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Superwetting hierarchical porous silica nanofibrous membranes for oil/water microemulsion separation

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Support information

Materials

Poly(vinyl alcohol) (PVA, M_w=88000), tween 80, aniline, paraformaldehyde, p-hydroxybenzaldehyde, phosphoric acid (H_3PO_4, 85%), trichloromethane, acetone, ethanol, sodium hydroxide, anhydrous magnesium sulfate, and SiO_2 NPs (7-40 nm) were purchased from Shanghai Chemical Reagents Co., Ltd., China. Tetraethyl orthosilicate (TEOS) and petroleum ether were purchased from Lingfeng Chemical Co., Ltd., China. Pure water was obtained from a Millipore system. All reagents were of analytical grade and used as received without further purification.

Preparation of pristine silica nanofibrous (SNF) membranes

The precursor solution was prepared by dissolving the PVA in pure water and heating in oil bath at 80 ^{o}C with vigorous stirring for 12 h. The silica sol solution was obtained via the hydrolysis and polycondensation reaction of the TEOS, then by dropwise addition of H_3PO_4 and pure water into as-prepared solution with the molar composition ratio of TEOS: H_2O: H_3PO_4 at 1: 1: 0.01 and stirring at room temperature for another 12 h. Following, 20.01 g of pre-synthesized silica sol solution was added into the 20 g of as-prepared PVA solution and continued stirring for another 5 h. The electrospinning process was performed by using a DXES-01 spinning equipment (Shanghai Oriental Flying Nanotechnology Co., Ltd., China) with an applied high voltage of 17 kV and a controllable feeding rate of 1 mL h^{-1}. The spinning temperature and humidity were stabilized at 25±2 ^{o}C and 50±5 %, respectively, the tip-to-collector distance of spinning process was kept at 20 cm. Finally, the composite membranes were calcined to 800 ^{o}C by gradually increasing the temperature with the heating rate of 5 ^{o}C min^{-1} in air to remove the PVA.

Synthesis of BA-CHO monomers

The BA-CHO was synthesized via one-step method of Mannich reaction by using p-hydroxybenzaldehyde, aniline, and paraformaldehyde, as shown in Fig. S1. Concisely, 20 g of p-hydroxybenzaldehyde, 15.24 g of aniline, and 9.84 g of paraformaldehyde were added into a three necked flask, and then the temperature was gradually increased to 105 °C with stirring in an inert atmosphere for 4 h. After the temperature of solution cooling to the room temperature, the obtained product was dissolved in 200 mL of trichloromethane. To further purify the sample, the solution was washed with 1 wt% sodium hydroxide and pure water, then treated with anhydrous magnesium sulfate and filtered, and dried at 60 °C for 2 h to obtain BA-CHO monomers. The details of structural confirmation by ^{1}H NMR spectroscopy were presented in Fig. S2.

Fabrication of SNF membranes

The pristine SNF membranes were firstly dipped in acetone solutions containing BA-CHO (1 wt%) and SiO_2 NPs with various concentrations (0.01, 0.1, 0.5, 1, and 2 wt%), and dried in an oven for 30 min. Then in situ polymerization of BA-CHO was carried out at 220 °C in vacuum for 1 h, leading to the formation of the Mannich bridge cross-linked structure, generating the cured thermosetting PBZ-CHO layer on the fiber surface which contained embedded SiO_2 NPs. Finally, the silica/PBZ-CHO membranes were calcined at 850 °C for 30 min with the heating rate of 4 °C min^{-1} under N_2 flow (the N_2 flow rate was 0.002 m^3 min^{-1}) to generate the hierarchical porous SNF membranes. The obtained samples with the SiO_2 NPs concentration of x wt% were denoted as SNF-x, and the pristine SNF membranes were denoted as SNF-0.

Emulsion separation experiments

Typically, the as-prepared SNF-2 membranes were sealed between one vertical glass tube with a diameter of 40 mm and one conical flask. The freshly prepared microemulsions were poured onto the SNF-2 membranes and spontaneously permeated quickly. The separation fluxes were estimated by calculating the permeated volume of emulsion within 1 min. To test the cycle performance, the membranes were washed with ethanol and dried at 60 °C for 30 min after each separation cycle.

Characterization

The ^{1}H NMR spectrum was recorded using the Bruker Avance 400, d_6-DMSO was used as the solvent. FT-IR spectra were measured with a Nicolet 8700 FT-IR spectrometer in the range of 4000-400 cm^{-1}. Field emission scanning electron microscopy images and energy-dispersive X-ray spectroscopy images were examined by Hitachi S-4800, Hitachi Ltd., Japan, all samples were coated by gold for 5 min. Transmission electron microscopy images were measured by using JEM-2100F, JEOL Ltd., Japan. N_2 adsorption-desorption isotherms were examined at 77 K by an ASAP 2020 physisorption analyzer (Micromeritics Co., USA). Water contact angle (3 μL), oil contact angle (OCA) (3 μL), and sliding angle (10 μL) measurements were performed by a contact angle goniometer Kino SL200B equipped with tilting base. The underwater OCA hysteresis was measured using the increment-decrement method. The mechanical properties of the membranes were measured on a tensile tester (XQ-1C, Shanghai New Fiber Instrument Co., Ltd., China), the size of samples were 3 × 40 mm^2, the thickness of the samples ranged from 20 to 40 μm, and the strain rate was 10 mm min^{-1}.

The determination of the adhesion work

The adhesion work was determined by the the Young Dupré's Equation: $W_{ad} = \gamma_{lv}(1 + \cos\theta_{lv})$, where the W_{ad} is the adhesion work, the γ_{lv} is the surface tension of liquid, and the θ_{lv} is the relevant liquid contact angle. For the SNF-0 membranes, the liquid contact angles (both the WCA and OCA) are 0° because of the superamphilicity in air. The surface tension for water and dichloromethane are 72 and 23 mN m^{-1}, respectively. Thus, for water, the $W_{ad} = 72 \times (1+ \cos 0°) = 144$ mN m^{-1}. For dichloromethane, the $W_{ad} = 23 \times (1+ \cos 0°) = 46$ mN m^{-1}.

The determination of the liquid adhesion forces

The determination of the liquid adhesion forces was on the basis of a well-known previous study (*J. Colloid Sci.*, 1962, 17, 309). In this paper, the authors proposed a theoretical method to calculate the adhesion force:

$$F = \theta_M\,(\gamma_A(\cos\theta_R - \cos\theta_A)/\rho)^{0.5}$$

where the F is the liquid adhesion force; the θ_A is the advancing contact angle; the θ_R is the receding contact angle; the θ_M is the arithmetic mean of θ_A and θ_R; the γ_A is the liquid/liquid interfacial tension; and ρ is the density of the liquid droplet. Therefore, the liquid adhesion forces of as-prepared SNF membranes were estimated by using this equations.

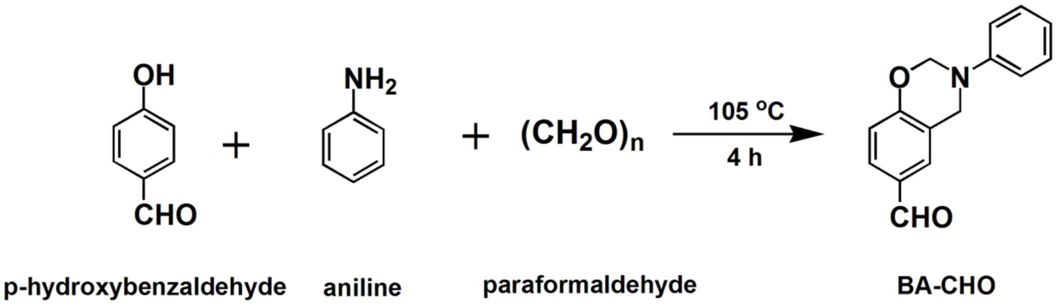


Fig. S1 Chemical synthetic route of BA-CHO monomers.

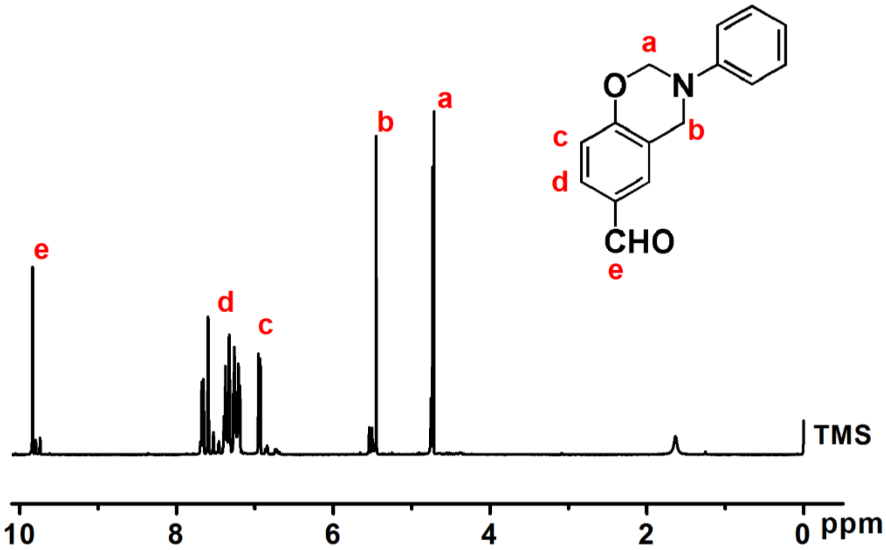


Fig. S2 ^{1}H NMR spectrum of as-synthesized BA-CHO.

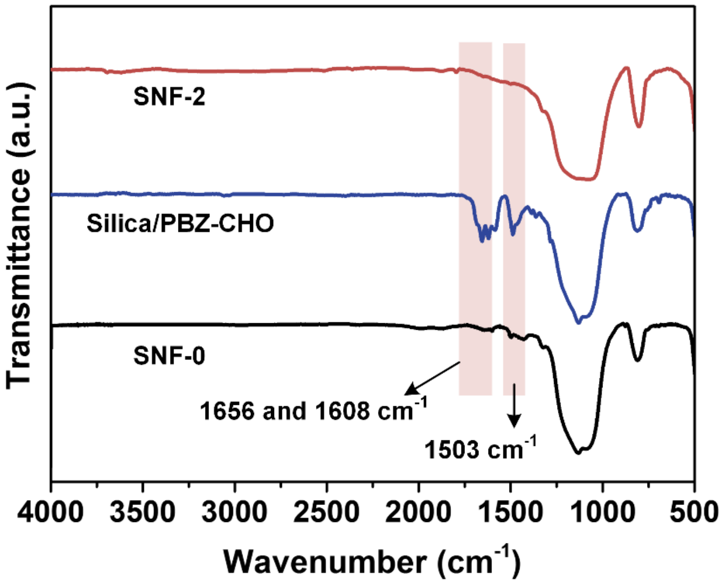


Fig. S3 FT-IR spectra of pristine SNF-0, silica/PBZ-CHO, and SNF-2 membranes.

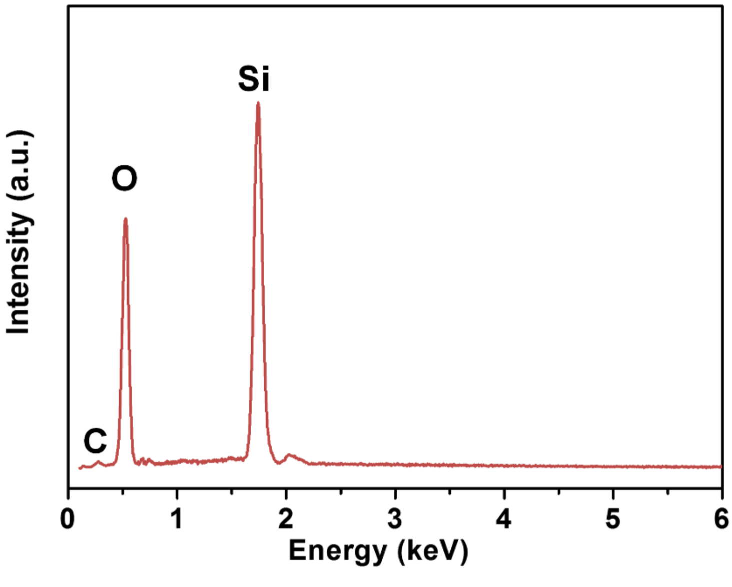
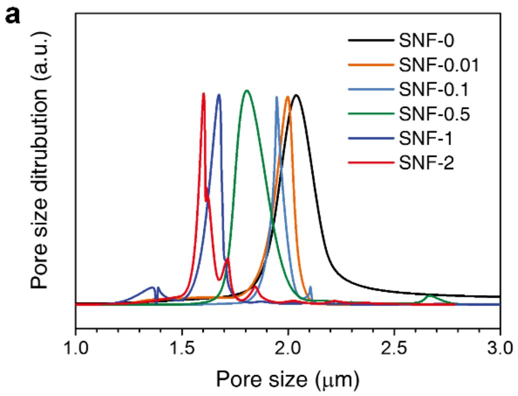


Fig. S4 EDX analysis of the SNF-2 membranes.



b

Samples	Mean pore size (μm)
SNF-0	2.03
SNF-0.01	1.99
SNF-0.1	1.94
SNF-0.5	1.80
SNF-1	1.67
SNF-2	1.60

Fig. S5 (a) Macropore size distribution and (b) mean pore size of the relevant SNF membranes.

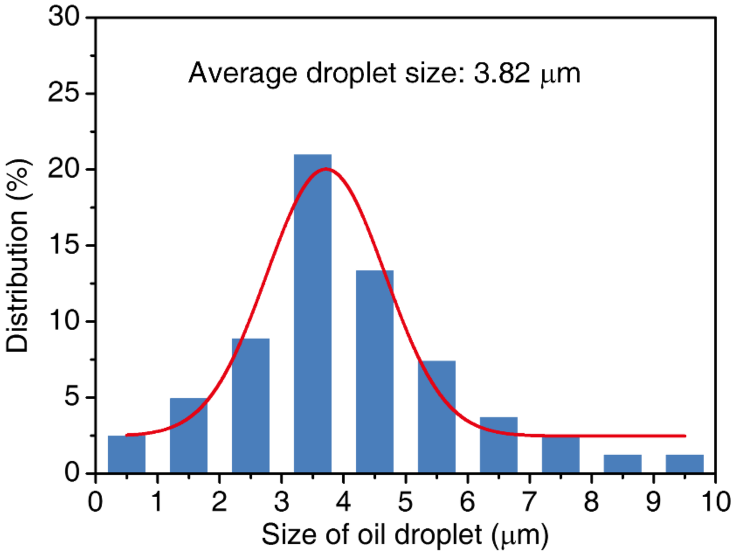


Fig. S6 Histogram showing the oil droplet size distribution of the as-prepared emulsions.

Table 1 Synthesis parameters and structure properties of various SNF membranes.

Samples	Concentration of BA-CHO (wt%)	Concentration of SiO_2 NPs (wt%)	Average fiber diameter (nm)	BET surface area (m^2 g^{-1})	BJH porosity (cm^3 g^{-1})
SNF-0	−	−	230	3.16	0.0056
SNF-0.01	1	0.01	286	5.95	0.013
SNF-0.1	1	0.1	274	14.03	0.019
SNF-0.5	1	0.5	271	38.21	0.071
SNF-1	1	1	281	46.65	0.107
SNF-2	1	2	295	64.48	0.251