

Theoretical study on electrical behavior of carbon chain inserted single-walled carbon nanotubes compared with Pt doped one

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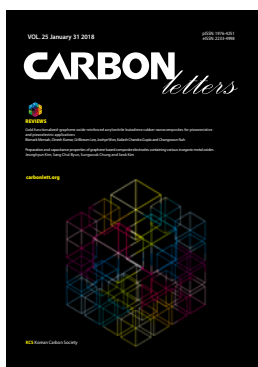
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Abstract

Carbon chain inserted carbon nanotubes (CNTs) have been experimentally proven having undergone pronounced property change in terms of electrical conductivity compared with pure CNTs. This paper simulates the geometry of carbon chain inserted CNTs and analyzes the mechanism for conductivity change after insertion of carbon chain. The geometric simulation of Pt doped CNT was also implemented for comparison with the inserted one. The results indicate that both modification by Pt atom on the surface of CNT and addition of carbon chain in the channel of the tube are effective methods for transforming the electrical properties of the CNT, leading to the redistribution of electron and thereby causing the conductivity change in obtained configurations. All the calculations were obtained based on density functional theory method.

Key words: carbon nanotubes, carbon chain, Pt

1. Introduction

Carbon nanotubes (CNTs) have been extensively studied due to their excellent physicochemical properties that provide them many potential technical applications including hydrogen storage media, sensors, and nanometer-sized semiconductor devices [1]. Linear carbon chains with pure *sp* hybridization have been in considerable focus of attention for a long time, which can be viewed as one-dimensional materials with a diameter of just one carbon atom [2]. These chains are therefore good candidates for applications in molecular devices regarding both electronic transport, and as field emitters on the atomic scale. Moreover, they are expected to further enrich the characteristics and functions of CNTs through the encapsulation of a carbon chain in a nanotube [3]. It has been demonstrated by high resolution transmission electron microscopy and resonance Raman spectra that the finite linear can be practically stable inside the CNTs under certain protected environment although its instability under common conditions because of the reactive cumulated unsaturated bonds inner the carbon chain [4]. Such carbon chains possess average conjugation length of about 8–12 carbon atoms with polyynic structure (...-C≡C≡C·), and once the carbon chain includes more than 20 atoms, they become energetically unstable [5].

The previous study has additionally proved that the insertion of carbon chain can improve the conductivity of metallic CNTs [6]. To the best of our knowledge, there are lack of mechanism analyses of how the carbon chains exert the impacts on the electronic behavior of a semiconducting CNT, and the effect of transition metal dopant on the electronic structure of chain/CNTs system. Studying on these issues are important as they are helpful to perfectly understand the effect of inserting carbon chains on the insolated CNTs, and compare the conductivity improving mechanisms of metal dopant

with that of carbon chain insertion. Because of good catalytic property, Pt atoms have been proved to be perfectly adsorbed on the CNT surface as their strong binding force for potential applications of gas sensing and fuel cell [7]. In this paper, the eight carbon atoms chain complied with the Pt dopant were determined to carry out the first-principle calculations, managing to resolve the points mentioned above and giving rise to some systemically understandings between surface modification and inside insertion of CNTs.

2. Experimental

In this work, the density functional theory method were performed to investigate the geometric structure and electronic behavior of chain/CNT and related Pt modified one. The whole calculations were implemented in the DMol³ package. The generalized gradient approximation was employed as described by Perdew, Burke, and Ernzerhof to treat the exchange and correlation [8]. The periodic boundary condition as $20 \text{ \AA} \times 20 \text{ \AA} \times 12.8 \text{ \AA}$ was adopted in order to preserve the interaction between adjacent units. We chose (8, 0) CNT as our representative sample because the stable geometry for carbon chain requires a diameter of tube to be 0.7 nm that similar to what we selected one according to the previous report [5]. The space orbital cutoff radius was set to 0.45 nm, whereas the Brillouin zone k -point sampling was performed in $1 \times 1 \times 3$ Monkhorst-Pack mesh that presents good approximation for (8, 0) single-walled CNTs [9]. The energy tolerance accuracy, maximum force, and displacement were set as 10^{-5} ha, 2×10^{-3} ha/Å, and 5×10^{-3} Å, respectively [10]. The core treatment was defined as density functional theory semi-core pseudopotentials to manage the interaction between the nucleus and valence electron.

3. Results and Discussion

The insulated carbon chain with eight carbon atoms, connected by staggered arrangement of single bond and triple bands, and insulated CNT acting as the carbon support were geometrically optimized as shown in Fig. 1a and Fig. 1b. Based on Fig. 1c, it can be found that after the Pt atom has modified on the sidewall of the tube, 0.056 electron was transferred from the tube to the Pt dopant, suggesting the electron affinity property of the transition metals [11]. Similarly, after a carbon chain inserts in the channel of the nanotube, presented in Fig. 1d, the total electron number of the chain is 0.018 (see in Table 1), suggesting the electron-transferring path from the chain to the CNT. When it comes to the Pt doped chain/CNT, it should be noted that total 0.033 e transfers from the tube to the Pt dopant as shown in Fig. 1e, while 0.053 e transfer to the tube from the carbon chain. Moreover, it can be concluded based on our calculations that the bond lengths inner the carbon chain in Pt-chain/CNT system are basically unchanged compared with those in chain/CNT system, which is in agreement with the little deformation in its geometry.

Overall, it can be inferred that the transition metal and carbon

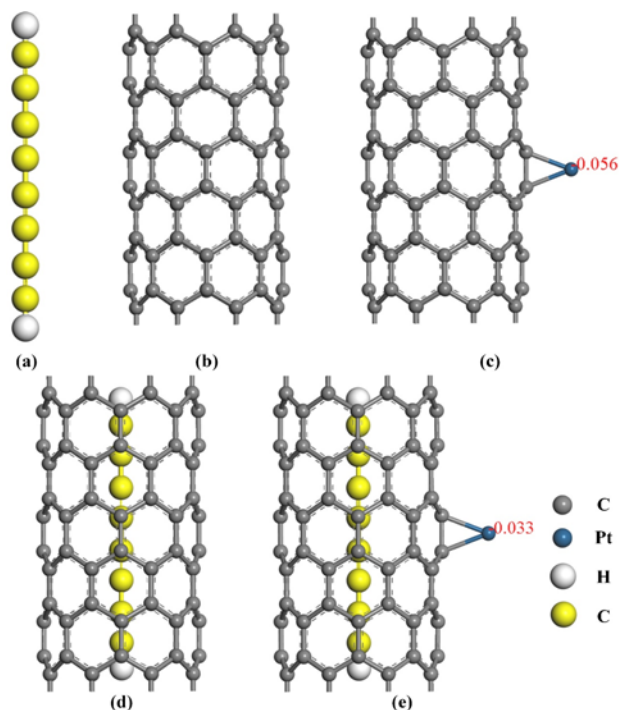


Fig. 1. Geometric structures of different systems. (a) Carbon chain; (b) (8, 0) CNT; (c) Pt-CNT; (d) chain/CNT; and (e) Pt-chain/CNT.

Table 1. Q_T , E_f (Fermi energy) and E_g of every system

Systems	Q_T (e)	E_f (eV)	E_g (eV)
Insolated CNT	/	-4.959	0.538
Chain/CNT	0.018	-5.030	0.496
Pt-CNT	/	-5.159	0.532
Pt-chain/CNT	0.053	-5.255	0.454

The Q_T is the carried electron number of carbon chain.

chain possess electron affinity and withdraw property, respectively. There results can not only confirm the participation of electron-transfer behavior for chain or Pt atom when interacted with the pure CNT, but also suggest the ionicity of binding nature for the two additives with the analyzed nano-support.

Focusing on the density of state (DOS) comparisons of these systems, the electronic performances and the conductivity change can be acquired. In Fig. 2a where the DOS comparison between chain inserted CNT and the intrinsic one are depicted, one can find that the DOS for the chain/CNT changes to a region lower than Fermi level compared with the one for intrinsic CNT. This can be attributed to the losing electron effect of the intrinsic CNT due to the increased effective Coulomb potential [12]. At the same time, the energy gap (E_g) of the chain/CNT system (0.496 eV) is obviously smaller than that in intrinsic CNT system (0.538 eV) as seen in Table 1, which accounts for the improved conductivity for the chain/CNT with respect to insulated CNT according to the previous report that lower E_g means higher electrical conductivity [13,14] Turning insights into Fig.

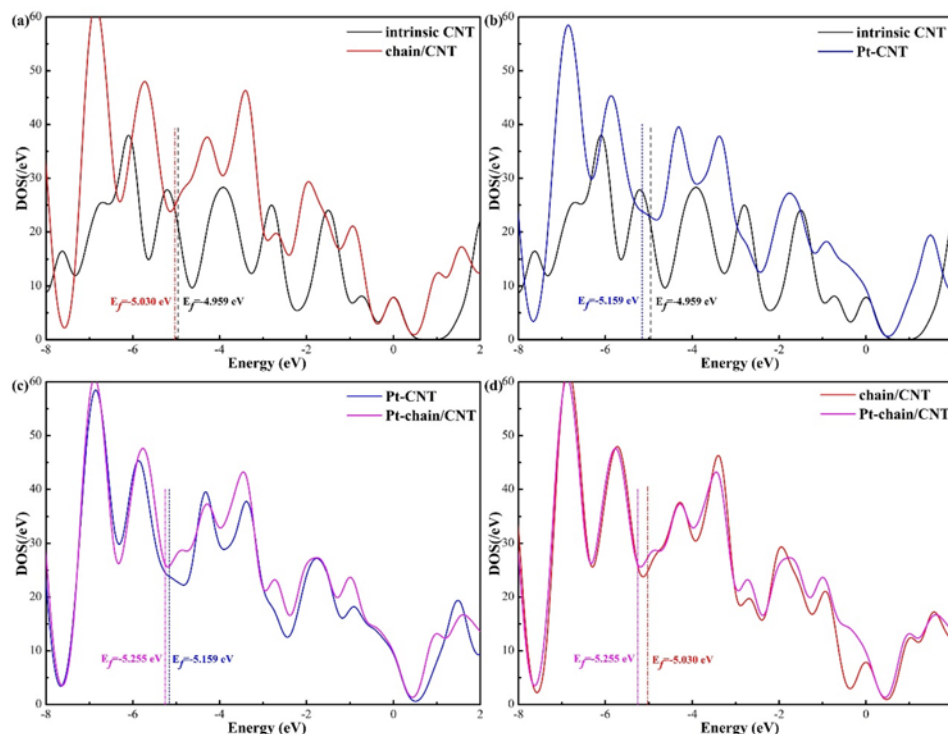


Fig. 2. DOS curves of various systems.

2b, the striking rise of the DOS peaks for Pt doped CNT can be seen when comparing with the one for intrinsic CNT, which to a large extent is resulted from the doping of Pt atom. Moreover, the new-emerged peak of DOS for Pt-CNT can be found, suggesting the induction of novel states within the E_g of the insulated (8, 0) CNT due to the chemical adsorption of Pt atom [15]. Simultaneously, the narrowed E_g (0.532 eV) in this system in comparison with that in intrinsic one can demonstrate the enhanced conductivity as well.

Further analyzing the variations from the chain/CNT to the Pt modified one, the apparent increase in the DOS peaks can also be found via Fig. 2c, due to the addition of Pt atom. Meanwhile, the slight right-shift for HOMO and left-shift for LUMO give rise to the narrower E_g (0.454 eV) in the Pt-chain/CNT system compared with the one (0.496 eV) without doping, thereby leading to the increased conductivity after the Pt dopant on the surface of the chain/CNT structure. This is in agreement with the above analysis that Pt dopant can contribute to the increasing conductivity for the carbon nano-support, so that causing the enhanced conductivity of the one doped by Pt atom. Also, the new induced small peak, namely novel states, around -4.8 eV within the band gap of Pt-chain/CNT in DOS curve can also account for the reduction of band gap for Pt-chain/CNT system compared with insulated Pt-CNT system. The comparison between Pt-CNT and Pt-chain/CNT systems are significant because it can provide more convincing evidence illustrating the effect of carbon chain on the pure CNT. To some extent, the analyses are similar to those in the comparison section between the chain/CNT and pure CNT systems. The total DOS of the Pt-chain/CNT is deformed towards a lower energy region from the chain/

CNT system according to Fig. 2d. The deformation can be understood as the increase in effective Coulomb potential due to the loss of charge as well. In addition, the noticeable shrinkage of E_g in Pt-chain/CNT system with respect to the Pt-CNT system is in good accordance with related values for the two systems, which accounts for the pronounced conductivity drop in Pt-CNT by forming carbon chain in the channel of the tube.

To further characterize the electronic property of Pt doped or chain inserted CNT associated with confirm our above results, frontier molecular orbital theory was employed with HOMO and LUMO distributions and their related energies shown in Fig. 3. We can find the orbital distributions along with their energies changed dramatically after carbon chain insertion or Pt doping. The HOMO-LUMO gaps narrow down subtly to 0.53 eV for Pt-doped CNT, to 0.50 eV for chain/CNT, respectively and sharply to 0.45 eV for Pt-chain/CNT. These coherent results of narrowed gap again correspond to the increasing conductivity of CNT through metal doping or carbon chain insertion, with demonstration that chain insertion has better effect on conductivity reducing than metal doping.

4. Conclusions

In this work, we perform the geometric simulation of carbon chain inserted CNT and the Pt doped one, in order to compare the electronic behaviors of these two methods on the pure CNT surface. The results show that both modification by Pt atom and addition of carbon chain in the channel of the tube can be effective methods for transforming the electrical properties of

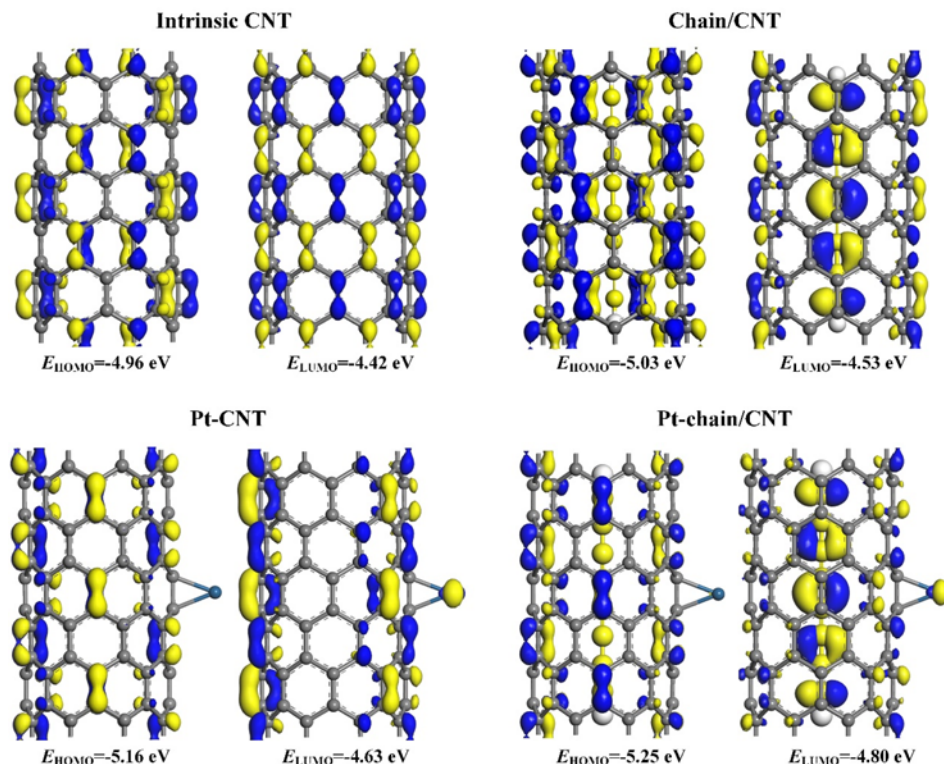


Fig. 3. HOMO and LUMO distributions of varying systems.

the CNT, leading to the redistribution of electron and thereby causing the conductivity change in obtained configurations. However, the chain/CNT system performs the dominated role in reducing the electrical resistance of the CNT. It can be assumed that the effect of the carbon chain is more profound than metal doping on the CNT referring to the electron behavior and physicochemical properties.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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Author contributions: X Zhang guided this work, H Cui performed it and wrote this manuscript while H Xiao and J Tang modified writing in order to improve its quality.

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