional theory (DFT) calculations. Bond lengths, tubular diameters, dipole moments, band gaps, and quadrupole coupling constants (C_q) have been calculated in four models of the investigated BNNT: pristine, S-doping at the boron (B) tip, S-doping at the nitrogen (N) tip, and S-doping at both the tips. The results indicated the influence of the S-doping on the electronic and structural properties of the (6,0) BNNT. The B–N bond lengths do not differ in the S-doped models but the tubular diameters at S-doped tips are increased. The values of dipole moments and band gaps are reduced in the S-doped models. The C_q parameters revealed that the S–N bonds could be weaker than the B–N bonds whereas the B–S bonds could be stronger. We have also indicated that the properties of the S-doped models are independent of the dangling effects.

1. Introduction

Ever since the carbon nanotube (CNT) was discovered by Iijima [1], the properties of this fascinating novel material have been investigated by numerous theoretical and experimental research projects [2,3]. Moreover, investigations have shown the stable structures of non-carbon based nanotubes in which boron nitride nanotube (BNNT) is among the most important ones [4]. The tubular structure of BNNT was initially stabilized by the calculations [5] and subsequently synthesized [6]. To this time, a rapidly growing number of experimental and theoretical investigations have been performed to study the structural and electronic properties of the BNNT [7–10]. In contrast with CNT, which is metal or semiconductor based on the tubular diameter and chirality, the BNNT is viewed as always semiconductors, which is independent of the structural factors [11]. Furthermore, the CNT is a non-polar material; however, the slight positive charges of boron (B) atoms and the slight negative charges of nitrogen (N) atoms make the BNNT a polar material. Therefore, instead of CNT, the BNNT is expected to be a more appropriate candidate to be employed in the electronic and mechanical devices for the specific purposes.

Earlier studies have demonstrated the influence of atomic doping on the electronic and structural properties of BNNT [12,13]. This kind of non-carbon nanotube is viewed as a III–V semiconductor; therefore, the atomic doping of BNNT by the atoms of group VI elements could make it an n-type semiconductor. To this time, to our knowledge, the atomic doping at the wall of the BNNT has been studied [12,13] but not the atomic doping at its tips. The zigzag BNNT has two hetero atomic tips, B-tip and N-tip, which play dominant roles in determining its electronic and structural properties [14]; therefore, the atomic doping at its tips could be an interesting subject of study. In the present research, we have investigated sulfur (s) doping at the tips of a representative zigzag BNNT. To achieve the purpose, we have performed density functional theory (DFT) calculations on four models of the (6,0) BNNT, which consist of pristine, S_B-doped, S_N-doped, and S_{BN}-doped models (Figs. 1 and 2). We discuss the parameters such as optimized bond lengths, tubular diameters, dipole moments, band gaps, and quadrupole coupling constants (Tables 1 and 2) to investigate the electronic and structural properties of the S-doping at the tips of the (6,0) BNNT.

2. Computational aspects

We have considered four models of the representative (6,0) zigzag single-walled BNNT in the present study (Figs. 1 and 2). Fig. 1 shows the pristine model, which consists of 24 boron (B) atoms and 24 nitrogen (N) atoms where the two tips of the nanotube are saturated by 12 hydrogen (H) atoms. Fig. 2a shows the S_B-doped model, which consists of 18 B atoms, 24 N atoms, and 6 sulfur (S) atoms where 6 B atoms of the B-tip are doped by 6 S atoms whereas the N-tip remains in its initial status. Fig. 2b shows the S_N-doped model, which consists of 24 B atoms, 18 N atoms, and 6 S atoms where 6 N atoms of the N-tip are doped by 6 S atoms whereas the B-tip remains in its initial status.

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The S_{BN}-doped model (Fig. 2c) consists of 18 B and 18 N atoms where both tips are doped by 12 S atoms. The tips of the nanotubes are saturated by the H atoms to avoid the dangling effects; therefore, we have also performed parallel calculations on the corresponding B-end (Fig. 2d), N-end (Fig. 2e), and BN-end (Fig. 2f) models to investigate the dangling effects on the calculated parameters of the S-doped models. In the new structures, the B-tip and N-tip are not saturated by the H atoms for the B-end and N-end models, respectively. Moreover, neither of the tips are saturated by the H atoms in the BN-end model. Initially, all-atomic geometries of the structures have been allowed to relax by performing optimization at the level of the BLYP exchange-functional and the 6-31G* standard basis set. By this process, the optimized bond lengths, the tubular diameters, the dipole moments and the band gaps have been evaluated (Table 1). Subsequently, the quadrupole coupling constants (C_q) have been calculated for the optimized structures at the same level of theory (Table 2).

The quantum chemical calculations yield electric field gradient (EFG) tensors in the principal axis system (PAS) with the order of $|q_{zz}| > |q_{yy}| > |q_{xx}|$; therefore, Eq. (1) is used to convert the calculated EFG tensors to the C_q parameters [15]. The C_q parameter measures the interaction energy between the nuclear electric quadrupole moment and the EFG tensors, which arise at the sites of quadrupolar nuclei such as ^{11}B, ^{14}N, and ^{33}S. The nuclear spin angular momentums, I, of these nuclei are greater than one-half. The standard Q values reported by Pyykkö [16] are employed in Ref. (1); $Q(^{11}B)=40.6$ mb, $Q(^{14}N)=20.4$ mb and $Q(^{33}S)=767.8$ mb. The DFT calculations have been performed by the Gaussian 98 package [17]. It is worth noting that the validities of the considered sizes of models and the employed level of theory for the study of the electronic and structural properties of the nanotubes have been examined by earlier works [18,19] and have also been approved by the results of this study.

$$C_q\,(\mathrm{MHz}) = e^2 Q q_{zz} h^{-1} \quad (1)$$

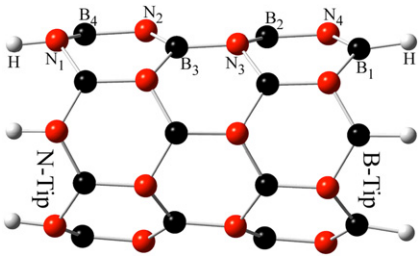

Fig. 1. 2D views of the pristine model of the (6,0) BNNT. Both tips of the nanotube are saturated by the H atoms.

3. Results and discussion

3.1. The optimized parameters

Table 1 presents the optimized parameters including the bond lengths, tubular diameters, dipole moments, and band gaps for four models of the investigated (6,0) BNNT (Figs. 1 and 2). The pristine model (Fig. 1) stands for the original structure of the BNNT consisting of B and N atoms where both tips are saturated by H atoms. The S_B-doped (Fig. 2a) and S_N-doped (Fig. 2b) models stand for S-doping at the B-tip and N-tip of the BNNT, respectively, where the other tip is still saturated by the H atoms in each model. The S_{BN}-doped model (Fig. 2c) stands for S-doping at both tips of the BNNT. The B–N bond lengths do not detect the effects of the S-doping in the considered models; however, different B–S and S–N bond lengths are observed where the latter is shorter than the former one. The tubular diameters of the two different tips, B-tip and N-tip, of the (6,0) BNNT show different values. The diameter of the N-tip is larger than the B-tip in the pristine model and this ratio also remains in the S_{BN}-doped model where both tips are in the S-doped status. However, the widening of the B-tip due to the S-doping is more significant than the N-tip. Interestingly, S-doping at one tip in the S_B-doped and S_N-doped

Table 1
The optimized parameters[a].

Parameter	Pristine	S_B-end	S_N-end	S_{BN}-end	B-end	N-end	BN-end
Bond length/Å							
B–N	1.46	1.46	1.46	1.46	1.47	1.47	1.47
B_4–S_1	—	—	1.86	1.86	—	—	—
S_2–N_4	—	1.77	—	1.77	—	—	—
Diameter/Å							
B-tip	4.85	6.25	4.87	6.25	4.03	4.87	4.03
N-tip	5.14	5.13	6.35	6.35	5.13	4.47	4.49
Band gap/eV	3.14	2.44	1.99	1.94	2.93	1.82	1.21
Dipole moment/Debye	8.15	7.61	6.21	7.08	7.20	5.72	6.67

[a] See Figs. 1 and 2 for details.

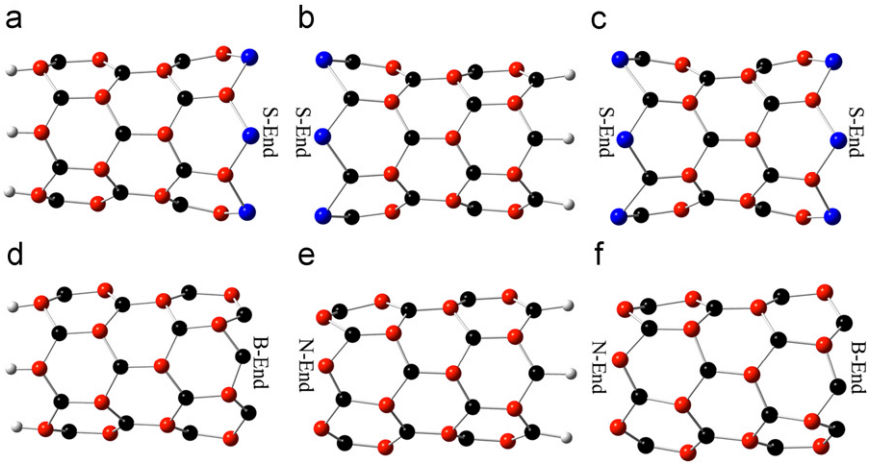

Fig. 2. 2D views of (a) the S_B-doped model, (b) the S_N-doped model, (c) the S_{BN}-doped model, (d) the B-end model, (e) the N-end model, and (f) the BN-end model.