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C-BN Single-Walled Nanotubes from Hybrid Connection of BN/C Nanoribbons: Prediction by *ab initio* Density Functional Calculations

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Subsequent to the discovery of carbon nanotubes (CNTs),[1] ternary boron carbonitride nanotubes (BCN-NTs) attracted increasing interest due to their unique electronic properties and potential applications in nanotechnology.[2] A prime advantage is that the band structure of BCN-NTs can be controlled by changing their atomic composition and configuration.[3,4] Experimentally, B and/or N doping and direct synthesis methods have been developed for synthesizing such novel BCN-NTs.[2,5] Hitherto, most studies of BCN-NTs have focused on random or ordered doping into single-walled carbon nanotubes (SWCNTs), synthesis of sequential BN-C nanodomains along the tube axis, or BN-C coaxial multiwalled NTs.[2,4−6]

Recently, low-dimensional graphene nanoribbons (GNRs) have been fabricated experimentally.[7] These developments have opened up exciting opportunities for the design of novel electronic devices and interconnects.[8] On the other hand, single hexagonal BN nanoribbons (BNNRs) have been also studied extensively.[9] C and BN single-walled nanotubes (SWNTs) can be considered to be rolled from GNRs and BNNRs, respectively.[10] An intriguing question, however, is whether it is possible to form novel C-BN NTs via hybrid connection of a BNNR with a GNR? To explore this question, we report below a series of calculations to study the $C_x(BN)_{1-x}$ NTs constructed from a GNR/BNNR hybrid connection. We find that armchair and zigzag $C_{0.5}(BN)_{0.5}$ SWNTs are gapless and narrow gap semiconductors, respectively. Most interestingly, *ab initio* molecular dynamics (AIMD) simulations reveal that a $C_{0.5}(BN)_{0.5}$ armchair SWNT can be spontaneously formed via the interaction of a BNNR and a GNR at room temperature. Our results suggest an interesting route for synthesizing specific types of BNC-NTs, which may have potential application in BNC-based nanodevices.

A series of single-walled $C_x(BN)_{1-x}$ (10, 10) armchair NTs with a varied ratio of GNR/BNNR ($x = 0.1-1.0$) was built, and all the geometries were first optimized before calculating their bandstructures[11] (see computational details in the Supporting Information, SI). The $C_x(BN)_{1-x}$ SWNTs remained largely undeformed due to a small lattice mismatch between BN and graphene. The C−B and C−N bond lengths at the heterointerface are calculated to be 1.531 and 1.387 Å, respectively. Remarkably, when x is greater than 0.3 and less than 0.9, $C_x(BN)_{1-x}$ (10, 10) nanotubes displayed negligible band gaps around the Fermi level, similar to the behavior observed in graphene. The band gap is open if x is smaller than 0.3, which is in good agreement with a recent study by Wang et al. reporting the conversion of metallicity in SWCNTs into semiconductivity by B/N Codoping.[5]

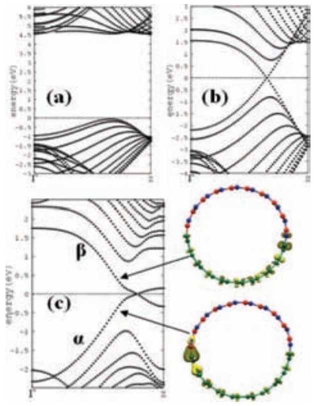

Figure 1. Band structure for (a) BN, (b) C, and (c) $C_{0.5}(BN)_{0.5}$ (10, 10) nanotube and band decomposed charge density for highest occupied valence band (α) and lowest unoccupied conduction band (β). Red, blue balls and yellow surface represent B, N atoms and iso-surface, respectively.

Figure 1a−c presents band structures for (10, 10) BN, C, and $C_{0.5}(BN)_{0.5}$ armchair NTs, respectively. Clearly, the BN-NT is a wide gap semiconductor while the armchair CNT shows metallic behavior. However, two linear bands in the CNT became flat (localized) around the Fermi level in the $C_{0.5}(BN)_{0.5}$ nanotube. It can therefore be inferred that the conductance will be greatly enhanced. To explore the origin of this phenomenon, the partial charge density for the highest occupied band (α) and lowest unoccupied band (β) were plotted as shown Figure 1c. Clearly, the C−B interface affects the valence band maximum (α), and a flat minimum conduction band (β) is attributed to the C−N interface. We have also computed the band structure for (6, 6) and (16, 16) $C_{0.5}(BN)_{0.5}$ SWNTs with very similar results (see SI); hence it is expected that the observed phenomenon of gapless bands is essentially independent of the diameter of the armchair $C_{0.5}(BN)_{0.5}$ SWNTs.

We now focus on (10, 0) and (12, 0) $C_x(BN)_{1-x}$ zigzag SWNTs with different hybrid ratios of GNR/BNNR. Figure 2 presents the calculated band structures for BN, C, and $C_{0.5}(BN)_{0.5}$ (10, 0) and (12, 0), respectively. Clearly, there is no major difference between the electronic structures of the (10, 0) and (12, 0) BN-NTs, whereas (10, 0) and (12, 0) C-NTs show a striking contrast (semiconducting and metallic). However, the band structures for (10, 0) and (12, 0) $C_{0.5}(BN)_{0.5}$ SWNTs are quite similar. The calculated band gaps are

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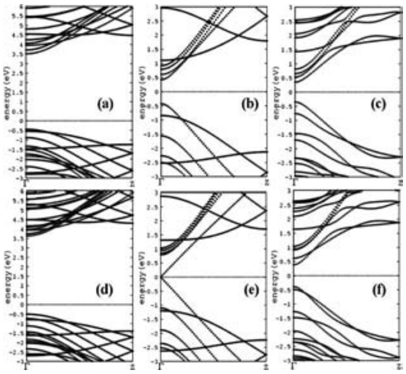

Figure 2. Band structures for a (10, 0) (top panel) and a (12, 0) (bottom panel) BN, C, and $C_{0.5}(BN)_{0.5}$ zigzag nanotube.

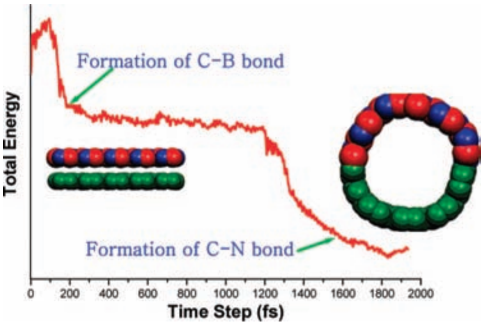

Figure 3. Variation of total energy as a function of Car–Parrinello molecular dynamics time step.

0.703 and 0.774 eV, respectively. On the basis of these preliminary results, it may therefore be anticipated that all the zigzag $C_{0.5}(BN)_{0.5}$ SWNTs should possess a narrow direct band gap (less than 1.0 eV). We have also computed band gaps for $C_x(BN)_{1-x}$ zigzag SWNTs at different x ($x = 0.1-1.0$) and found these to range from 0.4 to 0.8 eV (see SI). These consistently small band gaps indicate that $C_x(BN)_{1-x}$ zigzag SWNTs may be promising as semiconductors for visible light emission as in the case of a layered BC_2N compound.[12]

Having studied the electronic structure of these novel $C_x(BN)_{1-x}$ NTs, it is also relevant to explore a possible synthetic route using AIMD simulations. To this end, a bare 10-GNR and bare 10-BNNR (both preoptimized) with zigzag edges at the open ends are positioned at a large separation of 4 Å, such that the interaction between them is initially very weak. AIMD (Car–Parrinello) simulation is then performed at room temperature.[13] Figure 3 presents the variation of the total energy as a function of the AIMD time step. The C–B and C–N bonds are formed at ~200 and 1400 fs, respectively, and $C_{0.5}(BN)_{0.5}$ in a tubular form evolves at ~2 ps. This indicates that the reaction barrier should be very small if there is any at all; i.e., the formation of armchair $C_{0.5}(BN)_{0.5}$ SWNTs via the hybrid GNR/BNNR connection is both thermodynamically and kinetically favorable. In contrast, we could not observe the formation of a (10,0) $C_{0.5}(BN)_{0.5}$ *zigzag* SWNT from the hybrid connection of the corresponding armchair-type BNNR and GNR partners within 2 ps. Limitations of computational feasibility prevent us at this point from pushing to longer AIMD run times; however, the implication is that the activation barrier should be significant at room temperature. This contrasting reactivity can be understood by the fact that a flat band across the Fermi level occurs in the case of graphene nanoribbons with zigzag edges, which will induce higher chemical reactivity in this case as found previously.[10]

In summary, we have demonstrated by ab initio density functional calculations that $C_{0.5}(BN)_{0.5}$ armchair SWNTs are gapless semiconductors, independent of tube diameter. Most interestingly, the direct synthesis (in vacuum) of armchair $C_{0.5}(BN)_{0.5}$ via the hybrid connection of GNR/BNNR partners is found to be both thermodynamically and dynamically favorable. Armchair $C_{0.5}(BN)_{0.5}$ NTs can be spontaneously formed via the hybrid connection of a BNNR and a GNR at room temperature. Such novel armchair $C_{0.5}(BN)_{0.5}$ SWNTs should possess enhanced conductance, which is comparable to graphene. Additionally, the zigzag $C_{0.5}(BN)_{0.5}$ SWNTs are narrow direct band gap semiconductors (<1 eV), which may potentially be used as new light emitting materials. In light of recent experimental progress and the enhanced degree of control in the synthesis of GNRs and BNNRs,[8,9] our results suggest an interesting avenue for exploration to synthesize novel types of C-BN nanotubes with tunable electronic properties, leading to potentially important applications in BNC-based nanodevices.

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Supporting Information Available: Computational details, bandstructures for (10, 10) and (10, 0) $C_x(BN)_{1-x}$ SWNTs at different x, (6, 6) and (16, 16) $C_{0.5}(BN)_{0.5}$ SWNTs, a movie depicting formation of $C_{0.5}(BN)_{0.5}$ armchair SWNT via hybrid connection of BN/C nanoribbons during AIMD simulation. This material is available free of charge via the Internet at http://pubs.acs.org.

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