## **Supporting Information**

Ultradurable Underwater Superoleophobic Surface by Vapor-

synthesized Layered Polymer Nanocoatings for Highly Efficient

Oil-water Separation

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## **Experimental Details**

*Materials*: Precursors of isocyanatoethyl methacrylate (97%), hydroxyethyl methacrylate (98%) and *tert*-butyl peroxide (TBP, 98%) were purchased from TCI (China), J&K (China) and TCI (Japan), respectively. Aminostyrene (AS, 96%) was purchased from J&K (China). All chemicals were used as received without further purification. PVDF membranes were purchased from Taoyuan Chemicals (China).

*Initiated chemical vapor deposition*: Vapor deposition of polymer thin films was conducted in a custom-built reactor equipped with a parallel array of Nichrome filament as described previously.<sup>1</sup> Precursors of IEM, HEMA and TBP were vaporized at 55 °C, 75 °C, and 30 °C, respectively, and metered into the reactor by needle valves (Swagelok) with a predetermined order as listed in Table S1, resulting in the sequential deposition of the three layers of film. The filament was resistively heated to around 200 °C during deposition and the samples were maintained at about 30 °C controlled by the circulating water equipped on the backside of the deposition stage. Both temperatures were monitored by directly attached thermal couples. During each stage of deposition, a reference wafer was placed close to the fabric or membrane. The thickness of each layer of the film on the reference wafer was monitored in situ by an interferometry system (Table S1) with a 633nm He-Ne laser (JDS Uniphase).<sup>2</sup> The corresponding coating thickness on the wafer to each cycle on the interferometer was previously calibrated using variable-angle spectroscopic ellipsometry. The actual thickness of coatings on wool fabric and membrane varies from coatings on reference wafer, due to the larger specific area of these porous substrates, which consumes more monomer molecules per apparent area than their planar counterpart in order to produce the same thickness of coating. The precise thickness of coatings on wool or membrane was measured under SEM. After deposition, the synthesized coating was annealed in a vacuumed oven at 80 °C for 10

h to facilitate the reactions between isocyanate groups with hydroxyl groups in the middle layer and the functional groups on wool surface. As PHEMA chains deposited at the third stage may not be all grafted to the coating surface, the coated fabrics and membranes were thoroughly rinsed and soaked in DI water for 30 minutes to remove ungrafted PHEMA chains.

*Characterizations*: Fourier transform infrared (FT-IR) measurements were implemented using a Nicolet 6700 FT-IR spectrometer equipped with a DTGS detector under the transmission mode. All FT-IR measurements were conducted on coatings deposited on the reference wafer, while the compositions of coating on fabrics and membranes are similar. X-ray photoelectron spectroscopy (XPS) was carried out using a Shimadzu Axis Utltradld spectroscope with a Mg-Ka radiation source. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) were implemented using a Hitachi S-4800 SEM. The EDS elemental analysis was conducted on the cross section of a layered coating deposited on a wool fiber with a thickness of approximately 620 nm.

In-air water contact angle and underwater oil contact angle (OCA) were measured using a goniometer (Kruss DSA 100, Germany) equipped with an automated liquid dispenser at room temperature. For underwater OCA measurements, the coated substrates were first fixed underwater. A 10  $\mu$ L oil droplet was then placed underneath the substrate using a syringe and the contact angle was recorded and calculated. The contact angle of each sample was averaged from five measurements on different spots. For the measurement of underwater OCAs in different pH solutions, 10  $\mu$ L silicone oil drops were placed in aqueous solutions with the pH of 0, 2, 4, 10, 12 and 14. The acidic solutions contain HCl and the basic solutions contain NaOH with the corresponding concentrations. NaCl solution was prepared by dissolving NaCl in water with the concentration of 3.4%, which is close to the salinity in seawater. The residue oil content in the

filtrated water was analyzed using a Total Organic Carbon (TOC) Analyzer (MultiN/C 2100, Analytik Jena).

*Adhesion test*: The adhesion strength of coatings on fabrics was tested following a revised version of ASTM D3359. A piece of coated wool fabric cut to 2 X 2 cm<sup>2</sup> was annealed and then ultrasonicated in deionized (DI) water for 2 h, followed by boiling in DI water for 2 h. The fabric was then dried in air, and a scotch tape (3M, Scotch 600) was pressed on the top with a uniform pressure across the surface. The tape was then peeled off and the surface morphology of the fabric was observed under SEM. Tape test was also conducted on a reference PHEMA-coated wool fabric, but without sonication or boiling, as PHEMA dissolves in water.

*Durability test:* Durability test includes repetitive washing and sandpaper abrasion of coated fabric. One washing cycle consisted of washing the coated fabric in a flask with DI water under 200 rpm for 15 min, followed by drying using a hair-dryer. One abrasion cycle consisted of dragging the coated fabric under 5 kPa pressure on a 800-grit sandpaper by loading a 100 g standard weight for 20 cm with a moving speed of 4 cm s<sup>-1</sup>. After certain cycles of washing or abrasion, the fabric was used to separate 10 ml of vegetable-oil-water mixture. The residue oil content in the filtrate was then analyzed using TOC analyzer.



**Fig. S1** FT-IR spectra of as-synthesized PIEM, poly(isocyanatoethyl methacrylate-*co*-aminostyrene) (P(IEM-*co*-AS)), and poly(aminostyrene) (PAS) using iCVD (deposition conditions are listed in Table S2). The spectrum of P(IEM-*co*-AS) shows absorption bands of – C=O and -N=C=O stretching from IEM, along with the stretching absorption bands of benzene rings from aminostyrene moiety.<sup>3</sup> The reaction between isocyanate group from IEM and amino group from AS moiety is evidenced by: 1) the drastic reduction of the intensity ratio between – N=C=O stretching (2276 cm<sup>-1</sup>) and -C=O stretching (1728 cm<sup>-1</sup>) compared to that of PIEM homopolymer; and 2) the appearance of the absorption bands at 1660 cm<sup>-1</sup> and 1550 cm<sup>-1</sup> assigned to the -C=O stretching and -N-H bending from the generated urea groups.<sup>4</sup>



**Fig. S2** EDS elemental analysis of a 620 nm P(IEM-*L*-HEMA) film coated on a wool fiber along the direction perpendicular to the film surface. The film has the same three-layered structure as the thin coating in Table S1, except the thickness of each layer is larger. The X-axis represents the distance of the analyzed position to the wool surface. As the theoretical atomic concentration of O (27.3%) in IEM repeating unit is slightly lower than that of HEMA (33.3%) and the atomic concentration of N in IEM (9.1%) is a little higher than that of HEMA (0%) (excluding H), higher O content and lower N content thus indicates a higher concentration of HEMA moiety. The elemental content distribution qualitatively reveals a higher N and lower O content close to the top surface of the coating, indicating a higher HEMA concentration; thereby proving a PIEM-enriched primer and a HEMA-enriched surface.



**Fig. S3** Optical and SEM images of P(IEM-*L*-HEMA)-coated a) Si wafer and c) wool fibers; and PHEMA-coated b) Si wafer and d) wool fibers after adhesion test.



**Fig. S4** The permeation flux of the P(IEM-*L*-HEMA)-coated wool fabric separating vegetableoil-water mixture after different cycles of separation, washing and drying, and abrasion. The left columns represent the initial flux, while the middle column represents the flux after 50 cycles of separation, washing and drying, and abrasions. The right columns represents the flux after 100 cycles of separation, 150 cycles of washing and drying, and 150 cycles of abrasion.

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**Fig. S5** SEM image of P(IEM-*L*-HEMA)-coated wool fibers after abrasion against sandpaper for 150 cycles.



**Fig. S6** SEM images of P(IEM-*L*-HEMA)-coated PVDF membranes after a) 1 h sonication and b) 1 h boiling in DI water. The white dashed lines indicate the coatings wrapping around the fiber.



**Fig. S7** The permeation flux (striped) of coated membranes after 1 h sonication or boiling in DI water separating toluene-in-water emulsion, and the corresponding residue oil content (blank) in the filtrates.

Stage	Flow rate (sccm)			Pressure	Deposition	Estimated coating	
	IEM	HEMA	TBP	(mTorr)	time (min)	reference wafer*	
Stage 1	0.6	0	0.6	200	12	~200 nm	
Stage 2	0.2	1.2	0.6	300	15	~400 nm	
Stage 3	0	1.2	0.6	300	8	~100 nm	

**Table S1.** Precursor flow rate, deposition pressure, and deposition time during the three deposition

 stages of P(IEM-*L*-HEMA) film.

\* The actual thickness of each layer of coatings on wool and PVDF membrane is much less than the thickness on planar wafer as measured from SEM images due to the larger specific surface area of porous substrate.

**Table S2.** Precursor flow rate and deposition pressure during deposition of different reference films.

Sample		Pressure				
Sample	IEM	HEMA	AS	TBP	(mTorr)	
PIEM	0.6	/	/	0.6	200	
P(HEMA-co-IEM)	0.2	1.2	/	0.6	300	
P(IEM-co-HEMA)	0.6	0.2	/	0.6	300	
PHEMA	/	0.6	/	0.6	200	
P(IEM-co-AS)	0.5	/	0.2	0.6	400	
PAS	/	/	0.2	0.6	200	

**Table S3.** Binding energy and area of each peak resolved from the XPS C1s spectrum of as 

 deposited PIEM film.

Peak number	1	2	3	4	5+5'
Binding energy (eV)	285.0	285.6	286.6	287.2	289.2
Number of carbon atom	2	1	1	1	2
Area (normalized to peak 2)	2.7	1	0.99	0.993	1.8

## **References:**

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- 2. Y. Mao and K. K. Gleason, *Langmuir*, 2004, **20**, 2484-2488.
- 3. J. J. Xu and K. K. Gleason, *Chem. Mater.*, 2010, **22**, 1732-1738.
- 4. N. Risangud, T. R. Congdon, D. J. Keddie, P. Wilson, K. Kempe and D. M. Haddleton, *J. Polym. Sci., Part A: Polym. Chem.*, 2016, **54**, 2698-2705.

Movie S1. Ultralow adhesion of a crude oil droplet on P(IEM-*L*-HEMA)-coated fabric underwater.

Movie S2. Ultralow adhesion of a silicone oil droplet on coated fabric underwater.

Movie S3. Sliding of a vegetable oil droplet on coated fabric underwater.

Movie S4. Separation of free oil-water mixture using coated fabric.

Movie S5. Pristine wool fabric does not show any separation capability.

Movie S6. Separation of oil-in-water emulsion using P(IEM-*L*-HEMA)-coated PVDF membrane.