The computational design of junctions by carbon nanotube insertion into a graphene matrix

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Abstract. Using first-principles density functional theory calculations, two types of junction models constructed from armchair and zigzag carbon nanotube (CNT) insertion into a graphene matrix have been envisioned. It has been found that the insertion of the CNT into the graphene matrix leads to the formation of C–C covalent bonds between graphene and the CNT that distort the CNT geometry. However, the hydrogenation of the suspended carbon bonds on the graphene resumes the graphene-like structure of the pristine tube. The calculated band structure of armchair CNT insertion into graphene or hydrogenation graphene opens up a band gap and converts the metallic CNT into a semiconductor. For the zigzag CNT, the sp³ hybridization between the graphene and nanotube alters the band structure of the tube significantly, whereas saturating the dangling bonds of terminal carbon atoms of graphene makes the CNT almost keep the same character of the bands as that in the pristine tube. The synthesis of our designed hybrid structures must be increasingly driven by an interest in molecules that not only have intriguing structures but also have special functions such as hydrogen storage.

As one-dimensional (1D) nanostructures, carbon nanotubes (CNTs) have evolved into one of the most intensively studied materials in the field of carbon-based nanoelectronics [1]. They owe their success in the nanotechnology field to a unique combination of atomic-scale perfection, structural stability, and beneficial thermal and electrical properties [2, 3]. The conductance of

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CNTs depends sensitively on the precise way a graphene layer is rolled up into the tubular structure, and is identified by the chiral index \((n, m)\) [4]. Combined with their ballistic electronic transport characteristics [5], this opens exciting possibilities for the designing of novel electronic components [6]. Furthermore, the functionalization of CNTs might lead to new opportunities in carbon-based nano-electronic devices [7]–[13].

Recently, the rise of 2D graphene science has been accelerated by the new technological expectations that have emerged in the field of carbon-based nanoelectronics [14]–[16]. As a 2D atomic crystal [17], graphene has triggered tantalizing enthusiasm for new discoveries [18, 19]. It is found that the chiral nature of charge excitations in 2D graphene has been shown to result in unconventional quantum transport features, such as unusual quantum Hall effects [20, 21]. To construct logic circuits based on graphene and CNT units, it is necessary to join them in particular ways. One possible method to connect them is by using irradiation by energetic electrons [22] or atoms [23] in order to introduce topological defects such as pentagons, heptagons and octagons into a perfectly hexagonal lattice. Subsequently, the graphene and CNTs could be connected by the formation of new C–C bonds at the interface. Alternatively, chemical reactions could be applied to form covalent linkages between graphene and CNTs, for this method has been attempted to fabricate CNT junctions between various CNTs with different diameters [24, 25]. First-principles calculations have validated that linear, T- and H-shaped junctions within the connection modes between CNT and graphene nanoribbon units could be constructed [26]. Moreover, the simulation results of non-equilibrium Green’s function predicted that the proposed models had potential applications in nanoelectronics.

In this paper, we use first-principles calculations to probe the possibility of building basic CNT–graphene junctions via the covalent attachment of a single layer graphene to the sidewall of CNTs. The main motivation of this work is to establish a basic physical picture of junction construction between a CNT and graphene by the insertion of a tube into a graphene matrix. We chose the embedding medium as the \(8 \times 8\) graphene supercell so as to minimize the tube–tube strain presented in the neighboring supercells. Another underlying condition for reduced strain is the selection of CNT diameters such that the CNT–graphene distances are consistent with typical van der Waals values. For these reasons, we choose the armchair (5,5) CNT and zigzag (8,0) CNT as the candidates for our study. We find that the placement of a CNT in the graphene matrix leads to the formation of C–C covalent bonds between the graphene and the sidewall of the CNT that distort the CNT geometry. In particular, the interaction of hydrogen atoms with the suspended carbon bonds on the graphene leads the CNT to resume its pristine graphene-like structure. Since graphene introduces a partial sp\(^3\) character into the sp\(^2\) graphitic network of (5,5) tube, it opens up a band gap and converts the metallic (5,5) CNT to a semiconductor. For the semiconductor (8,0) CNT, the sp\(^3\) hybridization between the graphene and nanotube induces impurity states on the Fermi level, whereas hydrogenation on the suspended C atoms of graphene narrows down the range of its fundamental band gap.

Our study is based on the first-principles plane-wave pseudopotential density functional theory as implemented in the CASTEP code [27]. For the exchange and correlation term, the generalized gradient approximation (GGA) is adopted, as proposed by Perdew–Burke–Ernzerhof (PBE) [28]. We use ultrasoft pseudopotentials [29] for the carbon atoms and a plane-wave cutoff of 300 eV. The Brillouin zone integration is performed within the Monkhorst–Pack scheme [30]. Considering the larger number of atoms in the supercell and expensiveness of the calculation time, only the \(\Gamma\) point is used for the Brillouin zone sampling during the structural optimization and more K points along the tube axis are considered in the
calculation of the band structure. Optimal atomic positions are determined until the magnitude of the forces acting on all atoms becomes less than $0.01 \text{ eV Å}^{-1}$. By this criterion, the geometry is optimized within $10^{-3} \text{ Å}$, leading to a convergence of the total energy within $10^{-5} \text{ eV}$. In addition, a finite basis set of corrections are also included. Calculations have been carried out within the periodically repeating supercell geometry because of the necessity of using periodic boundary conditions with the plane-wave method. We use an $8 \times 8$ hexagonal graphene supercell with lattice constants $a_{sc}$, $b_{sc}$, and $c_{sc}$. The lattice constants $a_{sc}$ and $b_{sc}$ are chosen such that the interaction between the nearest neighbor tubes is negligible (the minimum C–C distance between the nearest neighbor tubes is taken as 9.84 Å). The lattice constant along the axis of the tube $c_{sc}$ is taken to be equal to four times (for an armchair tube) and twice (for a zigzag tube) that of the 1D lattice parameter $c$ of the tube, insuring no interaction between the neighboring graphene layers. The tube axis is taken along the $z$-direction, and the circular cross section lies in the $(x, y)$-plane. We started with the built supercell, which had the carbon atoms removed from the center and was suitable for placing an armchair (5,5) CNT or a zigzag (8,0) CNT at the center hole.

Figures 1(a) and (b) show the imaginary picture of a 3D network based on tube insertion into a graphene matrix. The initial configurations for a (5,5) CNT and an (8,0) CNT are at the center of a hollow of graphene. This 3D network could be the prototype of next-generational carbon-based microelectronic circuits: the basic logic circuits are constructed by the CNT, and the sheets of circuits are bridged by graphene. Allowing for ionic relaxation of the initial structures results in the formation of a number of C–C bonds between graphene and the CNT, as shown in figure 2. The (5,5) and (8,0) nanotubes in the relaxed configurations are anchored at many sites. As is evident from figures 2(a) and (c), the formation of the C–C bridges is accompanied by large distortions of the nanotube. A range of bond lengths and angles is found for the C–C bridges in the distorted configuration of (5,5) CNT in figures 2(a) and (b). The C–C bond lengths for these bridges range between 1.488 and 1.601 Å. A larger variation is found for the C–C–C angles that range between 103.4° and 130.4°. The formation of numerous C–C–C bridges also results after ionic relaxation when an (8,0) CNT is placed in the graphene hollow. Like in the (5,5) CNT case, the formation of these bridges results in significant CNT distortions, albeit of a lesser degree as compared to the (5,5) CNT, due to the difference in diameter. The C–C bond lengths for the bridges between graphene and the (8,0) tube range between 1.509 and 1.578 Å. The variation for the C–C–C angles of the bridges in the (8,0) case ranges between 105.3° and 134.8°. The average length of C–C bonds on the bridge in both cases is longer than the perfect C–C bond length of 1.42 Å in a CNT or graphene [4]. This indicates that the $\pi$ electrons of the C–C bonds on bridges between the tube and graphene are not strictly localized on such bonds, but tend to delocalize over the nearby graphene and tube units.

The large distortion on the sidewall accompanying the functionalization of graphene, however, is an undesirable effect. In order to take advantage of the encapsulation without distortion caused by CNT–graphene bonding, we investigated the effect of hydrogenation on the carbon atoms at the edge of the graphene hole. We allowed for H atoms to saturate the carbon atoms at the edge of the graphene hole in the initial un-relaxed structure and then re-relaxed it. A single hydrogenation step of this kind results in the breakup of a C–C bridge between the graphene and the tube. As seen in figures 3 and 4, one end of the bridge relaxes back towards the graphene matrix with CH groups, and the other C atom of the bridge relaxes back to assume a configuration closer to the pristine tubular structure of the CNT. Tsetseris et al [31] investigated the CNT–SiO$_2$ interface of an embedded CNT using first-principles calculations. Their results
Figure 1. Initial configuration (no relaxation allowed) of CNT insertion into the hole of a graphene matrix, (a) (5,5) CNT and (b) (8,0) CNT.

showed that strong Si–O–C bonds were formed and subsequent hydrogenation eliminated all the Si–O–C bonds, which proves that our relaxed structure after hydrogenation is reasonable.

Having established that graphene forms strong covalent bonds with nanotubes and hydrogenation eliminates the C–C bond between the graphene and the CNT, we next investigate the effect of functionalization on the electronic structure of CNTs. The band structures for the isolated (5,5) CNT, (5,5) CNT suspended graphene and (5,5) CNT suspended hydrogenation graphene are shown in figure 4. Figure 4(a) shows that the armchair (5,5) CNT is metallic, due to the fact that there are two energy bands near Fermi energy and the two bands cross with the Fermi level at $k \approx 2/3$ of the Brillouin zone, which is required by symmetry and suggested by the band-folding theory [32]. The most interesting case comes when considering the (5,5) CNT suspended by graphene or hydrogenation graphene, where the pristine CNT is metallic.
Figure 2. Configurations of figure 1 after relaxation. The insertion of CNT into a graphene matrix leads to the formation of C–C covalent bonds between graphene and CNT that distort the CNT geometry; (a) and (b) are the top and side views of (5,5) CNT encapsulated graphene, (c) and (d) are the top and side views of (8,0) CNT encapsulated graphene.

Here, the addition of graphene or hydrogenation graphene on the sidewall of the CNT reduces the symmetry and introduces additional couplings between the conduction band and valence band states of the CNT that open an energy gap of about 0.2 eV near the original Fermi level. Due to the isoelectronic character of the graphene and CNT, the Fermi level remains in the midgap region and the CNT is thus a semiconductor (figures 4(b) and (c)). The functionalization of graphene or hydrogenation graphene on the sidewall of the CNT, therefore, seems to provide a new and simple route to the interconnection of CNTs that would be semiconducting: if their chirality were such that they were metallic, the graphene or hydrogenation graphene encapsulation would turn them into semiconductors. Further calculations on the band structure of additional graphene or hydrogenation graphene on the sidewall of the metallic armchair (4,4) CNT also show a similar trend of gap opening.

The band structure $E(k)$ of the pristine (8,0) zigzag CNT is shown in figure 5(a) as a representative for other semiconducting nanotubes. Our calculations show that the (8,0) CNT
Figure 3. The relaxed structures of the configurations in figure 1 after the hydrogenation of the suspended carbon bonds in the graphene; (a) and (b) are the top and side views of (5,5) CNT encapsulated hydrogenation graphene, (c) and (d) are the top and side views of (8,0) CNT encapsulated hydrogenation graphene.

has an energy gap of 0.65 eV, which is consistent with the result of local density approximation (LDA) calculations by Blasé et al [33]. The effects of graphene and hydrogenation graphene on the electronic structure of the (8,0) CNT are shown in figures 5(b) and (c), respectively. In figure 5(b), the bands for the configuration in figure 2(c) or (d) have small dispersion and are strikingly different than those of figure 5(a), confirming that the creation of C–C–C bridges alters the CNT electronic properties significantly. We find that the sp$^3$ hybridization between the graphene and nanotube induces impurity states on the Fermi level of the (8,0) tube. By encapsulating the graphene on the sidewall of the (8,0) semiconducting tube, the existence of a band-gap would not be preserved. Our further calculations on the band structure of the (9,0) CNT encapsulated graphene on its sidewall show that the functionalization of graphene enlarges the energy gap of the pristine tube from 0.08 to 0.85 eV. Furthermore, the energy gap of the (9,0) CNT now is decided by the energy value of HOMO and LUMO corresponding to the Z point in the Brillouin zone. It proves that the bands for the semiconductor zigzag CNT encapsulated graphene are strikingly different than those of the pristine one. On the other hand, comparing
Figure 4. The band structures of (5,5) CNT (a), (5,5) CNT encapsulated graphene (b) and (5,5) CNT encapsulated hydrogenation graphene (c). The dotted line indicates the Fermi level.

the calculated bands in the band structure of the hydrogenation graphene functionalized (8,0) CNT in figure 5(c) with those of the pristine nanotube in figure 5(a), we conclude that the bands of the (8,0) zigzag semiconductor CNT encapsulated hydrogenation graphene have a similar character as that of the (8,0) pristine tube. However, the functionalization of hydrogenation graphene has narrowed down the range of its fundamental band gap, which is reduced in numerical value (0.28 eV) with respect to its pristine CNT analogue (0.65 eV). In spite of the energy gap of the tube having minor changes, our further calculation of the band structure of the (9,0) CNT encapsulated hydrogenation graphene proves that the functionalization by addition of hydrogenation graphene to its sidewall almost keeps the character of the bands as that in the (9,0) CNT. Tsetseris et al [31] found that hydrogenation eliminated all the Si–O–C bonds, leading to floating CNTs in SiO$_2$ with electronic properties very close to those of pristine CNTs in a vacuum. This may be the reason that SiO$_2$ is an insulator and would not alter the electronic property of the CNT. Our results show that the graphene on the sidewall of the semiconductor zigzag CNT has a great impact on the electronic structure of the CNT and hydrogenation on the dangling bonds on graphene significantly reduces the impact.

In summary, using first-principles DFT calculations, the geometries and electronic properties of junctions constructed by a CNT insertion graphene matrix have been investigated.
Figure 5. The band structure of (8,0) CNT (a), (8,0) CNT encapsulated graphene (b) and (8,0) CNT encapsulated hydrogenation graphene (c). The dotted line indicates the Fermi level.

systematically. We find that the insertion of the CNT into the graphene matrix leads to the formation of C–C covalent bonds between graphene and the CNT that distort the CNT geometry. However, the hydrogenation of the suspended C bonds on the graphene resumes the graphene-like structure of the pristine tube. The calculated band structure of an armchair CNT encapsulating graphene or hydrogenation graphene opens up a band gap and converts the metallic CNT into a semiconductor. For a zigzag CNT, the sp³ hybridization between the graphene and nanotube alters the band structure of the tube significantly, whereas the functionalization by the addition of hydrogenation graphene on its sidewall almost keeps the character of the bands as that in the pristine CNT if ignoring the minor changes in the energy gap. Our model suggested by successfully computational design supplies a novel hybrid composite nanostructure CNT–graphene. It was recently shown that incorporating CNTs within a metal-organic framework enhances its surface area, stability and hydrogen uptake capacity [34, 35]. The composite nano-material we studied here shows an enhanced surface area in a 3D space, which could be due to an increase in the hydrogen storage capacity at room temperature [36]. Our computational design also presents a new direction for achieving novel hybrid materials between the two spotlighting materials, viz. CNTs and graphene [37]. We note that organic synthesis will be increasingly directed to producing bio-inspired and newly
designed molecules [38], such as DNA sequence motifs for structure-specific recognition and separation of CNTs [39]. The synthesis of our studied hybrid structures must be increasingly driven by an interest in molecules that not only have intriguing structures, but also have special functions.

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