Supporting Information

Constructing Scalable Superhydrophobic Membrane for Ultrafast Water/Oil Separation

Xi Quan Cheng ^a, Yang Jiao ^a, Zekun Sun ^a, Xiaobin Yang ^b, Qing Bai ^a, Zhongjun Cheng ^b, Yingjie Zhang ^a, Kai Wang ^a, Lu Shao ^b*

^a School of Marine Science and Technology, State Key Laboratory of Urban Water Resource and Environment (SKLUWRE), Sino-European Membrane Technology Research Institute, Harbin Institute of Technology, Weihai 264209, P.R. China.

^b MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemical Engineering and Technology, State Key Laboratory of Urban Water Resource and Environment (SKLUWRE), Harbin Institute of Technology, Harbin 150001, P.R. China.

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1. Materials and methods

1.1. Chemical and materials

Polyvinylidene fluoride (PVDF) (Mw=320000) was purchased from Meryer Chemical Technology Co., Ltd (Shanghai, China). Polydimethylsiloxane (PDMS) was supplied by Dow Corning Co., Ltd (Shanghai, China). N, N-Dimethylformamide (DMF) was purchased from Tianjin Yongda Chemical Reagent Co., Ltd (Tianjin, China). Span 80 was obtained from Zhiyuan Chemical Reagent Co., Ltd (Tianjin, China). Tetrahydrofuran (THF) and Toluene were both provided by Yantai Far Eastern Fine Chemical Co., Ltd (Yantai, China). *n*-octane was obtained from Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Absolute ethanol was provided by Shuangshuang Chemical Co., Ltd (Yantai, China). All other reagents or chemicals mentioned were of analytical grade.

1.2. Characterizations

1.2.1. Scanning electron microscopy (SEM)

The microstructures of prepared PVDF, PVDF/PDMS, PVDF-co-PDMS, and PVDF-co-PDMS-AS membranes were observed with a SEM (**MERLIN Compact, Zeiss Company**) after sprayed with gold. To observe the morphology structure of the cross-section of the asprepared membranes, the membranes were brittlely fractured in liquid nitrogen before sprayed with gold. Energy dispersive microanalysis of the membranes was conducted with an INCAEnergy EDS System, **Oxford Instruments, UK**. The membranes were mapped to obtain the distribution of F and Si elements.

1.2.2. Confocal Laser Scanning Microscope (CLSM)

CLSM was measured to analyse the roughness of membranes by a CLSM device. 3D images of the membrane surface with RSa values can be used to characterize roughness.

1.2.3. Contact angle measurement

Water (3 μ L) contact angle and underwater oil (3 μ L) contact angle of the membranes were evaluated with a contact angle measuring instrument (**SL200B/K Kino, America**). The dried membrane was fixed on the fixture, then was dropped with a liquid droplet on the surface of the membrane to get the contact angles (5 points per sample). The dynamic wetting and adhesion state of water droplets on the membrane surface could be accurately recorded. In addition, when the droplet rolled, the sliding angle was estimated by measuring the vertical height and horizontal length of the slope and the tangent value (tan θ) of the slope was calculated.

The surface free energy was generally determined by the dispersion and polarity components of the membrane.¹ It could be calculated by measuring the contact angle of deionized water and ethylene glycol according to equation 1 and equation 2.

$$\gamma_l(1 + \cos\theta) = 2(\gamma_l^p \gamma_f^p)^{1/2} + 2(\gamma_l^d \gamma_f^d)^{1/2}$$
⁽¹⁾

$$\gamma_f = \gamma_f^d + \gamma_f^p \tag{2}$$

Where γ is the surface free energy, *l* and *f* respectively represent the solvent and membrane, *p* and *d* respectively represent the polar component and the dispersion component, θ represents the corresponding contact angle of water or ethylene glycol.

1.2.4. X- ray photoelectron spectroscopy (XPS)

XPS was characterized by a measuring instrument (**PHI-1600 X-ray photoelectron spectrometer**, **USA**) to investigate the chemical composition that exist on the surface of the

membrane under ultra-high vacuum (6×10^{-9} mbar). Mg K α was used as the source of emission and data was received from the SPECTRA version 8 operating system.

1.2.5. Fourier infrared spectrometer (FTIR)

Attenuated total reflectance Fourier transformed infrared spectroscopy (ATR-FTIR) was measured by FTIR equipment (**Nicolet 380, Thermo Electron**). It was used to analyse the chemical structure of the membranes.

1.2.6. Differential scanning calorimetry (DSC)

Differential scanning calorimeter (**DSC214, Germany**) was used to evaluate the enthalpy changes of the moisture in the membranes to investigate the affinity of the membrane and water. Firstly, the membrane was immersed in deionized water. Then the moist membrane was placed in an open Al crucible. The temperature range was set from -80 to 80 °C and the heating and cooling rate was set to 10 °C/min for all runs.

The melting enthalpy of water could be obtained by calculating the peak area of the curve, and then the content of non-frozen water in the membranes could be calculated by equation 3 - equation 5.

$$W_{s}(\%) = \frac{m_{1} - m_{0}}{m_{1}} \times 100\%$$
(3)

$$W_{fs}(\%) = \frac{\Delta H_{s}}{\Delta H_{w}} \times 100\%$$
(4)

$$W_{nfs}(\%) = W_{s} - W_{fs}$$
(5)

Where m_0 and m_1 represent the dry weight and wet weight of the membrane, ΔH_s is the sum of the melting enthalpy of the heating process, ΔH_w is the melting enthalpy of ice, W_s is the relative

water absorption ratio of membrane, W_{fs} and W_{nfs} represent the content of frozen and non-frozen bound water in the membrane, respectively.

1.2.7. Characterization of particle size in the emulsions

Optical microscopy photos of emulsion before and after separation were recorded by polarized optical microscopy (**BA210E**, **China**). Light scattering particle size and zeta potential meter (**Malvern Zetasizer Nano**, **UK**) measurements were applied to measure the droplet diameter and the size distribution of emulsions.

1.2.8. The lipophilicity of the PVDF based nanofiber membranes

The *n*-octane uptake of membranes was calculated as equation 6. The membranes were weighed and then immersed in *n*-octane for 24 h. Then, the *n*-octane on the surface of the membranes was wiped dry with a filter paper. The weight of wet membranes was measured.

$$U = \frac{m_1 - m_0}{A} \tag{6}$$

Where U stands for the increased mass per unit area of membrane, m_0 and m_1 represent the dry weight and wet weight of the membrane, A is the area of the tested membrane.

1.2.9. The pore structure of the PVDF based nanofiber membranes

The pore size distribution of the membrane was measured with a membrane pore size analyzer (**BSD-PB, China**). Ethanol was used as the infiltration liquid, and the test was carried out by atmospheric pressure infiltration.

1.2.10 The porosity of the PVDF based nanofiber membranes

The porosity of membranes was evaluated by the weight after being wet with absolute ethanol and the weight after being dried. Porosity (ε) was calculated by equation 7.

$$\varepsilon(\%) = \frac{\frac{\frac{m_1 - m_0}{\rho_1}}{\frac{m_1 - m_0}{\rho_1} + \frac{m_0}{\rho_0}} \tag{7}$$

Where m_0 and m_1 are the mass of the wetted and dried membranes, respectively, while ρ_1 and ρ_0 are the density of absolute ethanol and polymer, respectively.

1.2.11 The surface charge of the PVDF-based nanofiber membranes

The Surface Analyzer (**Surpass, Anton Paar GmbH**) was used to analyze the surface zeta potential of various PVDF-based nanofiber membranes. All characterization items were carried out at 25°C at pH=7.

1.2.12 The separation performance of the PVDF based nanofiber membranes

Firstly, Span 80 (0.1 g) was added into *n*-octane or toluene (198 ml), then deionized water (2 ml) was added. The mixture was stirred under 1000 rpm for 12 h to form the surfactant-stabilized water-in-oil emulsions. The permeance of the water-in-oil emulsion was measured by a laboratory-made emulsion separation device. The as-prepared PVDF-based membranes were sealed between two vertical glass tubes with a diameter of 1.5 cm. The freshly prepared emulsion was poured onto the membrane and permeated quickly by gravity (liquid level 10 ± 0.1 cm). The emulsion permeance was calculated by equation 8 in the first three minutes.

$$P = \frac{V}{A \times t \times \Delta P} \tag{8}$$

Where $P(L \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-1})$ represents the permeance of emulsion, V(L) is the volume of emulsion infiltrating through the membranes, $A(m^2)$ is the effective membrane area, t(h) is the penetration time, ΔP (bar) is the pressure of the liquid column on the membrane.

The finally obtained filtrate was collected for purity tests. Then the separation efficiency of water-in-oil emulsion was calculated by equation 9.

$$R(\%) = (1 - \frac{C_p}{C_f}) \times 100\%$$
(9)

Where C_p and C_f are the water concentrations in the permeate solution and the feed solution, respectively. The concentration of water droplets in the emulsion was measured with a trace moisture analyzer (BCS-600, China). Each data point is an average of three repetitions of each test.

Furthermore, the permeance of the membranes in 20 cycles was performed to explore the antipollution mechanism. In every cycle, the membrane was simply rinsed with absolute ethanol after filtration of 3 min and then dried. The flux recovery rate (FRR) was calculated using equation 10.

$$FRR(\%) = \frac{P_1}{P_0} \times 100\%$$
(10)

Where P_1 represents the emulsion permeance after 20 cycles and P_0 is the initial emulsion permeance.

2. Experimental

2.1. Preparation of the nanofiber membranes



Figure S1. The preparation process of PVDF nanofiber membrane with asymmetric structure

Many studies have proved that the composition of the polymer solution has an effect on nanofibers.² In this study, we adjust the concentration of PVDF and PDMS to optimize the performance of the membranes. According to the method mentioned above, 10%, 12%, 15%, and 17% PVDF solution are applied to obtain pristine PVDF membranes. Subsequently, 8%, 10%, and 13% PDMS solutions are deployed for enhancing the separation performance of the pristine PVDF membranes. Under the optimum membrane fabrication conditions, pristine PVDF and PVDF-co-PDMS nanofiber membranes are fabricated by electrospinning and coaxial electrospinning, respectively.

2.2. Effects of PVDF concentration on the properties of the nanofiber membranes

2.2.1. Effects of PVDF concentration on the membrane morphologies

With PVDF concentration increasing from 10 wt.% to 17 wt.%, the diameter increases by 254% from 91 nm to 321 nm. It could be observed that there are some oval beaded structures which are commonly obtained for the PVDF based nanofiber membranes caused by the phase inversion of the PVDF solution under high electrostatic voltage.³ Notably, when the concentration of PVDF solution is lower than 10 wt.%, the membrane is not strong enough to separate the water in oil emulsions.



Figure S2. The morphologies of the pristine PVDF nanofiber membranes fabricated by different PVDF concentrations: a) 10wt.%, b) 12 wt.%, c) 15wt.%, and d) 17 wt.%

2.2.2. Effects of PVDF concentration on the membrane hydrophobicity and porosity

As hydrophobic materials, PVDF nanofiber membranes demonstrate a high water contact angle around 136°. Notably, the hydrophobicity of the membrane changes little with the increment of the PVDF concentration, indicating that the hydrophobicity of the membrane is mainly dependent on the intrinsic hydrophobicity of the materials. Interestingly, the porosity of the pristine PVDF nanofiber membranes increases with the increment of the concentration of PVDF solutions. That might be due to the fact that coarser nanofibers always create larger pores.^{4, 5}



Figure S3. The properties of the pristine PVDF membranes: a) water contact angle; b) porosity.

2.2.3. Effects of PVDF concentration on the membrane separation performance

With the increment of the PVDF concentration from 10wt.% to 15wt.%, the permeance of nanofiber membranes increases by 46% while the rejection performance keeps constant. When the PVDF concentration is 17 wt.%, the permeance reaches up to 17676 L m⁻² h⁻¹ bar⁻¹, which is about triples of the nanofibers fabricated by 10 wt.%. As discussed above, the increment of porosity and pore size promotes the emulsion passing through the nanofiber membranes. Notably, when the concentration achieves at 17wt.%, the rejection declines to 95%

correspondingly. It might be possible that nanofiber membranes with asymmetric structure through constructing the support layer with 17 wt.% PVDF solution and the selective layer with 10 wt.% PVDF solution might demonstrate both high rejection and high permeances.



Figure S4. The separation performance of the pristine PVDF nanofiber membranes.

2.3. Effects of PDMS concentration on the properties of the nanofiber membranes

2.3.1. Effects of PDMS concentration on the membrane morphologies

PDMS solution is applied to enhance the hydrophobicity of the PVDF membranes through coaxial electrospinning technology. To investigate the effects of PDMS concentration on the separation performance, the symmetrical PVDF-co-PDMS membranes are developed. Besides oval beaded structure, PDMS micro-sphere with diameter of about 6.5 µm to 8.6 µm could be found on the surface of the nanofiber membranes. Notably, when the concentration increases to 10 wt.%, nano-scaled bulges appear on the surface of PDMS microsphere. However, once

the concentration continues to increase, the micro-spheres and nanofibers would be entangled with each other which makes the nano-scaled bulges disappear gradually. In addition, the nanofiber becomes coarser when coaxially electrospinning with PDMS solution.



Figure S5. The morphology of the PVDF-co-PDMS membranes fabricated with different PDMS concentrations: a) 8 wt.%. b) 10 wt.%, and c) 13 wt.%

2.3.2. Effects of PDMS concentration on the membrane hydrophobicity

Interestingly, the hydrophobicity of the nanofiber membranes increases significantly with a water contact angle nearly 160°, confirming that the PDMS solution plays an important role in constructing the superhydrophobic surface. The addition of PDMS could reduce the surface energy of PVDF nanofiber further and increase the micro-nano hierarchical structure of micro-sphere as mentioned in the main text. The increasing diameter of the nanofiber also contributes to the increment of the porosity.⁶ Notably, the porosity of the membranes does not change significantly with the increment of PDMS concentration.



Figure S6. The properties of the PVDF-co-PDMS membranes: a) water contact angle; b) porosity.

2.3.3. Effects of PDMS concentration on the membrane separation performance

Only appropriate concentration of PDMS could improve the emulsion permeance. The permeance of water-in-*n*-octane emulsion increases to 10778 L m⁻² h⁻¹ bar⁻¹ when 10% PDMS solution is added. Moreover, the addition of PDMS could promote the separation efficiency of the membranes. However, excessive PDMS would lead to a decrease in membrane separation efficiency. Due to more excellent separation performance, 10% is selected as the optimum concentration to prepare for the super-hydrophobic oil-water separation membranes.



Figure S7. The separation performance of the pristine PVDF nanofiber membranes.

2.4. Effects of the thickness of the selective layer on the separation performance of the PVDF-co-PDMS-AS membranes.

"When the spinning time of the support layer was about 6 hours, the thickness of the support was about 65 μ m. As the spinning time of selective layer increased from 1 hour to 4 hours, the thickness of the membranes increased from 11 μ m to 40 μ m. With the increment of the thickness of the selective layer, the permeance of the nanofiber membranes decreased and the separation efficiency of the nanofiber membranes increased first and then fluctuated around 99.6 %, correspondingly. Notably, When the spinning time of the selective layer is 2 hours, the separation efficiency achieves to 99.6% and the permeances of the membranes are still as high as 17331 L m⁻² h⁻¹ bar⁻¹. The results indicate also that the formation of the asymmetric structure promotes the emulsion passing through the membranes.

Table S1. The relation between the spinning time and the thickness of the selective layer

Item	PVDF-co-PDMS-AS membranes					
Item	Support	ort Selective layer				
Spinning time (h)	6	1	2	4	6	
Thickness (µm)	65±2.0	11±1. 2	24±1.3	31±1.7	40±2.1	



Figure S8. The effects of spinning time on the separation performance of the PVDF-co-PDMS-AS membranes.

2.5. The morphologies of the PVDF based nanofiber membranes

As shown in **Figure S9**, the F element distributes evenly on the surface of the pristine PVDF membrane while almost no Si element could be found. This proves that no extra Si element would be introduced during the membrane preparation process. Interestingly, the F element and Si element both distributes uniformly on the as-prepared PVDF-co-PDMS-AS membrane. This is similar to the PVDF-co-PDMS nanofiber membrane. Moreover, the Si element mainly appears on the selective layer while the F element distributes over the whole cross-section (**Figure S9e**). This indicated the membranes were asymmetric, which is consistent with the conclusion in the major.



Figure S9. The element distribution on the pristine PVDF nanofiber membrane(a-b), the surface(c-d) and cross-section(e) of PVDF-co-PDMS-AS nanofiber membrane.

As shown in **Figure S10**, the 3D structure of the PVDF based nanofiber membranes is characterized for clarifying the roughness of the membranes. Compared with PVDF membranes, PVDF membranes with PDMS have higher roughness, which is mainly due to the existence of PDMS micro-sphere. PVDF-co-PDMS have the largest roughness because the diameter of the PDMS micro-sphere on the membrane surface is the biggest. For the PVDF-co-PDMS-AS membranes, the selective layer is developed on the PVDF support layer. As the surface of the support layer is not that flat, the roughness of the PVDF-co-PDMS-AS membranes decreases.



Figure S10. The roughness of the PVDF based nanofiber membranes: a) pristine PVDF membranes, b) PVDF/PDMS membranes; c) PVDF-co-PDMS membranes; d) PVDF-co-PDMS-AS membranes.

2.6. The pore structure of the PVDF based nanofiber membranes

The introduction of PDMS increases the average pore size and porosity of the membrane. This might be caused by the insertion of microspheres and the thickening of nanofibers. When the nanofibers accumulate continuously, the pore size and porosity of the membrane gradually become smaller and the pristine PVDF nanofiber membrane shows the smallest pore size and porosity. Once the micro-spheres are inserted between the nanofibers, the pore size and porosity of the membrane are enlarged. For asymmetric nanofiber membrane, the support layer is composed of thicker nanofibers with larger pores. This leads to a larger pore size distribution and higher porosity. In addition, the asymmetric nanofiber membrane has a thinner selective layer which makes the pore size larger as shown in **Figure S12**.



Figure S11. The pore structure study on the PVDF-based nanofiber membranes: a) the pore size distribution of the PVDF-based membranes. b) the porosity of the PVDF-based membranes.



Figure S12. The Schematic diagram of membrane pore size changing with the thickness of the selected layer.

2.7. The hydrophobicity study of the PVDF-based nanofiber membranes

Table S2 showed the apparent surface energy of different PVDF-based membrane. Generally, the smaller the surface energy, the more hydrophobic the object. During the coaxial electrospinning process, the diffuse of the PDMS into PVDF nanofibers led to the decrease of the surface energy of the nanofiber. Moreover, the hierarchical micro-nano microspheres

embedded between the nanofibers reduces the surface energy of the membranes further as discussed in the main text.

	Contact angle (°)				
Sample	Water	Ethylene	γ^{p} (mN/m)	γ^{d} (mN/m)	γ _S (mN/m)
		glycol			
PVDF	137.463	47.329	43.62	164.43	208.05
PVDF/PDMS	153.112	136.900	0.16	2.34	2.50
PVDF-co-PDMS	155.139	140.175	0.19	1.92	2.11
PVDF-co-PDMS-AS	157.380	142.528	0.14	1.48	1.62

 Table S2. Surface energy of PVDF-based membranes



Figure S13. The optical images of the mirror-like phenomena when the membranes immersed in water.



Figure S14. The *n*-octane uptake of the PVDF-based nanofiber membranes.

Water is present in the membranes in different forms, for example, free water, freezable water, and non-freezable water.⁷ The fraction of non-freezable water is tightly connected to the membrane. The lower the proportion of non-freezable water is, the more difficult it is to form water layers on the surface of the membranes, which results in a poorer affinity for water. Therefore, compared with the pristine PVDF membrane, the introduction of PDMS especially by coaxial electrospinning improves the hydrophobicity of the membranes.

	(%) (%)	W_{fs} (%)	W _{nfs} (%)
PVDF 1.4	449	0.070	1.379
PVDF/PDMS 0.9	971	0.136	0.835
PVDF-co-PDMS 0.3	381	0.075	0.306
PVDF-co-PDMS-AS 0.4	455	0.081	0.373

 Table S3. The content of different forms of water in the membrane

2.8 The surface charge of the PVDF-based nanofiber membranes

In general, the PVDF-based nanofiber membranes show negative surface charge, when the pH of aqueous solution is 7. It is noteworthy that the continuous phase is octane or toluene, non-polar aprotic solvents, in which the membranes and water droplets show less possibility to be ionized. In this case, the electrostatic repulsion (Donnan effect) plays little role in removing the droplets from the emulsions

Sample	Zeta potential (mV	
	pH=7	
PVDF	-29.4	
PVDF/PDMS	-37.8	
PVDF-co-PDMS	-28.1	
PVDF-co-PDMS-AS	-32.9	

Table S4. The surface charge of PVDF-based nanofiber membranes

2.9. The separation performance of the PVDF-based nanofiber membranes

In order to further characterize the properties of the emulsion before and after filtration, the emulsion is irradiated with a laser pointer. Light scattering and Tyndall phenomenon could be obviously observed for the feed solution of the emulsion since the size of droplets ranges from 100 nm to 3000 nm. After filtration, the scattering disappears since the size of the droplets is only about 100~200 nm. Meanwhile, the Tyndall effect had become insignificant since the concentration of the water droplets is as low as 55 ppm.



Figure S15. The Tyndall effect of feed, filtrate, and pure oil.



Figure S16. The water concentration in the filtrate after filtration with PVDF-based membranes.



Figure S17. The comparison of the separation performance for water-in-toluene emulsion of as-prepared membrane in this work with the membranes reported in literatures.⁸⁻¹⁹

Figure S17 shows the separation performance comparison of our membrane with the previously reported membranes for water-in-toluene emulsion. It could be seen from the figure that our membranes with a emulsion permeance of up to $35751 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ is far superior to most of the membranes reported previously, and located far above the up-bound lines.⁸⁻¹⁹

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