

Gated Chemical Transport and Enhance Flow through Carbon Nanotube Membranes

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ABSTRACT

A promising architecture for ion-channel mimetics is a composite membrane structure containing vertically aligned carbon nanotubes, with inner core diameters of 7 nm, passing across a polystyrene matrix film. Plasma oxidation during the fabrication process introduces carboxylic acid groups on the CNT tips that are modified using carbodiimide mediated coupling between carboxylic acid on the CNTs and accessible amine groups of the functional molecule. Relative selectivity of the permeates was seen to vary from 1.9 to 3.6 as a function of tip-functionalization chemistry. Anionic charged functional groups are seen to sharply increase flux of cationic permeates. Biologically active desthiobiotin was also shown to be reversibly coordinated to streptavidin, showing a reduction in ionic flux through CNT. Pressure driven flux of a variety of solvents (H₂O, hexane, decane ethanol, methanol) are 4-5 orders of magnitude than conventional Newtonian flow. There are also experimental indications of the ordering of polar solvents inside CNT pores. Dual functional CNTs (that is different functionality at each end of a CNT) have also been produced by reacting each side of the membrane with different functional solution, then subsequent removal of polymer matrix..

Keywords: carbon nanotube, membrane, chemical separations, drug delivery, fluid flow

1 INTRODUCTION

Synthesis and characterization of ordered nanoporous materials with non-tortuous and well controlled pore diameter is an active research area with applications that include separations, catalysis, molecular sensing, and controlled drug delivery.^{1,2} Synthesis of a suitable membrane structure with highly ordered vertical orientation of pores is a difficult challenge.³ A promising approach for obtaining vertically oriented membrane structure has been controlled reduction of pore size of existing ordered porous structures like anodized alumina or track etch polycarbonate membranes.⁴ A flurry of research activity for reducing pore size by electroless deposition⁵ or CVD⁶ has demonstrated improvement in separation coefficients.

Critical to membrane separations is fine control of pore size. The inner core of carbon nanotubes offer an alternative route to uniform membrane pore diameter with fine control determined by catalytic particle size.⁷ Transport mechanisms through the graphitic hydrophobic cores of the CNTs is also of scientific interest that needs further experimental verification of theoretical studies.⁸ Recently vertically aligned carbon nanotube membranes with CNT cores (~7 nm diameter) traversing across a thin solid polymer film have been synthesized.⁹ Ionic and gas transport through CNTs is seen to be consistent with the geometry. Not only does pore size, but functional molecules attached to the pore surfaces can also lead to highly selective separations forcing chemical interaction between the permeate and the functional molecule.¹⁰ Since the oxidation process selectively functionalizes the entrances/tips of CNT cores, these membranes offer a unique nano-scale scaffolding to permit 'gate-keeper' interactions possibly increasing both flux and selectivity. Transport through hydrophobic carbon nanotube is analogous to biological membrane channels. Biological membrane systems are abundant in examples where protein molecules facilitate transport of ions or molecules. Motivation for the present study stems from such biological systems, in which molecules regulate the transport properties of molecules or ions in highly hydrophobic environments

2 EXPERIMENTAL

2.1 Membrane Fabrication

CNT membranes were fabricated using the previously described method.⁸ Briefly, an aligned array of multiwalled CNTs is grown by chemical vapor deposition using ferrocene/xylene feed gas. The volume between CNTs is filled with polystyrene and the composite film is removed from quartz substrate by HF etching. Excess surface polymer as well as Fe nanocrystals at CNT tips are removed by H₂O plasma oxidation,¹¹ resulting in a membrane structure with CNT cores traversing the polystyrene film and carboxylate functionalization at CNT tips.

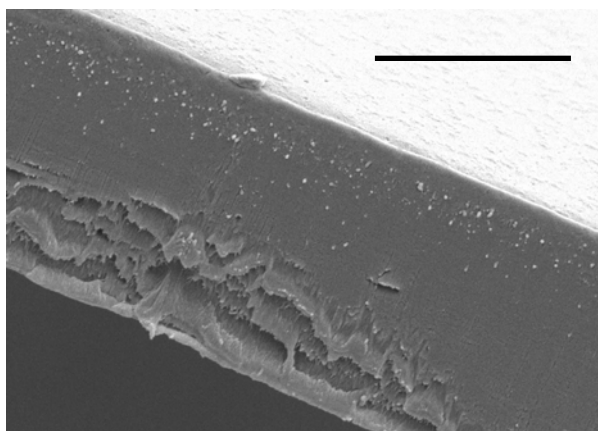


Figure 1. Cross sectional view of free-standing aligned CNT/polystyrene composite film membrane. Scale bar is 5 μm .

2.2 Chemical Functionalization

The entrances to CNT cores in the membranes were functionalized using well known carbodiimide chemistry. The following chemicals were used for these reactions: 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC, 98%, Aldrich), nonyl amine (C9, 98%, Aldrich), Direct Blue 71 (dye, Aldrich), 8-amino caprylic acid (ACA, 99%, Aldrich), Kemamine P-298D, (C22, Crompton Corporation, USA), 2-N-morpholino ethanesulfonic acid (MES, 99%, Sigma), isopropyl alcohol (99.5%, EMD), Ethyl alcohol (Aaper Alcohol and Chemical Co., Kentucky). For reactions in water, D.I. water ($\sim 18 \text{ m}\Omega$ resistance) was used.

For the water soluble molecules, C9 and dye, appropriate amount of C9 and dye were added to 4 ml solution of 0.1(M) MES buffer to make it 50 mM. 8 mg of EDC was dissolved in the solution and then the membrane was added to it. The reaction was carried out for 12 hours at ambient temperature after which the membrane was washed with MES buffer and IPA to remove the excess reagents. The functionalized membranes will henceforth be referred as CNT-9 and CNT-dye. Kemamine is a commercial fatty

amine containing about 90% C22. It is insoluble in water, but soluble in IPA at 35^o C. 32.36 mg of C22 & 8 mg of EDC was added to 4 ml of IPA along with the membrane and kept in a water bath at 35^o C. The reaction was carried out for 12 hours and was washed with Ethyl alcohol.

2.3 Transport Measurement

The pore density of the membranes was estimated using KCl diffusion through the membrane. The feed solution was 7.5 cc of 669 ppm of KCl (standard solution). The volume in the permeate is 1.5 cc. The maximum concentration measured is 25 ppm. Thus, the total mass of KCl in the feed solution is about 2 orders of magnitude greater than that in the permeate, eliminating depletion effects. Both the feed and the permeate cells were stirred with a magnetic stirrer. The conductivity of the permeate was monitored by a conductivity electrode (Microelectrodes Inc.), connected to a conductivity meter (Orion 150 A+ conductivity meter) and the data was collected in a spread sheet using Balance Talk SL (Labtronics) every 15 min. The conductivity meter was calibrated using 66.9 ppm standard solution before the start of any experiment. The conductivity data was converted into flux data using an appropriate calibration curve of ppm of KCl vs. conductivity. The permeable pore area (A_p) can be estimated from the equation

$$A_p = D \cdot c / J \cdot l$$

Where D is the bulk diffusivity of KCl at 21^oC ($\sim 1.96 \cdot 10^{-5} \text{ cm}^2/\text{s}$), c is the concentration of the feed ($8.97 \cdot 10^{-3} \text{ M}$), l is the membrane thickness (from SEM cross sectional pictures), and J is the experimental steady state flux of KCl (moles/s). A representative example of ionic flux data is shown in Figure S1. The permeable pore density can be calculated from:

$$\text{Permeable pore density (\#/cm}^2\text{)} = (A_p/A_m) / (\pi d^2/4)$$

Where, d is the pore diameter (7 nm), and A_m is the membrane area exposed in the diffusion experiment (0.19 cm^2).

A simple pressure-flow experimental apparatus was

Liquid	Permeable pore density (# per cm^2)	Membrane thickness (micron)	Initial permeability ($\text{cm}^3/\text{cm}^2\text{-min-bar}$)	Flow velocity normalized at 1 bar (cm/s)	Viscosity (cP)	Calculated Newtonian flow velocity at 1 bar (cm/s)	Slip length (micron)
Hexane	$3.4 \cdot 10^9$	126	0.44	5.6	0.3	$5.16 \cdot 10^{-4}$	9.5
Decane	$3.4 \cdot 10^9$	126	0.053	0.67	0.9	$1.72 \cdot 10^{-4}$	3.4
Water	$1 \cdot 10^9$	34	0.58	25	1.0	$5.7 \cdot 10^{-4}$	54
	$3.4 \cdot 10^9$	126	1.01	43.9		$5.7 \cdot 10^{-4}$	68
	$3.4 \cdot 10^9$	126	0.72	9.5		$1.5 \cdot 10^{-4}$	39
0.017(M) KCl	$3.4 \cdot 10^9$	126	1.25	19.6		$1.5 \cdot 10^{-4}$	108
EtOH	$3.4 \cdot 10^9$	126	0.35	4.5	1.1	$1.4 \cdot 10^{-4}$	28
IPA	$3.4 \cdot 10^9$	126	0.088	1.12	2	$7.7 \cdot 10^{-4}$	13

Table 1. Summary of observed pressure driven flow through aligned MWCNT membrane.

made. All associative liquids (water, isopropal alcohol (IPA), ethanol (EtOH)) are boiled in a vacuum oven for a period of 12-24 hours and allowed to cool in vacuum. For measurements of different liquids on the same membrane, it is dried in air for 12 hours and then soaked in the solvent for 1-2 hours prior to the experiment. The syringe is then filled with the liquid and the pipe line is purged with the liquid at 2.5 ml/min flow rate, keeping the valve completely open so that any air in the pipes is driven away. Thereafter, the valve is gradually closed manually to increase pressure inside the flow cell. Once a drop of liquid is seen coming out of the nipple, the data acquisition in the computer is started. Time dependent pressure data is also collected manually.

For diffusion experiments to show size selective chemical separations at the entrance to CNT cores, a simple U-tube cell with o-ring seals to have the membrane separate feed from permeate solution. The liquids in the two chambers were maintained at the same level to avoid any pressure induced transport. The probe molecules: Methyl viologen dichloride hydrate and Ruthenium bi-pyridine hexahydrate were purchased from Aldrich. The probe molecules were chosen for their ease of detection by UV-vis and the ability to directly compare fluxes and selectivities directly with other nano-porous systems.² The permeate was periodically pipetted out, the probe molecules readily quantified by UV-vis spectroscopy (HP 8543 Spectrophotometer) and then was transferred back to the chamber. Ru-(bipy)₃⁺² has two peaks at wavelengths of 452 and 286 nm, whereas MV⁺² has a peak at 260 nm. The peak at 452 nm is used to quantify the amount of Ru-(bipy)₃⁺². MV⁺² peak at 260 nm has interference from the amount of Ru-(bipy)₃⁺², due to the peak at 286 nm. So, the contribution at 260 nm from the peak at 452 nm is deducted from the absorbance value at 260 nm and then used to quantify MV⁺². For quantifying the amounts of Ru-(bipy)₃⁺² and MV⁺² 6 point calibration curves (from 5x10⁻⁴(M) to 1x10⁻⁶(M)) were used.

3 RESULTS AND DISCUSSION

In general, flow velocity of liquids (v) through porous membranes can be predicted using Haagen-Poiseuille equation given by

$$v=(r^2\Delta P)/(8\mu L)$$

Where r is pore radius (7nm for our system), P pressure applied, μ dynamic viscosity, and L length of pore. The basic assumptions of this equation are laminar flow and 'no-slip' at the boundary layer, i.e. the velocity of the fluid at CNT wall is zero. From ionic diffusion experiments, we have an accurate measurement of available nanotube pore area (# of nanotubes times individual pore area). Table 1 summarizes observed flow velocities (measured volume rate/CNT pore area) are 4-5 orders of magnitude faster than conventional fluid predictions using Haagen-Poiseuille equation. In fact the observed flow velocity of water is close to the theoretical prediction of 90 cm/s (1 bar pressure) due to cooperative H-bond ordering and minimal CNT interaction.⁸ It is necessary to mention that since the flow of water through the membrane is declining with time, there is a slight systematic underestimate of the initial flow rate. 3 different measurements of H₂O flow are shown in Table 1. This experimental observation of extremely high velocity supports the hypothesis that the transport of water through carbon nanotubes is frictionless and is independent of the length of the channel.¹² From diffusion studies we also found that the diffusivity of large molecules do not change significantly from bulk, suggesting a frictionless flow inside the smooth interiors of carbon nanotube. The slip lengths for the solvents on the Carbon Nanotubes can be calculated from the equation¹³:

$$V(\lambda)/Vns = 1 + 4\lambda/r$$

Where, V(λ) is the experimentally observed flow velocity (cm/s), Vns is the flow velocity calculated from the Haagen-Poiseuille Equation, λ is the slip length and r is the radius of the nanotube. Higher slip lengths were observed

Membrane Tip Functionality	Size of Molecule (Ang.)	MV ⁺² Flux (nmoles/hr) (90% confidence)	Ru(bi-py) ₃ ⁺² Flux (nmoles/hr) (90% confidence)	α	Pore Size Calc. from α (Ang.)
CNT	0	4.21(±1.0)	2.45 (±0.39)	1.7	67
CNT-9	11.4	6.40 (±2.18)	2.12 (±0.90)	3.0	37
CNT-dye	28	21.05 (±2.32)	9.57 (±0.91)	2.2	47
CNT-22	26	1.84 (±0.48)	0.93 (±0.22)	2.2	50
CNT-40	52	0.65 (±0.13)	0.18 (±0.02)	3.6	33

Table 2. Summary of transport measurements across CNT membrane (0.3cm² area, 5mmol of each source) from a 2-component source solution. Separation factor was experimentally measured for the membranes and pore size was calculated from the model using separation factor and hindered diffusion model at CNT entrance (model i). CNT-9 refers to membrane functionalized with 1-amino nonane, CNT-dye with Direct Blue 71, CNT-22 kermanine, CNT-40 4 polypeptides links (C8) terminated with 1 amino hexane.

for the polar molecules. Both for the polar and non-polar liquids, the slip lengths decrease with the chain length of the hydrocarbon, which is consistent with the fact that better wetting of CNT wall decreases the slip length. Surprisingly the initial flow of water is much higher than hexane which is opposite to conventional expectations of a hydrophobic membrane and lower viscosity liquid to have higher flow through a CNT. This suggests that hydrogen bond coupling of the fluid as well as minimal interaction with CNT wall is a dominant mechanism for enhanced fluid flow. Interestingly for the hydrogen bonded liquids, the initial flow velocities also follow the same trend water>EtOH>IPA, suggesting that hydrogen bonding is the source of initial high flow.

Table 2 summarizes observed separation coefficients between Ru-(bipy)₃⁺² and MV⁺². with indicated 'gate keeper' selective chemical functionality at CNT core entrance. The length of the gatekeeper molecule at CNT core entrance is seen to increase size-based selectivity. Longer aliphatic lengths of functional molecules have poor solvation resulting in reduced selectivity, indicating the importance of functional molecular configuration. Using anionically charged dye molecules as gatekeepers dramatically improves cationic transport through the membrane due to Coloumbic attraction.

4 CONCLUSIONS

In general, the transport through the CNT core shows nearly no enhancement in ionic diffusion, modest N₂ gas flow, but incredible enhancement (4-5 orders of magnitude) of fluid flow. In the former case of ionic diffusion and Knudsen diffusion, the non-interacting CNTs offer no advantages, essentially acting like a mirror for ions and molecules to bounce off of. This random scattering would not enhance transport rate and in fact would closely correlate with bulk diffusivity. In the case of the much denser fluid flow, dramatic enhancement is observed because of the nearly frictionless interface of the fluid and the CNT. This allows for very high wall velocity. The boundary condition of non-zero velocity at the CNT wall does not require the viscous transfer of momentum from a 'core' velocity, as is seen in conventional pores that have strong chemical interactions between pore and fluid and have high roughness at the atomic scale.

Chemical functionalization at the entrance to CNT cores affects the selectivity of chemical transport across an aligned membrane structure. Since the selectivity of transport is modified through chemical functionality, the observed flux through the membrane cannot be through macroporous cracks in the polymer matrix. The length of the gatekeeper molecule at CNT core entrance is seen to increase size-based selectivity. Longer aliphatic lengths of functional molecules have poor solvation resulting in reduced selectivity, indicating the importance of functional molecular configuration. Using anionically charged dye molecules as gatekeepers dramatically improves cationic

transport through the membrane due to Coloumbic attraction. A hindered diffusion model with lowered diffusion near the entrance to CNT cores and with bulk diffusion along the length of CNTs was consistent with observed separation coefficients (α) as a function of chemical functionality. Thus the overall chemical flux through CNT membranes is largely limited by chemical interactions of functional molecules at the CNT core entrances.

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