Structures, stability and electronic properties of two- or four-segment BN/C nanotubes

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Abstract: The structures, stability and electronic properties of some novel two- or four-segments BN/C nanotubes are systematically investigated using the density functional theory based first-principle calculations. Our calculations reveal that the structures, stability and electronic properties of these hybridized nanotubes are dependent on their diameters, compositions and hybridizing manners.

Kewwords: Boron nitride nanotubes; Carbon nanotubes; electronic properties.

Introduction

The quasi one dimensional (1D) carbon nanotubes (CNTs) [1, 2] can be metal or insulator, depending on their chirality and diameters [3]. And the boron nitride nanotubes (BNNTs) [4, 5] always behave as wide gap insulators [6] independent of their chirality and diameters. Recently, some novel two-segment BN/C hybridized nanotubes (BNCNTs) with tunable band gaps are proposed by Aijun Du et. al [7]. Their ab initio molecular dynamics simulations reveal that armchair single wall BNCNTs can be spontaneously formed via the interaction of the two segments of ZBNNR and ZGNR at room temperature. Another work of molecular dynamics simulations and total energy calculations [8] indicated that these two-segment BNCNTs hold stability comparable to CNTs and may stable well at room temperature if their diameters are larger than 0.4 nm. Inspired by the hybridizing ideas in these researches, some four-segment armchair single walled BNC-BNCNTs and BNC-NBCNTs with diameter larger than 0.8 nm are proposed and their structures, stability and electronic properties are investigated. Our calculations reveal that the structures, stability and electronic properties of these hybridized nanotubes are dependent not only on their diameters, compositions but especially on their hybridizing manners.

Models and Method

As show in the left panel in Fig.1, the nanotubes considered in our calculations are the pure CNTs, the two-segment BNCNTs, the four-segment BNC-BNCNTs and BNC-NBCNTs as well as the pure BNNTs with 12, 16 and 20 zigzag chains. We adopt VASP [10] to investigate their stability and electronic properties. The kinetic cutoff energy is set to be 420 eV and the Brillouin zone (BZ) is sampled using a 1x1x11 Gamma-centered Monkhorst-Pack grid in our calculations. All systems are fully optimized up to the residual force on every atom is less than 0.01 eV/Å through the conjugate-gradient algorithm.

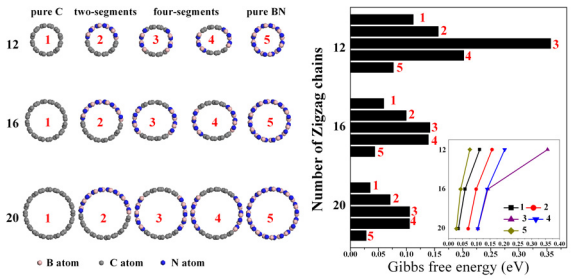

Fig.1: Shown in left are the optimized structures of the pure CNTs (1), two-segments BNCNTs (2), four-segment BNCB-NCNTs (3), BNC-BNCNTs (4) and pure BNNTs (5) with 12 (top), 16 (center) and 20 (bottom) zigzag chains, respectively; In right are their corresponding Gibbs free energies.

Results and Discussion

As shown in Fig. 1, all the fully optimized nanotubes are still cylinders except for the four-segment ones containing zigzag chains less than 20, who are staved

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due to the unbalanced strains in the narrow segments of ZBNNR and ZGNR. Two equivalent (inequivalent) ZGNR segments in BNC-BNCNTs (BNC-BNCNTs) are strained by unbalanced (balanced) external forces at their two sides and their curvatures are produced. The calculated Gibbs free energies of these nanotubes are shown in Fig.1. An obvious diameter-dependent stability in these tubes can be found in the dotted lines inserted in Fig. 1. From the histogram, we can see that the pure CNTs and pure BNNTs are more favorable that the multi-segment ones. Both the four-segment BNC-BNCNTs and BNC-NBCNTs are less stable than the two-segment BNCNTs due to their double unstable B-C and C-N interfaces, respectively. These results indicate that the ZBNNR segments and ZGNR segments prefer to separate from each other to form pure BNNTs and CNTs. In views of the forming of the multi-segment tubes from hybridizing the segments of ZBNNR and ZGNR [7, 8] and the successful synthesizing of the mixed B-C-N single walled nanotubes [9], it is necessary and interesting to investigate the electronic properties of these multi-segment tubes, especially of the four-segment ones.

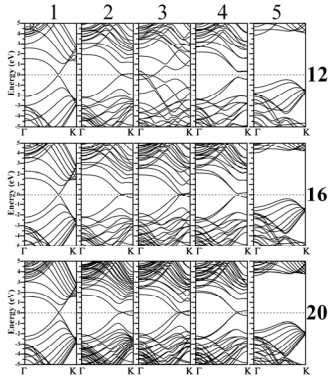

Fig.2: Band structures for the pure CNTs (1), two-segment BNCNTs (2), four-segment BNCB-NCNTs (3), BNC-BNCNTs (4) and pure BNNTs (5) with 12 (top), 16 (center) and 20 (bottom) zigzag chains, respectively.

The calculated band structures of the pure CNTs, two-segments BNCNTs, four-segment BNCB-NCNTs, BNC-BNCNTs and pure BNNTs with 12, 16 and 20 zigzag chains are shown in Fig. 2. We can see that all the pure CNTs are narrow band gap semiconductors and all the pure BNNTs are wide band gap insulators. All two-segment tubes are semimetals with tiny band gaps. Interestingly, the electronic properties of the four-segment tubes are dependent on their hybridizing manners. All the BNC-BNCNTs are semiconductors with narrow band gaps decreasing as the diameters increases, but all the four-segment BNC-NBCNTs are metals. These differences in the electronic properties are mainly derived from the different doping effects of ZBNNR segments on ZGNR segments in these two types of four-segment tubes. In the BNC-BNCNTs, the two segments of ZGNR locating at the same chemical environment are equivalent. Both two ZGNR segments containing both B-C and C-N interfaces are doped by the interfacial B and N atoms with both n-type and p-type, respectively, and behave as semiconductors. In the BNC-NBCNTs, the two segments of ZGNR locating at very different chemical environment are inequivalent. The one with only B-C interface is doped with only n-type and another one with only C-N interface is doped or p-type, resulting in a metallic properties in the BNC-NBCNTs.

Conclusion

Using the first-principles calculations, some four-segments BNC-BNCNTs and BNC-NBCNTs have been proposed and investigated. Our results indicate that these tubes can be metals or semiconductors depending on their hybridizing manners.

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