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Supporting information for

Photo-bactericidal thin film composite membrane for forward osmosis

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Experimental

Materials

Polyethersulfone (PES) was purchased from Solvay Co., Ltd. N-methyl-2-pyrrolodinone (NMP, > 99.5%) and polyethylene glycol 400 (PEG, Mn = 400g/mol) were purchased from Merck. The deionized water used in the experiments was produced by a Milli-Q ultrapure water system (Millipore, USA). m-Phenylenediamine (MPD, >99%), 1,3,5-benzenetricarbonyl trichloride (TMC, 98%) and 2, 7-dichlorofluorescein diacetate (DCF-DA dye) were purchased from Sigma-Aldrich Chemical Co. Hexane, ethanol, sodium chloride (NaCl) and sodium hydroxide (NaOH) were purchased from Merck. 5,10,15,20-Tetrakis(4-aminophenyl)-21H,23H-porphine was purchased from Tokyo Chemical Industry Co. All chemicals were used as received.

Membrane fabrication

The PES support was prepared by the Loeb-Sourirajan wet-phase inversion method. The PES polymers were first dried overnight to remove the moisture content. The composition of the casting solution was PES/PEG-400/NMP/water (wt%) = 20/37.9/37.9/4.2. The casting solutions were de-gas prior to the casting, followed by a casting onto a glass plate with a 100 µm casting knife. After that, the as-cast membranes were immediately immersed into a water coagulation bath at room temperature and kept for ~24 h to ensure complete precipitation.

For the fabrication of TFC membranes, the membrane substrate was first immersed in a 2 wt% MPD in deionized water for 1 min. After that, a filter paper was used to remove the water droplets on the membrane surface. The top surface of the membrane was then brought to contact with a 0.05 wt% TMC solution in n-hexane for 30 s, leading to the formation of a polyamide thin film layer. To prevent the hydrolysis of acyl chlorides, the freshly-prepared TFC membranes were immediately immersed in the ethanol solution with different porphyrin concentrations (0 M, 10^{-7} M, 10^{-6} M, 10^{-5} M, and 10^{-4} M) for 30 min, and the resultant membranes were named as Por0-TFC, Por1-TFC, Por2-TFC, Por3-TFC, Por4-TFC, respectively. In a final step, the as-fabricated membranes were stored in deionized water at room temperature before use.

Characterization of the TFC membranes

Composition, morphology, surface roughness and contact angles of the TFC membranes. Diffuse reflectance UV-vis (DR-UV) spectra of the porphyrin-grafted membranes were recorded on a CARY 5000 Varian spectrometer using a 110 mm PTFE integrating sphere. The reflectance spectrum was obtained against the Teflon standard reflectance spectrum. A Bio-Rad FTIR FTS 135 was used to monitor the changes of the functional moieties on the membrane surface in the range of 600-4000 cm^{-1} using the attenuated total reflectance (ATR) mode. The morphology of membranes was examined by field emission scanning electric microscopy (FESEM, JEOL JSM-6700F). The FESEM samples were prepared with liquid nitrogen, followed by a platinum coating using a Jeol-1100E Ion Sputtering device. The surface roughness of the TFC membranes was assessed by atomic force microscopy (AFM, Nanoscope IIIa, Digital Instrument, USA) at room temperature in the tapping mode. Images in the range of 5 µm × 5 µm were obtained and the mean roughness (Ra) was determined. Photoluminescence was recorded on a PerkinElmer LS55 fluorescence spectrometer. The water contact angle was measured by a Contact Angle Gniometer (Rame Hart) at room temperature using Milli-Q deionized water as the probe liquid to determine the surface hydrophilicity of the membranes. Immediate contact angles were recorded and calculated by the software once the water drops touched the membrane surface. We obtained ten readings, randomly at different locations, and an average contact angle was calculated to minimize the experimental error.

Determination of the TFC membrane performance in FO. The FO experiments conducted in this work were similar to previous studies.[1, 2] In a particular setup, the membrane test module consists of one water channel on each side of the membrane with a dimension of 2.0 cm in length and 1.0 cm in width. The effective membrane area was 2.0 cm^2. No spacer was used in the testing. Both draw solution and feed solution flowed, in a counter-current mode, through the filtration cell at the same volumetric flow rate of 0.3 L/min, and the solutions were re-circulated. Two different membrane orientations were tested at room temperature, with either the selective layer against the feed solution (FO mode) or against the draw solution (pressure retarded osmosis (PRO) mode).

The water permeation flux, J_w (L/m^2/h, LMH), is determined by Eq. (1) on the basis of the absolute weight change of the feed and the effective membrane area, A_m (m^2):

$$J_w = \frac{\Delta w}{\Delta t} \frac{1}{A_m} \qquad Eq. (1)$$

Where Δw (kg) is the absolute weight change of water that has permeated across the TFC-FO membrane over a pre-determined time Δt (h) during the FO tests.

The reverse salt flux, J_s (g/m^2/h, gMH) was determined from the conductivity increment in the feed when deionized water was used as the feed solution:

$$J_s = \frac{(C_t V_t) - (C_0 V_0)}{\Delta t} \frac{1}{A_m} \qquad Eq. (2)$$

Where C_t (mol/L) and V_t (L) are the salt concentration and the volume of the feed solution at time t, respectively; C_0 (mol/L) and V_0 (L) are the initial salt concentration and the volume of the feed solution, respectively.

Antibacterial ability assessment. The *Escherichia coli* (*E. coli*) strain was cultured in Lysogeny broth (LB) and incubated in an Isotemp incubator (FisherScientific, Inc., Pittsburgh, PA) under shaking (150 rpm) at 37 ^oC overnight. This culture was then centrifuged for 10 min at 3000 rpm, and the pellet was re-suspended in the LB solution. The resulting cell suspension was served as a bacterial stock solution, which was further diluted to ~10^5 colony-forming units (CFU)/ml before use. To assess the antibacterial properties of the as-fabricated TFC membranes, disk experiments were performed. In a typical disk experiment, an aliquot (30 µL) of *E. coli* solution was spread (in triplicate) onto the plate of LB agar. After that, the membrane samples with different porphyrin concentrations were placed onto the agar plate with the active layer in contact with the agar surface. The agar plate was then illuminated with white light (a 7 W LED light bulb, Outrace Co., Ltd) for 6 h. After that, the plate was incubated overnight in darkness at 37 ^oC to allow the individual bacteria to grow and form visible colonies.

In addition, two groups of Por3-TFC membrane samples with and without light irradiation were immersed in 100 mL of *E. coli* suspension (1.0×10^5 CFU/mL) with shaking at 150 rpm for 24 hours at 37 ^oC. The bacteria were then fixed in 3 vol.% glutaraldehyde PBS solution for 5 h at 4 °C, and rinsed with PBS solution several

times to remove any remaining glutaraldehyde on the surface. After fixation, the samples were dehydrated with an ethanol series (25, 50, 75 and 100%), air-dried, and coated with platinum (20 mA, 30 s) using the sputter coater for SEM observation.

ROS detection. The production of ROS in the presence of the porphyrin-grafted TFC membranes was measured by using a fluorescent dye DCFH-DA and a fluorescent spectrometer. In a typical experiment, in order to cleave the acetate group, 20 ml of sodium hydroxide (0.01 M) was introduced to 500 µl of DCFH-DA (5 mM), and the mixture was incubated at room temperature for 30 min. After that, 100 ml of sodium phosphate buffer (25 mM, pH 7.2) was added to quench the reaction. In the dark room, 5 ml of DCFH solution was then introduced into the tubes of the TFC membranes grafted with different amount of porphyrin. After that, the samples were exposed to light radiation to stimulate the photochemical reaction, and the fluorescent intensity was recorded at the excitation and emission wavelength of 488 and 525 nm, respectively. The experiments were done in triplicate.

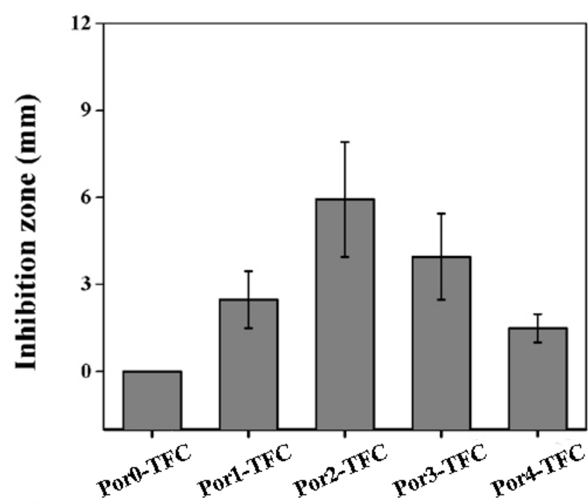

Figure S1. Photodynamic inhibition zones of the TFC membranes grafted with a different amount of porphyrin.

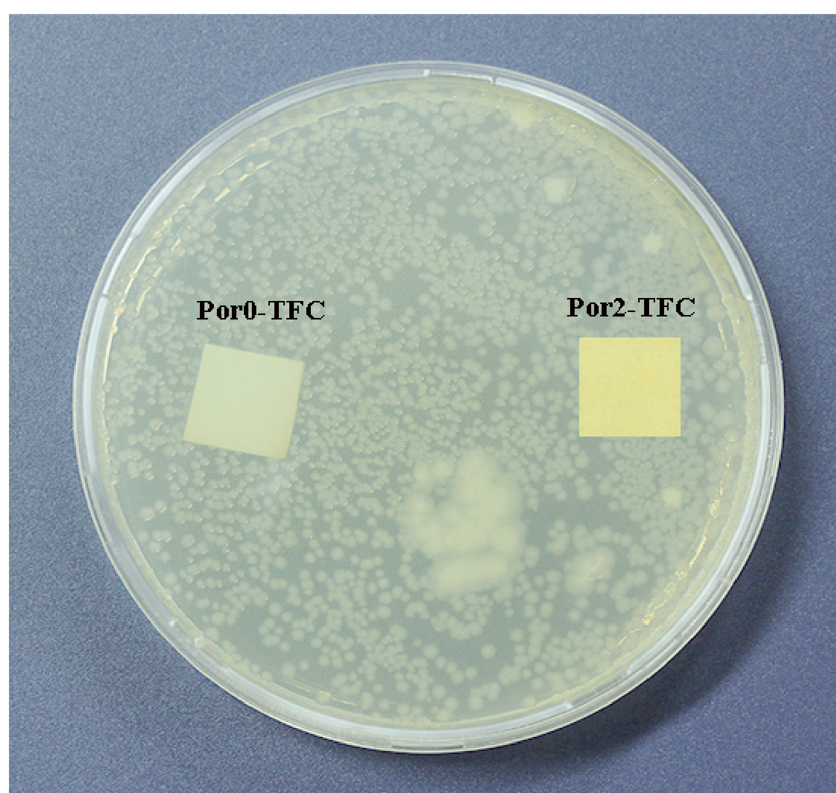

Figure S2. Agar diffusion assay for the Por0-TFC and Por2-TFC membrane incubated under dark condition.

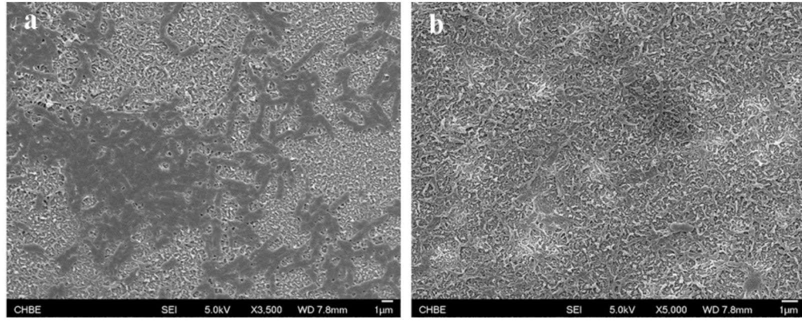

Figure S3. Representative SEM images of Por2-TFC membrane incubated in diluted *E. coli* solution at 37 ˚C (a) in the absence and (b) presence of light exposure.

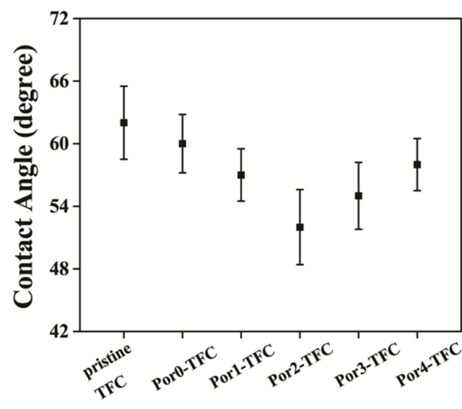

Figure S4. Water contact angles of the membrane surfaces.

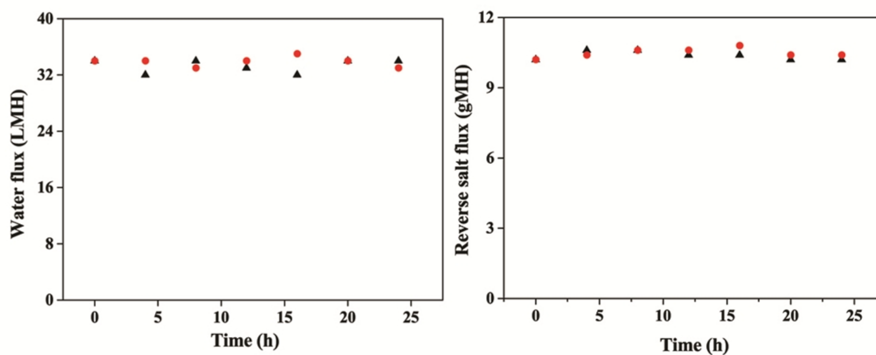

Figure S5. Por3-TFC membrane performance with (▲) and without (●) light exposure as a function of time in the FO mode.

Table S1. The performance of the pristine and porphyrin-grafted TFC membranes in the FO process.[a]

Sample	FO mode		PRO mode	
	J_w (LMH)	J_s/J_w (g L^{-1})	J_w (LMH)	J_s/J_w (g L^{-1})
Pristine TFC	16±1.2	0.26±0.02	26±2.2	0.24±0.01
Por0-FO	24±3.0	0.40±0.03	38±3.0	0.31±0.02
Por3-FO	34±1.4	0.29±0.02	44±3.2	0.28±0.02

[a] Draw solution: 2 M NaCl solution; feed solution: deionized water.

References

1. X. Li, S. Zhang, F. Fu and T.-S. Chung, *J. Membr. Sci.*, 2013, **434**, 204-217.
2. G. Han, S. Zhang, X. Li and T.-S. Chung, *J. Membr. Sci.*, 2013, **440**, 108-121.