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Charged Carbon Nanotubes

Devashree Atre and Shashank Pant

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Abstract

As the degree of functionalization on CNTs greatly affects its properties, the structure and dynamics of water confined inside pristine and functionalized/charged carbon nanotubes (CNTs) is of prime importance. The presence of charges on the surface of CNTs results in hydrophobic to hydrophilic transitions which increase its occupancy of the water molecules thereby breaking down 1D water wires, as seen in pristine CNTs.

Keywords: carbon nanotubes, breakdown of 1D water wires, functionalization, confined water, density fluctuations

1. Introduction

1.1. What are carbon nanotubes?

Carbon nanotubes (CNTs) are carbon allotropes having a cylindrical nanostructure. This nanostructure has unusual properties which increases its applications in the field of biology, electronics, water desalination, material science and optics. This material has significantly higher stiffness and exceptional strength. CNTs have been constructed in a wide range of diameter to length ratio [1]. In addition to the mechanical strength and stiffness, it has high thermal conductivity and wide range of electrical properties. Owing to this extremely high strength, CNTs have found a place in the materials used for designing bats, car parts etc. [2, 3]

CNTs belong to the fullerene family and the name is derived from their long and hollow structure where walls are formed by carbon atoms sheets called graphene [4]. These graphene sheets are rolled at a specific angle, which decides the properties of CNTs. Nanotubes can be broadly divided into two types:

1. Single wall carbon nanotubes (SWNTs).
2. Multi wall carbon nanotubes (MWNTs).

Individual CNTs can align themselves by pi-pi stacking and Van der Waals interactions. In more chemical terms, carbon nanotubes bond due to sp² hybrid carbon atoms. These bonds are stronger than the alkanes and provide CNTs which extremely high in strength. A typical carbon nanotube is show in **Figure 1**.

The wrapping of the graphene sheets is represented by a pair of indices (n,m) where n and m denote the number of unit vector in the crystal structure of graphene as shown in **Figure 2**.

MWNTs can consist of many rolled up graphene sheets and the process can be done either by using concentric single walled nanotubes or by rolling up a single graphene sheet around itself. Recently, many modifications of CNTs morphology have been reported [5–7].

1.2. Application of carbon nanotubes

Owning to its stiffness, mechanical strength, conductivity and structure carbon nanotubes have widespread applications in the area of sports, transistors, material science, biology etc. [8–14]. The Easton-Bell Sports Inc. has been using CNT, in partnership with Zyvex Performance Materials, in designing bicycle components like handlebars, seatposts, crank etc. Owning to the nanometer sized diameter and tunable length which can reach up to a few centimeters CNTs can be a drug vehicle for therapy purposes [15]. The sp² hybridized orbitals and a large porous surface area can be easily exploited to load large quantity of drugs inside the tube. Not only drug but specific molecules which can increases the targeting ability can be easily loaded in the nanotubes. Drugs like doxorubicin (DOX) can be absorbed on the CNT surface by pi-pi stacking [16], this type of loading is usually pH dependent thus proving a handle to release drugs.

Figure 1. A typical carbon nanotube (a) side view and (b) showing the carbon nanotube pore.

Figure 2. The (n,m) naming scheme of nanotubes can be thought of as a vector C in an infinite graphene sheet; this will describe how to roll up the sheet to form the nanotube. Also, a_1 and a_2 denotes the unit vector for the graphene.

In addition to the drug delivery the optical properties of CNTs provide NIR (Non Infrared Radiation) region of absorption [17, 18]. In contrast, biological tissues and cells provide maximum transmission in this range, thus making it a suitable candidate for bio-imaging, tracing, diagnosis etc. If chemotherapeutic drugs are combined with CNT optical properties it might increase the treatment effectiveness. The low toxicity of CNTs makes it an utmost important candidate for biomedical applications. We can tune the toxicity of the CNTs by varying the length, aggregation, surface functionalization etc. thus, care must be taken before using them. But the usual MTT assays cannot be used for testing the cytotoxicity of CNTs because MTT-formazan crystals might stick to the surface of the CNTs thereby making it less soluble in isopropanol and DMSO [19].

Carbon nanotubes serve as a robust material for water desalination and in water decontamination. The CNT hollow pores provide frictionless transport of water molecules and the tunable diameter can be used for removing unwanted particles. The functionalized CNTs can also be employed to selectively remove particular particles by specific or non-specific interactions. Thus, CNTs can be used as a “Gate-Keeper” molecule [20–27]. The smooth hydrophobic walls and the pore diameter of CNTs allow ultra-efficient water transport. A prototype of CNT membrane is shown in **Figure 3**.

1.3. Functionalization of carbon nanotubes

The chemical modifications of carbon nanotubes (CNTs) are an emerging area of research as it provides a handle to tune the solubilization [28] of CNTs. The reaction for the modification of CNTs can be broadly divided into two areas:

Figure 3. A water desalination setup where 4 CNTs form the membrane, yellow balls represents impurity and red-white molecules are the water. Movement of water through the CNT membrane is seen while impurity does not move through the membrane.

1. Direct attachment of groups on the graphitic carbon atoms.
2. Modifications on the CNT bound- carboxylic acids.

The fluorination [29] of CNTs has been extensively studied and this modification has resulted in the solvated individual CNTs in alcohol type solvents, while the second modification results in changes in the CNT properties as it might lead to the shortening of the nanotubes. Further different methods have been incorporated especially ester modification at the terminal carbon of CNTs. This modification can be easily removed by acid-base chemistry, thus enabling us to get back to the initial state of CNTs.

Figure 4. Carbon nanotube modification scheme.

In order, to solubilize CNTs attachment of large chemical group is needed. These larger chemical groups can be certain chemical compounds or can also be certain polymers. These chemical compounds wrap around the CNTs and hinder the formation of CNT bundles in the solvent, thereby solubilizing it in the solvent. The solubility of CNT can be easily modulated by varying the nature of the functional groups. As, the chemical modification [30–35] of CNT greatly alters the chemical and the electronic structure of the nanotubes, good attention has been paid to the non-covalent and non-specific modifications. This type of modification results in almost the same effect without altering the chemical and electronic nature of the nanotube. A typical scheme for modification is shown in **Figure 4**.

2. Properties of solvent inside carbon nanotubes

2.1. Structure of water

Water is ubiquitous yet the most anomalous substance on earth, the origin of its anomalous properties is yet to be fully understood [36–42]. Water is tetrahedral in structure and it forms 4 hydrogen bonds in the fluid state and 6 hydrogen bonds in its solid state i.e. ICE. It is formed by 2 hydrogen and 1 oxygen molecule with the presence of two lone pairs on the oxygen. Due to polarization effect there is a presence of partial positive charge on the hydrogen atoms and partial negative charge on the oxygen atom. Due to its wide range of applications, water is a prime candidate under study for almost all the systems. Its structure along with its dynamic and thermodynamic properties of water confined under nanopores of carbon nanotubes has been widely studied. It has been observed that the properties of confined water are distinctly different from that of bulk or non-confined water. Despite of the hydrophobic nature of carbon nanotubes, it is occupied by 4–5 water molecules. The most interesting feature of water inside the 6,6 pristine CNT is the presence of 1 D water wires (1 dimensional) [43]. The water molecules entering the nanotube channel lose on average two hydrogen bonds and only a fraction of lost energy can be recovered by the VdW interactions between water and the nanotube. The presence of 1D water wire inside pristine 6,6 CNT is shown in **Figure 5**.

Further, extensive amount of work has been put in to study the structure of water confined inside carbon nanotubes. Molecular dynamics simulations suggested the presence of ice like structural ordering of water at room temperature [44–46]. The presence of ice like structures has been quantified by various matrices like the calculation of order parameter, radial distribution curves and snapshots of system. Before moving further, I would like to explain how one of the most important parameter, radial distribution works and what type of information we get from it. Radial distribution function or RDF gives us the structure of the system under study and it works under the assumption that the system should be radially symmetric. It gives us an idea about the variation of the density with respect to the distance. Although, it will not gives us the idea about the instantaneous density of the system but averaged density. In much coarse terms it gives us the probability of finding a particle at a distance of “ r ” from the central particle.

Figure 5. Presence of 1 D water wires inside 6,6 pristine CNT. Hydrogen bonds are shown in black.

The structure (RDF) of confined water is shown in **Figure 6**. The figure clearly shows the presence of peaks at regular intervals which suggest a ordered structure. No such peak was observed in the case of bulk water. A typical snapshot of the simulations performed by Koga et al. is shown in **Figure 6(b)**. The presence of ordered water nanotubes was seen in the simulation at room temperature but under axial pressure, the presence of square, pentagonal and hexagonal water nanotubes was observed in (14, 14), (15,15) and (16,16) nanotubes.

These structural studies suggests the presence of well ordered ice like structure of water inside CNTs at room temperature. Further, this ice-like ordered structures were seen even at a high temperatures like 320 K. Very recently, there has been an effort to study the properties of confined water inside functionalized CNTs. The functionalization was done by incorporating charges on the surface of CNTs i.e. by placing charge on the carbon atoms as shown in **Figure 7**. The presence of charge results in decreasing the ordered ice like structure of water. The main reason for such disordering or absence of an ice-like ordered structure is the hydrophobic to hydrophilic transition in the CNT. Due to the presence of charges on the CNT surface, it does not behave like a hydrophobic wall and there is a loss in the ordering [47–52] as shown in **Figure 8**. It clearly shows the decrease in the peak intensity

Figure 6. (a) Radial distribution curve along the axis of 6,6 pristine CNT. It shows the presence of regular spaced peaks, (b) snapshots of quenched water co-ordinates in (a) square, (b) pentagonal, (c) hexagonal ice nanotubes in (14,14), (15,15) and (16,16) SWNTs, (d–f) shows the corresponding liquid phase. The ice nanotubes were formed upon cooling under axial pressure of 50 MPa in molecular dynamics simulations. Figure taken from Koga et al. [44].

and the absence of equally spaced peaks. Thus the presence of charge on the CNT surface although increases its solubility in water but greatly affects the properties of confined water.

Now, an interesting question arises on the presence of 1D water wires inside functionalized CNTs. The very first study by Pant et al. clearly shows the breakdown of the 1D water wires rather the presence of 3 linear water wires inside such a confined space was observed as shown in **Figure 9**. The presence of 3 water wires was surprising because earlier the presence

Figure 7. Distribution of charges on CNT. The blue area shows the presence of charged carbon atoms.

Figure 8. Decrease in the ordering of confined water inside CNT.

Figure 9. Presence of 3 water wires in functionalized CNT.

of 1D water wire in 6,6 pristine CNT was correlated to the diameter of the CNT and its hydrophobic nature of CNT. Although the functionalization of CNT does not change its diameter but it does change its hydrophilic nature, thus it suggests the presence of 1D wires in pristine CNT is only dependent on its hydrophobic nature and not on its diameter.

Now, a question arises on how the degree of functionalization affects the confined water? In-order to answer this question we can increase the functionalization and also distribute the functional groups on the CNT surface in the form of various patterns. This can provide us with an easy handle to change the properties of the tube and it can even be use to mimic the properties of complex biological systems like aquaporins [53].

2.2. Permeation, diffusion of water through carbon nanotubes

A single permeation event is considered when a water molecule enters from one of CNT and leaves from the other end. The permeation or flow of water from the CNT has been extensively studied and enhanced water flow was observed. This can be related to the breaking of the hydrogen bonds i.e. in the pristine 6,6 CNT presence of 1D water wires was observed where each water molecule on average forms 1–2 hydrogen bonds which is in contrast with bulk water as it forms 4 hydrogen bonds. Thus the movement of water is less hindered inside the tube and it experiences less resistance from the neighboring water molecules. On, the other hand in the presence of functionalization there is a significant amount of decrease in the water flow. Due to the effect of functionalization, the nature of the tube changes from hydrophobic to hydrophilic and this transitions breaks the formation of 1D water wires, also presence of functional groups on the CNT surfaces results in the formation of hydrophilic-hydrophilic interactions between water and functional groups. These forces results in the decrease of water flow as shown in **Figure 10**.

Figure 11 clearly shows the decrease in the flow rate with the increase in the charge % on the surface of CNT. This can be further explained by the variation of hydrogen bonds between the confined water molecules because in the 6,6 pristine CNT, one water molecule on an average

Figure 10. Variation of flow with the charge %.

Figure 11. (a) Shows the variation of the hydrogen bonds with the charge %. (b–d) Shows the behavior of the water dipole moment and the decrease in the number of flipping events with the increase in the charge %.

forms 1–2 hydrogen bonds but in the presence of functionalized groups on CNT surface the number of hydrogen bonds almost linearly increases due to the breakdown of 1D water wire as shown in **Figure 11(a)**. This linear increase in the number of hydrogen bonds also prevents the dipole moment of water from flipping inside the CNT as shown in **Figure 11(b)**. A flip event for water is defined if Θ passes through 90° , thus the increase in the number of hydrogen bonds results in a potential barrier for the water's dipole moment to flip. This behavior is only affected by the presence of charges and not on the pattern of charge distribution.

As, we can observe from **Figure 11(a)**, the average number of hydrogen bonds for the highest charged system almost reached 3.5, which matches well with the number of hydrogen bonds in the bulk solvent, thus suggesting that degree of functionalization provides us with a good handle to tune the properties of the system under study.

Now, I would to talk about the macroscopic details of the confined spaces, like pores of carbon nanotubes which can be understood by studying the water density fluctuations. Water density fluctuations gives us the information about the nature of the confined space i.e. it help us to understand if the pore is hydrophobic or hydrophilic in nature. The water density fluctuation can be calculated by the following formula:

$$\kappa = \frac{(\langle N^2 \rangle - \langle N \rangle^2)}{\langle N \rangle} \quad (1)$$

Figure 12. Normalized variance as the function of degree of hydrophobicity.

where K is the variance in the variance in the occupancy of water molecules normalized by its mean value. The ratio of variance and the mean value approaches $\rho k_B T \chi_t$, where χ_t is the isothermal compressibility, in macroscopic limits. **Figure 12**, shows fluctuations in the density of confined water inside pristine and functionalized carbon nanotubes. The two horizontal lines indicate two limiting cases for fluctuations in bulk water and in ideal gas. The relative fluctuations in the highest charged CNTs increases by almost 5 times compared to that of pristine CNTs. This suggests that the compressibility of water near the hydrophobic CNTs is more owing to the wet-dry transitions [45, 54].

3. Conclusion

In conclusion charged or functionalized carbon nanotubes behave quite differently compared to pristine CNTs. Functionalization not only affects properties like band gap, conductivity and metallic nature of CNTs but it also greatly affects the properties of confined fluids. The functionalization of CNTs changes the overall nature of the CNTs and increases the hydrophilicity, which varies almost linearly with the degree of functionalization. As the degree of functionalization provides us with a handle on the properties of confined water, it might be interesting to see if we can use carbon nanotubes as a prototype for studying complex biological system like aquaporins.

Author details

Devashree Atre¹ and Shashank Pant^{2*}

*Address all correspondence to: pant5@illinois.edu

1 Civil and Environmental Engineering, University of Illinois, Urbana-Champaign, IL, USA

2 Center for Biophysics and Quantitative Biology, University of Illinois, Urbana-Champaign, IL, USA

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