

Supporting Information

Pine-branch-like TiO₂ Nanofibrous Membrane for High Efficient Strong Corrosive Emulsion Separation

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Experimental section

1.1. Materials

Polyvinylpyrrolidone (PVP, Mw~1,300,000, AR) was purchased from Sigma-Aldrich company; Titanium butoxide (TBT), Ethanol, acetic acid, hexadecane, petroleum ether, isooctane, methylbenzene, Tween-20, HCl (36~38 wt%) were purchased from Beijing Chemical Works, gasoline and diesel were purchased from Sinopec. All the chemical reagents were used as received without further purification. All the aqueous solutions were prepared with deionized water.

1.2. Fabrication of the pine-branch-like TiO₂ nanofibrous membrane:

Typically, PVP, ethanol and anhydrous acetate acid were mixed in a weight ratio of 1/5/1 with continuous stirring for 12 h. Then TBT were dripped to the above mixture in a weight ratio of 3/7, and stirred for 24 h at room temperature till a homogenous solution was obtained. Then the as prepared solution was loaded into a plastic syringe positioned vertically with 19-Gauge blunt stainless nozzle. The vertical distance between the nozzle and the collector was 20 cm. The voltage was set at 19-25 kV by a high voltage power unit. The electrospun fibrous membranes were calcined at 600°C for 2 h at a heating rate of 1°C min⁻¹. Finally, the membranes were put into autoclaves containing water, HCl, TBT solution in a volume ratio of 30/30/1.5 at 150°C for 4h, then the pine-branch-like TiO₂ nanofibrous membranes were obtained.

1.3. Instrumentation and Characterization

Scanning electron microscopy (SEM) images of the surfaces were obtained using a field emission scanning electron microscope (JEOL, JSM-7500F, Japan). X-ray diffraction (XRD) patterns were collected on an XRD-6000 (shimadzu). Contact angles were measured by measuring five different positions of the same sample using the sessile drop method on an OCA20 machine (Data-Physics, Germany) at room temperature in air, under water. The probe (water, oil, or air) drops (about 4 μL) were dropped carefully onto the surfaces, which were in air, immersed in water. The average value of five measurements performed at different positions on the same sample was adopted as the measured data. The adhesion force between the probe drops and the surfaces was measured using a high-sensitivity microelectro mechanical balance system (Data-Physics DCAT 11, Germany) under water. A probe drop (about 4 μL) was suspended with a copper cap, and the surface was placed in a water channel on the balance table. The surface was moved upward to contact the probe droplets at a constant speed of 0.2 mm/s. Then the surfaces were moved down at the same speed until the probe droplets broke away from the surfaces. The forces were recorded by the balance and measuring process was recorded by a charge-coupled-device (CCD) camera system. Droplet size distributions of the oil-in-water emulsion samples and filtrate solutions were obtained by dropping an emulsion droplet on a glass sheet for imaging with an optical microscope (OLYMPUS BX51, Japan). The Tyndall phenomenon was characterized by using a beam of red light to irradiate the emulsion and filtrate. The emulsion droplet size distribution curves were calculated by the Dynamic Light Scattering (DLS) analyzer. The oil content in the filtrate was measured by the infrared spectrometer oil content analyzer (Oil 460 Beijing China invent Instrument Tech. Co. Ltd., China).

1.4. Oil-in-Water Emulsion Separation Experiments

Oil-in-water emulsions were prepared by injecting oil (namely, isooctane, n-hexadecane, petroleum ether, toluene, gasoline and diesel) into water or strong acid, alkali and high-concentration salt aqueous solution (4 mol L^{-1} HCl, 4 mol L^{-1} NaOH, 4 mol L^{-1} NaCl) in a volume ratio of 1:100 under ultrasonication with 0.1g surfactant like Tween-20 per 100 mL water, which was continued for 1 h at 250 W to obtain a homogeneous white emulsion. Commonly, the as-obtained petroleum ether-in-water emulsion could remain stable for 8 h, while the isooctane-in-water, toluene-in-water emulsions could remain stable for 12 h, and the gasoline-in-water emulsion, n-hexadecane-in-water and diesel-in-water could remain stable

for 24 h when stored under ambient conditions. The as-prepared pine-branch-like was placed on a filtration apparatus with a diameter of 17 mm, and then a certain volume of oil-in-water emulsion was added into the apparatus. The separation processes were respectively carried out under gravity solely. The filtrate water was collected, and the oil content in the water was determined by an infrared spectrometer oil content analyzer.

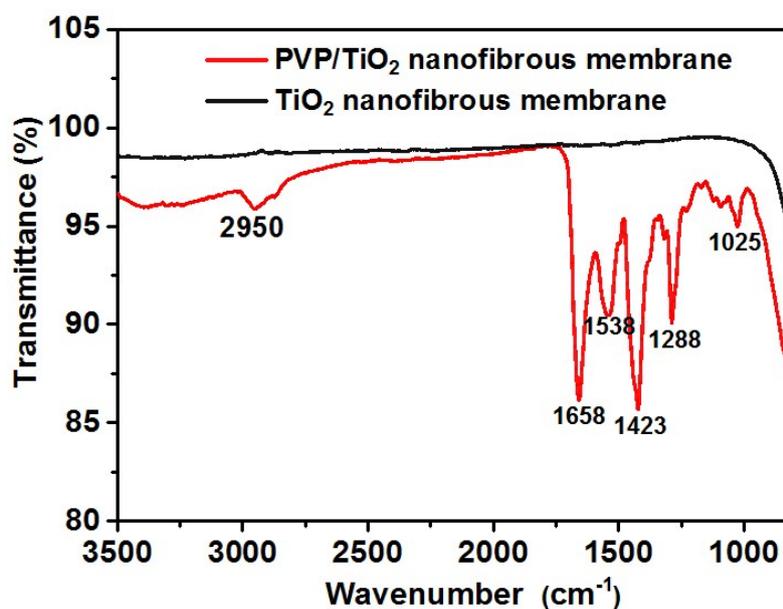


Figure S1 FTIR spectrums PVP/TiO₂ nanofibrous membrane and the TiO₂ nanofibrous membrane.

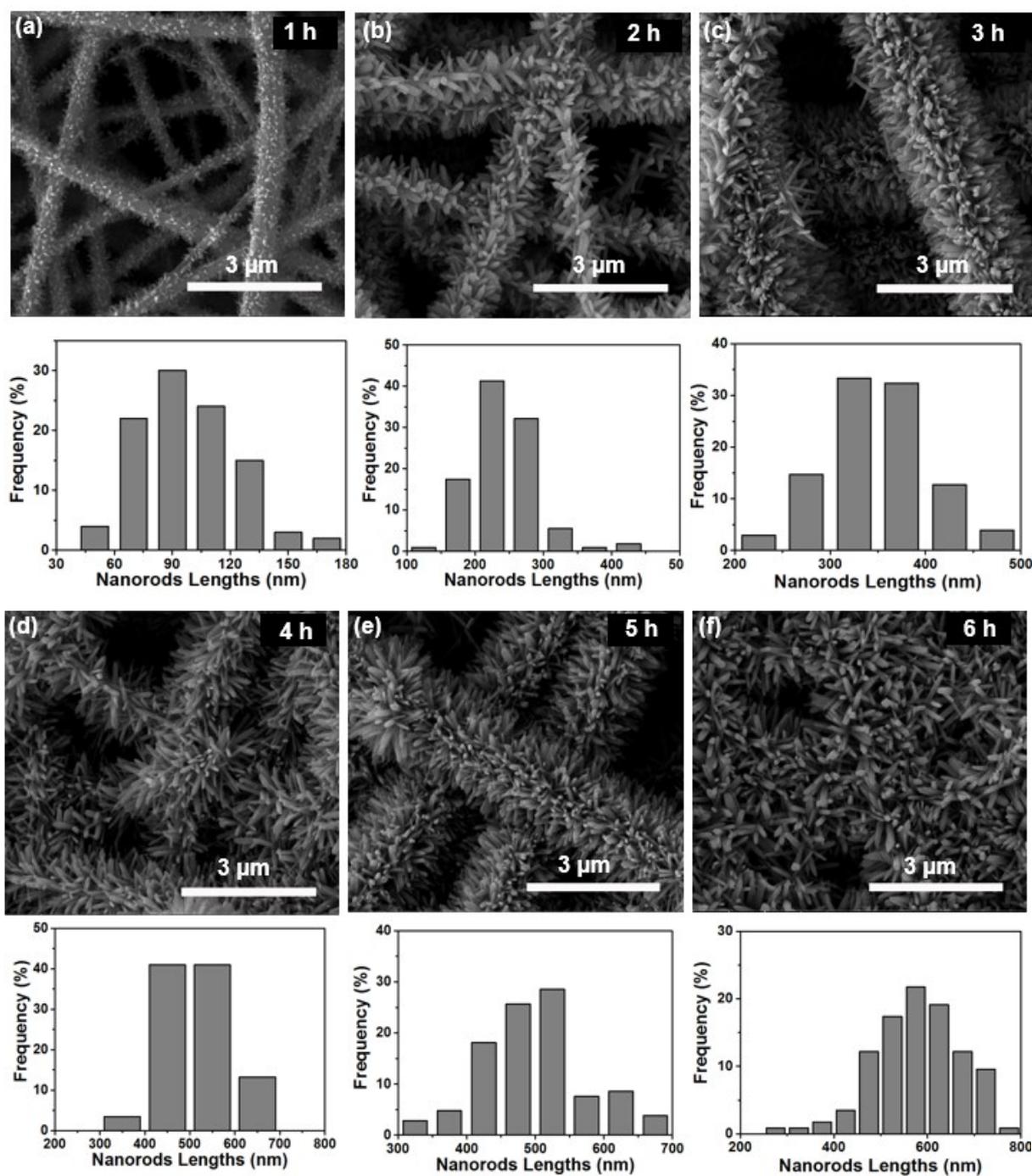


Figure S2 SEM images of TiO₂ pine-branch-like structures growing on TiO₂ calcinated membrane with different hydrothermal reaction time at 150°C with constant volume ratio of TBT/deionized water/ hydrochloric acid=1.5/30/30: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h, (e) 5 h, (f) 6 h, respectively (bottom pictures are the corresponding nanorods lengths distribution). The corresponding nanorods lengths with the above membranes were 100.0 ± 13.8 nm for 1 h, 247.6 ± 11.2 nm for 2 h, 413.7 ± 30.9 nm for 3 h, 570.0 ± 22.9 nm for 4 h, 532.0 ± 30.8 nm for 5 h and 602.7 ± 10.9 nm for 6 h, respectively.

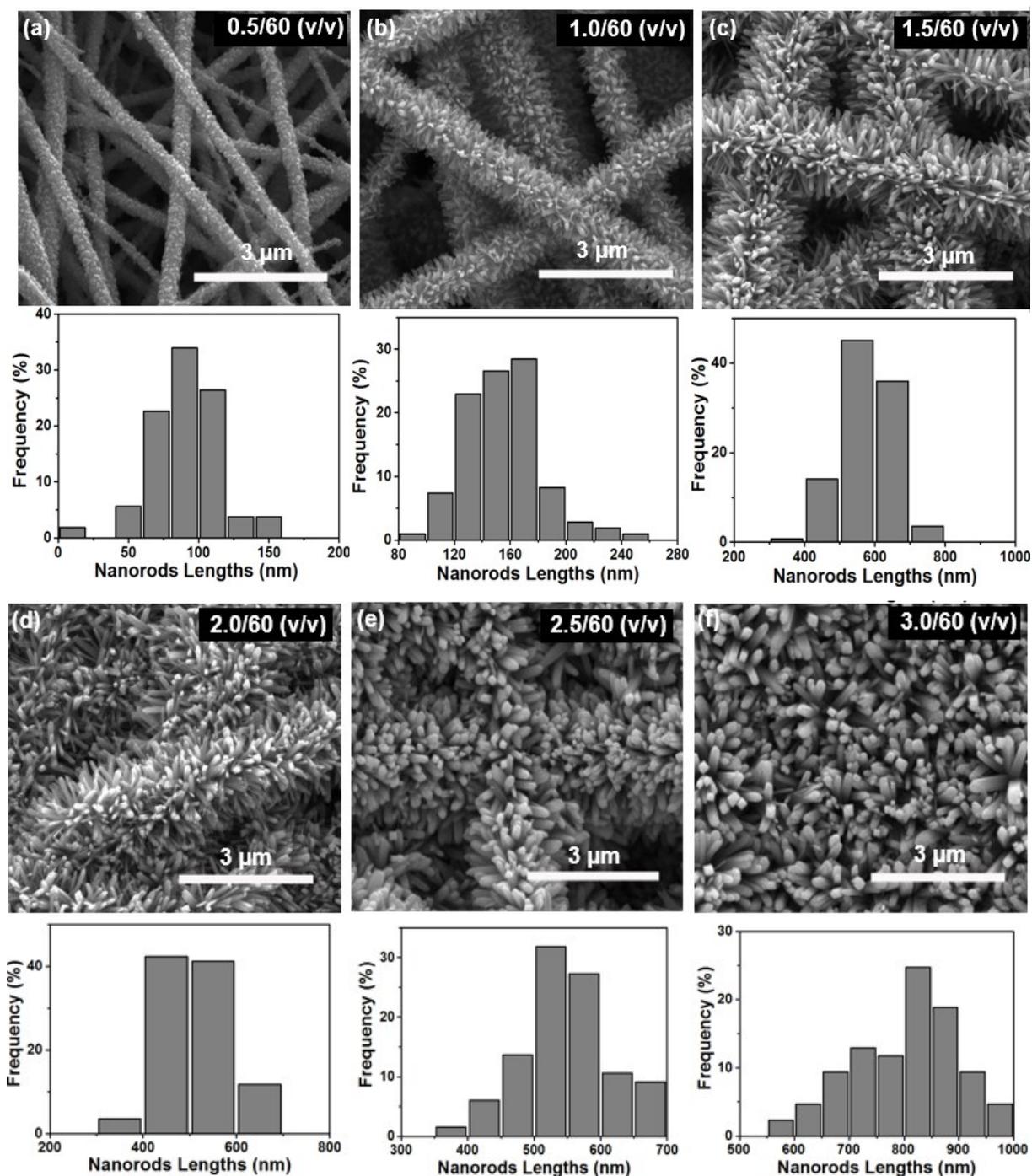


Figure S3 SEM images of TiO₂ pine-branch-like structures growing on TiO₂ calcinated membrane with different TBT hydrothermal solutions at 150°C for 4 h, 30 ml deionized water, 30 mL hydrochloric acid concentration: (a) 0.5 mL, (b) 1.0 mL, (c) 1.5 mL, (d) 2.0 mL, (e) 2.5 mL, (f) 3.0 mL, respectively (bottom pictures are the corresponding nanorods lengths distribution). The corresponding pines lengths with the above membranes were 94.4 ± 9.3 nm for 0.5 mL, 164.2 ± 16.8 nm for 1.0 mL, 584.2 ± 6.3 nm for 1.5 mL, 560.7 ± 5.6 nm for 2.0 mL, 548.9 ± 15.9 nm for 2.5 mL and 811.7 ± 14.3 nm for 3.0 mL, respectively.

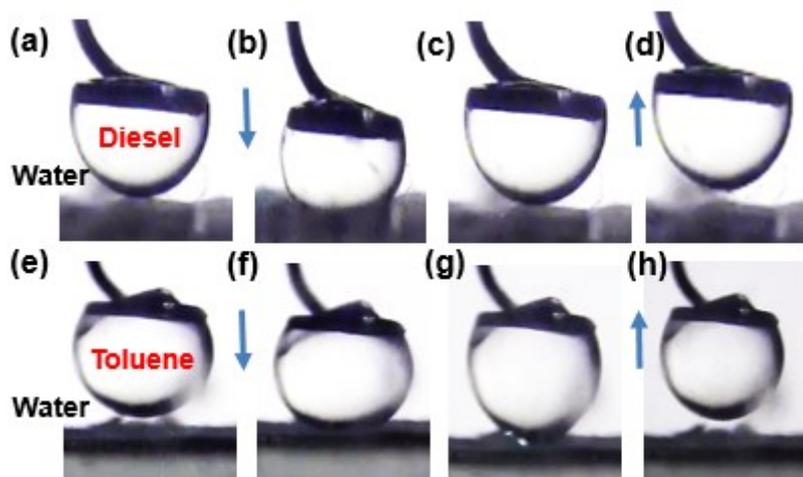


Figure S4 The characterization of adhesive force for different oil on the membrane underwater. The advancing and receding processes of diesel (a-d) and toluene (e-h) to the membrane underwater.

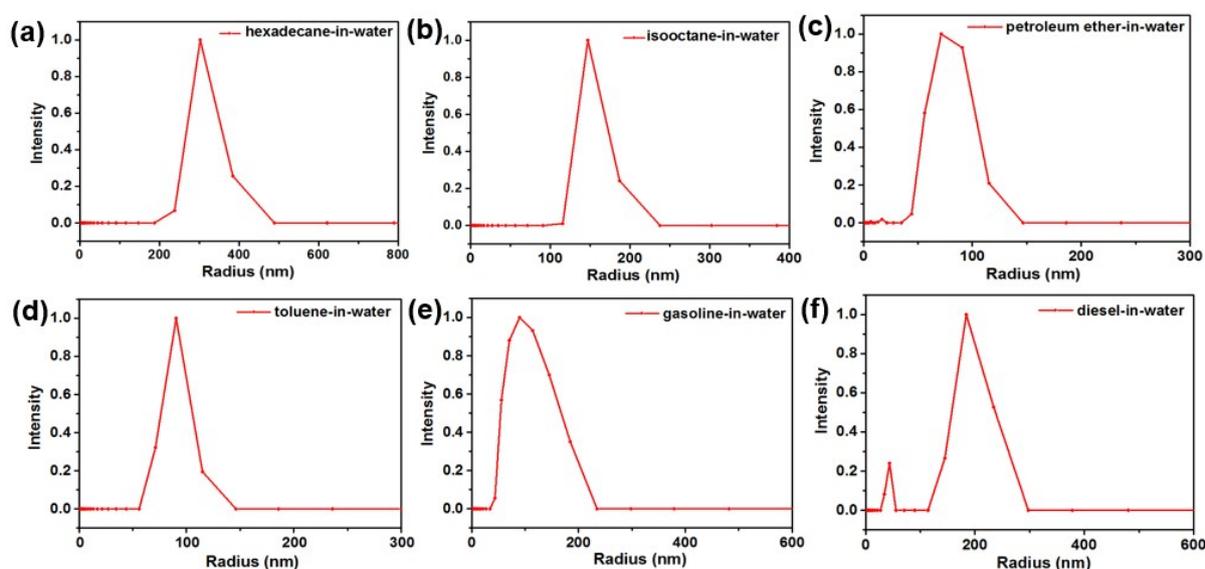


Figure S5 Dynamic light scattering (DLS) of (a) hexadecane-in-water emulsion, (b) isooctane-in-water emulsion, (c) petroleum ether-in-water emulsion, (d) toluene-in-water emulsion, (e) gasoline-in-water emulsion and (f) diesel-in-water emulsion. The average radius of the dispersed phase were 313.5 nm for hexadecane, 154 nm for isooctane, 75.6 nm for petroleum ether, 88.7 nm for toluene, 96.12 nm for gasoline and two peaks 41.1 nm, 190.7 nm for diesel, respectively.

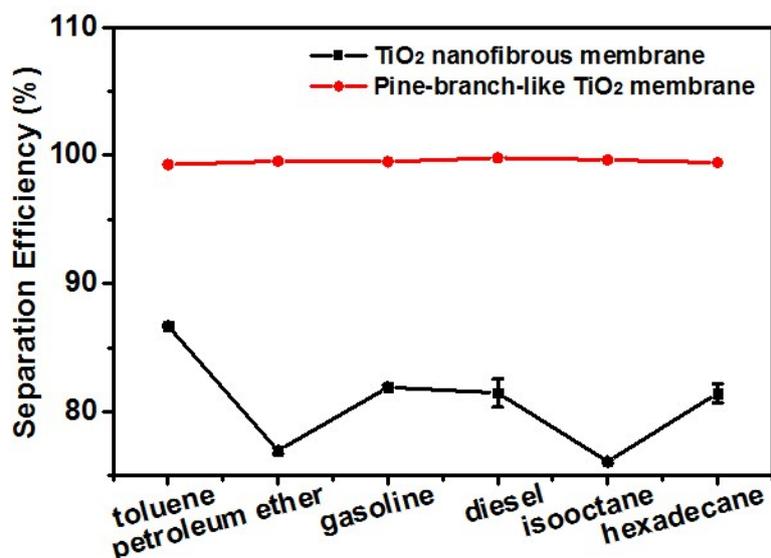


Figure S6 Separation efficiencies of TiO₂ nanofibrous membrane and pine-branch-like TiO₂ membrane. The corresponding TiO₂ nanofibrous membrane separation efficiencies were all lower than 87% (toluene (86.69% ± 0.10%), petroleum ether (76.94% ± 0.25%), gasoline (81.90% ± 0.16%), diesel (81.45% ± 1.10%), isooctane (76.09% ± 0.13%) and hexadecane (81.42% ± 0.78%)). As a comparison, the pine-branch-like TiO₂ membrane separation efficiencies were all higher than 99% (toluene (99.29% ± 0.03%), petroleum ether (99.55% ± 0.04%), gasoline (99.51% ± 0.11%), diesel (99.81% ± 0.04%), isooctane (99.65% ± 0.05%) and hexadecane (99.44% ± 0.09%)).

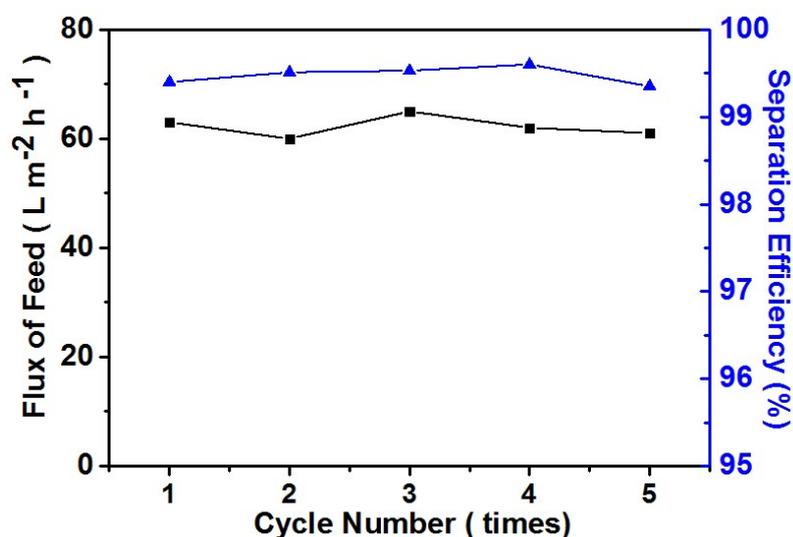


Figure S7 Change of fluxes and filtrates purities with cycle times when separating isooctane-in-water emulsion stabilized by Tween-20. In one cycle, a certain volume of emulsion was permeated through the pine-branch-like TiO₂ membrane and the membrane was then carefully washed by water and dried in a vacuum oven at 60°C for 30 min.

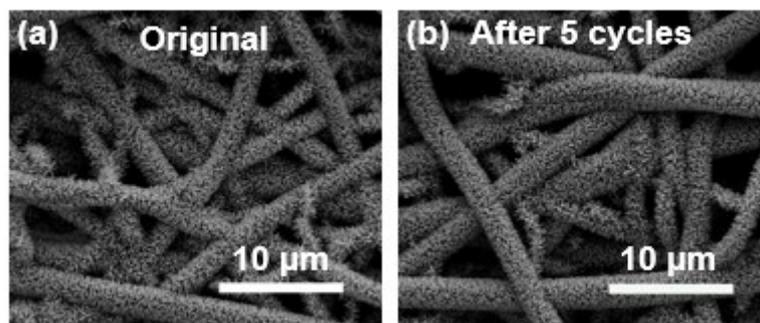


Figure S8 SEM images of original (a) and after 5 cycles experiment (b) comparison.

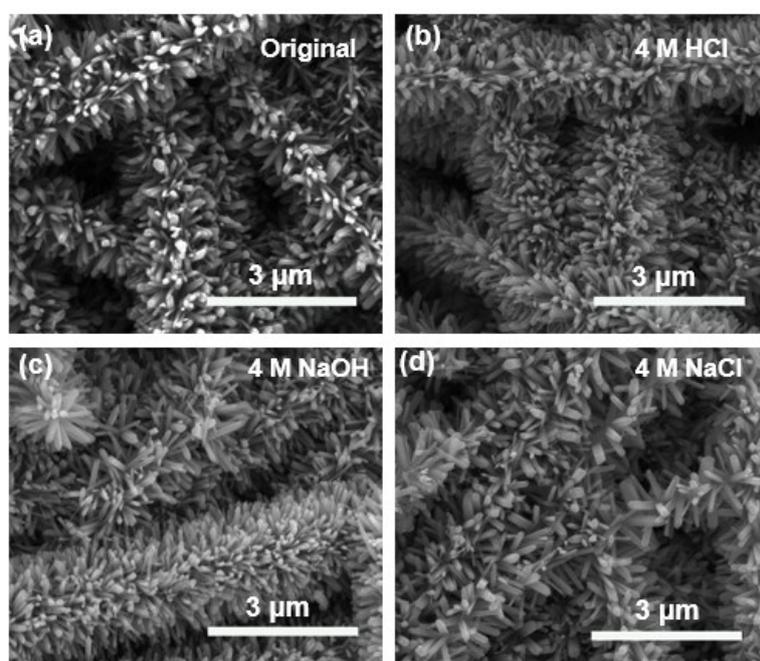


Figure S9 SEM images of hierarchical TiO_2 membrane before (a) and after (b-d) immersing in corrosive environments for one week, (b) 4 M HCl, (c) 4 M NaOH and (d) 4 M NaCl, respectively.

Reference:

1. C. Sun, N. Wang, S. Zhou, X. Hu, S. Zhou and P. Chen, *Chem. Commun.*, 2008, **28**, 3293.