

Nanofiltration of Electrolyte Solutions by Sub-2nm Carbon Nanotube Membranes

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ABSTRACT

Both MD simulations and experimental studies have shown that liquid and gas flow through carbon nanotubes with nanometer size diameter is exceptionally fast. For applications in separation technology, selectivity is required together with fast flow. In this work, we use pressure-driven filtration experiments to study ion exclusion in silicon nitride/sub-2-nm CNT composite membranes as a function of solution ionic strength, pH, and ion valence. We show that carbon nanotube membranes exhibit significant ion exclusion at low salt concentration. Our results support a rejection mechanism dominated by electrostatic interactions between fixed membrane charges and mobile ions, while steric and hydrodynamic effects appear to be less important. Comparison with commercial nanofiltration membranes for water softening reveals that our carbon nanotube membranes provides far superior water fluxes for similar ion rejection capabilities.

Keywords: carbon nanotube, membrane, ion exclusion, fast flow

1 INTRODUCTION

1.1 Properties of Carbon Nanotubes

By now carbon nanotubes (CNTs) have firmly established itself as the iconic molecules of nanoscience. Despite having a very simple chemical composition and structure, it is capable of displaying an astonishing variety of unique properties. A carbon nanotube is simply a nanometer-sized rolled-up graphene sheet that forms a perfect seamless cylinder capped at the ends by fullerene caps.

A carbon nanotube can have one (as in case of a single-walled carbon nanotube), or several concentric graphitic shells (as in case of multi-walled nanotubes). One of the most remarkable properties of this structure that makes it attractive for transport applications is its unique combination of its extremely high aspect ratio with small dimensions: a nanotube can reach up to several millimeters in length, yet retain a diameter of only a few nanometers.

The second important nanotube property that is critical for the transport applications is the remarkable atomic scale smoothness and chemical inertness of its graphitic walls.

Several methods of CNT production currently exist. In the laboratory environment catalytic chemical vapor deposition (CVD) is preferred over other methods such as arc discharge and laser ablation because it produces higher quality carbon nanotubes. CVD reactors can produce individual isolated nanotubes, as well as densely packed vertically-aligned arrays. Unfortunately, the ultimate goal of the carbon nanotube synthesis- producing a uniform population of nanotubes with a given chirality- still remains elusive. Several studies indicated that the size of the catalyst particle during the growth stage determines the size of the carbon nanotube to less than 10% [1]; yet the efforts to control the size of the carbon nanotubes with greater precision have been largely unsuccessful. Thus, synthesizing a vertically-aligned carbon nanotube array with a narrow distribution of sizes still remains a difficult endeavor requiring considerable process development and optimization efforts [1-3]. The task of describing the details of CNT synthesis goes well beyond the scope of this article; therefore we refer the readers to the recent reviews [4-6].

1.2 Molecular Dynamics Predictions and Experimental Observations of Fast Flow through Carbon Nanotubes

In the last few years, fluid transport through carbon nanotubes has been subject of intense research. A recent review summarizes [7] the state of the current theoretical and experimental effort toward understanding fluid flow through carbon nanotube channels.

Using MD simulations, G. Hummer and colleagues surprisingly found that water molecules spontaneously fill a (6,6) carbon nanotube (0.81 nm in diameter and 1.34 nm in length) [8]. Several experimental studies also provide some evidence of water filling of carbon nanotubes [9-12]. Weak interactions of water molecules with the hydrophobic walls combine with the smooth nature of the nanotube walls to enable nearly-frictionless, ultrafast transport of water in nanotubes channels [13].

Recently, extremely high, pressure-driven flow-rates of water have been reported through sub-2-nm DWNT membranes [14] and through MWNT membranes with larger pore diameters [15]. Measured flow rates correspond to enhancements of 4–5 orders of magnitude compared with the no-slip, hydrodynamic flow calculated using the Hagen–Poiseuille equation for MWNT membranes [15], and of at least 2–3 orders of magnitude for DWNT membranes [14]. Experimental water fluxes compare well with those predicted by MD simulations. With 100-atm osmotic pressure, ~12 water molecules flow through a CNT per nm² of cross-sectional area per ns [16]. Measured fluxes, extrapolated to the simulation pressure drop, correspond to 10–40 water molecules per nm² per ns [14].

For applications in separation technology, selectivity is required together with fast flow. In particular, for water desalination, coupling the enhancement of the water flux with selective ion transport could drastically reduce the cost of brackish and seawater desalting.

In this work, we study the ion exclusion properties of DWNT with sub-2-nm diameter CNTs whose entrance is decorated by negatively charged carboxylic groups. These DWNT span the whole thickness of an otherwise impermeable silicon nitride (SiN_x) membrane. We use pressure to drive the filtration of ionic solutions through the SiN_x/CNT composite membranes.

2 EXPERIMENTAL

2.1 Membrane Fabrication

SiN_x/CNT composite membranes are fabricated as explained elsewhere [14]. Briefly, a vertically aligned array of CNTs is encapsulated with low-stress SiN_x by an extremely conformal, low pressure CVD process. After encapsulation, the membrane undergoes a series of etching steps to remove excess SiN_x from the tips of the CNTs, followed by oxygen plasma to uncap the CNTs. The resulting free standing membrane is located in 89 windows (50 μm in diameter) etched on a silicon support (Figure 1) [14].

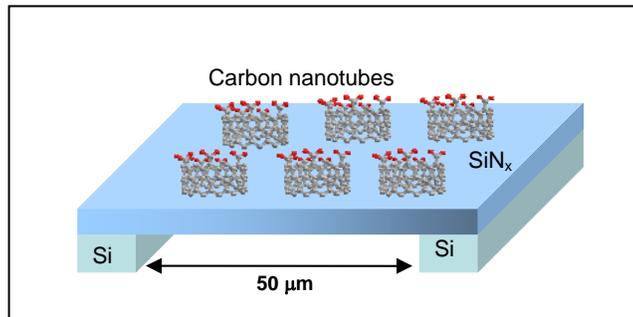


Figure 1: Schematic representation of a 50 μm window containing the free standing SiN_x/carbon nanotube membrane.

TEM of thinned-down sections of our double-walled CNT (DWNT) membranes shows pores with less than 2 nm in diameter, consistent with diameters of as-grown nanotubes. The absence of nano- or microvoids larger than the nanotube diameter is also demonstrated by the full retention of 2 nm gold nanoparticles during filtration of colloidal gold solution [14].

2.2 Nanofiltration

Figure 1 shows a schematic of the nanofiltration set-up. A CNT membrane is mounted in a filtration cell so that it divides the cell in two chambers. The top chamber (feed) is filled with about 2 ml of salt solution. The feed solution is pressurized at 0.69 bar, while the permeate chamber is kept at atmospheric pressure. Permeate flow rate is recorded as variation of the column height of the feed solution with respect to time. At the end of a nanofiltration experiment, solution samples from both feed and permeate are collected and analyzed by either capillary electrophoresis (Hewlett Packard 3D CE capillary electrophoresis system, Agilent Technologies, Santa Clara, CA) or UV-vis spectroscopy (PerkinElmer, Waltham, MA). The rejection coefficient R for an ion i is calculated as:

$$R = 1 - \frac{c_i^p}{c_i^f} \quad (1)$$

where c_i^f and c_i^p , are the ion concentrations in the feed and permeate, respectively.

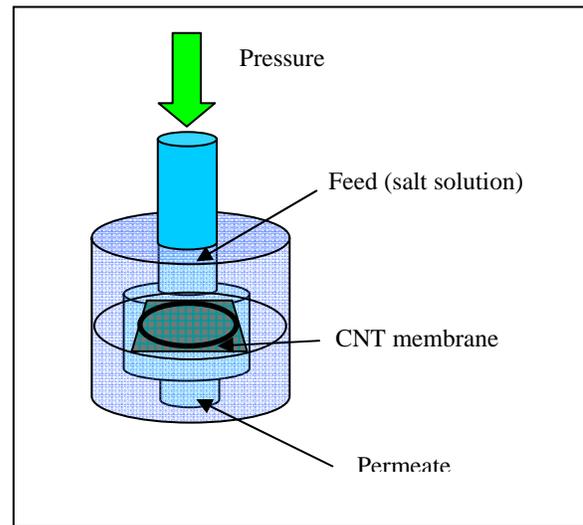


Figure 2: Schematic representation of the experimental nanofiltration cell

3 RESULTS

Capillary electrophoresis (CE) analysis of the ion concentration before and after nanofiltration shows that the DWNT membranes exclude a large part of the feed solution ionic content. Moreover, carbon nanotube membranes maintain the ultrafast rates of water flow reported in our previous study [14]. Measured rejection ratios are comparable to the rejection ratios exhibited by a tight nanofiltration membrane tested under the same conditions. Note that our DWNT membranes provide an order of magnitude higher flux than the tested commercial nanofiltration membrane.

To test if electrostatic interactions are an important determinant of the ion exclusion in silicon nitride/ sub-2-nm CNT composite membranes, we study ion rejection as a function of solution pH and ionic strength. Nanofiltration of solution of ions of different valences was used to further understand the underlying mechanism of ion exclusion. More details are reported in Reference [17].

Our experimental observations indicate that the electrostatic forces between carboxylic groups on the CNT rim and the free ions play a significant role in the rejection of electrolytes during salt solution nanofiltration [17].

4 CONCLUSIONS

We have used pressure-driven nanofiltration of ionic solutions through sub 2-nm carbon nanotube membranes to study ion rejection by carbon nanotubes that have carboxylic groups on their rim. Analysis of ion concentration in the feed and permeate reveals that these membranes are able to significantly reject small ions while maintaining ultrafast water transport rates.

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