
Theoretical investigations on the tip-functionalised carbon nanotubes interacting with water

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Abstract: Interactions between single-walled carbon nanotubes (SWNTs) and water molecules were studied using first principle calculations and molecular dynamics simulations. The SWNTs were modelled by varying the diameter ranging from the chiral vector (6, 0) to (9, 0) and by modifying the tube ends terminated with hydroxyl (-OH) and carboxyl (-COOH) functional groups. Water and SWNT molecules were modelled using the SPC model and a flexible model based on the OPLS force field respectively. The first principle NBO charges were used for describing the tube-water electrostatic interactions. The results indicate that the movement of water into the COOH-SWNT is rather different from the pristine and OH-functionalised nanotubes. Water molecules prefer to localise around the SWNT's tips than other parts. Hydrophilic behaviour of functionalised SWNT is improved over the pristine tube in agreement with experiments. The COOH-SWNT also shows the confinement of water molecules that may be useful for H₂O transport.

Keywords: Carbon Nanotube; CNT; Single-Walled Carbon Nanotube; SWNT; functionalisation; molecular dynamics; first principle; water orientations.

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1 Introduction

Carbon nanotubes (CNT) were first discovered in 1991 by Iijima (1991). After that discovery, research on CNT reaches a critical mass in many areas of physics and chemistry. Because of its remarkable electronic and mechanical properties, CNT is one of the best candidate materials for use in various applications including biosensors, nanocomposites and gas storage (Terrones, 2003). CNTs can also be employed as a simple model for biological channels to study the transport of various molecular species through cell membrane (Roux and Karplus, 1994; Fu et al., 2000). A common aspect of these applications involves the interaction of CNT with the surrounding medium and more specifically the surrounding water molecules. However, in general, it was found that the pristine CNTs are insoluble in water and common solvents (Scrivens and Tour, 1993; Ruoff et al., 1993) which hinders ordinary chemical approaches and preparation of nanocomposite materials. In the biological viewpoint, the insolubility of pristine CNTs also makes them highly toxic (Bianco et al., 2005). To overcome this obstacle, many approaches were employed to functionalise CNTs such as adding surfactants or hydrophilic groups (i.e., hydroxyl (OH), carboxyl (COOH) and aliphatic amines) to the open ends of nanotubes which is defined as tip functionalisation (Huang et al., 2003; Tasis et al., 2003; Riggs et al., 2000). After the tip functionalisation, these tubes are able to solubilise and become well-dispersed in common solvents since such functional groups can prevent the aggregation of CNTs and increase chemical interactions between the tubes and their environment.

From a theoretical point of view, quantum mechanics (QM) and molecular dynamics (MD) simulations have been widely used for studying the behaviour of CNTs with water molecules at the atomic level. For example, Walther et al. (2001) examined hydrophobic behaviour of a pristine CNT by investigating the structural properties of surrounding water using MD simulations (Walther et al., 2001; 2004; Werder et al., 2001). Hummer et al. (2001) explored whether CNT could be used as a molecular channel to transport water by tuning the local channel polarity and solvent conditions (Mashl et al., 2003; Zhu and Schulten, 2003). Lu et al. (2005) employed density functional theory to map the potential energy surface of armchair (6,6) CNT interacting with a water molecule. Although several computational and theoretical studies have been reported in the literature on the pristine tube-water interaction, study on behaviour of the tip functionalised tube-water interaction is rather limited. A work by Zheng et al. (2005) on MD simulations of sidewall functionalised tube-water interaction reported that COOH group assists in the transport of water into the CNT inner wall. It was found that water molecules easily enter into the hydrophilic COOH-SWNT but encounter a difficulty to flow through the tube.

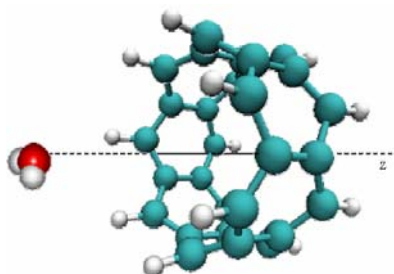
Although the tip-functionalised CNTs exist in the real experiments, theoretical works aimed to explain the behaviour of such systems are scarce. In the present study, the behaviours of water interacting with functionalised CNTs have thus been addressed by using first principles calculations and MD simulations. The goal of this work is to lay down fundamental understanding of the hydration structures, the orientation of water molecules around the tip-functionalised tubes, the diameter size effect and hydrophobic-hydrophilic behaviour.

2 Method and technical details

2.1 QM of nanotube-water interaction

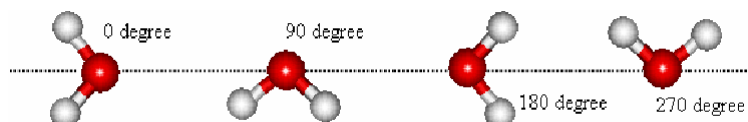
The cyclacene structure (single-walled CNT or SWNT having a length of one unit-cell as shown in Figure 1) was used throughout this study to represent CNT. Size dependency was studied by varying the diameter ranging from the chiral vector (6,0) up to (9,0). Both open ends of SWNTs were terminated by hydrogen atoms to avoid the boundary effects from the dangling bonds. Functionalisation was modelled by chemically modifying the open-ends of the (9,0) SWNT with hydroxyl (-OH) and carboxyl (-COOH) functional groups. The geometries of all model tubes were fully optimised based on the semi-empirical AM1 method (Dewar et al., 1985) using the GAMESS software (Schmidt et al., 1993). Interactions of model SWNTs with one water molecule were studied based on the density functional theory B3LYP using 6-31G* basis set (Kumeda et al., 2001) (denoted by B3LYP/6-31G*). Potential energy surfaces based on a longitudinal trajectory of water into the nanotube's centre (Figure 1) having various orientations (Figure 2) were calculated. On such trajectory, the water's oxygen atom was moved along the tube axis z and the hydrogen atoms were symmetrically placed giving the water molecule a fixed orientation. At first, the smallest (6,0) SWNT was chosen for studying the effect of water orientation on the tube-water interactions. Then, the effects of diameter size and functional group on the tube-water interactions were investigated respectively.

Figure 1 Definition of the longitudinal trajectory for a water molecule interacting with SWNT (see online version for colours)



Note: The water having a fixed orientation was placed at various positions along the tube axis.

Figure 2 The orientations around an inertial axis of a water molecule (see texts) (see online version for colours)



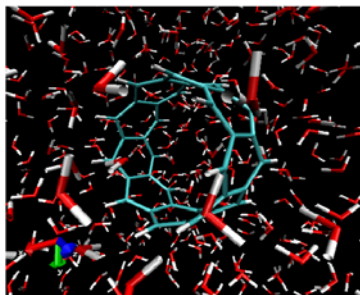
2.2 MD simulation of nanotubes in water

The hydration structure and hydrophobic-hydrophilic behaviour of the functionalised SWNTs have been studied using MD technique within GROMACS software package (Berendsen et al., 1995). The open-ended (9,0) SWNTs terminated with hydrogen (H-SWNT), hydroxyls (OH-SWNT) and carboxylic (COOH-SWNT) were simulated in aqueous environment. The structures of all functionalised SWNTs employed in the simulations were obtained by geometry optimisations based on the semi-empirical AM1 method. B3LYP/6-31G** was employed to compute atomic NBO charges (Glendening et al., 1996) for describing the tube-water electrostatic interactions. Hence, the AM1 method is good enough for geometry optimisation of the nanotubes (Udomvech et al., 2003) while the B3LYP/6-31G** level was found to be more reliable for charge calculation (Koch and Holthausen, 2001). The simulations were performed at the constant volume and temperature in a rectangular box containing one SWNT and 871 water molecules (see Figure 3). Therefore, total number of atoms in the simulation box is 2,667, 2,685 and 2,721 for the H-SWNT, OH-SWNT and COOH-SWNT systems, respectively. SWNTs were represented by a flexible model based on OPLS force field (Jorgensen and Tirado-Rives, 1988) as well as the SPC water model (Teleman et al., 1987). The SWNT-water and water-water interactions were given by a sum of the Lennard-Jones and Coulomb potentials.

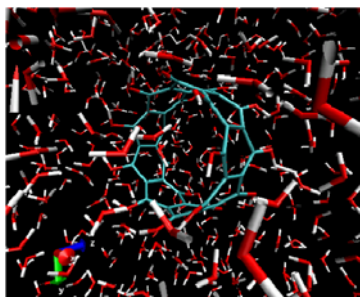
$$V_{LJ}(r_{ij}) = 4\epsilon_{ij} \left(\left[\frac{\sigma_{ij}}{r_{ij}} \right]^{12} - \left[\frac{\sigma_{ij}}{r_{ij}} \right]^6 \right) + \frac{q_i q_j}{r_{ij}} \quad (1)$$

Here, ϵ and σ are Lennard-Jones parameters, and q_i and q_j represent the charges on atom i and atom j , respectively.

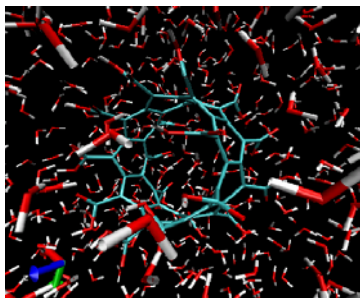
Figure 3 The simulation snapshots of (a) H-SWNT, (b) OH-SWNT and (c) COOH-SWNT in water at 298 K (see online version for colours)



(a)



(b)



(c)

Initially, water molecules and a SWNT were placed in the rectangular box having a dimension in x-, y- and z-axis of 3.00 nm to reproduce the water density of 1 g/cm³. All simulated systems were controlled via a temperature coupling bath to maintain the temperature at 298 K. Density control was achieved by Berendsen pressure coupling (Berendsen et al., 1984). The box was scaled every time step. In consequence, the volume of the system was adjusted in the equilibration phase to match the desired density of water. After equilibration, the system was run for 1,000 picoseconds with a time step of 0.5 fs. Trajectories were stored every 100-time steps for subsequent analyses.

3 Results and discussion

3.1 Interaction energy

After geometrical optimisation using the AM1 method, the average C-C bond lengths of all tubes, including the tip-functionalised ones, are nearly the same and close to the C-C bond length in the perfect nanotube with sp^2 hybridisation (1.42 Å) (see Table 1). It thus confirms that adsorption of molecular entities at the tips of an open-ended tube does not bring about any structural distortion to the tube, in contrast to adsorption at the sidewall that strongly affects the tube structure (Park et al., 2005), e.g., weakening the C-C bond to a ~ 1.52 Å length. The HOMO-LUMO energy gaps of all model tubes exhibit the small-gap semi-conducting properties. The COOH-SWNT has the smallest energy gap while the H-SWNT has the largest one. It can be seen that such functional groups somewhat affect the HOMO-LUMO energy gap of the short tube.

Table 1 The average C-C bond-lengths obtained from geometry optimisation and electronic properties of H-, OH- and COOH-SWNTs calculated by B3LYP/6-31G* method

System	C-C (Å)	HOMO (eV)	LUMO (eV)	E_{gap} (eV)
H-SWNT	1.417	-3.734	-2.630	1.104
OH-SWNT	1.424	-2.774	-1.859	0.915
COOH-SWNT	1.424	-5.704	-4.884	0.820

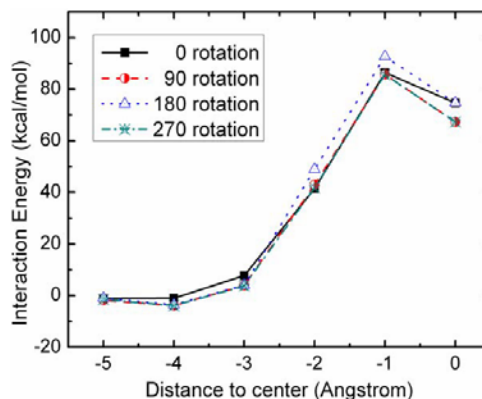
The single point calculations with B3LYP/6-31G* method were performed to find the total energy of each system. In order to evaluate the interactions between these model tubes and water molecule, the interaction energies are evaluated via the equation:

$$E_{\text{int}} = E(\text{SWNT-water}) - E(\text{SWNT}) - E(\text{water}) \quad (2)$$

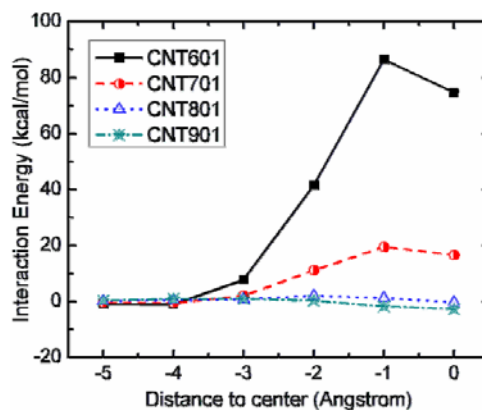
where $E(\text{SWNT-water})$ denotes the total energy of the model SWNTs (pristine or functionalised) presented with one water molecule. $E(\text{SWNT})$ represents the total energy of the model tubes and $E(\text{water})$ for the water molecule.

The effect of water orientation on the tube-water interactions of (6,0) H-SWNT was demonstrated in Figure 4(a). It was found that the water molecule encounters a difficulty to move into the (6,0) H-SWNT, which has a diameter size of 4.8 Å, in agreement with a previous study on H_2O adsorption inside the 4 Å armchair and chiral CNTs using LDA and GGA methods (Agrawal et al., 2007). E_{int} is in a range of 85–90 kcal/mol at the tip of nanotubes. For such a small-diameter tube, it seems that the orientation of water has no effect on the water-tube interactions since the large repulsive interactions dominate the potential energy surface. Therefore, investigation of the effect of water orientation on the tube-water interactions using larger diameter nanotubes would be more informative. The potential energy surfaces for SWNTs with varying diameter interacting with a water molecule are displayed in Figure 4(b). The potential energy barrier appears to decrease rapidly when the diameter size of CNT increases. From the results, water molecule can enter into a pristine tube only when the tube diameter is larger than 7.0 Å. Therefore, the (9,0) SWNT was chosen for studying the tube-end functionalisation and a water molecule was varied in its orientation.

Figure 4 Potential energy surface for (a) (6,0) SWNT interacting with a water molecule that rotates along the centre of mass and (b) SWNTs with varying diameter interacting with a water molecule having fixed orientation at various positions along the z-tube axis (see online version for colours)



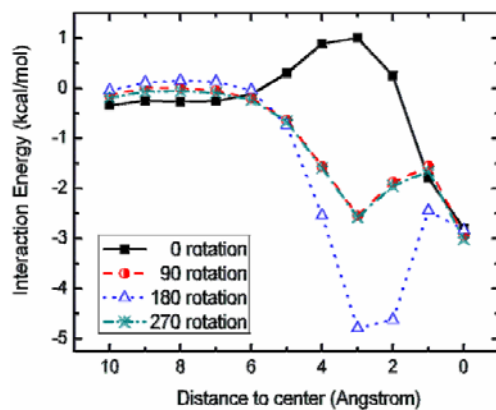
(a)



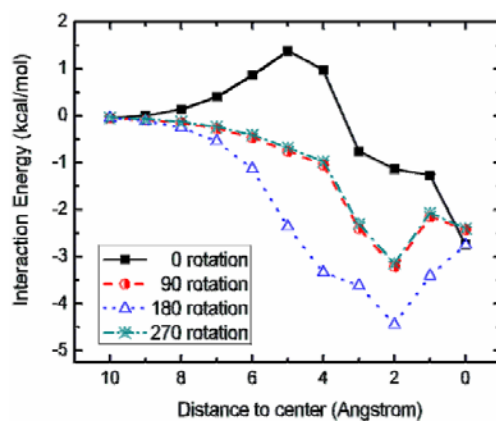
(b)

The interactions of functionalised SWNTs with a water molecule were displayed in Figure 5. In case of H-SWNT [see Figure 5(a)], when a water molecule moves into the tube with 0° orientation, the H-SWNT has a slight potential barrier in the range of 2–4 Å from the centre of nanotube. The potential barriers reduce when the water molecule interacts with the tube in other orientations. The behaviour of OH-SWNT as shown in Figure 5(b) is rather similar with H-SWNT but the potential barrier moves to a farther distance from the tube. However, such energy barrier is not high enough to hinder water entrance into the interior of H- and OH-SWNTs at room temperature. The water molecule prefers to occupy in front of the open ends of H- and OH-SWNTs with the 180° orientation. Specifically for COOH-SWNT [see Figure 5(c)], there is a deep potential well (~ 10 kcal/mol) in front of the tubule open end that can localise the water molecule with 0° orientation in contrast to the H- and OH-SWNTs. As a result, tip functionalisation by COOH functional group affects the penetration of water molecule inside the CNT. In the latter case, the terminal ends will be solvated by water.

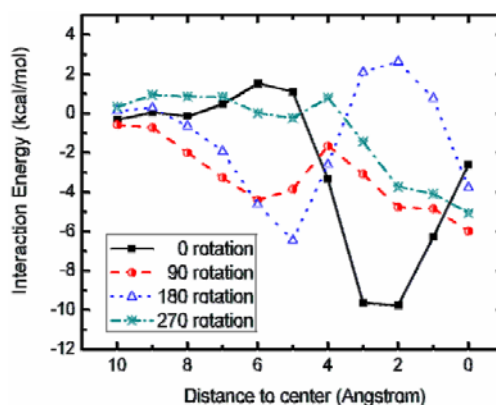
Figure 5 Potential energy surface for (a) H-SWNT (b) OH-SWNT and (c) COOH-SWNT interacting with a water molecule that rotates along the centre of mass (see online version for colours)



(a)



(b)



(c)

Note: All nanotubes have (9,0) configuration.

3.2 Hydration shell and hydrophobic-hydrophilic behaviour

The hydration structure of functionalised SWNTs can be extracted from the MD simulation data in terms of atom-atom radial distribution function analysis (RDF), $g_{X-Y}(r)$ which represents the probability of finding an atom of type y in a spherical volume of radius r around the central atom of type x as defined in the following equation:

$$g_{X-Y}(r) = \frac{1}{\langle \rho_Y \rangle_{local}} \frac{1}{N_X} \sum_{i \in X} \sum_{j \in Y} \frac{\delta(r_{ij} - r)}{4\pi r^2} \quad (3)$$

where $\langle \rho_Y \rangle_{local}$ denotes the particle density of type Y averaged over all spheres around particles X .

In order to evaluate the average y atoms number in a spherical volume of radius r around the central atom of type x , the corresponding running integration numbers, $n_{X-Y}(r)$, are calculated by using the integration of RDF,

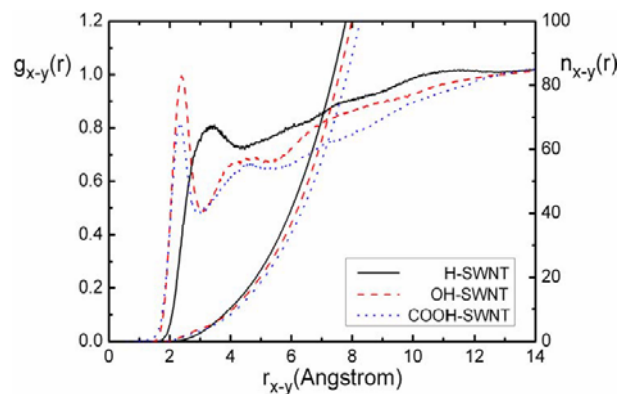
$$n_{X-Y}(r) = 4\pi\rho_0 \int_0^r r'^2 g_{X-Y}(r') dr' \quad (4)$$

where ρ_0 is the density number of y atoms.

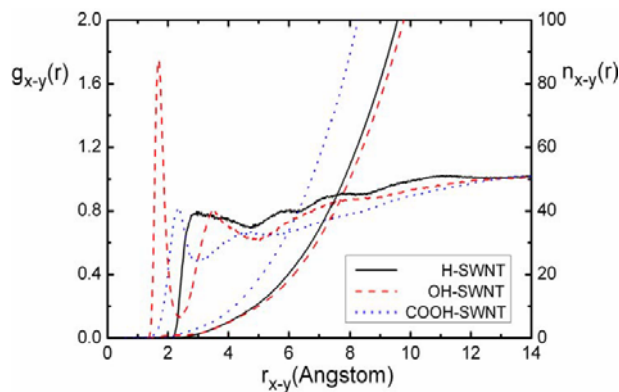
The RDFs, $g_{X-Y}(r)$ and their corresponding running integration numbers, $n_{X-Y}(r)$, from the tips of each tube (H atoms of each tube) to the H and O atoms of water molecules are shown in Figure 6(a) and 6(b), respectively. From Figure 6(a), only one RDF peak was found for H-SWNT which positions at 3.47 Å, whereas for OH-SWNT and COOH-SWNT it appears two RDF peaks. The first sharp and the second shoulder peaks position at 2.39 and 4.83 Å for OH-SWNT, 2.35 and 4.75 Å for COOH-SWNT, respectively. From Figure 6(b), the RDF peaks position at 3.01 Å, 1.67 Å and 2.33 Å for H-SWNT, OH-SWNT and COOH-SWNT, respectively. These results indicate that water molecules prefer to localise at the tips of the functionalised tube (OH-SWNT and COOH-SWNT) closer than that of the pristine tube (H-SWNT). The functional groups increase the interactions between the tube and water molecules at the tips of nanotube. Therefore, the probability of finding water molecules surrounding the functionalised tube is higher than that of the pristine tube. The number of water molecules surrounding the tips of both OH-SWNT and COOH-SWNT can be calculated using equation (4) as shown in Figure 6(a) and 6(b) ($n_{X-Y}(r)$). Integration of the RDF up to the minima of the first peaks at 3.07 and 2.41 Å corresponds to four hydrogen and one oxygen atoms of water for OH-SWNT. In case of COOH-SWNT, the minima of the first peaks position at 3.03 and 2.87 Å corresponds to two hydrogen and three oxygen atoms of water. It implies that the H atoms of water turn toward the tips of OH-SWNT whereas directing the O atoms of water toward the tips of COOH-SWNT. The results are in good agreement with potential energy surface obtained by first principles calculations above.

The RDF plot for the centre of mass (CoM) of water toward CoM of each model tube is displayed in Figure 7. H-SWNT does not yield any sharp peak whereas tip-functionalised tubes show one little sharp peak at 1.7 Å. The peaks of all functionalised tubes indicate that water molecules can occupy more closely to the centre of nanotube. The functionalised groups may help to confine the water inside the hydrophobic tube's interior.

Figure 6 RDFs, $g_{x-y}(r)$, and their corresponding running integration numbers, $n_{x-y}(r)$, from (a) H atoms and (b) O atoms of water molecule to the H atoms of H-SWNT, OH-SWNT and COOH-SWNT (see online version for colours.)

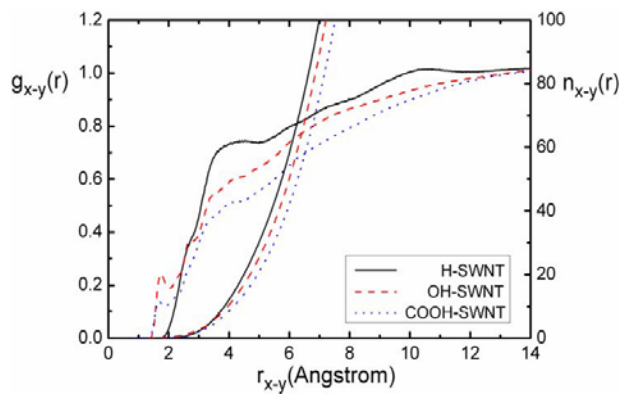


(a)



(b)

Figure 7 RDFs, $g_{x-y}(r)$, and their corresponding running integration numbers, $n_{x-y}(r)$, from the CoM of water to the CoM of tubes (see online version for colours)



Based on the overall characteristics of RDF peaks in Figures 6 and 7, one can conclude that water molecules favour to bind to the tips of tubes and the interactions between the water molecules with pristine tube are rather weak in comparison with the functionalised ones.

The average number of tube-water and water-water hydrogen bonds were calculated and given in Table 2. In case of the functionalised tubes, it was found that the average number of water-water hydrogen bonds decreases whereas that of tube-water hydrogen bonds increases, comparing to the pristine tube. Hydrogen bonding is a special type of attractive interactions that exists between certain chemical groups of opposite polarity in which the donor-acceptor distance is within 3.5 Å range and the orientation of the O-H donor bond is within 60° aligned to the acceptor oxygen (Jeffrey, 1997). It means that after functionalisation, the water molecule has more attractive interactions with such tubes. The hydrophilic behaviour has an increasing trend depending on the functional groups.

Table 2 Average number of hydrogen bonds for tube-water and water-water

<i>CNT type</i>	<i>Number of H-bonds</i>	
	<i>Tube-water</i>	<i>Water-water</i>
H-CNT	–	1501.09
OH-CNT	23.29	1463.04
COOH-CNT	23.77	1435.08

The mean square displacement (MSD) of CNTs in aqueous environment can be computed as follows:

$$MSD(t) = \left\langle (r_i(t) - r_i(0))^2 \right\rangle \quad (5)$$

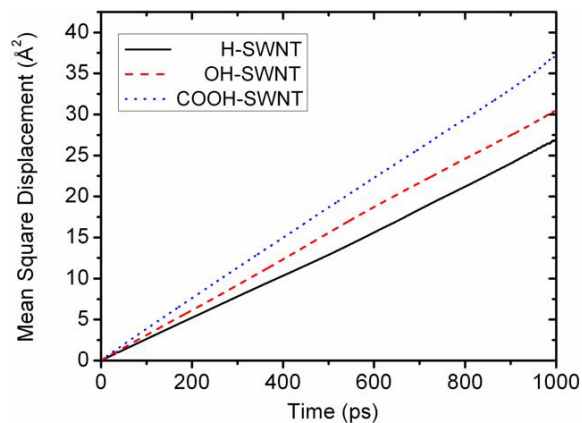
where r_i is the CoM coordinates of the CNTs.

The MSD of model tubes was shown in Figure 8. However, the motion of CNTs can be explained in terms of the diffusion constant (D) which is calculated by the slope of the MSD fitted from time 100 to 900 picoseconds using the Einstein relation:

$$D = \frac{1}{6t} \lim_{t \rightarrow \infty} (MSD(t)) \quad (6)$$

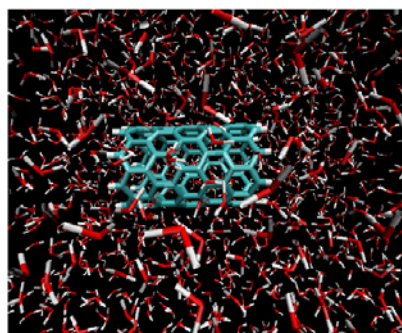
The diffusion constants of H-, OH- and COOH-SWNT are 4.44×10^{-5} , 5.13×10^{-5} and $6.07 \times 10^{-5} \text{ cm}^2/\text{s}^{-1}$, respectively. These results suggest that the diffusivity develops with the tip modification by OH and COOH functional group. In consequence, the tip functionalised SWNT is a better dispersion in water than the pristine tube is, corresponding with the experimental results (Huang et al., 2003; Tasis et al., 2003; Riggs et al., 2000).

Figure 8 MSD versus time of model CNTs in aqueous environment (see online version for colours)

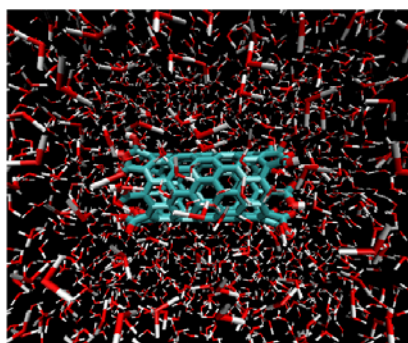


To affirm the accuracy of using one unit cell for representing model SWNTs, the hydration structure of H- and COOH-SWNTs having 14-Å tubular length was additionally simulated in 2,032 water molecules as shown in Figure 9.

Figure 9 The simulation snapshots of 14-Å long (a) H-SWNT and (b) COOH-SWNT in water (see online version for colours)



(a)

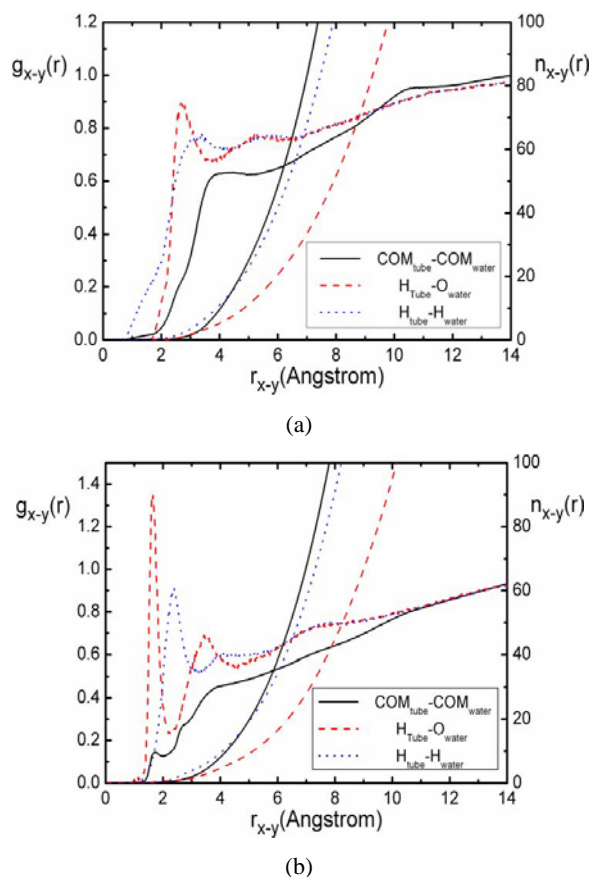


(b)

The $g_{x-y}(r)$ and $n_{x-y}(r)$ from the tips and CoM of 14-Å long H-SWNT and COOH-SWNT to CoM, O and H atoms of water molecules are displayed in Figure 10(a) and 10(b), respectively.

From Figure 10, it can be seen that the RDF plots of both 14-Å long H- and COOH-SWNT are in agreement with the shorter model SWNTs. Based on the first peak, $g_{\text{H-O}}$ and $g_{\text{H-H}}$ for 14-Å long H-SWNT appear at 2.71 and 3.39 Å and their corresponding numbers are 3.8 O and 13 H atoms, respectively. For 14-Å long COOH-SWNT, it shows the two layers of hydration shells around the tips of nanotube. The orientation of water around the tip of 14-Å long SWNT is similar to those of the shorter model SWNTs. As a result, one unit cell can be used to represent the nanotube having three unit cells (14-Å long) as well.

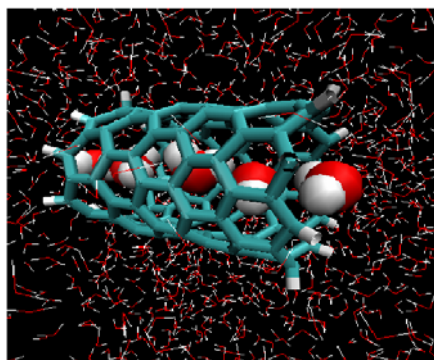
Figure 10 RDFs, $g_{x-y}(r)$ and corresponding running integration numbers, $n_{x-y}(r)$, for 14-Å long (a) H-SWNT and (b) COOH-SWNT (see online version for colours)



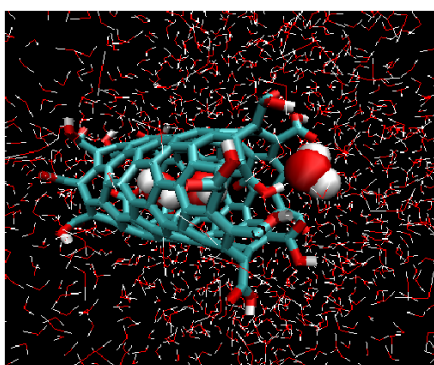
To observe water orientation inside the tubes, the simulation snapshots of 14-Å long H-SWNT and COOH-SWNT were investigated as displayed in Figure 11(a) and 11(b), respectively. Water molecules are seen to move into and out of the H-SWNT during the time of observation. The average number of water molecules inside the H-SWNT is about five and these water molecules line up to a single line. The transport behaviours of water

in H-SWNT are in accordance with the study of water dynamics inside armchair CNT by Zhou and Lu (2007). Specifically for COOH-SWNT, two water molecules were confined inside the tubes for the whole period of the simulation. These finding may imply that COOH-SWNT will be useful in nano-encapsulation or H₂O storages.

Figure 11 The simulation snapshots showing the orientation of water molecule inside (a) H-SWNT and (b) COOH-SWNT (see online version for colours)



(a)



(b)

4 Conclusions

The interactions between various SWNTs and water molecules have been studied using first principle calculations and MD simulations. Based on a study of potential energy surface using QM calculation, it was found that the movement and orientation of water molecule into the COOH-SWNT are rather different from H- and OH-SWNTs while the diameter of nanotube also plays an important role. The water molecule can enter into a pristine zigzag nanotube when the tube diameter is larger than 7.0 Å. The results from MD simulations indicate that the hydration shell of functionalised nanotubes is located at ~2–3 Å from the tube edges while the hydration shell of the pristine system is located farther at ~3–4 Å. The water molecules prefer to surround the tips of nanotubes rather than the sidewall. In the functionalised systems, the number of tube-water hydrogen

bonds is higher than that in the pristine system whereas the number of water-water hydrogen bonds has the opposite trend. From this study, it can be concluded that the hydrophilic behaviour of functionalised SWNT is improved over the pristine tube, in agreement with previous experimental works. In addition, the tip functionalisation using COOH functional groups can confine water molecules in the CNT.

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