

Chemical Functionalization of Carbon Nanotubes by Carboxyl Groups on Stone-Wales Defects: A Density Functional Theory Study

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Chemical functionalization of carbon nanotubes with Stone-Wales (SW) defects by carboxyl (COOH) groups is investigated by density functional calculations. Due to the localized donor states induced by the SW defect, the binding of the COOH group with the defective carbon nanotube is stronger than that with the perfect one. A quasi-tetrahedral bonding configuration of carbon atoms, indicating sp^3 hybrid bonding, is formed in the adsorption site. The charge distribution analysis shows that, in comparison with benzoic acid, the localized or delocalized π states on the nanotube would affect the polarities of chemical bonds of the COOH group without losing the acidity. Furthermore, it is found that the double-adsorption system (two COOH groups are respectively adsorbed on two individual carbon atoms of the SW defect) is more energetically favorable than the monoadsorption one. The adsorption of COOH groups leads to a significant change of the electronic states around the Fermi level, which is advantageous for the electrical conductivity. The functionalization by introducing functional groups on the topological defects provides a pathway for applications of carbon nanotubes in chemical sensors and nanobioelectronics.

I. Introduction

Chemical functionalization of carbon nanotubes by introducing molecules and groups has attracted a lot of attention as a significant way to modify their physical and chemical properties. Typically, the electronic structures and transport properties of carbon nanotubes can be obviously modified upon exposure to gaseous molecules^{1,2} (such as NO_2 , NH_3 , and O_2) and chemical decoration on the sidewall or open end with organic groups^{3,4} (such as carboxyl and hydroxyl groups). In substance, chemical modification makes carbon nanotubes more amenable for various potential applications, such as associating individual tubes in high-strength fibers,⁵ improving the sensitivities of chemical sensors,⁶ and opening hollow cavities for gas storage or lithium intercalation.⁷

As a main prototype for functionalization, the carboxyl groups (COOH) were usually found on the tube sidewall or open end after the oxidation of carbon nanotubes by strong acids,^{8,9} or other oxidizing agents.^{10,11} The COOH groups would make further chemical modifications of carbon nanotubes more convenient, as they enable the covalent coupling of molecules through the creation of amide and ester bonds.¹² Thus, carbon nanotubes equipped with a variety of functional moieties could be potentially useful as building blocks for nanoelectronic and nanobioelectronic devices.¹³ For instance, the functionalizing effects of COOH groups¹⁴ and dibenzothiophene¹⁵ adsorbed on the defect-free sidewall of perfect tubes have been theoretically studied, and the related adsorption behaviors and interaction mechanisms have been probed. On the other hand, it is very difficult in reality to synthesize perfect carbon nanotubes without

defects.¹⁶ Meanwhile, it was experimentally shown that the acidic oxidation treatment could yield much more defective sites on the sidewalls of nanotubes.¹⁷ Some recent theoretical studies demonstrated that the adsorption of atoms^{18,19} and molecules^{20,21} on defects is more stable than that on the smooth sidewall, and the physical properties induced are obviously different. Thus, it is more important and practical to investigate the interaction between COOH groups and defects and to explore possible effects on the structures and properties of carbon nanotubes.

The Stone-Wales (SW) defect is a typical topological defect in the nanotubes and is comprised of two pairs of five-membered and seven-membered rings.²² It was suggested that SW defects could act as nucleation centers for the formation of dislocations in the originally ideal graphite network and constitute the onset of the possible plastic deformation of a carbon nanotube.²² With a local deformation, the nanotube containing SW defects might be more favorable for subsequent reactions. In this paper, using the density functional theory, we systematically study the adsorption of COOH groups on zigzag single-walled carbon nanotubes (SWNTs) with SW defects. Then, we explore the nature of the interaction between COOH groups and SW defects and explain the associated adsorption behavior from the localized electronic states. Finally, we evaluate the effect of functionalization of SWNTs by introducing COOH groups on SW defects and predict possible applications in chemical sensors and nanobioelectronics.

II. Calculation Method and Model

We use the DMol³ package²³ within the framework of density functional theory to implement structural optimizations and electronic structure calculations. All-electron calculations are performed with the double numerical basis set and the generalized gradient approximation^{24,25} for the exchange-correlation potential. To explicitly study the interaction between COOH groups and a SW-defective (10,0) SWNT (as shown in Figure

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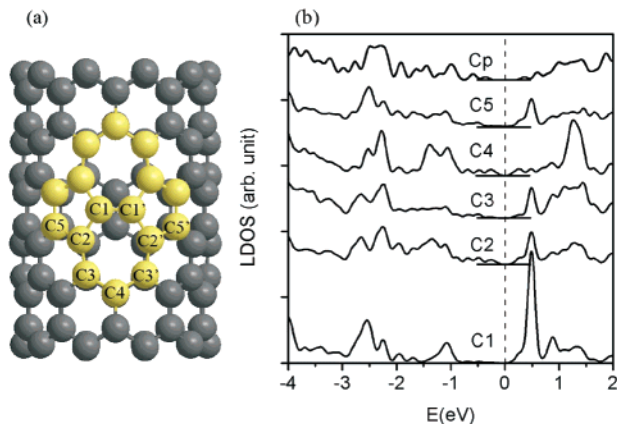


Figure 1. (a) SW defect (in yellow) in the zigzag (10,0) carbon nanotube. According to the symmetry, the carbon atoms of the defect are labeled by C1 (C1'), C2 (C2'), C3 (C3'), C4, and C5 (C5'), respectively. (b) The local density of states of carbon atoms at the SW defect sites and at perfect tube (named as C_p). The Fermi level is at zero energy and marked by the dashed line.

1a), we employ a tetragonal supercell of $25 \text{ \AA} \times 25 \text{ \AA} \times 8.52 \text{ \AA}$, containing 80 C atoms for the SWNT stem and one COOH group (mono-adsorption mode) or two COOH groups (double-adsorption mode), together with periodic boundary conditions. The Brillouin-zone integration is performed with $1 \times 1 \times 19$ Monkhorst–Pack \mathbf{k} points. Structural optimizations are deemed sufficiently converged when the residual forces on all ions are less than 10^{-3} au.

III. Results and Discussion

Compatible with the local deformation shown in Figure 1a, the SW defect induces a significant change of the electronic properties of the SWNT. Typically, the defect states introduced dominate the conduction band edge near the Fermi level and fill the original band gap of the zigzag (10,0) SWNT, and correspondingly, the band gap is reduced from 0.73 eV of the perfect tube to 0.36 eV of the defective one. The calculated local density of states (LDOS) of carbon atoms at the SW defect sites are shown in Figure 1b and compared with the perfect tube. The LDOS at the tube body and the SW defect are similar below the Fermi level. For both cases, two broad peaks are observed around 2.20 and 1.07 eV from the Fermi level in the valence band. However, above the Fermi level, differences in the LDOS between the tube body and the SW defect exist. A sharp LDOS peak is observed at 0.48 eV above the Fermi level, corresponding to the localized donor states. This peak is mainly contributed by carbon atoms at the SW defect, and especially, 2p atomic orbitals of C1 and C1' have the most significant contribution. These characteristics of electronic structure are different from those induced by only one pentagon–heptagon pair on SWNTs.²⁶ Importantly, the property that the donor states are mostly localized at or originated from central atoms (i.e., C1 and C1') of the SW defect would determine that the activities of atoms at the SW defect are not identical.

A. Mono-adsorption. In the study of the mono-adsorption where one COOH group is adsorbed on the SW-defective (10,0) SWNT, five adsorption sites (as shown in Figure 1a) are considered according to the symmetry of the SW defect. Similar to the case of the perfect tube,¹⁴ when the COOH group is attached to the SW defect, a local sp^3 rehybridization of C–C bonding between them occurs and an evident local radial distortion is observed on the tube wall. The shape of the cross section of the tube is changed from circular to oval. Table 1

TABLE 1: Adsorption Site, Binding Energy (Absolute Value), E_b (eV), and Bond Length, d (Å), between the COOH Group and the Host in the SW-Defective (10,0) Tube^a

	adsorption site	E_b (eV)	d (Å)
perfect tube	C_p	0.92	1.573
SW-defective tube	C1	2.00	1.540
	C2	1.34	1.565
	C3	1.32	1.562
	C4	1.45	1.561
	C5	1.26	1.566

^a The data in the perfect tube are also given for comparison.

summarizes the binding energy of the COOH group attached to the tube and the C–C bond length between the COOH group and the tube (i.e., C–COOH bond length). Herein, the binding energy (absolute value), E_b , is defined as $E_b = E_t(\text{CNT} + \text{COOH}) - E_t(\text{CNT}) - E_t(\text{COOH})$, where $E_t(\text{CNT} + \text{COOH})$, $E_t(\text{CNT})$, and $E_t(\text{COOH})$ are the total energies of the tube with the COOH group, of the tube, and of the COOH group, respectively.

Table 1 clearly shows that all binding energies of the COOH group on the SW defect sites are much larger than that on the perfect tube. This implies that the localized π states induced by defects are more advantageous for doping or oxidation than the delocalized π states in carbon nanotubes, which has been verified by oxidation experiments.^{20,27} Among all sites at the SW defect, the C1 (C1') site is the most energetically favorable for the adsorption of the COOH group. The corresponding binding energy (2.00 eV) is 0.55 eV larger than that of the second favorable site (C4 site). This coincides with the fact that the defect states at the conduction band edge are mainly contributed by 2p states of C1 (C1') (as shown in Figure 1b). Correspondingly, the C1–COOH bond length (1.54 Å) is somewhat smaller than the others (~ 1.56 Å) but is larger than the calculated C–C bond lengths of carbon nanotubes (~ 1.42 Å). This also reflects that the covalent bonding in such adsorption is much weaker than the substantial C–C covalent bonding in the stable structures (for instance, the binding energy is 7.42 eV/atom for carbon nanotubes²⁸). Meanwhile, it is noted that the calculated C–COOH bond length in the perfect tube (1.573 Å) is larger than the value (1.547 Å) obtained by Zhao et al.¹⁴ using CASTEP,²⁹ an ultrasoft pseudopotential plane-wave method. This discrepancy in calculated bond length may mainly come from the different basis sets used (i.e., the double numerical basis set in DMol³ and the plane-wave basis set in CASTEP) and the different computational codes implemented and computational parameters (e.g., the size of vacuum layer) adopted in these two works.

To obtain profound insight into chemical functionalization, we study in detail the structural and electronic properties of the most stable system in which the COOH group is attached to the C1 site of the SW defect. It is found that the COOH group pulls out the C1 atom a little from the tube wall, leading to a significant change of local geometry of the SW defect. The forming C–COOH bond is nearly perpendicular to the tube axis, and the three associated angles are 111.6, 111.3, and 114.2°, respectively, as shown in the inset of Figure 2a. For the SW defect on the tube, the C–C bond lengths are increased from 1.52, 1.52, and 1.37 Å (shown in Figure 2b) to 1.60, 1.62, and 1.50 Å (shown in Figure 2a), and correspondingly, the bond angles are reduced from 120.5, 120.5, and 111.9° (shown in Figure 2b) to 106.9, 106.6, and 105.8° (shown in Figure 2a). These C–C bond angles significantly deviate from the standard angle of sp^2 hybridization, 120°. This indicates that the carbon

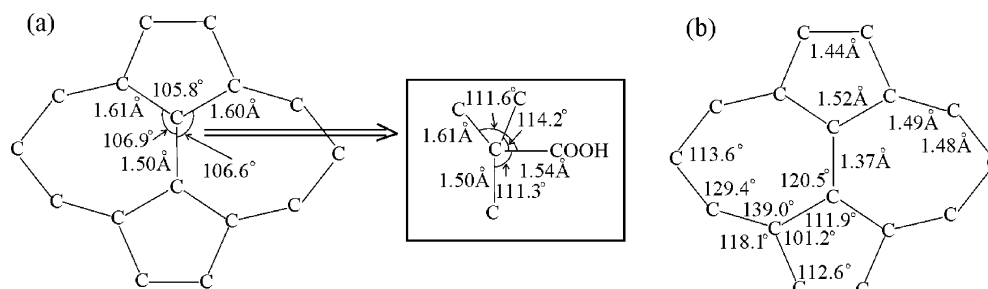


Figure 2. Optimized morphologies of (a) the SW defect with the COOH group and (b) the SW defect on the (10,0) SWNT. The associated bond lengths and bond angles between the COOH group and the SW defect are shown in the inset.

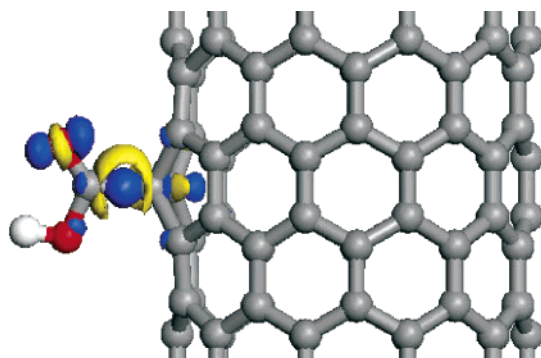


Figure 3. Charge density difference between the SW-defective tube with one COOH group and the sum of the isolated COOH group and SW-defective (10,0) SWNT. The isosurfaces at the values 0.05 and -0.05 au are depicted by the blue and yellow, respectively. The grey, red, and white balls correspond to C, O, and H atoms, respectively.

TABLE 2: Mulliken Population Data for the Isolated COOH Group, the COOH Groups Attached to Perfect and SW-Defective Tubes, the COOH Groups in Acetic Acid and Benzoic Acid, and Two COOH Groups Attached to the SW-Defective Tube^a

atom	isolated COOH	perfect tube with COOH	defective tube with COOH	acetic acid	benzoic acid	double adsorption C1-C1'
C	0.356	0.561	0.511	-0.175	0.434	0.563
O1	-0.351	-0.370	-0.400	-0.419	-0.384	-0.370
O2	-0.261	-0.390	-0.390	-0.411	-0.393	-0.405
H	0.256	0.282	0.283	0.269	0.274	0.285
sum	0.0	0.083	0.044	-0.736	-0.069	0.073

^a O1 and O2 represent, respectively, the oxygen atom forming a double bond with the carbon atom and the oxygen atom binding with the hydrogen and carbon atoms in the COOH group. Positive and negative symbols correspond to the release and capture of electrons, respectively.

atoms of the SW defect near the adsorption site, C1, change to sp^3 hybridization from sp^2 hybridization. With the near- sp^3 hybridized bond between the COOH group and the tube, a quasi-tetrahedral bonding configuration of carbon atoms such as the methane molecule, CH_4 , is formed at the adsorption site.

In principle, the calculated charge density difference (Figure 3) and the Mulliken populations³⁰ (Table 2) can be used to understand the interaction between the COOH group and the SW defect, and to evaluate the induced effects on the functional group. From Figure 3, we can see that the dangling bond at the C atom of the COOH group is saturated, and subsequently, a hybridized bond is formed in the connection. Furthermore, Table 2 indicates that the charge distributions of the COOH groups attached to perfect and defective tubes are more similar to that in benzoic acid rather than that in acetic acid, due to the similar interaction mechanisms (the hybridization between the unsaturated electron of the COOH group and the π states of carbon

nanotubes or benzene). However, the opposite directions of the charge transfer between the COOH group and the host might be related to the fact that the properties of π bonds in nanotubes and benzene are a bit different. In addition, small charge transfer between the COOH group and the perfect or defective tube indicates the formed sp^3 hybridized bond is a “rigid” covalent one. The extent of covalent bonding (i.e., bond order) between the COOH group and the defective tube is somewhat pronounced compared with that between the COOH group and the perfect one, which is well compatible with the calculated binding energies and bond lengths listed in Table 1.

On the other hand, it is found that the charges of the COOH groups on the nanotubes are slightly redistributed in comparison with those in benzoic acid. Typically, the charge transfers (from the C to O1 atom) in different systems descend in the following sequence: defective tube ($0.4e$), benzoic acid ($0.384e$), and perfect tube ($0.37e$). However, the charge transfers (from the C to O2 atom) in them descend in the following sequence: benzoic acid ($0.119e$), perfect tube ($0.108e$), and defective tube ($0.107e$). This reveals that, compared with the cases in benzoic acid, the chemical bonds of COOH groups on the perfect and defective tubes have different changes because of the different π states involved. In the perfect tube with *delocalized* π states, the polarities of the C-O1 and C-O2 bonds are slightly reduced, whereas, in the defective tube with *localized* π states, the polarity of the C-O1 bond is slightly increased and that of the C-O2 bond is slightly reduced. Simultaneously, the carbon nanotubes induce nearly a same charge transfer from the H to O2 atom of the COOH group as that in benzoic acid. This means that the acidity (or the ionicity of H atom) of the COOH group on the nanotubes is almost the same as or might be slightly larger than that of benzoic acid. In addition, Table 2 also shows that the perfect and defective carbon nanotubes capture more electrons from the COOH groups, and thus, the carbon atoms in COOH groups have a large amount of positive charge and are more electrophilic. This will facilitate the functional applications of nanotubes in chemical and biological areas, by further modifications based on subsequent coupling reactions with other functional groups.³¹

One purpose of functionalization is to significantly modify the electrical conductivity of the system, especially for chemical sensors and nanobioelectronic devices. Figure 4 shows the band structures of perfect and defective zigzag (10,0) SWNTs before and after COOH group adsorption. Compared with the perfect tube (Figure 4a), the adsorption of COOH groups not only causes the visible splitting of bands used to be degenerate due to the breaking of nanotube mirror symmetry³² but also clearly introduces a new band (marked by arrows in Figures 4c and d) in the original energy gap of perfect or defective tubes. Typically, this band of the perfect tube with the COOH group is almost dispersionless (Figure 4c), corresponding to the highly localized state,¹⁴ whereas, for the defective tube with the COOH

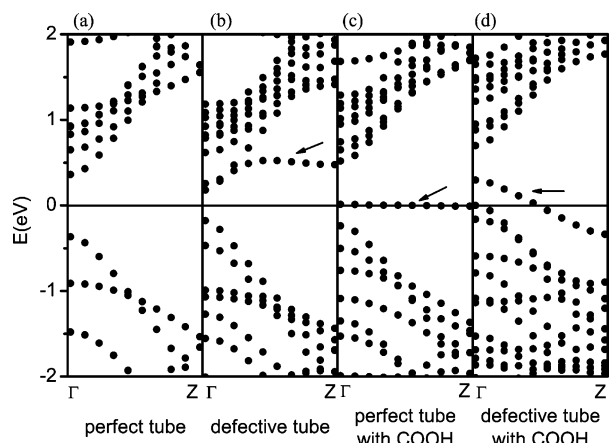


Figure 4. Band structures of (a) perfect and (b) SW-defective zigzag (10,0) carbon nanotubes and (c) perfect and (d) SW-defective ones with the COOH groups. The Fermi level is at zero energy and marked by the solid line. The bands marked by arrows correspond to defective states in the systems.

group, the new band crosses the Fermi level and is much broader (Figure 4d), indicating that this state is no longer localized at one COOH group but extends over the tube. Herein, we propose the chemical functionalization mechanism of the defective tube by the COOH group as follows: when the COOH group is attached to the SW defect, the unsaturated electron of the carbon atom in the COOH group directly interacts with the donor states localized at the C1 site (the defect band just above the Fermi level, marked by the arrow in Figure 4b). The strong rehybridization interaction causes obvious downward shifts of the states from the two bonding C atoms to the lower energy region (in Figure 4d). This can explain the phenomenon that the defect band in Figure 4b shifts down after the adsorption of the COOH group (in Figure 4d). It is interesting to see that the defect band induced is partially occupied and has a large dispersion. Such a partially occupied band should be favorable for the increase of the electrical conductivity of the system. This is different from the case of perfect sidewall adsorption of the COOH group,¹⁴ in which the flat functionalizing band might have less contribution on the electrical conductivity of the tube.

Moreover, the LDOS in Figure 5 shows that this partially occupied band is contributed by the atoms of the SW defect (especially the C1' atom at the center of the SW defect) (major) and of the COOH group (minor). In comparison with the LDOS of the SW defect (in Figure 1b), we can affirm that the formation of one C–COOH bond on the defect causes the redistribution

of electronic states on the carbon atoms in the SW defect. Especially, the LDOS at the Fermi level for C1', C5', C3', and C2' obviously increase, and correspondingly, a local radical center (containing C1', C5', C3', and C2') is present. This makes certain that these carbon atoms are more active and thus greatly facilitate the subsequent chemical reactions, such as the formation of the second bond with another functional group.

B. Double Adsorption. Herein, we examine four sites (i.e., C1', C2', C3', and C5') for the adsorption of the second COOH group. We find that the binding energy, E_b' , of the second COOH group³³ for the double adsorption on C1–C1' sites is 2.44 eV, larger than those on C1–C2' sites (1.57 eV), C1–C3' sites (1.74 eV), and C1–C5' sites (1.85 eV), which is well compatible with the LDOS for C1', C5', C3', and C2' in the mono-adsorption system, as shown in Figure 5b. Since the E_b' value for the C1–C1' double-adsorption system is obviously larger than the E_b value (2.0 eV) for the mono-adsorption on the C1 site, we can confirm that the monofunctionalized SW-defective nanotube would be a short-lived or unstable intermediate, while the double-functionalized SW-defective tube (i.e., the C1–C1' system) is more energetically favorable.

In the most stable double-adsorption C1–C1' system, the spatial orientations of the two adsorbed COOH groups are almost “antiparallel” with the angle between the tube axis and COOH groups being about 38.1° (as shown in Figure 6a). The C1 and C1' atoms in the SW defect are pulled a little out of the sidewall of the carbon nanotube, and the C1–C1' bond length increases to 1.57 Å from 1.37 Å in the pure defective tube and 1.50 Å in the mono-adsorption system. The formed C–COOH bonds with the identical length of 1.552 Å remain nearly perpendicular to the tube axis, but the three associated angles change to 114.8, 108.4, and 102.0°, respectively, as shown in Figure 6c. The two individual COOH groups have the same deformation effect on the SW defect, and the resulting geometry of the deformed SW defect (Figure 6b) is the following: the C–C bond lengths are 1.57, 1.61, and 1.62 Å, and the bond angles are 113.1, 112.1, and 105.5°. This indicates that the quasi-tetrahedral bonding configurations of carbon atoms based on sp^3 hybridization are formed at the C1 and C1' sites in the double-adsorption defective nanotube. Simultaneously, the Mulliken population analysis³⁰ shows that these two adsorbed COOH groups have the same charge distribution, as listed in Table 2. In particular, compared with the cases of mono-adsorption, in the double-adsorption system, there are more charge transfers to the carbon nanotube from COOH groups (0.073e per COOH group), the carbon atoms in the COOH groups have

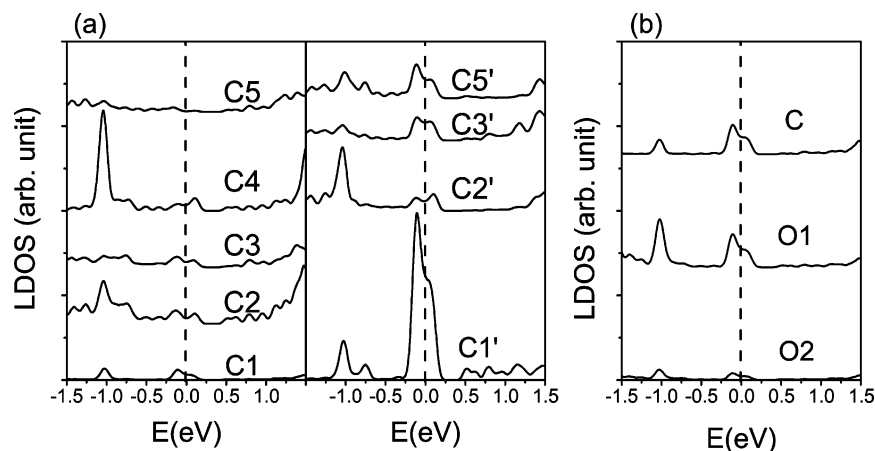


Figure 5. Local density of states in the SW-defective tube with the COOH group. The Fermi level is at zero energy and marked by the dashed lines. C1–C5 and C1'–C5' represent the carbon atoms of the defect (as denoted in Figure 1a).

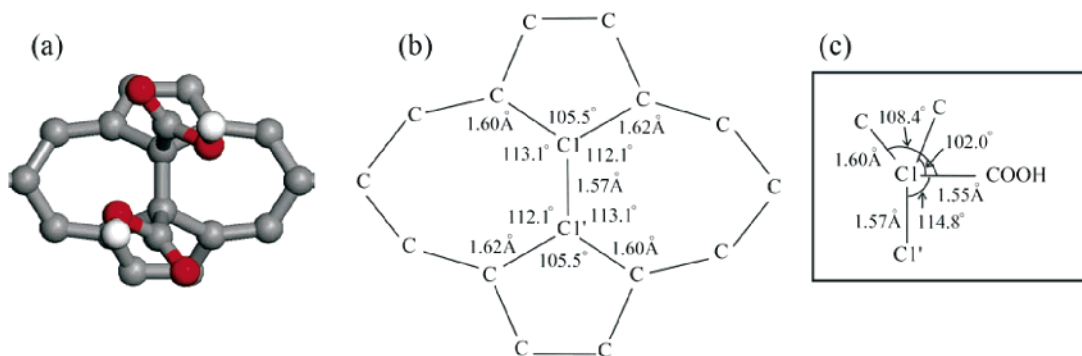


Figure 6. (a) Atomic structure of the double-adsorption defective nanotube. The grey, red, and white balls correspond to carbon, oxygen, and hydrogen atoms, respectively. (b) Optimized morphologies of the SW defect with two COOH groups. (c) The associated lengths and angles of the C–COOH bond in the double adsorption.

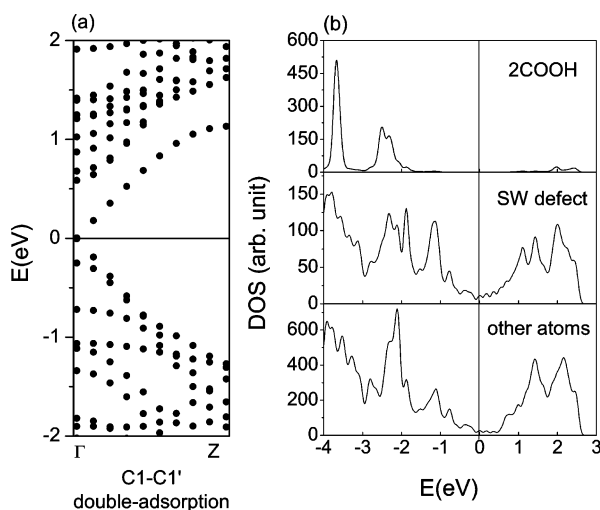


Figure 7. (a) Band structure and (b) local density of states of the double-functionalized SW-defective carbon nanotube. 2COOH, SW, and other atoms represent, respectively, the sums of local density of states for two COOH groups, for the SW defect, and for the other carbon atoms in the tube.

more positive charge ($0.563e$) and are more electrophilic to create amide and ester bonds, and the polarity of the O–H bond is increased. This might result from the complete saturation by the second COOH group for the unpaired electron states around the Fermi level in the mono-adsorption SW-defective carbon nanotube.

Furthermore, the double adsorption of COOH groups significantly changes the band structure and electronic properties of the defective carbon nanotube. The partially occupied band crossing the Fermi level in the mono-adsorption case (Figure 4d), which is mainly contributed by the $C1'$ atom, obviously shifts downward because of the strong interaction between $C1'$ and the second COOH group. In particular, different from the case of the defective nanotube without adsorption (Figure 4b), the double-adsorption $C1$ – $C1'$ system can be regarded as metallic (or semimetallic) with a calculated gap of less than 0.01 eV at the Γ point (Figure 7a). For the double-adsorption SW-defective nanotube, the bands near the Fermi level have a large dispersion (Figure 7a), and the calculated LDOS (Figure 7b) shows that the COOH groups do not contribute to these states. It is suggested that double adsorption of the COOH groups will significantly enhance the electrical conductivity of the defective tube.

In short, we can expect that as the COOH groups are readily derivatized by a variety of reactions,³¹ the preparation of a wide range of functionalized nanotubes with topological defects

should be possible, which may lead to molecular sensors or nanoelectronic devices with potential applications in many areas of chemistry and biology.

IV. Conclusion

Using the density functional theory, we systematically study the chemical functionalization of zigzag SWNTs by the COOH group adsorption on the SW defects. The donor states induced by the SW defect are advantageous for the adsorption of the COOH groups or oxidation. Especially, the two atomic sites at the center of the SW defect are the most energetically favorable adsorption sites. The COOH group leads to the significant change of local geometry of the SW defect, and a quasi-tetrahedral bonding configuration of carbon atoms is formed in the adsorption site, indicating sp^3 hybrid bonding. The charge redistribution reveals that the polarities of the chemical bonds of the COOH group attached to the nanotubes are somewhat changed compared with those in benzoic acid, but its acidity is perfectly maintained. When only one COOH group is adsorbed on the defective nanotube, the partially occupied band with a large dispersion, contributed by the atoms of the SW defect and of the COOH group, is introduced in the original energy gap, and may result in an increase of the electrical conductivity of the defective tube. It is found that the adsorption of two COOH groups on the two central atoms of the SW defect leads to a more energetically stable structure, the double-functionalized SW-defective nanotube. Double adsorption of COOH groups makes the COOH groups more active and is also advantageous for the electrical conductivity of the defective tube. Our work suggests the topological defects have important promoting effects on functionalizing modification of the electronic properties of SWNTs induced by organic groups, so they would have unique application potential in chemical sensors and nanobioelectronic devices.

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- (33) The binding energy of the second COOH group is defined as the energy gained by the second functionalizing adsorption: $E_b' = E_t(\text{CNT} + 2\text{COOH}) - E_t(\text{CNT} + \text{COOH}) - E_t(\text{COOH})$, where $E_t(\text{CNT} + 2\text{COOH})$, $E_t(\text{CNT} + \text{COOH})$, and $E_t(\text{COOH})$ are the total energies of the defective tube with two COOH groups, of the defective tube with one COOH group, and of the isolated COOH group.