

Modulation of the Electronic Structure of Semiconducting Nanotubes Resulting from Different Metal Contacts

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Received: January 31, 2005; In Final Form: March 9, 2005

Examined in this paper is the role of the metal electrode influencing the structure and electronic properties of semiconducting carbon nanotubes near the interface at low bias. Specifically, we present quantum-chemical calculations of finite sections of a (8,0) semiconducting single wall nanotube contacted with gold and palladium clusters. The calculations at the density functional level of theory, which included full geometry optimizations, indicate the formation of bonds between the metal atoms of the electrode and the carbon atoms of the nanotube. The local work function of the metal electrode can be expected to exhibit significant variations as a result of this bond formation. Compared to the gold-contacted nanotubes, the palladium-contacted nanotubes have a small but interesting increase in both length and diameter. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the gold-contacted nanotube are shown localized at the edges. In contrast, the HOMO and LUMO of the palladium-contacted nanotube are extended over the entire nanotube and the metal cluster contacted to it, providing thereby a better conduction path in the contact region of the electrode and the nanotube. The involvement of the highly directional d orbitals in the interactions involving the palladium cluster leads to an enhanced π electron density in the nanotube. This enhanced π electron density is synonymous with an improved electron transmission.

Introduction

A lot of interest has recently been evinced on the development of single-walled carbon nanotubes (SWNTs) as quantum wire field-effect transistors.^{1–5} It is evident from several studies that the observed electrical properties of SWNTs exhibit variations due to the quality of the nanotube material, the device geometry, and the nature of the contact. Though dramatic experimental advances in the fabrication of SWNT based transistors have been made, little is known about the nature of the interface or the contact.^{1,5,6–10} Thus, one would like to know the nature of the contact in terms of (i) the chemical nature of the metal electrode, (ii) the charge transferred between the metal electrode and the SWNT, (iii) the changes in the electronic structure of the carbon nanotube and hence its transport characteristics.

Most experimental investigations of SWNTs to date have been limited to their electrical characteristics using a single metal contact; i.e., there has been no comparison of the effects of different metal contacts in the same study. However, recent experimental evidence seems to suggest that palladium— or gold—titanium contacts are better than gold contacts.^{1,3,4,11} Because both palladium and gold have similar work functions, the above experimental evidence seems to indicate that a detailed understanding of the local chemistry of the contact and its effect on the carbon nanotube is essential.

To date, most theoretical investigations of semiconducting SWNT—metal electrode contacts have been carried out using a tight-binding approximation with a jellium model representing

the metal electrode.^{6–10,12} There has been a recent report of a density functional study of the contact between a semiconducting SWNT and aluminum electrodes.⁸ Surprisingly, all these theoretical investigations neglect the detailed electronic structure of both the metal electrode and the SWNT at the interface and most calculations have been carried out on fixed geometries of the SWNT and the metal electrode. Given the different chemistries of the metal electrodes and the fact that most experiments employ high temperatures to process these contacts, the interface chemistry would play a very important role on the electronic characteristics of the SWNT.^{2,5} To shed more light on the chemistry of the interface, we present detailed quantum-chemical calculations of a short semiconducting SWNT (8,0) contacted to different metal leads.

Computational Methodology

The electronic structure calculations in this study were carried out using the double- ζ plus polarization basis set (DZP) for all the species. The LYP version of the generalized gradient approximation (GGA) was used for the electron exchange and correlation, and optimized BLYP pseudopotentials are used for the atomic cores. The atomic structures of the SWNT, metal clusters, and SWNT—metal systems were fully optimized, with residual forces less than 0.1 eV/Å.¹³ We also carried out full geometry optimizations of the systems at the B3LYP (Becke's three-parameter hybrid method using the Lee—Yang—Parr correlation functional) level using the 3-21G basis set for the carbon and hydrogen atoms (see Table 1).^{14,15} Correspondingly, the metal atoms were represented by the CRENBS basis sets.¹⁶

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TABLE 1: Selected Geometrical Features of the Optimized Geometries of All Systems Investigated in This Study

system/distance ^a	1	2	3	4	5	6
R_L	7.112	7.108	7.166	8.571	8.580	8.585
R_{W1}	6.373	6.480	6.234	6.377	6.481	6.321
R_{W2}	6.341	6.323	6.356	6.348	6.336	6.359

^a The optimizations were carried out at the B3LYP/3-21G level of theory. See Figure 2, for definitions of R_L , R_{W1} , and R_{W2} . All distances are in units of Å.

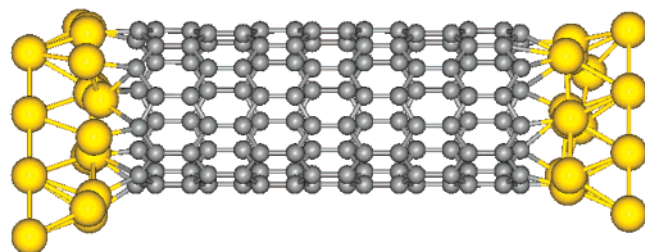


Figure 1. Optimized structure of a four unit cell (8,0) nanotube contacted to two layers of gold electrodes. While the atoms in the two outer layers were fixed, the distance between the two outermost metal containing planes was allowed to vary. The optimization was carried out using the SIESTA program.¹⁴

In this metal basis set, the core electrons are replaced by effective core potentials (ECPs). The electron density analysis was carried out using the AIMPAC suite of programs.¹⁷

One of the most critical issues in modeling the carbon nanotube–metal electrode interface is the representation of the atomic structure of the interface. Because the actual atomic structure of the electrode–SWNT interface is unknown and is likely to change from sample to sample under identical experimental conditions, we have carried out calculations using finite ensembles of metal atoms to represent the metal electrode. Though such an approach can lead to some problems because of plausible difference in structures when compared to the case of extended metal electrode systems, it has been previously shown that theoretical calculations employing quantum-chemical cluster methods provide a fairly accurate description of the interactions prevailing at the metal–semiconductor interface.¹⁸ Quantum-chemical calculations of isolated nanotubes have also been found to yield nearly similar results to the corresponding band structure calculations.¹⁹

Results and Discussion

The choice of the structures investigated in this study emerged from a full geometry optimization of a four unit-cell (8,0) carbon nanotube coupled to two layers of gold or palladium electrodes (Figure 1).¹³ The optimized structure indicates that all the terminal carbon atoms of the nanotube form strong bonds with the Au or Pd atoms, as a result of a significant relocation of the surface metal atoms. Experimentally, a high-temperature annealing precedes electrical measurements.^{2,5,11} Although the aim of this annealing is to remove oxygen at the contact region, high temperatures also lead to significant structural changes in the surface layer of metals.²⁰ Because the fundamental difference at the contact region of the carbon nanotube and the metal electrode seem to stem from the formation of metal–carbon bonds, we have investigated these model structures (Figure 2), wherein a cluster composed of a ring of metal atoms interacts with the carbon nanotube. It is of interest to note at this juncture that the bond formation involving the surface atoms of the metal electrode can also have a bearing on its work function. Although two unit cells of the semiconducting (8,0) nanotube were

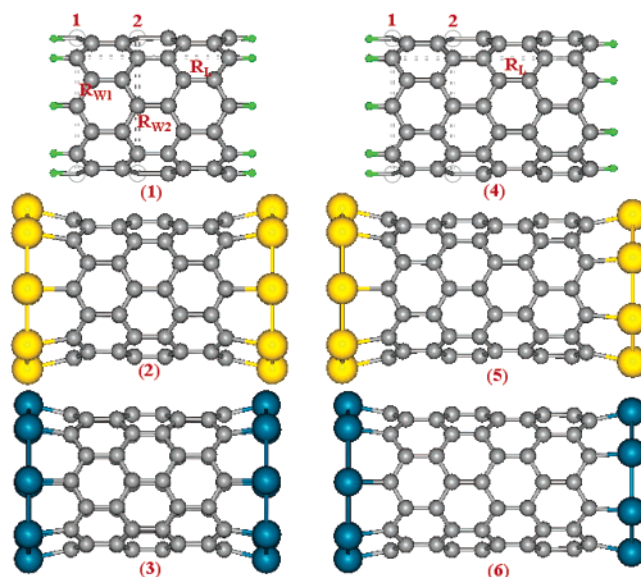


Figure 2. B3LYP/3-21G optimized structures of a two-unit cell (8,0) nanotube contacted to hydrogen atoms (1), gold (2), and palladium (3). An extra ring of carbon atoms was added to the structures 1–3 to yield structures 4–6. R_{W1} and R_{W2} correspond to the distances between the unshaded carbon atoms.

considered in structures 1–3, an extra ring of carbon atoms was added to the nanotube in structures 4–6.

It can be seen from Figures 1 and 2 that the geometry changes of the carbon nanotube are characteristic of the metal atom binding it. Compared to the hydrogenated nanotube, the gold-contacted nanotube is characterized by a negligible decrease in the length of the carbon nanotube (R_L), a small increase in the diameter of the terminal carbon rings (R_{W1}) and a decrease in the diameter of the inner carbon rings (R_{W2}). In sharp contrast, the palladium-contacted nanotube is characterized by an increase in both R_L and R_{W2} . Because the terminal carbon atoms are directly bonded to the metal atoms, one can readily accept the changes in the diameter of the terminal rings (R_{W1}). The changes in R_L and R_{W2} are, however, difficult to anticipate and in a way distinguish the geometrical changes in the nanotube as a result of binding to different metal clusters. Thus, binding to palladium atoms leads to an increase in both the length and diameter of the nanotube. The rationale for this increase is discussed later.

In two very recent studies, the nature of contacts of metal electrodes to semiconducting (8,0) nanotubes was investigated in correlation with the corresponding binding energies.^{21,22} However, we feel that charge reorganization resulting from the interaction of metal with the nanotube is a more effective indicator than the binding energies. In this context, it has been shown in the course of our work on weak interactions involving π systems that substantial charge reorganization and geometrical changes can result from relatively weak interactions.²³

Because changes in the geometries of these nanotubes are intricately linked to both the separation and features of the band edges, it is useful to examine the changes in the profiles of the molecular orbitals. It can be seen from Figure 3 that the HOMOs and LUMOs of the hydrogen- and gold-contacted nanotubes (1 and 2) are mainly localized on the edges of the nanotube and have negligible amplitude at the center. The profiles of the HOMOs and LUMOs of the palladium-contacted nanotubes (3) are delocalized along the entire length of the nanotube including the metal cluster. Although it is difficult to discuss the relevance of these results in the case of bulk nanotubes contacted to extended electrodes, it is interesting to note the three factors

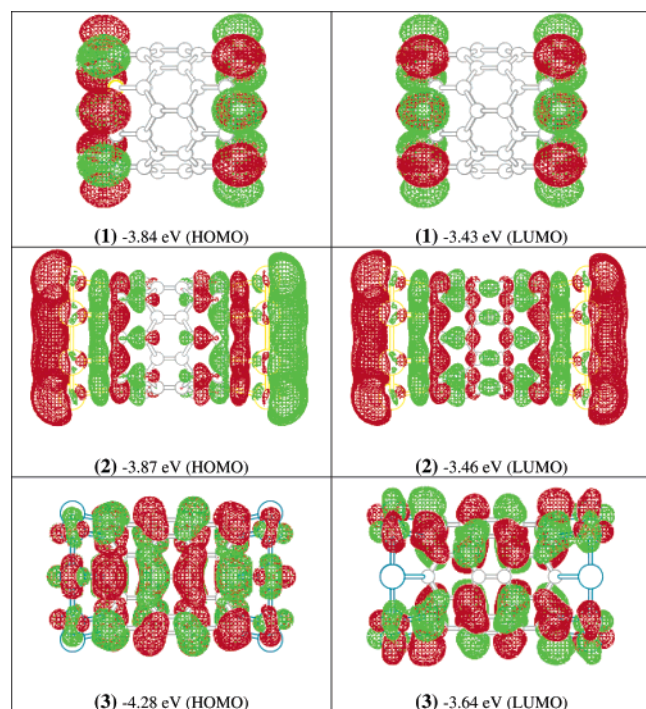


Figure 3. Plots of the HOMO and LUMOs of structures 1–3. Note the extended nature of the HOMO and LUMO in the case of the palladium-contacted nanotube (3).

determining the contribution of a molecular orbital to the total current, i.e., (i) its position relative to the Fermi energy, (ii) its bridging extent (extended or localized), and (iii) its coupling to the leads.^{24,25} On the basis of these factors, it can be inferred that at least for these short (8,0) nanotubes, palladium is a better contact than gold. Though there are no theoretical calculations to support this assertion for bulk nanotubes, the available experimental evidence seems to indicate that palladium forms better contacts.^{2,5}

In light of the differences noted in the potentials of the platinum- and gold-contacted nanotubes,²⁶ we examine the characteristics of the electron density distributions of the gold- (2) and palladium-contacted (3) nanotubes in Figure 4. It can be seen from Figure 4a,b that the electron density distributions of the gold- and palladium-contacted nanotubes are nearly similar along a slice of the longitudinal axis of the nanotube. However, the electron density distributions on a plane 4.25 Å above the center of the nanotube clearly indicate that the π electron density above the surface of the tube is significantly higher in the case of the palladium-contacted nanotube. Transmission calculations carried out on benzene and tetramethylbenzene contacted to palladium electrodes indicates that tetramethylbenzene with its higher π electron density is more conducive to electron transmission than benzene.²⁷ Though the veracity of the above findings can only be verified by ab initio calculations carried on longer nanotubes contacted to realistic metal contacts, we believe that the modulation of the π electron density of the nanotubes by the metal contacts constitutes one of the significant effects of the contact.

In earlier calculations carried out using tight-binding methods, the authors have shown that the electron density in the SWNT channel is decreased when the nanotube is contacted to high work function metals such as Au or Pd.¹⁰ Though the strength of the interface coupling does not effect the band lineup at regions far away from the interface,¹² the extent of charge transfer was found to be larger in the case of contacts involving Pd.¹⁰ The differing characteristics of the Pd- and Au-contacted

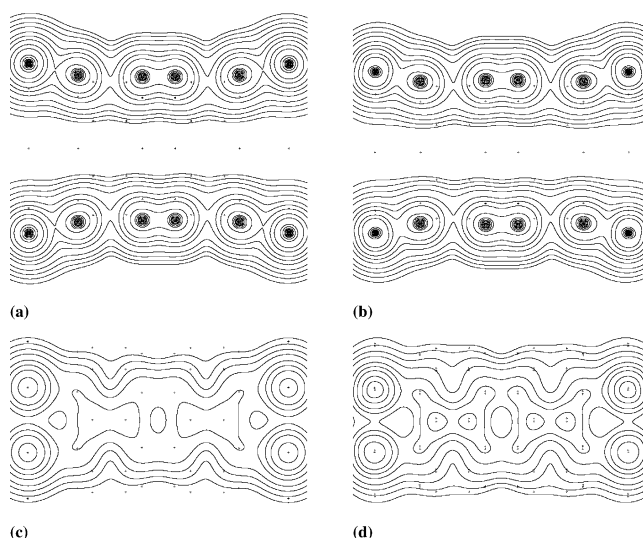


Figure 4. Electron density $\{\rho(r)\}$ plots of a plane cut along the longitudinal axis of the nanotube in structures 2 (a) and 3 (b) and a plane 4.25 Å above the center of the nanotube in structures 2 (c) and 3 (d). The contour values, which are similar for all the structures, correspond to values of 0.001, 0.002, 0.004, 0.008, 0.02, 0.04, 0.08, 0.2, 0.4, and 0.8 atomic units.

metal nanotubes were in part explained by the different characteristics of the frontier orbitals (spherically symmetric 6s orbital in case of Au, directional 4d orbitals in case of Pd) involved in the binding with the carbon nanotube.

Given the large size of the systems, it is difficult to interpret the molecular orbital diagrams for the systems investigated in this study. However, the stabilization of the palladium-contacted nanotubes emerges from the very similar energies of the 4d orbitals of Pd and the nanotube antibonding orbitals. The presence of the Pd 4d electrons in the nanotube antibonding orbitals would lead to an increase in the C–C bond lengths because of a decrease in the bond order. An increase in the diagonal C–C bond lengths is synonymous with an increase in the diameter of the carbon nanotube. It is of interest to note that a recent work on olefin exchange at Pd(0) also indicated a very small energy gap between the Pd-4d and the olefin- π^* orbitals.²⁸ The small energy gap together with the directional nature of the Pd 4d orbitals was reported to be responsible for the effective charge exchange between Pd and the olefin.

Concluding Remarks

The present work details high-level quantum-chemical calculations of a short (8,0) semiconducting nanotube contacted to different metal clusters. Our results indicate that metal electrode atoms possessing very similar work functions could induce different changes in the contact region of the nanotube at low bias. A significant dislocation of the surface atoms of the metal electrode as a result of bond formation with the nanotube can be expected to influence the metal work function. The geometrical changes in the palladium-contacted nanotube include an increase in both its diameter and length. The HOMOs and LUMOs of the palladium-contacted nanotubes are extended over the entire nanotube and the metal cluster. The contact with the metal cluster results in small amounts of charge exchange and substantial reorganization of the electron density of the nanotube. As a result, the π electron density of the palladium-contacted nanotubes is larger than that of the gold-contacted nanotubes. On the basis of transmission calculations of benzene and tetramethylbenzene, it can be inferred that a higher π

electron density results in a better electron transmission profile. Although our calculations have been performed on short nanotubes, the results could provide insights regarding the series resistance of the nanotube transistors. Naturally, calculations at the present level of theory performed with longer nanotubes contacted with a multilayer of metallic atoms are required for understanding the charge transfer and the full interface surface chemistry of the contact resistance.

Acknowledgment. We acknowledge the use of the 1024 grand cluster system installed at the Korea Institute of Science and Technology in carrying out some of the calculations reported in this study.

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