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Electronic Supplementary Information

Inverse Desert Beetle-Like ZIF-8/PAN Composite Nanofibrous Membrane for Highly Efficient Separation of Oil-in-Water Emulsions

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This file contains 15 supporting figures, 1 supporting table and 3 Movies.

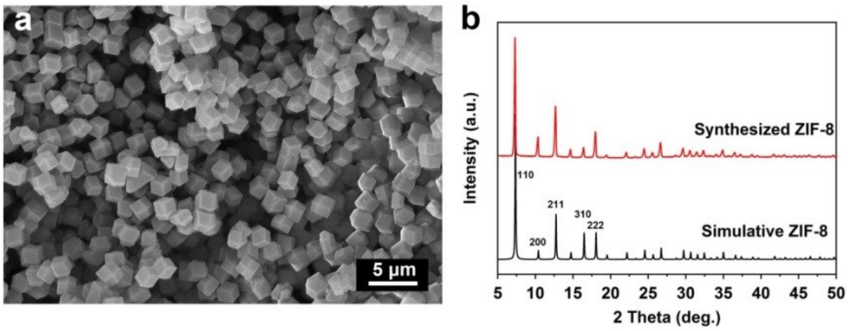

Fig. S1 FE-SEM and XRD of synthesized ZIF-8 particles.

The synthetic hydrophobic ZIF-8 particles are regular dodecahedron with particle size of about 2 μm (Fig. S1a), which can be used to absorb oil droplets at the nanoscale in the surfactant-stabilized oil-in-water emulsion. For the XRD of ZIF-8 particles, the synthesized ZIF-8 is in agreement with that of the simulated one, indicating its bulk phase purity (Fig. S1b).

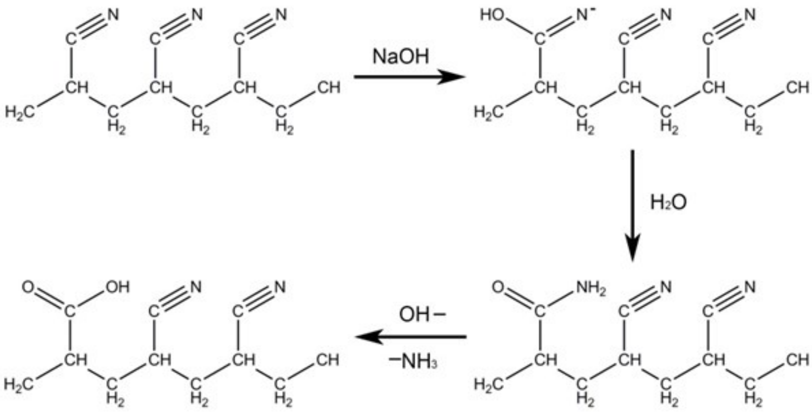

Fig. S2 The hydrolysis reaction process of the PAN membrane.

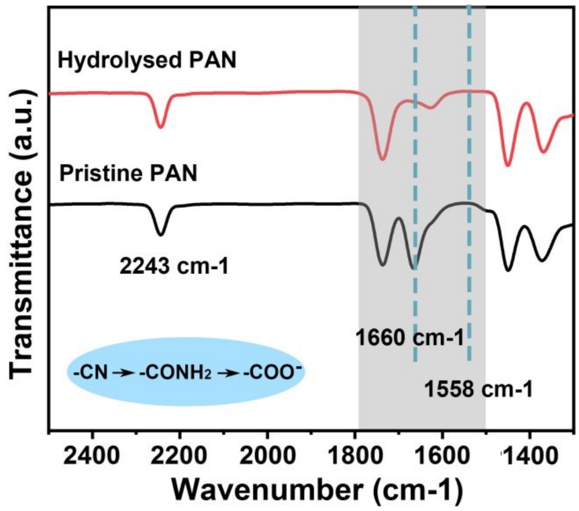

Fig. S3 FI-TR of PAN membrane before and after hydrolysis.

The reaction process and FT-IR spectra of partial hydrolysis of PAN is shown in Fig. S2-3 and the final product of hydrolysis mainly contains carboxyl group and amide group, which are beneficial to hydrophilicity.

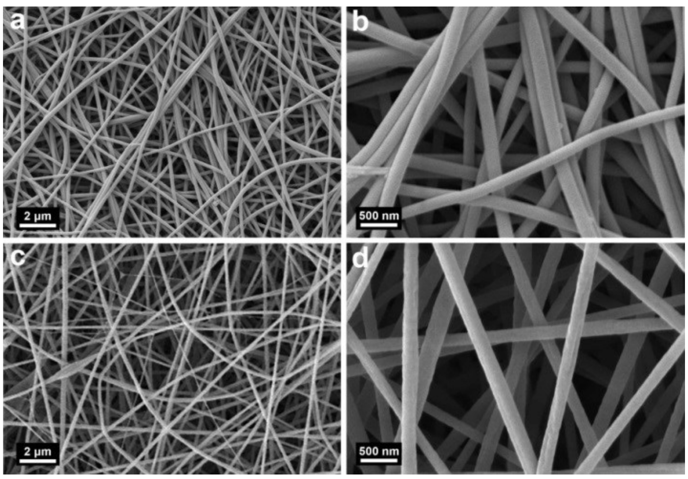

Fig.S4 The morphology of the fibers before a, b) and after c, d) hydrolysis.

Partial hydrolysis can increases hydrophilicity but do not change morphology of PAN. Fig. S4 is the low and high-magnification images of the hydrolyzed PAN nanofibrous substrate with the pore size of 204.4 nm.

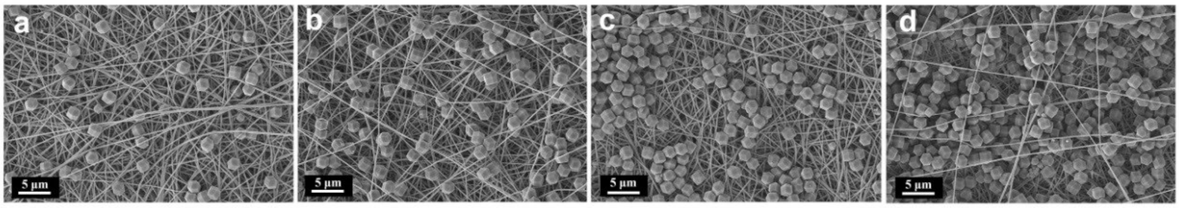

Fig. S5 FE-SEM of different concentration of ZIF-8/PAN membrane. a-d) represents 5 mg/mL, 10 mg/mL, 20 mg/mL^{-1}, and 50 mg ml^{-1}, respectively.

We have carefully monitored this spin coating process. When the suspension concentration is low (5 mg/mL), a few microspheres were decorated on the fibers, however, the surface is very sparsely covered (Fig. S5a). Upon increasing the concentration to 10 mg/mL, the beetle like bumps become continuous and distribute uniformly on the fiber surface. Thus, an interesting continuous coating of beetle-back like structure is formed on the membrane, which would be beneficial for oil capture and passage of water. Further increasing the suspension concentration up to 20 mg/mL resulted in a large number of aggregation formed and few exposure of the hydrophilic surface (Fig. S5c). For concentrate close to 50 mg/mL, the membrane was completely covered and there is almost no exposed sub-layer area (Fig. S5d). In this case, water cannot pass through effectively due to the covered hydrophobic particles. Therefore, the ZIF-8 particle concentration of 10mg/mL was selected to form a desert beetle like structure.

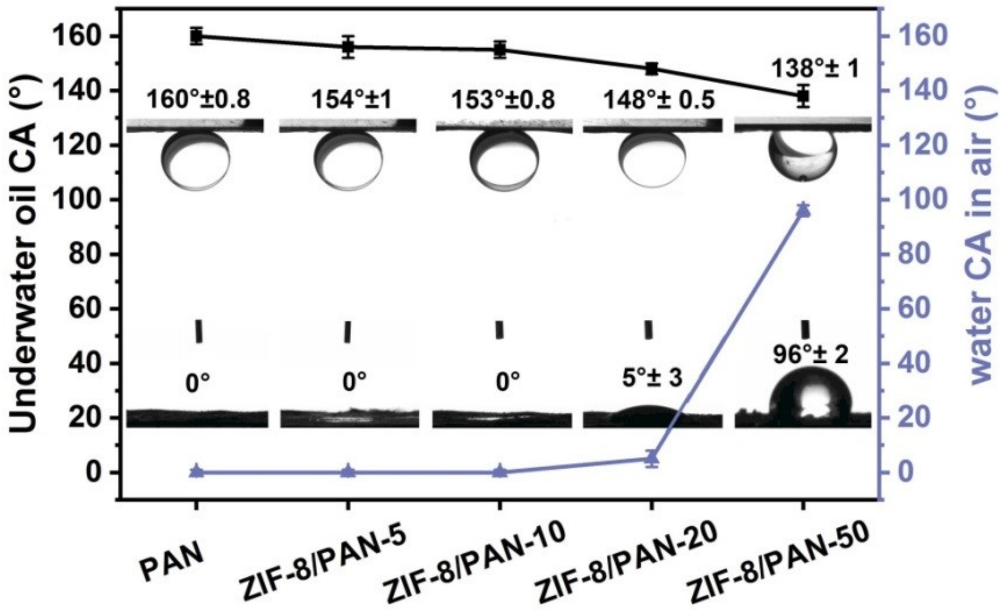

Fig. S6 The influence of ZIF-8 concentration on wettability of membrane.

We further study the influence of ZIF-8 concentration on wettability (Fig. S6). At low concentration (less than 10 mg/mL), the wettability had almost no change and remained superhydrophilicity/underwater superoleophobicity. With increasing ZIF-8 concentration to 20 mg/mL, the membrane's water CA increased to 5.2±3° and the underwater oil CA decreased to 148± 0.5°. At this point, the membrane is no longer underwater superoleophobicity. Further increasing ZIF-8 concentration to 50 mg/mL, the water CA was 96± 2° and the underwater oil CA was 138 ± 1°. These results further indicate that in order to acquire desert beetle-like structure and wettability of OL-SOB (UW), the ZIF-8 concentration need to be controlled at 10mg/mL.

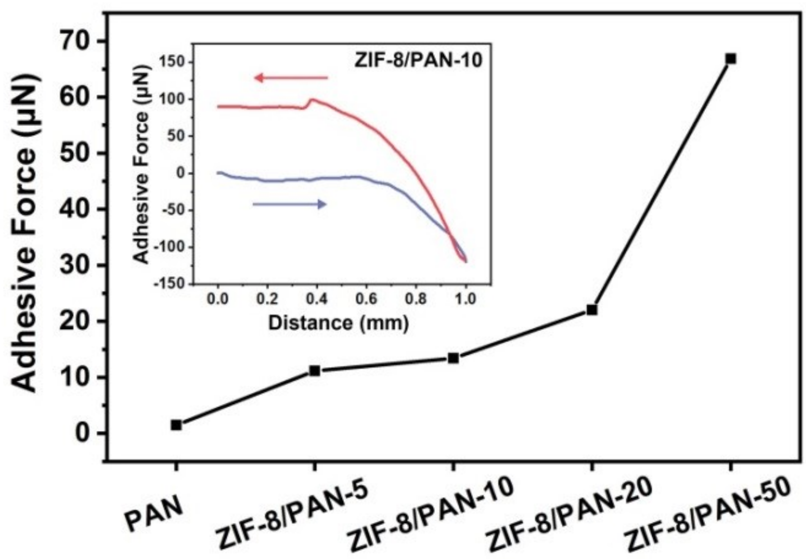

Fig. S7 The influence of ZIF-8 concentration on oil adhesion force of membrane.

The oil adhesion force of ZIF-8/PAN nanofibrous membranes was tested by petroleum ether droplets (10 μL) in water circumstance (Fig. S8). With the addition of ZIF-8 particles, the adhesion force increases continuously. This is because the hydrophobic particles decreased the average surface energy of ZIF-8/PAN membrane and therefore increased the adhesion of oil droplets on it[1]. ZIF-8/PAN membrane possesses a small adhesion force with 1.47 μN which is benefit for subsequent oil detachment.

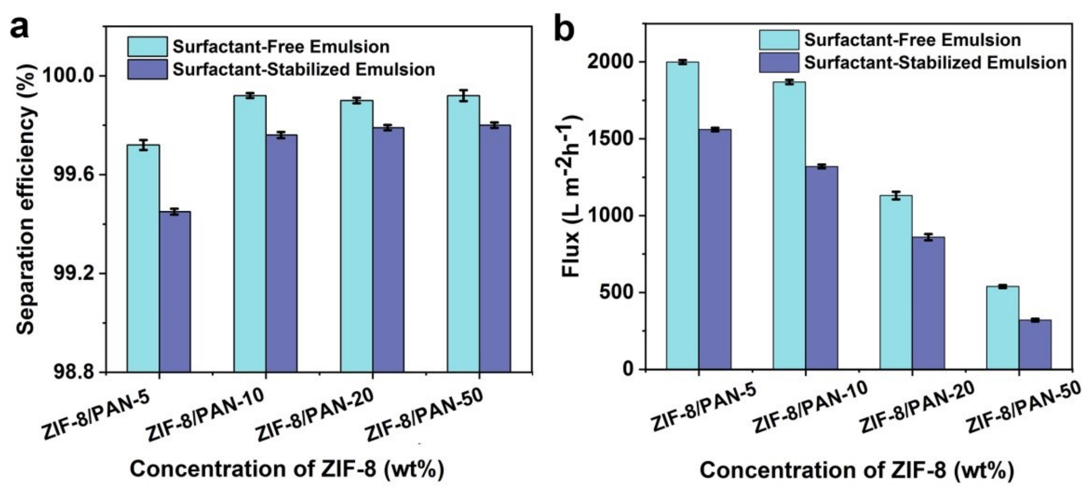

Fig. S8 The influence of ZIF-8 concentration on water purity and flux of membrane.

The concentration of ZIF-8 particle has a great influence on the separation efficiency and flux (Fig. S8). With the increase of particle concentration, the separation efficiency increases and the separation flux decreases, and we chose an optimal ZIF-8 concentration of 10mg/mL. Compared to the pure PAN membrane, the optimal ZIF-8/PAN membrane greatly improved the separation efficiency and the flux did not decrease.

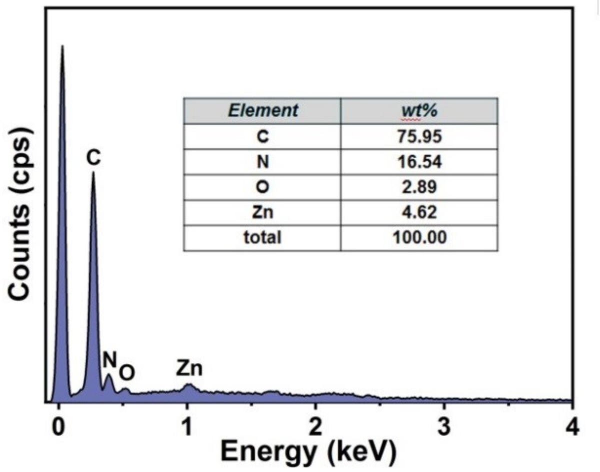

Fig. S9 EDS analysis of ZIF-8/PAN membrane.

EDS analysis of ZIF-8/PAN shows that a main peak was ascribed to C element with the atomic percent of 75.95 %. In addition, there were three main peaks belonging to N, O, and Zn element. This was attributed to the ZIF-8 coating layer.

Table S1 Comparison of various membrane materials used to separate surfactants-stabilized oil-in-water emulsion.

Material	Method	Separation efficiency (%)	Permeating Flux (L m^{-2} h^{-1})	Reference
Janus Cotton Fabric	Immersing and annealing	99.97	1500 (gravity)	2
PAA-g-PVDF Membranes	Salt template method	99.9	1140(0.1 bar)	3
PVDF/(DA-TEOS) membrane	Reaction Coating	none	140 (1 bar)	4
Cellulose nanosheet membranes	Filtration	96.5%	1591 (1 bar)	5
ZIF-8/PAN membrane	Electrostatic spinning and spinning coating	99.92	2550 (0.85 bar)	This work

Abbreviation: PAA, poly(acrylic acid); PVDF, Polyvinylidene fluoride; DA, dopamine; TEOS, tetraethoxysilane; none, not measured.

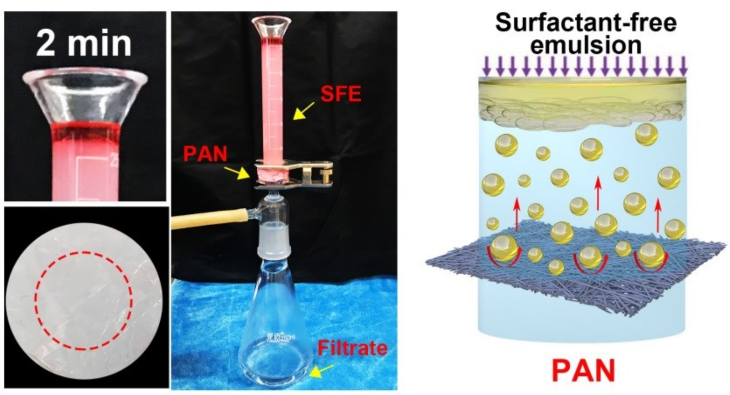

Fig. S10 Digital images and mechanism of the separation process for surfactant-free oil-in-water emulsion by PAN membrane.

A clear floating oil layer can be found on the feed solution only after 2 min separation due to their self-aggregation. And the membrane was white and no oil residue was visible from the digital photo. After separating by PAN, filtrate becomes transparent proved that separation of SFE is relatively easy due to the formation of layered oil-water mixtures.

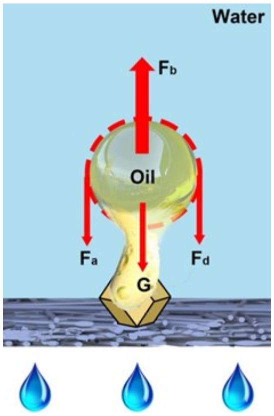

Fig. S11 The force analysis of oil droplets in “oil detachment” of separation process.

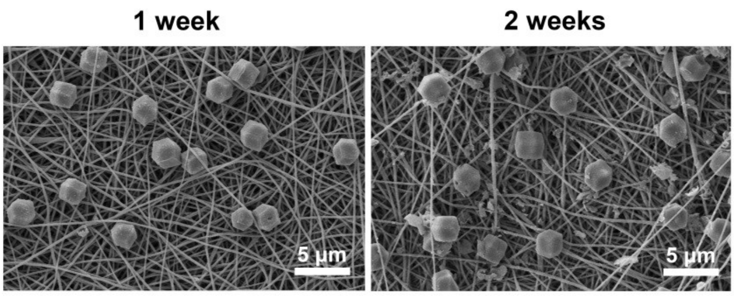

Fig. S12 FE-SEM of ZIF-8/PAN membranes after being immersed in water for 1 week and 2 weeks.

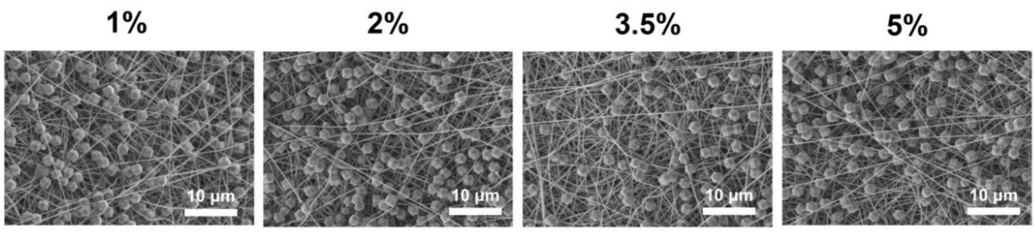

Fig. S13 FE-SEM of ZIF-8/PAN membranes after being immersed in different concentration of NaCl aqueous solution for 1 h.

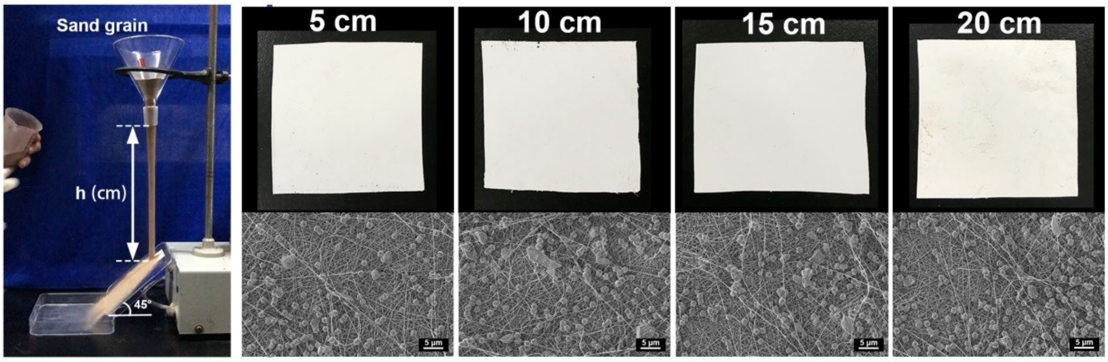

Fig. S14 Digital Photograph and FE-SEM of ZIF-8/PAN membranes after sand impact test for different flow height.

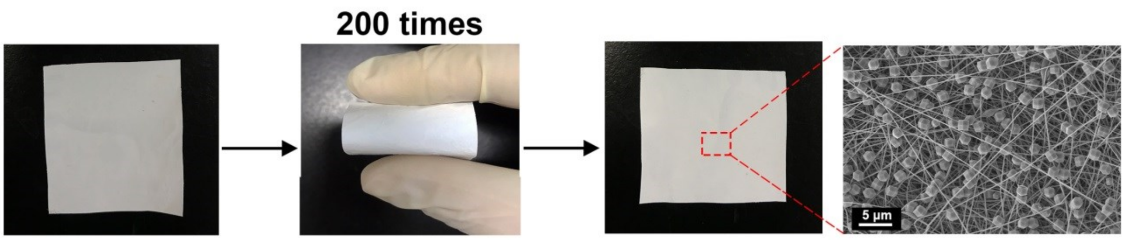

Fig. S15 Bending test of ZIF-8/PAN membranes and FE-SEM of ZIF-8/PAN membranes after being bent 200 times.

Stability of membrane was tested under water and salt solution. After two weeks in water, only a few ZIF-8 particles decomposed, hence the membrane can survive the water exposure at least 2 weeks (Fig. S12). Four concentrations of NaCl solution were performed to test the stability of membrane. Of these, 3.5 % NaCl solution simulated seawater environment (Fig.S13). After immersing for 1h, the surface of membrane has no change. The above result illustrates that the membrane shows good stability in seawater environment. Relevant robustness test includes hand touch, bending and mechanical abrasion were also constructed which normally happen to a membrane surface in practical application (Fig.S14-15).

Movie S1. The video of PAN membrane separating surfactants-stabilized emulsion.

Movie S2. The video of ZIF-8/PAN membrane separating surfactants-stabilized emulsion.

Movie S3. The video of PAN membrane separating surfactant-free emulsion.

Reference

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