

Evolution of the Electronic Properties of Metallic Single-Walled Carbon Nanotubes with the Degree of CCl₂ Covalent Functionalization

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The changes in energetic, structural, and electronic properties of the metallic (5,5) single-walled carbon nanotube (SWNT) with the degree of sidewall covalent functionalization of CCl₂ are investigated extensively by using density functional theory calculations. The saturation concentration of CCl₂ covalent functionalization is predicted to be 33.3%. The cycloadducts always adopt an open structure. A band gap opens as the functionalization concentration reaches 11% and then basically increases with increasing functionalization concentration. These results are in agreement with available experiments and can be applied to accurately predict the band gap of metallic SWNTs produced by the HiPco method at a given CCl₂ functionalization concentration.

Carbon nanotubes have attracted much attention due to their unique structural and electronic properties. Single-walled carbon nanotubes (SWNTs) can be either metallic or semiconducting depending on their chirality and diameter.¹ Manipulation of electronic properties of SWNTs is the requisite step for using them to realize a functional device. A metallic SWNT can be converted into a semiconducting one and vice versa upon proper treatment. So far, several routes are developed or suggested to control the electronic properties of SWNTs: (1) mechanical methods,^{2–7} such as stretching, twisting, or squashing; (2) application of an external field, such as a very inhomogeneous electric field,⁸ uniform transverse electrical field,^{9,10} potentials with angular dependence,¹¹ or a magnetic field;¹² (3) ionic chemistry doping,^{13,14} which introduces electrons or holes to the electronic bands of SWNTs and can easily transform a semiconducting SWNT into a metallic one. The electronic properties of metallic SWNTs, however, are less sensitive to ionic chemistry doping. On the other hand, it was shown in recent experiments^{15,16} that the intensity of far-infrared (FIR) adsorption of the SWNT characteristic of a metal is decreased with increasing degree of covalent functionalization of dichlorocarbene (CCl₂) on the sidewall of SWNTs. 50% and 90% of the intensity are removed when the ratio of Cl:C is $n = 12\%$ and 16%, respectively. The degree of functionalization to

completely disrupt the electronic band structure of the metallic SWNTs is estimated to be about 22%. These results suggest that controlling the degree of covalent functionalization is an effective route to modulate the electronic structure of metallic SWNTs and realize a metal-to-semiconductor transition (MST) of metallic SWNTs. Previous theoretical works^{17–19} have found that covalent functionalization of metallic SWNTs by chemical groups such as H, F, COOH, and others can lead to a MST of metallic SWNTs. However, the accurate evolution process of the electronic properties of the metallic SWNTs with the degree of covalent functionalization has not been established.

In this paper, we have examined in detail the evolution process in energetic, structural and electronic properties of the metallic armchair SWNT with the increasing degree of CCl₂ chemical functionalization on the sidewall by using the density functional theory (DFT) method. These investigations reveal an evolution of the armchair SWNT from a metal to a small band-gap semiconductor and then to a moderate band-gap semiconductor with increasing functionalization concentration and explain the experiments^{15,16} nicely.

The SWNT sample used in the works of Haddon^{15,16} is produced by the HiPco (high-pressure CO) method and has a diameter of about 7 Å.²⁰ The (5,5) SWNT (diameter $d = 6.78$ Å) is chosen as representative of the metallic SWNTs produced by the HiPco method. The supercell is constructed with a size of $19 \text{ Å} \times 19 \text{ Å} \times 7.34 \text{ Å}$, corresponding to three unit cells of the (5,5) SWNT in the z direction (the total number of C atoms per supercell is 60). The number of CCl₂ per supercell in our model ranges from 1 to 10, corresponding to Cl:C ratios of 3.3–33.3%. Full geometry optimization was performed for both the atomic positions and lattice lengths by using the ultrasoft pseudopotential²¹ plane-wave program, Castep,²² with two k

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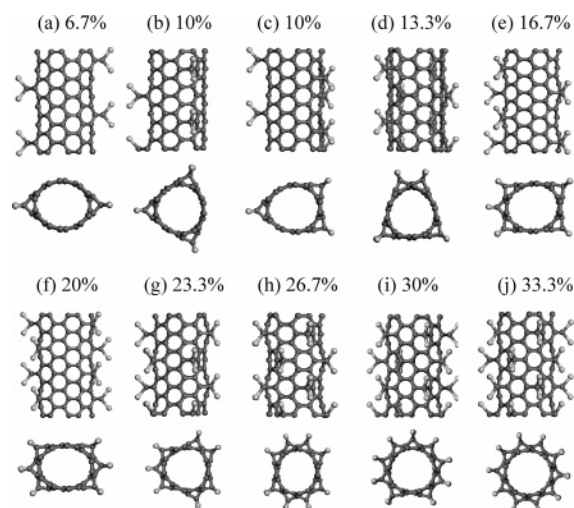


Figure 1. Structures of the lowest energy isomers of CCl_2 -modified (5,5) SWNTs at different functionalization concentrations. White ball, Cl; dark ball, C. The two isomers shown in (b) and (c) are isoenergetic.

points. The plane-wave cutoff energy of geometry optimization is 240 eV, and the convergence tolerance of force on each atom is 0.05 eV/Å. Static total energies of the relaxed structures are calculated with a larger 310 eV cutoff energy. There are two types of C–C bonds on the (5,5) SWNT. It is found that [2+1] cycloaddition on the C–C bond perpendicular to the tube axis is more favorable than that orientated along the tube axis^{23–25} due to its larger curvature. In our calculations, we found that [2+1] cycloaddition of CCl_2 on the C–C bond perpendicular to the tube axis is more favorable than that orientated along the tube axis by over 1 eV. Therefore, we only consider the addition on the C–C bond perpendicular to the tube axis in this paper. The generalized gradient approximation by Perdew, Burke, and Ernzerhof (PBE) is employed for the exchange-correlation functional.

To determine the distribution feature of addends on the sidewall of the nanotube, we calculate all possible distribution of two CCl_2 groups on the sidewall of the supercell. The total energy has a decreasing tendency with increasing separation between the two CCl_2 groups. The configuration with two adjacent CCl_2 groups is most energetically unfavorable, while the lowest energy configuration has maximum separation between two CCl_2 groups. The energy difference between the two extreme configurations is about 1 eV. Therefore, to obtain the lowest energy isomer at higher functionalization concentrations, the distance between CCl_2 groups should be maximized; especially adjacent CCl_2 groups should be avoided.

The most stable isomers of CCl_2 -functionalized (5,5) SWNTs at different modification ratios obtained in this work are shown in Figures 1a–j. It has been found that the [2+1] cycloaddition of single CH_2 , NH , SiH_2 , and O can open the sidewall of the SWNTs with smaller diameters.²⁵ At higher functionalization concentrations, each CCl_2 functional group still opens the sidewall of the (5,5) SWNT as long as none of CCl_2 groups is adjacent (two bridge C atoms belonging to different cycloaddition structures are covalently bonded). The highest functionalization concentration that does not contain two adjacent CCl_2 groups is 33.3%, whose configuration is displayed in Figure 1j. In this five-fold-symmetric configuration, five CCl_2 groups occupy the first layer of C atom, and the other five CCl_2 groups occupy the fourth layer of C atom. Another isomer in which the five adducts on the fourth layer of C atom take close three-membered ring (3MR) structures is 1.45 eV higher in energy.

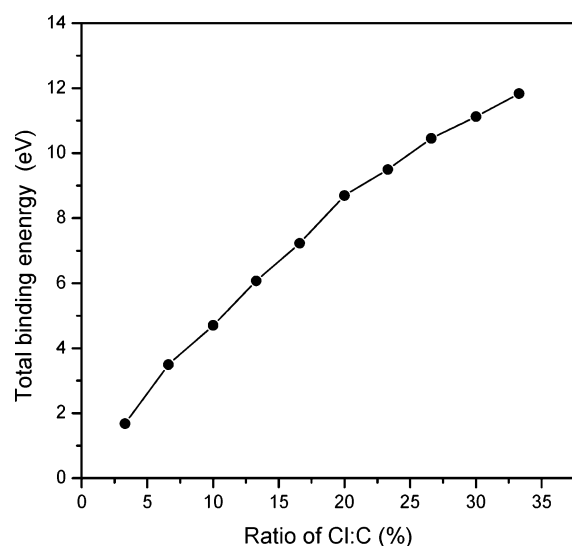


Figure 2. Total binding energies of CCl_2 to the (5,5) SWNT at different functionalization concentrations.

This highest functionalization concentration that does not contain two adjacent CCl_2 groups can be expanded to other (*n,n*) armchair SWNTs. The lowest energy isomers at lower functionalization concentrations are obtained by removing one or more CCl_2 groups from the structure shown in Figure 1j. These lowest energy isomers have no adjacent CCl_2 groups and always take open structure. Addition of F atoms on SWNTs also gives rise to large deformation of the nanotube sidewall,¹⁷ but no C–C bond of the nanotube sidewall is open.

The change of the total binding energy of CCl_2 groups to the (5,5) SWNT with functionalization concentration in the lowest energy isomer is plotted in Figure 2. The total binding energy is defined as

$$E_b = E(\text{tube}) + E(n\text{CCl}_2) - E(\text{tube} + n\text{CCl}_2)$$

As Figure 2 shows, the total binding energy always increases with the increasing degree of functionalization as long as the modification ratio is less than 33.3%. On the other hand, further CCl_2 functionalization beyond $n = 33.3\%$ turns out to be rather difficult due to spatial limitation. Therefore, the saturation concentration of CCl_2 functionalization on the sidewall of the (5,5) SWNT is 33.3%. The calculated average binding energy per CCl_2 group on the (5,5) SWNT is 1.2–1.8 eV, suggestive of a higher thermal stability of CCl_2 adsorption. This appears consistent with the experiment which showed that thermal treatment of CCl_2 -functionalized SWNTs above 300 °C did not restore the original electronic structure of SWNTs. We notice that in Figure 2, two points corresponding to $n = 6.7\%$ and 20% show slight deviation from the smooth $E_b - n$ curve and appear to be two local stable points. The CCl_2 functionalization concentration achieved in the experiments of Haddon et al. varied between 12% and 23%.^{15,16} It appears that the functionalization in their work is stopped on the second local stable point. Further functionalization is possible if the reaction barrier is overcome from the present theoretical calculations.

Figures 3 and 4 display the electronic structures of CCl_2 -modified (5,5) SWNT as a function of modification ratio in the lower and higher concentrations, respectively. The pure (5,5) armchair SWNT is a metal with two subbands crossing the Fermi level, which can be obtained from the zone folding of the band of a graphite sheet.¹ At the concentrations of $n \leq 10\%$, the CCl_2 -modified (5,5) SWNT remains a metal despite of the

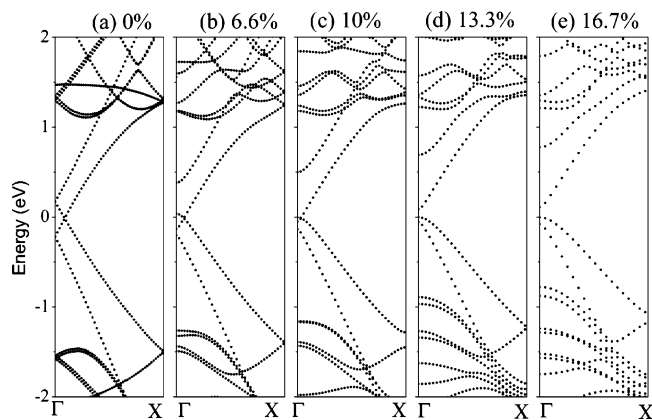


Figure 3. Band structures of the lowest energy isomers of CCl₂-functionalized (5,5) SWNTs at lower functionalization concentrations. The band structure at $n = 10\%$ comes from the structure shown in Figure 1b. The subbands of the structure shown in Figure 1c have larger overlap at the Fermi level. The Fermi level is set to zero.

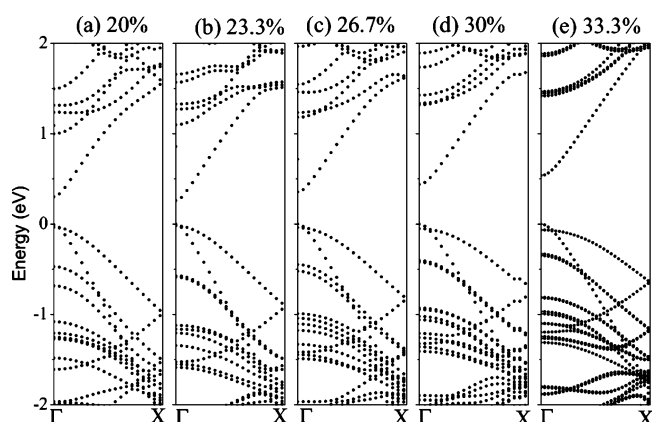


Figure 4. Band structures of the lowest energy isomers of CCl₂-functionalized (5,5) SWNTs at higher functionalization concentrations. The Fermi level is set to zero.

breaking of mirror symmetry. The overlap of two subbands near the Fermi level, however, is reduced with increasing functionalization concentration and nearly vanishes at $n = 10\%$ (0.05 eV). At the functionalization concentration of $n = 13.3\%$, a tiny gap of 0.09 eV opens, indicating a transition of metal to small band-gap semiconductor. The onset of a band gap is estimated to be at about $n = 11.2\%$ from a simple linear interpolation. This agrees well with the far-IR data, which showed that 50% of the intensity characteristic of a metal is removed when the ratio of Cl:C is $n = 12\%$.¹⁶ The opened band gap basically increases with increasing functionalization concentration (Figure 5), and reaches 0.30 and 0.54 eV at $n = 20$ and 33.3%, respectively. One exception is from $n = 20$ –23.3%, where the band gap is reduced from 0.31 to 0.26 eV. This exception appears consistent with the conjecture that $n = 20\%$ is a possible local stable point. The maximum band gap of the (5,5) SWNT at 33.3% CCl₂ coverage is comparable with those of moderate-gap semiconducting SWNTs.²⁶ In the work of Dai et al.,²⁷ the SWNT, used as a transistor, has a band gap of 0.35–0.50 eV. A CCl₂-functionalized SWNT at the maximum coverage, therefore, has a band gap suitable for a semiconductor device.

The moderate band gaps at $n \geq 20\%$ imply a complete disruption of the electronic band structure of the (5,5) SWNT. This is also consistent with the far-IR data, which suggest that the degree of functionalization to completely disrupt the electronic band structure of the metallic SWNTs is about

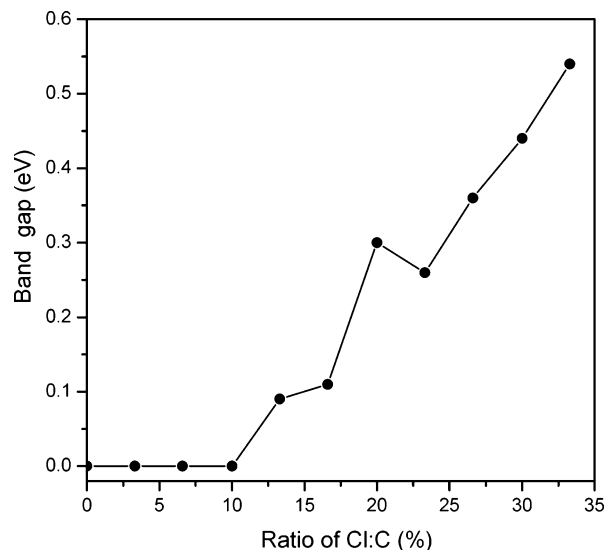


Figure 5. Band gap change of the lowest energy isomers of CCl₂-functionalized (5,5) SWNTs with functionalization concentration.

22%.^{15,16} The electronic band structures of CCl₂-functionalized SWNTs are sensitive to the pattern of functionalization. All the band gaps of the lowest energy isomers appear at the Γ point, whereas the positions of the band gaps of the higher energy isomers are not in the Γ point. Because the most stable isomers at different concentrations always have an open structure with the bridge C–C atom distances greater than 2.0 Å, no sp³ hybridization of the C atoms of the sidewall of SWNTs occurs. Therefore, sp³ hybridization of the C atoms of the sidewall is not requisite to MST of metallic SWNTs. Although the sidewall C atoms connecting to CCl₂ group retain their sp² hybridization, the sp² hybridization angle has been changed. Therefore, the electronic structure of the SWNT is inevitably affected by CCl₂ addition and the alteration in the electronic structure of the SWNT increases with increasing CCl₂ functionalization concentration.

In a very recent DFT investigation²⁸ with double numerical plus d atomic orbital basis set,²⁹ the band structures for CCl₂-functionalized (6,6) SWNTs at a few functionalization concentrations are calculated and a MST is also found at the higher functionalization concentration. However, the lower-energy isomers of CCl₂-functionalized (6,6) SWNTs have not been searched in that work. For example, at $n = 25\%$, the proposed isomer has six pair adjacent CCl₂ groups, and all CCl₂ groups are found to give rise to an open structure. By using the same method, we found that closure of the twelve open structures lowers the total energy by 1.8 eV. As pointed out above, this isomer with close structures remains far away from the lowest energy isomer because it contains adjacent CCl₂ groups. Therefore, it is not surprising that their predicted critical concentration for the band gap opening of $n = 18\%$ ²⁸ is apparently overestimated compared with the experiments^{15,16} and their calculated positions of the band gap deviate from the Γ point. In fact, the overestimation to the critical concentration for band gap opening also takes place when we use higher energy isomers.

The addition of CCl₂ to SWNTs was carried out in solution phase (dichlorobenzene),¹⁵ and thus the actual electronic structure of CCl₂-functionalized SWNTs is probably different from our calculated ones due to the interaction between SWNTs and the solvent. However, the difference is likely to be insignificant if the interaction between SWNTs and the solvent

is van der Waals type and does not change the sp^2 hybridization angle of the sidewall C atoms significantly.

In conclusion, the evolution process of the electronic structures of the metallic (5,5) SWNT with the concentration of CCl_2 chemical functionalization has been revealed by DFT calculations. A metal-to-semiconductor transition can take place at a CCl_2 functionalization concentration of about 11%, and the band gap nearly increases with increasing functionalization concentration. These calculations are in accordance with the available experiments. Therefore, once CCl_2 covalent functionalization concentration is given, the band gap of functionalized metallic SWNTs produced by the HiPco method can be accurately predicted. SWNTs are typically grown as mixtures of metallic and semiconducting tubes. Very recently, metallic SWNTs have been enriched to 80% in a large-scale way;³⁰ this lays a foundation of manipulating the electronic structures of metallic SWNTs in a large-scale way.

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