

# Electronic Supplementary Material

## **Bicontinuous porous membranes with micro-nano composite structure using a facile atomization-assisted nonsolvent induced phase separation method**

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### **Supplementary Materials:**

Figure S1-S9

Table S1.

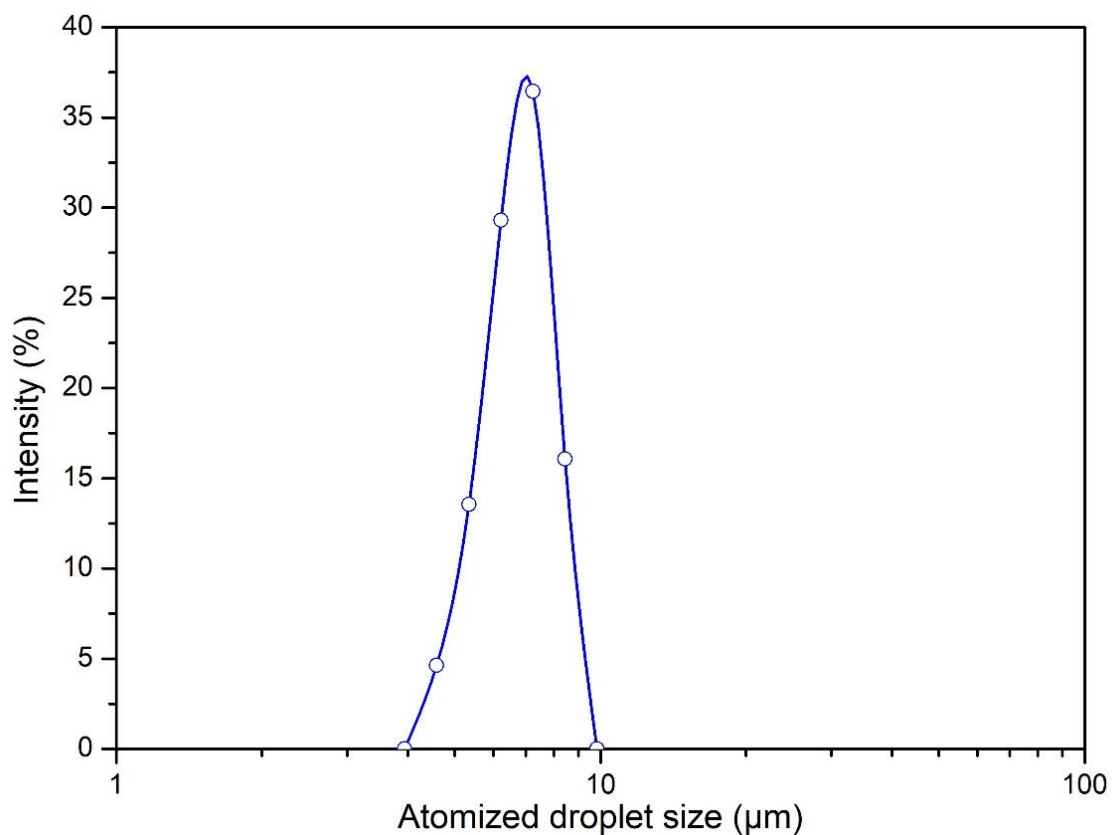
Movie S1: Membrane with anti-oil-adhesion property-1 (MP4)

Movie S2: Membrane with anti-oil-adhesion property-2 (MP4)

Movie S3: Beaker with anti-oil-adhesion coating (MP4)

Movie S4: Beaker without anti-oil-adhesion coating (MP4)

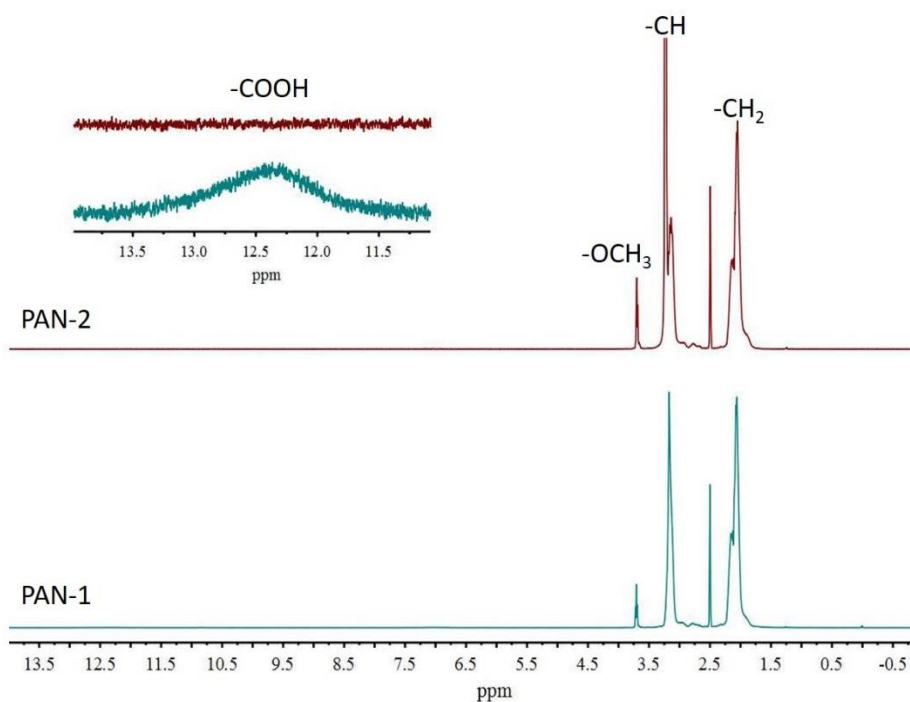
## 1. The size distribution of atomized water droplets



**Fig. S1.** The size distribution of atomized water droplets measured by laser particle scanning analyzer.

## 2. PAN raw material and PAN/PVP membrane composition analysis

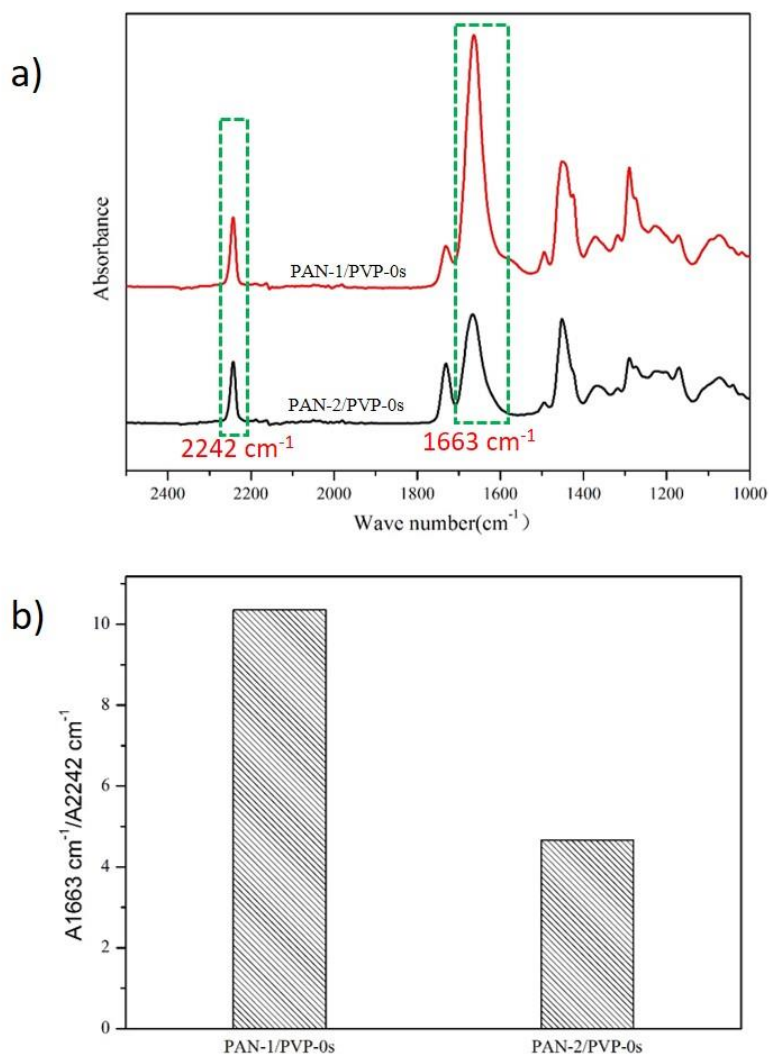
The PAN raw material used in the main text, denoted as PAN-1, is a copolymer of acrylonitrile (AN), methyl acrylate (MA) and a small amount of carboxyl-containing monomer. Another PAN raw material without carboxyl comonomer, denoted as PAN-2, is a copolymer of AN and MA ( $M_w=85000$ , purchased from Macklin). Their compositions were verified by NMR technology, and the analysis is as follows:



**Fig. S2.** The <sup>1</sup>H NMR spectra of PAN-1 and PAN-2.

It can be seen from **Fig. S2** that the signals of AN and MA can be observed in the <sup>1</sup>H NMR spectra of the two PAN copolymers. The difference is that the carboxyl hydrogen signal can only be observed in PAN-1, not in PAN-2. The mole fraction of AN in PAN-1 and PAN-2 can be calculated from the NMR spectra, which are 97.6% and 96.4%, respectively. The molar contents of the acrylonitrile component in the two PAN raw materials are very close.

For the two PAN copolymers, the same formula and preparation conditions as in the main text were used to prepare PAN/PVP ultrafiltration membranes via NIPS method. The following is the analysis of the influence of carboxyl groups on remaining PVP content in the PAN/PVP membrane.



**Fig. S3.** a) ATR-FTIR spectra of PAN/PVP membranes. b) Comparison of ATR-FTIR absorbance ratio of carbonyl group ( $1663\text{ cm}^{-1}$ ) to cyano group ( $2242\text{ cm}^{-1}$ ) of two membranes.

As shown in **Fig. S3**, the peak at  $2242\text{ cm}^{-1}$  corresponds to the cyano group ( $\text{C}\equiv\text{N}$ ) absorption peak that belongs to PAN. The peak at  $1663\text{ cm}^{-1}$  corresponds to the carbonyl group ( $\text{C}=\text{O}$ ) absorption peak that belongs to PVP. ATR-FTIR can reflect the absorbance of the surface to a depth of 2-3  $\mu\text{m}$  and the molar contents of the acrylonitrile component in the two PAN raw materials are very close. Therefore, the absorbance ratio of carbonyl group ( $1663\text{ cm}^{-1}$ ) to cyano group ( $2242\text{ cm}^{-1}$ ) can be used as a semiquantitative indicator to reflect the change of PVP content in the membrane. The change in the ratio of  $A_{1663\text{ cm}^{-1}}/A_{2242\text{ cm}^{-1}}$  means that the content of PVP in PAN-2/PVP-0s is significantly lower than that in PAN-1/PVP-0s. This is because the complexation between PAN and PVP via hydrogen bonding reduces the leaching of

PVP into water.

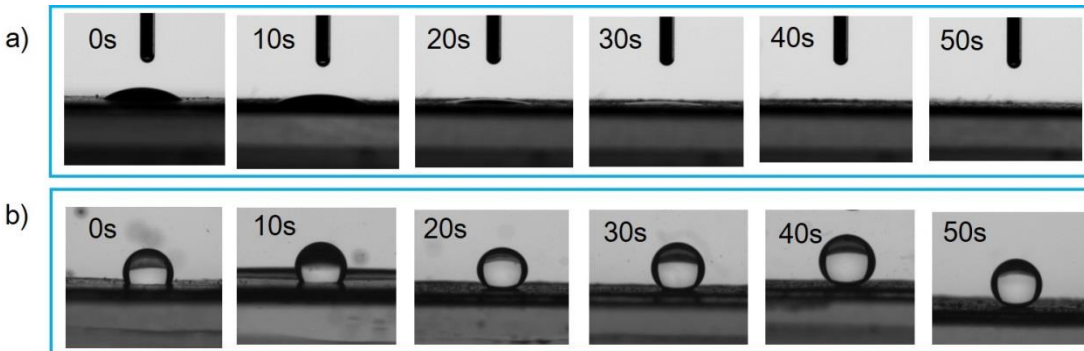
### 3. Calculation of adhesion work of micro-nano composite surface to water and oil

According to Young Dupre's Equation: [1]

$$W_{ad} = \gamma_{lv}(1 + \cos \theta_{lv})$$

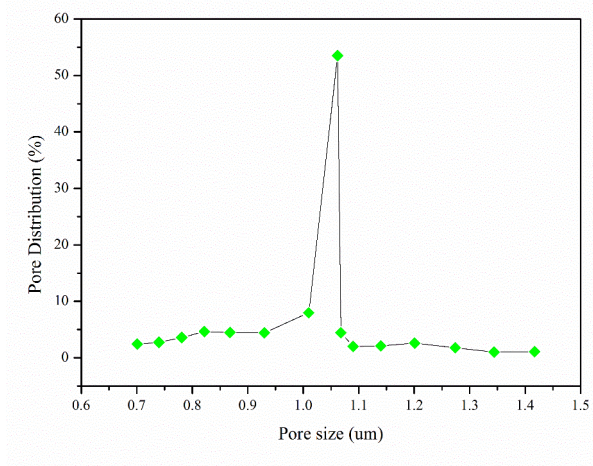
where  $W_{ad}$  is the adhesion work,  $\gamma_{lv}$  is the surface tension of the liquid-gas surface, and  $\theta_{lv}$  is the relevant liquid contact angle in air. For the PAN/PVP-30s membrane, the water contact Angle (WCA) and oil contact Angle (OCA) in the air are both  $0^\circ$ , and the surface tension of water and 1,2-dichroethane in the air are about  $72 \text{ mN m}^{-1}$  and  $23 \text{ mN m}^{-1}$ , respectively. Therefore,  $W_{ad,water}=144 \text{ mN m}^{-1}$ ,  $W_{ad,oil} = 46 \text{ mN m}^{-1}$ . The adhesion work of membrane to water is significantly higher than that to oil. This indicates that the water absorbed by the membrane is difficult to be replaced by oil, thus ensuring the robust underwater superoleophobicity.

### 4. The CA physical graph with different atomization pretreatment time



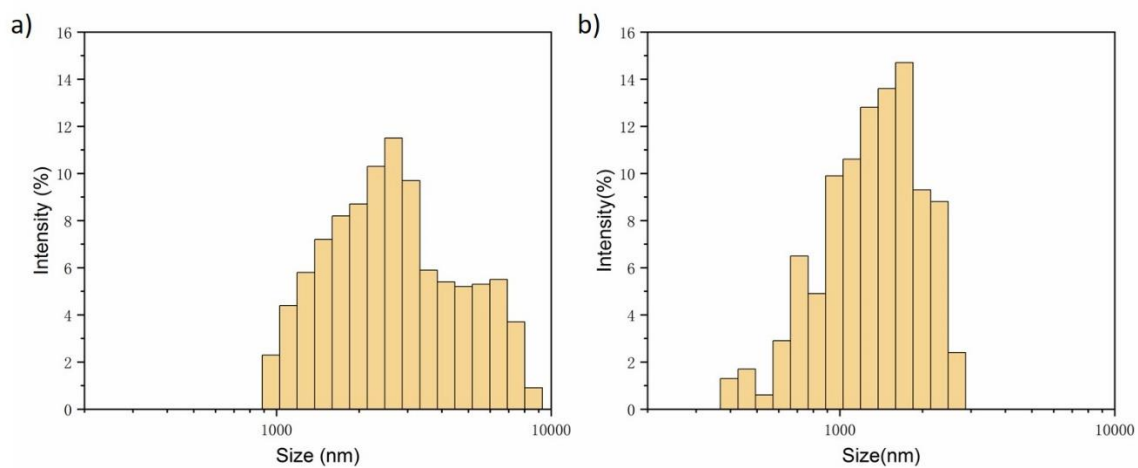
**Fig. S4.** a) Water CA in air and b) underwater oil CA images of the membrane with different atomization pretreatment time.

## 5. The distribution of pore diameter of PAN/PVP-30s membrane



**Fig. S5.** The distribution of pore diameter of PAN/PVP-30s membrane.

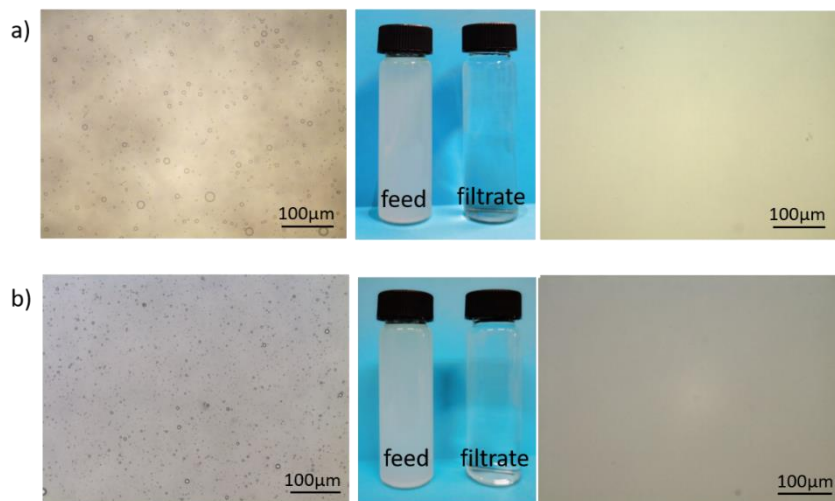
## 6. The size distribution of emulsified oil



**Fig. S6.** The oil droplet size distribution of a) surfactant-free emulsions and b) surfactant-stabilized emulsions.

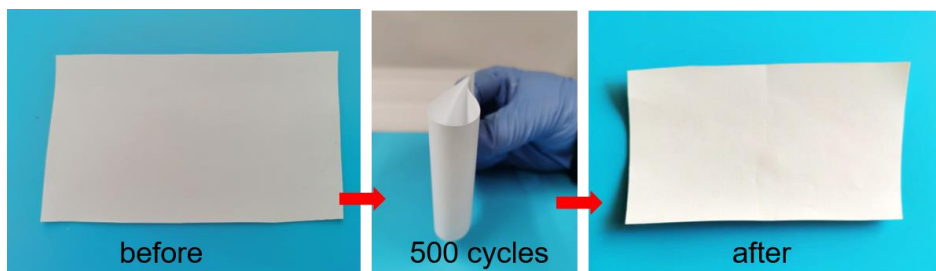
## 7. Optical microscopy images of oil-in-water emulsions before and after filtration

As shown in **Fig. S6**, surfactant-free diesel/H<sub>2</sub>O and SDS-stabilized diesel/H<sub>2</sub>O emulsions have large amounts of oil droplets in micron and sub-micron scale in the feeds. In the corresponding filtrates, no oil droplets are observed in the whole image.



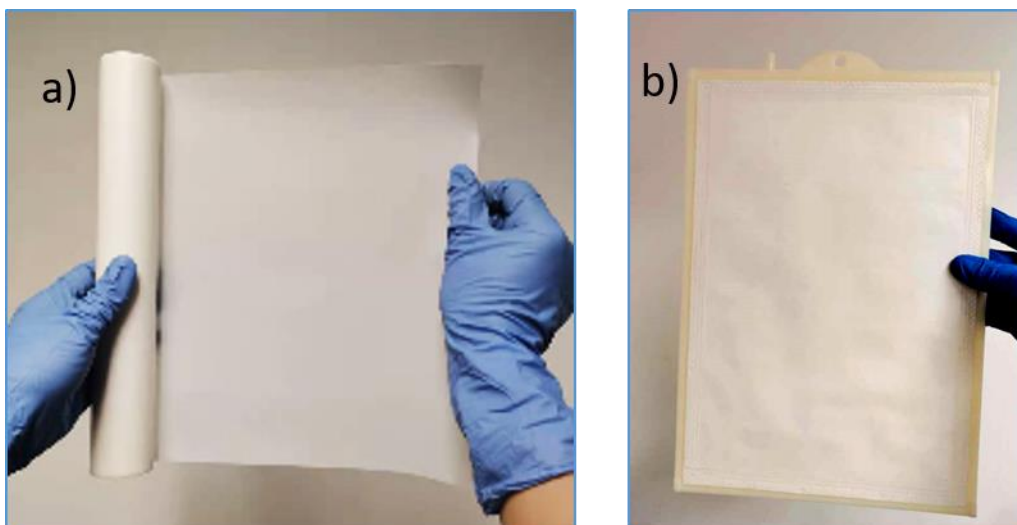
**Fig. S7.** Optical microscopy images of a) diesel/H<sub>2</sub>O and b) SDS/diesel/H<sub>2</sub>O before and after filtration.

## 8. The flexibility of PAN/PVP-30s membrane



**Fig. S8.** Photographs of PAN/PVP-30s membrane before and after bending. No cracks were found after bending 500 cycles, indicating an excellent flexibility and robustness of the membrane.

## 9. Continuous fabrication of PAN/PVP bicontinuous porous structure membrane



**Fig. S9.** a) The PAN/PVP-30s membrane and b) the plate and frame PAN/PVP bicontinuous porous structure membrane module obtained by the continuous fabrication process.

**Table S1.** TOC vales of related emulsions.

Oils	TOC of surfactant-free emulsion /mg L <sup>-1</sup>	TOC of surfactant-stabilized emulsion/mg L <sup>-1</sup>
Hexane	4483	3144
Diesel	5910	5380
Soybean oil	6973	2038

### References

1. Agarwal S, Arnim V, Stegmaier T, Planck H, Agarwal A. Role of surface wettability and roughness in emulsion separation. *Separation and Purification Technology*, 2013, 107: 19-25