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Intrinsic current–voltage characteristics of metal-carbon nanotube networks: A first-principles study

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ABSTRACT

The interconnections involving metal atoms in single-walled carbon nanotube (SWNT) networks are crucial for building nanoscaled devices. The influence of the metal-(η^6-SWNT) interconnects in the electrical conductivity of SWNT film have been reported in recent experiments [X. Tian et al. *Nano lett*. 2014,14,3930]. Using non-equilibrium Green's function with density function theory, we performed theoretical calculations on the electron transport properties of (Cr, Li, Au)-SWNT systems. We revealed the roles of transition metal Cr, alkalis metal Li and inert metal Au in improving the electrical conductance of metal-SWNT systems. Our calculated results show that transport properties along the inter-tube direction are strongly dependent on the connecting metal atoms varying over many orders of magnitudes. Gold atoms fail to enhance the electrical conductance of SWNT systems. Meanwhile, negative differential resistances are demonstrated in semiconducting inter-tube models, which would have potential applications in the electronic device. Our results provide a promising way to optimize the performance of SWNT based networks.

1. Introduction

The synthesis of carbon nanotubes (CNTs) started a new and exciting field in nanoscience and nanotechnology [1], due to their incredible strength and fascinating electronic properties. CNTs are endowed with exceptional electrical [2–4], thermal [5], chemical and mechanical [6,7] properties. Although some of these excellent properties can be preserved in well-aligned CNT bundles, a wide range of conductivities, from 12.5 S/cm [8] to 6600 S/cm [9,10], have been reported in CNT films. The low conductivity was expected to be related to the four reasons: (a) different fabrication methods; (b) chiralities and diameters of CNTs; (c) microstructures in CNT films; and (d) poor electronic tunneling at inter-tube junction. The last one may hold a dominant position. Theoretical and experimental studies have shown that the electrical [11] and thermal [12] resistances at CNT junctions are at least one order of magnitude higher than those of individual CNTs [13,14]. This offers a promising approach to improve the conductivity of carbon films, i.e., by building conductive inter-tube junctions. Chemical functionalization of CNTs with conductive polymers was commonly employed in this approach. However, chemical functionalization may interrupt the π-conjugation in CNTs, forming charge trapping or steric hindrance [9], which leads to a loss of conductivity and mobility in these systems [15].

The recent experiments showed that the electrical conductivity of single-walled carbon nanotube (SWNT) film is greatly enhanced by high vacuum e-beam deposition of metals [16–19]. The bis-hexahapto-metal bonds formed in the covalent (η^6-SWNT)-M-(η^6-SWNT) interconnects in the SWNT films are responsible for increase of electrical conductivity. A series of delicate experiments completed by *Tian* et al. [16] indicated that metal Cr, Li and Au atoms had subtle different mechanisms and effects in increasing the conductivity of SWNTs film. However, from a theoretical point of view, the electron tunneling through the (η^6-SWNT)-M-(η^6-SWNT) interconnects at atomic scale, which is quite crucial for improving the efficiency of SWNT-based electronic devices [20], remains unclear.

In this work, we performed theoretical calculations on the electron transport properties of (Cr,Li, Au)-SWNT networks with metal-mediated interconnection using non-equilibrium Green's function (NEGF) with density function theory (DFT), which was employed in many other systems [20–23]. Currents along the tube (in-tube direction) and across the tube(inter-tube direction) were

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investigated separately. The significant different I–V curves responses of metal-SWNT systems to Cr, Li and Au adsorption were elaborately presented. An appropriate hybridization between Cr's *3d*-orbitals and SWNT's π-orbitals plays an important role in contribution to the inter-tube conductance of the transition metal Cr mediated SWNT systems, while charge transfer to the SWNTs is responsible for the increase in the conductivity of Li-mediated SWNT systems. Gold atoms do not have obvious effect in increasing the conductivity of SWNT systems. Cr atom at inter (6,6) SWNT can induce one order of magnitude increase in current, while other doping configurations cannot. For semiconducting (8,0) CNT, both Cr and Li atoms can lead to the same order of magnitude current increase. Moreover, an intriguing negative differential resistance (NDR) phenomenon is observed in metal-(8,0)SWNT systems. Our calculation results offer theoretical insights into understanding electrical conductive properties of metal-SWNT systems.

2. Computational methods and models

All the geometry relaxation and electronic structure were calculated by the ab initio package known as SIESTA [24–26]. A localized linear combination of numerical atomic-orbital (LCAO) basis sets was adopted for the valence electrons, while norm-conserving nonlocal pseudopotentials were constructed using the Trouiller-Martins scheme [27] to describe the interactions between the valence electrons and the atomic core. Double ζ-plus-polarization (DZP) basis sets were employed to expand the electron wavefunctions. A generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) [28] was employed to account for electron–electron interactions. The charge density was projected onto a real-space grid with an equivalent cutoff of 350 Ry. The convergence criterion for the density matrix was taken as 10^{-4}. A conjugate gradient (CG) method was used to relax all the coordinates until the maximum absolute force on each atom was less than 0.01 eV/Å, and the stress on the supercell was less than 0.02 GPa. Brillouin zone (BZ) integration was carried out using an $1 \times 1 \times 20$ k-point mesh for relaxation of isolated SWNTs according to the Monkhorst-Pack grid [29].

The electron transport properties were simulated by a NEGF technique within the Keldysh formalism, based on DFT as implemented in the TranSIESTA module [30] within the SIESTA package. To save computation resources, a single ζ-plus-polarization (SZP) basis set was used. We also performed test calculations with larger basis set (DZP) and obtained almost the same results. The electrical current (I) through the contact region was calculated using Landauer-Buttiker formula [31], which can be expressed as:

$$I(V_b) = G_0 \int_{\mu_L}^{\mu_R} T(E, V_b)[f_L(E-\mu_L) - f_R(E-\mu_R)]dE$$

where $G_0 = 2e^2/h$ is the unit of quantum conductance and $f_{L(R)}$ is the Fermi-Dirac distribution function for the left (right) electrode with electrochemical potential $\mu_{L(R)}$. $T(E,V_b)$ is the transmission probability of electrons incident at an energy E through the device under the potential bias V_b. The electrochemical potential difference between the left and right electrodes is $V_b=(\mu_L-\mu_R)/e$.

The metal-SWNT systems were treated as a two-probe model. Two representative cases of SWNTs, (6,6) and (8,0) SWNTs, were considered in this study. The electrodes were modeled by the SWNTs. We focused on two typical electron transport pathways: one is within a SWNT along the axial direction (in-tube pathway), the other is across the interconnection between SWNTs (inter-tube pathway). The electron transport properties of pristine SWNTs (denoted as iso_CNT) were also calculated for purpose of comparison. The isolated SWNT with adsorbing metal atoms (M = Cr, Li, Au) is denoted as M@iso_CNT. Two SWNTs linked by metal atoms are referred to as M@CNT. The three models employed to study the in-tube transport are depicted in Fig. 1(a–c). The inter-tube transport was simulated using a M@inter_CNT model as shown in Fig. 1(d). The preferential adsorption sites of Cr, Li and Au atoms on SWNTs are the hollow sites, in good agreement with previous reports [32–34]. All the systems were fully relaxed using DFT

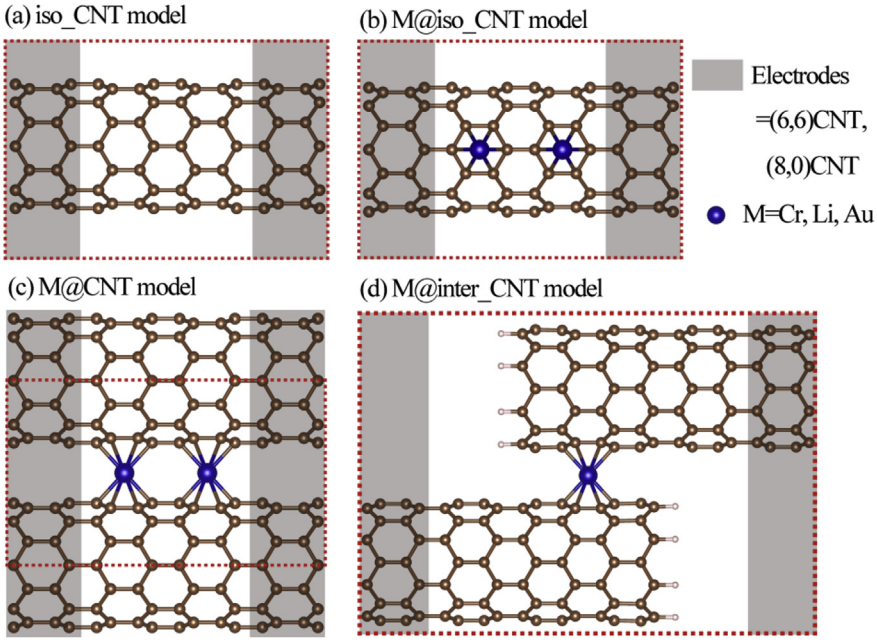

Fig. 1. Models of transport systems: (a) iso_CNT model, (b) M@iso_CNT model and (c) M@CNT model are three different models of the in-tube transport system. (d) M@inter_CNT model is the inter-tube transport system. M=Cr, Li, Au and CNT=(6,6) CNT, (8,0) CNT.