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Effect of curvature and chirality for alkanethiols interaction with single-walled carbon nanotubes: *ab initio* investigation

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Abstract: *First-principles* calculations have been performed to investigate the dependence of alkanethioles interaction with single-walled carbon nanotubes (SWCNTs) on nanotube's type, curvature and chirality. The *ab initio* calculations at the density functional level of theory can provide useful information about the nature of alkanethioles adsorption in SWCNT selected sites and the binding under different curvatures and chiralities of the tube walls. The author's results have shown that the affinities of ethanethiol molecule for the semiconducting and metallic SWNTs are rather close, about 10% stronger in the former case. Our *first-principles* calculations indicate also that the binding energy of alkanthiols is increased for adsorption on larger-diameter CNTs with lower-curvature while, it is decreased for adsorption on the larger-chiral angle one.

Keywords: Alkanethiols; SWCNTs; Chirality; Curvature; Adsorption; Density functional theory.

Introduction

Carbon nanotubes (CNTs) are considered to possess unique properties compared with the corresponding bulk materials due to the quantum confinement effect, and have great potential applications in both nanotechnology and nanoscale engineering [1–5]. A number of recent investigations focus on the interaction between carbon nanotubes and organic compounds such as alkylamines [6–10] and organo-sulfur compounds [11, 12], to form hybrid materials that benefit from the electrical and mechanical properties of CNTs. Aspects of particular interest to the organo-sulfur compounds, particularly alkanethiol molecules (C_nH_{2n+1}–SH), are the covalent functionalization of the CNT probe tip for chemical force microscopy [3, 4] and increasing the solubility of single-walled CNTs [5–7], their self-assembly on metal surface [13, 14] which have provided model systems for understanding fundamental physical, chemical, and biological interfacial processes [11, 12]. Particular attentions have been devoted to nanoscale field-effect transistors (FETs) since they can serve as high-mobility transport channels [15]. However, precise position and alignment of CNTs is still not available in current growth and assembly technology. Therefore, there is a growing body of research on the development of carbon nanotubes network FETs [16, 17]. Electrical detection of deoxyribonucleic acid and biomolecules using carbon nanotubes network FETs have been demonstrated [18, 19]. Such devices have been also found to be sensitive to various gases and thus can be used as chemical sensors [20]. The sensing behaviors of these network devices strongly depend on the electrical characteristics in their as-produced state. Therefore, optimizing the performance of these devices requires a better understanding of the method for adjusting their electrical characteristics prior to further applications in electronics and molecular detection [21]. In one recent work, Roh *et al*. [12] investigated the adsorption behaviors of alkanethiol molecules on the surface of single-walled CNT with vibrational spectrophotometer. They confirmed their experimental results with the molecular dynamics simulation calculations. They reported that alkanethiol molecules adsorbed strongly on the SWNT surface and suggested that the active adsorption sites in the nanotube surface might be Stone–Wales defects (5–7 ring defects) [12]. We investigated, in the previous work [22], the adsorption of alkanethiol molecules, such as ethanthiol and buthanthiol, on the zigzag (10, 0) single-walled carbon nanotube with and without structural defects. The obtained results indicated that alkanethiol molecules adsorbed rather strongly on the single-walled

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carbon nanotubes surface and introduce defects do not have an important contribution to the adsorption mechanism of alkanethiols on SWNTs.

The main purpose of the present study is to model the adsorption of alkanethiol in SWNTs with tubes of different diameters and types or, in other words, *curvature* and *chirality*, by using appropriate simulation techniques. It is obvious that theoretical calculations in this field can be extremely useful in attaining a thorough and quantitative understanding of the elementary steps concerning the gas adsorption phenomenon that takes place in the aforementioned materials.

Among the well-established computational techniques are used to study molecular adsorption in porous materials is the density functional theory (DFT), which is a first principles quantum mechanics method. Generally, the theoretical calculations employed in this research field can be classified according to the approximations that they are based on [23]. In the *ab initio* theoretical studies, both chemisorption [24, 25] and physisorption [26, 27] were investigated within the DFT method. Only with the use of high accuracy computational techniques we can understand the nature of the alkanethiol interaction with the SWNts.

Computational methods

The aim of the *ab initio* study is to calculate the binding energy between the alkanethiols and the walls of carbon nanotubes of different diameters and chiralities. In order to treat our system with high accuracy *ab initio* methods we employed a supercell approach in all our calculations. In the direction perpendicular to the tube axis, a distance of at least 16 Å was kept between repeated units to avoid interactions between adjacent CNTs. We used a 1 × 1 × 3 Monkhorst–Pack grid for *k*-point sampling of the Brillouin zone.

The structural optimizations of carbon nanotubes and alkanethiols are carried out using the recently developed DFTB+ code [28-31]. The Slater-Koster (S-K) type parameter set [32] was implemented. The dispersion corrects for the van der Waals interaction have also been considered via the Slater-Kirkwood type model [33].

The total energy calculations for the interaction between CNTs and alkanethiols are carried out using the *ab initio* DFT code SIESTA [34, 35]. We used the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange-correlation potential [36]. The core electrons are represented by improved Troullier-Martins pseudopotentials, and a numerical atomic orbital basis with polarization is used for the valance electrons. All total energy calculations were done with a double-ζ plus polarization (DZP) basis set.

The adsorption energy E_{ads} of an alkanethiol molecule on the nanotube wall can be calculated as follows:

$$E_{ads} = E_{CNT-A} - E_{CNT} - E_{A} \qquad (1)$$

where E_{CNT-A} is obtained from the potential energy of the SWNT-alkanethiol molecule structure, E_{CNT} is the energy of the pure CNT, and E_A is the energy of the isolated alkanethiol molecule.

Results and discussion

We model the interaction of alkanethiols with SWNTs, using ethanethiol (C2H4)-SH as a particular example. Armchair (6, 6) structure is considered here as typical metallic nanotube with similar diameter (7.83 Å) with zigzag (semiconducting) (10, 0) nanotube (8.14 Å) which used in the previous work [22]. Ethanethiol–SWCNT system is optimized starting from two different initial geometrical configurations. In all cases the thiol (-SH) active site is initially oriented so that the sulfur atom is the closest to the nanotube, and the free electron pair of sulfur is directed perpendicular to the SWNT surface. In the starting configuration A, the sulfur atom of ethanethiol is situated over a hexagon of carbon atom of the nanotube, with molecular axis parallel to the tube axis while in the configuration B, the molecular axis is perpendicular to the tube axis. The orientation schemes employed in modeling ethanethiol adsorption are represented in figure 1.

After full structural optimization of the considered systems, we find that the ethanethiol molecule prefers to be adsorbed on the hexagon of carbon nanotube with a parallel orientation of molecular axis with respect to the tube axis, configuration A. The calculated binding energy for the favorable energetically configuration and the equilibrium distance between the closest atom between carbon nanotube and ethanethiol are about –1.62 eV (–37.41 kcal/mol) and 2.130 Å, respectively. The relatively far equilibrium ethanethiol–carbon substrate separation and small binding energy suggest the involvement of only non-covalent interactions in the adsorption. The present results reveal also that alkanthiols are weakly bound to the outer surface of the nanotube, having adsorption energies comparable to that for amino acids, nucleic acid bases and gas molecules on carbon nanotubes [37 and 42]. Comparing the present results with those obtained for the ethanethiol/CNT (10, 0) system [22], we clearly see that the affinities of ethanethiol molecule for the semiconducting and

metallic SWNTs are rather close, about 10% stronger in the former case. We now investigate the adsorption of ethanethiol on the outer surface of the (13, 0) SWCNT. Similar initial orientations were selected for the ethanethiol molecule approaching the surface of the tube and then the similar calculations were carried out for the considered configurations. The orientation schemes employed in modeling ethanethiol adsorption on the (13, 0) SWCNT are shown in figure 2. Our first-principles calculation results show a binding energy of about -2.11 eV for the energetically most favorable state which corresponds to the parallel approach of the molecule with respect to the nanotube axis. From the obtained result for the (13, 0) nanotube, we clearly see that the binding energy of the alkanethiols is increased for adsorption on larger-diameter CNTs with low curvature. Although the high curvature allows the molecule to approach the surface more closely but however, the majority of the carbon atoms in high curvature CNT are actually further removed from the atoms of the ethanethiol than in the corresponding case on a low curvature CNT.

Figure 1. Model for two different adsorption states for an ethanethiol molecule on the sidewall of the (6, 6) CNT above a heptagon substrate with the molecular axis (a) parallel and (b) perpendicular with respect to the tube axis. Atom colors: grey—carbon, white—hydrogen, yellow—sulfur.

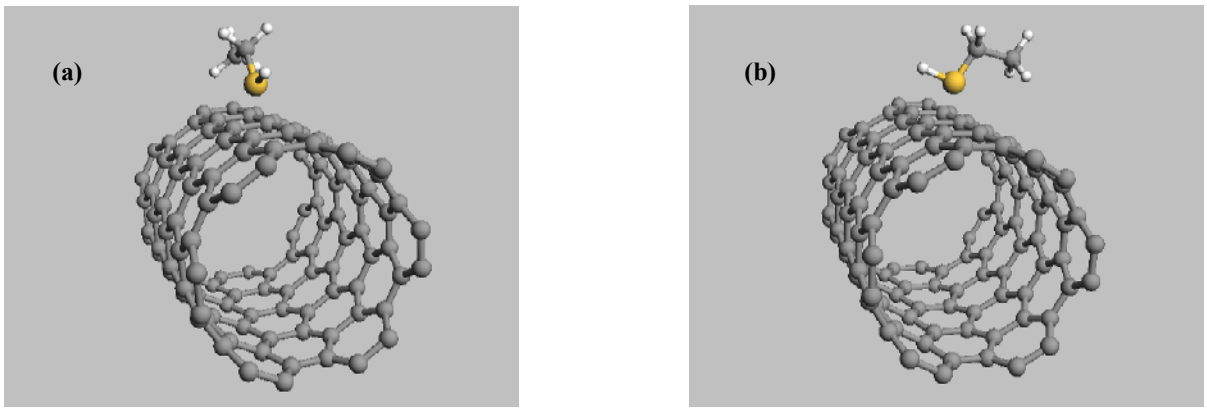
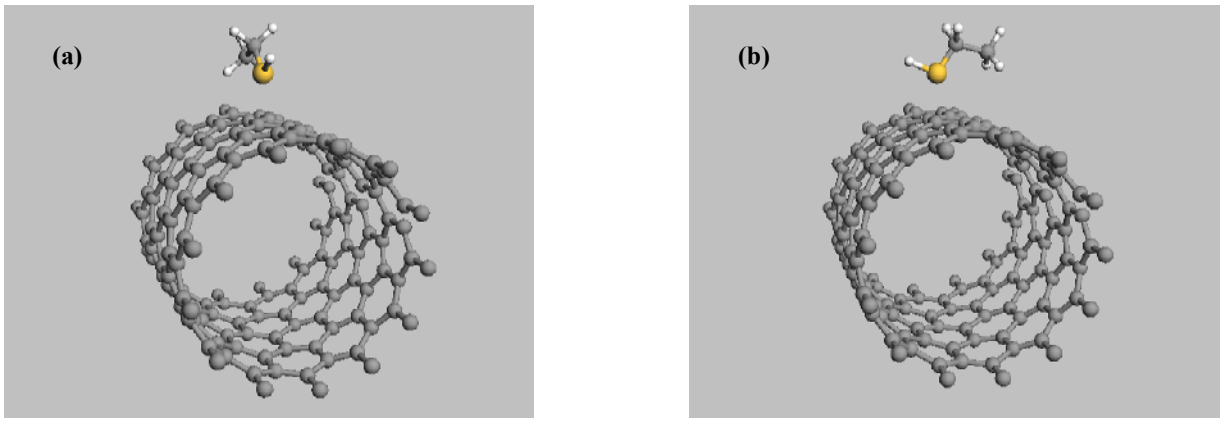


Figure 2. Model for two different adsorption states for an ethanethiol molecule on the sidewall of the (13, 0) CNT above a heptagon substrate with the molecular axis (a) parallel and (b) perpendicular with respect to the tube axis.



To study the effect of nanotube's chirality on alkanethiols adsorption on the carbon nanotube surface we have examined the binding of the ethanethiol on the (8, 4) nanotube which is a semiconducting nanotube with a chiral angle of about 19°. Following a similar procedure employed in the previous systems, we started by carrying out the optimization process for the ethanethiol molecule approaching to the sidewall of the (8, 4) SWCNT. The orientation schemes employed in modeling ethanethiol adsorption on the (8, 4) SWCNT are shown in figure 3. Our calculation results show that ethanethiol molecule prefers to interact with the hollow position of the tube with molecular axis perpendicular to the tube axis with a binding energy of -1.55 eV. It can be found from the obtained results that the binding energy of the alkanthiols is decreased for adsorption on the nanotubes with a larger-chiral angle ((8, 4) nanotube in comparison to the (10, 0) nanotube with a chiral angle of 0°)

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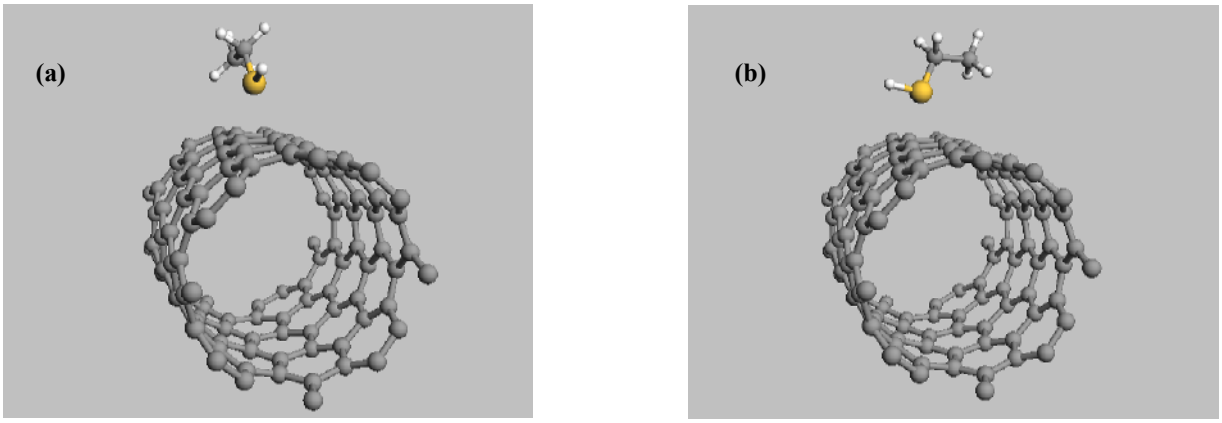
Figure 3. Model for two different adsorption states for an ethanethiol molecule on the sidewall of the (8, 4) CNT above a heptagon substrate with the molecular axis (a) parallel and (b) perpendicular with respect to the tube axis.



Conclusions

In this study, the *ab initio* method at the density functional level of theory (DFT) has been employed to investigate the dependence of alkanethiols interaction with single-walled carbon nanotubes (SWCNTs) on the nanotube's type, curvature and chirality. The use of *ab initio* DFT calculations provides in general useful information concerning the nature of alkanethiol adsorption in SWCNTs selected sites and the binding under different curvatures and chiralities of the tube walls.

The results obtained from this computational technique have shown that all the considered factors play rather an important role in the adsorption process. It can be found that the affinities of ethanethiol molecule for the semiconducting and metallic SWNTs are rather close, about 10% stronger in the former case. Our first-principles calculations indicated also that the binding energy of alkanthiols is increased for adsorption on the larger-diameter CNTs with lower-curvature while it is decreased for adsorption on the larger-chiral angle. Consequently, we could say that alkanethiols adsorbed rather strongly on the single-walled carbon nanotubes surface and they prefer to be adsorbed on the semiconducting nanotubes with lower-curvature (larger-diameter) and smaller-chiral angle.

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