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 m-(trifluoromethyl)aniline alcohol) (PVA, Mw=88000), (tfa), paraformaldehyde, p-hydroxybenzaldehyde, phosphoric acid (H_3PO_4) 85%), tricholoromethane, acetone, sodium hydroxide, anhydrous magnesium sulfate and hydrophobic Al₂O₃ NPs (6-30nm) were purchased from Shanghai Chemical Reagents Co., Ltd., China. Tetraethyl otrhosilicate (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** m-(trifluoromethyl)aniline was synthesized using (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 tricholoromethane. 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:H₃PO₄:H₂O=1:0.01:11 was prepared by hydrolysis and polycondensation, by drop wise addition of H₃PO₄ 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, d_6 -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 μ L), oil contact angle (OCA) (3 μ L) and sliding angle (10 μ L) 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.

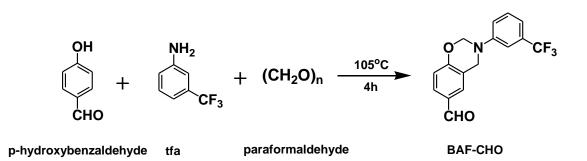


Fig. S1 Chemical synthetic route of BAF-CHO.

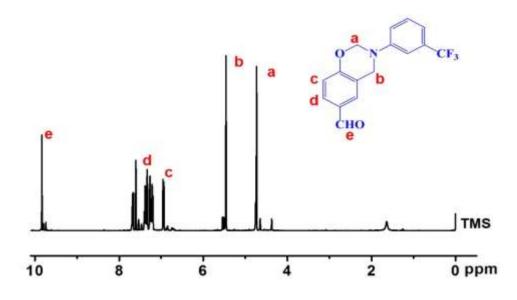


Fig. S2¹H NMR spectrograph of BAF-CHO

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.

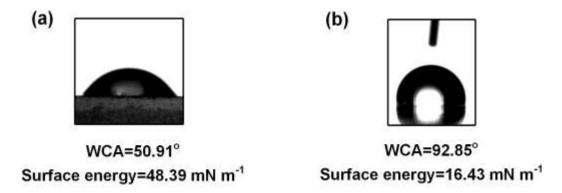


Fig. S3 Optical profiles of water droplets on the (a) flat silica casting films and (b) flat F-PBZ casting films. The relevant surface energies were determined based on the relevant WCA values.

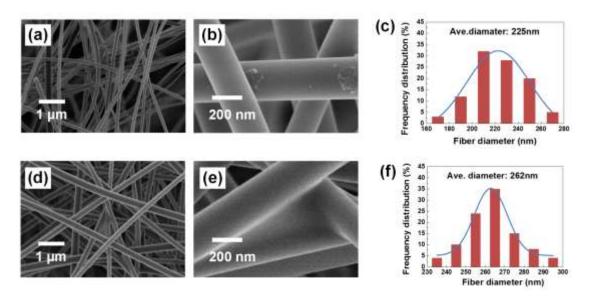


Fig. S4 (a) Low and (b) high magnification FE-SEM images of SNF membranes. (c) Histogram showing the fiber diameter distribution of SNF membranes. (d) Low and (e) high magnification FE-SEM images of F-SNF membranes. (f) Histogram showing the fiber diameter distribution of F-SNF membranes.

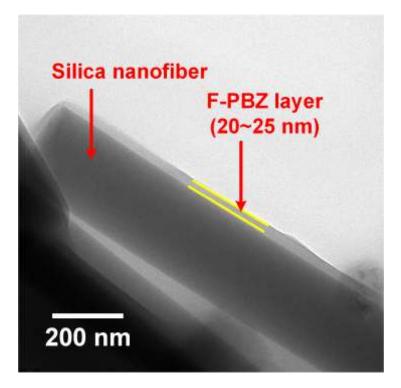


Fig. S5 TEM image of the F-SNF membranes shows the well coated F-PBZ layer with the uniform thickness of 20~25 nm.

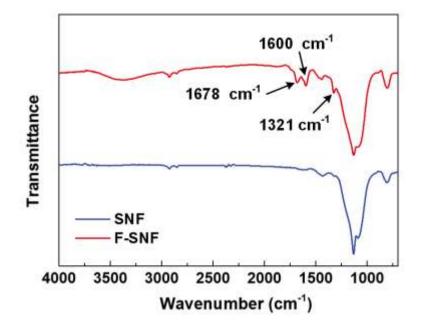


Fig. S6 FT-IR spectra of SNF and F-SNF membranes shows the polymerization of BAF-CHO monomers on fibers surface.

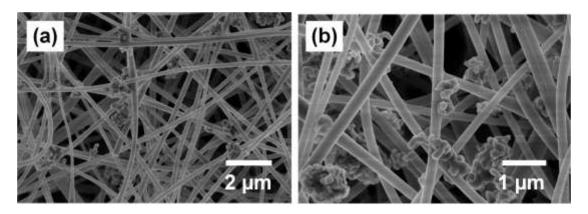


Fig. S7 (a) Low and (b) high magnification FE-SEM images of F-SNF/Al₂O₃ membranes after 10 separation cycles.

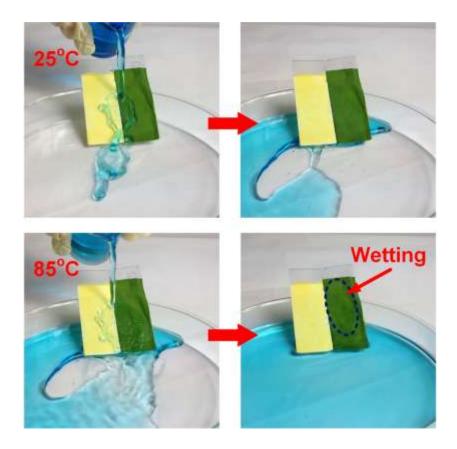


Fig. S8 Optical photos of cool water (25° C) and hot water (85° C) dumped on the surface of lotus leaves (right green one) and F-SNF/Al₂O₃ membrane (left yellow one), the water was dyed by methyl blue.

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.