Chemical Physics 479 (2016) 42–52

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Functionalized single walled carbon nanotubes as template for water storage device

Sanjib Paul, Srabani Taraphder *

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

ARTICLE INFO

Article history:
Received 12 July 2016
In final form 8 September 2016
Available online 9 September 2016

ABSTRACT

Single walled carbon nanotubes, endohedrally functionalized with a protonated/unprotonated carboxylic acid group, are examined as potential templates for water storage using classical molecular dynamics simulation studies. Following a spontaneous entry of water molecules into the core of model functionalized carbon nanotubes (FCNTs), a large fraction of water molecules are found to be trapped inside FCNTs of lengths 50 and 100 Å. Only water molecules near the two open ends of the nanotube are exchanged with the bulk solvent. The residence times of water molecules inside FCNTs are investigated by varying the length of the tube, the length of suspended functional group and the protonation state of the carboxylic acid group. Favorable energetic interactions between the functional group and water, assisted by a substantial gain in rotational entropy, are found to compensate for the entropy loss resulting from restricted translational diffusion of trapped water molecules.

1. Introduction

Single and multiwalled carbon nanotubes (CNTs) have been widely used in chemistry, biology and material science to probe the effect of hydrophobic confinement on the properties of water [1,2]. They serve not only as useful mimics of biological water channels [3–6], but also, for instance, as templates for fabrication of nanodevices for drug delivery [7,8], molecular detection [9], membrane separation [10], solvent purification [11,12] and solid phase extraction [13]. Many of these applications require a spontaneous flow of charged and dipolar species across the hydrophobic core of the tube. The simulation results of an accelerated diffusion of highly viscous ionic liquids (comprised entirely of ions) through CNTs furnish one such intriguing case[14]. However, their usage for storage purposes is much less investigated. The use of CNTs as porous carbon materials for creating charge storage devices has been demonstrated only recently [15,16]. In this article, yet another seemingly counter-intuitive application of the CNTs is explored. We use molecular dynamics simulation studies to assess SWCNT as a prototype of water storage devices.

Three different aspects need to be taken into consideration for the model storage. First, water molecules should easily enter the storage unit. It should also stay inside till some external perturbation facilitates its removal from the unit. At the fundamental level, several experimental [17–19] and simulation [20,21] studies now support the viability of a spontaneous filling of narrow CNTs by water molecules when dipped in a water reservoir [22]. In the core of a (6,6) narrow, open ended single walled carbon nanotube (SWCNT), water molecules are found to form a single file, hydrogen bonded chain extended along the tube axis. In wider nanotubes, water molecules are found to form stacked ring-like structures with the computed rate of conduction depending on the model of water used [23]. Based on these results, a narrow SWCNT is selected as the simplest basic unit for our design. Following a spontaneous entry, we need to ensure a substantially long retention period of water molecules inside the tube. The hydrophobic core of a SWCNT has been shown to fluctuate between an empty and a filled state [24–26]. An attractive interaction between water molecules and carbon atoms on the wall (higher than a certain threshold value) is required for significantly high average occupancy of water molecules inside the CNT cavity [24]. By tuning the attractive interaction between CNT and water molecules with an adjustable parameter, λ, a threshold value for $\lambda$was found to promote the filled state [25]. It is also noted that the structure and dynamics of confined water are significantly modulated in several functionalized carbon nanotubes (FCNTs) [17,27–30]. Accordingly, an endohedral functionalization of SWCNT with at least one polar group (such as a -COOH or -COO^-) seems an appropriate choice for a hydrophobic core suitably tuned to facilitate increased average occupancy by water molecules. The functional group present within the core would be expected to promote the entry of water molecules in the tube. It may also hold them inside for a long time through hydrogen bonding interactions, for instance. Finally, we contemplate the release of water from the designed SWCNTs. Wetting and dewetting of the inner pore of CNT are known to be

* Corresponding author.
E-mail address: srabani@chem.iitkgp.ernet.in (S. Taraphder).

http://dx.doi.org/10.1016/j.chemphys.2016.09.013
0301-0104/

influenced by electric fields applied orthogonal to the tube axis [31]. Higher electric fields have been shown to favor the dry state and reduce the residence time of water molecules inside CNT [31]. These results indicate the possibility of using an external electric field for an easy release of the stored water on demand.

It is also important to evaluate the thermodynamic feasibility of the proposed storage process. Entropy generation has long been a critical issue in fabricating microfluidic devices with optimum efficiency [32,33]. The entry and partial or full occupancy of water molecules inside SWCNT appear to be thermodynamically favorable, although the relative contributions of energy/enthalpy and entropy changes are highly debated [25,34–36]. The relative importance of entropy and enthalpy changes in the filling of CNTs by water is reported to depend on the size [37] and type [38] of nanotubes being used. In narrow CNTs (of diameter 0.8–1.0 nm), the filling is found to be driven by both translational and rotational entropy. Medium sized nanotubes (of diameter 1.1–1.2 nm), in contrast, shows stabilization of water molecules on account of favorable enthalpy changes. In larger nanotubes (of diameter 1.3–2.7 nm), translational entropy is found to be the major driving force of water transfer into the hydrophobic channel [37]. Estimation of free energy of binding of water molecules with (5,5) and (6,6) CNTs (using thermodynamic integration and thermodynamic cycling) reveals that initial loading of water molecules is driven by entropy but the later stages are energetically driven by strong dipolar interactions among the water molecules inside CNT pore [38]. In view of these results, our current model, employing functional groups to assist in lining up water molecules inside the pore, appears to be suitable in terms of thermodynamic parameters.

In an earlier work [39], we have used extensive molecular dynamics simulations to study the behavior of water molecules inside the core of a series of endohedrally functionalized CNTs (FCNTs). Each FCNT was prepared *in silico* using a (6,6) SWCNT and covalently attaching an analog of a polar amino acid side chain to its inner wall. Five different FCNTs were generated by incorporating *uncharged* side chain analogs of histidine (His), aspartic acid (Ash), glutamic acid (Glh), threonine (Thr) and serine (Ser). The structure and dynamics of water molecules inside these FCNTs were compared with those residing inside a pristine CNT. The average residence time per water molecule (τ_R) inside the FCNTs was shown to depend crucially on the functional group that is suspended from the inner wall and extend into the core of the tube. The value of τ_R was found to be maximized in Ash-FCNT, followed closely by Glh-FCNT. Our preliminary estimates indicated that in the presence of the carboxylic acid groups in their protonated forms, water molecules inside these FCNTs gain substantial amount of rotational entropy favoring longer retention of water molecules within the core. The residence times increased with increasing length of the nanotube.

Based on the observations cited above, in the present article we propose a set of four FCNTs, endohedrally functionalized with carboxylic acid groups in different states of protonation, as models for storage devices of water molecules in the nanometer and sub-nanometer scale. The residence times and dynamics of water molecules trapped inside the CNT core, along with thermodynamics of transfer of bulk water into the hydrophobic core, are reported in support of the viability of our proposal.

2. Method

2.1. Model

In the present work, model FCNTs have been generated starting from open ended, (6,6) single walled carbon nanotubes having three different lengths equal to 15.6, 51.9 and 101.6 Å. For the ease of reference, we label these lengths as 15, 50 and 100 Å, respectively, in the rest of the article. In each case, an endohedral functionalization of the CNT has been carried out in the gas phase using the utility of DMol3 [40] where one of the C-atoms on the wall close to the middle of the tube is modified from sp^2 to sp^3 hybridization. In the next step, a desired functional group is covalently attached to the modified C-atom such that it extends inside the hydrophobic core of the tube [41]. The resultant structure has been optimized by density functional theory [42]. It may be noted that the structures of only shortest FCNTs (of length 15 Å each) have been optimized. For each of the longer tubes, the optimized 15 Å long functionalized unit is extended on both sides using DMol3 [40] by replicating carbon atoms on the wall only.

As mentioned earlier, we have used two carboxylic acid groups for the functionalization in their respective protonated and unprotonated forms. The resultant structures are.

(i) Ash-FCNT when functionalized with $-CH_2-COOH$,
(ii) Asp-FCNT when functionalized with $-CH_2-COO^-$,
(iii) Glh-FCNT when functionalized with $-CH_2-CH_2-COOH$ and
(iv) Glu-FCNT when functionalized with $-CH_2-CH_2-COO^-$.

These are shown in Fig. 1. Twelve different FCNTs have thus been prepared by varying the functional group, its protonation state and length of the nanotube.

2.2. Details of simulation

Each of the model FCNTs described above has been used in classical molecular dynamics simulation by adopting the following steps. A single FCNT molecule is solvated by around 5000–10,000 TIP3P [43] water molecules depending on the length of FCNT used. The simulation system was minimized to remove bad contacts first by constraining the atoms belonging to carbon nanotubes and then by carrying out an all atom minimization. The minimized system is subsequently heated slowly from 0 K to 300 K and equilibrated in

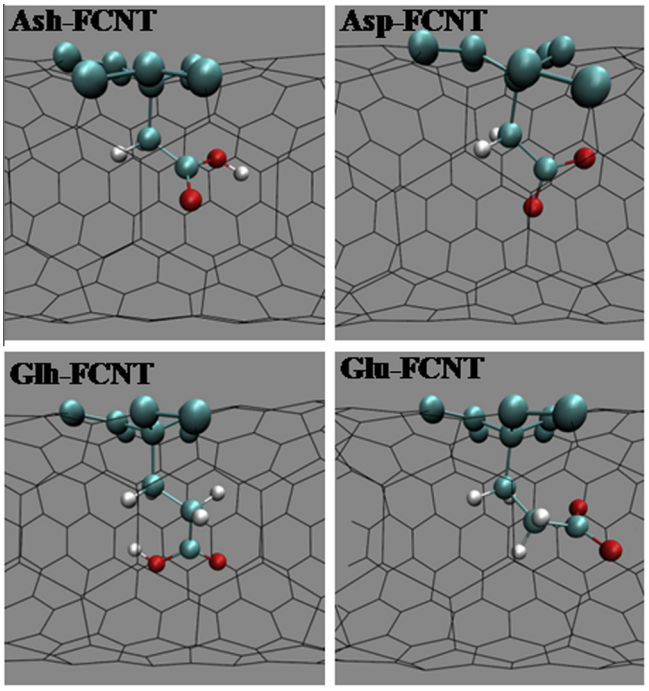

Fig. 1. Endohedral functionalization on the inner wall of SWCNT for Ash-, Asp-, Glh- and Glu-FCNTs. The blue, red and white balls represent carbon, oxygen and hydrogen atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)