

Supplementary Information

Unprecedented scaling/fouling resistance of omniphobic polyvinylidene fluoride membrane with silica nanoparticle coated micropillars in direct contact membrane distillation

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Supplementary Information

Method S1: Fabrication of polydimethylsiloxane (PDMS) mold and micro-pillared poly (vinylidene fluoride) (PVDF) membrane;

Method S2: Calculation of membrane surface energy;

Method S3: Calculation of wetting state factor for MP-PVDF membrane;

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Figure S1: Experimental MD setup;

Figure S2: Size distribution of silica nanoparticles (SiNPs);

Figure S3: The durability of SiNPs and 17-FAS coating after 30 min bath sonication;

Figure S4: Membrane autopsy after Casein fouling test for C-PVDF and MP-PVDF membrane based on module location

Figure S5: SEM image and water contact angle of MP-PVDF membrane with SiNPs but not 17-FAS coating

Method S1 Fabrication of polydimethylsiloxane (PDMS) mold and micro-pillared poly (vinylidene fluoride) (PVDF) membrane.

Polydimethylsiloxane (PDMS) mixed with the curing agent at a weight ratio of 10:1. Before casting onto the silicon wafer with micropillar arrays, the mixture was de-gassed by the vacuum pump to remove any air bubbles from the mixture. Afterwards, the mixture together with silicon wafer was cured for 3 h at 60 °C. The PDMS mold was then peeled off carefully and stored in a clean container. Resultant PDMS mold with an ordered cylindrical hole array was used as a substrate for further casting process.

Before casting, poly (vinylidene fluoride) (PVDF) polymer solution was prepared by mixing the PVDF polymer powder (15 wt.%), N, N-Dimethylacetamide (57.6 wt.%) and Diethylene glycol (27.4 wt.%) at 90 °C for 12 h. Obtained PVDF polymer solution exhibited a homogeneous phase and was stored at 90 °C for 12 h to remove air bubbles from the solution.

During the casting process, an appropriate amount of the casting solution was spread on the PDMS mold to a thickness of 600 µm using a home-made stainless-steel casting knife. Liquid film by casting was further subjected to vapor (75 °C) exposure for 10 s and subsequently immersed into the DI water (75 °C) bath for 15 min to allow for precipitation. Afterwards, the obtained membrane was rinsed by DI-water to remove solvent and additives, followed by being dried in a oven at 30 °C for 48 h.

Method S2 Calculation of membrane surface energy

Membrane surface energy was determined based on Boo's method [1]. The dispersion (γ_{sv}^d) and dipole-hydrogen (polar) bonding forces (γ_{sv}^p) (i.e., $\gamma_{sv} = \gamma_{sv}^p + \gamma_{sv}^d$) of the two components were estimated according to the Owens-Wendt method [2] using the experimentally determined intrinsic contact angles of water (θ_{water} with $\gamma_{\text{water}} = 72.1$ mN/m) and methylene iodide ($\theta_{\text{M-I}}$ with $\gamma_{\text{M-I}} = 50.8$ mN/m):

$$\sqrt{\gamma_{\text{water}}^d} \sqrt{\gamma_{sv}^d} + \sqrt{\gamma_{\text{water}}^p} \sqrt{\gamma_{sv}^p} = \frac{(1 + \cos(\theta_{\text{water}})) \gamma_{\text{water}}}{2}$$

$$\sqrt{\gamma_{\text{M-I}}^d} \sqrt{\gamma_{sv}^d} + \sqrt{\gamma_{\text{M-I}}^p} \sqrt{\gamma_{sv}^p} = \frac{(1 + \cos(\theta_{\text{M-I}})) \gamma_{\text{M-I}}}{2}$$

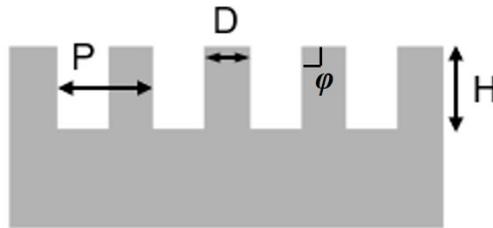
The values of the dispersive and polar components for water were taken from literature as, $\gamma_{\text{water}}^d = 21.8$ mN/m and $\gamma_{\text{water}}^p = 51.0$ mN/m and $\gamma_{\text{M-I}}^d = 49.5$ mN/m and $\gamma_{\text{M-I}}^p = 1.3$ mN/m for methylene iodide [2].

Method S3 Calculation of wetting state factor for MP-PVDF membrane

Based on the theoretical approach by Grewal et al [3], the wetting state of MP-PVDF membrane can be determined by the calculation of wetting state factor, which is defined as below [3]:

$$\zeta = \frac{(\sqrt{2}S_f - 1)}{2a_r} \tan(\theta_a - \varphi)$$

where S_f indicates the spacing factor (ratio of pitch to diameter) and a_r is aspect ratio given by height and diameter of pillar on the membrane. θ_a is advancing angle and φ is the interior angle as a geometrical factor (= 90° for cylindrical pillars). Physics meanings of these parameters and experiment conditions for the calculation are found below. A suspended state to transition state occurs at $\zeta < 0.5$, whereas a transition state to pinned state occurs at $0.75 > \zeta > 0.5$ and a pinned state is observed at $\zeta > 0.75$.



$$S_f = P/D$$

$$a_r = H/D$$

Type	Spacing factor	Aspect ratio	Interior angle/°	Advancing angle/°	Wetting state factor
MP-PVDF	2	2	90	157	0.92

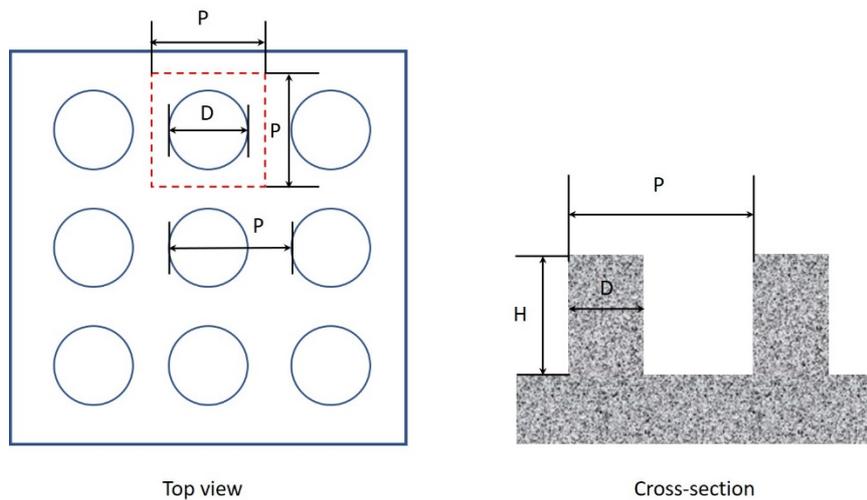
Method S4 Calculation of area fraction (f_1 and f_2) and roughness factor (r_2) for determining the wetting state of SiNPs-MP-PVDF membrane

Based on the theoretical approach by Wu et al [4, 5], area fraction f represents the solid fraction for a surface containing only one type of asperities, and roughness factor r is defined as ratio between the total surface area and the projected surface area (Schematic diagram shown below). Subscript 1 and 2 represent micropillar and silica nanoparticle, respectively. Notably, spherical structure (i.e. silica nanoparticles) can be simplified to a cylindrical structure, where height (H) and diameter (D) of cylindrical structure is equal to the diameter of spherical structure.

For the area fraction f , it is defined as below:

$$f = S_{solid}/S_{total}$$

being S_{solid} the area of solid membrane and S_{total} the total area, as shown in the schematic illustration below.



The schematic diagram indicates that the area of solid membrane S_{solid} and the total area S_{total} can be defined as below:

$$S_{solid} = \pi D^2 / 4$$

$$S_{total} = P^2$$

$$f = S_{solid} / S_{total} = \pi D^2 / 4P^2$$

where D and P represent the diameter and period of cylindrical structure, respectively. As a result of the simplification, the value of D for the silica nanoparticle is equal to the diameter (644 nm) of silica nanoparticle.

For the roughness factor r , it is defined as below:

$$r = S_{surface} / S_{projected}$$

being $S_{surface}$ the total surface area and $S_{projected}$ the projected area of solid membrane. It is noted that the total surface area $S_{surface}$ is different from the total area S_{total} . $S_{surface}$ and $S_{projected}$ are defined as below.

$$S_{surface} = P^2 + \pi DH$$

$$S_{projected} = P^2$$

where P , D and H represent the period, diameter and height of cylindrical structure, respectively. As a result of the simplification, the value of D and H for the silica nanoparticle is equal to the diameter (644 nm) of silica nanoparticle. Hence, the roughness factor r for silica nanoparticle is given by:

$$r = (P^2 + \pi DH) / P^2 = 1 + \pi DH / P^2$$

$$r = 1 + \pi D^2 / P^2$$

Type	Diameter	Height	Period	f	r
Micropillar	5 μm	10 μm	10 μm	~ 0.20	/
Silica nanoparticle	644 nm	644 nm	644 nm	~ 0.79	~ 4.14

Criteria for suspended and pinned wetting states for surfaces with dual-scale roughness.

Wetting state	Equations [4, 5]
Suspended	$\cos \theta < f_1 f_2 \cos \theta_0 + f_1 f_2 - 1$; $\cos \theta < \sim -0.83$, $\theta > 146^\circ$
Pinned	$\cos \theta > f_1 r_2 \cos \theta_0 + f_1 - 1$; $\cos \theta > \sim -0.73$, $\theta < 137^\circ$

f_1 and f_2 : area fractions of microstructure (i.e. micropillar) and nanostructure (i.e. silica nanoparticles), representing the solid fraction of a surface containing only one type of asperities;

r_2 : roughness factor of nanostructure, defined as ratio between the total surface area and the projected surface area.

θ_0 represents the intrinsic contact angle of substrate material and that of PVDF polymer is 85° [6], and $\cos \theta_0$ is ~ 0.09 .

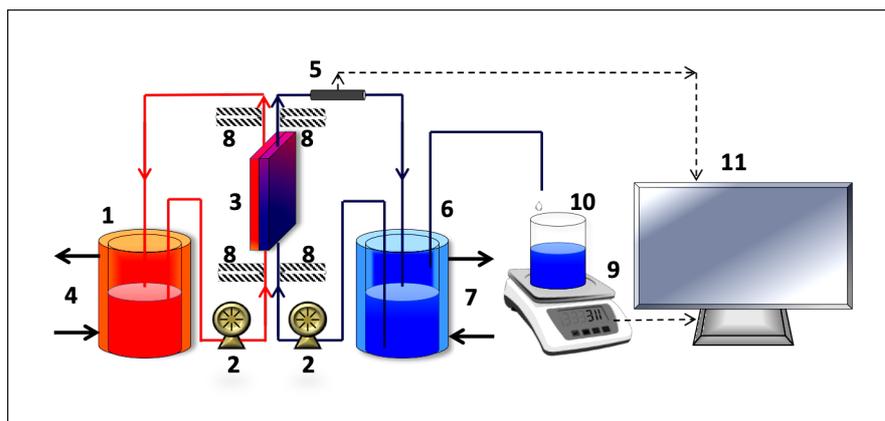


Fig. S1 Schematic diagram of the DCMD test unit (1: feed tank; 2: pumps; 3: flat sheet membrane module; 4: heating exchange; 5: conductivity sensor; 6: permeate tank; 7: cooling exchange; 8: thermometer; 9: digital balance; 10: overflow tank; 11: log computer) [7].

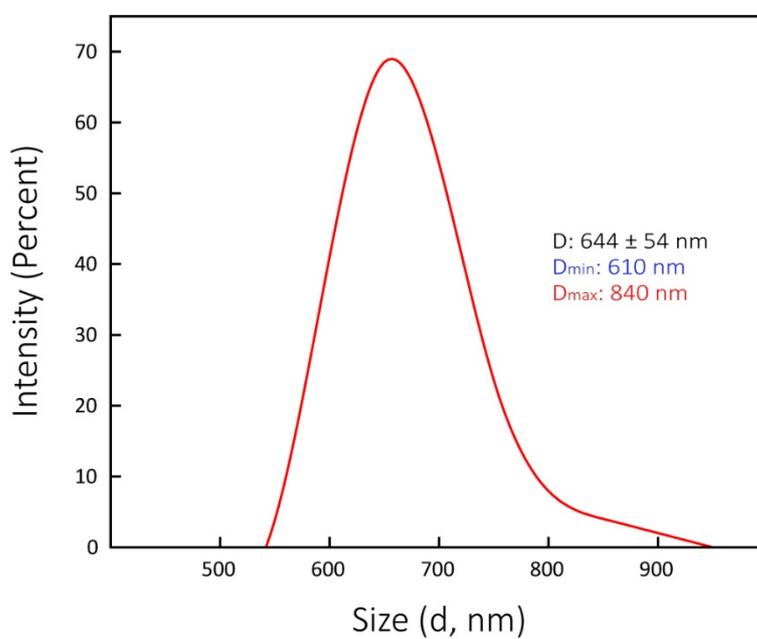


Fig. S2 Particle size and size distribution of silica nanoparticles (SiNPs) via SEM images analysis.

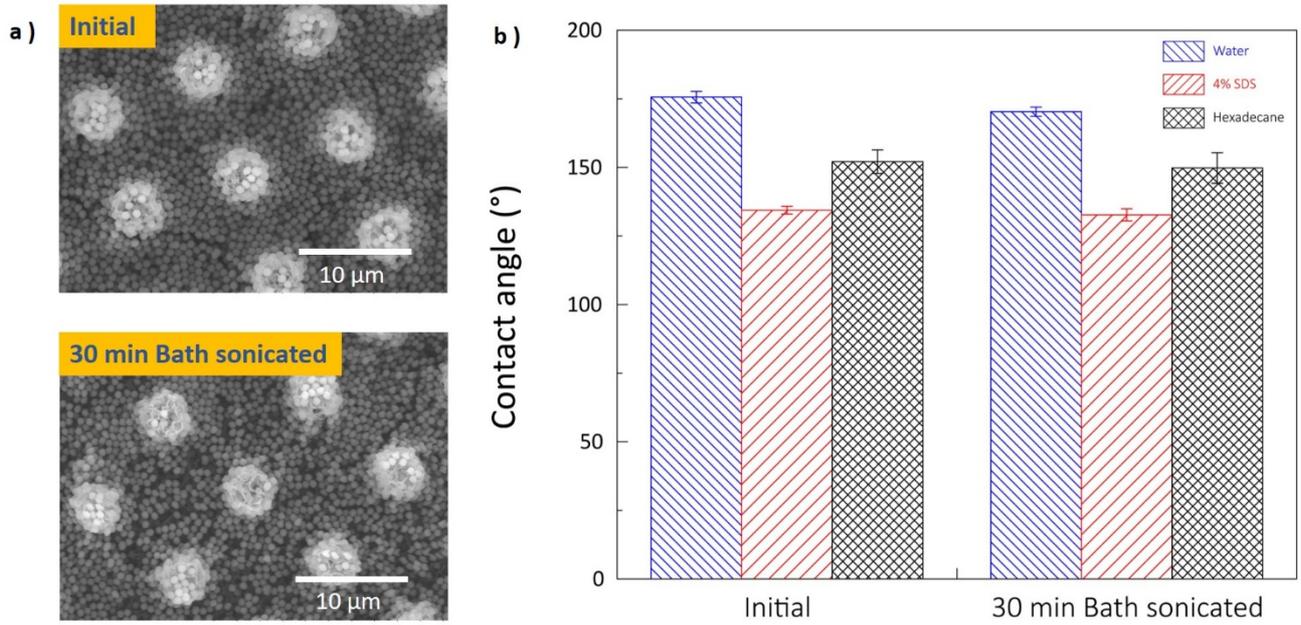


Fig. S3 Contact angles of DI water, 4% SDS and hexadecane on the SiNPs-MP-PVDF membrane surface and surface morphology measured after surface modification (labeled as initial) and after the SiNPs-MP-PVDF was subjected to the bath sonication for 30 min. Error bars represent standard deviations of five independent measurements.

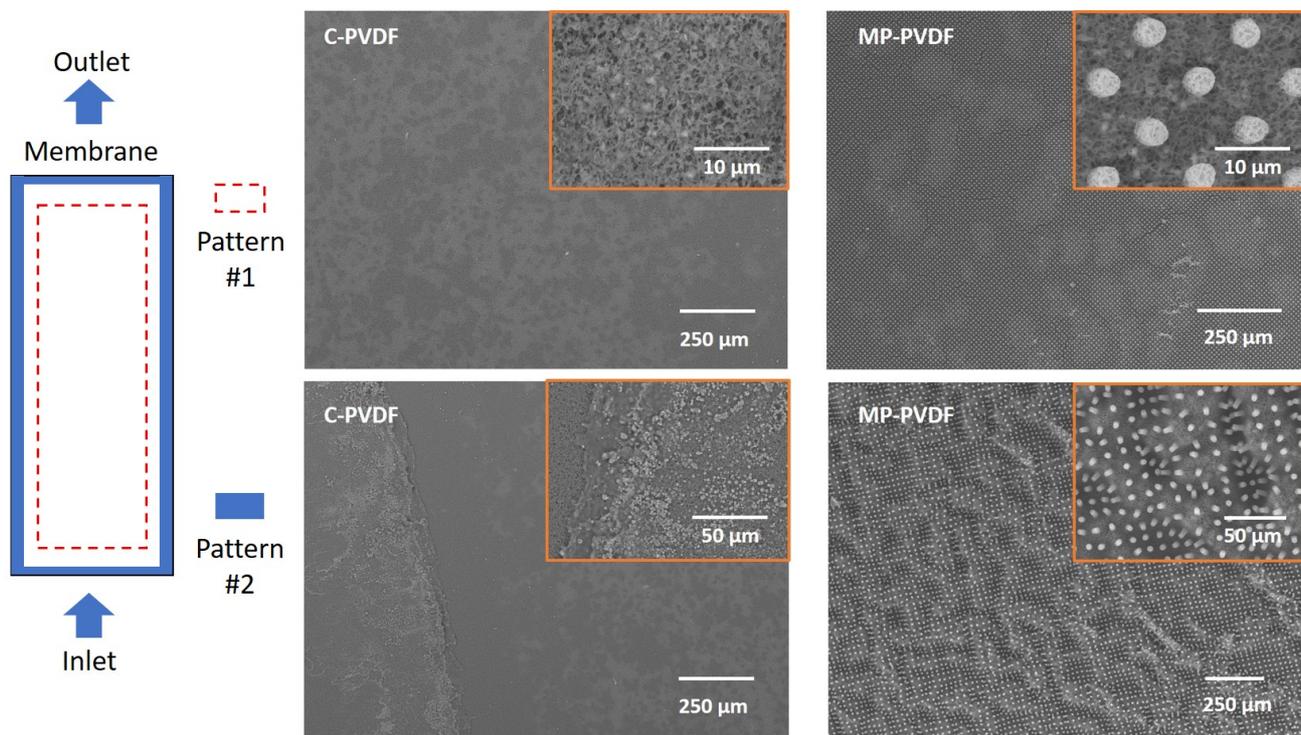


Fig. S4 Membrane autopsy after Casein fouling test for C-PVDF and MP-PVDF membrane based on module location.

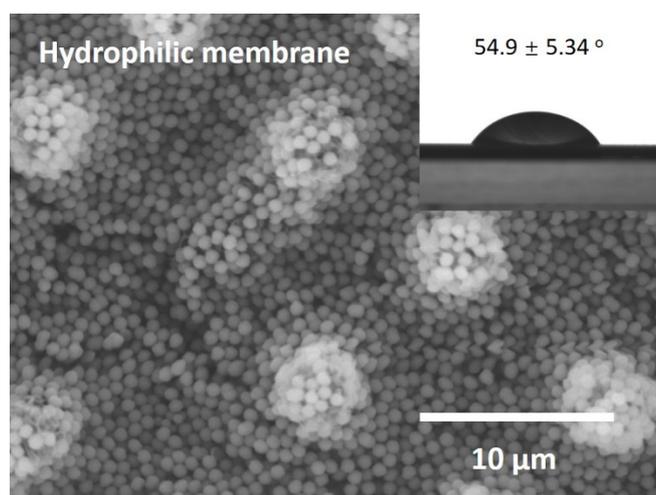


Fig. S5 SEM image and water contact angle of MP-PVDF membrane with SiNPs but not 17-FAS coating

References

- [1] C. Boo, J. Lee, M. Elimelech, Engineering surface energy and nanostructure of microporous films for expanded membrane distillation applications, *Environmental science & technology* 50 (2016) 8112-8119.
- [2] D.K. Owens, R. Wendt, Estimation of the surface free energy of polymers, *Journal of applied polymer science* 13 (1969) 1741-1747.
- [3] H.S. Grewal, C. Il-Joo, O. Jae-Eung, Y. Eui-Sung, Effect of topography on the wetting of nanoscale patterns: experimental and modeling studies, *Nanoscale* 6 (2014) 15321-15332.
- [4] W. Bing-Bing, W. Hua-Ping, Z. Zheng, D. Chen-Chen, C. Guo-Zhong, Thermodynamic analysis of stable wetting states and wetting transition of micro/nanoscale structured surface, *ACTA PHYSICA SINICA* 64 (2015).
- [5] H. Wu, K. Zhu, B. Wu, J. Lou, Z. Zhang, G. Chai, Influence of structured sidewalls on the wetting states and superhydrophobic stability of surfaces with dual-scale roughness, *Applied surface science* 382 (2016) 111-120.
- [6] A. Kaynak, T. Mehmood, X. Dai, K. Magniez, A. Kouzani, Study of radio frequency plasma treatment of PVDF film using Ar, O₂ and (Ar+ O₂) gases for improved polypyrrole adhesion, *Materials* 6 (2013) 3482-3493.
- [7] R. Zheng, Y. Chen, J. Wang, J. Song, X.-M. Li, T. He, Preparation of omniphobic PVDF membrane with hierarchical structure for treating saline oily wastewater using direct contact membrane distillation, *Journal of membrane science* 555 (2018) 197-205.