

Gravity driven separation of emulsified oil/water mixtures utilizing in-situ polymerized superhydrophobic and superoleophilic nanofibrous membranes

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Support information

Materials

Poly(vinyl alcohol) (PVA, $M_w=88000$), *m*-(trifluoromethyl)aniline (tfa), paraformaldehyde, *p*-hydroxybenzaldehyde, phosphoric acid (H_3PO_4 , 85%), trichloromethane, acetone, sodium hydroxide, anhydrous magnesium sulfate and hydrophobic Al_2O_3 NPs (6-30nm) were purchased from Shanghai Chemical Reagents Co., Ltd., China. Tetraethyl orthosilicate (TEOS) was purchased from Lingfeng Chemical Co., Ltd., China. Pure water was obtained from a Millipore system. All chemicals were of analytical grade and were used as received without further purification.

Synthesis of BAF-CHO monomer

The BAF-CHO was synthesized using *m*-(trifluoromethyl)aniline (tfa), paraformaldehyde, and *p*-hydroxybenzaldehyde through Mannich reaction, as shown in Fig. S1. Briefly, 24.4 g of tfa, 32.2 g of *p*-hydroxybenzaldehyde and 6 g of paraformaldehyde were added into a three necked round bottom flask. Then the temperature was gradually increased to 105°C with continued stirring for 4 h in an inert atmosphere. After cooling to room temperature, the obtained product was dissolved in 250 mL of trichloromethane. The solution was purified by washing with 1 wt% sodium hydroxide and pure water, then treated with anhydrous magnesium sulfate and filtered, and dried at 60°C for 4 h to acquire BAF-CHO powder. The detail of structural confirmation by 1H NMR spectroscopy were presented in Fig. S2.

Preparation of silica nanofibers (SNF)

The precursor solution was prepared by dissolving the PVA powder in pure water at 80°C with vigorous stirring for 12 h. A silica gel with the molar composition of $TEOS:H_3PO_4:H_2O=1:0.01:11$ was prepared by hydrolysis and polycondensation, by drop wise addition of H_3PO_4 to TEOS with stirring at room temperature for another 12 h. The 10 g resultant silica gel was added into the PVA (10 g) solution and stirred

for another 4 h. Following the electrospinning process was performed by using a DXES-1 spinning equipment (Shanghai Oriental Flying Nanotechnology Co., Ltd., China) with an applied high voltage of 20 kV and a controllable feed rate of 1 mL/h. To obtain the pure SNF, the composite membranes were calcined to 800°C by gradually increasing the temperature at the heating rate of 5 °C/min in air to remove the PVA.

Fabrication of F-PBZ/Al₂O₃ NPs modified SiO₂ nanofibrous membranes

The F-PBZ/Al₂O₃ NPs modified membranes were obtained by first dipping the SNF membranes in acetone solutions with 1 wt% of BAF-CHO and 1 wt% of Al₂O₃ NPs. Following the membranes were dried in the oven for 20 min at 60°C, and then in situ polymerization of BAF-CHO was carried out at 200°C in vacuum for 1 h, leading to the formation of the Mannich bridge cross-linked structure, and finally generating functional membranes (F-SNF/Al₂O₃) with cured thermosetting F-PBZ layer on the fiber surface. In addition, the membranes without Al₂O₃ NPs (F-SNF) were also prepared for comparison.

Emulsion separation experiment

Typically, the as-prepared F-SNF/Al₂O₃ membranes was sealed between one vertical glass tube with a diameter of 38 mm and one conical flask. The 100 mL freshly prepared emulsion was poured onto the F-SNF/Al₂O₃ membrane and spontaneously permeated quickly. The flux was determined by calculating the permeated volume of an emulsion within 1 min. To test the cycle performance, the membrane was washed with ethanol and dried in 50 °C for 30 min after each separation cycle.

Characterization

The ¹H NMR spectrum was recorded using the Bruker Avance 400, d₆-DMSO was used as the solvent. FT-IR spectra were measured with a Nicolet 8700 FT-IR spectrometer in the range 4000-400 cm⁻¹. The morphology of membranes was imaged by field emission scanning electron microscopy using S-4800, Hitachi Ltd., Japan, all

samples were coated with carbon for 5 min before analysis. N₂ adsorption-desorption isotherms were examined at 77 K by an ASAP 2020 physisorption analyzer (Micromeritics Co., USA). Water contact angle (WCA) (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 water contact angle hysteresis was measured using increment decrement method.

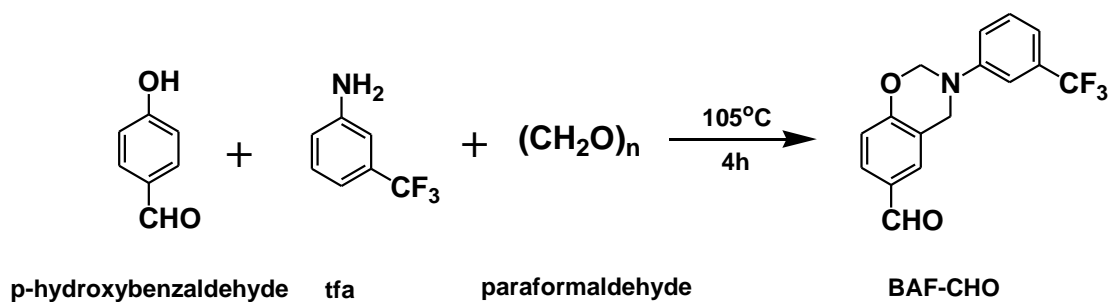


Fig. S1 Chemical synthetic route of BAF-CHO.

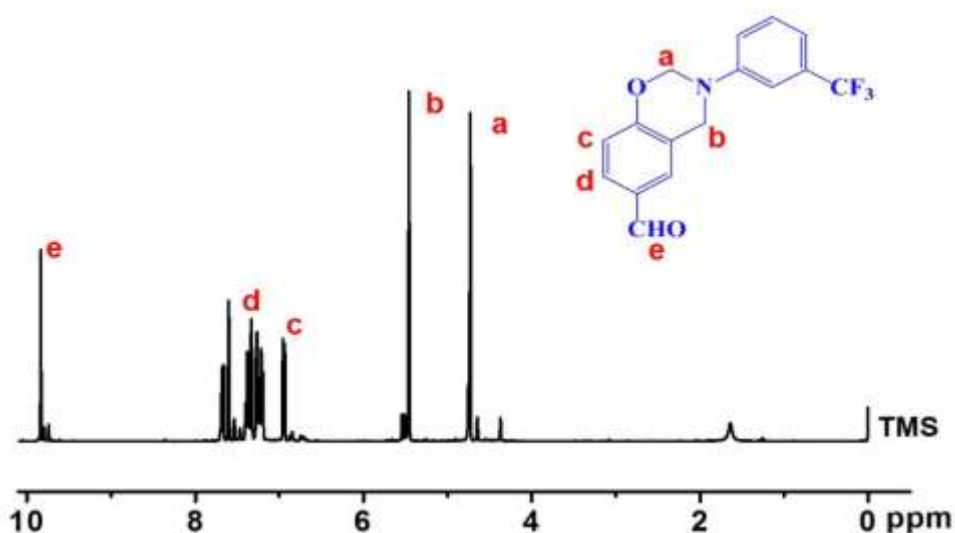


Fig. S2 ¹H NMR spectrograph of BAF-CHO

The as-synthesized BAF-CHO monomer after purification was subjected to ¹H NMR spectroscopic analysis, as shown in Fig. S2. Specific for oxazine ring, the peaks for Ar-CH₂-N and N-CH₂-O are observed in ¹H NMR, which are distinctive of benzoxazine monomers. For BAF-CHO monomer, the characteristic protons of Ar-CH₂-N and N-CH₂-O appeared at 4.71 and 5.45 ppm. Moreover, aromatic protons have given their chemical shift in the range of 6.92-7.67 ppm. The proton for aldehyde group has been appeared at 9.83 ppm. Acquisition of quantitative resulting from ¹H NMR analysis has confirmed the chemical structure of BAF-CHO.

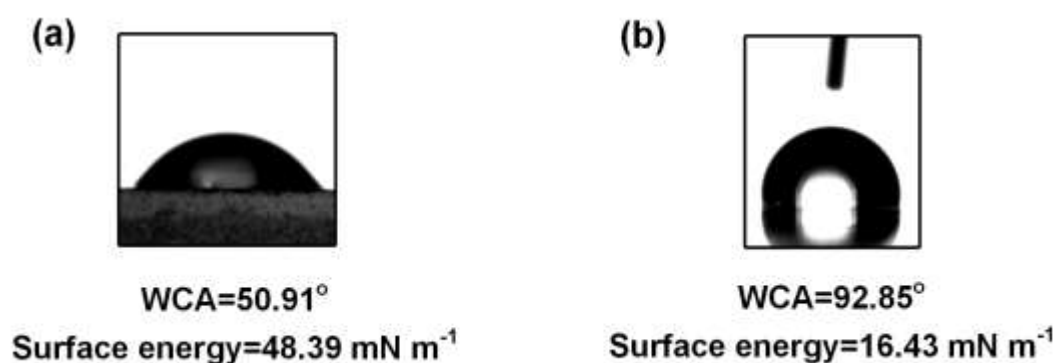


Fig. S3 Optical profiles of water droplets on the (a) flat silica casting films and (b) flat F-PBZ casting films. The relevant surface energies were determined based on the relevant WCA values.

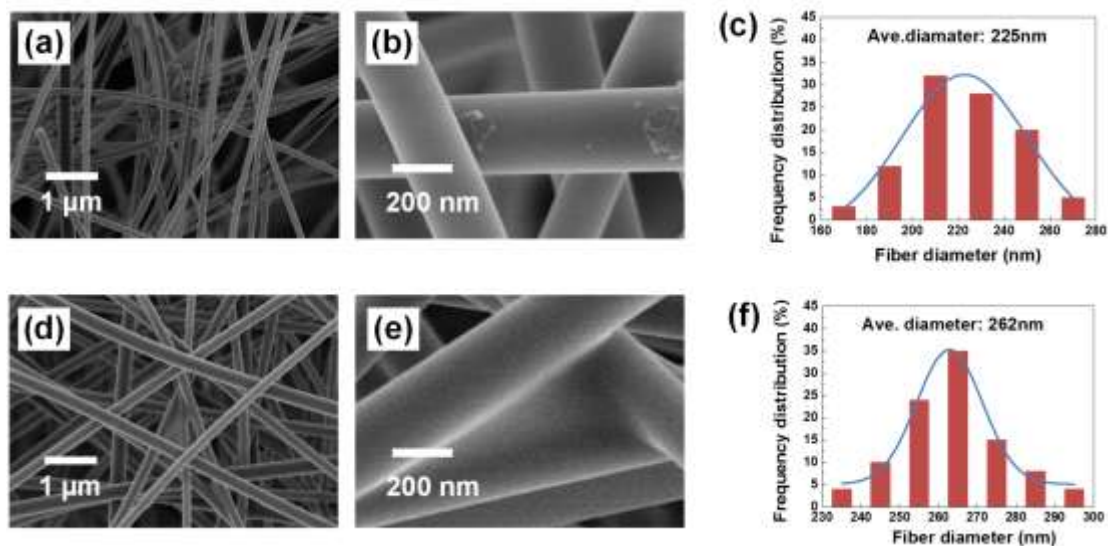


Fig. S4 (a) Low and (b) high magnification FE-SEM images of SNF membranes. (c) Histogram showing the fiber diameter distribution of SNF membranes. (d) Low and (e) high magnification FE-SEM images of F-SNF membranes. (f) Histogram showing the fiber diameter distribution of F-SNF membranes.

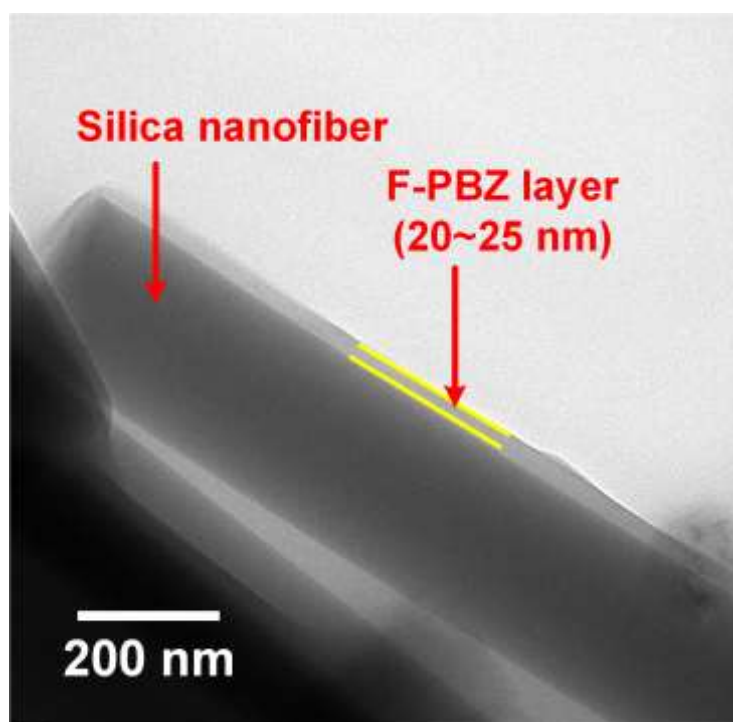


Fig. S5 TEM image of the F-SNF membranes shows the well coated F-PBZ layer with the uniform thickness of 20~25 nm.

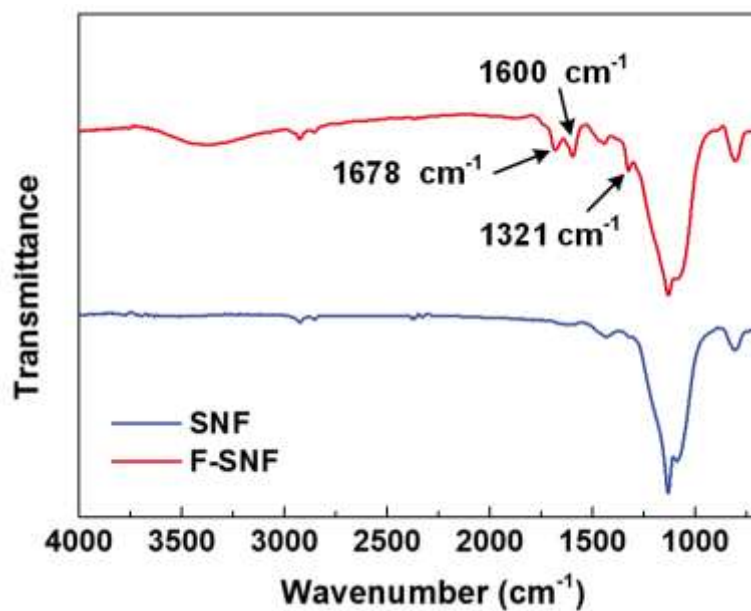


Fig. S6 FT-IR spectra of SNF and F-SNF membranes shows the polymerization of BAF-CHO monomers on fibers surface.

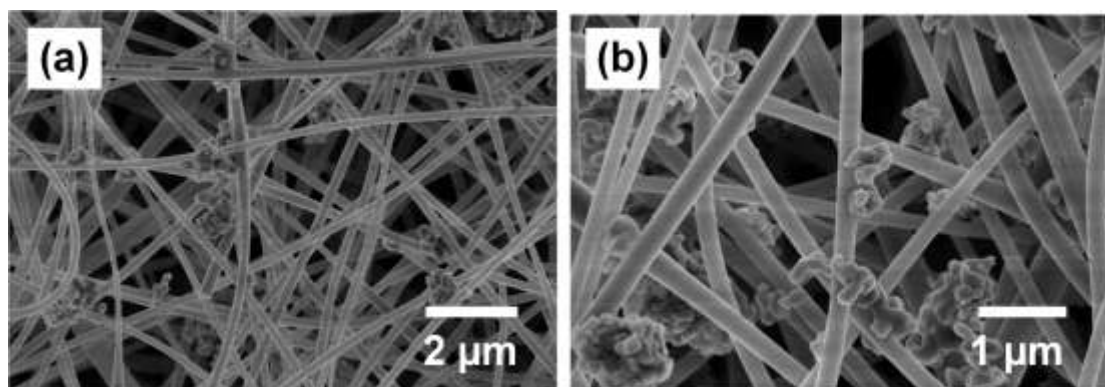


Fig. S7 (a) Low and (b) high magnification FE-SEM images of F-SNF/Al₂O₃ membranes after 10 separation cycles.

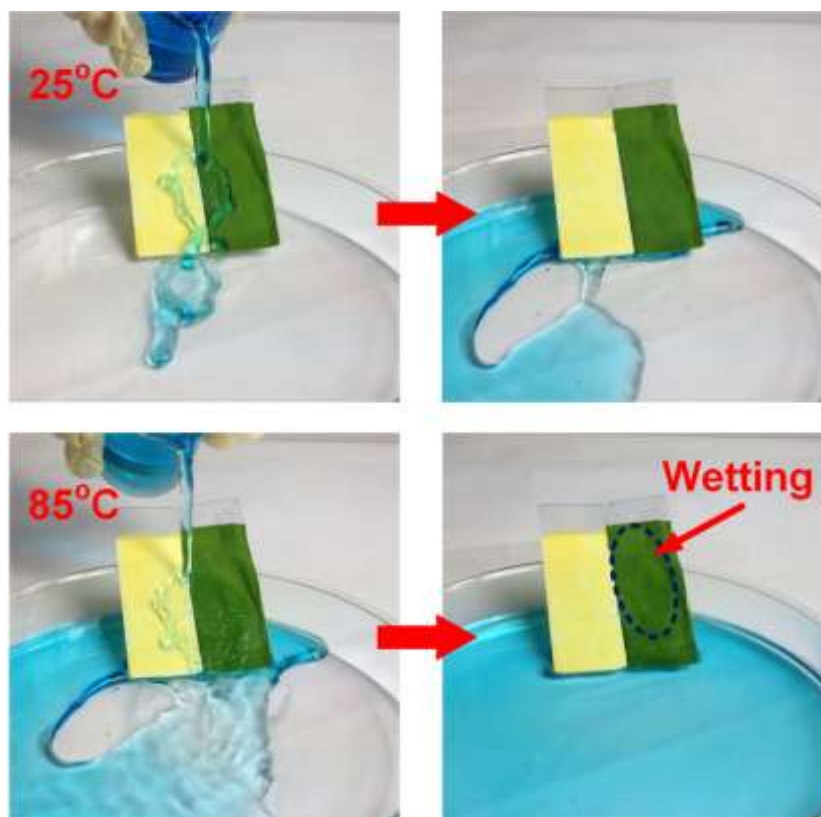


Fig. S8 Optical photos of cool water (25°C) and hot water (85°C) dumped on the surface of lotus leaves (right green one) and F-SNF/Al₂O₃ membrane (left yellow one), the water was dyed by methyl blue.

Generally, the separation membranes should enable to handle hot oil-water emulsified mixture in real industrial application. The repellent characteristics of F-SNF/Al₂O₃ membrane and the classic superhydrophobic lotus leaves to hot water were presented in Fig. S4, and see also Movie S2. It can be seen that both the lotus leaves and F-SNF/Al₂O₃ membrane exhibited good repellency towards water with 25°C. Meanwhile, the lotus leaves showed hydrophilic properties to hot water (85°C) with obvious wetting behavior (indicated by dotted circle). The F-SNF/Al₂O₃ membrane, in contrast, still possessed robust hydrophobicity upon hot water without any wetting, thus implying good thermal stability towards real applications.



Fig. S9 Photograph shows the large-scale (60×60 cm) of SNF nanofibrous membranes.