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ORIGINAL PAPER

Adsorption properties of SCN^- on (6,0), (7,0), (8,0), and Al-doped (6,0) zigzag single-walled carbon nanotubes: a density functional study

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Abstract The behavior of the thiocyanate anion (SCN^-) adsorbed on the external surface of H-capped (6,0), (7,0), (8,0), and Al-doped (6,0) zigzag single-walled carbon nanotubes was studied by using density functional calculations. Geometry optimizations were carried out at the B3LYP/6-31G* level of theory using the Gaussian 03 suite of programs. We present the nature of the SCN^- interaction in selected sites of the nanotubes. Our results show that the pristine carbon nanotubes cannot significantly detect SCN^-. The calculated binding energy of the Al-doped (6,0) single-walled carbon nanotubes indicated that SCN^- can be adsorbed significantly on the C and Al sites and these nanotubes can therefore be used for SCN^- storage. Binding energies corresponding to adsorption of SCN^- on the Al site in the Al-doped (6,0) single-walled carbon nanotubes was calculated as –286.38 kJ mol^{-1}. The calculated binding energies for SCN^- in N-down orientation are higher than those in S-down orientation for all of the configurations. More efficient binding could not be achieved by increasing the nanotube diameter. We also report the effects of SCN^- adsorption on the electronic properties of the nanotubes.

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Keywords Carbon nanotube · Adsorption · Binding energy · DFT

Introduction

Since the discovery of carbon nanotubes (CNTs) [1], single-walled carbon nanotubes (SWCNTs) have attracted great interest owing to their physical and chemical properties [1–3] and applications as novel materials [4, 5]. SWCNTs have a wide range of applications in nanoelectronics, nanoscaling biotechnology, and biosensors [3, 6–9]. Because of their size, large surface area, and hollow geometry, SWCNTs are being considered as prime materials for gas adsorption [10–14], biological, chemical, and electromechanical sensors, and nanoelectronic devices [15–17]. For example, CNTs have been experimentally investigated for the detection of gas molecules [18–20], organic vapors [21, 22], biomolecules, and different ions [23–25]. The doped or defective CNTs improved sensitivity when used in detecting molecules like CO, H_2O, 1,2-dichlorobenzene, or gaseous cyanide and formaldehyde [26–28]. The possibilities of using chemically doped CNTs as highly sensitive gas sensors are also under intensive investigation [18, 29]. Moreover, electronic conductance of a CNT semiconductor can be changed upon exposure to gas molecules, serving as a basis for nanotube molecular sensors.

Sensitivity of CNTs to the thiocyanate anion (SCN^-) has been indicated by quantum mechanics calculations. The determination of the structure of adsorbed SCN^- on CNT surfaces is important for understanding its bonding and reactivity in catalysis and other surface phenomena. The thiocyanate anion, a particularly stable species, has been generated by the reaction between CS_2 and NH_2^-

species. Also, SCN$^-$ can be generated by the reaction $CH_3SCN + e^- \rightarrow SCN^- + CH_3\cdot$ [30, 31].

The study of the chemical reactions of the thiocyanate anion on CNT surfaces is of scientific interest because SCN$^-$ is important in the atmosphere and environmental issues; moreover, SCN$^-$ exists in interstellar ice and dust clouds [32]. However, to our knowledge, no experiments and theoretical investigation have been reported on adsorption of SCN$^-$ on CNT surfaces. The understanding of the physisorption of SCN$^-$ on CNT surfaces is important for SCN$^-$ storage. In this study, we report the results of density functional model calculations on the physisorption of SCN$^-$ on (6,0), (7,0), (8,0), and Al-doped (6,0) zigzag SWCNTs with two molecular orientations, N- and S-down, at four distinct sites.

Results and discussion

SCN$^-$ can approach the nanotube walls from outside (out), which is the most common case, and from the inside (in). Zigzag configurations of (6,0), (7,0), and (8,0) SWCNTs have two different C–C bonds (C1–C2 and C2–C3; Fig. 1a, b; Table 1). For the adsorption of SCN$^-$ (N-down and S-down) on the CNTs, we considered four possible sites [i.e., the C site (center site) above the hexagon, the C2, C3 sites above the carbon atoms, and the Z site above the zigzag and axial C–C bond] as described in Fig. 1a and b. The notation N-down and S-down denotes an SCN$^-$ perpendicular to the surface via N and S, respectively. The Al-doped (6,0) SWCNTs have two different Al–C bonds (Al–C2 and Al–C6; Fig. 1c, d; Table 1). For the adsorption of SCN$^-$ (N-down and S-down) on the CNTs, we considered three possible sites (i.e., the Al site above the aluminum atom, and the C2, C6 sites above the carbon atoms) as described in Fig. 1c and d.

We limited our analysis to the interaction of SCN$^-$ with the nanotubes' outer walls. Considering each site and configuration, we ended up with 16 different approaches of SCN$^-$ to the CNTs walls. For each of these cases we investigated the CNT–SCN$^-$ potential energy surface (PES). The binding energies of SCN$^-$ (N-down and

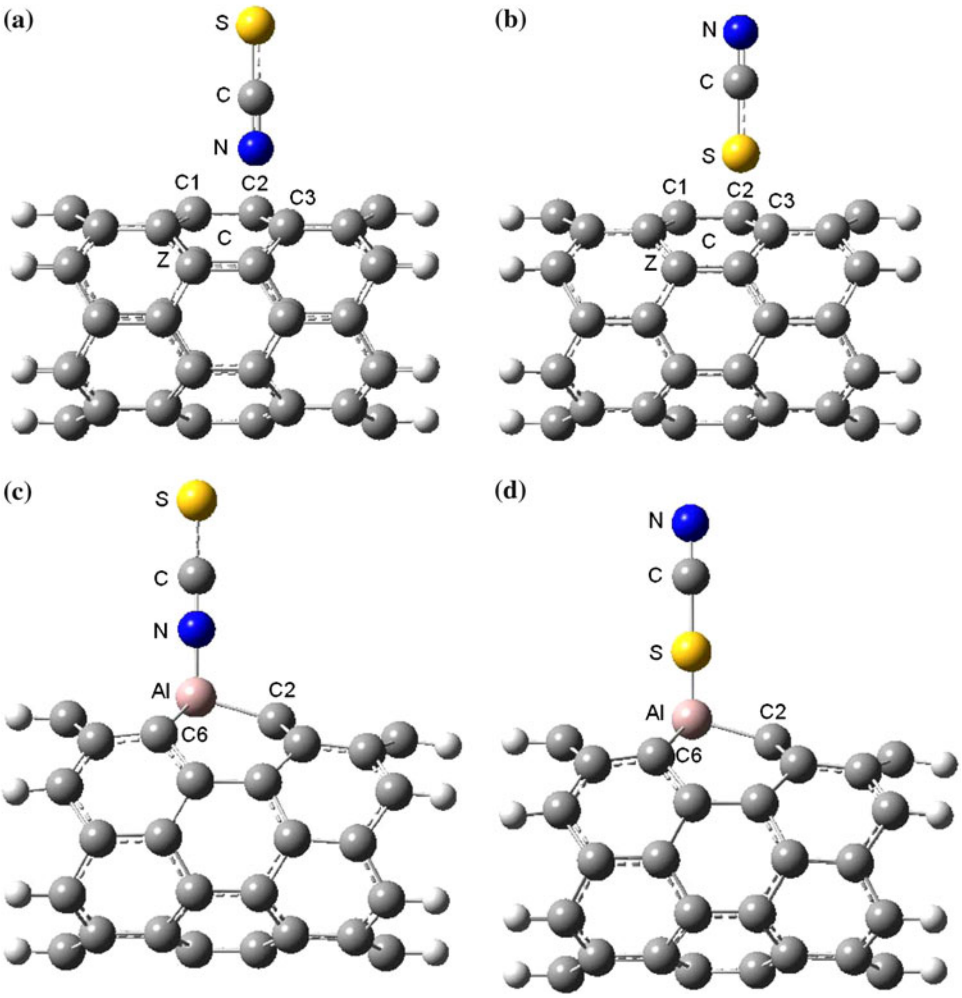

Fig. 1 **a**, **b** Adsorption configurations of SCN$^-$ (N-down and S-down) on CNTs. **c**, **d** Adsorption configurations of SCN$^-$ (N-down and S-down) on Al-doped (6,0) SWCNTs

Table 1 Binding energy value/kJ mol^{-1}, band gap/eV of pristine CNTs, and equilibrium distance (rd)/Å of SCN$^-$ on zigzag (6,0), (7,0), (8,0), and Al-doped (6,0) CNTs

Model	Length/Å	Band gap/eV	Configuration		Site			
					C2	C3	Z	Center
(6,0)	C1–C2 = 1.435	0.44	N-down	Binding energy	−26.08	−17.14	−15.94	−17.96
	C2–C3 = 1.431			rd	3.0	3.0	3.0	3.0
			S-down	Binding energy	−13.74	−6.03	−16.67	−13.16
				rd	3.5	3.5	3.5	5.0
(7,0)	C1–C2 = 1.431	0.5	N-down	Binding energy	−23.91	−19.38	−21.46	−21.68
	C2–C3 = 1.430			rd	4.0	3.0	4.0	3.0
			S-down	Binding energy	−18.05	−16.66	−20.80	−14.94
				rd	4.0	4.0	3.5	4.5
(8,0)	C1–C2 = 1.438	0.42	N-down	Binding energy	−18.59	−19.91	−19.61	−19.36
	C2–C3 = 1.424			rd	3.0	3.0	3.0	3.0
			S-down	Binding energy	−18.20	−18.20	−18.39	−16.19
				rd	4.0	3.5	3.5	3.5
Al-doped (6,0)	Al–C2 = 1.853	$\alpha = 0.54$	N-down		C2	C6	Al	–
	Al–C6 = 1.896	$\beta = 0.73$		Binding energy	−86.70	−36.19	−286.38	–
				rd	2.5	3.0	2.0	–
			S-down	Binding energy	−83.26	−35.88	−90.69	–
				rd	2.5	3.0	3.0	–

S-down) at the four sites on the zigzag configurations of (6,0), (7,0), (8,0), and at the three sites on the Al-doped (6,0) SWCNTs are plotted in Fig. 2, and the binding energy with the equilibrium distance in each case is summarized in Table 1.

In all pathways for the zigzag (6,0), (7,0), and (8,0) the potential is attractive presenting a well of maximum −27 kJ mol^{-1}, which does not characterize a chemisorption process. The binding energies obtained from these calculations are slightly dependent on orientations and locations of SCN$^-$, and the interaction becomes rapidly repulsive as the molecule approaches the CNT wall. The calculated binding energy (BE) of the CNTs indicated that SCN$^-$ cannot significantly be adsorbed on the sites, BE for the sites have very small differences in total energy (<12 kJ mol^{-1}), and the calculated BE for SCN$^-$ in N-down is more than that in S-down. The most stable configuration of SCN$^-$ for N-down in the (6,0) CNT is the C2 site, the perpendicular approach of SCN$^-$ (N-down) to the (6,0) CNT wall on the upper carbon atom, and the current calculation shows that the adsorption energy for this site is −26.08 kJ mol^{-1} with equilibrium distance (rd) 3.0 Å.

The most stable configuration of SCN$^-$ for N-down in the (7,0) and (8,0) CNTs are the C2 and C3 sites. The current calculation showed that the adsorption energies for these sites are −23.91 and −19.91 kJ mol^{-1} with rd of 4.0 and 3 Å, respectively. We observed that when the CNT diameter increases, the BE of SCN$^-$ at each particular site of the interaction is different. For example, SCN$^-$ (N-down) binds on the Z site of a (6,0) CNT with −15.94 kJ mol^{-1}, whereas it binds on the Z site of a (7,0) and (8,0) CNT with −21.46 and −19.61 kJ mol^{-1}. An interesting conclusion that can be drawn from these pathways is that only the type of the tube (CNT) plays an important role in determining the BE of SCN$^-$ and not the diameter of the tube as observed in previous cases [33]. All the results are clearly demonstrated in Table 1. The results show that pure CNTs cannot significantly detect SCN$^-$, because it cannot be adsorbed on the surface completely. Therefore to solve this problem, we used the Al-doped (6,0) SWCNTs for the adsorption of SCN$^-$, because sensitivity of the single wall carbon nanotubes can be increased substantially through either doping technology or surface engineering [34–36]. The calculated BE of the Al-doped (6,0) SWCNTs indicated that SCN$^-$ can be adsorbed significantly on the C and Al sites, and the calculated BE for SCN$^-$ in N-down is higher than that in S-down. The most stable configuration of SCN$^-$ for N-down in the Al-doped (6,0) CNT is the Al site, the perpendicular approach of SCN$^-$ (N-down) to the Al-doped (6,0) CNT wall, and the current calculation shows that the adsorption energy for this site is −286.38 kJ mol^{-1} with rd of 2.0 Å, which characterizes a chemisorption process.

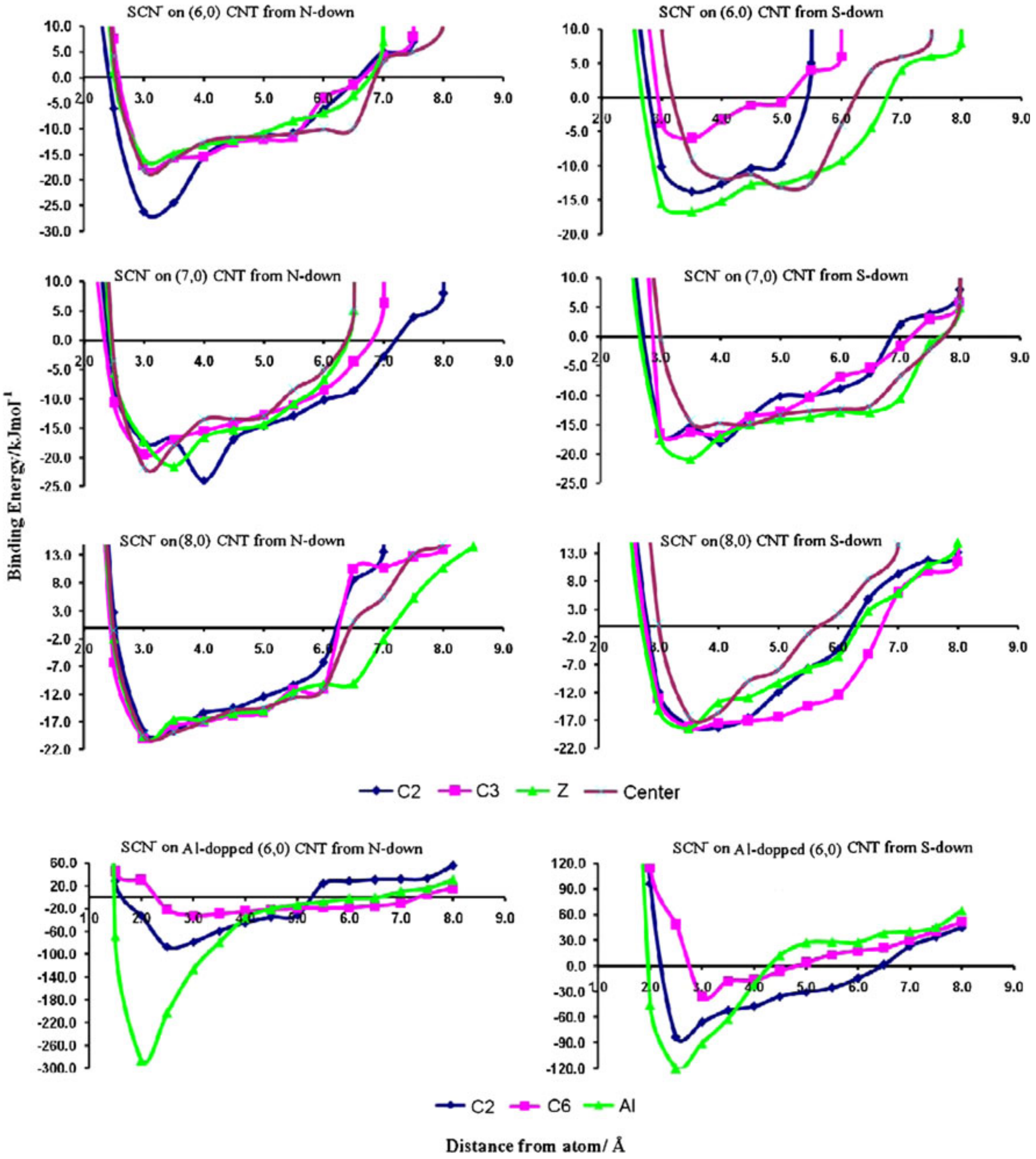

Fig. 2 Binding energy curves of SCN⁻ (S-down and N-down) adsorption at C2, C3, Z, and center sites on zigzag (6,0), (7,0), and (8,0) CNTs and at C2, C6, and center on Al-doped (6,0) SWCNTs

Electronic properties

Finally, we studied the influence of SCN⁻ adsorptions on the electronic properties of the CNTs. The total densities of states (TDOS) of these tubes are shown in Fig. 3. As is evident from Fig. 3, the calculated band gaps of the clean perfect (6,0), (7,0), and (8,0), zigzag SWCNTs are 0.44, 0.50, and 0.42 eV and the calculated band gaps of the Al-doped (6,0) zigzag SWCNTs for α and β molecular orbitals are 0.54 and 0.73 eV. The effects of SCN⁻ on adsorption energies in the CNTs relate to their electronic structure. When SCN⁻ is adsorbed on the CNTs, the interaction between them being weak, the electronic properties of these tubes are changed obviously and the band gaps are calculated as about 0.40, 0.29, and 0.35 eV. The DOS of these tubes show some significant changes due to SCN⁻ adsorptions in the gap regions of the TDOS plots. Therefore, the adsorption of SCN⁻ on the CNTs slightly decreases the energy gap of the pristine CNTs, and increases their electrical conductance. But for the Al-doped (6,0) zigzag SWCNTs, the interaction between SCN⁻ and the Al-doped CNT is much further from the interaction of

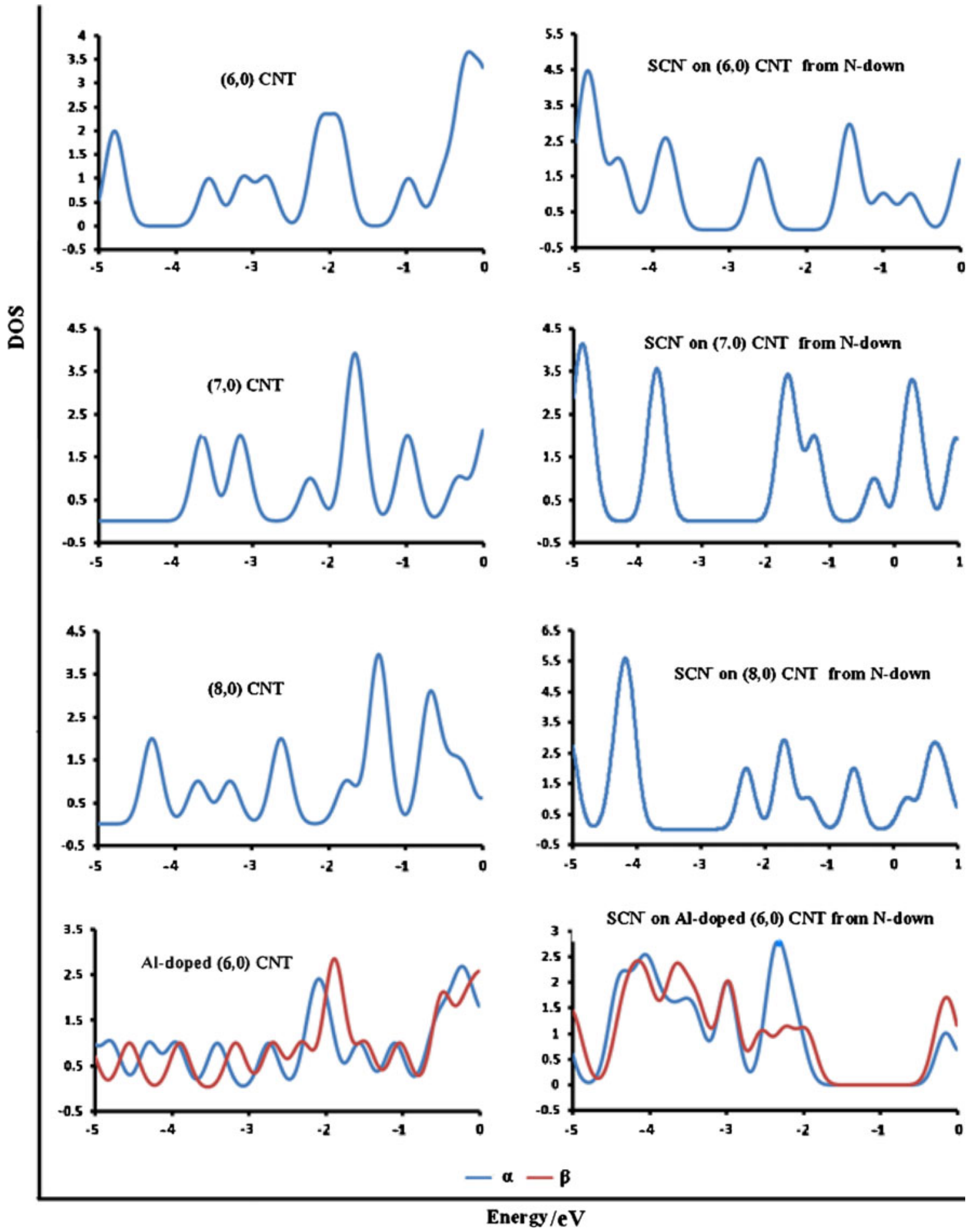

Fig. 3 Total densities of states (TDOS) for different models of the CNTs

between SCN$^-$ and the CNTs. The DOS of the Al-doped CNT show significant changes due to SCN$^-$ adsorptions in the gap regions of the TDOS plots. Therefore, the band gap of the Al-doped CNT will change significantly. Band gaps of the Al-doped (6,0) zigzag SWCNTs for α and β molecular orbitals are calculated as 1.93 and 1.75 eV. However, the adsorption of SCN$^-$ on the Al-doped significantly increases the energy gap of the Al-doped CNTs, and reduces their electrical conductance.

Conclusions

We studied the adsorptions of SCN^- on zigzag configurations of (6,0), (7,0), (8,0), and Al-doped (6,0) SWCNTs by means of density functional theory (DFT) calculations. On the basis of our calculations, it seems that the pristine CNTs cannot significantly detect SCN^- because it cannot be adsorbed on the pure CNT surface completely. The calculated BE of the Al-doped (6,0) SWCNTs indicated that SCN^- can be adsorbed significantly on the C and Al sites and the Al-doped (6,0) SWCNTs can therefore be used for SCN^- storage. We compared all the BE curves of SCN^- interacting with all possible sites of adsorption on nanotube walls in several structural configurations. The calculated BE for SCN^- in N-down configuration is higher than that in S-down. We showed that by increasing the nanotube diameter, more efficient binding could not be achieved. Furthermore, in this study, the presence of SCN^- on the Al-doped CNTs increases their energy gap and reduces their electrical conductance.

Methods

In the present work, the adsorption behavior of SCN^- on the SWCNTs was studied by using representative models of (6,0), (7,0), (8,0), and Al-doped (6,0) zigzag SWCNTs, in which the ends of the nanotubes are saturated by hydrogen atoms. The hydrogenated (6,0), (7,0), (8,0), and Al-doped (6,0) zigzag SWCNTs consist of 60 ($C_{48}H_{12}$), 70 ($C_{56}H_{14}$), 80 ($C_{64}H_{16}$), and 60 ($C_{47}H_{12}Al$) atoms. In the first step, the structures were allowed to relax by all atomic geometrical parameters in the optimization at the DFT level of B3LYP exchange-functional and 6-31G* standard basis set. The BE of SCN^- on the CNTs wall was calculated as follows:

$$BE = E_{CNT-SCN^-} - (E_{CNT} + E_{SCN^-}) \quad (1)$$

$$BE = E_{Al-CNT-SCN^-} - (E_{Al-CNT} + E_{SCN^-}) \quad (2)$$

where $E_{CNT-SCN^-}$ was obtained from the scan of the potential energy of the CNTs–SCN^-, E_{CNT} is the energy of the optimized CNT structure, and E_{SCN^-} is the energy of an optimized SCN^-. All calculations were carried out by using the Gaussian 03 suite of programs [37].

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