Electronic structure and transport properties of carbon nanotube adsorbed with a copper chain
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The authors have studied the electronic structure and transport properties of hybrid nanowires made of a copper chain adsorbed on a single-wall carbon nanotube (CNT) using first principle methods. Results have shown that after the adsorption of the Cu chain, the density of states and the transmission coefficients of the CNT (5, 5)/Cu nanowire have been increased, while the band gap of CNT (10, 0)/Cu have been significantly reduced. These results imply that the conductivity of CNTs, either metallic or semiconducting, have been enhanced by the adsorption of a copper chain. These hybrid nanowires with enhanced conductivity may be suitable for nanoelectronics.

Keywords: carbon nanotube; copper; adsorption; electronic structure; transport

1. Introduction
Carbon nanotubes (CNTs) [1] have received wide attention due to their unusual material properties, including the high symmetric arrangement, possible defect free structure which leads to high strength and stiffness [2], and the high Young’s modulus [3] as well as the extraordinary flexibility. In addition, CNTs have shown special electric conduction capabilities. For instance, the armchair type CNT ((n, n) type) has been proved to be metallic with a low resistivity of $\sim 10^{-5} \Omega \text{cm}$ [4], a large current carrying capacity [5], and ballistic transport properties [6]. All these make metallic carbon nanotubes a good candidate for nanoelectronic applications [7].

However, CNTs do have intrinsic limitations on electric applications [8,9] in terms of its low free electron density. On the other hand, metals like copper are rich in free electrons and it may be used as doping agent to CNT to form Cu/CNT hybrid nanowire with both the large mean free path (from CNTs) and the large free electron density (from copper) at the same time. Although predications have been made that it is possible to achieve ultra-low resistivity in CNT-based metal composites [10,11], available experiment on such composites [12,13] could not produce similar low resistivities as theoretically predicted. Therefore, more further and deeper studies are needed to elaborate the underlying fundamentals.

The authors have conducted a numerical study on this matter. The main work of this study was to investigate the electronic and transport properties of CNT/Cu hybrid nanowire with density functional theory (DFT) and non-equilibrium Green functions (NEGF) approaches. The goal of this work was to understand the basics of the conduction mechanism of Cu/CNT hybrid wire and to guide for further development of the materials.

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2. The calculation method and the simulation model

The electronic/transport properties of the Cu/CNT hybrid nanowire and the optimization in geometry were performed by the Quantum Wise/ATK2008.10 (Copenhagen, Denmark) package [14–17]. In the relaxation process, authors employed local density approximation with the Perdew–Zunger (PZ) exchange-correlation functional [18]. 1 × 1 × 30 k points sampling and double-zeta polarized basis set were used for both carbon and copper atoms during the relaxation process. Figure 1 (left) shows the atomic structure of a hybrid nanowire consisted of a semiconducting CNT (10, 0) and a copper chain, and Figure 1 (right) shows another Cu/CNT nanowire consisted of a metallic CNT (5, 5) and a copper chain. Both structures were fully relaxed until the maximum force was less than 0.05 eV/Å. The relaxed geometry can be seen in Figure 1.

Zigzag single-wall CNT (SWCNT) (10, 0) is semiconducting and armchair CNT (5, 5) is metallic. For Cu/CNT (10, 0) nanowire, there are two Cu atoms in one unit cell. While for the Cu/CNT (5, 5) nanowire, there’s one Cu atom in one unit cell. The initial distance between one Cu atom and its nearest carbon atom in both cases are kept at around 1.5 Å, and the final distance varies after the relaxation.

The electronic structure and the transport properties are calculated using the relaxed geometries. In this part, the generalized gradient approximation with the Perdew–Burke–Ernzerhof exchange-correlation functional [19], and a Monkhorst–Pack grid of 1 × 1 × 100 were used. A tolerance of 1 × 10−5 of the total energy was used as the convergence criterion.

3. Results and discussion

3.1. Electronic structure

3.1.1. Band structure

Figure 2b shows the bandstructure of the CNT (10, 0) with a Cu chain. As a comparison, the bandstructure of the distorted CNT (Figure 2c) as well as the freestanding Cu chain (Figure 2a) have also been calculated. The geometry of the distorted CNT has been obtained by removing the Cu chain from the relaxed hybrid system, while the geometry of the freestanding Cu chain is achieved by removing the CNT from the relaxed hybrid system.

Bandgaps are observed in both the hybrid nanowire and the distorted CNT (10, 0). When a Cu chain is absorbed, the bandgap is only a little reduced than that of the distorted CNT. That implies that the addition of the Cu chain does not change the semiconducting nature of the CNT (10, 0). By comparing the bandstructures of the three components (Figure 2a–c), we could see that two new bands around the Fermi level have been derived by the adsorption of the Cu chain, with one above and one below the Fermi level. In addition, the bandgap is narrowed due to the adsorption of the Cu chain.

The bandstructure of CNT (5, 5)/Cu system (Figure 3) has shown some difference in comparison to that of the CNT (10, 0)/Cu system. First, for the distorted CNT (5, 5) (Figure 3c), it shows a cross at two-thirds of the distance between Γ and Z point [20],
implying its metallic characteristics. Second, the bandstructure of CNT (5, 5) has been modified after the adsorption of the Cu chain. As shown in Figure 3b, the bandstructure of CNT (5, 5)/Cu nanowire (Figure 3b) could be viewed as a superposition of the bandstructure of CNT (5, 5), and that of Cu. By comparing (b) and (c), one would find that in Figure 3b the Fermi level has been shifted upwards, toward the conduction band of the CNT. Similar behavior has been observed in the case that a single Cu chain wrapped inside of a CNT [21]. In addition to the shift, more bands crossing the Fermi level are also derived by the existing of Cu chain and the conductance of the system has been increased.

3.1.2. Density of states

A better insight into the electronic interaction between CNT and Cu chain is the density of states (DOS). The DOS for the CNT (10, 0)/Cu system is presented in the Figure 4 (left), while the DOS for the CNT (5, 5)/Cu system is shown in the right part of Figure 4.

In Figure 4 (left), the top part (a) shows the DOS for the distorted (10, 0) CNT, while the middle part (b) shows the DOS for the free-standing Cu chain and the bottom part (c) indicates that of hybrid CNT (10, 0)/Cu. The integration of the Cu chain does not change the DOS of the system around the Fermi level (c). However the gap of the DOS has been shrunk.

Results on metallic CNT (5, 5)/Cu are shown in Figure 4 (right) as a comparison to the semiconducting CNT (10, 0)/Cu. The top part (a) is for the DOS of CNT (5, 5)/Cu system, the middle part (b) shows the DOS for the distorted CNT (5, 5), and the bottom part (c) shows the DOS for the free-standing Cu chain. The adsorption of Cu chain creates some additional states around the Fermi level, as shown in Figure 4 right (c), which enhances the conductivity of CNT (5, 5). It is also indicated that the density of states of the CNT

Figure 2. Band structure of (a) the free standing Cu chain, (b) the CNT(10,0)/Cu hybrid system, and (c) the distorted CNT(10,0).

Figure 3. The band structure of (a) the free standing Cu chain, (b) CNT (5, 5) with a Cu chain and (c) the distorted CNT (5, 5).
(5, 5)/Cu is not a simple superposition of the DOS of CNT (5, 5) and that of Cu chain. This means that there is interaction between the CNT and the copper chain and this interaction changes each other’s electronic structure.

3.2. Transmission spectrum

The calculated transmission spectrum at the zero bias for the two hybrid systems are presented in Figure 5. The left figure of the Figure 5 is the transmission spectrum for the CNT (10, 0)/Cu system, while the right part of the Figure 5 is the transmission spectrum for the CNT (5, 5)/Cu system.

According to Figure 5 (left), a transmission gap retains for the CNT (10, 0) after a Cu chain has been absorbed onto it. It means that the CNT (10, 0) remains its semiconducting nature even after the addition of the Cu chain. However, the transmission gap has been decreased. This result agrees well with the DOS results (Figure 4) as well as the band structure of the CNT (10, 0)/Cu system (Figure 3).

In comparison to the transmission coefficient of CNT (10, 0) at Fermi level, the transmission of CNT (5, 5) has been significantly enhanced after the absorption of the Cu chain.
According to Figure 5 (right), the transmission coefficients around the Fermi level for the pure CNT (5, 5) is 2, in agreement with the well-known results. However, the transmission coefficient at the Fermi level is 2.999992 for the CNT (5, 5)/Cu and 0.9999622 for the Cu chain. The transmission coefficient for the CNT/Cu is not the exactly superposition of the Cu and the CNT, which indicates interaction between the CNT and the Cu chain.

3.3. Transmission eigenchannel of the CNT/Cu nanowire

Transmission eigenstate is also called transmission eigenchannel, which indicates the electronic states that contribute to the conductance [22]. Since the CNT (10, 0) is semiconducting and it has a gap in its band structure, it is reasonable to analyze the transmission eigenstates not at the Fermi level. In this study, 0.32 eV above and below the Fermi level is chosen, which is almost the same value of its band gap energy. By performing the eigenchannel analysis, we found there is only one eigenchannel at each case (+0.32 eV, −0.32 eV). Figure 6a shows the transmission eigenstates at 0.32 eV below the Fermi level. In this case, the eigenstates is not localized in the Cu atoms alone, but it also includes the electronic states of the carbon atoms. That means electrons can pass the system both through the CNT and the copper chain, or both the Cu and the C atoms are contributing to the conductance of the system. While for the case of 0.32 eV higher above the Fermi level (see Figure 6b), the transmission eigenstates concentrate on the Cu atoms. Comparing the band structure of the CNT (10, 0) with a Cu chain system, it is concluded

Figure 6. Transmission eigenstates at 0.32 eV below (a) and higher (b) than the Fermi level for CNT (10, 0) with a Cu chain, and at the Fermi level for CNT (5, 5) with a Cu chain (c)–(e). (a) CNT (10, 0)/Cu at 0.32 eV below the Fermi level, (b) CNT (10, 0)/Cu at 0.32 eV above the Fermi level, (c) CNT (5, 5)/Cu eigenstate 0 at the Fermi level, (d) CNT(5, 5)/Cu eigenstate 1 at the Fermi level, and (e) CNT (5, 5)/Cu eigenstate 2 at the Fermi level.
that the highest valence band originates from the combined system of Cu and CNT, while the lowest conduction band originates from the Cu chain.

The CNT (5, 5) with a Cu chain system is metallic and by performing the eigenchannel analysis at Fermi level, it can be found that the number of eigenstates is 3, the same as its transmission coefficient at Fermi level. The three transmission eigenstates at the Fermi energy are listed in Figure 6c–e, respectively. All the three transmission eigenstates are found to be contributed by the Cu/CNT (5, 5) hybrid systems, which proves that this is typically a metallic system.

4. Conclusions
In summary, authors have employed the DFT and the NEGF to investigate the electronic structures and the transport properties of the CNT/Cu system. The results have proved that the incorporation of a Cu chain enhances the DOS, the transmission coefficient at Fermi level of the metallic CNT (5, 5), and thus the conductivity of the hybrid system. The incorporation of a Cu chain reduces the band gap of a semiconducting (10, 0) zigzag CNT. Analysis of the transmission eigenstates near the Fermi level for CNT (10, 0)/Cu system has shown that not only the copper chain but also the CNT contributes to the resultant conductance of the system. The integration of a copper chain would increase the conductivity of both the metallic and the semiconducting CNTs. Therefore, the hybrid CNT/Cu nanowires and nanocomposites with unprecedented electric conductivities can be developed.

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