Electronic structures of an (8, 0) boron nitride/carbon nanotube heterojunction*

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Abstract: The electronic structure of the heterojunction is the foundation of the study on its working mechanism. Models of the heterojunctions formed by an (8, 0) boron nitride nanotube and an (8, 0) carbon nanotube with C–B or C–N interface have been established. The structures of the above heterojunctions were optimized with first-principle calculations based on density functional theory. The rearrangements of the heterojunctions concentrate mainly on their interfaces. The highest occupied molecular orbital and the lowest unoccupied molecular orbital of the heterojunctions distribute in the carbon nanotube section. As the band offsets of the above heterojunctions are achieved with the average bond energy method, the band structure is plotted.

Key words: boron nitride/carbon nanotube heterojunction; density functional theory; the average bond energy method; electronic structures

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1. Introduction

One-dimensional (1D) heterojunctions, especially nanotube heterojunctions, have attracted tremendous interest because of their distinctive structures and properties, which are of importance for both scientific fundamentals in nanoscience and potential application in nanoelectronics[1]. Most of the previous studies on nanotube heterojunctions focused on those formed by bulk material and nanotubes[2, 3], while those formed by nanotubes alone are rarely studied. This is attributed to the difficulty in the fabrication of these nanotube heterojunctions. With the development of fabrication technology in nanometer materials, heterojunctions formed between nanotubes have recently been synthesized. Chandra *et al.* prepared a nanotube heterojunction constructed by carbon nanotubes (CNTs) with different chiralities[4]. Vertically aligned multiwalled CNT heterojunction arrays were formed with successive plasma-enhanced chemical vapor deposition (PECVD)[5]. Heterojunctions formed between CNTs and CN_x nanotubes have also been fabricated[6].

The boron nitride nanotube (BNNT) and the CNT are two types of nanotube materials intensively studied in theory and they can be massively synthesized in experiments[7, 8]. The heterojunction formed by these two nanotubes is the most possible one to fabricate. The structure is helpful to its fabrication and the electronic structure is the foundation of the modeling of heterojunction devices.

In this paper, the structures of the heterojunction formed by an (8, 0) BNNT and an (8, 0) CNT are achieved through geometry optimization based on density functional theory (DFT). The electronic structures of the heterojunction are then obtained with the same method. The band offsets of the heterojunction are calculated by means of the average bond energy method, which utilizes the band structures of the corresponding isolated nanotubes. Finally, a band schematic diagram of the heterojunction is plotted.

2. Model and method

As the model of the heterojunction is the basis of the study on the electronic structures with first-principle calculations, a heterojunction supercell was established, in which 64 carbon atoms, 32 boron atoms and 32 nitrogen atoms were included. The interface of the heterojunction was formed via C–B bonds (named model I) or C–N bonds (named model II). The structure of model I is shown in Fig. 1. Replacing the B atoms with N atoms in BNNT section, model II was obtained. The supercell is large enough for our calculation[9]. Due to the influence of the structure of the heterojunction on its electronic structures, geometry optimization was realized before the calculation of the electronic properties, which was implemented with the Cambridge Serial Total Energy Package (CASTEP).

In calculations, ultrasoft pseudopotentials were used to describe the interactions between electron and ion and the generalized gradient approximation (GGA) indicated the exchange-

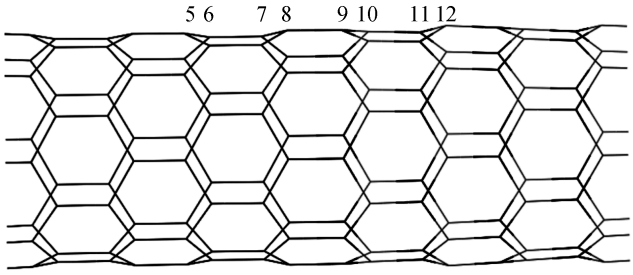

Fig. 1. Structure of BN/CNT heterojunction. The left 8 layers are the CNT section and the right 8 layers BNNT.

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Table 1. Diameters of the layers in model I and their changes.

Layer type	Layer number	Diameter (Å)	ΔD
C	5	6.260	−0.004
C	6	6.273	0.009
C	7	7.280	0.016
C	8	6.348	0.084
B	9	6.324	−0.032
N	10	6.456	0.007
B	11	6.375	0.019
N	12	6.442	−0.007

correlation potential. The Monkhorst and Pack scheme of k point sampling was used for integration over the first Brillouin zone and 8 k points along the tube axis in reciprocal space were used. In geometry optimization, the maximal force, stress and displacement were set as 0.05 eV/Å, 0.05 GPa and 5×10^{-4} Å.

3. Results and discussion

3.1. Electronic structures of the heterojunction

The electronic structures of the heterojunction are influenced by its structure. To obtain the structure of the heterojunction, the geometry optimization of the heterojunction has been realized. Similar work on the isolated nanotubes was implemented to achieve changes in structures in the form of the heterojunction. The diameter of the (8, 0) CNT is 6.264 Å, which is consistent with Song *et al.*'s result of 6.26 Å[10]. The B–N bond in the BNNT is 1.44 Å, which agrees with the results of Zhang *et al.*[11]. The diameters of the nitrogen layers and the boron layers are 6.449 Å and 6.356 Å, respectively. These results indicate that our method is reasonable for the study of the structure of the heterojunction.

The optimized structure of the heterojunction shows that rearrangement is mainly concentrated on the interface (layer 8 and layer 9), which is acquired by observing the changes of the diameters of the layers near the interface (the diameters and their changes in model I are shown in Table 1). The variations of the diameters of layer 8 and layer 9 are 0.084 Å and –0.032 Å, which are much larger than those of the other layers. However, the changes are much smaller than those in a (10, 0) BNNT/AlNNT heterojunction[9], which is attributed to the smaller difference between the diameters of the CNT and BNNT. The same result is found in model II.

The molecular orbitals of the BNNT/CNT heterojunction were calculated. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the BNNT/CNT heterojunction are presented in Figs. 2(a) and 2(b). These two orbitals mainly concentrate on the CNT section, which means that the top of the valence band and the bottom of the conduction band are located on the CNT section. The calculated density of states (DOS) of the isolated CNT and BNNT show that their band gaps are 0.42 and 3.04 eV, respectively.

3.2. Band offsets of the heterojunction

The band offsets are the discontinuities between the valence and conduction band edges of the heterojunction, which are important parameters[12, 13]. The average bond energy

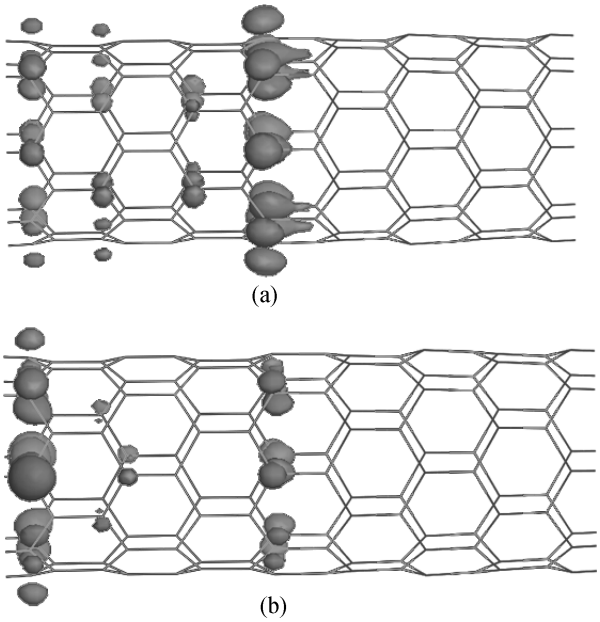

Fig. 2. (a) HOMO and (b) LUMO of the heterojunction.

method is an effective method for the calculation of band offsets of a heterojunction[14, 15], and utilizes the band structures of the (8, 0) CNT and the (8, 0) BNNT. The average bond energy E_{m} was achieved by averaging the eigenvalues of the $E_{\mathrm{n}}(k)$ of the four highest valence bands and four lowest conduction bands in the whole Brillouin zone, which is represented as follows:

$$E_{\mathrm{m}} = \frac{1}{8N} \sum_{n=1}^{8} \sum_{k} E_{\mathrm{n}}(k). \tag{1}$$

The band offset parameter E_{mv} could be obtained by

$$E_{\mathrm{mv}} = E_{\mathrm{m}} - E_{\mathrm{v}}, \tag{2}$$

where E_{v} is the energy of the top of the valence band. Then, the valence band offset of the heterojunction was determined by

$$\Delta E_{\mathrm{v}} = E_{\mathrm{mvBN}} - E_{\mathrm{mvC}}, \tag{3}$$

where E_{mvC} and E_{mvBN} are the band offset parameters of the CNT and BNNT, respectively. Finally, the conduction band offset of the heterojunction was achieved through

$$\Delta E_{\mathrm{c}} = \Delta E_{\mathrm{g}} - \Delta E_{\mathrm{v}}, \tag{4}$$

in which ΔE_{g} is the difference of the energy gaps of the materials forming the heterojunction. The calculated valence and conduction band offsets of the heterojunction for model I are 1.83 and 0.79 eV, respectively.

3.3. Band structure of the heterojunction

The work functions of the CNT and BNNT are the other essential parameters to plot the band structure of the heterojunction. Su *et al.* have studied the work functions of CNTs with DFT calculations and the achieved work function of the (8, 0) CNT is about 4.72 eV[16]. The BNNT may end with B

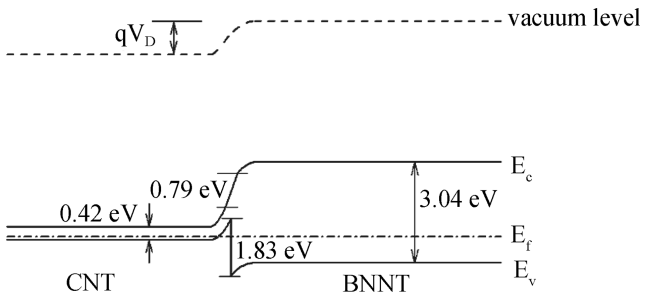

Fig. 3. Band diagram of the heterojunction (model I). The vacuum level is set as the reference level.

atoms or N atoms. The difference in structure results in different work functions. The work functions of the (8, 0) BNNT are 5.78 eV at the B end and 7.03 eV at the N end[17].

A band diagram of the heterojunction of model I is shown in Fig. 3. We can see that the band of the CNT section bends up, while that of the BNNT section bends down near the heterojunction interface. This is because the electrons transfer from the CNT section to the BNNT section when the nanotubes form the heterojunction. The other obvious feature in the band diagram of the heterojunction is that the discontinuities between the valence and conduction band edges lie at the interface. In the valence band, there is a peak in the CNT section and a valley in the BNNT section at the interface. It is obvious that both the top of the valence band and the bottom of the conduction band are located on the CNT section, which is consistent with the results of the molecular orbital. The difference in work functions between the two models results in a higher potential barrier in model II with a value of 1.25 eV.

4. Conclusion

In summary, to study the properties of the heterojunction formed by (8, 0) CNT and BNNT, a supercell was established, in which 64 carbon atoms, 32 boron atoms and 32 nitrogen atoms were included. The structures of the heterojunction and corresponding isolated nanotubes were optimized with a method based on DFT. Rearrangement of the heterojunction occurs mainly on its interface. The valence and conduction band offsets of the heterojunction are 1.83 and 0.79 eV, which were gained with the average bond energy method. Utilizing the known work functions of the CNT and BNNT, the band structure of the heterojunction has been obtained. Our results are meaningful for the modeling of nanotube heterojunction devices.

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