Electronic Supplementary Information

Nanoporous Organosilica Membrane for Water Desalination

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Experimental Section

Preparation of nanoporous organosilica hybrid membranes

The organosilica hybrid membranes were prepared via the sol-gel method under acidic conditions. First, 1.0 g of BTESE was pre-hydrolysed in 1.26 g of ethanol with 0.61 g of 0.01 M hydrochloric acid (HCl, 37%, Aldrich) at 35 °C for one hour. Second, 0.28 g of non-ionic triblock copolymer surfactant Pluronic F68 was dissolved in ethanol under stirring for 2 hours. Finally, the two mixtures were combined under stirring to give a final molar ratio of 1BTESE : 8.7ethanol : 6H$_2$O : 0.0022HCl : 0.006 F68.

Dip-coating was carried out in a class 100 laminar flow cabinet to prevent from dust contamination on the membrane surface. The organosilica membrane was deposited by dip-coating the prepared sol as aforementioned on (a) glass slides (for TEM analysis sample) and (b) alumina substrate (PALL, length 100mm, outer diameter 10mm, thickness 1.7mm, for desalination test) with titania as intermediate layer (pore size 5nm) at a withdrawal speed of 10 cm min^{-1} and holding time of 1 min. After dip-coating, the membrane was dried in air overnight, and then cured at 150°C for 12hrs for the complete cross-linking and self-assembly of organosilica network before surfactant removal through calcination in air at 300°C for 4hrs with heating rate of 1°C min^{-1}. The remaining sol was dried on a petri dish to form a thin layer and grinded for SAXS and N$_2$ adsorption analyses.

Characterization

Transmission electron microscopy (TEM) analysis was performed by JEOL JEM-1010 and JEM-2100 electron microscopes operated at accelerating voltage of 100kV and 200kV, respectively. TEM sample was prepared by scraping out the calcined thin films from glass slides, and mixed with ethanol to form slurry then dropped on holey carbon film coated Cu grid. The mesostructure of calcined organosilica membrane was investigated by small-angle X-ray scattering (SAXS) with lower starting angle of 2 θ < 0.5° using a Anton Paar 'SAXSess' which was equipped with both CCD and image plate detection. Fourier transform infrared spectroscopy was performed using a Shimadzu IRAffinity-1 FT-IR Spectrometer, from 4000-500cm^{-1} wavelength. Nitrogen adsorption and desorption isotherms were

measured at 77K using a Micromeritics Tristar 3020 analyzer. Prior to the adsorption measurements, the samples were outgassed under vacuum at 180°C for 12 hrs. The mean pore size and pore size distribution were calculated from the adsorption branch of the isotherm using nonlocal density functional theory (NLDFT) method. The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method and total pore volume was calculated by the amount of nitrogen adsorbed at $P/P_0 = 0.99$. ^{29}Si and ^{13}C nuclear magnetic resonance (NMR) were measured by a solid state Bruker Avance III spectrometer with a 7T (300 MHz for ^{1}H) magnet and a zirconia rotor, 4 mm, rotated at 7kHz. Thermogravimetric analysis (TGA) was performed using a Shimadzu TGA-50 with a temperature ramp rate of 1°C min^{-1} to 700°C under an air flow at 100ml min^{-1}. The surface morphology of the calcined membrane was observed using scanning electron microscopy (SEM; JCM-5000 Neo Scope, JEOL, Japan) in the secondary electron imaging mode with an acceleration voltage of 10kV under high vacuum.

Performance test of organosilica membrane in desalination

Desalination test of organosilica and pure silica membrane were performed through a continuous flow system of vacuum membrane distillation (VMD) as shown in Figure S1. Membrane module resembling shell-and-tube heat exchanger with varied temperature of feed solution was transported inside the tube lumen and vacuum of 80mbar was applied at the shell side. Sodium chloride solution with varied concentrations (10, 35, 50, 75, 150 g L^{-1} of NaCl) was used as the feed solution that represent the range of brackish water (10 g L^{-1}), seawater (35 g L^{-1}) and brine solution (> 50 g L^{-1}) available in the natural environment. Effect of feed temperature to permeate flux was studied at 20, 40 and 60°C. The feed and permeate conductivities were measured by a labCHEM CP conductivity meter, which was calibrated over a range of salt concentrations (0.1 to 150 g L^{-1}). The permeate flux through the membrane, F (kg m^{-2} hr^{-1}) was calculated by $F = m/A{\cdot}t$, where m is the mass of permeate collected, A as the membrane tube active area and t is the duration time of permeation test. Salt rejection, R (%) of the membrane was calculated by the following equation: $R = (C_f - C_p)/C_f \times 100\%$, where C_f and C_p were the feed and permeate concentrations (wt%), respectively.
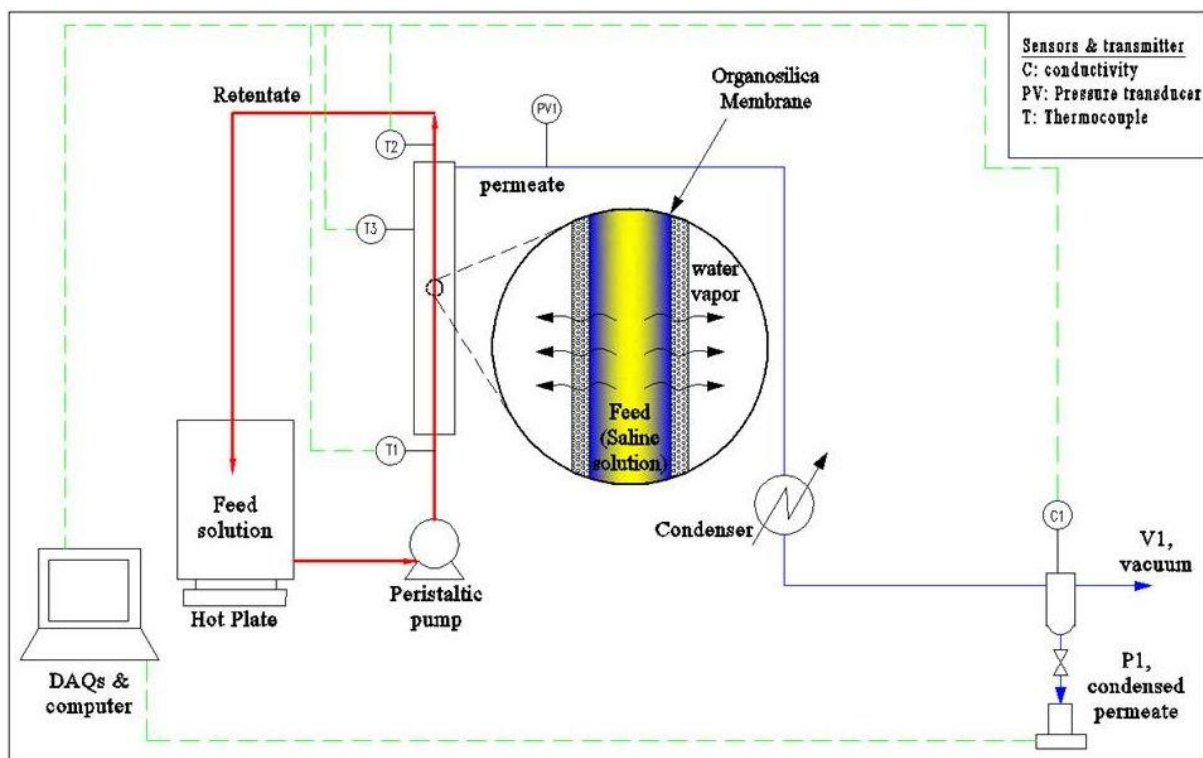
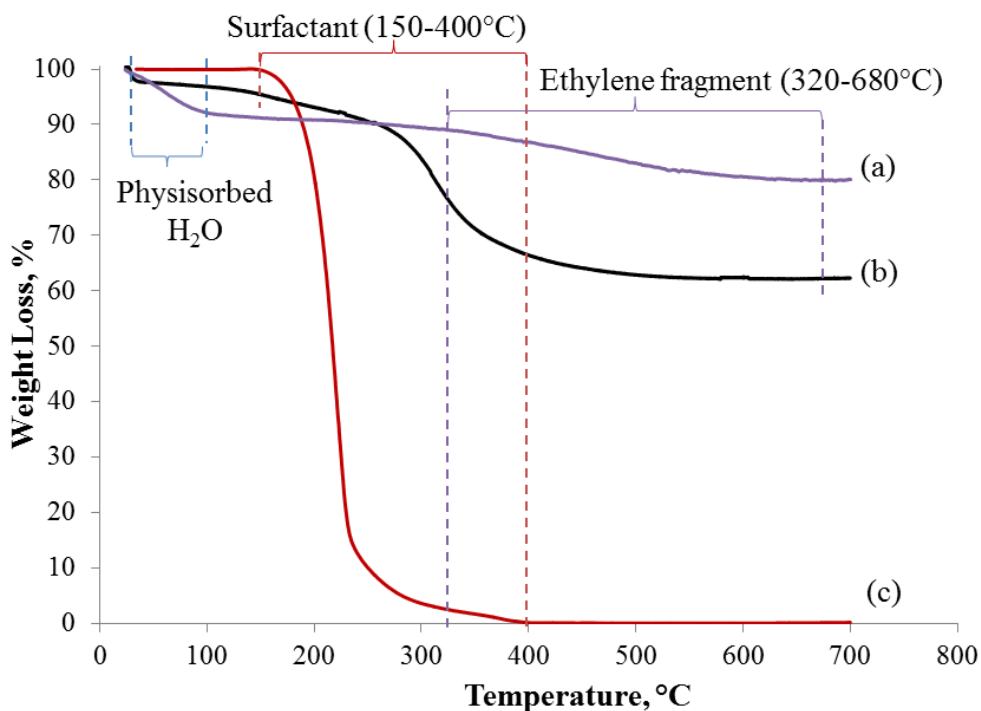**Figure S1 Schematic diagram of vacuum membrane distillation test rig**

Figure S2 TGA curve of the as-synthesized (a) organosilica without template; (b) organosilica templated with F68 and (c) pure Pluronic F68 as recorded under an air atmosphere.

A clear trade-off exists between surfactant removal and retention of organic moieties within the silica network as to completely remove the surfactant a calcination temperature of 400°C would be required, as shown by thermogravimetric analysis (TGA) (Figure S2(c), ESI). However, a calcination temperature this high would have adversely affected the organosilica matrix, indeed the TGA curve for the organosilica sample without surfactant template (Figure S2(a), ESI) demonstrates that Si-C bonds begin decomposition at approximately 300°C – 320°C. TGA data for the templated organosilica sample (Figure S2(b), ESI) shows two major mass losses between 140°C – 280°C, related to surfactant decomposition, and between 280°C – 420°C, related to the combined surfactant decomposition and cleavage of the ethylene fragment in the organosilica, suggesting that cleavage of a fraction of the Si-C bonds is unavoidable during surfactant removal.
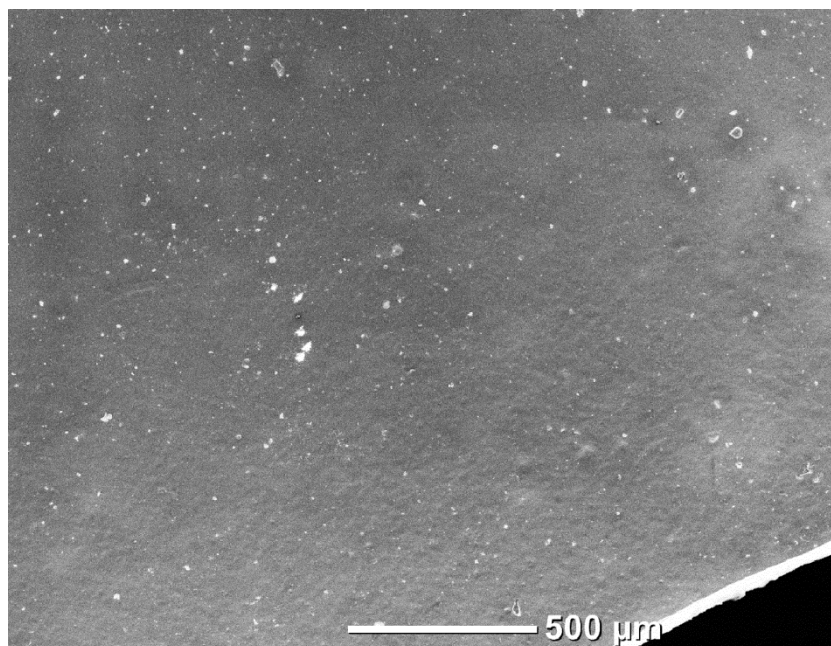
Figure S3 SEM image of top plane view of organosilica membrane showing the large area of uniform coating without cracks or defects.