Interaction of Au and Boron Nitride Nanotube: A DFT Study

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Abstract In this work, structural and electronic properties of zigzag single-walled boron nitride nanotube (BNNT) are considered through density functional theory. In order to reduce the large band gap of BNNT, the effects of 2-5 Au atoms are reported as impurities in two different patterns. We selected two dispersions for Au atoms: one for the random dispersion and the other for the chain dispersion. Our results show that the chain modes have lower formation energy and their band gap is smaller, as well. We could tune the large band gap of BNNT from 5.96 eV to 0.41 eV in chain mode. In the random mode, the band gap could reach a minimum level of 1.01 eV.

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1. Introduction

Honeycomb nanostructures of boron and nitrogen are interesting subjects for scientists. Two dimensional Boron nitride nanosheets like as graphene has many attractions. Very small nanocluster of boron nitride honeycomb recently are considered [1,2]. BNNTs have a honeycomb structure similar to that of carbon nano tubes (CNT). In the past two decades, many scientists studied various properties of carbon nanotubes (CNT). Two of the most important reasons that are fascinating scientists are the excellent physical properties and chemical stability of these structures at room temperature [3,4,5,6,7,8,9]. The electronic properties of such materials were investigated by many scientists and it has been shown that the electronic properties of these structures strongly depend on their chirality [10]. This may be one issue in order to manufacture electronic devices. So scientists motivated to find another nanostructure with similar geometrical structure but more stable electronic properties[11]. Now boron nitride nanotubes is a candidate.

While the on-site energies of nitrogen and boron are different with each other, preliminary calculations have shown that there must exist a band gap in these structures. Rubio et al. predicted the existence of BNNT for the first time [10]. Immediately after this prediction, Chopra et al. synthesized multi-walled BNNT via arc discharge methods [12]. Blase et al. showed that pristine BNNTs have a large band gap, which is independent of the chirality and radius of the structures [13]. BNNTs have attracted many researchers because of their interesting properties. Good mechanical properties [14], strong piezoelectric features [15], a high chemical stability [16], and independent band gap with chirality are some aspects of these structures. Hydrogen storage is a strategic subject on energy saving industry [17], recently scientist proved that BNNTs have better hydrogen storage capability rather than carbon nanotube [18].

Experimental measurements based on Cathodoluminescence method show that the pristine BNNTs have a band gap ranging from 5.3 to 5.4 eV [19,20]. Because of the large band gap, BNNTs are not suitable to be used in electronic devices. Many researchers have tried to modify the band gap by doping BNNTs with the elements of periodic table [21,22,23,24]. The effects of one Au atom on electrical properties of zigzag BNNT was reported by Bagheri et al [21]. They found that when B atom is substituted by Au atom, the structure is more stable. In this situation, Au creates three successful chemical bonds with the nitrogen neighbors [21]. They reported that the Au atom induced an acceptor level in the HOMO-LUMO gap and reduced the pristine gap to 2.43eV. The magnitude of this HOMO-LUMO gap is still large for practical purposes. While the simulations showed doping Au at B site was more stable, to reach the applicable purpose, we planned a new structure with doping more Au atoms at B sites such that to reduce the HOMO-LUMO gap. Considering that the effect of Au on electrical properties of BNNTs is an interesting and a serious challenge, it seems that collecting various properties of this structure with heavily Au contamination is of more necessity. Regarding that the experimental results show Au can enhance electrical properties of BNNT [25], another research showed that boron nitride nanosheet on Au substrate has a good ability to reduce oxygen [26]. Improving the electrical properties and opening new horizons in energy storage devices regarding the ability of oxygen reduction in presence

of gold are our motivations for considering electrical properties of these structures.

2. Computational Details

Density functional theory is used to simulate electronic properties of BNNT. This method is a good approach to predict physical properties of nanoclusters made of boron and nitrogen [1,2,17,21,22]. The relaxed structures and energies are calculated by GAMESS (US) package [27]. Effective core potentials along with d polarization functions are used as basis sets [28,29]. The hybrid B3LYP functional is used to describe exchange-correlation interaction [30,31]. The convergence of gradient tolerance is set to 0.0001 Hartree/Bohr. In this work, a nanocluster (10,0) BNNT is considered. The nanocluster is made of 60 boron, 60 nitrogen, and 20 hydrogen atoms. The length and the radius of the structure are 1.1604Å and 8.042 Å, respectively. Figure 1a illustrates the relaxed structure of pristine BNNT. The formation energy (FE) for Au-doped BNNT is calculated as [18,19]:

$$FE = E_{dop}\left[H_{20}N_{60}B_{60-n}Au_n\right]$$
$$-E_{BNNT}\left[H_{20}N_{60}B_{60}\right]-n\mu_{Au}+n\mu_B \qquad (1)$$

Where µx (x=Au or B) is the atomic chemical potential of Au or B. The cohesive energy (CE) is calculated as:

$$CE = E_{dop}\left[H_{20}N_{60}B_{60-n}Au_n\right]-n\mu_{Au}$$
$$-\left(60-n\right)\mu_B-60\mu_N-20\mu_H. \qquad (2)$$

Chemical potential is calculated as the total energy per atom of the most stable allotrope of the elements [22]. While N_2, B_4, and H_2 are the most stable known allotropes of nitrogen, boron, and hydrogen, the chemical potential of N, B, and H have been calculated using the energy calculation of the relaxed N_2, B_4, and H_2 molecules [18]. In Eq. 1 and Eq. 2, n is the number of Au atoms substituted at B sites. FCC structure is used to calculate the chemical potential of Au. The tube is free to charge and the Mulliken charge was calculated to extract the total net charges Au atoms gained from the tubes. For this purpose, Hessian calculations were performed. Since there were not seen any negative frequency, the systems were on the global minima.

3. Results and Discussions

This section has been divided by two parts. First part describes structural properties of Au doped BNNT and second part describe electronic properties of Au doped BNNT. In this article we compared results of two different structures. Gold atoms can distribute randomly on the tube surface or they can seat in a chain model. We show random distributed structure with R-$N_{60}B_{60-n}Au_n$ and the other structure will show as C-$N_{60}B_{60-n}Au_n$. As mentioned before we only considered the B-Site substitution.

3.1. Structural Properties

In this section we have reported the bond length and the bond angels between Au atoms and their neighbors.

Figure 1 presents the relaxed structure of pristine and Au-doped BNNTs. Bond length of B-N is 1.46Å for pristine BNNT. As can be seen, Au atoms make three successful chemical bonds with their neighboring nitrogen atoms. Since the effect of doping one Au atom has been investigated earlier [18], we focused on higher concentrations of Au contaminations. We use two different patterns for Au dispersion; i.e., a random dispersion of Au atoms and a chain arrangement along a plane perpendicular to the tube axis. The effects of 2-5 Au atoms were considered in Figure 1b to 1i respectively. Since the radii of Au are larger than those of N and B, it moves radially outward from the surface of the tube. Table 1 contains average value of Au-N and Au-Au bond lengths. As can be seen the average bond length of Au-N for R-$N_{60}B_{60-n}Au_n$ is equal to 2.01 and it is fixed, but for C-$N_{60}B_{60-n}Au_n$ it is not fixed. As can be seen the Au-Au bond length in C-distribution decreases with the increment of Au atoms. And it reach 2.64 angstrom for n=4,5.
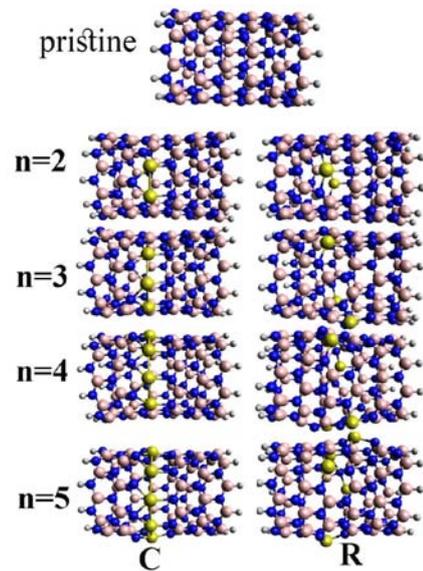

Figure 1. Relaxed structure of pristine and Au doped BNNT. (a) pristine, (b) C-Au2B58, (c) RAu2B58, (d) C-Au3B57, (e) R-Au3B57, (f) C-Au4B56, (g) R-Au4B56, (h) C-Au5B55, (i) R-Au5B55

Table 1. Average value of Au bond length (pristine N-B length is 1.54 Å)

	Chain		Random	
n	Au-N(Å)	Au-Au(Å)	Au-N(Å)	Au-Au(Å)
2	2.02	2.67	2.23	-
3	2.01	2.69	2.06	-
4	2.01	2.64	2.1	-
5	2.01	2.64	2.08	-

The surface of the tube by doping deforms after doping and this deformation is very important for scientists and engineers who want design semiconductor devices. Most important effect of this deviation is the deviation of hexagonal rings from its pristine shape. Alongside of this deviation, Au doping increases the roughness of the surface. This phenomena is illustrated in Figure 2. As can be seen the roughness of C-mode is higher than R-mode. Increasing the roughness of nanostructures are one ways that use to bond them to a surface [32].
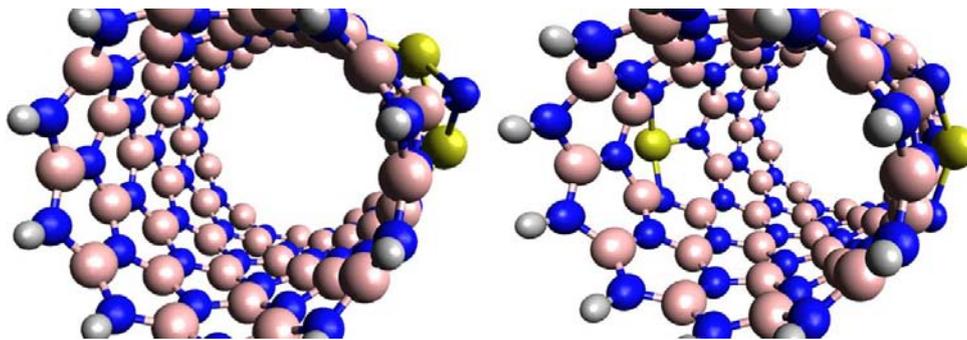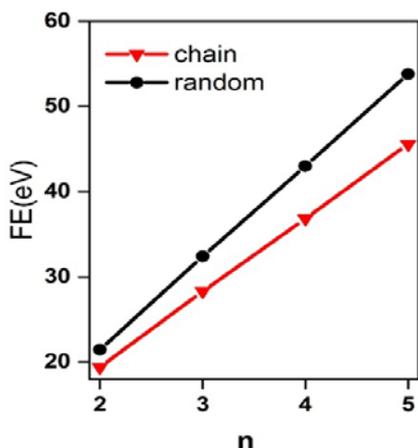
Figure 2. Changing of roughnes of tube by doping

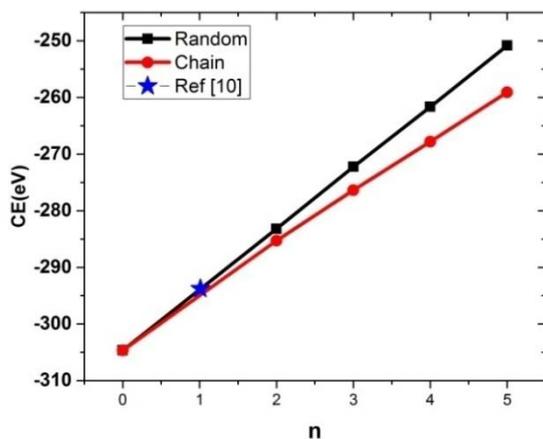**Figure 3.** Formation energy of chain modes and random modes

Figure 4.

Figure 3 shows formation energy of two types of doping. As can be seen, the case of the random modes needs more energy to construct. Studying the formation energy reveals that the work needed to dope BNNT with a chain of gold is smaller than that required for the random mode with the same number of atoms. In the case Au atoms are placed in a chain shape, the distance between them is 2.61 Å to 2.67 Å. To our knowledge, the lattice constant of gold is 4.07Å so the bond length of Au in the FCC lattice is equal to 2.84 Å. It seems, in this case, that the distance between two Au neighbors is very close to their stable FCC structure, leading to the formation of chemical bonds among Au valance orbitals. So, the main cause for lower formation energy in the chain mode is the attraction interaction of d-orbitals of the Au atom. Figure 4 depicts the CE of two types of doping. As can be seen, the CE increases by adding more Au atoms. The chain modes have a more negative CE compared with random modes. Since more negative CE means a more stable structure [33,34], we expect the chain modes to be more stable than random modes.

3.2. Electronic Properties

Figure 5 shows the density of states for pristine (a) and Au-doped BNNTs (b to i). Because the nitrogen and hydrogen amounts are fixed, we labeled chain structures by the phrase $C\text{-}Au_nB_{60-n}$ and random structures by $R\text{-}Au_nB_{60-n}$. As can be seen, the band gap of pristine BNNT is 5.96 eV, which is in good agreement with experimental reports [8,9]. The energy band of the structure is presented along with the DOS curve. The LUMO level is shown by a red dash-dot line while the HOMO level is shown by a blue dot line. Au atoms induced an empty level near the valence band so the systems are converted to the p type semiconductors and, consequently, the HOMO-LUMO gap is reduced by an increase in Au concentration. Figure 6 presents the HOMO-LUMO gaps of Au-doped BNNTs versus Au concentration. The figure exhibits the value of HOMO-LUMO gap of an Au-doped BNNT, obtained from ref [10], by a blue star symbol. The exact values of these gaps are listed in Table 2. As can be noted, with the same concentration of Au, chain modes have a lower HOMO-LUMO gap versus the random modes. The oxidation numbers of gold (i.e., ±1, ±2, ±3, and 5) can be used to explain this behavior. In a random mode, Au makes three chemical bonds, making it act like as a 3-valent element. Furthermore, while Au creates 5 chemical bond in chain mode, it acts like as a 5-valent element. As Figure 1 shows, the Au atoms located at the beginning and the end of a chain have one less bonding, which make these atoms behave like holes. It is noteworthy that these two extra holes lead to a better conductivity compared with the random mode. In order to investigate the charge transfer from Au atoms to the tube, we used the Mulliken method. Table 3 illustrates the total charges of Au atoms. In all cases, the Au atoms take positive charges, suggesting that Au acts as an electron acceptor. These are total net charges that Au atoms take from the tube.
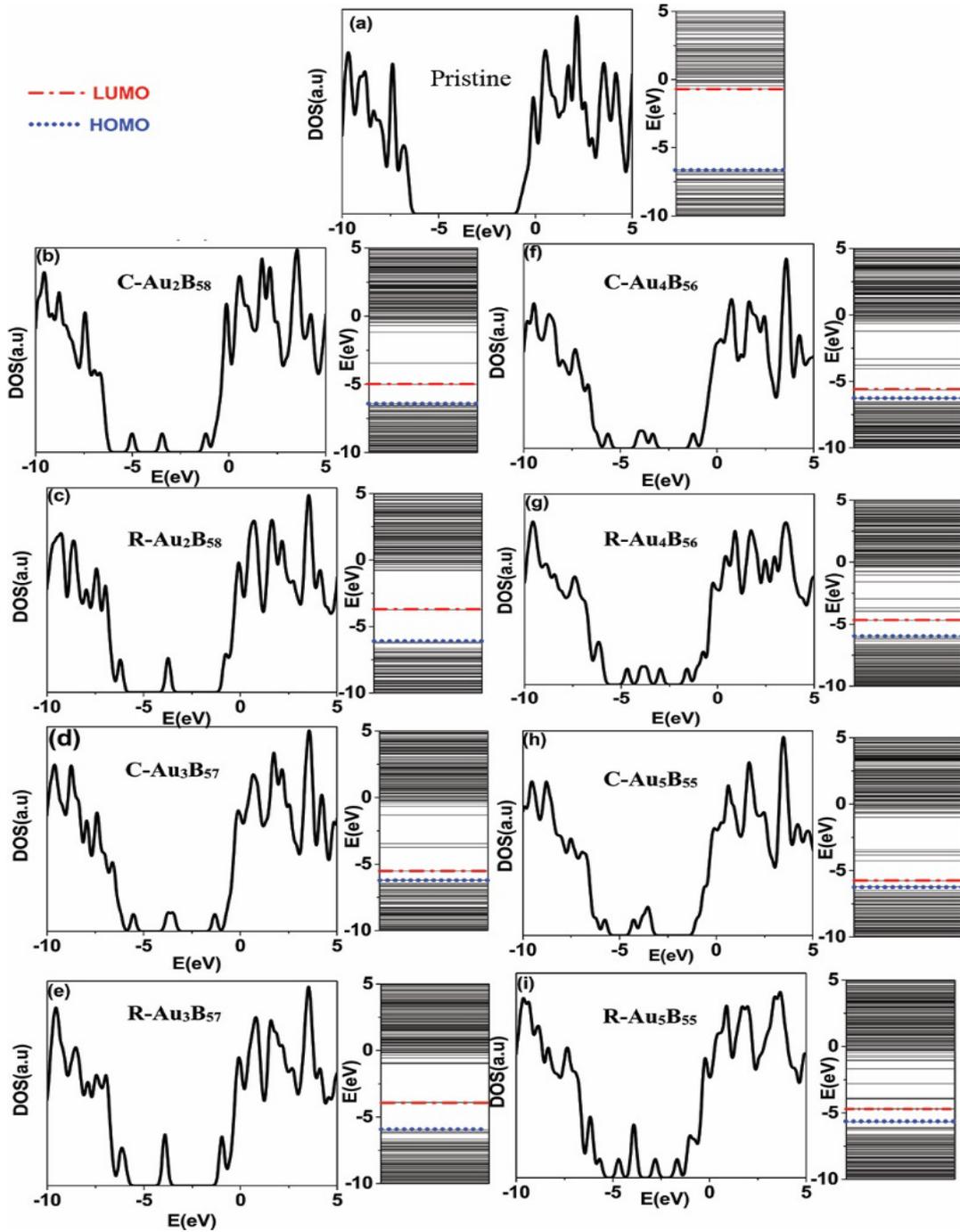
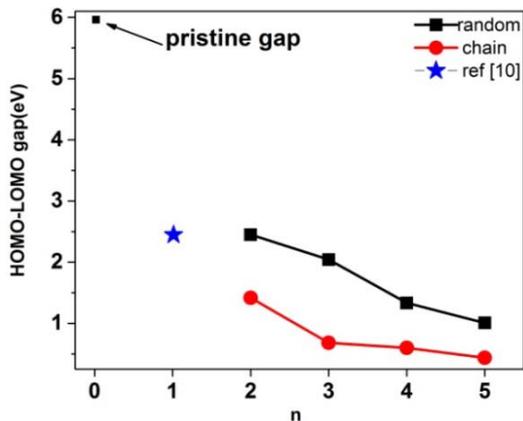**Figure 5.** DOS and band energy of pristine and Au doped BNNTs

Figure 6. HOMO-LUMO gap of chain modes and random modes

Table 2. The amount of HOMO and LUMO of various Au doped BNNT

BNNT	HUMO (eV)	LUMO (eV)	|HOMO-LUMO|(eV)
C-Au$_2$B$_{58}$	-6.42	-5.00	1.42
R-Au$_2$B$_{58}$	-6.18	-3.73	2.45
C-Au$_3$B$_{57}$	-6.20	-5.52	0.68
R-Au$_3$B$_{57}$	-5.96	-3.92	2.04
C-Au$_4$B$_{56}$	-6.23	-5.63	0.6
R-Au$_4$B$_{56}$	-6.01	-4.68	1.33
C-Au$_5$B$_{55}$	-6.20	-5.79	0.41
R-Au$_5$B$_{55}$	-5.69	-4.68	1.01
Prictine	-6.64	-0.68	5.96

Table 3. Total Mulliken charge of Au atoms.

BNNT	Mulliken charge |e|
C-Au_2B_{58}	0.85
R-Au_2B_{58}	0.88
C-Au_3B_{57}	1.29
R-Au_3B_{57}	1.36
C-Au_4B_{56}	1.52
R-Au_4B_{56}	1.73
C-Au_5B_{55}	1.92
R-Au_5B_{55}	2.16

4. Conclusions

Electrical and structural properties of heavily Au doped BNNT are considered in two different patterns random modes and chain modes. Because of attractive d-orbital correlation, the chain modes require less energy to construct. Formation energy has a linear shape as Au concentration and the random mode change with a steep slope compared to the chain one. In all cases, Au acts as an electron acceptor but the HOMO-LOMO band gap takes smaller value in chain modes. The band gap decreases monotonically with an increase in Au concentration. We could obtain a p-type semiconductor with 0.43 eV and 1.01 eV HOMO-LUMO gap by doping 5 Au at B site of a zigzag BNNT in chain mode and random mode, respectively. In the chain mode, by doping 4 Au atoms the HOMO-LUMO gap reached 0.6 eV, which is comparable with the band gap of Ge. In contrast, with the 5 Au doping in random mode, a 1.01 eV HOMO-LUMO gap could be achieved which is comparable with the band gap of Si.

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