

Ultrasound-assisted dopamine polymerization: rapid and oxidizing agent-free polydopamine coatings on membrane surfaces

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Materials

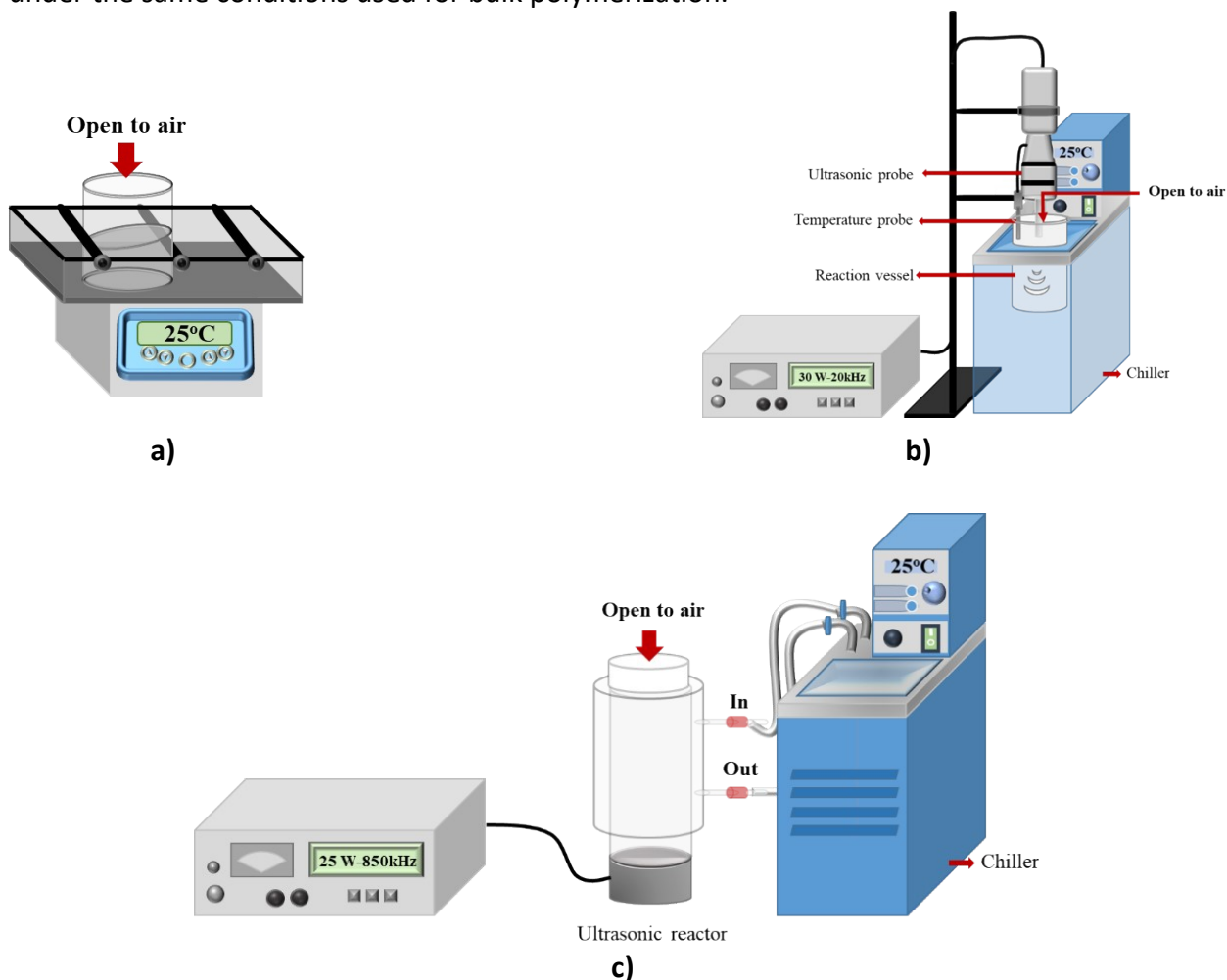
Dopamine hydrochloride, Tris-HCl buffer, L-ascorbic acid, Cysteine, nitrotetrazolium blue chloride (NBT) were purchased from Sigma-Aldrich. Polysulfone (PSF) (Mw= 35 kDa) purchased from Sigma-Aldrich, and Sulfonated polyethersulfone (SPES) (Mw= 80 kDa, Sulfonation degree (SD)<30%) kindly donated by Konishi Chemicals, Japan, were used to prepare flat sheet membranes. 1-methyl-2-pyrrolidone (NMP, 99.5%) and N, N-Dimethylacetamide (DMAc, 99%) purchased from Fluka and Sigma-Aldrich, were used to dissolve the polymers. NaOH, HCl, polyethylene glycol (PEG: 35 kDa) and polyethylene oxide (PEO: 100 kDa) were purchased from Sigma-Aldrich. The water/paraffin emulsion used to determine the fouling resistance of the membranes was kindly supplied by Işıksan Kimya Corporation and Polyester non-woven fabric (05TH-100) (thickness: 161 μm and base weight: 100 g/m²) was purchased from Hirose Paper Mfg. Co. Ltd, Japan, and used as a support layer for manufacturing the membranes. All chemicals were used without further purification and solutions were prepared using deionized (18.2 M Ω cm) water.

Preparation of Flat Sheet Membranes

PSF and PSF-SPES blend membranes were prepared by the non-solvent induced phase inversion technique. The polymers were dried in a vacuum oven at 80 °C for 24 h to remove moisture. Dried PSF and the PSF:SPES blend (blending ratio is 3:1) were dissolved in NMP and DMAc:NMP mixture (DMAc:NMP ratio of 2:1), respectively by stirring at 100 rpm for 24 h. In order to eliminate air bubbles, solutions rested for 24 h without stirring and then were cast on a clean glass plate and non-woven with the help of an automated film applicator (Sheen Instrument Ltd., model number: 1133N). The initial thickness of the cast membranes was adjusted using a four-sided applicator with a gap size of 200 μm . Following casting, the glass plate was immediately immersed into the coagulation bath including only deionized (18.2 M Ω cm) water at 25 °C. The polymer concentration in both casting solutions was adjusted to 20 wt.%.

Conventional and Ultrasound-Assisted Polymerization of Dopamine

Dopamine hydrochloride (2 mg/mL) was dissolved in Tris-HCl buffer solution (10 mM, pH 8.5, 25 °C). For conventional polymerization (Scheme 1a), the reaction solution (100 mL) was gently shaken at 70 rpm and room (25 °C) temperature. For ultrasound-assisted polymerization, an ultrasonic horn (Scheme 1b) and an ultrasonic reactor (Scheme 1c) operated at 30 W (frequency 20 kHz) and 25 W were used. In both experimental setup, the dopamine solution (100 mL) was not stirred, and the temperature was controlled by a chiller. At specific time intervals, the sample was removed to measure the formed polydopamine intensity using UV-vis spectroscopy. For coating the membranes, the sample coupons were immersed in the dopamine solution for 1 h under the same conditions used for bulk polymerization.



Scheme 1 a) Conventional polymerization set-up, **b)** Ultrasonic horn polymerization set-up **c)** Ultrasonic reactor polymerization set-up

Characterization of Membranes

The chemical structure of the bare and modified membranes was determined by Attenuated Total Reflectance Fourier Transformed Infrared Spectrometer (ATR-FTIR), (Perkin Elmer). Spectra were collected at ambient temperature over a scanning range of 4000-650 cm^{-1} with a resolution of 4.0 cm^{-1} . The water contact angle of the membranes was measured (Attension Optical tensiometer) with a 5 μL water droplet ($n=5$). The surface free energy (SFE) calculations based on the OWRK method (Owens, Wendt, Rabel and Kaelble) were carried out using the contact angle measurements of water and diiodomethane. The X-ray photoelectron spectra (XPS, Thermo Scientific) analysis at the emission angle of 0° was used to determine the elemental composition of the membranes ($n=3$). The surface morphology of the membranes was characterized using a scanning electron microscope (SEM) (FEI Quanta 250 FEG). Before taking the images, the membrane surfaces were coated with gold nanoparticles with a Magnetron Sputter Coating Instrument. The surface roughness of the membranes (arithmetic mean (R_a) and root-mean-square (R_q)) was determined using an atomic force microscope (AFM) (MMSPM Nanoscope 8, Bruker). $5 \times 5 \mu\text{m}^2$ sample area was scanned at a rate of 1 Hz using tapping mode in the air at room temperature by the TAP150 model tip (Bruker) ($n=3$). Prior to analysis, all the membranes were dried in a vacuum oven (Memmert) at 25°C . (n is the number of repeated experiments). The surface free energy (SFE) values were determined by the OWRK method.¹ Equation 1 describes the surface tension of the solid (σ_s) with respect to the interfacial tension between solid and liquid (σ_{sl}) and the surface tension of the liquid (σ_l) by the Young equation:

$$\sigma_s = \sigma_{sl} + \sigma_l \cdot \cos\theta \quad (1)$$

The OWRK method requires contact angle measurements with at least two liquids, one polar (water) and the other nonpolar (diiodomethane) to calculate σ_s and the σ_l from Equation 2.

$$\sigma_l = \sigma_l^d + \sigma_l^p, \quad \sigma_s = \sigma_s^d + \sigma_s^p \quad (2)$$

where σ_l^d/σ_s^d and σ_l^p/σ_s^p are the disperse and polar components of the liquid and solid, respectively. The OWRK model uses geometric mean to combine the solid and liquid contributions as follows:

$$\sigma_{sl} = \sigma_s + \sigma_l - 2 \left(\sqrt{\sigma_s^d \cdot \sigma_l^d} + \sqrt{\sigma_s^p \cdot \sigma_l^p} \right) \quad (3)$$

Substituting this term for σ_{sl} in the Young equation (1) and solving the unknowns results in a linear expression.

$$y = mx + c \quad (4)$$

where

$$y = \frac{1 + \cos\theta}{2} \frac{\sigma_l}{\sqrt{\sigma_l^d}}, \quad x = \sqrt{\frac{\sigma_l^p}{\sigma_l^d}}, \quad m = \sqrt{\sigma_s^p}, \quad c = \sqrt{\sigma_s^d} \quad (5)$$

Thus, plotting y versus x enables the calculation of σ_s^p from the slope, and σ_s^d from the intersection with the vertical axis.

Membrane Filtration Performance

The filtration performance of membranes was determined by a 50 mL dead-end stirred cell (Millipore, Amicon Stirred Cell 8050) with an effective area of 13.4 cm². Before filtration, membrane coupons were compacted until a constant flux is reached. Next, pure water was filtered at 1 bar and collected permeate volume was recorded for specific time intervals. The volumetric flux was calculated from the slope of the permeate volume vs. time graph and converted to hydraulic pure water permeability (PWP) using following equation:

$$PWP = \frac{\Delta V}{A \Delta t \Delta P} \quad (6)$$

where ΔV is the volume of permeated water (L), A (m²) is the membrane area, Δt (h) is the permeation time and ΔP (bar) is the transmembrane pressure difference applied through the membrane. To determine the rejection characteristics of the membranes, 1 g/L aqueous solutions of 35 kDa PEG and 100 kDa PEO were filtered at 1 bar. The concentrations of the permeate, retentate and feed solutions were measured by Rudolph-J357 Automatic Refractometer. The solute rejection (%) was calculated using the equation:

$$R(\%) = \left(1 - \frac{C_p}{\frac{C_f + C_r}{2}} \right) \times 100 \quad (7)$$

where C_p , C_r and C_f are the concentrations of permeate, retentate and feed solution, respectively. To eliminate concentration polarization, the solution was stirred at 300 rpm. The fouling behaviour of the membranes was evaluated by filtering of water/paraffin emulsion at 1 bar. Following filtration, the membrane coupons were rinsed with pure water for 30 min and water flux was re-measured to calculate the flux recovery ratio (FRR).

$$FRR(\%) = \left(\frac{J_R}{J_W} \right) \times 100 \quad (8)$$

where J_W and J_R are the pure water fluxes of the clean and the washed membranes. The experiments were carried out at room (25 °C) temperature. ($n=3$ where n is the number of repeated experiments).

The hydraulic resistance of the porous bare and PDA coated membranes is defined as follows:²

$$R_i = \frac{\Delta p}{\mu J_i} \quad (9)$$

where Δp is the transmembrane pressure, μ is the viscosity of the feed solution, J_i is the steady-state water flux and R_i is the hydraulic resistance of the membrane.

Equation 9 can be employed for coated membranes to quantify the effect of PDA coating on membrane flux. The coating layer adds resistance to the membrane's overall hydraulic resistance, and it can be expressed as:

$$J_{PDA} = \frac{\Delta p}{\mu(R_0 + R_{PDA})} \quad (10)$$

where J_{PDA} is the pure water flux of PDA coated membrane, R_0 is the hydraulic resistance of bare membrane, R_{PDA} is the hydraulic resistance of the PDA coated membrane. By combining equations 9 and 10, R_{PDA} can be calculated as follows:

$$R_{PDA} = \frac{\Delta p}{\mu} \left(\frac{1}{J_{PDA}} - \frac{1}{J_0} \right) \quad (11)$$

where J_0 is the steady-state pure water flux of bare membrane.

Stability of Coating Layer

The chemical stability of the PDA-coating layer on membranes was evaluated in a strong acidic and alkaline environment. To this end, coated membranes with 1.5 cm x 1.5 cm sizes were immersed in 5 mL 0.1 M NaOH and 0.1 M HCl for 24 h. Next, the leached PDA in solution was quantified by measuring the absorbance of the solution at 420 nm with UV-vis spectroscopy.³

Table S1. Peak area of the bare and PDA coated membranes.

Membranes	Peak Area		
	$\nu(\text{N-H})$ and $\nu(\text{O-H})$ peaks at 3300 cm^{-1}		
	Bare	CP	USP
PSF	41.1	400.5	515.2
PSF-SPES	345.7	2030.1	3918.4

Table S2 Contact angles of the bare and PDA coated membranes.

Membranes	Contact Angle (°)			The change in Contact Angle (%)	
	Bare	CP	USP	$(\theta_B - \theta_{CP})/\theta_B$	$(\theta_B - \theta_{USP})/\theta_B$
PSF	97.4±0.2*	76.9±0.6*	69.9±0.6*	21.0	28.2
PSF-SPES	72.9±0.8**	58.9±0.8**	46.8±0.1**	19.1	35.9

θ_B , θ_{CP} , θ_{USP} are the contact angle of bare, CP, and UPS membranes, respectively.

*represents statistically significant difference ($p < 0.05$) in contact angle of the bare and coated PSF membranes.

**represents statistically significant difference ($p < 0.05$) in contact angle of the bare and coated PSF-SPES membranes.

Table S3. Surface free energy and its components of the PDA coated membranes.

Membranes	Coating technique	Contact Angle (°)		SFE components (mN/m)			$(\sigma_s^p - \sigma_{s0}^p)/\sigma_{s0}^p$	$(\sigma_s - \sigma_{s0})/\sigma_{s0}$
		Water	Diiodomethane	σ_s	σ_s^d	σ_s^p		
PSF	CP	76.9±0.6	32.2±0.4	47.1	43.3	3.8	250.9	0.080
	USP	69.9±0.6	31.7±0.4	49.9	43.5	6.4	427.5	0.146
PSF-SPES	CP	58.9±0.8	29.6±0.3	55.7	44.4	11.3	1.2	0.130
	USP	46.8±0.1	31.3±0.5	61.9	43.7	18.2	2.6	0.255

σ_{s0} : The total surface free energies of the modified membranes.

σ_{s0}^d and σ_{s0}^p : Dispersive and polar components of the surface free energies of the modified membranes.

$(\sigma_s - \sigma_{s0})/\sigma_{s0}$ describes the change in σ_s of the PDA coated membranes in comparison to that of the bare one.

A high value of $(\sigma_s - \sigma_{s0})/\sigma_{s0}$ means that the total surface free energy of the membranes after the PDA coating increases.

Table S4. Surface free energy and its components of the bare membranes.

Membranes	Contact Angle (°)		SFE components (mN/m)		
	Water	Diiodomethane	σ_{so}	σ_{so}^d	σ_{so}^p
PSF	97.4±0.2	31.6±0.5	43.6	43.5	0.015
PSF-SPES	72.9±0.8	29.8±0.4	49.3	44.3	5.048

σ_{so} : The total surface free energies of the bare membranes.

σ_{so}^d and σ_{so}^p : Dispersive and polar components of the surface free energies of the bare membranes.

Table S5. XPS analysis of the bare and PDA coated membranes.

Membranes	Coating technique	S%	C%	O%	N%	N/S	C/O
PSF	*	3.86	82.74	13.4	-	-	6.17
	CP	3.00	76.82	16.14	4.04	1.35	4.76
	USP	1.82	74.83	19.11	4.24	2.33	3.92
PSF-SPES	*	7.86	71.12	21.02	-	-	3.38
	CP	4.91	73.61	19.53	1.95	0.40	3.77
	USP	3.73	69.03	21.88	5.36	1.44	3.15

* Bare membrane.

Table S6. Surface roughness of the bare and PDA coated membranes.

Membranes	R_a (nm)	R_q (nm)
PSF	2.53±0.16	3.15±0.19
PSF_CP	5.41±1.45	7.22±2.01
PSF_USP	3.70±0.76	4.67±0.98
PSF-SPES	3.34±0.01	4.26±0.24
PSF-SPES_CP	8.52±3.18	12.01±4.89
PSF-SPES_USP	4.03±0.45	5.23±0.70

Table S7. Influence of PDA deposition on membrane hydraulic resistance.

Membranes	Hydraulic Resistance x 10^{-10} (m^{-1})	
	PSF	PSF-SPES
Bare	415.7	39.4
PDA coated membranes with CP	1547.8	10.7
PDA coated membranes with USP	3549.9	69.1

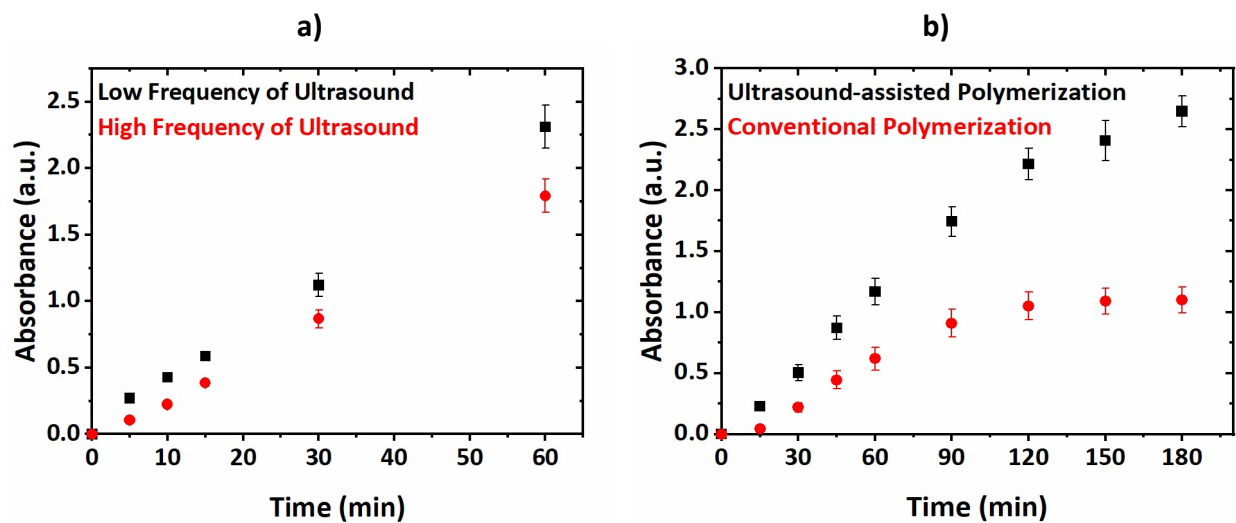


Fig. S1 The rate of dopamine polymerization **a)** Effect of ultrasound frequency on the absorbance of dopamine solution **b)** Absorbance of blue NBT formazan at 560 nm as function of time.

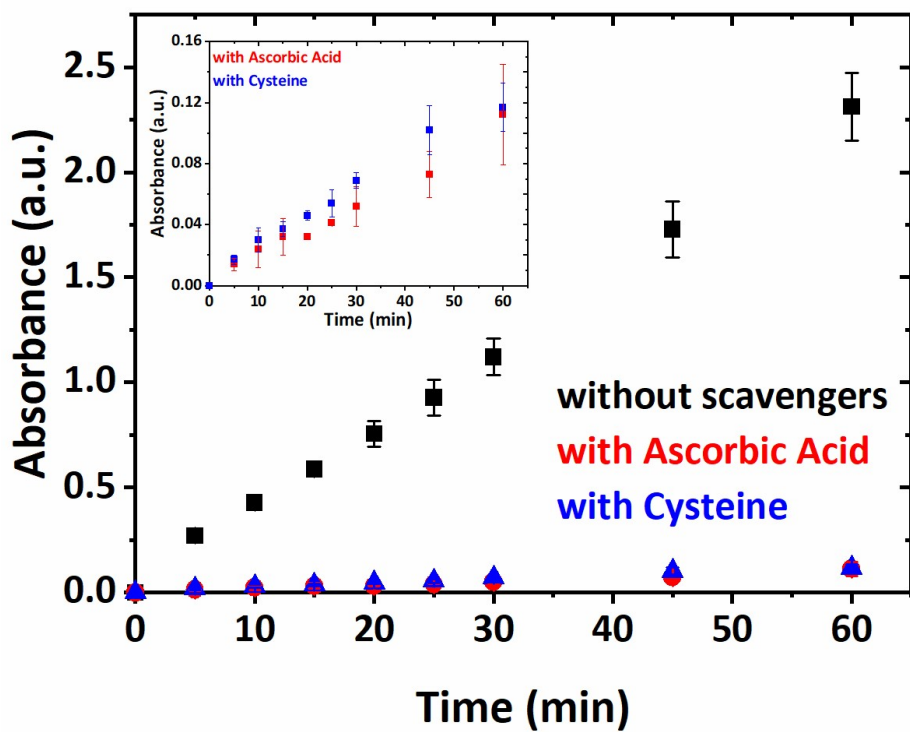


Fig. S2 The effect of scavengers on the absorbance of dopamine solution.

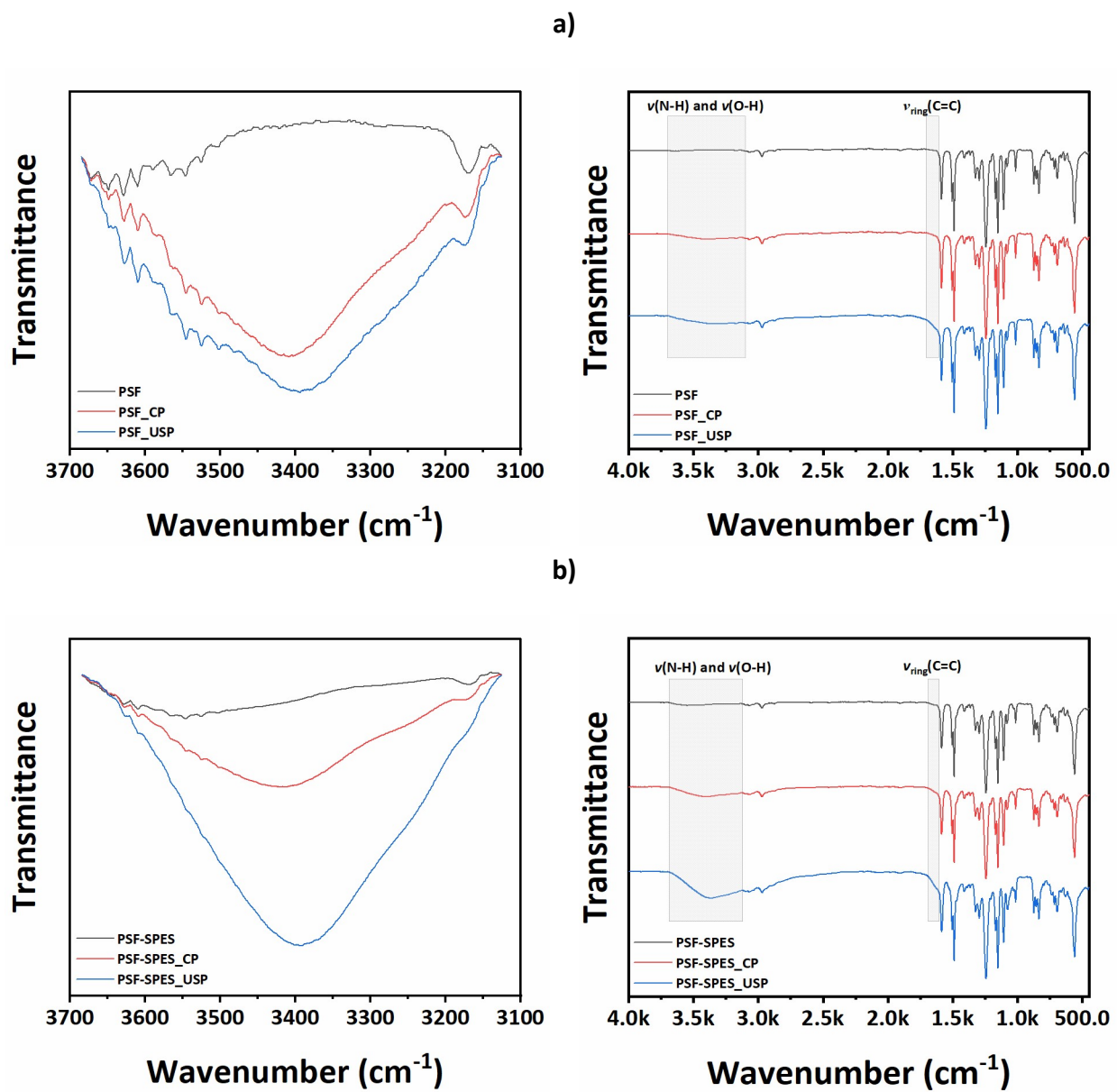


Fig. S3 ATR-FTIR spectra of the bare and modified a) PSF and b) PSF-SPES membranes.

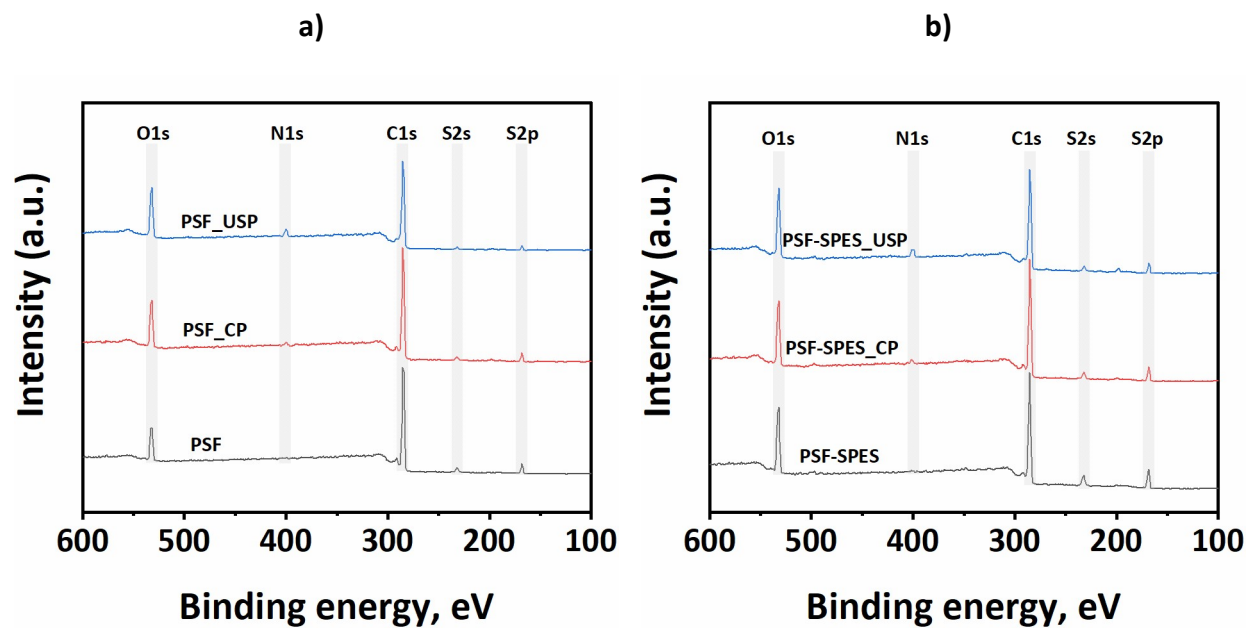
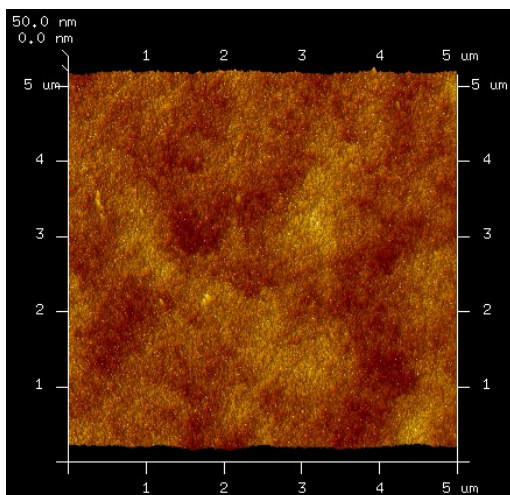
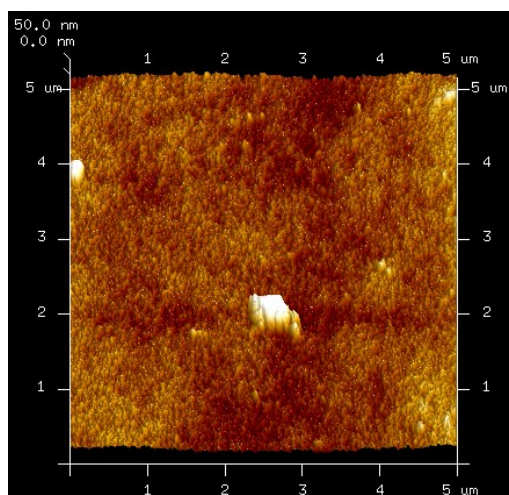


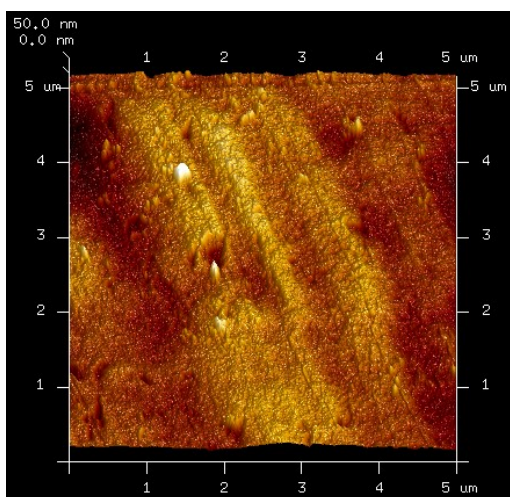
Fig. S4 The general survey of the bare and modified **a)** PSF and **b)** PSF-SPES membranes.



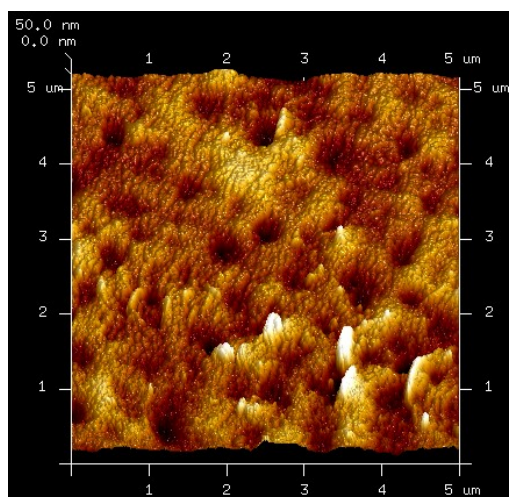
PSF



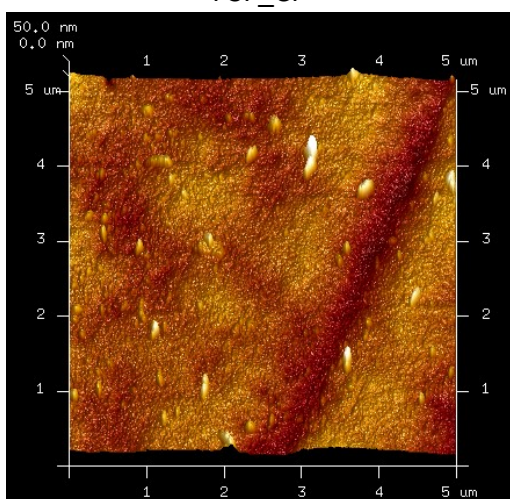
PSF-SPES



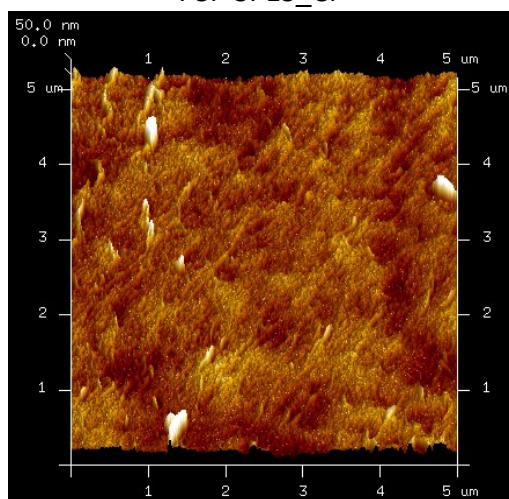
PSF_CP



PSF-SPES_CP

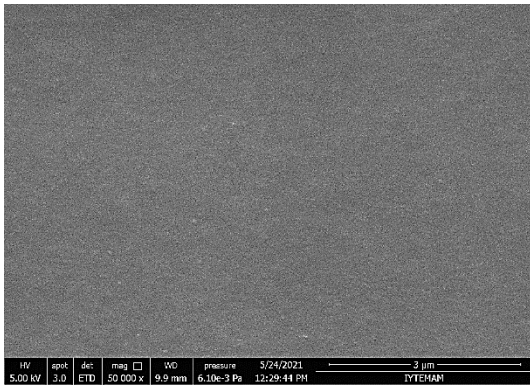


PSF_USP

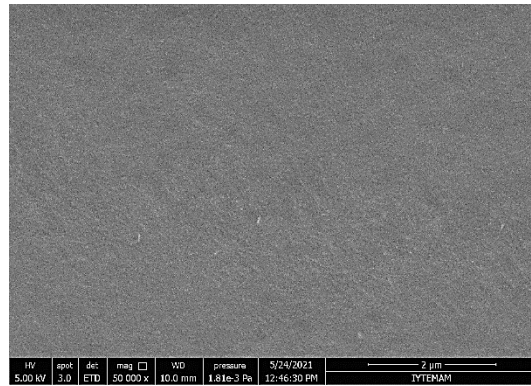


PSF-SPES_USP

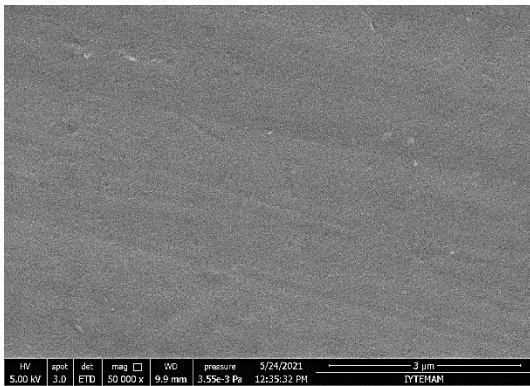
Fig. S5 AFM images of the bare and PDA coated membranes.



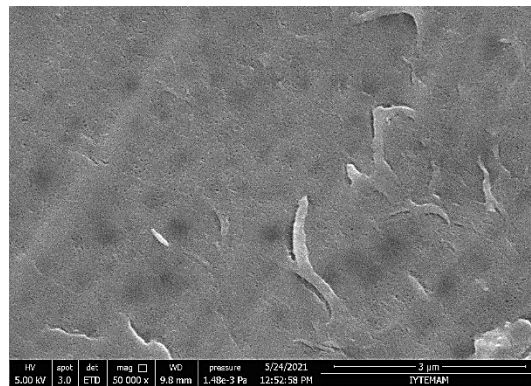
PSF



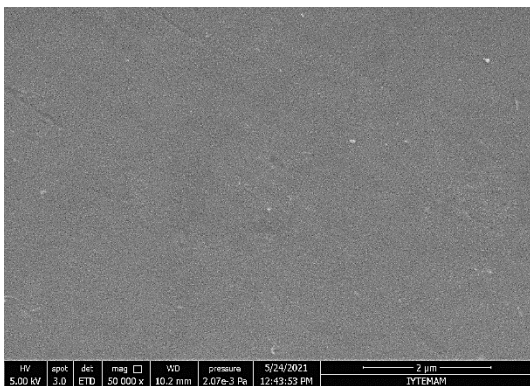
PSF-SPES



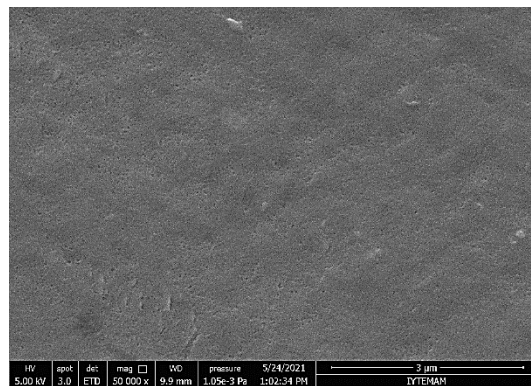
PSF_CP



PSF-SPES_CP



PSF_USP



PSF-SPES_USP

Fig. S6 Surface SEM images of the bare and PDA coated membranes.

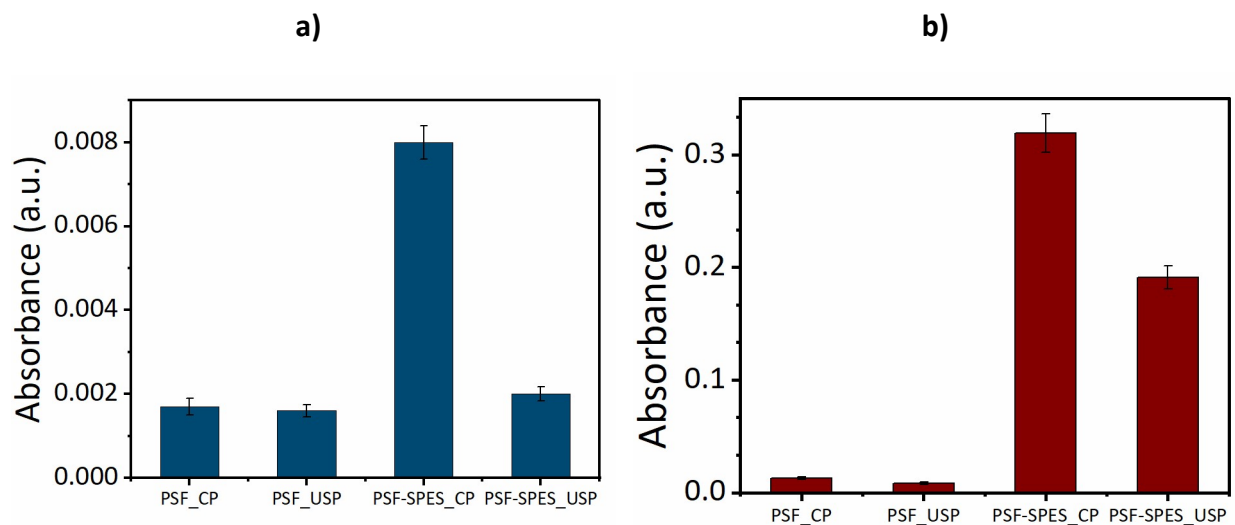


Fig. S7 UV-visible spectra of the eluent of PDA coated membranes immersed in strongly acidic and alkaline solutions: **a)** 0.1 M HCl, **b)** 0.1 M NaOH solutions. The immersion time is 24 h.

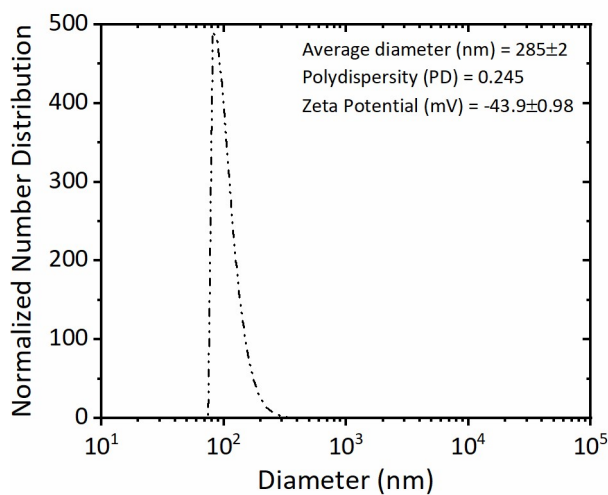


Fig. S8 Size distribution and zeta potential of water/paraffin emulsion used as synthetic foulant in the experiments.

Notes and references

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