True Nanocable Assemblies with Insulating BN Nanotube Sheaths and Conducting Cu Nanowire Cores

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Nanocable models comprised of BN nanotubes filled with close-packed Cu nanowires were investigated by gradient-corrected density functional theory (DFT) computations. The optimal distance between the sidewall of BN nanotubes and the atoms in a copper nanowire is about 0.35 nm, with a weak insertion energy (ca. −0.04 eV per Cu atom). Hence, such nanocables are assembled by weaker van der Waals (vdW) forces, rather than by chemical bonding interactions. The electronic band structures of the BN/Cu hybrid systems are superposition of those of the separate components, the BN nanotubes, and the Cu nanowires. Since charge density analyses show that the conduction electrons are distributed only on the copper atoms, charge transport will occur only in these inner nanowires, which are effectively insulated by the outer BN nanotubes. On the basis of these computational results, BN/Cu hybrid structures should be ideal nanocables.

Introduction

The concepts of nanoelectronics and nanoelectromechanical systems (NEMS)[1] have led to the experimental realization of many novel one-dimensional (1-D) nanostructures such as nanotubes, nanowires, nanorods, and nanobelts. These have been used as building blocks in nanoelectronics and NEMS. Though metallic nanowires are important components for the interconnection of nanoscale electronic elements,[2] there are serious limitations. Metallic nanowires are usually unstable chemically and the environment may affect their transport properties.[3] Furthermore, the electronic and transport properties of nanoelectronic devices or NEMS using metallic nanowires as building components may be disturbed by unwanted interactions with their nearby nanowire neighbors. Therefore, true nanocables, with a metallic nanowire core protected by an insulating, chemically stable outer sheath, are desirable.

The "nanocables" first found experimentally referred to the coaxial structures of several layers of nanotubes and/or clusters; many investigations have been carried out. In 1997, Colliex et al.[4] found a sandwich C−BN−C structure closely resembling a coaxial nanocable during the synthesis of carbon and boron nitride (BN) nanoparticles. In 1998, Zhang et al.[5] reported coaxial nanocable structures consisting of a β-phase silicon carbide core, an amorphous silicon oxide intermediate layer, and separated boron nitride and carbon layered radial outer shells. Since then, many materials with coaxial nanocable-like structures have been prepared experimentally,[6] including B/SiO2,[7] SiC/SiO2,[8] TiO2/SiO2,[9] ZnO/SiO2,[10] Zn/ZnS,[11] Zn/ZnO,[12] ZnS/C,[13] Ag/C,[14] Ga2O3/C,[15] etc. However, most of these nanostructured materials only resemble cables in structure, but not in their electrical capabilities. A true nanocable should be defined as a 1-D nanostructure consisting of a metallic core and an insulating sheath; the outer sheath should have negligible influence on the transport properties of the inner metallic nanowire.

Carbon nanotubes with a large aspect ratio (defined by the ratio between axial and transverse lengths) should be possible templates for fabricating nanotube-based 1-D hybrid structures.[6,16] Filling of carbon nanotubes with metals, metal oxides, etc. by capillarity or wet-chemistry methods has been carried out successfully for a decade.[6,16−21] Novel electronic and magnetic properties of metal-filled carbon nanotubes have been predicted,[22−24] but the strong coupling between the encapsulated transition-metal (Fe, Co, etc.) wires and the carbon nanotubes may lead to substantial modification of their electronic states. The electronic structures of carbon nanotubes themselves depend on the type of tube (the chirality), and it is hard to select only semiconducting carbon nanotubes to function as nanocable shields. Moreover, exposure to gases such as O_2 and NO_2 may affect the electronic properties of carbon nanotubes considerably.[25] Therefore, such hybrid carbon nanotube/metal nanowire structures do not appear to have promise as nanocables with conducting properties.

Recent preparations of novel inorganic nanotubes[26−28] have provided more candidate materials for nanocables. Among them, BN nanotubes, one type of III−V compounds with tubular structure, have been of wide interest recently.[29−34] Due to the

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highly ionic character of the bonding, BN nanotubes possess many properties, which differ from those of carbon nanotubes. In particular, BN nanotubes have stable insulating properties (~5.5 eV wide band gap) weakly dependent on the diameter, the helicity, and the number of tube walls.[29] Moreover, graphitic-like BN is chemically inert and thermally stable. For example, BN nanotubes were found to exhibit significant resistance to oxidation at high temperatures.[32] Therefore, BN nanotubes appear to be ideal as insulating sheaths of nanocables encapsulating conducting metallic nanowires or metallic nanotubes. Enyashin et al. proposed that a large-diameter BN nanotube, filled with a smaller metallic carbon nanotube, might result in a prototype nanocable.[35] However, the preparation of such double walled nanotubes, comprised of an outer BN shell and an inner carbon shell with controlled conductivity, is unlikely to be realized in practice.

Recently, Bando's group has encapsulated Mo clusters as well as Ni, Co, Fe, or Fe−Ni alloy nanorods/nanowires into BN nanotubes via a newly developed two-stage experimental process.[36−39] Zettl's group reported encapsulation of 1-D potassium halide single crystals within BN nanotubes.[40] The emerging field opened by such successful uses of BN nanotubes to enclose metal fragments or other compounds might lead to new BN nanotube applications. In this paper, we propose true nanocables composed of insulating BN nanotubes and highly conductive Cu nanowires. Here we choose Cu for the following reasons: (1) Cu is a commonly used material as the conducting core in the macroscopic electrical cables; (2) the filled 3d electron shell of Cu atoms might result in weaker coupling with the nanotube sheath than the other open-shell transition metals such as Fe, Co, and Ni; (3) Cu nanowires have been experimentally encapsulated inside carbon nanotubes,[18] and a Cu wire−BN tube composite nanocable should also be able to be synthesized. According to our DFT computations on such 1-D hybrid structures, it is shown that the BN nanotube−Cu nanowire interactions are weak. Consequently, the outer BN tubes do not affect the conductance of the individual Cu wires. Such BN nanotubes with encapsulated Cu nanowires might function as true nanocables in the same way as the macroscopic cables in electronic devices.

Computational Methods

Since BN nanotubes only adopt zigzag structures experimentally,[41,42] our computations were restricted to such models. (The same nomenclature is employed for BN (n, m) and C (n, m) nanotubes.) The tube−wire interactions and electronic band structures of the BN/Cu 1-D hybrid nanostructures were investigated by using all-electron DFT methods with generalized gradient approximations (GGA), as implemented in the DMol program.[43,44] A double numerical plus polarization (DNP) basis set[43] and the PW91 exchange-correlation functional[45] were used. Self-consistent field (SCF) calculations employed convergence criteria of 10^{-6} au for the total energy. Geometry optimizations employed convergence criteria of 2×10^{-3} au on the maximum energy gradient and 2×10^{-3} Å on the maximum displacement of each atom without any symmetry constraint. 1-D periodic boundary condition was applied along the nanotube axis. Higher thresholds have been tested and no significant improvement has been found. We used 3 **k** points to sample the 1-D Brillouin zone during the geometry optimization. Band structures, based on the equilibrium structures, were computed by using 30 **k** points along the 1-D Brillouin zone.

Technically it is not possible to include basis set superposition error (BSSE) within DMol. The calculated energy does not
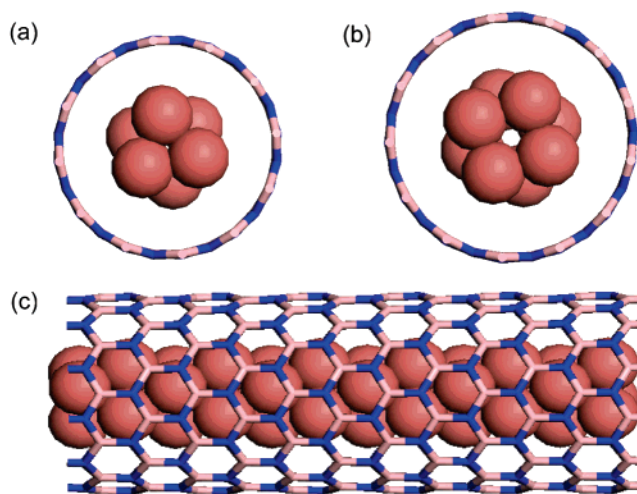

Figure 1. Atomic structures of the most stable BN nanotube/Cu nanowire nanocable structures: (a) top view of (12, 0) BN nanotube filled with six Cu atoms per unit cell; (b) top view of (13, 0) BN nanotube filled with eight Cu atoms per unit cell; (c) side view of the nanocable structure in (a) with six repeated unit cells.

include BSSE, and the exact insertion energy may change slightly after BSSE correction, but it will not affect the general conclusion. Also, it is known that DFT does not describe the weak van der Waals (vdW) interactions very well. Thus, the computed interaction energies reflect the intrinsic inaccuracies of the DFT method due to the exchange-correlation functionals chosen. Typically GGA underestimates vdW interaction energies, while local density approximation (LDA) results are usually higher. Therefore, the strength of tube−wire interaction measured by the insert energy per Cu atom might be somewhat underestimated at the current GGA level. However, the trends (energy vs wire−tube distance) should be correct when the same theory was employed uniformly, so the major conclusions made in this paper should be qualitatively valid regardless of the adopted approximation.

Results and Discussion

We considered a variety of BN zigzag nanotubes, from (9,0) to (16,0), with tube diameters from 0.7 to 1.3 nm. One unit cell of the BN nanotubes along tube axis was included in the computational supercell. As shown in Figure 1, the BN nanotubes were filled with Cu nanowires having either *ABAB* staggered triangle or square close-packed structures with six or eight atoms per unit cell, respectively. The individual BN nanotubes and Cu nanowires were also computed separately to investigate the tube−wire interaction.

The insertion energy of Cu nanowires can be defined by the total energy gained by encapsulating the Cu wire inside the BN nanotube, all at their equilibrium geometries: $E_i = E_{tot}(tube+wire) - E_{tot}(tube) - E_{tot}(wire)$. Figure 2 displays the insertion energies per atom for the two Cu nanowires filling various BN nanotubes of different diameters. BN tubes with smaller diameter, i.e., tube−wire distance less than 0.3 nm, exhibit strong Cu wire−BN tube repulsions. As the BN tube diameter increases, the tube−wire interactions become attractive. At the GGA level, the strongest attraction, about −0.04 eV per Cu atom, occurs at an equilibrium tube−wire distance of about 0.35 nm, for both Cu nanowires studied. Though the absolute insertion energies may be underestimated by the GGA approximation, such weak interaction energies are due to vdW attractive forces rather than to chemical bonding (for the standard vdW energy for gas adsorption on graphite and carbon
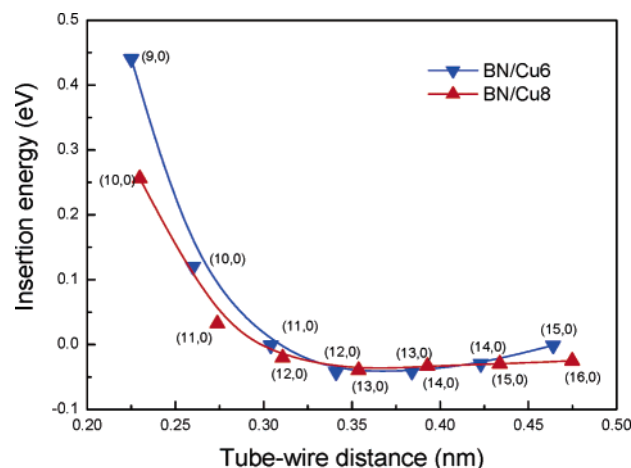
Nanocable Models Comprised of BN Nanotubes

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Figure 2. Insertion energies per atom of Cu nanowires filling various BN nanotubes as a function of the tube−wire distance. The latter is the difference between the radii of the outer BN tubes and the inner Cu wires.

nanotube surfaces, please refer to ref 46 and references therein). The tube−wire interactions are less attractive when the BN tube diameters are larger. The BN (12, 0) and (13, 0) nanotubes are the best outer sheaths to encapsulate the staggered triangle and square close-packed Cu nanowire structures, respectively. Figure 1 represents the most stable configurations for the BN (12, 0)/Cu(6) and BN (13, 0)/Cu(8) hybrid structures. Consistent with the weak interaction, only slight changes in the geometries of both the Cu nanowires and the BN nanotubes occur in going to the filled nanocable structures.

The interaction between outer BN tubes and inner Cu wires was investigated by computing the electronic band structures for the BN (12, 0)/Cu(6) (Figure 1a) and BN (13, 0)/Cu(8) (Figure 1b) nanocables (see the middle panels of Figure 3). The band structures of the individual BN tubes and Cu wires are also shown for comparison respectively in the right and left panels of Figure 3. The wide band gaps (∼4.5 eV) show pristine BN nanotubes to be insulators, whereas free-standing Cu nanowires show metallic characteristics, since there are two or three bands crossing the Fermi level. The band structures for the BN/Cu nanocables (the BN nanotube−Cu nanowire composites) are clearly a superposition of the band structures of the individual BN tubes and the Cu wires. This emphasizes the weak interaction between the outer BN nanotubes and the inner Cu nanowires, which has almost no influence on their electronic structures. Thus, the bands crossing the Fermi level in the BN/Cu nanocables all originate from the inner Cu nanowires, whereas the outer BN tubes remain insulating with large band gaps. It is known that the number of conduction channels for the ballistic electron transport of metallic nanowires (or metallic carbon nanotubes) is directly associated with the number of electron bands crossing the Fermi level.[2] Hence, the quantum conductance for the Cu(6) and Cu(8) nanowires would be $2G_0$ and $3G_0$, respectively, which would not be modified when these nanowires are filled inside the BN tube to form nanocable. Moreover, such ballistic quantum conductance is rather robust and is not easily disrupted by the local structural defect on the nanowires.[2]

The electronic and transport properties of the BN/Cu nanocables can be assessed further by analyzing the charge density distribution of the conduction electrons of the bands crossing the Fermi level. As shown in Figure 4 for the BN (12, 0)/Cu(6) nanocable, the conduction electrons are localized on the inner Cu wire region. Thus, electron transport will occur only through
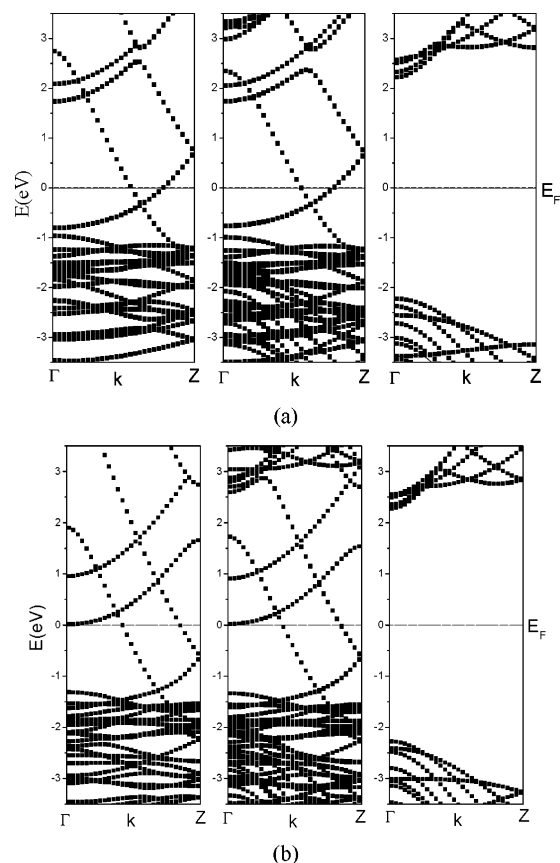

(a)

(b)

Figure 3. Electronic band structures for BN (12, 0)/Cu(6) (a) and BN (13, 0)/Cu(8) (b) nanocables. Left panels: Free-standing Cu nanowires. right panels: Pristine BN nanotubes. Middle panels: BN/Cu nanocables. The dashed lines denote the Fermi level positions.
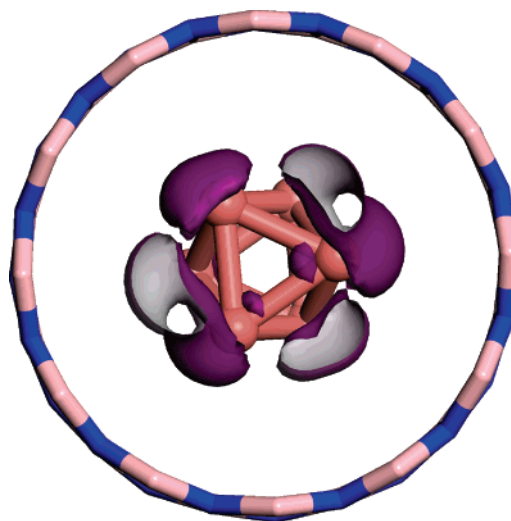

Figure 4. Isosurface for the electron density (in purple) of the conduction electrons on the two bands crossing the Fermi level (see Figure 3a) for the (12, 0)BN/Cu6 nanocable. Clearly, the conduction electrons are only distributed on the Cu nanowires.

the encapsulated Cu nanowires; the inert outer BN nanotubes serve well as insulating cable sheaths. Both these features are very important for applications of nanocables in future nanoscale devices. The chemical inertness and the high thermal stability of BN tubes make the proposed BN−Cu nanowires even more promising.

From the above discussions, we have established the electronic properties and the nature of the tube−wire interactions

in a few BN/Cu nanocables. These models are only illustrative; many more are possible. The structures of the inner Cu nanowires and the diameters of the outer BN nanotubes can differ from our models. For example, multiwalled instead of single-walled BN nanotubes are possible and the packing of the Cu atoms of the metal wire could even be amorphous. If other coinage metals, Ag and Au, and main group metals, like Al, etc., behave like Cu, they might also serve as nanowire components inside BN nanotubes. Note that it is possible that the infinite 1D periodic metals can suffer Peierls distortion and transform into nonmetallic,[47,48] so wires different from Cu_6 and Cu_8 but with higher cohesive energies may be better synthesis targets. However, the requirements for true nanocables should be followed: (1) the tube−wire interactions should be weak and (2) the outer BN sheath should not affect the electron conductance of the encapsulated metallic nanowire.

Conclusion

In summary, our extensive DFT investigations on nanocable structures composed of BN nanotube sheaths filled with Cu nanowires showed that the interactions between these components are weak. At the optimum tube−wire distance of ∼0.35 nm, the insertion energy is only about −0.04 eV per Cu atom, far less than that expected for chemical bonding. Consequently, the electronic structures, either of the individual BN tubes or of the Cu wires, are not modified significantly by the encapsulation: the electronic band structures of the BN/Cu nanocables are superposition of the electronic bands of the isolated individual systems. The densities of the conduction electrons only are associated with the inner Cu nanowire. Therefore, the electronic transport will occur in the inner Cu nanowires; the outer BN nanotubes only function as insulating sheaths. Such true nanocables have technological potential, for example, in NEMS and in nanoelectronics.

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