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Transport properties of boron nanotubes investigated by *ab initio* calculation*

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We investigate atomic and electronic structures of boron nanotubes (BNTs) by using the density functional theory (DFT). The transport properties of BNTs with different diameters and chiralities are studied by the Keldysh nonequilibrium Green function (NEGF) method. It is found that the cohesive energies and conductances of BNTs decrease as their diameters decrease. It is more difficult to form (N, 0) tubes than (M, M) tubes when the diameters of the two kinds of tubes are comparable. However, the (N, 0) tubes have a higher conductance than the (M, M) tubes. When the BNTs are connected to gold electrodes, the coupling between the BNTs and the electrodes will affect the transport properties of tubes significantly.

Keywords: nonequilibrium Green function, transport properties, boron nanotubes
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1. Introduction

Low-dimensional nano-structures have received much attention due to their potential applications in future electronic devices.[1−5] The basic electronic properties of organic-molecule-based electronic devices have been investigated.[6−9] Carbon nanotubes (CNTs) and boron nanotubes (BNTs) are two of the most popular research fields because of their excellent properties.[10−13] All the BNTs are metallic, which is different from CNTs that are either conductors or semiconductors depending on their chiralities.[14] The geometric structure significantly affects the stability and transport properties of BNTs. Several studies of the boron nanostructures have been completed.[15−18] For example, Yan *et al* predicted a large family of stable boron monoelemental fullerenes and investigated their stability.[17] Liu *et al* showed the vertically-aligned single-crystalline boron nanowire arrays and investigated their field-emission behaviour.[4] However, less work has been done on the transport properties, which are important for further applications in nano-electronic devices.

In the present paper, we investigate several configurations of typical BNTs, for example, (3, 3), (6, 0), (6, 6), and (12, 0) by DFT calculations. The relaxed geometric structures and the stability properties are obtained together with the transport properties by NEGF calculations. Chiralities and diameters of BNTs are considered as key factors for the structure stability and the transport properties.

2. Method

In order to investigate the effects of diameter and chirality on the stability and transport properties of the tubes, we calculate (6×0), (12×0) BNTs, (3, 3), and (6, 6) BNTs with different chiralities. The (12×0) tube has a diameter close to that of the (6, 6) BNT, therefore the chiral effect will dominate their difference.

We relax the structures of (6, 0), (6, 6) and (12, 0) BNTs based on the density functional theory, which is implemented in the code of the Vienna *ab initio* simulation package (VASP).[19] The core electrons are treated in an ultrasoft pseudopotential.[20] Local-density approximation (LDA) is employed,[21] and a 310 eV energy cutoff is set. We use a hexagonal lattice to maintain the symmetry of the nanotubes. The vacuum layer is carefully checked to make sure that the interaction between adjacent tubes can be ignored. 5×5×15 k-sampling is used. For the (3, 3) structure,

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the relaxation using the VASP cannot converge. So we optimize the structure with the 6–31G* basis set and B3LYP exchange-correlation functional by using the Gaussian03 program package.[22] Five primitive unit cells are chosen as a cluster to be relaxed. We do not saturate the ends with hydrogen atoms. After the optimization, the endpoints become closed. Then we pick up the middle unit cell to build the nanotube. Buckled and un-buckled (3, 3) BNTs are obtained. The net force on each atom is small enough for the further calculation of the transport properties.

For the transport properties of BNTs, we use a state-of-the-art quantum transport technique[23] which is based on the Keldysh nonequilibrium Green's function (NEGF) formalism combined with the DFT. The basic idea of the NEGF-DFT formalism is to calculate the Hamiltonian and electronic structure of the device by the DFT, populate the electronic structure by using the NEGF, which properly takes into account nonequilibrium quantum statistics, and deal with open device boundaries directly by using the real-space numerical technique. The calculation code we used is MatDCal, which is developed by Hong Guo's group.

3. Results and discussion

3.1. Geometric structures

Ihsan Boustani *et al* found that boron clusters were stable if they followed the Aufbau principle:[15,16] simply put, stable boron nanoclusters could be constructed from only two elemental units, i.e. pentagonal and hexagonal pyramids. Boron nanotubes are therefore rolled up like carbon nanotubes. The difference is that the two-dimensional sheet is a triangular lattice (6-coordinated), buckled into some configurations. Recently, a new stable boron 2D sheet was considered to be even more stable than the structures discovered before.[24,25] It was actually a mixture of 6-coordinated and 5-coordinated structures. Some atoms were removed from the triangular lattice. The special three-center, two-electron bond in the boron based materials makes it difficult to explore the global minimum in the potential energy surface in such electron-lacking systems.

The optimized structure of the (6, 0) BNT is shown in Fig.1(a). In this case, the isosurface of the electron density has a network distribution in which each boron atom is 4-coordinated (see Fig.1(b)). It is quite different from the electron distribution in the "perfect boron nano sheet," in which each boron atom is 6-coordinated. This is also different from the (M, M) BNTs, which will be discussed later.

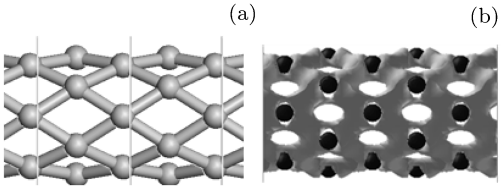

Fig.1. (a) Side view of a (6, 0) BNT structure and (b) isosurface of electron density of (6, 0) BNT.

For the (6, 6) BNT, to reduce the interaction between adjacent BNTs, we enlarge the supercell to 30 Å (1 Å=0.1 nm) and optimize its structure. The optimized structure is shown in Fig.2(a). Unlike the (6, 0) BNT in which the electron distribution is a network, the isosurface of the electron density shows itself to be of an isolated chain structure. The bond length between the nearest boron atoms on the chain is 1.61 Å, and the distance between different chains is 1.82 Å.

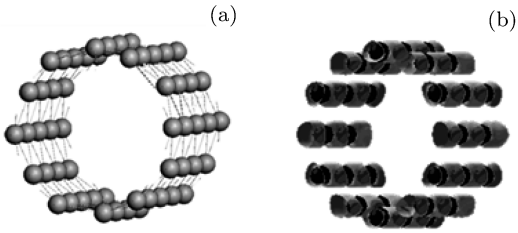

Fig.2. (a) Geometric structure of (6, 6) BNT and (b) isosurface of electron density of (6, 6) BNT.

The (12, 0) BNT has a diameter similar to that of the (6, 6) BNT. We optimize the structure and analyse the electron density distribution. The electrons also show a chain-like distribution which is the same as that of (6, 0) BNT.

Table 1. Diameters and cohesive energies of several types of BNTs.

N×M	diameters/Å	cohesive energies/eV
6×0	3.62	6.40
6×6	6.33	6.77
12×0	6.60	6.64

The cohesive energies and diameters of these three BNTs are listed in Table 1. The (6, 6) BNT has a higher cohesive energy than (12, 0) BNT though they have similar diameters, which means that the (6, 6) BNT is much more favourable than (12, 0) BNT in energy when forming BNTs of similar diameters. We

also find out that the cohesive energies of (6, 6) and (12, 0) BNTs are higher than those of (6, 0) BNTs, indicating that a BNT of large diameter is more stable than the one of small diameter.

3.2. Transport properties

The transport properties of nanotubes are very important in future nano electronic devices. To our knowledge, there is no research concerning the transport properties of BNTs. First, we investigate transport properties of pure BNT, in which the BNT itself serves as an electrode. We calculate the density of states (DOS), the transmission coefficient (T) and the tunneling current (I) for the (3, 3) buckled tube, the (3, 3) un-buckled tube, the (6, 6) and (12, 0) nanotubes. We also calculate the (8, 8) tube to confirm the relationship of the conductance changing with diameter, with the chirality being unchanged. The (8, 8) tube is not relaxed. We use an average bond length of (6, 6) BNT (1.76 Å) to construct the tube since we have found that the relaxation here does not cause any notable difference.

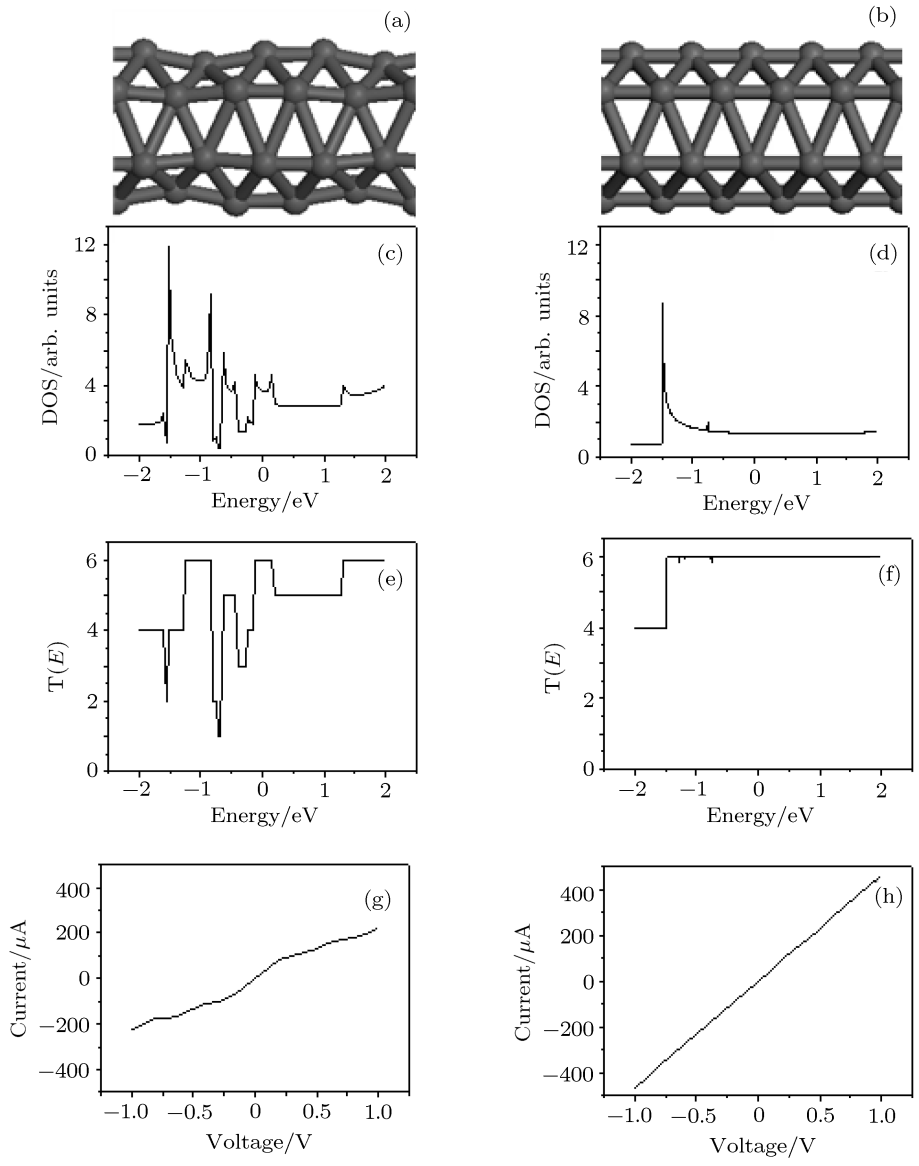

Fig.3. The left panels (a, c, e, g) are for the properties of buckled (3, 3) BNT. The right panels (b, d, f, h) are for the properties of un-buckled (3, 3) BNT. Panels (a) and (b) are for the geometric structures, panels (c) and (d) DOS properties, panels (e) and (f) transmission properties, and panels (g) and (h) the I–V curves.

Figure 3 shows structures, values of DOS, T and I of buckled and un-buckled (3, 3) BNTs. From the calculation results, we can find that the buckled structure has more states than the un-buckled structure at small scattering energy. When the scattering energy is from –2 eV to 2 eV, there are 10 peaks on the DOS curve for the buckled structure, but there exists only one peak for the un-buckled structure. From the corresponding transmission curve, we can find that each scattering state contributes one peak to the transmission coefficient, which means that there is no reflection in each scattering channel. The transmission of the un-buckled structure is larger than that of the buckled structure. So we can see from the I–V curve that the conductance in the un-buckled structure is larger than that in the buckled structure.

The diameters of (12, 0) BNT and (6, 6) BNT are comparable (see Table 1), but the chiralities are different. From Fig.4, we can find the different transport properties of the zigzag structure and the armchair structure. Figures 4(a) and 4(d) show the DOS and the T(E) of (12, 0) BNT, figures 4(b) and 4(e) display the DOS and the T(E) of (6, 6) BNT, and figures 4(c) and 4(f) indicate the DOS and the T(E) of (8, 8) BNT. Compared with (3, 3) BNT, these BNTs are larger in diameter, DOS and T(E). From our calculation results, it can be seen that they are similar to those for (3, 3) BNT, each scattering state contributes one peak to the transmission coefficient. The transmission curve shows that the conductance of (8, 8) BNT is largest, the conductance of (6, 6) BNT is smallest, and the conductance of (12, 0) BNT is between those of (6, 6) BNT and (8, 8) BNT. So we can predict that the conductance of the (N, 0) BNTs is larger than that of (M, M) BNTs when their diameters are comparable. And the conductances of BNTs with larger diameters are larger when BNTs have the same kind of chirality (both are of armchair in this case).

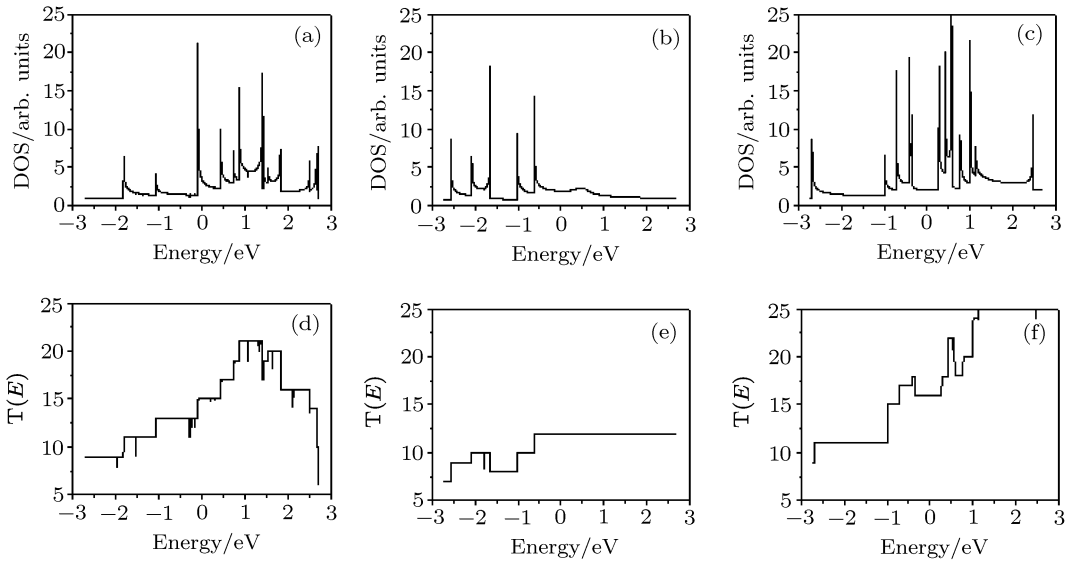

Fig.4. DOS properties ((a)–(c)), and transmission coefficient properties ((d)–(f)) of (12, 0), (6, 6) and (8, 8) BNTs, respectively.

The above calculations are performed with perfect infinite BNTs. But for practical applications, we may connect the BNTs with one electrode of the same kind or other kind. Here we use the (3, 3) buckled BNT and the gold electrode as an example. We investigate the transport properties of an Au-BNT-Au system. We also change the coupling strength between the BNT and gold electrodes by adjusting the distance in between. The calculation results are shown in Fig.5.

The transmission coefficient of the Au-BNT-Au system decreases significantly due to the contact between the gold electrodes and the central BNT compared with that of the perfect infinite BNTs, and in this case it does not hold true that each scattering state contributes one peak to the transmission coefficient. So the conductance and the current of the Au-BNT-Au system are far lower. For example, when the bias voltage across the two electrodes is 0.5 V, the current of the Au-BNT-Au system is 21 μA, and the current of the BNT-BNT-BNT system is 134 μA.

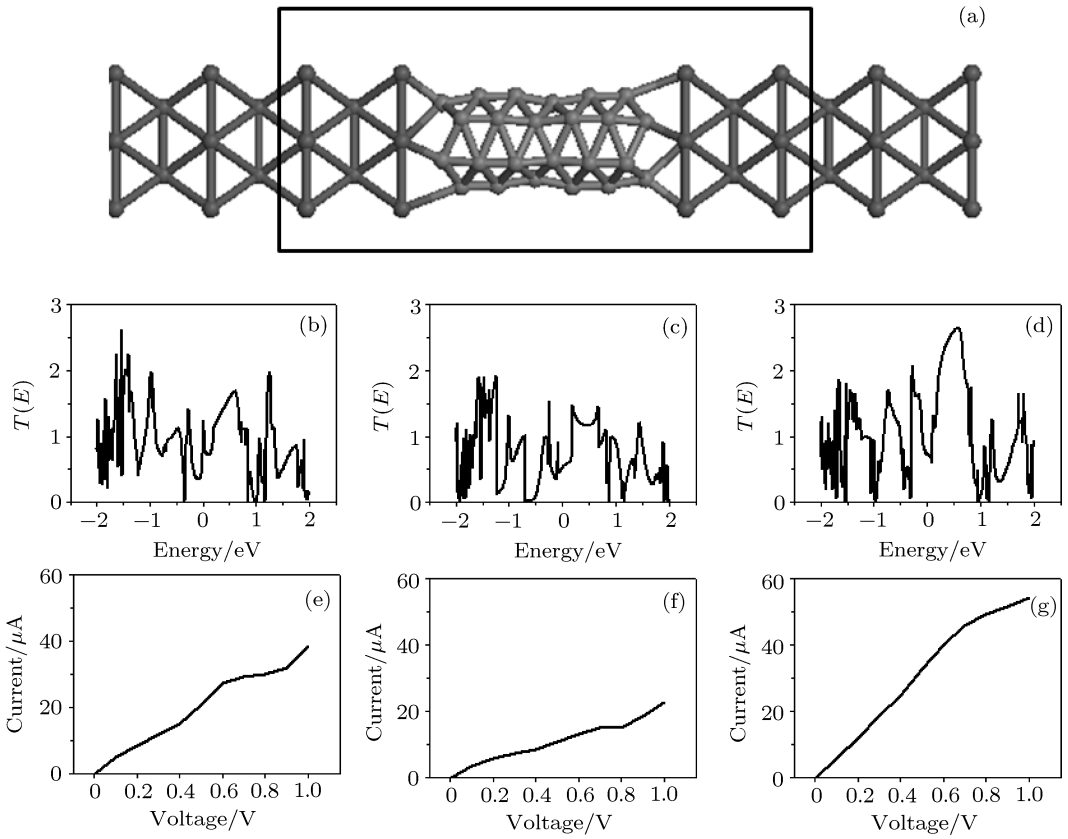

Fig.5. (a) Structure of the (3, 3) buckled BNT contact with two gold electrodes; (b) and (e) transmission coefficient and I–V curve for a normal contact (a typical bond length between gold and boron is 2.2 Å); (c) and (f) T(E) and I–V curves when the distance between the BNT and the electrodes is increased by 0.5 Å; (d) and (g) T(E) and I–V curves when the distance between the BNT and each of the electrodes is reduced by 0.5 Å.

The coupling strength can also change the conductance of the Au-BNT-Au system. When the distance between the central BNT and each of its gold electrodes is increased by 0.5 Å, the current at 0.5 V is reduced down to 11 μA. When the distance is reduced by 0.5 Å, the current at 0.5 V increases up to 33 μA. This means that if we increase the distance between the central BNT and each of the gold electrodes, the coupling strength is weakened, and the conductance and the current decrease accordingly. When we reduce the distance between the central BNT and each of the gold electrodes, the coupling is strengthened, and the conductance and current increase correspondingly.

4. Conclusions

The structure and transport properties of BNTs with different diameters and chiralities are investigated based on DFT and NEGF methods. The calculation results indicate that it is difficult to grow small diameter BNTs, and it is much more difficult to form (N, 0) tubes. All BNTs are metallic regardless of their chiralities. (N, 0) BNTs tend to have a larger conductance than the (M, M) tubes if their diameters are close. Conductance increases when the diameter increases, and so does the cohesive energy. When a BNT is sandwiched between two electrodes, the resistance comes mainly from the contact. Therefore, for applications in future electronic devices, the electrodes should be selected carefully.

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