

Chemical Reactivity of Single-Walled Carbon Nanotubes to Amidogen from Density Functional Calculations

Mingwen Zhao,^{*,†} Yueyuan Xia,[†] James P. Lewis,[‡] and Liangmo Mei[†]

Department of Physics, Shandong University, Jinan 250100, China, and Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602-4658

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We study the chemical reactivity of the sidewall of single-walled carbon nanotubes (SWNTs) (n, n), with n ranging from 5 to 16 using density functional theory calculations. We find that the exterior surface of SWNTs is reactive to amidogen, which can be chemically bound to a carbon atom, with the binding energy between 1.71 and 2.12 eV. The binding energy of SWNTs with amidogen decreases as the radius of the tubes increases. However, the interior surface of SWNTs is inert to amidogen, making them promising candidates as containers for the chemical reactions involving amidogens. The introduction of 7–5–5–7 topological defects into the wall of a (5, 5) SWNT improves the chemical reactivity of the tube wall. The bond between amidogen and the carbon atoms in the region of the topological defect can be further stabilized by about 1.05 eV. We also discuss the modification in the electronic properties of SWNTs caused by decoration of amidogen on the exterior surface.

Introduction

Single-walled carbon nanotubes (SWNTs) described as enroled graphene sheets exhibit interesting physical and chemical properties,^{1–4} making them very promising for application in various domains ranging from electron field emitters⁵ to nanodevices.^{6–8} The electronic structure of SWNTs can be either metallic or semiconducting, depending on their chiral vectors (n, m).^{2–4} Meanwhile, SWNTs are also unique among solid-state materials in that every atom is on the surface. Surface chemistry could therefore be critical to the physical properties of SWNTs and their applications. Moreover, the hybridization of the graphite σ , π , σ^* , and π^* states caused by the curvature of SWNTs^{2–4,9} makes a difference in the chemical reactivity on both the exterior surface and the interior surface of the tubes.

The chemical reactivity of the exterior surface of SWNTs to many kinds of molecules and atoms has been revealed both experimentally and theoretically.^{10–16} Molecules such as O_2 , H_2O , NO_2 , NH_3 , and H_2 will physisorb on the exterior surface through weak interactions with binding energies of less than 1.0 eV. This adsorption changes the electronic structure of SWNTs, and in turn imposes modifications in the electronic properties of the tubes. Thus, SWNTs as gas sensors^{8,14} are a promising application. Many kinds of atoms, such as H, F, K, Al, and N, can chemisorb on the exterior surface of SWNTs, changing the electronic properties of these tubes. The adsorption of K on the sidewall of SWNTs was found to enhance the conductivity of SWNTs.¹⁰ The p-doped feature of SWNTs caused by the adsorption of nitrogen atoms on the exterior surface of SWNTs, contrary to that of N-substituted SWNTs, has also been predicted on the basis of first-principles calculations.¹⁵

Recently, interest in the chemical reactivity on the sidewall of SWNTs has greatly increased to improve the solubility and

processibility of chemical functionalization in SWNTs.¹⁷ The main focus has been to couple the unique properties of SWNTs with those of other materials. Studies of chemical reactivity of SWNTs to free radicals including amidogen are therefore highly desirable. The exterior of the sidewall of perfect SWNTs is less reactive compared to other fullerenes, because there are no strongly curved regions that could serve as reactive targets for direct additions.¹⁸ But the introduction of defects, such as a topological defect, may locally change the chemical activity of SWNTs, which benefits the sidewall decoration.

In addition, compared with the exterior surface of SWNTs, the interior surface is less reactive and is predicted to be inert to nitrogen atoms.¹⁵ On the basis of this result, a promising application of closed SWNTs as containers for chemical radicals was proposed.^{15,19} However, the chemical reactivity on the interior surface of SWNTs to free radicals has not been reported so far and needs further investigation. In this paper, we study the chemical reactivity on both the exterior and interior surfaces of (n, n) SWNTs to an amidogen radical for n ranging from 5 to 16 using density functional theory calculations.

Theoretical Approach and Computation

Density functional (DF) calculations were performed by using an efficient *ab initio* tight-binding code known as FIREBALL.^{20–23} This code uses a localized linear combination of an atomic basis set for the description of valence electrons and a norm-conserving nonlocal pseudopotential for the atomic core. We employed a double numerical (DN) basis set, ss^*pp^* , for nitrogen and a single numerical (SN) basis set, sp^3 , for carbon. These basis sets have been revealed to provide reasonable accuracy with a low demand on computation resources.²⁴ The localized pseudoatomic orbitals were constructed with a confinement radius of 3.70 a_B for the 2s state and 4.10 a_B for the 2p state of nitrogen, while the 2s and 2p orbitals of carbon were confined in spheres with radii of 4.00 and 4.40 a_B , respectively. For the exchange correlation potential, we used the generalized gradient approximation (GGA) corrections in

* To whom correspondence should be addressed: E-mail: zmw@sdu.edu.cn.

[†] Shandong University.

[‡] Brigham Young University.

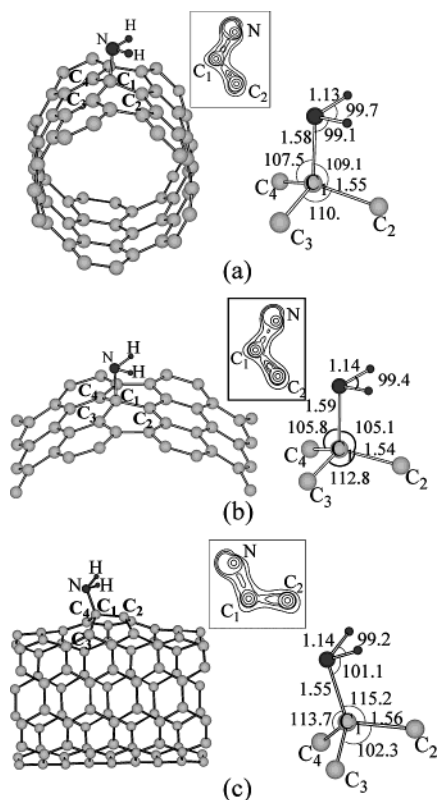


Figure 1. Equilibrium configurations of SWNTs with an adsorbed amidogen on their exterior surface: (a) (5, 5) SWNT; (b) (10, 10) SWNT; (c) (5, 5) SWNT with a 7-5-5-7 topological defect. The electron density contours in the plane containing the nitrogen atom of the adsorbed amidogen and two carbon atoms, C_1 and C_2 , on the sidewall of the (5, 5) SWNTs, as well as some structural parameters, are also presented in the insets of this figure.

the form of Becke,²⁵ Lee, Yang, and Parr.²⁶ Periodical boundary conditions along the tube axis were used for SWNTs under study. We chose supercells with 10 layers of carbon atoms for these SWNTs. To determine the equilibrium structures of the systems under study, we relaxed all the atomic coordinates, reaching the energy convergence within 1.0×10^{-3} eV/atom. The binding energy $E_b(\text{SWNT}-\text{NH}_2)$ between SWNT and amidogen was obtained from the expression $E_b = E_t(\text{SWNT}) + E_t(\text{NH}_2) - E_t(\text{SWNT} + \text{NH}_2)$, where the total energy of a SWNT adsorbed with an amidogen is $E_t(\text{SWNT} + \text{NH}_2)$, the total energy of a SWNT is $E_t(\text{SWNT})$, and the total energy of an isolated amidogen is $E_t(\text{NH}_2)$.

Results and Discussion

The average bond length of a C-C bond in a (5, 5) SWNT was found to be 1.45 Å in our calculations, slightly longer than the result based on other methods, 1.42 Å.^{27,28} When an amidogen adsorbs on the exterior surface of a (5, 5) SWNT, local distortion takes place in the region around the adsorption site, as shown in Figure 1a. The carbon atom (C_1) extrudes out with its distance to the nearest carbon atoms (C_2 , C_3 , C_4) elongated to about 1.55 Å. The distance between the carbon atom (C_1) and the nitrogen atom in the adsorbed amidogen is 1.58 Å, which is much longer than the bond length of a single C-N bond, 1.36 Å, and that of a typical double C=N bond, 1.32 Å (in cytosine).²⁹

The electron density contours in the plane containing the nitrogen atom of the adsorbed amidogen and two carbon atoms, C_1 and C_2 , on the sidewall of the (5, 5) SWNTs are shown in the inset of Figure 1a. Clearly, a covalent C-N bond is formed

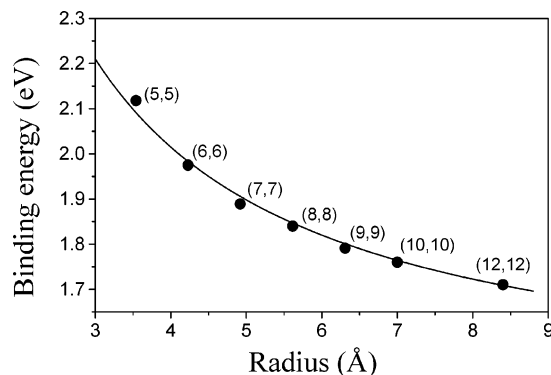


Figure 2. Variation of the binding energy (eV) between the exterior surface of SWNTs and an amidogen with the radius of the tubes. The solid line is the fit to $E_b = E_0 + D/R$ (see the text).

between the carbon atom C_1 and the nitrogen of amidogen. The bonding energy of this C-N bond is about 2.12 eV, in good agreement with the result of 2.11 eV obtained from the DF calculations within the SIESTA package.³⁰ This indicates that the adsorption of amidogen on a (5, 5) SWNT is chemical. This is quite different from the physical adsorption of NH_3 molecules on (10, 0) SWNTs, which has a binding energy only 0.18 eV.¹⁴ The bond angles $\angle(C_2-C_1-C_3)$ and $\angle(C_2-C_1-N)$ are close to the standard bond angles of sp^3 hybridization (109°), indicating that the hybridization of carbon atom C_1 transfers from sp^2 to sp^3 through the adsorption of an amidogen. Apparently, there are three symmetric geometries of an amidogen adsorbing on the exterior surface of a (5, 5) SWNT around the 3-fold symmetry axis through the C-N bond. The difference in binding energies of these geometries is less than 0.003 eV. The rotational barrier around the symmetry-related geometry is about 90 meV from our calculations, significantly larger than the thermal energy at room temperature (26 meV).

The equilibrium structure of amidogen adsorbed on the exterior surface of a (10, 10) SWNT is shown in Figure 1b (local map), where the length of the C-N bond is 1.59 Å, slightly longer than that of the C-N bond in the (5, 5) SWNT. The stable 1.76 eV binding energy of amidogen adsorbed on the (10, 10) SWNT is also weaker compared to that on the (5, 5) SWNT. This is consistent with the difference of electron density contours where the overlap of electron clouds between the SWNT and the adsorbed amidogen is smaller for the (10, 10) SWNT than that for the (5, 5) SWNT.

The binding energies between the exterior surface of (n , n) SWNTs and an adsorbed amidogen for n ranging from 5 to 12 are represented by the solid circles in Figure 2. It is obvious that the binding energy of amidogen decreases with increasing radius (decreasing curvature) of the tubes, and will saturate at the value corresponding to the case of an amidogen adsorbing on a sheet of graphite. This suggests that an increase of the curvature of the carbon framework leads to a more pronounced pyramidalization of the sp^2 -hybridized C atoms and therefore an increased tendency to undergo addition reactions.¹⁸ The variation of binding energy in amidogen adsorption on the exterior surface of SWNTs, E_b , as a function of the tube radius R can be fitted to the data given by the expression $E_b = E_0 + D/R$, where E_0 is the binding energy of an amidogen adsorbed on graphite. The fitting parameters E_0 and D were calculated to be 1.39 and 2.50 eV Å. The value of E_0 obtained by extrapolation is in good agreement with that obtained by the calculation of an amidogen adsorbed on graphite. The fitting expression presented herein is quite similar to those of hydrogen, nitrogen, and aluminum atoms adsorbed on SWNTs.^{13,15,27}

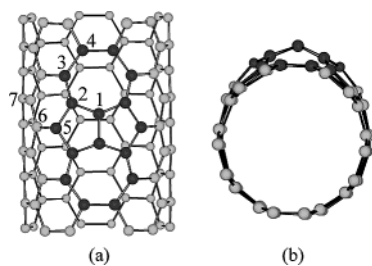


Figure 3. Configuration of a (5, 5) SWNT containing a 7-5-5-7 topological defect. The black balls in this figure represent the carbon atoms of the defect. (a) is the side view, and (b) is the top view.

TABLE 1: Binding Energy, E_b , of an Amidogen Adsorbed on the Exterior Surface of a (5, 5) SWNT with a 7-5-5-7 Topological Defect^a

| adsorption site | E_b (eV) | ΔE (eV) |
|---|------------|-----------------|
| NH ₂ adsorbed on carbon atom 1 | 3.172 | 1.054 |
| NH ₂ adsorbed on carbon atom 2 | 2.531 | 0.413 |
| NH ₂ adsorbed on carbon atom 3 | 2.322 | 0.204 |
| NH ₂ adsorbed on carbon atom 4 | 2.688 | 0.570 |
| NH ₂ adsorbed on carbon atom 5 | 2.494 | 0.376 |
| NH ₂ adsorbed on carbon atom 6 | 2.078 | -0.040 |
| NH ₂ adsorbed on carbon atom 7 | 2.182 | 0.064 |

^a ΔE is the difference in binding energy of an amidogen adsorbed on the exterior surface of a (5, 5) SWNT with and without a 7-5-5-7 topological defect.

In addition, SWNTs always contain many kinds of defects, such as pentagons, heptagons, vacancies, and dopants, which have been revealed to drastically modify the electronic and mechanical properties of these tubes.¹⁷ Among these defects, the 7-5-5-7 topological defect is a typical form which affects the properties of SWNTs.^{31,32} The equilibrium structure of a (5, 5) SWNT containing a 7-5-5-7 topological defect represented by black circles is shown in Figure 3. This defect causes remarkable distortion on the sidewall of the tube, where some carbon atoms extrude out, locally changing the curvature of the tube wall.

Table 1 lists the binding energies of amidogen adsorbed on different sites of the tube wall of a (5, 5) SWNT with a 7-5-5-7 topological defect, as shown in Figure 3a. Most of the binding energies increase except for that of amidogen adsorbed on the carbon labeled 6, which decreases. This is related to the differences in curvature of these sites from that of the perfect (5, 5) SWNT caused by the existence of a 7-5-5-7 defect. The adsorption of amidogen on the carbon labeled 1 of the tube wall has the highest binding energy, being 1.054 eV greater than that of amidogen adsorbed on a perfect (5, 5) SWNT. Moreover, the highest occupied molecular orbital (HOMO) of a (5, 5) SWNT with a 7-5-5-7 topological defect was found to localize in the two carbon atoms shared by the two pentagons (carbons labeled 1 and 8 in Figure 3a) rather than other sites. On the basis of these results, we predict that the most reactive sites of a (5, 5) SWNT with a 7-5-5-7 topological defect to amidogen are the two carbon atoms shared by the two pentagons.

The equilibrium configuration of amidogen on carbon 1 of the (5, 5) SWNT with a 7-5-5-7 defect (see Figure 3a) is presented in Figure 1c. The bond length of C-N is shorter than that of the C-N bond between a perfect (5, 5) SWNT and an adsorbed amidogen by about 0.03 Å. The overlap of electron clouds between carbon 1 and the adsorbed amidogen is also enhanced compared with the case in a perfect (5, 5) SWNT. These results are consistent with the higher binding energy between the adsorbed amidogen and the (5, 5) SWNT with a

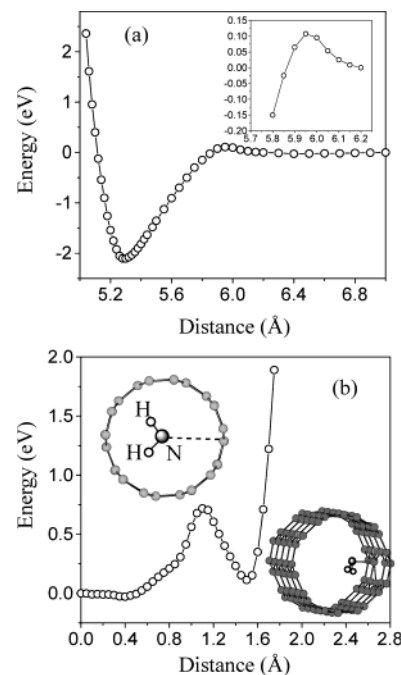


Figure 4. The relative energy of a (5, 5) SWNT containing an amidogen varies with the approach of the amidogen from (a) the exterior and (b) the center of the tube toward a carbon atom of the tube wall. The horizontal axis is the distance from the center of the tube to the nitrogen atom of the amidogen. The inset in (b) indicates the path of the amidogen approaching the interior wall of the tube.

defect. All these results clearly indicate that introducing a 7-5-5-7 topological defect into the sidewall of SWNTs can locally improve the chemical reactivity of SWNTs to amidogen and therefore facilitates the covalent sidewall functionalization of SWNTs.

To evaluate the chemical reactivity on the exterior surface of SWNTs to amidogen, we calculated the potential profile for an amidogen approaching carbon atom C₁ of the (5, 5) SWNT (as shown in Figure 1a) from the exterior of the tube (as shown in Figure 4a). It is clear that there is an energy barrier of about 0.12 eV for an amidogen adsorbing on the exterior surface of the (5, 5) SWNT. This barrier may be related to the energy cost of the sp² to sp³ hybridization transition of carbon atom C₁. Similar results have been revealed for the exohedral approach of a nitrogen atom to a carbon atom of C₆₀.³³ This value is much lower than the barrier of 1 eV for hydrogen atom chemically adsorbing on a perfect (5, 5) SWNT,³⁴ and higher than the result of ref 35, which demonstrated that the reaction barrier for hydrogen chemisorption on a torsionally strained nanotube is smaller compared to kT at 300 K.

The inertness on the interior surfaces of SWNTs and fullerenes to nitrogen has been revealed in the literature.^{15,33} We found that the energetically most favorable configuration of amidogen trapped inside a (5, 5) SWNT is when it locates in the center of the tube with the plane containing the three atoms of amidogen perpendicular to the tube axis, as shown in the top inset of Figure 4b. The adsorption of amidogen on the interior surface of the (5, 5) SWNT (bottom inset of Figure 4b) is energetically unfavorable relative to that at the center of the tube by about 0.14 eV from our calculations. Figure 4b plots the relative energy of amidogen as it approaches the tube wall. For each step, the distance between the nitrogen atom of amidogen and a carbon atom of the tube wall was fixed during geometry relaxation. We can see from this figure that the endohedral adsorption configuration of an amidogen on the (5,

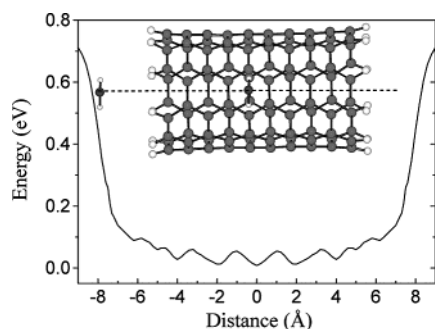


Figure 5. Energetics of a typical diffusion path calculated for an amidogen moving through an open (5, 5) SWNT. The inset in this figure indicates the diffusion path.

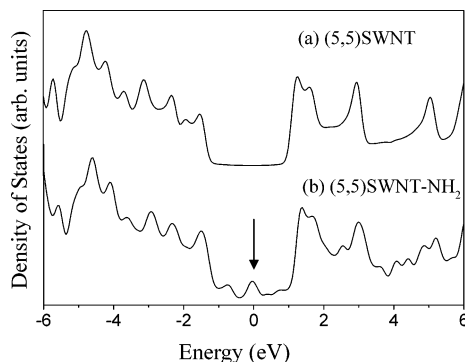


Figure 6. Density of states near the Fermi level of a bare (5, 5) SWNT and a (5, 5) SWNT with an adsorbed amidogen on the exterior surface. The arrow in this figure indicates the local state appearing near the Fermi level of the bare (5, 5) SWNT caused by the adsorption of an amidogen.

(5, 5) SWNT is metastable and the energy barrier between the most stable and metastable geometries is about 0.74 eV. It is obvious that the interior surface of the (5, 5) SWNT is inert to amidogen, in good contrast with its exterior surface. This difference is related to the hybridization of the graphite σ , π , σ^* , and π^* states caused by the curvature of the tubes,^{2–4,9} making the frontier orbitals localize on the exterior surface rather than on the interior surface. Moreover, the total energy of a (5, 5) SWNT containing amidogen is lower than the sum of the total energy of an empty (5, 5) SWNT and a free amidogen by about 1.12 eV. This means that an open-ended (5, 5) SWNT may soak up free amidogens into the tube. To understand the movement of amidogen through open-ended nanotubes, we have calculated the diffusion barriers for an amidogen inside the (5, 5) SWNT with the density functional technique. For the (5, 5) SWNT, both ends were stabilized by saturating the nanotube tips with hydrogen atoms (as shown in the inset of Figure 5). This structure was then relaxed prior to the insertion of amidogen. Figure 5 plots the energetics of a typical diffusion path calculated for an amidogen moving through an open (5, 5) SWNT. The main results are as follows. For the (5, 5) SWNT, there is no energy barrier for the amidogen to enter the open tube. The net decrease in the energy of the system shows that the nanotube actually acts as an attractor for the amidogen. Once inside the nanotube, the barrier for amidogen diffusion is about 50 meV. The inertness on the interior surface of SWNTs and the attraction of open tubes to amidogen make them promising candidates as containers for the chemical reactions involving amidogens.

As amidogen adsorbs on the exterior surface of the (5, 5) SWNT, the charge transfer from the (5, 5) SWNT to the adsorbed amidogen is -0.018 e, and a slight redistribution of atomic charges also takes place in regions near the adsorption

site. This may modify the electronic properties of SWNTs. The density of states (DOS) near the Fermi level of a bare (5, 5) SWNT and a (5, 5) SWNT with an adsorbed amidogen on its exterior surface (as shown in Figure 1a) are shown in Figure 6.³⁶ Clearly, a sidewall-decorated SWNT with an amidogen surface has an acceptor energy level (denoted by the arrow in this figure) in the band gap of the perfect SWNT. Therefore, these amidogen-decorated SWNTs can be regarded as p-type semiconductors because the electrons in the valance bands of SWNTs can transfer to the acceptor levels caused by adsorption of amidogens. Considering that amidogens can stably adsorb on the exterior surface of SWNTs, the sidewall decoration of amidogen is also an efficient way to improve its conductivity.

Conclusions

The exterior surface of SWNTs, especially small-radius SWNTs, is reactive to amidogen, and amidogen can chemically adsorb on it with a binding energy of 2.12 eV for a (5, 5) SWNT. The chemical reactivity of SWNTs to amidogen can also be further improved by introducing a 7–5–5–7 topological defect into the tube wall, and therefore facilitates the covalent sidewall functionalization of SWNTs. Contrary to the exterior surface, the interior surface of SWNTs is inert to amidogens, making the tubes promising candidates as containers for chemical reactions involving amidogen. The complexes of SWNTs with adsorbed amidogens are predicted to have the character of p-type semiconductors.

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