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Ab initio study on the carbon nanotube with various degrees of functionalization

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Abstract

We present our ab initio results on carbon nanotubes functionalized with dichlorocarbene (CCl_2). We find that the electronic properties of carbon nanotubes are significantly modified depending on the site of $[2 + 1]$ cycloaddition. The random addition of dichlorocarbene is found to reduce the band gap of semiconducting nanotubes while those of metallic nanotubes are increased. This is related to the quasi-bound states within the energy gap originated from dichlorocarbene, which are revealed at the large supercell calculation.
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The carbon nanotube is one of the promising nanoscale materials with well-defined electronic properties. Depending on the way the hexagonal graphene sheet is folded, the nanotube becomes metallic or semiconducting [1]. The use of nanotubes for practical application critically depends on their electronic properties. For example, the field emission display using nanotube as an electron gun exploits the metallic conductivity of carbon nanotubes [2]. On the other hand, the nanotube-based field effect transistor device proposed to date, adopts the semiconducting carbon nanotube as a carrier channel [3]. Therefore, it is desirable to use nanotubes with uniform electronic properties depending on the targeted application. Since it is practically not feasible at the present time to selectively grow the nanotube with a specific physical property, engineering the electronic properties of as-grown carbon nanotube through the functionalization has been a hot issue in recent nanotube researches. The study on functionalized nanotube has been greatly accelerated with the advent of the experimental technique to disperse nanotube bundles in the solution phase [4]. With the sidewall of the nanotube

exposed to various solutes, it becomes possible to attach a wide range of covalent functional groups, such as amine, carboxyl, fluorine, dichlorocarbene, and enzyme on the sidewall of nanotube [5–8]. Due to the fully saturated sp^2 C–C bonding within the nanotube sidewall, the large chemical reactivity is required for the covalent functionalization.

Recently, it was found that dichlorocarbene (CCl_2) forms the covalent bonds with the carbon nanotube and open a band gap at the Fermi level, changing the electronic properties from metallic to semiconducting [9,10]. The ab initio calculations have demonstrated the sidewall opening or band gap opening of armchair nanotube upon 20% modification ratio, as defined by the number of chlorine atoms divided by that of carbon atoms at the sidewall [11–13]. It was claimed in those calculations that one type of binding is energetically favorable than the others, e.g., the perpendicular site versus slant one in the armchair nanotube, and the detailed investigation has been performed only on the specific or highly ordered binding configurations. However, we point out that at the typical radius of single-walled carbon nanotubes, the difference is quite small compared to the binding energy itself, as will be shown below. Therefore, the realistic modeling would consider various binding configurations simultaneously.

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In this Letter, we report on the comprehensive ab initio calculations on the dichlorocarbene-functionalized nanotube as we address the realistic situation occurring in the experiment. We find that the functionalization with dichlorocarbene exerts opposing effects on the band gap of semiconducting and metallic nanotubes; the band gap of the semiconducting nanotube is reduced while those of metallic nanotubes increase. This is closely related to the molecular states induced by the functionalization.

We carry out density-functional calculations using the computational code of Vienna ab initio simulation package (VASP) [14]. To check any effect of different implementation of first-principles method, some of the results are repeated using PwSCF program employing the similar computational framework [15]. The density-functional calcula-

tions [16] are performed using the generalized gradient approximation [17]. The ionic potentials are described by the projector augmented-wave (PAW) pseudopotential [18]. The energy cutoff to describe electronic wave functions is chosen to be 280 eV. We choose the $(9, 0)$ and $(10, 0)$ zigzag tubes, the $(5, 5)$ armchair tube and the $(7, 3)$ chiral tube [1]. The $(10, 0)$ and $(7, 3)$ nanotubes are semiconducting with energy gap of $\sim$0.8 eV, while $(9, 0)$ and $(5, 5)$ nanotubes are metallic or semimetallic. All of the nanotubes considered here have similar radii, about 3.5–4 Å. The 5, 6, 1 k-points are sampled in the Brillouin zone along the tube axis (z-direction) for zigzag, armchair, and chiral nanotubes of unit repetition. To minimize the interaction between neighboring cells in xy-direction, the vacuum spaces of more than 7 Å are inserted. The geometry optimization is performed until the magnitude of Hellmann-Feynman force on each atom is reduced to within 0.05 eV/Å.

In Fig. 1, the binding configurations of dichlorocarbene adsorbed at the sidewall are shown for zigzag, armchair and chiral nanotubes. From the preliminary tests searching possible local geometries, the dichlorocarbene is found to be locally stable only when the carbon atom is above the middle of C–C bond as shown in Fig. 1, confirming the $[2 + 1]$ cycloaddition typical for carbene, silyene, and germylene [11,13]. The C–C bond lengths of pristine nanotubes to which dichlorocarbene binds are 1.42 and 1.44 Å for zigzag, 1.43 and 1.43 Å for armchair, and 1.42, 1.43, and 1.42 Å for chiral nanotubes in the order of increasing type number. This indicates that C–C bond strengths are uniform.

We first study the size effect of supercell length along the nanotube axis. This is a useful step to identify states originated from the functionalizing addend. In Fig. 2, the band structures of semiconducting $(10, 0)$ nanotubes with CCl_2 attached in type-I (see Fig. 1a) configuration are shown. The repeating period of CCl_2 increases from 2-unit cell (80 C atoms) to 10-unit cell (400 C atoms). The zigzag $(10, 0)$ nanotube in the pristine state exhibit the band gap of 0.69 eV. The band structures change substantially with respect to the repeating period of CCl_2 with the maximum influence appear in the shortest period. At the 2-unit cell
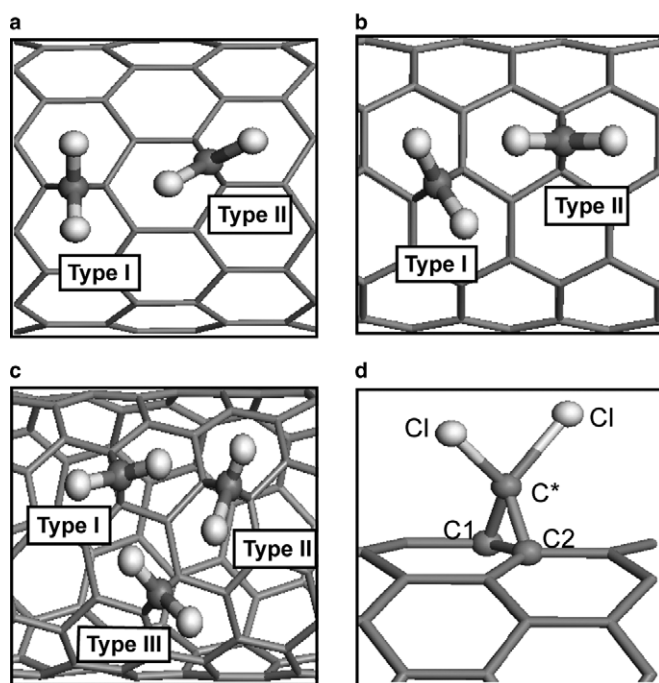

Fig. 1. The binding geometries of dichlorocarbene attached at: (a) zigzag $(9, 0)$, (b) armchair $(5, 5)$, and (c) chiral $(7, 3)$ nanotubes. (d) The side view of (a). The lighter (darker) gray indicates chlorine (carbon) atoms.
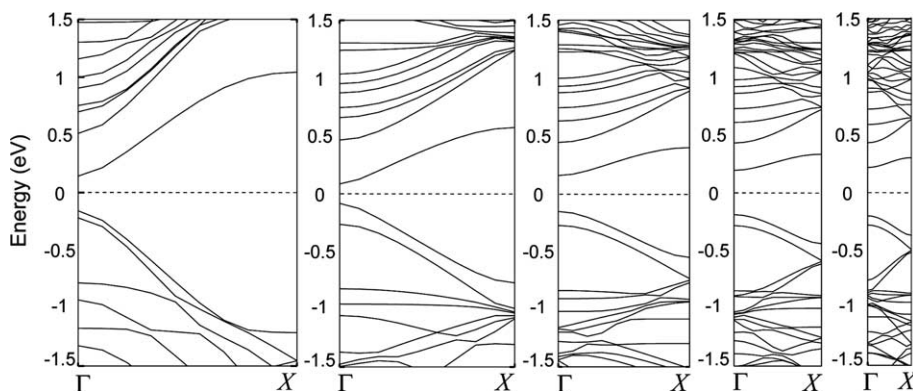

Fig. 2. Band structures of dichlorocarbene attached $(10, 0)$ nanotube with supercell length ranging from 8.52 to 42.6 Å. (2-, 4-, 6-, 8-, and 10-unit cells, respectively) The development of quasi-bound states is clearly visible.

repetition, the π^* band of the pristine nanotube shifts down by 0.3 eV and the band gap of functionalized CCl_2 is reduced to 0.4 eV. However, as the supercell length increases, the extended π^* state changes into the quasi-bound state, with the flat energy dispersion along k-points, in contrast to those of extended states. With another quasi-bound state developing just above the valence band, there are two quasi-bound states within the energy gap. If these states are set aside, the original gap of 0.69 eV is almost recovered at the largest supercell. From the decomposition into atomic orbitals, we find that spatial distribution of quasi-bound states are very similar to those of π or π^* states with their maximum intensities around the attached dichlorocarbene and slowly decaying throughout the cell. This is in contrast with the monovalent functionalization where pronounced localized states are usually found [19,20]. The creation of quasi-bound states with characters similar to π and π^* states will increase the optical oscillator strength of the semiconducting nanotubes near the energy gap, which could be monitored by the optical spectroscopy.

In Table 1, the computational results on the binding geometry, binding energy, and the energy gap of the nanotube with the dichlorocarbene attached as shown in Fig. 1. To identify the binding properties of the isolated dichlorocarbene, we use the 8-, 16-, and 1-unit cell period for zigzag, armchair, and chiral nanotubes, respectively. The binding energy E_b between the addend and the carbon nanotube is defined as follows:

$$E_b = E(CCl_2) + E(nanotube) - E(CCl_2/nanotube), \quad (1)$$

where E means the total energy. We first note that the binding geometries are quite different between binding types. In type-I, the C1–C2 bond, to which the dichlorocarbene is attached, is slightly elongated compared to the C–C length in pristine nanotube (1.42 Å) and becomes comparable to the single bonding (1.54 Å). On the other hand, the C1–C2 bond in type-II geometry (type-I in (7,3) nanotube) is almost broken with the bond length as large as 2 Å, indicating the sidewall opening of the nanotube. The C–C bond lengths in the pristine nanotube are shown in the parenthe-

sis and one can find that the C1–C2 distance between the functionalized and the pristine nanotubes is rather uncorrelated. Therefore, it is likely that the shape of π and π^* states determined by the finite circumference length plays a significant role in determining the C1–C2 distance. The binding energy for each configuration, on the other hand, depends strongly on the chirality. For $(n,0)$ nanotube, type-I geometry is slightly favorable while type-II and type-I is far more stable in (5,5) and (7,3) nanotube, respectively. The energetic differences between types are certainly consequences of the small diameter of the nanotubes (~ 7 Å) because all the bonds in the nanotube are equal in the limit of infinite radius. In fact, for the dichlorocarbene attached at the (10,10) nanotube, which represents the typical size of nanotube found in experiment, we find that the binding energies of type-I and type-II differ only by 0.1 eV to be compared with 0.7 eV in (5,5) nanotube. (The C1–C2 bond lengths in the functionalized (10,10) nanotube are 1.57 and 2.13 Å for type-I and type-II geometries, respectively.) This indicates that in real situation, it is likely that the dichlorocarbenes are randomly attached with little site preference. As will be shown below, this has profound effect in estimating the energy gap of functionalized nanotubes.

In Fig. 3, we present the band structure of (10,0) and (5,5) nanotubes functionalized with one dichlorocarbene per supercell with a length about 40 Å along the nanotube. The results on the energy gap are summarized in the last

Table 1
The binding geometry, adsorption energy, and energy gap change of the nanotube functionalized with dichlorocarbene repeated with the 8-, 16-, and 1-unit cell period for zigzag, armchair, and chiral nanotubes, respectively

Nanotube	Type	d_{C1-C2} (Å)	d_{C1-C^*} (Å)	E_b (eV)	E_g (eV)
(9,0)	I	1.53	1.53	1.24	0.17 (0.16)
	II	1.82	1.52	1.06	0.15 (0.16)
(10,0)	I	1.54	1.53	0.90	0.38 (0.69)
	II	2.12	1.50	0.89	0.70 (0.69)
(5,5)	I	1.57	1.53	0.91	0.07 (0.00)
	II	2.21	1.52	1.62	0.00 (0.00)
(7,3)	I	2.19	1.51	1.44	0.84 (0.86)
	II	1.55	1.53	0.90	0.52 (0.86)
	III	1.62	1.53	0.77	0.83 (0.86)

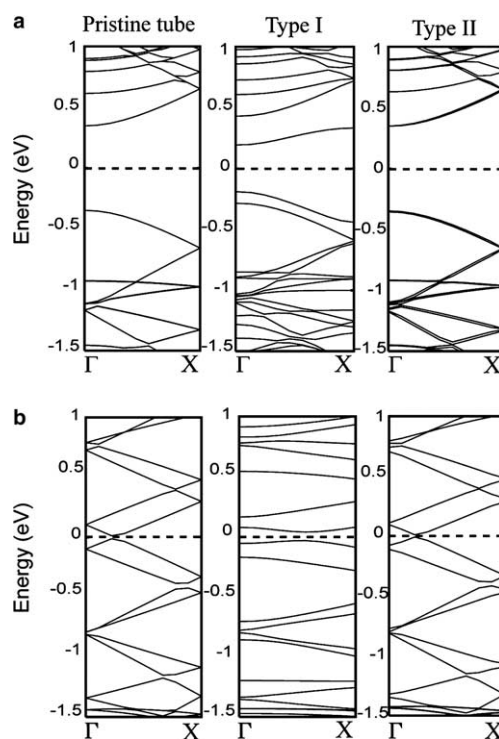The energy gaps in the parenthesis indicate those of pristine nanotubes.

Fig. 3. The band structures of dichlorocarbene-attached: (a) (10,0) and (b) (5,5) carbon nanotubes calculated with the 8 and 16-unit supercells for zigzag and armchair nanotubes. From the left to the right, the band structures on pristine, type-I, and type-II functionalized nanotubes are shown.

column of Table 1. We find that the localized band with small dispersion is notable in type-I geometry. For all the nanotube indices studied in this work, the quasi-bound states appear when d_{C1-C2} is around 1.5–1.6 Å rather than completely broken (~ 2 Å), that is to say, when the graphene network is less perturbed on the nanotube. Although the relatively larger supercell length is used, there still exists small dispersions, indicating that the state has a long decaying tail through a strongly coupling with the extended π or π^* states. In $(5,5)$ nanotube, the quasi-bound state discernible from the extended states is not found but the band gap changes depending on the type. In the type-II geometry, the mirror symmetry of the nanotube is maintained, which renders the nanotube strictly metallic [21].

As shown above, the site preference for functionalization is rather weak for typical radius of single-walled nanotubes and the random addition is more realistic than ordered ones [12]. To address this, we attach dichlorocarbene randomly with the degree of functionality ranging from 15 to 30%. The functionality ratio is defined by the number of Cl atoms divided by that of C atoms at the sidewall. For mutiple runs, we choose 2- and 4-unit supercell for zigzag and armchair nanotubes, respectively, and attach 5–12 dichlorocarbene randomly to the C–C bonds in the sidewall. Five configurations were selected for calculations with a condition that distances between atoms in different addends are bigger than 2 Å to avoid the steric hindrance. The computational results are summarized in Table 2. Due to the relatively small supercell, there are fluctuations in the computational results. The binding energy is a decreasing function of the modification ratio, which is due to the disruption of π-bonding network of the nanotube. The binding energy of each run is more or less uni-

form in the zigzag nanotubes, which can be understood by the similar energetics of type-I and type-II addition. The binding energy of metallic nanotubes are larger than those of semiconducting nanotubes, which is explained by the electron density at the Fermi level [22].

The energy gap is deduced from the band structure of each configuration. We observe almost direct band gap for all cases but the k-points at which minimum energy gap occurs are rather varied between samples. It is found that the energy gap of the metallic nanotube opens up over the whole range of ratio, at variance with that in [12]. This is due to the type-I addition which was completely excluded in [12]. On the other hand, the band gap of semiconducting nanotubes is *reduced* by 0.2–0.4 eV and the energy gap of metallic nanotube increase. This is due to the band formation of quasi-bound states within the original energy gap. Our results are in good agreement with the experimental observation of weakening of metallic oscillator strength in far-infrared absorption [9]. One interesting observation is that the average band gap is more or less uniform regardless of degree of functionality. The opposing effects of functionalization on the band gap of semiconducting and metallic nanotubes are similar to the results of bond-rotation defects [23].

In summary, we have calculated on the functionalized nanotube with dichlorocarbene as the addend. It is found that the effect of functionalization on the electronic structure of nanotube is strongly dependent on the sites to which the dichlorocarbene is attached. In the high level of modification ratio up to 30%, it is found that energy gap of semiconducting nanotube is reduced, but never closed, while those of metallic tubes are opened. This indicates that with the delicate control of modification ratio, it may be possible to engineer the band gap of single-walled nanotube to be semiconducting with the uniform energy gap.

Table 2
The binding energy and band gap of functionalized nanotubes with various degrees defined by $(Cl/C_{wall})\%$

Nanotube	15%		23%		30%	
	E_b (eV)	E_g (eV)	E_b (eV)	E_g (eV)	E_b (eV)	E_g (eV)
$(9,0)$	1.08	0.64	0.84	0.37	0.83	0.74
	1.08	0.73	0.91	0.52	0.76	0.42
	0.96	0.75	0.83	0.75	0.67	0.36
	0.91	0.14	0.79	0.54	0.58	0.23
	1.06	0.57	0.83	0.43	0.68	0.70
	1.02	**0.57**	**0.84**	**0.52**	**0.70**	**0.49**
$(10,0)$	0.82	0.08	0.79	0.62	0.67	0.65
	0.88	0.50	0.60	0.59	0.51	0.44
	0.84	0.52	0.56	0.30	0.54	0.11
	0.8	0.06	0.55	0.70	0.71	0.46
	0.89	0.39	0.54	0.43	0.57	0.51
	0.85	**0.31**	**0.61**	**0.53**	**0.60**	**0.43**
$(5,5)$	1.25	0.27	0.74	0.17	0.86	0.50
	0.89	0.12	0.85	0.05	0.78	0.50
	1.31	0.44	0.76	0.27	0.83	0.07
	1.19	0.51	0.88	0.12	0.56	0.05
	0.85	0.14	0.93	0.37	0.73	0.04
	1.10	**0.30**	**0.83**	**0.20**	**0.75**	**0.23**

The average values are given in boldface. The binding energy is per one dichlorocarbene.

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