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Effects of Sidewall Functionalization on Conducting Properties of Single Wall Carbon Nanotubes

Hyoungki Park,[†] Jijun Zhao,^{*,‡} and Jian Ping Lu^{*,†}

Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, and State Key Laboratory of Materials Modification by Laser, Electron, and Ion Beams & College of Advanced Science and Technology, Dalian University of Technology, Dalian 116024, China

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ABSTRACT

We investigated the conducting properties of functionalized single wall nanotubes (SWNTs) with a finite addend concentration. Robust differences are found between monovalent and divalent additions. For the former a small number of addends can significantly disrupt the ballistic conductance of nanotubes near the Fermi level. As the concentration increases the conductance decreases rapidly and approaches zero at addend to C ratio around 25%. In contrast, divalent functionalizations have weak effects, and the nanotube quantum conductance remains above 50% of that of a perfect tube even for an addend concentration as large as 25%. These differences can be attributed to the formation of impurity states near the Fermi level for monovalent additions, while divalent addends create impurity states far away from the Fermi level.

It is recognized that covalent sidewall functionalization is one of the promising methods of modifying electric properties of carbon nanotubes (CNTs) for many applications.¹ Sidewall chemical functionalizations disrupt the π -bonding system and break the translational symmetry of single-walled carbon nanotubes (SWNTs) by introducing saturated sp^3 carbon atoms. As a result, electronic and transport properties of SWNTs are significantly altered. There have been many experimental^{2–6} and theoretical^{7–11} studies in this area. Ballistic transport has been reported in defect-free multi-walled^{12–14} and single-walled nanotubes^{15–17} with the quantum conductance unit $G_0 = 2e^2/h$. Individual SWNTs have been recognized as coherent electron waveguides and electron resonators.^{18–21} These behaviors, however, can be significantly changed when there are scattering centers such as covalent addends and local structural defects.^{22–24} While all experimental results are obtained with finite concentration of addends, there have been no corresponding theoretical investigations.

In this paper, we present numerical studies on the conducting properties of covalently functionalized metallic SWNTs. Systematic dependence on the addend concentration is investigated for both monovalent and divalent sidewall additions. We found that for monovalent bonding the addend-induced impurity state resides near the Fermi level; thus it acts as a strong scattering center and the ballistic conducting

properties can be significantly affected. The conductance decreases rapidly with the addend concentration and approaches zero at around 25% addend to C ratio. In contrast, the divalent addend has a very small effect on the conductance near the Fermi level. With increasing addend concentration, the conductance is reduced gradually. Even at 25% concentration, the conductance still remains more than 50% of that of a perfect nanotube.

The geometrical structure for the conductance study was composed of two leads (left and right, both are pristine SWNTs) separated by the central section where the covalent functionalization groups are added (Figure 1d). Only metallic armchair SWNTs are studied. Figure 1a shows an example of monovalent additions: a single chemical bond is formed between the molecule and the CNT. For divalent additions two chemical bonds are formed between the molecule and two neighboring C atoms on the CNT. Previous studies^{6–8} have shown that there are two possible configurations: the C–C bond of the two affected atoms on the CNT can be either broken (Figure 1b) or not (Figure 1c). The open structure was slightly favored at low addend concentrations. The conductance is calculated by the Landauer–Büttiker formalism²⁵ with the nonorthogonal localized-orbital based Green's function method.^{26,27} A four-orbital (one s and three p) nonorthogonal tight-binding Hamiltonian^{28,29} is used for the carbon–carbon interactions within the SWNT, and the extended Hückel approximation³⁰ was employed for the tube–addend interactions. This type of Hamiltonian has been successfully used to study the electronic structure of small

* Corresponding authors. E-mail: jpl@physics.unc.edu; zhaojj@dlut.edu.cn.

[†] University of North Carolina at Chapel Hill.

[‡] Dalian University of Technology.

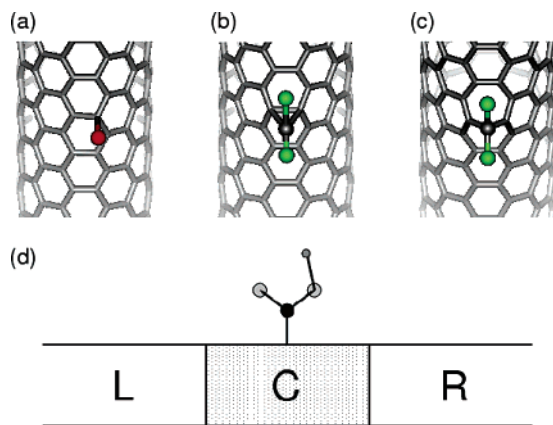


Figure 1. A schematic representations of (a) monovalently functionalized SWNT, (b) divalently functionalized SWNT without sidewall opening, (c) divalently functionalized SWNT with sidewall opening, and (d) the structure across which the conductance is calculated: two semi-infinite leads (L (left) and R (right), both are pristine tubes) are connected to the functionalized region (C).

radius SWNTs^{31,32} and was shown to reproduce well the ab initio band structures of functionalized tubes near the Fermi level.¹⁰

Figure 2a shows the calculated conductance and the local density of states (LDOS) for metallic (6, 6) SWNTs with a single monovalent addend ($-\text{COOH}$) attached. Different types of addends (F, COOH , NH_2 , H, OH, and CH_2) were investigated for systematic studies.¹⁰ All show qualitatively similar results. The local sp^3 rehybridization of the carbon atom at the functional site induces a localized impurity state near the Fermi level, thus strongly disrupting the conducting π and π^* states.^{9,10,23} The functionalization site acts as a strong scattering center. This hinders dramatically the ballistic conducting property of CNT. The conductance of a nanotube has a significant dip near the Fermi level. Each addend exhibits the conductance minimum at a specific energy which correlates well with the position of the addend induced impurity state relative to the pure nanotube Fermi energy in the band structure calculations of the previous study.¹⁰ Thus, we can attribute the scattering effect near the Fermi energy to the impurity state induced by the functionalization.

In the cases of divalent functionalization, two impurity states induced by two neighboring functional sites will be shifted away from the Fermi level due to the rehybridization into bonding and antibonding states.⁸ As a consequence, the overall electronic structures of metallic nanotubes near the Fermi level are not strongly affected by the divalent sidewall functionalizations at low concentrations of addends. Our calculations show that the conductance near the Fermi level is almost unaffected by the divalent functionalization with a single addend ($>\text{NH}$, $>\text{CCl}_2$, $>\text{CH}_2$, and $>\text{O}$ were considered in our study). Regardless whether the sidewall is open (C–C bond on the CNT is broken, Figure 2b) or closed (the C–C bond is not broken, Figure 2c) the same conclusion is found, even though there are structural differences between two cases. This result can be understood by examining the electronic states created by the addend. The rehybridization of the two neighboring impurity states create strong localized

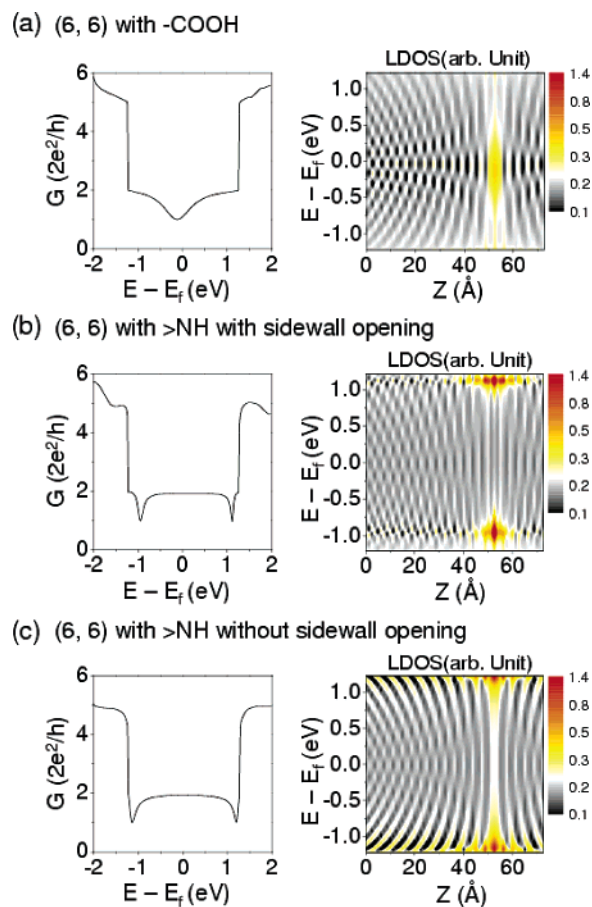


Figure 2. The calculated conductance and LDOS near the Fermi level as a function of energy for a (6, 6) tube. The addend is located $Z = 51.66 \text{ \AA}$ in all three cases. (a) Monovalent $-\text{COOH}$ addition. The addend-induced localized impurity state can be seen to be near the Fermi level in the LDOS plot. There is corresponding conductance dip. (b) Divalent $>\text{NH}$ addition with sidewall opening, and (c) divalent $>\text{NH}$ addition without sidewall opening. In both cases the rehybridized impurity states can be seen to locate far away from the Fermi level in the LDOS plots. The corresponding conductance show little change near the Fermi level.

bonding and antibonding states which are located far away from the Fermi level. This can be clearly seen in Figure 2b and Figure 2c, where significant changes in conductance are showing up 1 eV above/below the Fermi level. This suggests that the C–C bond, even when it is not broken, is significantly weakened due to the interaction with the addend.

Recent experimental results^{2,4,33,34} show that sidewall functionalization with high addend-to-carbon ratio is possible. Thus, it is very desirable to systematically investigate the dependence of the conducting properties on the addend concentration. For such studies, we gradually increased the number of addends in a fixed size section of the nanotube. There are many possible ways of arranging the functionalization sites for a given concentration. Energetically we did not find any significant differences among different configurations. Thus, to ensure that our results are qualitatively relevant, we performed calculations for 30 random configurations at each concentration. The results are shown in Figure 3 with the solid line representing the average and the gray

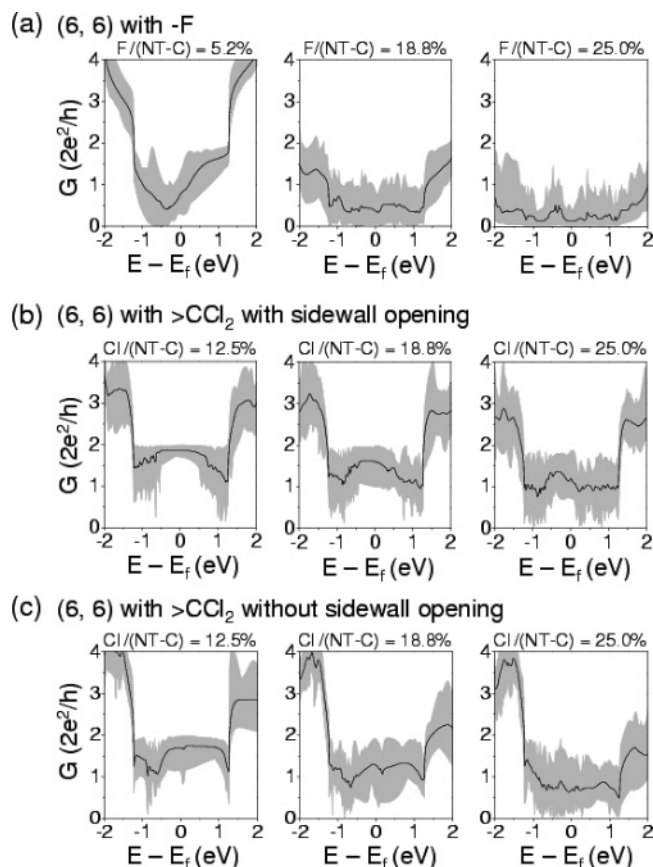


Figure 3. Conductance calculations (on 30 different configurations of addends for each modification ratio in all graphs) of (a) monovalently functionalized (6, 6) with F addends, (b) divalently functionalized (6, 6) with $>\text{CCl}_2$ with sidewall opening, and (c) divalently functionalized (6, 6) with $>\text{CCl}_2$ without sidewall opening. Three different modification ratios are shown for each case. Solid lines and shaded areas represent the average conductance and max–min ranges of the conductance fluctuations, respectively.

area indicating the spread of conductance value over the 30 configurations.

In the case of monovalent addends, the conductance spectrum near the Fermi level carries the molecular signature of the addend impurity state at low concentrations of addends. As the concentration increases, this signature is washed away and the conductance decreases rapidly for a wide range of energies, independent of the functionalization group. Figure 3a shows results of a monovalently functionalized (6, 6) tube with F addends at different modification ratios ($\text{F}:\text{C} = 5.2\%$, 18.8% , and 25% , respectively). The conductance minimum, at the energy of molecular specific impurity state level (ca. -0.4 eV for $-\text{F}$), is clearly seen at the low modification ratio of 5.2% . This feature is no longer there in the case of 18.8% addend, and the average conductance near the Fermi level is substantially reduced. At 25% concentration, the conductance approaches zero. This feature is generally observed for the other monovalent addends studied. Thus, we conclude that monovalent functionalized CNTs lose their metallic character at high addend concentrations.

In contrast, effects of divalent functionalization on conducting properties are much weaker. Examples of our

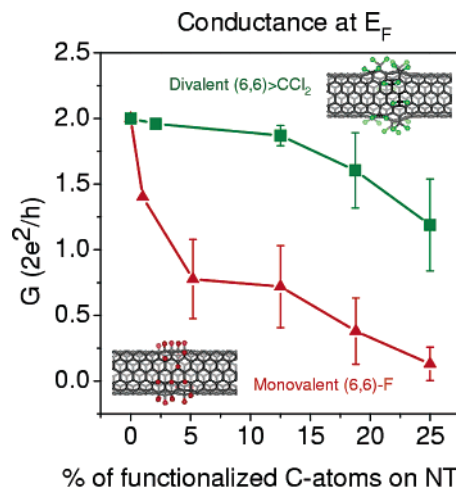


Figure 4. The conductance at the Fermi level vs the addend concentration for monovalent ((6, 6) with F addends) and divalent ((6, 6) with $>\text{CCl}_2$, with sidewall opening) functionalization. Error bars represent the standard deviation range from the average value. The graph shows that monovalent functionalizations decrease the conductance rapidly, and the CNT loses metallicity around 25% modification ratio, while for divalent addition the conductive properties of CNT remain robust.

calculation for CCl_2 functionalized (6, 6) tube are also shown in Figure 3b for the case of no sidewall opening (no broken C–C bond), and in Figure 3c for the case with sidewall opening (broken C–C bond). In all three concentration ratios, 12.5% , 18.8% , and 25% studied, the metallic behavior is found to be robust near the Fermi level. Even at 25% , the average conductance near the Fermi level is still above 50% of that of a perfect tube. Qualitatively we found the same results whether the sidewall is open or not. This suggests that the bonding–antibonding rehybridization effect of the addend induced impurity states is still prevailing even at high concentration ratios of divalent addends.

The dramatic difference between the monovalent and the divalent cases can be more clearly seen in Figure 4, where we plotted the conductance at the Fermi level vs the addend concentration. The conductance of the monovalently functionalized tube decreases rapidly with the increasing addend concentration, and the nanotube loses its metallicity around 25% of modification. While for the divalent cases, the CNTs remain substantially conductive.³⁵

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- (35) Note: It is worthy to point out that in our present conductance calculations (Figure 3), the Fermi level shifts can be disregarded because only a small part of the SWNT is perturbed by chemical groups. In reality, when a large section of a nanotube is functionalized, the Fermi level can be shifted at high concentrations of addends. Our previous study¹⁰ shows that at relatively low concentrations of addends the shift is negligible. Using our tight-binding calculations, we estimate that the shift is about 0.13 eV for 25% periodically functionalized (6, 6) tube with F addends. This shift will not affect the conclusions of our present study as we can see from the window of energy ranges we studied in Figure 2 and Figure 3. Also in our conductance calculations, we did not take into account the effect of spin polarization due to the unpaired electron with F or COOH addends. From our ab initio calculations, we found that total energy difference between the result calculated from spin-polarized GGA calculation and that from the unpolarized GGA is only about 0.1 eV (with 1 F and 40 carbon atoms of the (5, 5) tube). Moreover, the energy difference between the spin doublet state and spin quartet state is found to be about 0.4 eV (with 1 COOH and 120 carbon atoms of the (5, 5) tube), indicating that high-spin states are not favorable. Therefore, we believe that the spin polarization effect is small and negligible in our formalism and would not affect our qualitative conclusions.

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