High-flux water desalination with interfacial salt sieving effect in nanoporous carbon composite membranes

Wei Chen¹⁴, Shuyu Chen², Tengfei Liang²⁵, Qiang Zhang¹, Zhongli Fan¹, Hang Yin¹, Kuo-Wei Huang¹, Xixiang Zhang¹, Zhiping Lai¹*, Ping Sheng²³*

¹Division of Physical Science and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia

²Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

³Institute for Advanced Study, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

⁴CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai, China

⁵School of Astronautics, Northwestern Polytechnical University, Xi’an, China

Freshwater flux and energy consumption are two important benchmarks for the membrane desalination process. Here we show nanoporous carbon composite membranes, comprising a layer of porous carbon fiber structures grown on a porous ceramic substrate, can exhibit 100% desalination effect with 3 to 20 times higher freshwater flux compared to existing polymeric membranes. Thermal accounting experiments found the carbon composite membrane to save over 80% of latent heat consumption. Theoretical calculations combined with molecular dynamics simulations revealed the unique microscopic process in the membrane. When the salt solution is stopped at the openings to the nanoscale porous channels and forms a meniscus, the vapor can fast transport across the narrow gap to condense on the permeate side, driven by the chemical potential gradient and aided by the unique smoothness of the carbon surface. The high thermal conductivity of the carbon composite membrane insures that most of the latent heat is recovered.

*Emails: zhiping.lai@kaust.edu.sa, sheng@ust.hk
Owing to the increasing trend of freshwater usage being not balanced by the available supply\textsuperscript{1-3}, water desalination is becoming more important as a means of supplying freshwater to a thirsty world. Traditional desalination approaches involve either the process of distillation which needs large amount of energy, or the filtration approach using polymeric membranes which need to achieve both high salt rejection rate and high freshwater flux. Most desalination units have adopted the energetically efficient reverse osmosis (RO) membrane process\textsuperscript{3, 4}, while membrane distillation (MD) and forward osmosis (FO) have also attracted intense attention in recent years\textsuperscript{5} because of their potential for integration with renewable energies. In all the filtration approaches, membrane flux constitutes a common challenge. High flux membrane is highly desirable not only for reducing the membrane area, but also for increasing productivity.

Based on the solution-diffusion mechanism, the polymeric membranes used in the RO and FO desalination processes are necessarily dense. In contrast, membranes used in the MD process are microporous, in which the hydrophobic micropores allow the transport of water vapor by Knudsen diffusion, while blocking the transport of liquid. In all of these polymeric membrane processes the flux is limited by either the low permeability of the dense membrane structure or the low density of the transported water vapor. Recently, water was found to transport superfast along aquaporin\textsuperscript{6} and carbon nanotube\textsuperscript{2, 7-9} channels. A number of simulation studies\textsuperscript{10, 11} have proposed that if the tube diameter is less than 1.1 nm, then salt can be effectively rejected through a molecular sieving mechanism. However, how to control the tube diameter and how to seal the gaps between tubes still remain as big challenges in membrane fabrication. So although aligned carbon nanotube layers have showed enhanced water flux\textsuperscript{12, 13}, but to the best of our knowledge their application to water desalination has yet to be demonstrated. To seal the gaps a common approach is to make mixed matrix membranes\textsuperscript{10, 11, 14-16}. Indeed, a commercial made by this approach gives a high water flux of 7 liters per square meter per hour (LMH) in the FO processes\textsuperscript{17}; while a carbon nanotube/polyamide composite membrane was able
to improve the specific water flux up to 3.6 LMH/bar in the RO processes\textsuperscript{18, 19}. However, the mixed matrix membrane approach suffers from many challenges such as poor dispensability, low loading rate, improper alignment and defects, etc. As a result, only limited success has been achieved by this approach. Graphene and graphene oxide membranes have also showed promising potentials in gas and liquid separations\textsuperscript{20-22}. In particular, Abraham et al. recently reported the use of epoxy to encapsulate graphene oxide membranes to limit the swelling issue and successfully achieved good salt rejection up to 97\%\textsuperscript{23}. However, these membranes are hard to scale-up and their real water flux are still low.

Here we report the synthesis of a nanoporous carbon composite membrane containing a layer of carbon fibers on porous ceramic support; it has a relatively open structure with a minimum pore size of ~30 nm. The membrane was successfully applied to all three membrane desalination processes and showed 100\% salt rejection with 3 to 20 times higher freshwater flux when compared to existing polymeric membranes. From a combination of vacuum membrane distillation (VMD), FO, and energy accounting experiments, water was found to transport through the gaps of the carbon fibers. From molecular dynamics simulations, a novel interfacial salt sieving effect is found to account for the high salt rejection rate, which differs fundamentally from the solution-diffusion mechanism in polymeric membranes; it also differs from the molecular sieving mechanism that is expected in carbon nanotubes and graphitic materials. Owing to the rather smooth and high thermal conductivity of the carbon surface, desalination with high freshwater flux and low energy consumption is achieved.

**Membrane structure**

Our carbon composite membrane was fabricated on a hollow yttrium-stabilized zirconia (YSZ) tube (Fig. 1(a)) with a porous wall. The obtained composite membrane is denoted as C-DP-X, where P denotes the nickel deposition power in Watts and X denotes the growth time in minutes.
Figure 1 | Structure of the membrane. (a) SEM image of an as-prepared C-D35-2 membrane on the surface of the hollow YSZ tube. The square denotes the area to be zoomed in for a magnified view in (b). (b) The FIB-SEM image of the interface between YSZ and carbon layer. The sharp interface between carbon and YSZ is clearly delineated. The nano-sized pores on the carbon side can also be seen. The pore size is seen to be the smallest in the vicinity of the carbon fiber-ceramic interface, about 31 nm as determined by gas permeation. (c) HRTEM image of a typical single carbon nano-fiber in the C-D35-2 membrane. The arrow points to the “bamboo-knot-like” structure inside the carbon fiber that divides the interior space into compartments.

The typical membrane structure is shown in Fig. 1. The thickness of the entire carbon layer is about 10 μm with a loose outer surface and a dense interface that separates the carbon layer and YSZ support, as evidenced in Fig. 1(b) as well as by EDX mapping analysis (see Fig. S2 in Supplementary Information (SI)). The effective region of the membrane, consisting of a dense growth of carbon fibers at the interface with the YSZ substrate, is only several hundreds of nanometers in thickness. The average pore size and porosity, as determined by gas permeation\textsuperscript{24}, are 31 nm and 22%, respectively. Detailed studies of many carbon fibers by high resolution transmission electron microscopy, one of which is shown in Fig. 1(c), and Raman spectrum (Fig. S3 in SI) revealed that every fiber studied has a multiwall carbon nanotube structure, but the inner channels are always blocked by bamboo-knot-like structures, indicated by an arrow in Fig. 1(c).

Liquid entry pressure and membrane distillation

Water cannot penetrate through the nanoporous carbon membrane unless an applied pressure is higher than the liquid entry pressure (LEP). The measured LEPs for membranes with different pore sizes
follow the relation $\text{LEP} = 4 \gamma | \cos \theta | / (\text{pore size})$ (see SI and Fig. S4), with $\theta = 93^\circ$ obtained by fitting the experimental values of LEP with the simulated water-vapor interfacial tension of 58 mN/m (see below). Therefore, the nanoporous carbon membrane is equivalent to a porous (slightly) hydrophobic membrane that can be used for seawater desalination via membrane distillation.

An illustration of a vacuum membrane distillation setup is shown in Fig. 2(a), where a C-D35-2 membrane was immersed into a salt solution with one end sealed by epoxy resin and the other end connected to a vacuum pump through a condensation cold trap. The latter can use either liquid nitrogen or cold water at 2 °C, with the cold water showing only 1% less freshwater collected. NaCl solutions were used as synthetic seawaters. The salt concentration was measured by conductivity at room temperature. In all the experiments the conductivity of the collected water after VMD is less than 2 μS/cm, equivalent to 1 ppm salt concentration, i.e., the salt rejection rate is over 99.99%. The freshwater fluxes of C-D35-2 membrane, at different temperatures and different salinities of salt solutions, are shown in Fig. 2(b). The flux increases as temperature increases. Above 40 °C, the water flux increases almost linearly with temperature. At 90 °C, approximately 1.34 liter freshwater was collected from a 5 wt% NaCl solution after 48 hours over a membrane area of $1.26 \times 10^{-4}$ m$^2$, which gives a water flux of 221.6 LMH. Reducing the salinity of the feed solution can increase the water flux up to 413.5 LMH when freshwater is used as the feed solution. These values are not only significantly higher than the highest values reported for polymeric membranes operated in the direct contact mode, which was around 80 LMH to the best of our knowledge$^{25}$, but also 15 to 20 times higher than that obtained by using the non-contact mode, in which only vapor was in contact with the membrane. In Fig. 2(b), the blue stars indicate the non-contact mode results. For comparison, we show the water flux on a commercial polytetrafluoroethylene (PTFE) membrane (W.L. Gore®), in the direct contact mode, on the same setup as red open squares in the inset figure. The data match very well with the Knudsen
diffusion predictions, with the absolute values in the range of 5 to 10 times lower than that of the nanoporous carbon membrane.

We attribute the high freshwater flux of the carbon membrane, in the contact mode, to result from the short Knudsen diffusion path. That is, salt solution can penetrate the loose carbon layer and stop at a certain position of the dense carbon layer due to the slight hydrophobicity of carbon. The vapor transport path is hence greatly reduced as compared to the non-contact mode. The salt concentration polarization in our carbon composite membrane is strong because of the high flux, leading to a significant decrease of freshwater flux as the salinity of feed solution increases. In contrast, salt solution cannot enter the polymeric membranes used in membrane distillation, such as PTFE, polyvinylidene fluoride (PVDF), polypropylene (PP), etc., due to their strong hydrophobicity. Hence, even in the direct contact mode they do not exhibit significant difference on freshwater flux in the two modes, nor the sensitivity on salinity.

We have also conducted VMD desalination process on seawater taken from the Red Sea, with a salinity of 4.1%. Quantitative details are shown in Figs. S7 and S8 in the SI. Excellent desalination performance was obtained (Fig. S7), even though the freshwater flux is slightly lower when compared to NaCl solution with the same salinity, owing mainly to the presence of divalent ions in seawater that can reduce the water flux much more than monovalent ions\(^2\). Similar reduction in the freshwater flux has been observed on commercial membranes\(^27\), \(^28\). Scalability of our desalination approach was tested by using multiple membranes in parallel, and found the total flux to be a linear function of the number of membranes (see SI, section (4.2)).
Figure 2 | Freshwater transport through the C-D35-2 membrane. (a) A schematic illustration of the VMD setup. (b) The measured freshwater flux plotted as a function of temperature (red lines) at different salt concentrations. Blue stars denote the water flux predicted by Knudsen diffusion (labelled as Knudsen calculation), based on the measured data using methane gas, which has very similar molecular weight as water vapour. The green open circles denote the water flux in the non-contact mode when the membrane was exposed to only vapour (obtained by bubbling N₂ through water); good agreement with the Knudsen diffusion is seen. The inset shows the results over a PTFE membrane (pore size ~100 nm) in the direct contact mode, where the red lines are measured freshwater fluxes at different salt concentrations and the blue line is the calculated flux by Knudsen diffusion. (c) The membrane freshwater flux in the FO process at two different temperatures (maintained to be the same on both sides of the membrane) plotted as a function of the draw solution salinity. The freshwater flux for the PTFE membrane is seen to be more than an order of magnitude lower. Inset: A schematic illustration of the FO process.

Forward and reverse osmosis

A FO process is illustrated in the inset to Fig. 2(c) in which the membrane separates pure water from the salt solution, denoted the draw solution. The temperatures on both sides are maintained to be the same. Pure water would diffuse across the membrane to the draw solution through vapor diffusion, driven by the chemical potential gradient. Figure 2(c) shows the FO water fluxes at different concentration of the draw solution at 20 °C and 80 °C. As a comparison, we tested a commercial PTFE membrane in the same way and the results are denoted as star symbols in Fig. 2(c). The magnitude of the water flux for the nanoporous carbon membrane is seen to be more than an order of magnitude higher than that of the PTFE membrane, and also substantially higher than that for the commercial FO membranes, typically in the range between 5-10 LMH². In spite of the salt ion concentration gradient
in the reverse direction, the salt leakage rate from the draw solution was almost zero, as the salt concentration detected in the pure water stream was below 1 ppm during the 2-days measurement, indicating the salt rejection rate to be higher than 99.9%.

Similar high freshwater flux was measured in the RO process (see SI and Fig. S9a). A pressure of 3 bars, necessarily less than the LEP of the membrane, was applied to the salt solution side. The salt solution is at the concentration of 2000 ppm, in the brackish water salinity range. The applied pressure of 3 bars allowed the extraction of freshwater from salt solution. At 20 °C, the specific water flux of the RO process was around 12 LMH/bar with ~100% salt rejection rate. At 80 °C, the specific water flux increased to 29 LMH/bar. Figure S9b shows the water flux vs. the salt rejection trade-off diagram of existing membranes\(^3\). It can be seen that even at 20 °C the overall performance of the nanoporous carbon membrane is an order of magnitude better than any other membranes. Since in the RO process the applied pressure should be higher than the osmotic pressure, hence the LEP of C-D35-2 membrane, around 3.9 bar, would severely limit the application of this membrane to high salinity water. In what follows, we focus on the energy accounting and the theoretical modeling of the MD and FO processes, which have no such limitation.

**Energy accounting**

Energy consumption counts significantly in the total desalination cost\(^3\). The composite carbon membrane showed high flux in all the three membrane processes, a feature favorable to the possibility of integrating all three processes together to improve the flux. To study whether such an integration will benefit from the energy point of view, an energy accounting setup was designed, shown schematically in Fig. 4. One stream is fresh water and the other is salty water. The temperature of the fresh water is higher than that of the salty water. Hence, the whole process can be viewed as combination of the MD and FO processes. The temperature at the inlet and outlet of both streams were
measured and denoted as $T_1$, $T_2$, $T_3$ and $T_4$. The parameters $h_0$ and $h_m$ shown in Fig. 4 are the heat transfer coefficients to account for the heat loss to the environment and the heat conduction between the two streams, respectively. The values of $h_0$ at different temperatures were determined by a separate experiment using an impermeable membrane (see SI, section (5.1)). From the temperature data, measured in-flow and out-flow rates $P$, $F$, respectively, and the membrane flux $V$ on the two sides of the membrane, plus the known values of latent heat and specific heats of water, an energy consumption coefficient $\bar{m}$, defined as the ratio of the measured energy consumption over the theoretical latent heat consumption, can be obtained (see SI, section (5.2)). The results are listed in Table 1. They show the energy consumption coefficient $\bar{m}$ increases with $T_i$, but even at 80 °C only ~10-20% of the theoretical latent heat is consumed. However, when a PTFE membrane was used, $\bar{m} >100\%$ for temperatures over 30°C. These results are consistent with the data shown in Fig. 2(b). It means that the intrinsic energy consumption of this process (FO plus temperature gradient) is reduced by at least 80% in the nanoporous carbon membrane as compared to the PTFE membrane. In Table 1 is also shown the order of magnitude difference in the transported freshwater fluxes between the two membranes.

**Figure 3 | Energy accounting experiment.** A schematic illustration of the setup to measure the temperature change of the desalination process. The terms $h_0A_0\Delta T_0$ and $h_0A_0\Delta T_0'$ represent the heat loss to environment where $h_0$ and $A_0$ are the module heat transfer coefficient and surface area and $\Delta T_0$ and $\Delta T_0'$ the average temperature difference between the streams and the environment at the feed and permeate side, respectively. The term $h_mA_m\Delta T_m$ represents the heat conduction between the two streams where $h_m$ and $A_m$ are the membrane heat transfer coefficient and membrane area, respectively, and $\Delta T_m$ the average temperature difference between the two streams. $F$ and $P$ denote the constant flow rates of the pure water and salt water streams, respectively, and $V$ is the transported freshwater flux.
from $F$ to $P$. The energy accounting measurements can yield the value of $V$ and the energy consumption coefficient $\bar{m}$.

**Table 1:** Ratio of the measured energy consumption over the theoretical latent heat consumption and the total freshwater flux.

| $T_1$ (°C) | C-D35-2 membrane | PTFE membrane |
|------------|------------------|---------------|
|            | $\bar{m}$ | V(LMH) | $\bar{m}$ | V(LMH) |
| 30         | 3%   | 43.4   | 64%   | 0.98   |
| 40         | 6%   | 46.5   | 208%  | 1.24   |
| 50         | 9%   | 51.1   | 249%  | 1.81   |
| 60         | 12%  | 56.7   | 313%  | 2.57   |
| 70         | 15%  | 62.8   | 231%  | 4.64   |
| 80         | 18%  | 69.5   | 186%  | 7.69   |

**Desalination mechanism**

From the liquid entry pressure studies, it is clear that because the nanoporous carbon membrane is slightly hydrophobic, a meniscus will necessarily be formed on the feed side. During the RO and FO processes, another meniscus will also be formed on the permeate side. The two menisci are separated by a gap. Such a microstructure is completely different from that of the dense polymeric membranes.

To clarify the mechanism for the three salient features of the carbon composite membrane comprising: a) high salt rejection rate, b) high flux, and c) low energy consumption; we have performed large scale molecular dynamics simulations on the water vapor transport characteristics in the vicinity of the menisci and the gap in-between. The simulations are mainly focused on two aspects: a) salt distribution near the menisci, as illustrated in Fig. 4a-b, and b) dynamic transport of water molecules in the gap between the two menisci, as schematically illustrated in Fig. 4c, and detailed below as well as in the SI section 6-7.
**Figure 4 | Desalination mechanism.** (a) Left panel: a molecular view of the simulated system. The concentration of the salt solution is about 3.5 wt%. Right panel: top figure shows the densities of salt ions (green line) and the water (blue line). Mass density is in units of g/liter. Two to three atomic layers of pure water is seen at the water-vapour interface, indicated by the light blue line. Bottom figure shows the same at the carbon-salt solution interface. A monolayer of pure water is seen to exist at the carbon surface. The surface water layer is noted to have lower density than the bulk. Center of the first carbon atomic layer is located at -5.35 nm. So there is a small “air gap” of around 3 Angstroms. (b) The blue line indicates the anisotropic component of the stress tensor whose integral (red line) gives the surface tensions. It is seen that besides the water-vacuum interfacial tension of 58 mN/m, there is a small interfacial tension between pure water and the saline solution that prevents mixing of the salt ions with the surface water layer. (c) An illustration of vapor diffusion and the interfacial salt sieving effect. The bottom panel is a magnified illustration of the dense section of the carbon membrane closest to the YSZ substrate. It shows two menisci separated by a gap in which fast water vapor transport through Knudsen diffusion takes place. An explanation of the freshwater transport process is given in the text.
The simulation results in Fig. 4b indicates that there is a small interfacial tension, \( \sim 4 \text{mN/m} \), between pure water and the saline solution that prevents mixing of the salt ions with the surface water layer. As a consequence, as illustrated in Fig. 4a, there exists a thin layer between the salt water and the carbon surface, as well as between the salt water and its vapor, containing no salt. This interfacial salt sieving effect is the same as the formation of solvation shells in which each salt ion is enveloped by a layer of structured water molecules\(^{31,32}\), thereby preventing the salt ions to be in direct contact with the water-vapor or the graphitic interface\(^{33}\) at which water molecules also form the layered structures\(^{34}\). For a salt ion to leave the meniscus, it has to either exit from the solvation shell, or bring the whole solvation cluster with it. In both scenarios the energy required is prohibitively high. From the molecular dynamic simulation, it was also found that water vapor can rarely condense to form stable droplets on the carbon surface due to the relatively large pore size (\( \sim 30 \text{ nm} \)), the slight hydrophobicity of the carbon surface, as well as the sub-saturated or near-saturated vapor environment in the MD or FO/RO process. This excludes the possibility of surface diffusion of water droplets. Hence, the freshwater flux through the carbon composite membrane is realized by vapor transport, and the salt rejection mechanism is no different from the evaporation process.

We use a resistance-in-series model to simulate the water flux in the FO and VMD processes, as well as the energy consumption in the energy accounting experiment. Figure 5(a) shows a schematic illustration of the model. For the energy accounting experiment, the net heat flux \( Q \) has the following relationship with the latent heat flux \( Q_{\text{vapor}} \),

\[
Q = \frac{R_0}{\Sigma R_i} Q_{\text{vapor}} + \frac{T_{b2} - T_{b1}}{\Sigma R_i}
\]

(1)

where \( R_i \) is the thermal resistance of each part, and \( T_{b1} \) and \( T_{b2} \) are the temperatures of bulk streams on the two sides indicated in Fig. 5. The factor before \( Q_{\text{vapor}} \) is less than \( 2 \times 10^{-7} \) because of the low
thermal resistance of carbon fibers between the two menisci $R_0$ (see SI, section 6.1). Hence, the net heat flux $Q$ measured in the experiment is not sensitive to the latent heat flux $Q_{\text{vapor}}$. If the vapor transport flux is large, $Q_{\text{vapor}}$ can be much larger than the net heat flux $Q$. In that case, most part of $Q_{\text{vapor}}$ is recovered through the carbon fibers between the two menisci.

**Figure 5** | Predicted heat and mass transport by theoretical model and MD simulation in carbon composite membrane. (a) A resistance-in-series model to predict the transport through the carbon composite membrane. (b) Freshwater flux in the VMD experiment plotted as a function of temperature. Here the stars are experimental results, the curves are the theoretical fitting (see below and SI section 6.3). (c) Freshwater flux in the FO experiment plotted as a function of the salt concentration of the draw solution. Blue and red symbols are experimental results at 20 °C and 80 °C, respectively, while the blue and red solid curves are the theory predictions, respectively. The nonlinear behavior seen in both the experimental data and the theory is the manifestation of concentration polarization.

From molecular dynamics simulations, the transport resistance of vapor across the gap between the two menisci is obtained (see SI section 7), which is much lower than that predicted by an analytical model\textsuperscript{35} developed under the assumptions of diffuse vapor-surface scattering and Hertz relation. This discrepancy is attributed to two points: 1) the unique smooth surface of the carbon pore, and 2) the
non-equilibrium state of vapor in the narrow gap (see SI section 7). These findings are in agreement with many other simulation studies of the transport in graphitic materials\textsuperscript{36-38}. The high water flux will thus induce concentration polarization at the menisci which limits the overall flux. After considering the concentration polarization, the predicted VMD and FO water fluxes are plotted and compared with experimental results, shown in Fig. 5b-c (see SI section 6.2 and 6.3 for details). The results of VMD agree very well with the experimental results. It reveals that the reason for the salinity-dependent flux is due to concentration polarization when ions need to diffuse from the menisci to the bulk streams. The predicted flux of FO at 20 °C matches well with the experimental results, which suggests that even at room temperature, the mechanism of vapor transport can yield a rather high flux. However, the predicted flux at 80 °C is higher than the experimental result. This may indicate that the flow is severely limited by concentration polarization.

**Conclusions**

In summary, a nanoporous carbon composite membrane was found to display unprecedented high water flux in three membrane-based desalination processes. The large freshwater flux is attributed to the fast transport of water vapor through nano-scale carbon pores, while the excellent salt rejection rate is attributed to the interfacial sieving effect. This high-flux desalination mechanism, with latent heat recovery, opens the possibility of considerable energy savings for the desalination process, with the FO combined with a temperature gradient being a promising direction for its realization.

**Methods**

**Experimental**

**Growth of carbon nanostructures on the hollow fiber**
YSZ hollow fibers were custom-made from YSZ nanoparticles (30 to 60 nm from Inframat Advanced Materials Co.) through a phase-inversion/sintering process\textsuperscript{39, 40}. The diameter of YSZ hollow fiber was about 0.91 mm with average pore size of 100 nm and porosity of 40%. The outer surface of YSZ hollow fiber was uniformly coated with nickel nanoparticles (20 to 30 nm, Fig. S1c) using a rotational sputtering deposition. A carbon layer was grown on nickel deposited YSZ hollow fiber through a catalytic chemical vapour deposition (CVD) process, in which acetylene was used as carbon source in the presence of hydrogen gas (acetylene to hydrogen volume ratio 1:10) to grown carbon nanowires at 700 °C for 1 to 3 minutes. Then the CVD chamber was quickly cooled down to room temperature under argon flow. Following the same procedure a carbon composite membrane can also be grown on YSZ flat-sheet support.

**Membrane characterization**

Raman spectroscopy measurements were carried out on a Horiba Aramis confocal microprobe Raman instrument with He–Ne laser (\(\lambda = 632.8\) nm) at the outer surface of the carbon composite membranes. SEM images were taken by a FEI Nova Nano630 equipped with a focused ion beam (FIB), which facilitates in obtaining an ultra-smooth interface of carbon composite membrane while preserving the initial structure. The elemental distributions of the membrane were analysed by energy dispersive X-ray (EDX) mapping in SEM. Transmission electron microscopy images were obtained by using a Titan ST microscope (FEI Co.), operating at 300 kV.

**Energy accounting experiment**

Carbon composite membranes grown on YSZ flat-sheet supports were used for energy accounting experiments in order to have large room to house the temperature probes on both sides of the membrane. Commercial porous PTFE membrane (W.L. Gore®) and dense polyethylene (PP) sheet were used as references for comparison. The membranes were mounted into a permeation cell made
of polymethyl methacrylate (PMMA). Fresh water and draw solution (10 wt% NaCl) were recycled in each side of the membrane through circulation bathes. At each measurement point, the experiment was run for ~5 h to reach steady state, then the weight, conductivity, and temperatures at the inlet and outlet of each stream were recorded.

Theory

Molecular dynamics simulations

Molecular dynamics simulation was carried out by using the package GROMACS 4.6.7\textsuperscript{41}. Parameterized force fields were adopted to describe the atomic interactions in the system\textsuperscript{42-44}. The concentration of the NaCl solution was chosen to be ~3.5 wt%, similar to that of seawater. Carbon atoms were fixed at the crystallographic positions of the graphite lattice. All bonds of water molecules were constrained by using the SHAKE method\textsuperscript{45}. Simulation showing the salt rejection mechanism was performed for 5 ns in the canonical ensemble with Berendsen thermostat\textsuperscript{46} at a constant temperature of 300 K. The time step was set to be 1 fs. Long range electrostatic interactions were calculated with the particle mesh Ewald technique\textsuperscript{47} and the van der Waals interactions were cut off at 1.2 nm. A custom GROMACS version based on GROMACS 4.5.5 was used to compute the 3D stress tensor from the simulated data\textsuperscript{48}.

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Author contributions

Z.L. and W.C. contributed to the initial ideas and experimental design. S.C., T.L., and P.S. contributed to the desalination mechanism and the relevant simulations and data analysis. W.C., Q. Z., Z.F. and H.Y. carried out the experiments, and T.L. and S.C. carried out the MD simulations. K.W.H. contributed to data analysis. X.Z. contributed to characterization and data analysis. Z.L., W.C., and P.S. wrote the primary draft, Z.L., W.C., P.S., S.C., T.L., and X.Z. participated in its revisions.

Competing financial interests

The authors declare no competing financial interests.

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