Applied Surface Science 423 (2017) 154–159

Contents lists available at ScienceDirect

Applied Surface Science

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

Selective ion transport in functionalized carbon nanotubes

Olga N. Samoylova [a], Emvia I. Calixte [b], Kevin L. Shuford [b],*

[a] *Department of Biochemistry and Molecular Biology, University of Texas Medical Branch, 301 University Blvd, Galveston, TX 77555-0304, United States*
[b] *Department of Chemistry and Biochemistry, Baylor University, One Bear Place #97348, Waco, TX 76798-7348, United States*

ARTICLE INFO

Article history:
Received 24 February 2017
Received in revised form 16 May 2017
Accepted 10 June 2017
Available online 15 June 2017

Keywords:
Modified carbon nanotube
Selectivity
Ion current
Molecular dynamics

ABSTRACT

Ion transport through functionalized carbon nanotubes in an external electric field is studied using all atom molecular dynamics simulations. The surface of carbon nanotubes has been functionalized with hydrogens and hydroxyl groups, and ionic current passing through the nanochannels has been examined with respect to the extent of surface modification. We are able to dramatically increase the ionic current passing through the nanotube via the appropriate surface modification. An analysis of the electrostatic potential within the tube shows higher ionic currents result from an increase in accessible pathways coupled with a global shift toward more direct ion passage. Moreover, through judicious choice of structure, the current can be modulated to a large degree with ion selectivity.

1. Introduction

Structure and dynamics of confined fluids is drastically different from that of bulk due to large internal surfaces and geometric restriction. Variations in the local environment can lead to altered physical and chemical properties, and in some cases yield exotic system behavior. Examples include modified fluid structure, different thermodynamic, kinetic and correlation properties, size dependence and shift of critical parameters like temperature, pressure, and density, as well as spatial limitation and dimensional crossover effects on the dynamic properties such as diffusion and relaxation [1–5]. In our previous investigations of brines under confinement, we observed significant changes in fluid properties as the encapsulating pores decreased in size [6–9]. Specifically, we found reduced water densities, increased water and ion structuring at interfaces, reduced ion hydration, and disruption to the overall hydrogen bonded network. The increased hydrogen bond lifetimes coupled with higher hydrogen bond activation energies were due to unfavorable reorientation of water molecules as pore diameter decreased [9].

There is great interest in elucidating the characteristics of confined fluids and further developing systems that can actively control these properties on the nanoscale. Carbon nanotubes (CNTs) are promising candidates for such novel technologies due to their unique mechanical, electrical, and optical properties [10–12]. In particular, applications that incorporate nanotubes (sensing, nanofluidics, electrochemistry, etc.) may benefit greatly from controllable ion transport coupled to favorable surface interactions that can be manipulated in some way [13–18]. For example, the development of water purification technologies using CNTs is very attractive owing to their chemical and mechanical properties, low mass, large surface area, high aspect ratio, low cost and low impact on the environment [19]. These properties along with high flux and potential for selectivity make them highly favorable for next generation membrane technology [20,21]. However, pristine nanotubes tend to aggregate and fouling can also limit desalination. Surface modifications to CNT sidewalls can address these limitations and may also improve adsorption of contaminants and intensify water flux [19]. Other studies on ion entry have reported routes for selectivity based upon judicious choice and placement of functional groups [22,23]. More generally, it is expected that uncapped CNTs are inherently tip modified, and investigations into different forms of functionalization are highly relevant [24]. It is thus important to fully understand fluid transport through CNTs as you reduce tube size, and in turn how the surface chemical properties affect this.

In a previous molecular dynamics (MD) study, we examined ion and solvent transport through CNTs of different diameters in an external electric field [25]. For large diameter CNTs, ionic current was essentially linear with voltage. However, deviations from this behavior emerged as the CNT diameter decreased, until eventually no ions were able to pass. The aim of the current study is to increase the ionic current through small diameter CNTs by modifying the tube surface with different functional groups. The results are meant to emphasize the effects of surface chemistry and demonstrate how these interactions can be utilized to control transport, especially

---

* Corresponding author.

http://dx.doi.org/10.1016/j.apsusc.2017.06.120
0169-4332/

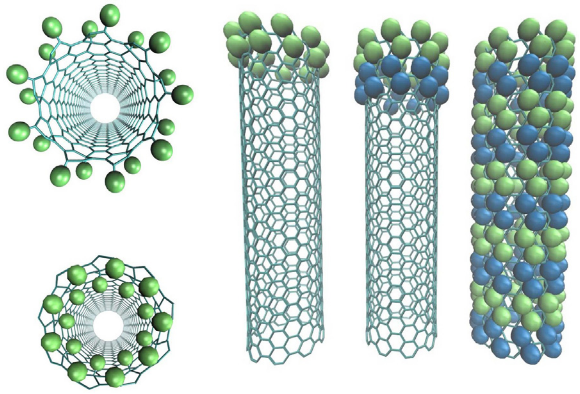

Fig. 1. Schematic representation of CNT modification from the outside or inside (left) and by rings (right). Spheres denote functional groups (OH or H atoms) bound to carbon atoms of the CNT. Green/blue rings represent odd/even number of modification rings (for visualization purposes only). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

in small CNTs that do not readily permit ion passage otherwise. We find that by altering the conditions at the interface, the ionic current can be increased significantly. Our analysis also provides insight into the mechanism and underlying principles driving this observation, which can be leveraged to design fluid transport vessels with enhanced properties. Through surface chemistry, we are able to modulate the current and provide a degree of ion selectivity not previously present in pristine CNTs of similar size. This yields a chemically intuitive approach toward controlling fluid transport properties within CNTs via existing methods of synthesis. Although not the focus here, we note there is a vast literature describing synthetic routes to functionalize CNTs. Most relevant for the theoretical studies below are those that result in sidewall addition of H or OH groups, which have been realized experimentally [26–32].

2. Theoretical methods

2.1. Model systems

We have examined armchair CNTs with chiral indices ranging from (6,6) to (9,9) that are 40 Å in length. Our previous studies found NaCl transport through unfunctionalized (9,9) CNTs to be substantially altered by confinement effects [25], thus CNTs of this size were specifically targeted in this work. In particular, we wanted to induce significant ionic transport in systems that did not readily allow ions to pass previously, while providing some degree of selectivity.

CNTs were constructed using the tcl code [33] with the C—C bond equilibrium distance set to 1.42 Å and an equilibrium angle between carbon atoms of $\Theta_0 = 120^\circ$. To model functional groups on the surface, pristine CNTs were modified by adding H or OH groups to selected carbon atoms. Experimental routes of sidewall addition lead to varying degrees of functionalization that are not saturated but can vary greatly (1–10%, perhaps more) [34]. To account for this broad range and extrapolate to levels beyond, we varied the extent of functionalization by modifying the CNT incrementally, one "ring" at a time starting from the top. We denote a ring as a series of connected benzene-like molecules that roll up to encompass a segment of the overall CNT length; stacking all the rings forms the tube. For a (n, n) CNT, each ring has n hexagons of carbon atoms connected in a circle. Our model for the modified CNT adds functional groups to $2n$ carbon atoms composing the ring – every second carbon atom along the top of a hexagon cell and every second carbon along the bottom of each hexagon cell, staggered from the top. Fig. 1 shows schematically the method of CNT modification by rings. For example, a (9,9) CNT with 1 ring of modified carbon atoms has 18 functional groups of atoms bound to certain carbons. The H or OH groups were added to the outside of the CNT, leading to different configurations for each CNT diameter examined. Note that functionalizing the CNT alters the charge distribution, which is represented in the simulations by a change in force field parameters at those sites (see Section 2.2). All modifications of pristine CNTs were performed using Avogadro [35], followed by an initial geometry optimization using MMFF94 force field [36]. The functionalized CNTs were then solvated with NaCl solution. Details about the model systems – the number of carbon atoms, OH/H groups added, sodium and chloride ions, and water molecules – can be found in Tables 1 and 2.

Table 1
Carbon nanotube systems of interest. Columns are labeled by CNT chiral vector indices (n, m), CNT radius, the number of carbon atoms in the CNT, and the number of ions and water molecules, respectively. The tube length is 40 Å in all cases.

(n, m)	Radius, Å	Carbon	Ions	Water
(6,6)	4.09	480	36	932
(7,7)	4.76	559	34	898
(8,8)	5.44	640	34	857
(9,9)	6.12	720	32	839

Table 2
CNT modification by rings with the numbers of H/OH functionalizations bound to carbon atoms. Columns are labeled by number of rings and CNT type.

Rings	(6,6)	(7,7)	(8,8)	(9,9)
1	12	14	16	18
2	24	28	32	36
⋮	⋮	⋮	⋮	⋮
10	120	140	160	180

Table 3
Bond parameters.

Atom pair	$k_{stretch}$, kcal/mol Å^2	r_0, Å
C—C	305.0	1.375
C—H	340.0	1.083
C—O	334.3	1.411
O—H	545.0	0.96

We have chosen to utilize a rather idealized model throughout these studies. The goal was not to represent a particular experimental system, but rather to explore the range of effects that could be achieved by introducing new interactions in a controllable manner. This approach allows us to glean insight from the model systems, which can then be used to develop a fundamental understanding of complex transport processes and routes to control them. Model variations that probe the vast complexities present in real experimental systems are under development currently.

2.2. Simulation approach

We used all atom molecular dynamics (MD) to simulate ion transport through CNTs of various radii in the presence of an electric field. Each tube was solvated by ~1 M NaCl solution in an orthorhombic simulation box with dimensions 24 Å × 24 Å × 70 Å. TIP3P water molecules [37] have been used for the simulations. Carbon atoms of the tube were harmonically restrained. The tube was aligned along the z-axis, corresponding to the long axis of the hexagonal system. All MD simulations have been performed using the program NAMD2.9 [38] with the CHARMM36 force field [39]. Force field parameters are shown in Tables 3–6.

The system was minimized and then equilibrated for 5 ns at 300 K using the NPT ensemble and a 1 fs time step. Periodic boundary conditions were applied in 3 dimensions, and the Particle