Enhanced Stability of Carbon Doped Boron Nanotubes: An ab-initio Approach

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Abstract. We have performed ab-initio calculations for investigating structural stability of carbon doped boron nanotubes. The considered structures are Armchair (3,3), Zigzag (5,0), and Chiral (4,2) nanotubes consists of 12, 20, and 56 atoms respectively. The ground state energies of relaxed nanotubes are calculated, thereby cohesive energy and formation energy. The cohesive energy is increased to a significant extent after carbon doping. Thus, carbon doped boron nanotubes are energetically more stable than pristine nanotubes. The enhancement of energetic stability is also supported by formation energy. It is found that the formation energy is higher for the higher stable structure in all the three nanotubes. It is also observed that carbon doped zigzag nanotube is most favourable nanotube among all the three considered nanotubes because of high formation energy.

1. INTRODUCTION

The nanoscale materials possess intriguing physical and chemical properties whereby scientist and engineers have been fascinated. Nanotube, one of the most important nanostructures is extensively studied and grouped into organic and inorganic nanotubes. Organic and inorganic nanotubes have been studied theoretically as well as experimentally. The organic nanotube i.e. Carbon nanotube (CNT) was investigated by Iijima [1] and subsequently it was investigated that the electronic properties depend on diameter and chirality [2]. Similarly, the nanotubes of inorganic materials include Boron Nitride [3-4], Silicon [5], Gold [6], etc. The boron nanotube was first proposed by Boustani [7] and subsequently various structural conformations of BNTs were proposed. The various conformations include Triangular [8], α-BNT [9, 10] and Hexagonal [11, 12] in contrast to only one conformation of CNT i.e. Hexagonal. It has been predicted that all the BNTs are found to be metallic and independent of diameter and chirality. The experimental synthesis of BNTs by Ciuparu et al [13] has confirmed the existence of boron nanotubes. Victor et al. [14] also synthesized the BNT and studied the field emission properties. The study of transport properties [15] revealed that BNTs are more conducting than that of CNTs. However, the atomic structure of BNTs has not been revealed yet. Moreover, it is predicted that α-BNTs are found to be highly stable while hexagonal to be least. In view of comparison with hexagonal CNTs, it becomes extremely essential to study CNT-like-BNT. Further, hexagonal BNTs of small diameter were found to be stable. However, the stability of hexagonal BNTs can also be enhanced by doping with foreign atoms i.e. carbon. It is our natural choice to prefer substitutional doping rather than other available methods of doping. We have used carbon atoms as impurity because of its size comparable to boron.

2. COMPUTATIONAL METHODOLOGY

The pseudopotential plane wave calculations for determining structural stability of ultrathin BNTs doped with carbon have been performed in the framework of density functional theory (DFT). All the calculations have been carried out using CASTEP simulation tool [16]. The exchange and correlation effects are described by generalized gradient approximation (GGA) [17] proposed by Perdew-Burke-Ernzehrof (PBE). The Vanderbilt [18] ultrasoft pseudopotential in the reciprocal space with plane wave basis set. The Brillouin zone is sampled with Monkhorst-Pack grid [19]. The structures are relaxed until the forces on the atoms are less than 0.01 eV/Å. The convergence criteria for energy and charge are set as 1×10⁻⁵ a.u. The calculations are performed for Armchair (3,3), Zigzag (5,0), and Chiral (4,2) nanotubes consists of 12, 20, and 56 atoms respectively.
wave cutoff energy 320eV has been used for geometry optimization. The integration is performed in the first brillouin zone [19] by using k-points generated by 1x1x8 grid parameters. The geometry is optimized until force on each atom becomes < 0.03 eV/ Å. The intertubular distance is set to be 10 Å in order to avoid periodic image interaction. The bond length B-B is chosen to be 1.67 Å. In addition, non-spin-polarized calculations are performed. The considered conformations of BNTs are of the three types viz. Armchair (3,3), Zigzag (5,0), and Chiral (4,2) consisting of 12, 20, and 56 atoms respectively. The concentration of carbon impurity is restricted to two atoms. The diameters of these tubes are 4.60Å, 4.78Å, and 4.87 Å for (5,0), (3,3), and (4,2) BNTs respectively.

3. RESULTS AND DISCUSSION

The effect of chemical doping of carbon atoms in BNTs have been investigated in the framework of density functional theory (DFT). We have put forth our efforts to explore the structural stability of carbon doped BNTs. In this study, three model of BNTs have been considered namely Armchair (3,3), Zigzag (5,0), and Chiral (4,2). The content of carbon impurity is limited two atoms in each model of BNTs. In our previous study [12], it has been investigated that pristine chiral (4,2) BNT is highly stable followed by zigzag (5,0) and armchair (3,3).

In this study, the structural stability is predicted on the basis of cohesive energy and formation energy. The cohesive energy $E_{coh}$ of the SWBNT was obtained from the total energy ($E_{tot}$), the energy of a single free boron atom ($E_1$), and the energy of the carbon atom ($E_2$) using the following relation:

$$E_{coh} = \frac{(E_{tot} - xE_1 - yE_2)}{x + y}$$

Where $x$ and $y$ are the numbers of boron and carbon atoms in the supercell respectively.

When single atom of carbon substitutes boron atom in armchair (3,3) BNT, the cohesive energy is found to be 6.48 eV while 6.34 eV correspond to two atom doped BNT. Thus, there is a very slight variation in cohesive energy. Consequently, carbon doped BNTs are energetically more stable as compared to pristine one. Similarly, substitution of carbon atoms in zigzag and chiral BNTs causes’ slight variation in cohesive energies correspond to single and double atom doped nanotubes. The variation of cohesive energies with impurity atoms is shown in figure (1). Thus, it is revealed from figure (1) that all the three models are equally stable.

![Figure (1): Variation of cohesive energy with impurity concentration](image)

Moreover, the formation energy of carbon doped boron nanotube is calculated by using ground state energy of relaxed structures. We determine the formation energy:

$$E_{formation} = \frac{E_{doped BNT} - E_{pristine BNT} - xE_{carbon}}{n}$$

Where $E_{doped BNT}$ is the total energy of our supercell with doped carbon atoms, $E_{pristine BNT}$ is the total energy of pristine BNT, $E_{carbon}$ is the total energy of an isolated carbon atom, $x$ is the total number of carbon atoms, and $n$ is the total number of atoms in the supercell.
Table 1: Variation of formation energy with impurity concentration

| Nanotubes     | Number of impurity atoms | Formation energy (eV) |
|---------------|--------------------------|-----------------------|
| Armchair (3,3)| 1                        | 10.71                 |
|               | 2                        | 9.20                  |
| Zigzag (5,0)  | 1                        | 12.35                 |
|               | 2                        | 14.14                 |
| Chiral (4,2)  | 1                        | 2.90                  |
|               | 2                        | 3.14                  |

The calculated formation energy for these BNTs is shown in Table (1). It is noteworthy that single atom doped armchair BNT possess high formation energy correspond to high cohesive energy as compared to two atom doped BNTs. The high formation energy reflects more favourable structure. Thus, for armchair (3,3) BNT, the formation energy is in good agreement with cohesive energy. Similarly for zigzag (5,0) and chiral (4,2) BNTs, the cohesive energy as well as formation energy increase with the concentration of carbon impurity. However, there is very slight variation in energies. Moreover, it is shown in Table (1) that the formation energy for zigzag (5,0) BNT is found to be highest which indicates that zigzag (5,0) BNT is highly favourable while chiral (4,2) is least stable among considered conformations.

4. CONCLUSION
Ab initio calculations have been performed for exploring structural stability of carbon doped hexagonal ultrathin boron nanotubes with conformations namely, armchair (3,3), zigzag (5,0) and chiral (4,2) BNTs. It is found that carbon impurity gives rise to higher stability to boron nanotubes. The formation energy is found to be highest for zigzag (5,0) followed by armchair (3,3) and chiral (4,2). The structural stability is found to be highest for armchair (3,3) followed by zigzag (5,0) and chiral (4,2) BNTs.

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