THE ROLE OF HETEROJUNCTIONS IN THE GROWTH OF TERNARY CBN HETERONANOTUBES

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Introduction

Carbon nanotubes (CNTs) are known to be intrinsically either semiconducting or metallic, depending upon the chirality. Whereas, boron nitride nanotubes (BNNT) are electrical insulators with a large band gap of ca. 5.5 eV, independent of their chirality. Due to the exciting, yet distinct properties discovered in CNTs and BNNTs [1], attention has recently switched to explore hybrid CBNNTs [2-5].

The effect of C_x:$(BN)_y$ heterojunctions (in terms of number and composition) on the stability and electronic structure of $[C_x$:$(BN)_y]_n$ heteronanotubes is still unknown. In order to address this issue, we have performed DFT calculations on ternary $[C_x$:$(BN)_y]_n$ heteronanotubes, where x and y denote the number of unit cells of each CNT and BNNT segment, and n denotes the number of repeating units of C_x:$(BN)_y$. In our calculations, prototype C and BN single-walled nanotubes (SWNT) (8,0) and (6,6) were chosen to model the general features of ternary $[C_x/(BN)_y]_n$ heteronanotubes having periodic *axial* heterojunctions (labeled with "/"), and shown in Figure 1 (a-d). The second type of C_x:$(BN)_y$ heteronanotubes having *continuous* heterojunctions all the way along tube axis (labeled with "–") are also included for comparison [see Figure 1 (e)]. It is known that SWCNT (8,0) and (6,6) are semiconducting and metallic, respectively, while SWBNNT (8,0) and (6,6) are both semiconducting. Thus, it is important to understand how the stability and electronic structure of *hybrid* CBNNTs evolve with respect to the CNT and BNNT building blocks, with varying x and y.

Computational Method

Geometry optimizations and electronic structure calculations were performed with DFT, as implemented in the Vienna ab-initio simulation package (VASP) [6]. The computational details have been described elsewhere [7].

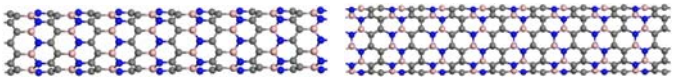
Results and Discussion

As shown in Figure 1, CBN heteronanotubes can be formed as nearly seamless tubular structures, via strong C-N and C-B covalent bonds, regardless of various x, y, and n. However, due to the lattice mismatch and strain at the heterojunctions, the formation of CBN heteronanotubes are energetically less favorable, as compared to pristine CNTs and BNNTs with the same chirality (Figure 2). The formation energies [defined as the energy released (eV/atom) by forming a nanotube from the gas-phase atoms] are increased with respect to x and y. Ultimately, the formation energy is expected to converge to that of a mixture of pristine CNTs and BNNTs (as shown by the dashed lines in Figure 2).

The calculated formation energies for C–(BN) heteronanotubes (8,0) and (6,6) are 7.26 and 7.31 eV, respectively. It can be seen that the formation of $C_x/(BN)_y$ heterojunctions have an adverse impact on the stability of $[C_x/(BN)_y]_n$ heteronanotubes, as smaller values of x and y lead to an increase in the number of such nodes. Due to their larger diameter (8.22 vs. 6.38 Å), (6,6) heteronanotubes have lower formation energies, as compared to (8,0) heteronanotubes. As compared to the size of experimentally-synthesized $[C_x/(BN)_y]_n$ heteronanotubes, the x and y values employed in our model are much smaller. From Figure 2, one can predict that $[C_x/(BN)_y]_n$ heteronanotubes with increased x and y values, which correspond to heteronanotubes with fewer junctions, will be thermodynamically competitive with respect to the corresponding CNTs and BNNTs. This helps explain the experimental observations that the growth of $[C_x/(BN)_y]_n$ can be realized via catalyst-assisted organization.

In Figure 3, we show the calculated total density of states (DOS) for ternary CBN heteronanotubes (8,0) and (6,6). As shown in Figure 3 (f) and (g), our calculated DOS agree with the consensus that SWCNT (8,0) and (6,6) are semiconducting and metallic, respectively, whereas SWBNNT (8,0) and (6,6) are both semiconducting. From Figure 3 (I), one can see that the (8,0) $C_{0.5}/(BN)_{0.5}$ and $C_1/(BN)_3$ nanotubes become more semiconducting with an increased HOMO-LUMO (HL) gap (i.e., 1.33 and 1.06 eV, respectively) as compared to pristine CNT (8,0) (i.e., 0.59 eV). Whereas, $C_3/(BN)_3$ and $C_3/(BN)_1$ become metallic with significant electron states populated at the Fermi level. Also, C–(BN) becomes slightly metallic. From (a)-(d) of Figure 3 (II), the $[C_x/(BN)_y]_n$ (6,6) nanotubes all made a shift from a metallic to a semiconducting state, with HL gaps of 1.17, 0.78, 0.30, and 1.75eV, respectively. In contrast, the C–(BN) heteronanotube remains metallic, with enhanced conductivity. This is evidenced by more states at the Fermi level when compared to those of pristine CNT (6,6), as shown in II (e) and (f) of Figure 3. Therefore, the electronic structure of ternary $[C_x/(BN)_y]_n$ heteronanotubes can be tuned by modifying the composition and size of C_x and/or the $(BN)_y$ unit, which can lead to either more metallic or more semiconducting behavior. We also find that the states around the Fermi level are mainly contributed from the whole lattice, rather than the interfacial C, B, and N states at the heterojunctions.

I II



(a) (a)

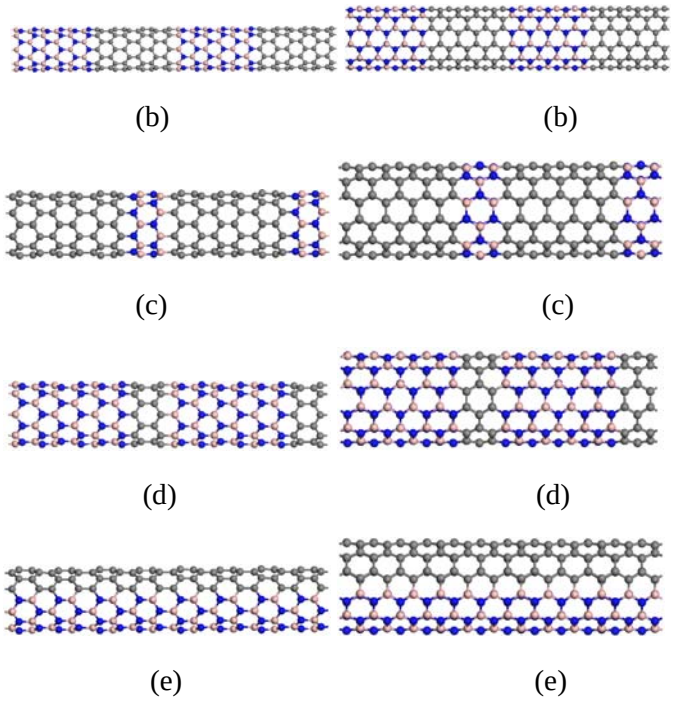


Fig. 1 Side view of ternary CBN heteronanotubes (8,0) and (6,6), represented in column I and II, respectively: Column I (a) $[C_{0.5}/(BN)_{0.5}]_8$, (b) $[C_3/(BN)_3]_2$, (c) $[C_3/(BN)_1]_2$, (d) $[C_1/(BN)_3]_2$, (e) $C_{2y}/(BN)_y$; Column II: (a) $[C_1/(BN)_1]_8$, (b) $[C_{4.5}/(BN)_{4.5}]_2$, (c) $[C_{4.5}/(BN)_{1.5}]_2$, (d) $[C_{1.5}/(BN)_{4.5}]_2$, (e) C_{2y}– $(BN)_y$.

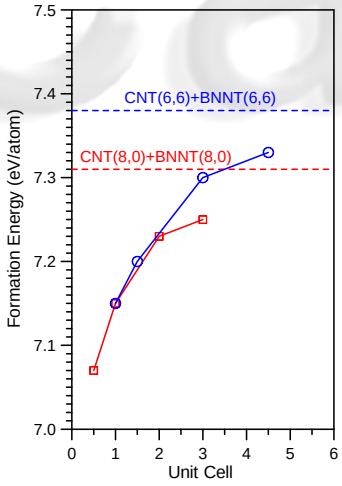
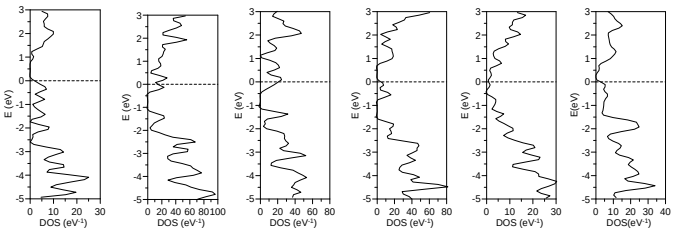
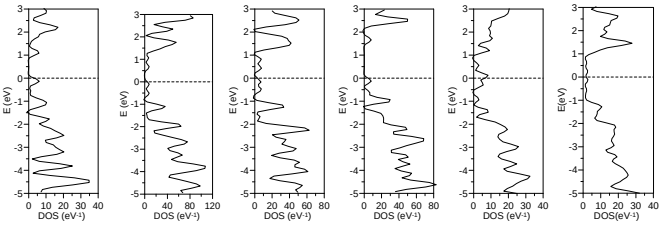


Fig. 2 Formation energy of ternary $[C_x/(BN)_y]_n$ heteronanotubes as a function of the unit cells of CNT and BNNT in the formation of $C_x/(BN)_y$ NT (x=2y). The compositions in the unit cell of SWNT (8,0) and (6,6) are $[C_{32}B_{16}N_{16}]$ and $[C_{24}B_{12}N_{12}]$, respectively.



(a)$C_{0.5}/(BN)_{0.5}$ (b)$C_3/(BN)_3$ (c)$C_3/(BN)_1$(d)$C_1/(BN)_3$(e)C−(BN) (f) C_2

(I)



(a)$C_1/(BN)_1$(b)$C_{4.5}/(BN)_{4.5}$(c)$C_{4.5}/(BN)_{1.5}$(d)$C_{1.5}/(BN)_{4.5}$(e)C−(BN)(f)C_3

(II)

Fig. 3 Calculated total density of states for ternary CBN heteronanotubes (I) (8,0) and (II) (6,6) as shown in Figure 1. Figures (f) and (g) are pristine CNT and BNNT. The Fermi level (dashed line) is shifted to zero eV.

Conclusions

We have investigated the stability and electronic structure of CBN heteronanotubes. We found that $[C_x/(BN)_y]_n$ heteronanotubes with fewer nodes can be thermodynamically stable, as compared to pristine CNTs and BNNTs. Moreover, the electronic structure of $[C_x/(BN)_y]_n$ heteronanotubes can be tuned by modulating the x and y combinations.

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