Electronic Supplementary Information (ESI)

Effects of CNT size on desalination performance of outer-wall CNT slit membrane

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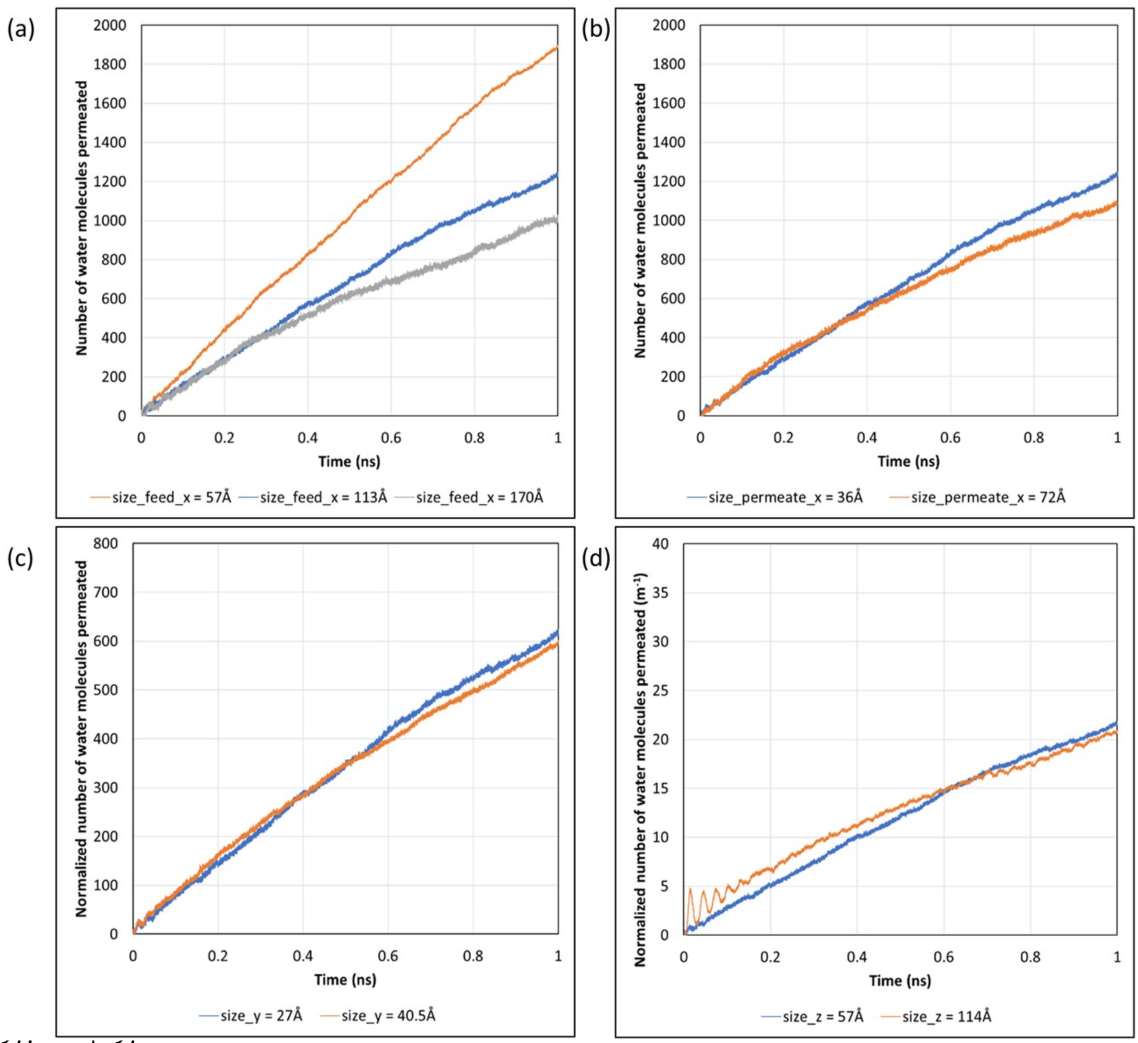
CONTENTS

S1. Domain sensitivity study for NEMD simulations

To decide the size of the simulation domain for NEMD simulations, a domain size sensitivity study is conducted. Previous low dimension membrane simulation studies done by our group, as well as many published work by others, used a simulation domain size of about 50 to 100 Å in the longitudinal direction (x direction in our case), and 30 Å by 30 Å in the lateral dimension.[1-5] A few MD studies have considered a longitudinal size larger than 100 Å with similar lateral dimensions.[6, 7] To decide the longitudinal size, 1ns simulation runs are conducted with varying longitudinal sizes using CNT_(5,5)_3.28 membrane to determine the sensitivity of the results with longitudinal size. The longitudinal x direction is generally made of up 2 components: the size of the feed solution (size_feed_x) and the size of the permeate (size_permeate_x). The two components are investigated independently in this work. Size_feed_x is varied from 57 to 170 Å and the water permeance behaviour for different size_feed_x considered is shown in Figure S1a. Results indicate that the size of the feed solution affects the simulation results significantly. Increasing size_feed_x from 57 to 113 Å reduces the water flow rate by 37%, while further increasing size_feed_x from 113 to 170 Å reduces the water flow rate by 17%. Bearing in mind the considerable computational cost that comes with the increase in domain size, a size_feed_x of 113 Å is adopted in our study. Conversely, increasing size_permeate_x does not seem to influence the results, and hence, it is kept at 36 Å (Figure S1b).

Further analysis is done on the size of the domain in the lateral directions (size_y and size_z). Two sizes are considered, 27 Å (corresponding to $2D_{CNT} + 2L_s$) and 40.5 Å (corresponding to



$3D_{CNT} + 3L_s$). The results are depicted in Figure S1c. Note that the results are normalized with

Figure S1 Domain sensitivity study results (a) Water permeance behaviour for varying size_feed_x (b) Water permeance behaviour for varying size_permeate_x (c) Water permeance behaviour for varying size_y normalized with respect to number of slits (d) Water permeance behaviour for varying size_z normalized with respect to size_z.

respect to the number of slits in the membrane. As can be seen, increasing the size of the domain in the y direction does not significantly change the results. Hence, size_y is kept at $2D_{CNT} + 2L_s$. Similarly, Figure S1d indicates that increasing size_z does not significantly affect the results as well. Therefore, size_z is chosen in our study to be 57 Å. On the side note, it can be seen from Figure S1d that increasing size_z leads to oscillatory permeance behaviour at the beginning of the simulation, when the pressure difference is applied. This is attributed to the longer CNT length, which takes a longer time to settle when a large pressure difference is applied across the domain. As a result of this domain sensitivity study, the final dimensions adopted for the NEMD simulations are depicted in Figure 1a in the main paper. The dimensions for the EMD simulations are set to be on par with the NEMD simulations, as marked in Figure 1b in the main paper.

S2. Effetcs of CNT chirality on the desalination performance of TFCM

To investigate the effects of chirality on the TFCM's desalination performance, three additional simulations were ran with TFCM made with CNTs of other chirality. The existing results used the armchair (5,5) CNT with a CNT diameter of 6.8 Å. To ensure that the CNT size is comparable, the following chirality are considered, with their corresponding CNT diameter stated in brackets: (6,4) CNT (CNT diameter of 6.85 Å); (8,1) CNT (CNT diameter of 6.7 Å); (9,0) CNT (CNT diameter of 7.0 Å). The water permeance behaviour of the four TFCMs are shown in Figure S2 below.

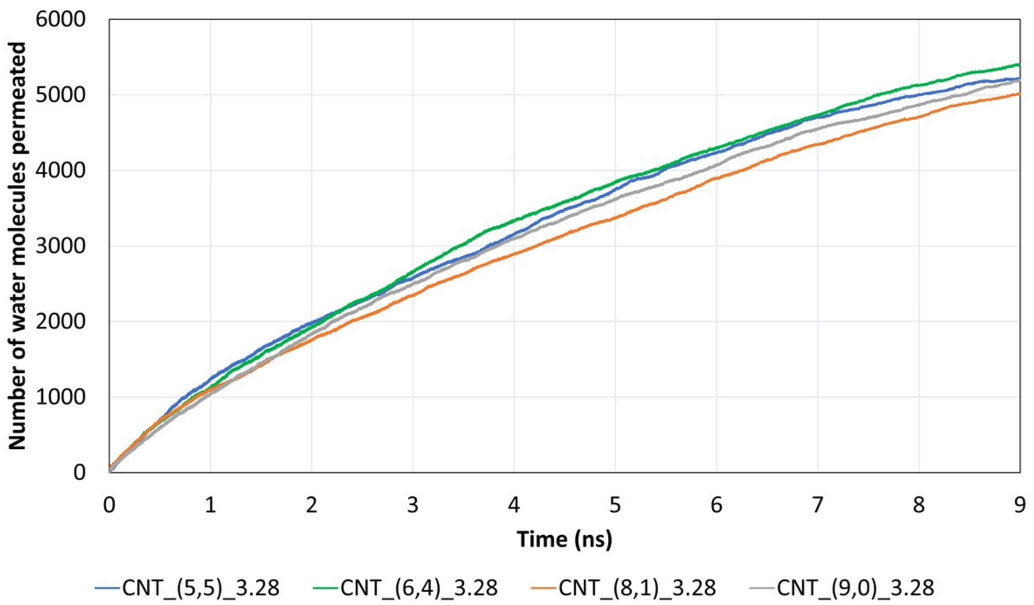


Figure S2 Comparison of water permeance history for TFCM made from different CNT chirality

As can be observed from Figure S2, the effects of CNT chirality on the water permeance behaviour of TFCM is negligible. After taking into account the membrane area, the final permeability recorded at the point where 80% of water has permeated is 1588 LMBH for CNT_(6,4)_3.28, 1457 LMBH for CNT_(8,1)_3.28 and 1417 LMBH for the CNT_(9,0)_3.28, membrane, as compared to 1609 LMBH recorded for CNT(5,5)_3.28 membrane. This is within 10% variation, which is on par with the statistical variance measured for the membrane at different initial conditions. In terms of salt rejection, the CNT_(6,4)_3.28 membrane has a final salt rejection of 98.2%, CNT_(8,1)_3.28 99.1% and CNT_(9,0)_3.28 98.9%, as oppose to 98.2% for the CNT_(5,5)_3.28 membrane. This is less than 1%

difference. Hence, it can be concluded that the effects of CNT chirality on the desalination performance of TFCM is negligible.

This chirality sensitivity study conducted confirms the fact that the desalination performance of TFCM is influenced predominantly by the slit size and CNT diameter. Although changing chirality changes atomistic interactions of the CNTs with its surrounding, thereby resulting in different electronic properties ((5,5) and (9,0) CNTs are metallic while (6,4) and (8,1) CNTs are semi conducting), adsorption and slip behavior [8, 9], this study shows that this effect is minute as compared to changes in slit and CNT sizes. This is consistent with observations made by Alessio and Kassinos in 2008, where they showed by studying a large class of CNTs with different chirality, that the density of water within CNTs are not significantly affected by changes in CNT chirality, but largely dependent on CNT size.[10] In a separate study done by the same authors, the self-diffusivity and hydrogen bonding of water molecules within CNTs of different chirality were additionally measured, and it was again found that these are dependent mostly on CNT size rather than chirality.[11] The slit sizes of TFCM influence the number of water molecules allowed within the membrane at any one time, and the CNT size affects the entrance and exit effects of the TFCM, both of which are much more dominant as compared to the change in atomistic interactions resulting from varying chirality.

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