ORIGINAL ARTICLE

Adsorption properties of CH$_3$COOH on (6,0), (7,0), and (8,0) zigzag, and (4,4), and (5,5) armchair single-walled carbon nanotubes: A density functional study

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Acetic acid;
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Adsorption

Abstract The behaviour of CH$_3$COOH molecule adsorbed on the external surface of H-capped (6,0), (7,0), and (8,0) zigzag, and (4,4), and (5,5) armchair single-walled carbon nanotubes was studied by using density functional calculations. Geometry optimizations were carried out at the B3LYP/6-31G** level of theory by using the Gaussian 03 suite of programs. We present the nature of the CH$_3$COOH interaction in selected sites of the nanotubes. Adsorption energies corresponding to adsorption of the CH$_3$COOH are calculated to be in the range 47–174 kcal mol$^{-1}$. The calculated adsorption energies for CH$_3$COOH in H-down orientation are higher than those in O-down and C-down orientation for all of the configurations. More efficient adsorption energies cannot be achieved by increasing the nanotube diameter. We also provide the effects of CH$_3$COOH adsorption on the electronic properties of the nanotubes.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) Iijima (1991), carbon nanotubes (CNTs) have attracted great interest owing to their extraordinary structural, mechanical, chemical, physical, and electronic properties (Iijima, 1991; Derycke et al., 2002; Liu et al., 1999). Numerous works have been performed to study the properties and applications of this fascinating novel material (Zurek and Autschbach, 2004; Nojeh et al., 2003). They have a wide range of application in nanoelectronics, nanoscaling biotechnology and biosensors (Zhou et al., 2002; Zhen et al., 1999; Baughman et al., 1999; Gao et al., 2003). Because of their size, large surface area and hollow geometry, single-walled carbon nanotubes (SWCNTs) are being considered as prime materials for gas adsorption (Rawat et al., 2007; Zhao et al., 2002; Gordillo, 2007; Choi et al., 2004; Byl et al., 2003), biological, chemical, electromechanical sensors and nanoelectronic device (Yang et al., 2007; Gowtham et al., 2007; Froudakis et al., 2003). For example, CNTs have

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been experimentally investigated for the detection of gas molecules (Kong et al., 2000; Belyarova et al., 2004; Peng et al., 2005), organic vapours (Li et al., 2003; Agnihoti et al., 2006), biomolecules and different ions (Chen et al., 2001, 2004; Kam and Dai, 2005). The key element that makes nanotubes so potentially useful as electrochemical storages is their structure (Hirsch et al., 2001). Recent studies have shown that the physical properties of single-wall carbon nanotubes (SWNTs) could be modified by adsorption of foreign atoms or molecules (Cheng et al., 2004; Peng et al., 2004; Cink et al., 2003). For example, it has been found that the exposure to O₂, NO₂ or NH₃ dramatically influences the electrical resistance and thermoelectric power of semi-conducting SWCNTs (Dag et al., 2003; Quang et al., 2006). Gas adsorption on carbon nanotubes and nanotube bundles is a great issue for both essential research and applied application of nanotubes. The adsorptive characteristics of SWCNTs in the gas phase enabled their use as gas sensors of pollutant gases, storage of fuels (Liu et al., 1999), and removal of hazardous pollutants from gas streams (Long and Yang, 2001a,b). The doped or defective CNTs can give improved sensitivity when used in detecting molecules similar to CO, H₂O, 1,2-dichlorobenzene or gaseous cyanide and formaldehyde (Peng and Cho, 2003; Fagan et al., 2004). The possibilities of using chemically doped CNTs as highly sensitive gas sensors are also under intensive investigation (Collins et al., 2000).

Furthermore, there are evidences indicating the great importance of molecular gaseous orientation on the energy of adsorption (Paredes et al., 2003; Sorescu et al., 2001). This effect is one of the major aspects of gas–nanotube interactions that has not been studied extensively. Sensitivity of CNTs to the acetic acid (CH₃COOH) has been indicated by quantum mechanics calculations. The determination of the structure of adsorbed CH₃COOH on CNT surfaces is important for understanding its bonding and reactivity in catalysis and other surface phenomena. However, to our knowledge, no experiments and theoretical investigation have been reported on adsorption of CH₃COOH on CNT surfaces. In this work, we theoretically studied the adsorption of CH₃COOH on various adsorption sites of the three zigzag (n,0) (n = 4,6,8) and two armchair (n,n), (n = 4,5) carbon nanotubes. Also three orientations of CH₃COOH molecules on the outside of the tubes, H-down, O-down, and C-down modes were considered.

2. Computational method

In the present work, adsorption behaviours of the CH₃COOH on SWCNTs were studied by using the representative models of (4,0), (6,0), and (8,0) zigzag, and (4,4), and (5,5) armchair single-walled CNTs in which the ends of nanotubes are saturated by hydrogen atoms. The hydrogenated (4,0), (6,0), and (8,0) zigzag, and (4,4), and (5,5) armchair single-walled CNTs have 48 (C₆₈H₄₈), 72 (C₇₀H₇₂), 80 (C₈₀H₈₀), 72 (C₇₀H₇₂), and 90 (C₉₀H₉₀) atoms, respectively. In the first step, the structures were allowed to relax by all atomic geometrical optimization at the DFT level of B3LYP exchange-functional and 6-31G* basis set. The optimized structures have diameters ~3.10, 4.66, 6.22, 5.39, and 6.73 Å, respectively. The adsorption energy of a CH₃COOH on the CNT wall was calculated as follows Eq. (1).

$$E_{ad} = (E_{CNT} + E_{CH₃COOH}) - E_{CNT-CH₃COOH}$$  

where $E_{CNT}$ is the energy of the optimized CNT structure, and $E_{CH₃COOH}$ is the energy of an optimized CH₃COOH and $E_{CNT-CH₃COOH}$ was obtained from the scan of the potential energy of the CNT–CH₃COOH. All the calculations were carried out by using the Gaussian 03 suite of programs (Frisch et al., 2003).

3. Results and discussion

CH₃COOH can approach the nanotube walls from outside (out), which is the most common case, and from inside (in). For the adsorption of the CH₃COOH (H-down, O-down and C-down) on the CNTs, we considered two sites (i.e., C site directly on top of carbon atoms, and B site on the middle of two nearest neighbour carbon atoms) as described in Fig. 1. The notation H-down, O-down and C-down denotes a CH₃COOH perpendicular to the surface via H, O and C, respectively.

We limited our analysis to the interaction of CH₃COOH with the nanotubes’ outer walls. Considering each site and configuration, we ended up with six different approaches of CH₃COOH to the CNT walls. For each of these cases we investigated the CNT–CH₃COOH potential energy surface (PES). The adsorption energies of the CH₃COOH (H-down, O-down, and C-down) at the two sites on zigzag (4,0), (6,0), and (8,0) and armchair (4,4), and (5,5) single-walled CNTs are plotted in Fig. 2, and the adsorption energy with the equilibrium distance in each case is summarized in Table 1.

In all pathways the potential is attractive, presenting a well of maximum ca. −175 kcal mol⁻¹, which is characteristic of a chemisorption process. The calculations showed that the obtained adsorption energies depend on orientations and locations of CH₃COOH, and the interaction becomes rapidly repulsive as the molecule approaches the CNT wall. And the calculated $E_{ad}$ for CH₃COOH in H-down is more than that

Figure 1  Adsorption modes of a CH₃COOH on CNTs: H-down (a), O-down (b), and C-down (c).
in O-down, and C-down. The most stable configuration of \( \text{CH}_3\text{COOH} \) for H-down in the (4,0) CNT is the C site, the perpendicular approach of \( \text{CH}_3\text{COOH} \) (H-down) to the (4,0) CNT wall on the upper carbon atom, and the current

Figure 2  Adsorption energy curves of \( \text{CH}_3\text{COOH} \) (H-down, O-down and N-down) adsorption at \( C \), and \( B \) sites on zigzag (4,0), (6,0), and (8,0), and armchair (4,4), and (5,5) CNTs. Distances are in Å.
calculation shows that the adsorption energy for this site is $-136.82$ kcal mol$^{-1}$ with equilibrium distance (rd) 1.0 Å. The most stable configurations of CH$_3$COOH for H-down in the (6,0), (8,0), (4,4), and (5,5) CNTs are the C, B, B, and C site, respectively. The current calculation showed that the adsorption energies for these sites are $-139.35$, $-174.31$, $-148.06$, and $-158.24$ kcal mol$^{-1}$ with equilibrium distance (rd) 1.0, 1.0, 1.0 and 1.0 Å, respectively. We observed that when the CNT diameter increases, the $E_{ad}$ of CH$_3$COOH at each particular site of the interaction is different. For example, CH$_3$COOH (H-down) binds on the B site of the (4,0) CNT with $-133.00$ kcal mol$^{-1}$, whereas it binds on the B site of the (6,0), (8,0), (4,4), and (5,5) CNTs with $-139.35$, $-126.15$, $-48.65$, and $-158.24$ kcal mol$^{-1}$, respectively. 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 adsorption energy of the CH$_3$COOH and not the diameter of the tube as observed in previous cases. All the results are clearly demonstrated in Table 1.

### 3.1. Electronic properties

Finally, we studied the influence of CH$_3$COOH adsorptions on the electronic properties of the CNTs. The calculated band gap energies of the clean perfect (4,0), (6,0), (8,0), (4,4), and (5,5) single-walled CNTs are about 2.64, 1.13, 2.59, 2.72, and 3.54 eV, respectively. The effects of the CH$_3$COOH on adsorption energies in the CNTs relate to their electronic structure. When the CH$_3$COOH is adsorbed on the CNTs, the interaction being strong, the electronic properties of these tubes are changed obviously, and the band gap for the CH$_3$COOH (8,0) zigzag CNT in the most stable configuration is calculated to be about 1.35 eV. Therefore, the adsorption of CH$_3$COOH on the CNTs further decreases the band gap of the pristine CNTs, and increases their electrical conductance.

### 4. Conclusions

We studied the adsorptions of CH$_3$COOH on zigzag configurations of (4,0), (6,0), and (8,0) and armchair (4,4), and (5,5) SWCNTs by means of density functional theory (DFT) calculations. On the basis of our calculations, it seems that pristine CNTs can be used as a CH$_3$COOH storage medium as long as CH$_3$COOH is adsorbed on the exterior walls of the CNTs because of the high adsorption energy. We compared all the adsorption energy curves of CH$_3$COOH interacting with all possible sites of adsorption on nanotube walls in several structural configurations. For the CNTs the calculated $E_{ad}$

<table>
<thead>
<tr>
<th>Model</th>
<th>Mode</th>
<th>Site</th>
<th>Adsorption energy ($E_{ad}$)</th>
<th>Equilibrium distance (rd) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4,0)</td>
<td>H-down</td>
<td>Adsorption energy</td>
<td>−136.82 kcal mol$^{-1}$</td>
<td>1.0 Å</td>
</tr>
<tr>
<td></td>
<td>O-down</td>
<td>Adsorption energy</td>
<td>−78.06 kcal mol$^{-1}$</td>
<td>1.5 Å</td>
</tr>
<tr>
<td></td>
<td>C-down</td>
<td>Adsorption energy</td>
<td>−67.77 kcal mol$^{-1}$</td>
<td>2.0 Å</td>
</tr>
<tr>
<td>(6,0)</td>
<td>H-down</td>
<td>Adsorption energy</td>
<td>−139.35 kcal mol$^{-1}$</td>
<td>1.0 Å</td>
</tr>
<tr>
<td></td>
<td>O-down</td>
<td>Adsorption energy</td>
<td>−105.83 kcal mol$^{-1}$</td>
<td>1.5 Å</td>
</tr>
<tr>
<td></td>
<td>C-down</td>
<td>Adsorption energy</td>
<td>−89.21 kcal mol$^{-1}$</td>
<td>2.0 Å</td>
</tr>
<tr>
<td>(8,0)</td>
<td>H-down</td>
<td>Adsorption energy</td>
<td>−126.15 kcal mol$^{-1}$</td>
<td>1.0 Å</td>
</tr>
<tr>
<td></td>
<td>O-down</td>
<td>Adsorption energy</td>
<td>−100.83 kcal mol$^{-1}$</td>
<td>1.5 Å</td>
</tr>
<tr>
<td></td>
<td>C-down</td>
<td>Adsorption energy</td>
<td>−89.48 kcal mol$^{-1}$</td>
<td>2.0 Å</td>
</tr>
<tr>
<td>(4,4)</td>
<td>H-down</td>
<td>Adsorption energy</td>
<td>−48.65 kcal mol$^{-1}$</td>
<td>1.0 Å</td>
</tr>
<tr>
<td></td>
<td>O-down</td>
<td>Adsorption energy</td>
<td>−121.00 kcal mol$^{-1}$</td>
<td>1.5 Å</td>
</tr>
<tr>
<td></td>
<td>C-down</td>
<td>Adsorption energy</td>
<td>−89.26 kcal mol$^{-1}$</td>
<td>2.0 Å</td>
</tr>
<tr>
<td>(5,5)</td>
<td>H-down</td>
<td>Adsorption energy</td>
<td>−158.24 kcal mol$^{-1}$</td>
<td>1.5 Å</td>
</tr>
<tr>
<td></td>
<td>O-down</td>
<td>Adsorption energy</td>
<td>−157.00 kcal mol$^{-1}$</td>
<td>1.5 Å</td>
</tr>
<tr>
<td></td>
<td>C-down</td>
<td>Adsorption energy</td>
<td>−80.17 kcal mol$^{-1}$</td>
<td>2.0 Å</td>
</tr>
</tbody>
</table>
for CH$_3$COOH in H-down is more than that in O-down and C-down. We showed that by increasing the nanotube diameter more efficient binding could not be achieved. Also, the adsorption of CH$_3$COOH on the CNTs further decreases the band gap of the pristine CNTs, and increases their electrical conductance.

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