Electronic Supplementary Information

Localized Heating by a Photothermal Polydopamine Coating Facilitates a Novel Membrane Distillation Process

Xuanhao Wu[1], Qisheng Jiang[2], Deoukchen Ghim[1], Srikanth Singamaneni[2, *] and Young-Shin Jun[1, *]

[1]*Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, Missouri, 63130, USA. E-mail: ysjun@seas.wustl.edu*

[2]*Department of Mechanical Engineering and Materials Science, Washington University in St. Louis, St. Louis, Missouri, 63130, USA. E-mail: singamaneni@wustl.edu*

Summary

15 pages, including experimental descriptions, 6 figures, and 2 tables.

Experimental Section

S1. Synthesis of FTCS-PDA-PVDF membrane.

A PDA coating on a commercial hydrophilic polyvinylidene fluoride (PVDF) membrane (0.45 µm pore size, 110 µm thickness, MilliporeSigma) was achieved via self-polymerization of PDA.[1, 2] Hydrophilic PVDF was chosen for easier PDA coating. Dopamine (DA, 2 mg/mL) was dissolved in 10 mM Tris-HCl (pH 8.5), and PVDF membranes were dipped in the solution. The solution was shaken (VWR Orbital Shaker, Model 3500) for 24 hours before the membrane was taken out and rinsed using deionized (DI) water (18.2 MΩ-cm, Barnstead Ultrapure water systems). The self-polymerization process was repeated for 7 days until the entire surface of the PVDF was uniformly coated by PDA (Fig. S1). Then, the membrane was rinsed with DI water and dried under N_2 gas. Next, the PDA-PVDF membrane was exposed to (tridecafluoro-1,1,2,2-tetrahydrooctyl)-trichlorosilane (FTCS) vapor at 70 °C for 3 hours, resulting in a dense coverage of PDA-PVDF by hydrophobic FTCS fluoro-silane.[3, 4]

S2. Characterization of FTCS-PDA-PVDF membrane.

Scanning electron microscopy (SEM; OVA NanoSEM 230, FEI) was used to image the morphology and microstructure of the FTCS-PDA-PVDF membrane surface and its cross-section at an acceleration voltage of 10 kV. The chemical composition of PDA and FTCS on the PVDF surface were identified using an attenuated total reflection Fourier transform infrared (ATR-FTIR; Thermo Scientific Nicolet Nexus 470 spectrometer equipped with a diamond crystal) spectroscopy and a Raman spectroscopy (inVia confocal Raman spectroscope, Renishaw, equipped with 514 nm wavelength diode laser). The reference peaks for FTIR are shown in Table S1. X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II, Ulvac-PHI with monochromatic Al Kα radiation (1486.6 eV)) was utilized to identify the N 1s, C 1s, and Si 2p peaks for the PDA-FTCS-PDA membrane. The surface roughness (root-mean-square, RMS) was measured using tapping mode AFM (Veeco Inc., Nanoscope V multimode SPM) and analyzed using the Nanoscope 7.20 software (Veeco Inc.). For each membrane, triplicate locations on the sample surface were measured to determine the roughness. The gravimetric method was used to quantify the porosity (ε) of the PDA-PVDF membrane.[5-7] Three 2 cm × 2 cm pieces were cut from a PDA-PVDF membrane sheet, weighed dry, and then submerged in DI water for 1 week before being taken out and weighed again wet. The porosity was calculated using the equation below to get the average values for triplicate samples:

$$\varepsilon = \frac{w_2 - w_1}{\rho_w V},$$

where ε is the porosity (%), w_2 (g) is the weight of the wet membrane, w_1 (g) is the weight of the dry membrane, ρ_w (g/cm^3) is the liquid density (DI water), and V (cm^3) is the volume of the membrane. ImageJ 1.80 software (National Institutes of Health, Bethesda, Maryland, USA) was used to determine the average pore diameter of pristine PVDF and FTCS-PDA-PVDF membranes by taking measurements of 100 pores from the SEM top surface images. A mean and a standard deviation were calculated for each size distribution. Considering that both pristine PVDF and PDA-PVDF are hydrophilic (contact angle ≈ 0º, Fig. 1A), it is difficult to evaluate the effect of the altered pore size and porosity by PDA coating on the membrane wetting property or MD performance. The actual amount of FTCS on the FTCS-PVDF (contact angle ≈ 120º) and FTCS-

PDA-PVDF (contact angle ≈ 125º) membranes could be different, which also makes it difficult to attribute the slight wetting resistance increase of FTCS-PDA-PVDF only to the PDA coating.

S3. Measuring the optical properties and surface temperature of FTCS-PDA-PVDF membranes.

The transmittance and reflectance of FTCS-PVDF and FTCS-PDA-PVDF membranes were measured using a micro-spectrophotometer (QDI 302, CRAIC Technologies) coupled to a Leica microscope (DM 4000M, Leica Microsystems). The surface temperatures of the FTCS-PVDF and FTCS-PDA-PVDF membranes were measured by an infrared camera (IR camera, Ti 100, FLUKE) after 600 secs light illumination using a solar simulator (Newport 66921 Arc Lamp) under both unfocused and focused irradiations (Fig. S3). Triplicate 1 cm × 1 cm pieces were cut from the membranes of interest and measured. The surface temperature of the membrane with water on top (water thickness = 8 mm) was monitored using a benchtop controller thermocouple probe (OMEGA CSI32K-C24, US) with a response time of 5 s and resolution of ±0.5 °C.

S4. Direct contact membrane distillation experiments.

DCMD experiments were carried out using a specially designed membrane distillation module. The setup of the system is shown in Fig. S4. The membrane distillation module consists of a 2-mm-thick quartz window with a diameter of 5 cm on the feed side to allow light illumination. A 1-mm-thick aluminum platform was placed in between the feed side and distillate side to support the membrane. The cross-flow velocities in the feed and distillate channels were 3.6 mL/min and 16.2 mL/min, respectively. Both DI water and 0.5 M NaCl aqueous solution (ACS grade, BDH, PA) were used as feed water, stored in a 500-mL Erlenmeyer flask, and DI water was used for the distillate stream at the bottom of the membrane. The 0.5 M salinity was chosen to mimic the average salinity of seawater.[8] The feed and distillate were continuously circulated through the membrane module using two peristaltic pumps respectively (Welco WPX1-F1 and Stenner 85MHP5). The flow rate of the feed water was changed by monitoring the DC supply (Extech 382203) controlling the feed pump. The distillate reservoir was kept on a weighing balance (Sartorius ELT402) to measure the collected permeate at 1 min intervals. The distillate reservoir was capped during MD tests to reduce the effects of evaporation. During solar MD tests, the light from the solar simulator (Newport 66921 Arc Lamp) was oriented to the membrane surface using a mirror. The light intensities at the membrane surface were measured to be 0.75 (unfocused) and 7.0 kW/m^2 (focused using a magnifying lens) by a spectroradiometer (SpectriLight ILT 950). The diameters of the active irradiation areas were 5 cm and 1.5 cm for 0.75 kW/m^2 and 7.0 kW/m^2 intensities, respectively. The solar efficiency was calculated by the following equation:

$$\eta = \frac{\dot{m} H_{vap}}{I},$$

where η is solar efficiency, $\dot{m}$ is the permeate flux (kg/m^2·h), H_{vap} is the enthalpy change (2,454 kJ/kg) from liquid to vapor, and I is the power density of the incident light (kJ/m^2·h).[9]

S5. Stability tests of the FTCS-PDA-PVDF membrane.

The chemical and mechanical stability of the FTCS-PDA-PVDF membrane was tested at three pH values (pH 4, 7, and 10), using both ultrasonic agitation for 6 hours (Bransonic 3510R, 335W) and vigorous shaking for 30 days (VWR Orbital Shaker, Model 3500) (Fig. S6A).

Triplicate 1 cm × 1 cm pieces were cut from the membrane and measured. The contact angles of the membrane after testing in pure water and saline water, were measured using a contact angle analyzer (Phoenix 300, Surface Electro Optics Co. Ltd) over 10 cycles of MD tests (1 cycle = 1 hour) (Fig. S6B). After every 2 cycles, the membrane was washed using DI water, dried using N_2 gas, and weighed to reveal the mass variation during MD tests. A chloride probe (VWR 89231-632) was used to measure the salt concentration in both the feed and distillate during 0.5 M NaCl MD tests. SEM images were further measured for the FTCS-PDA-PVDF membrane after MD tests to evaluate the morphology and microstructure alteration.

Supporting figures and tables

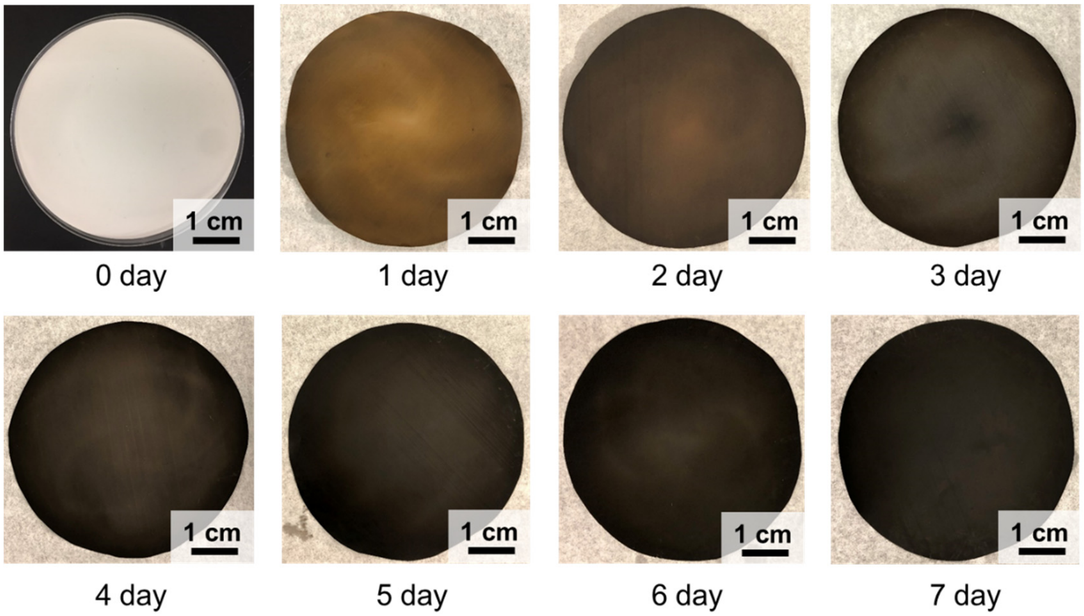

Fig. S1. Optical images showing the color change of the PVDF surface during the 7-day PDA self-polymerization proess.

Table S1. ATR-FTIR reference peaks for PDA coating on PVDF.

FTIR peak positions (cm^{-1})					
N-H bending vibrations	1510	1490	1506	1540	1520
C=C resonance vibrations in the aromatic ring	1600	1610	1600	1645	1610
O-H and NH_2 stretching vibrations	3100-3600	3100-3600	3100-3600	3000-3700	3100-3600
Reference	Jiang et al., 2011[10]	Cao et al., 2014[11]	Shao et al., 2014[12]	Sun et al., 2017[13]	This study

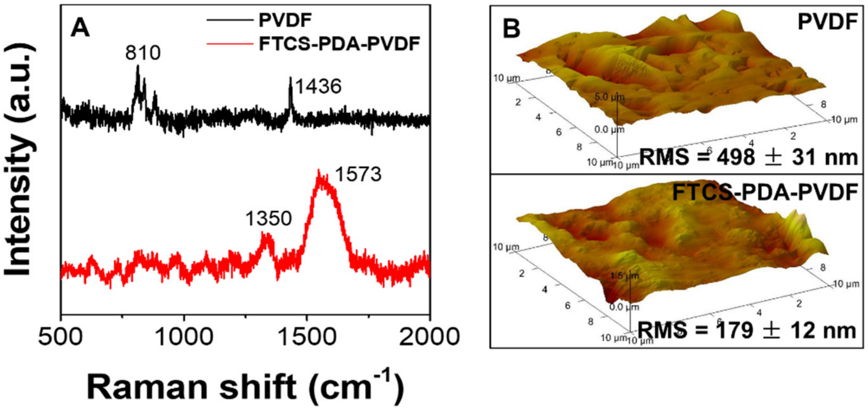

Fig. S2. (A) Raman spectra of pristine PVDF and FTCS-PDA-PVDF membranes; (B) Tapping mode AFM images (10 μm × 10 μm) showing the surface roughness (RMS) of pristine PVDF and FTCS-PDA-PVDF membranes.

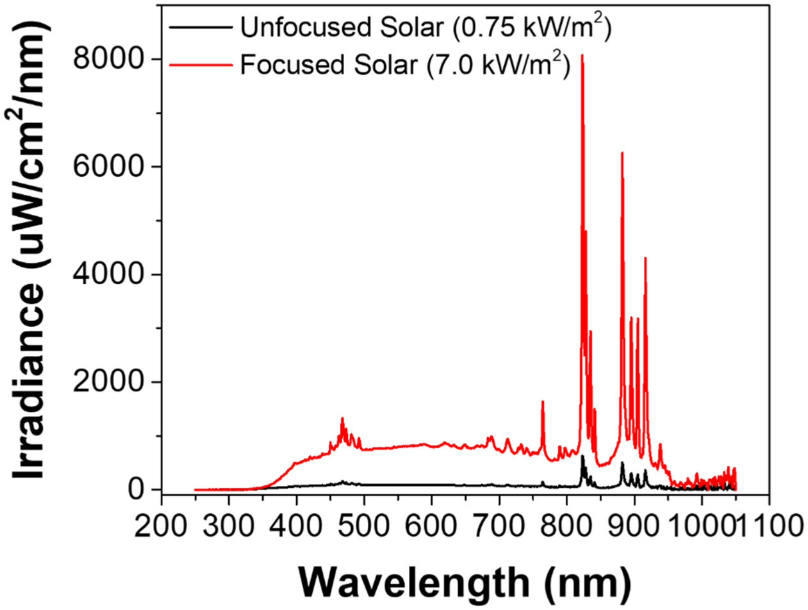

Fig. S3. Solar irradiance spectra of the solar simulator for unfocused (0.75 kW/m^2) and focused (7.0 kW/m^2) conditions.

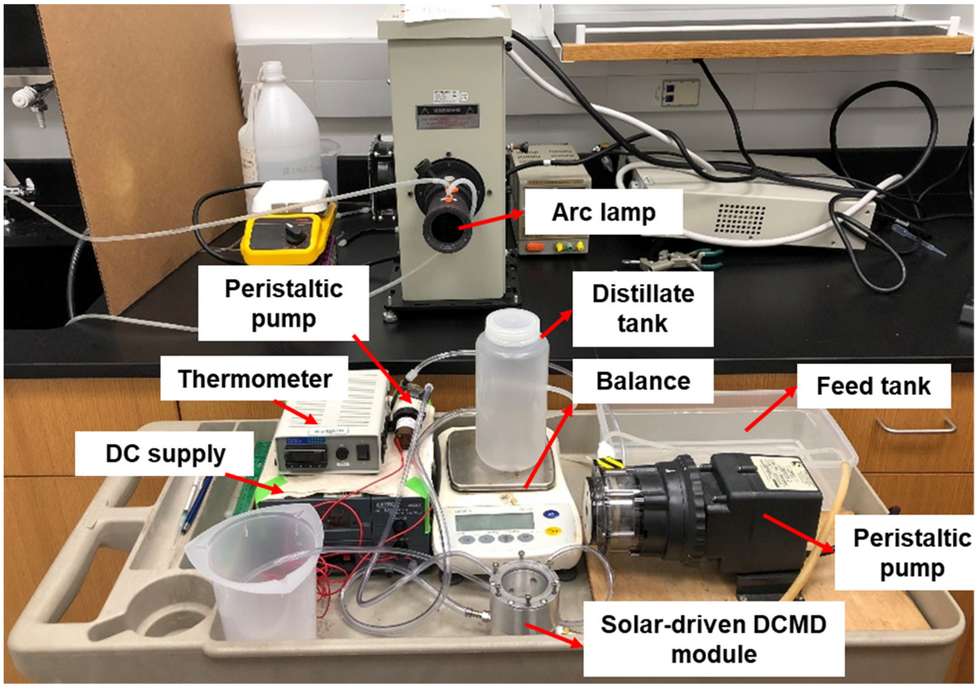

Fig. S4. Photo of the portable solar-driven direct contact membrane distillation system.

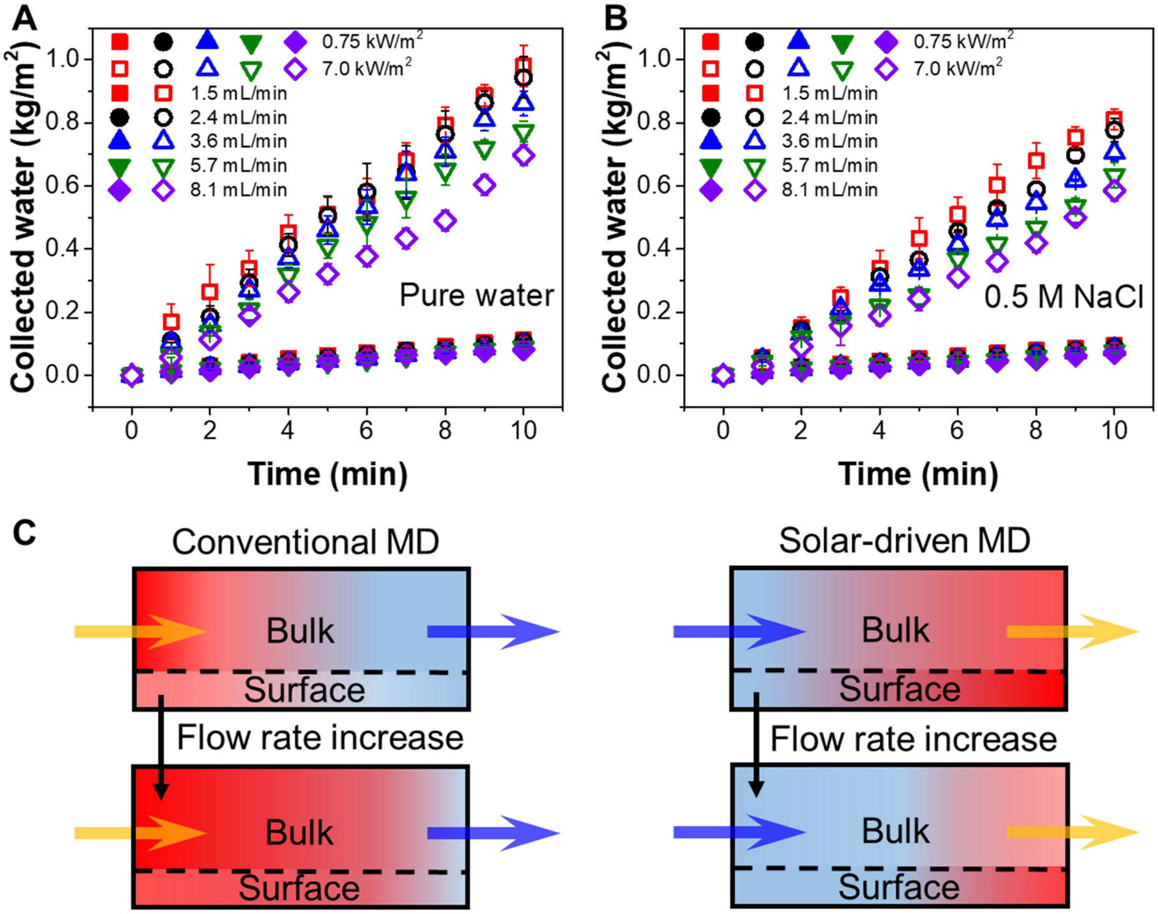

Fig. S5. Collected water (kg/m^2) for DCMD using pure water (A) and 0.5 M NaCl (B) with various feed flow rates (1.5–8.1 mL/min). (C) Schematic illustration depicting the temperature change in the feed side of a conventional MD system and solar-driven MD system with different feed flow rates. Red depicts high temperature and blue depicts low temperature.

Table S2. Comparison with other current photothermal MD membranes.

Materials	MD system[a]	Efficiency	T_{top} [b] (ºC)	Thickness of H_2O on top (mm)	Flux (kg/m^2 h)	Energy source	Hydrophobicity	Paper
PVDF-PVA-5.5wt%BC	DCMD	21.45%	20.8	1.5	0.22	solar	NA	Dongare et al., 2017[9]
PVDF-25%Ag NPs	VMD	29.6%	54.3	NA	25.7	UV	80.3º±3.6º	Politano et al., 2017[14]
Millipore nitrocellulose membrane	AGMD	31.8%	42–72[c]	4	0.35	solar	NA	Summers et al., 2013[15]
FTCS-PDA-PVDF	DCMD	45%	26	8	0.49	solar	126.1º±1.6º	This study

[a] VMD stands for vacuum membrane distillation. AGMD stands for air gap membrane distillation.

[b] Water temperatures of feed inlet and distillate for Dongare et al. and this study are 20 ºC. Politano et al. used an inlet of ~28 ºC. Summers et al. used an inlet of 26–30 ºC and a distillate of 20 ºC.

[c] Summers et al. used an electric heater besides the solar system.

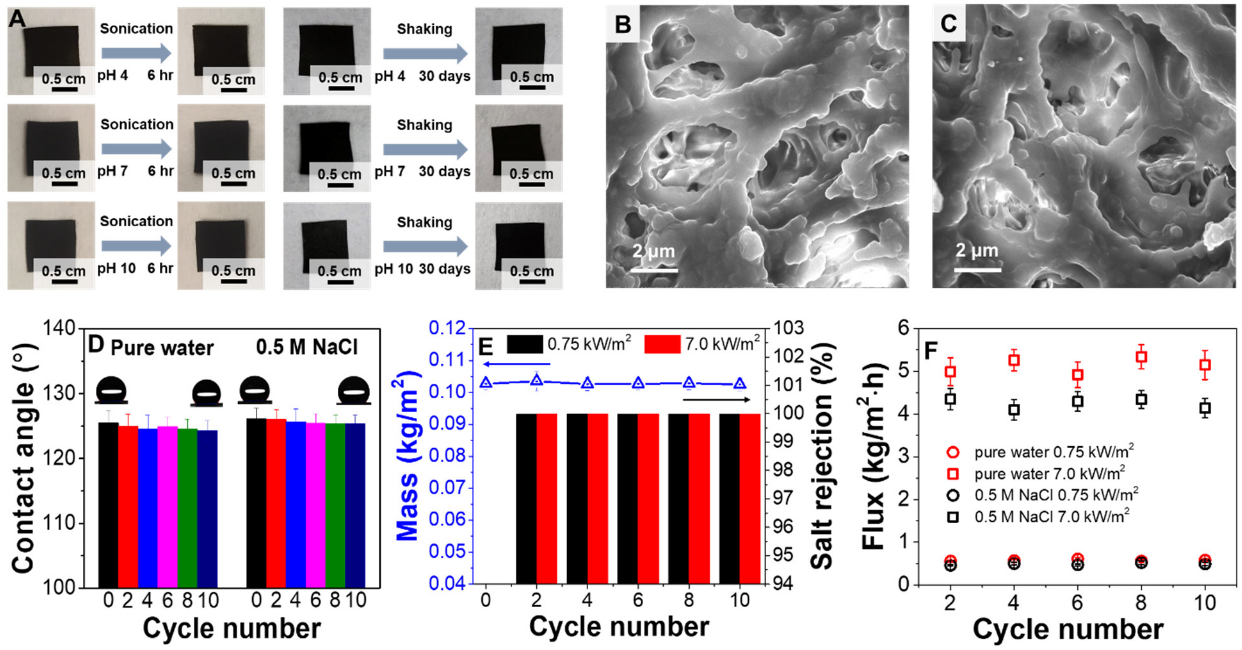

Fig. S6. (A) Photographs showing the chemical and mechanical stability of FTCS-PDA-PVDF membrane with ultra-sonication and shaking for an extended duration. SEM images of FTCS-PDA-PVDF membrane surface after 10 cycles using (B) pure water and (C) 0.5 M NaCl. (D) Contact angles of FTCS-PDA-PVDF membrane over 10 cycles of MD tests using pure water and 0.5 M NaCl. (E) *(Left y-axis)* Mass change of FTCS-PDA-PVDF membrane over 10 cycles of MD tests using 0.5 M NaCl, with 7.0 kW/m^2 irradiation; *(right y-axis)* Salt rejection of FTCS-PDA-PVDF membrane over 10 cycles of MD tests using 0.5 M NaCl, with both 0.75 and 7.0 kW/m^2 irradiations. (F) Flux performance of FTCS-PDA-PVDF membrane over 10 cycles of MD tests using pure water and 0.5 M NaCl, with both 0.75 and 7.0 kW/m^2 irradiations. Triplicate membrane samples were tested.

References

1. M. d'Ischia, A. Napolitano, V. Ball, C.-T. Chen and M. J. Buehler, *Acc. Chem. Res.*, 2014, **47**, 3541-3550.
2. H. Lee, S. M. Dellatore, W. M. Miller and P. B. Messersmith, *Science*, 2007, **318**, 426-430.
3. H. Jin, M. Kettunen, A. Laiho, H. Pynnönen, J. Paltakari, A. Marmur, O. Ikkala and R. H. Ras, *Langmuir*, 2011, **27**, 1930-1934.
4. M. E. Leitch, C. Li, O. Ikkala, M. S. Mauter and G. V. Lowry, *Environ. Sci. Technol. Lett.*, 2016, **3**, 85-91.
5. J. E. Efome, M. Baghbanzadeh, D. Rana, T. Matsuura and C. Q. Lan, *Desalination*, 2015, **373**, 47-57.
6. A. Khalifa, D. Lawal, M. Antar and M. Khayet, *Desalination*, 2015, **376**, 94-108.
7. U. Kuila, D. K. McCarty, A. Derkowski, T. B. Fischer and M. Prasad, *Fuel*, 2014, **117**, 1115-1129.
8. H. A. Loáiciga, *Geophys. Res. Lett.*, 2006, **33**.
9. P. D. Dongare, A. Alabastri, S. Pedersen, K. R. Zodrow, N. J. Hogan, O. Neumann, J. Wu, T. Wang, A. Deshmukh and M. Elimelech, *Proc. Natl. Acad. Sci.*, 2017, **114**, 6936-6941.
10. J. Jiang, L. Zhu, L. Zhu, B. Zhu and Y. Xu, *Langmuir*, 2011, **27**, 14180-14187.
11. C. Cao, L. Tan, W. Liu, J. Ma and L. Li, *J. Power Sources*, 2014, **248**, 224-229.
12. L. Shao, Z. X. Wang, Y. L. Zhang, Z. X. Jiang and Y. Y. Liu, *J. Membr. Sci.*, 2014, **461**, 10-21.
13. D. Sun, Y. Zhu, M. Meng, Y. Qiao, Y. Yan and C. Li, *Sep. Purif. Technol.*, 2017, **175**, 19-26.
14. A. Politano, P. Argurio, G. Di Profio, V. Sanna, A. Cupolillo, S. Chakraborty, H. A. Arafat and E. Curcio, *Adv. Mater.*, 2017, **29**.
15. E. K. Summers, *Desalination*, 2013, **330**, 100-111.