Supporting Information for

Bio-inspired Vertically Aligned Polyaniline Nanofibers Layer Enabling Extremely High-efficiency Solar Membrane Distillation for Water Purification

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Experimental section

Materials and chemicals: The hydrophobic polyvinylidene fluoride (PVDF) membrane (ISEQ00010) with a diameter of 0.2 μm was purchased from Millipore (defined as PVDF-m). All chemicals used in this work were analytical grade and were commercially available and used without any further purification.

Preparation of polyaniline (PANI) nanofiber dispersions: Aniline (0.02 M) and
ammonium persulfate (0.005 M) were dissolved in 150 mL of 1 M hydrochloric acid solution and rapidly mixed under stirring for 1 min and then standing for 12 h at room temperature to obtain PANI nanofiber dispersion (defined as PANI-HA nanofiber dispersion).

*Preparation of PVDF membrane with vertically-aligned PANI nanofibers:* Aniline (0.02 M) and ammonium persulfate (0.01 M) were dissolved in 50 mL of 1 M perchloric acid solution, respectively. After pre-cooling in an ice bath, the reaction solution was rapidly mixed under stirring. Meanwhile, 1 mL of PANI-HA nanofiber dispersion was added in 50 mL ethanol and vacuum-filtrated onto a PVDF-m (5.5 cm × 3.5 cm) and dried at 60 °C in an oven (the obtained membrane is defined as PANI0-m). Thereafter, the PANI0-m was floated in the aforementioned reaction solution wherein the side of PANI nanofibers was in contact with the reaction solution. The aniline polymerization took a certain time under continuous stirring at room temperature. Then, the obtained PVDF membrane with PANI coating was thoroughly rinsed with deionized water and placed in 0.1 M ammonium hydroxide for 2 h. Finally, the obtained PVDF membrane with vertically-aligned PANI nanofibers was thoroughly rinsed with deionized water and dried at 60 °C in an oven. The obtained PVDF membranes with vertically-arrayed PANI nanofibers after 2, 3, 4 and 8 h aniline polymerization were defined as PANI2-m, PANI3-m, PANI4-m, and PANI8-m, respectively.

*Preparation of PVDF membranes with PANI nanofibers (control sample):* Aniline (0.02 M) and ammonium persulfate (0.01 M) were dissolved in 50 mL of 1 M perchloric acid solution, respectively. After pre-cooling in an ice bath, the reaction solution was...
rapidly mixed under stirring. The PVDF-m (5.5 cm × 3.5 cm) was floated in the 
aforementioned reaction solution. The aniline polymerization took 4 h under 
continuous stirring at room temperature. Then, the obtained PVDF membrane with 
PANI coating was thoroughly rinsed with deionized water and placed in 0.1 M 
ammonium hydroxide for 2 h. Finally, the obtained PVDF membrane with PANI 
nanofibers (defined as PVDF4-m) was thoroughly rinsed with deionized water and 
dried at 60 °C in an oven.

**Instruments and characterizations:** The surface morphology of different membranes 
were observed on a Hitachi S4800 cold field emission scanning electron microscope. 
The chemical composition of different membranes were analyzed by a Nicolet 6700 
FTIR spectrometer and a Thermo Fisher Scientific ESCALAB 250Xi X Ray 
photoelectron spectrometer. The effective water contact angles were measured on an 
OCA20 machine (Data-physics, Germany). The surface roughness (root-mean-square, 
RMS) was measured using tapping mode of a Bruker Dimension Icon atomic force 
microscopy (Bruker, Santa Barbara, CA). Ion concentrations were measured with the 
inductively coupled plasma optical emission spectroscopy (ICP-OES) (Perkin Elmer 
Optima 8300, USA). The optical parameters (n and k) of single PANI nanofiber were 
measured using an M-88 spectroscopic ellipsometer (J. A. Woollam Co., Inc.). 

**Solar-driven membrane distillation measurements:** Solar-driven membrane 
distillation (SDMD) experiments were carried out using a custom-built membrane 
distillation module in a direct-contact mode. The setup of the SDMD system is shown 
in Figure S1. The membrane module consists of a 1-mm-thick quartz window (4 cm ×
2 cm) on the feed side to allow sunlight illumination. A 4-mm-thick polypropylene mesh spacer was commercially available and used on the distillate side. The cross-flow velocities in the feed and distillate channels were 0.0455 cm/min (flow rate, 0.01 mL/min) and 251.19 cm/min (flow rate, 50 mL/min), respectively. Saline streams with different salinities were chosen as the feed on the top of the membrane and stored in a 200-mL glass bottle. Deionized water was stored in a 100-mL beaker (distillate reservoir) and used for the distillate stream at the bottom of the membrane. To maintain stable temperatures on both sides of the membrane, the feed and distillate were cooled by 10-m-long chilling coils submerged in a low constant temperature trough before entering the SDMD module. The feed and distillate were continuously circulated through the membrane module in a countercurrent flow mode, using a peristaltic pump (Longer, BT100-2J) and a gear pump (Longer, WT3000-1JA), respectively, wherein feed and distillate streams flow in opposite directions. The distillate reservoir (a beaker of 100 mL) was kept on a weighing balance (Sartorius ELT402) to measure the collected permeate at 2 min intervals. During solar MD tests, the light from the solar simulator (Beijing Precise Technology Co., Ltd. PL-X300DF) was oriented to the membrane surface. The light intensities at the membrane surface were measured to be 1 kW m\(^2\) by a spectroradiometer (TES-132). The SDMD module was added a mask to ensure that only the phothothermal membrane received solar irradiation. The transmembrane pressure was increased by 0.1 bar increments at ~ 5 min intervals. The transmembrane pressure at which water permeated through the membrane was taken as the liquid entry pressure of the membrane. The distillate flux is the sum of the
evaporation rates of water with and without solar irradiation. The salt rejection was calculated according to the following equation:[1]

\[
\text{Salt rejection (\%)} = \left(1 - \frac{\sigma_d}{\sigma_f}\right) \times 100\%
\]

where \(\sigma_d\) is the conductivity of the distillate through the membrane, and \(\sigma_f\) is the conductivity of the feed. The conductivity of the distillate (\(\sigma_d\)) through the membrane was calculated using a mass balance on salt in the entire distillate reservoir:

\[
\sigma_d = \frac{M_b \times \sigma_b - M_a \times \sigma_a}{M_d}
\]

where \(M_a\) is the initial mass of solution in the distillate reservoir, \(\sigma_a\) is the initial conductivity of solution in the distillate reservoir, \(M_b\) is the final mass of solution in the distillate reservoir, \(\sigma_b\) is the final conductivity of solution in the distillate reservoir, \(M_d\) is the total mass of distillate through the membrane, \(\sigma_d\) is the conductivity of the distillate through the membrane.

The solar efficiency was calculated by the following equation:[2]

\[
\eta = \frac{m H_{\text{vap}}}{I}
\]

where \(\eta\) is solar efficiency, \(m\) is the distillate flux (kg m\(^{-2}\) h\(^{-1}\)), \(H_{\text{vap}}\) is the enthalpy change (2,454 kJ kg\(^{-1}\)) from liquid to vapor, and \(I\) is the power density of the incident light (kJ m\(^{-2}\) h\(^{-1}\)).

**Optical modelling and COMSOL simulation:** Optical modelling and electromagnetic simulation were carried out by a commercial software (COMSOL 5.5) to demonstrate the optical property of vertically-aligned PANI nanofibers layer. In the model presented in this work, an equal quantity of vertically-aligned PANI nanofibers were arranged
periodically on the surface of the PVDF membrane. These vertically-aligned PANI nanofibers have a diameter of 50 nm and a length of 600 nm. The PVDF membrane has a porosity of 65% and a thickness of 200 μm. The distance between PANI nanofibers of models was chosen as 81 nm, 99nm, and 140 nm, respectively. The optical parameters (n and k) of single PANI nanofiber were provided in Figure S13. All models were exposed to vertical solar irradiation with the wavelength of 550 nm and 810 nm, respectively. To calculate and compare the total absorption performance of different models, the total transmission and reflection efficiency were detected by two power monitors, and absorption efficiency was calculated by $A=1-R-T$. R and T are the reflection and transmission efficiency, respectively.
Supplementary Figures and tables

Fig. S1 a) Photograph of SDMD system. b) SDMD module before SDMD test. c) SDMD module with a mask during SDMD test.
According to the SEM image (Fig. S2b) and TEM images of the PANI-HA nanofibers (Fig. S2c-d), the PANI-HA nanofibers have branch-like morphology, diameters of 30-60 nm and lengths of 350-600 nm.
Fig. S3 Concentration of undoped PANI-HA nanofibers dispersion.

A certain volume (5, 10, 15 and 20 mL) of PANI-HA nanofibers dispersion were added in 50 mL ethanol and vacuum-filtrated onto a PVDF-m (5 cm × 3.5 cm) and dried at 60 °C in an oven, respectively. Then, the PVDF-m with PANI-HA nanofibers were placed in 0.1 M ammonium hydroxide for 2 h and thoroughly rinsed with deionized water and dried at 60 °C in an oven. The masses of original PVDF-m and PVDF-m with undoped PANI-HA nanofibers were measured by electronic balance to calculate the mass of undoped PANI-HA nanofibers. As shown in Figure S3, the mass undoped PANI-HA nanofibers and corresponding volume of PANI-HA nanofibers dispersion exhibit linear dependency in a range of volume from 0 to 20 mL. As a result, the slope of the fitted line was the concentration of undoped PANI-HA nanofibers dispersion, namely 0.074 mg mL⁻¹.
Fig. S4  c) Surface wettability of PVDF-m and PAN0-m. d) Growth density of vertically-aligned PANI nanofibers on PVDF4-m and PANI4-m.

Fig. S5  Effect of the aniline polymerization time on the growth mass of PANI nanofibers.

Fig. S6  a) FTIR and b) XPS spectra of PVDF-m and PANI4-m.
Fig. S7 Salinities of four primary ions in a simulated seawater sample before and after desalinated by PANI4-m.

Fig. S8 Salt rejection of PANI4-m over 10 cycles of SDMD tests using 1 wt% NaCl under one sun irradiation.

Fig. S9 a) Light absorption b) light reflectance and c) Light transmittance spectra of PANI4-m before and after 10-cycles SDMD tests using 1 wt% NaCl under one sun irradiation, respectively.
**Fig. S10** Top-view SEM images of PANI4-m before a) and after b) 10-cycles SDMD tests using 1 wt% NaCl under one sun irradiation, respectively.

**Fig. S11** Top-view SEM images of a) PANI2-m, b) PANI3-m, and c) PANI4-m, respectively. Cross-section SEM images of d) PANI2-m, e) PANI3-m, and f) PANI4-m, respectively. All scale bars are 1 μm.
**Fig. S12** Calculated light reflectance a) and transmittance b) of models with different PANI nanofibers densities at the wavelength of 550 nm and 810 nm. c) Calculated three-dimensional electric field distributions of models with the PANI nanofibers densities of 0.048 mg cm\(^{-2}\), 0.064 mg cm\(^{-2}\) and 0.088 mg cm\(^{-2}\), respectively, at the wavelength of 810 nm from left to right. Color bar: indicating the electromagnetic energy (THz) absorbed by PANI nanofibers.

**Fig. S13** Optical parameters of PANI nanofibers.
<table>
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<tr>
<th>Materials</th>
<th>Feed temperature (°C)</th>
<th>Distillate temperature (°C)</th>
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<th>Efficiency</th>
<th>Ref.</th>
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<td>CB/PVA-PVDF</td>
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References


