Supporting Information

Osmotic Transport across Surface Functionalized Carbon Nanotube Membrane

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1. Fabrication and characterization of CNT membrane

a. Gas Measurement during Etching process:

We measured N_2 gas permeance through our membrane during the etching process to confirm the membrane integrity and verify the opening of CNT pores in the VA-CNT membrane. The figure below shows the N_2 gas permeance measurement during the etching process of membrane.

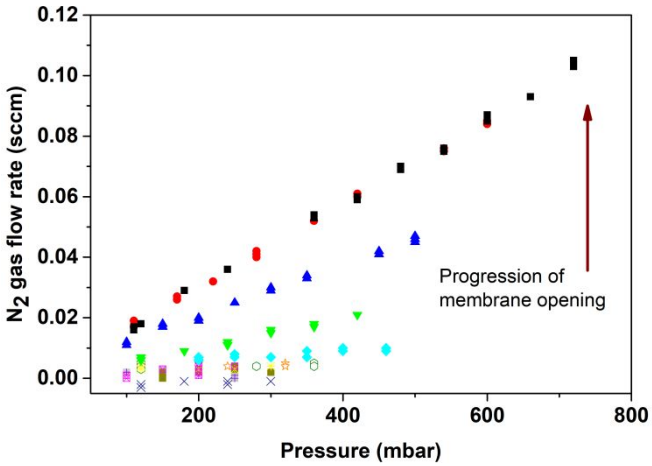

Figure S1. N_2 gas measurement during the stages of membrane etching and CNT pore opening

b. Membrane Layout and Area:

The projected membrane surface area was estimated from the optical microscope images of the backside-pit windows and then estimating the area using ImageJ software. Below is the optical image of one such window of our CNT membranes.

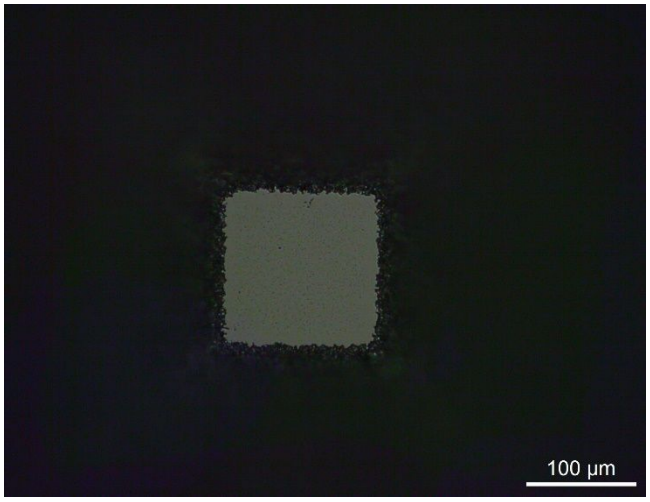

Figure S2. Backside optical image of window on the ODPA modified CNT membrane

c. Estimation of CNT areal density

We estimated the areal density of our vertically aligned CNTs using the steady-state NaCl permeation data from our non-functionalized CNT membrane together with Deen's hindered diffusion model[1].

$$Permeable\ CNT\ pore\ area,\ A_p = \frac{\dot{m}\, l_{CNT}}{\Delta C\, K_\lambda\, D_{NaCl}}$$

$$K_\lambda = 1 - 2.104\lambda + 2.09\lambda^3 - 0.95\lambda^5$$

$$\lambda = \frac{(r_{Na^+} + r_{Cl^-})}{2r_{CNT}}$$

Where ΔC is the salt concentration gradient, $\dot{m}$ is the flow rate of NaCl (moles/s), $l_{CNT} = 2.67\ \mu m$ is the thickness of the non-functionalized CNT membrane, D_{NaCl} is the bulk diffusivity of NaCl[2], K_λ is the diffusion hindrance factor, r_{Na^+} and r_{Cl^-} are the stokes radii[3] of the individual ions.

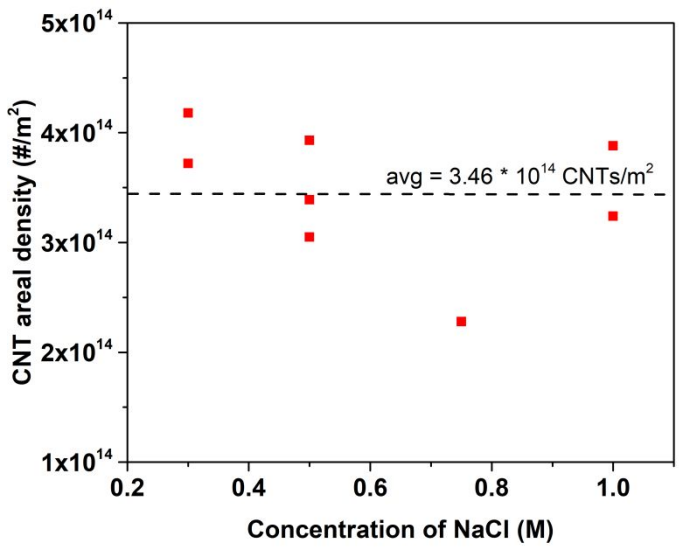

Figure S3. : Estimation of CNT areal density using steady state NaCl diffusive flow rate

2. Conductance measurements and correlation with salt flux

a. Calibration of conductivity probe for relating the measured conductivity to the feed-salt concentration

The conductance of the eDAQ dip-in conductivity probe (ET-915) was measured for a set of standard NaCl solutions. The Table S1 gives the values of the conductance measured. The EdaQ probe together with the accompanying software reads the values of conductance of solutions rather than conductivity. We used the same conductivity probe for all our experiments and thus our conductivities of solutions across all experiments correlate to the measured conductance across experiments.

Concentration (mM)	Conductance for NaCl (mS)	Conductance for KCl (mS)	Conductance for LiCl (mS)	Conductance for $MgSO_4$ (mS)
0 (MilliQ water)	0.00088	0.00128	0.00084	0.00052
0.01	0.00254	0.00289	0.00217	0.00441
0.1	0.01426	0.01620	0.01321	0.02719

Table S1. Conductance of salt solutions as measured using the conductivity probe for different concentrations

From the measurement of the conductances of the different salt solutions, a linear fit was obtained for different salts. For instance, for NaCl, it is

$$G_{NaCl} = 0.132\, c + 0.00104$$

Where G_{NaCl} is the measured conductance (mS) of feed from NaCl osmosis experiments, and c is the concentration of the solution in mM. The above equation was used to find the concentration of the feed and thereby determine the salt content on the feed side at the end of our osmosis experiments.

b. Measurement of salt flux

To measure the salt flux across the membrane from the draw to the feed side, we used the conductance measured for the duration of the experiment, when the osmotic water flow rate was calculated. The conductance measured during the experiment, G_{osm} was used in the conductance-concentration expression above to calculate the concentration of salt (e.g. NaCl) of the feed side in mM. The volume of the feed cell compartment in our diffusion cell was measured to be 7.9 mL.

$$Number\ of\ millimoles\ of\ NaCl\ permeated, m_{NaCl}\ (mMoles) = 0.0079\ c_{osm}$$

$$Mass\ of\ NaCl\ permeated\ (g) = 58.44 \times 10^{-3}\ m_{NaCl}$$

c. Reverse salt flux relative to the osmotic water flux

For the duration of the experiment, the measured osmotic water transport is V_{osm}. The reverse salt flux (g/L) is defined as,

$$Salt\ vs\ Water\ flux\ (g/L) = \frac{mass\ of\ solute\ (NaCl)\ permeated}{Volume\ of\ pure\ solvent\ (water) transported\ by\ osmosis}$$

3. Correlations between Osmotic Permeabilities and Hydraulic Permeabilities

a. Estimation of Osmotic Permeabilities (cm^3/s)

We used the unit – cm^3/s for comparing our data with osmotic permeabilities of AQP, CNT (simulations and experiment), BNT (simulation). Osmotic permeabilities are calculated using the relationship below.

$$Osmotic\ Permeability\ (cm^3/s)\ =\ \frac{Osmotic\ water\ flow\ rate\ (mol/s)}{\Delta C\ (mol/cm^3)}$$

b. Comment on stoppage of osmosis across CNT channels

We estimated the osmotic water transport rate and thus the permeabilities per CNT from the initial duration of the experiment (15 minutes). The time scale of stoppage of osmosis (order of 10's of minutes) is related to the concentration of the draw solutions and the type of constituent ions of the salt (e.g., Na+, K+, Li+). We looked at the concentration dependence (NaCl) and the salt dependence (LiCl, KCl, NaCl – at single concentration of 300 mM). We observed that at higher concentrations of draw solutions, the osmotic process stopped sooner. Among various draw salt solutions, i.e., LiCl, KCl, NaCl, at a constant draw concentration of 300 mM, we found out that the duration of observable osmosis, t, follows the order $t_{KCl} < t_{LiCl} < t_{NaCl}$, which we believe is related to cation-pi interactions of the hydrated ions on graphitic surfaces. We believe the osmotic water transport is stopped because of either (a) establishment of an equilibrium between osmosis and diffusio-osmosis or (b) ion accumulation inside the CNT due to ion-CNT wall interactions that eventually leads to negation of the gradients to continue to drive osmosis and diffusion-osmosis.

c. Estimation of osmotic pressure (π) from Osmolality

For the salts used during our osmosis experiments, we estimated the osmotic pressure from the osmolality measured using a freezing point depression based osmometer (OM-806, Loeser, Germany). The measured osmolality (mOsm/Kg) is related to the osmotic pressure (bar) using the following expression,

$$Osmotic\ Pressure\ (\pi,\ bar) = \frac{Osmolality\left(\frac{mOsm}{Kg}\right) \times 10^{-3} \times R\,T}{\rho_{H2O}}$$

Where R is the universal gas constant and T is the temperature of solutions (taken as 298 K)

Salt	Concentration (M)	Average Osmolality (mOsm/Kg)	Osmotic Pressure (bar)
NaCl	0.3	534.5	13.282
	0.5	919	22.837
	1	1855.5	46.110
KCl	0.3	552	13.717
LiCl	0.3	555	13.792
$MgSO_4$	0.3	301	7.480

Table S2. Measured osmolality of salt solutions

d. Measurement of hydraulic water permeabilities: pressure driven water transport

We measured the pressure driven water transport rates across the CNT membrane before and after ODPA functionalization. We used a dead end measurement

Hydrostatic pressure (mbar)	Hydraulic permeability (l_p) before ODPA functionalization (in $*10^{-21}$ $cm^3/Pa\cdot s$)	Hydraulic permeability (l_p) after ODPA functionalization (in $*10^{-21}$ $cm^3/Pa\cdot s$)
300	9.07	4.61
500	7.73	2.77

Table S3. Measured pressure driven water permeabilities of the CNT channels before and after ODPA functionalization of the CNT membrane

We measured the pressure driven water transport going from 300 mbar to 500 mbar. As is seen, the drop in permeability at the higher pressure is attributed to mild fouling before functionalization and a combination of reversible ODPA chain flexing and fouling for the measurement done after ODPA functionalization.

e. Estimation of non-ideality of CNT channels: Estimation of experimental and theoretical (geometrical) reflection coefficients

Using the above mentioned hydraulic permeabilities, we can estimate the theoretical maximum obtainable osmotic permeability using the relationship[4]

$$p_{f,\,estimated} = \frac{R\,T}{V_w}\, l_{p,exp} \quad \text{(eq. 1)}$$

Before functionalization, using the average hydraulic permeabilities from Table S3,

$$l_{p,\,average\ exp} = 8.4 * 10^{-21}\frac{cm^3}{Pa\cdot s}$$

Using equation (1),

$$p_{f,\ estimated} = \ 1.1562 * 10^{-12}\frac{cm^3}{s}$$

The estimated osmotic permeability will be the theoretically maximum permeability that can be observed with the CNT channel under condition of ideal semi-permeability. Since the CNTs used in our work do not exhibit ideal semi-permeability, but rather allow passage of ions. To account for the degree of non-ideality, one may evaluate the ratio of experimental osmotic permeability and estimated osmotic permeability, which is known as the *reflection coefficient (σ)*[5],

Therefore, we estimate the experimental reflection coefficient (σ_{exp})

$$\sigma_{exp} = \frac{p_{f,\,experimental}}{p_{f,\,estimated}} = \frac{0.4695 \times 10^{-12}\frac{cm^3}{s}}{1.1562 \times 10^{-12}\frac{cm^3}{s}} = 0.4061$$

We can also calculate the theoretical reflection coefficient (σ_{theor}) mainly from the geometrical consideration of the diameter of CNT channel and the ions.

$$\sigma_{theor,\,1D} = 1 - \left(1 - \frac{a}{r}\right)^2$$

$$\sigma_{theor,\,3D} = \left\{1 - \left(1 - \frac{a}{r}\right)^2\right\}^2$$

Where $\sigma_{exp,1D}$ and $\sigma_{exp,3D}$ are the reflection coefficients calculated solely from the dimensions of the channel (radius: r) and the permeating ions (radius: a), considering 1-dimensional and 3-dimensional transport respectively.

Using the values, r = 1.115 nm (∵ d_{CNT} = 2.23 nm) and hydrated radius of ion[3] (average of Na^+ and Cl^-), a = 0.345 nm

$$\sigma_{theor,\,1D} = 0.5231$$

$$\sigma_{theor,\,3D} = 0.2736$$

We therefore see that, our experimentally determined reflection coefficient (σ_{exp}) lies within the bounds of (σ_{theor}) considering 1-D and 3-D transport within the channels. Also, (σ_{theor}) was evaluated assuming water to be in a continuum state, which may not hold true even at dimensions of d_{CNT} = 2.23 nm. Future work in estimation of reflection coefficients of CNTs of different diameters will be useful to throw light on the solute-CNT interactions and therefore can be used indirectly to identify mechanisms of solute-CNT interactions.

4. Correlation between diffusio-osmosis and osmotic water permeance

a. Propensity for Diffusio-osmotic flow inside CNT channels

The diffusio-osmotic behavior of different symmetric n+:n- salts (NaCl, KCl, LiCl, $MgSO_4$) can be related to the osmotic permeance using a linear relationship.

$$U_{DO} = -\frac{\varepsilon}{4\pi\eta}\frac{kT}{Ze}\left[\beta\zeta - 2\frac{kT}{Ze}\ln\left(1-\gamma^2\right)\right]\frac{d\ln C_\infty}{dx}$$

Where,

$$\gamma = \tanh \frac{Ze\zeta}{4kT}$$

and,

$$\beta = \frac{D_+ - D_-}{D_+ + D_-}$$

e is the elementary charge of electron, k is the Boltzmann constant, ε, η and T are the permittivity, viscosity and temperature (T = 298 K) of the solutions. The above expression for the diffusio-osmotic velocity (U_{DO}) can be referred from Prieve (1984)[6] . C_∞ is the x dependent bulk salt concentration inside the tube far away from the CNT wall surface. Since we applied the same concentration gradient (300 mM) for all the experiments, $\frac{d\ln C_\infty}{dx}$ is constant. Bulk diffusivity of ions[2] was used to compute the β values.

The first part of the equation relates to the diffusio-osmotic flow arising from the difference in diffusivities between the cation and anion of the solute. The second part of the expression relates to the diffusio-osmotic flow arising from the concentration difference along the direction of flow.

For our analysis, we define diffusio-osmotic factor (unit: Volt/Coulomb) as,

$$\left[\frac{\beta\zeta}{Ze} - 2\frac{kT}{Z^2e^2}\ln\left(1-\gamma^2\right)\right]$$

Diffusio-osmotic factor therefore gives the propensity of each salt in inducing the diffusio-osmsotic flow.

b. Estimation of zeta potential

The adsorption of OH^- onto the interior walls of the CNT creates an induced negative charge on the CNT walls. This has been noted in general for hydrophobic surfaces and for CNTs [7, 8]. The estimated values of the surface charge density (C/m^2) lie in a broad range and there is no deterministic value from experiments yet. Therefore, in our analysis we assumed a surface charge density, $\Sigma \approx -0.1\ C/m^2$. Using Grahame's equation [9],

$$\Sigma = 0.117\sinh\left(\frac{\psi_0}{51.4}\right)[MX]^{0.5}$$

Where $[MX]$ is the salt concentration in moles/litre, while M^{n+} and X^{n-} being the cation and the anion of the salt. ψ_0 is the resultant surface potential (mV) due to the induced surface charge. We also assume that the slipping plane occurs at the walls of the CNT, which would mean that the zeta potential, $\zeta \approx \psi_0$. The valence factor, Z used in the above formulation is the average of the valences of the constituent cation and anion, $Z = (|n+| + |n-|)/2$.

The exact measurement of surface charge density of the interior wall of CNT is lacking in literature, the estimation of zeta done as here is appropriate for the analysis of the relationship between the observed osmotic permeance and the diffusio-osmotic factor. Additionally, we also show hereunder the estimated diffusio-osmotic factors when the surface charge density, $\Sigma \in (-0.15, -0.2)\ \mathrm{C}/m^2$. We see that at higher negative surface charge densities i.e. $\Sigma < -0.15\ \mathrm{C}/m^2$, the $MgSO_4$ seems to deviate from the theoretical scaling law, which might be used as an indicative upper bound for the surface charge density of ~ 2 nm CNT channels.

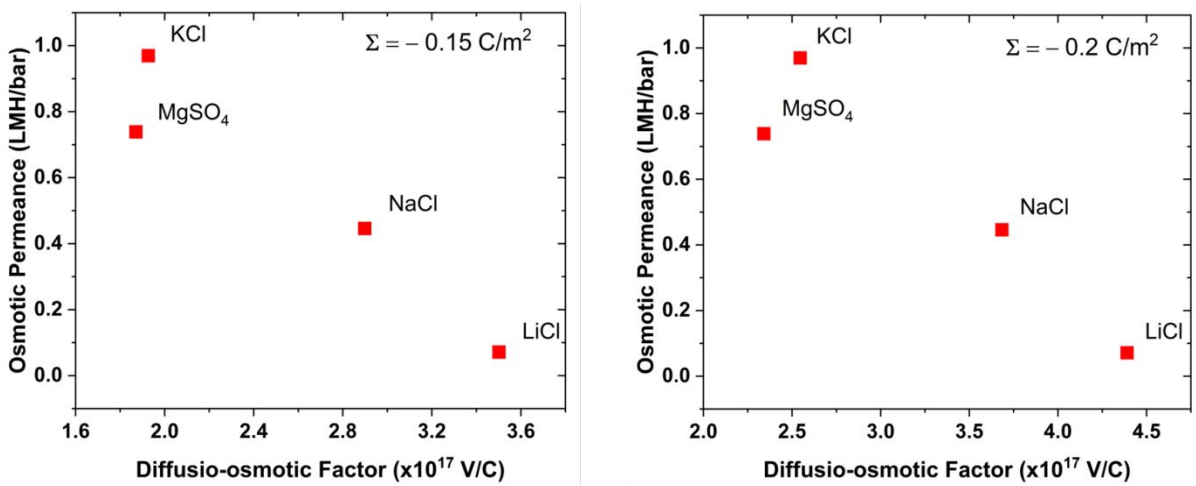

Figure S4. Relationship between observed osmotic permeance and estimated diffusio-osmotic factor for different surface charge densities (a) $\Sigma = -0.15\ C/m^2$ (b) $\Sigma = -0.2\ C/m^2$

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