

## Supplementary Information

### A Switchable Mesh for On-Demand Oil/Water Separation

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#### Experimental Details

**Materials.** Sodium decanoate ( $\text{CH}_3(\text{CH}_2)_8\text{COONa}$ , 99+%) was purchased from Tokyo Chemical Industrial Co. Ltd.; poly(methylhydrosiloxane) ( $((\text{CH}_3)_3\text{SiO}[(\text{CH}_3)\text{HSiO}]_n\text{Si}(\text{CH}_3)_3$ ,  $n \approx 35$ ), ethyl acetate, aluminum tri-sec-butoxide ( $\text{Al}(\text{O-sec-Bu})_3$ ), ethyl acetoacetate (EAcAc), and isopropyl alcohol (i-PrOH) were purchased from Aladdin Chemical Reagent Co. Ltd.; poly(vinyl acetate) (PVAc,  $M_w \sim 17\text{K}$ ) was purchased from J&K Chemical Co. Ltd.; sodium hydroxide, ethanol, chloroform, acetone, and 1,2-dichloroethane were purchased from Sinopharm Chemical Reagent Co. Ltd.; and poly(allyamine hydrochloride) (PAH,  $M_w \sim 15\text{K}$ ) was purchased from Aldrich Chemical Co. Ltd. All chemicals were used as received. The ultrapure water ( $18.2 \text{ M}\Omega \text{ cm}$  at  $25^\circ\text{C}$ ) generated by a PGeneral GWA-UN4 dispensing system was used for all experiments. Commercial stainless steel meshes of various pore sizes were purchased from a local metal materials supplier, cut into  $25 \times 25 \text{ mm}$  pieces, and ultrasonically cleaned in ultrapure water, ethanol, chloroform, acetone, and ultrapure water sequentially, each for 2 min, to get rid of inorganic and organic surface contaminants. The cleaned meshes were dried in an oven at  $120^\circ\text{C}$  for 30 min and then kept at room temperature before testing.

**Poly(methyl sodium silicate) (PMSS) Preparation.** Poly(methylhydrosiloxane) (10 g) was

placed into a 250 mL round bottom flask, and aqueous sodium hydroxide (30.94 g at 20% (w/w)) was added dropwise, with the resulting room temperature mixture subjected to violent agitation by magnetic stirring for 24 h. After pouring the mixture into a separations funnel, the bottom transparent aqueous phase containing PMSS was collected after 1-2 h.

**Porous Alumina Substrate Preparation.** Aluminum-sol (Al-sol) was prepared following a literature procedure:<sup>1</sup> Al(O-*sec*-Bu)<sub>3</sub> (12.316 g) and *i*-PrOH (37.8 g) were stirred together at room temperature over 1 h in a 250 mL round bottom flask. After adding EAcAc (6.507 g), stirring was continued for 3 h more. A mixture of water (3.6 g) and *i*-PrOH (37.8 mL) was then added dropwise to produce Al-sol through hydrolysis. To improve the adhesion of the sol to stainless steel mesh substrates,<sup>2</sup> PVAc (1 g at 18 wt.% in ethyl acetate) was added into the as-prepared Al-sol (9 g), and the mixture stirred for 1 h. The resulting, highly adhesive Al-sol was deposited on a cleaned stainless steel mesh by immersion, and afterwards, the newly coated mesh was heated to 400 °C for 10 min, submerged in boiling water for 10 min, dried, reheated to 400 °C for 10 min more and stored in a desiccator before use.

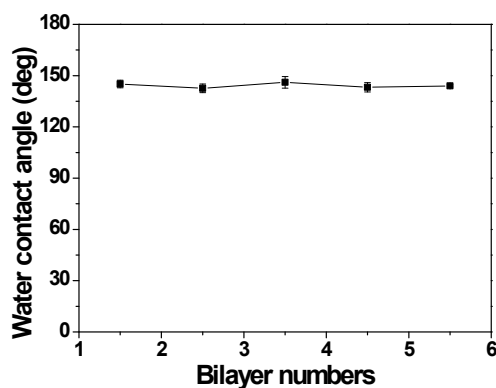
**PEM Deposition.** A (PAH/PMSS)<sub>2.5</sub> PEM film was fabricated on the alumina-coated stainless steel mesh by alternating 15 min dippings of mesh into PAH (1.0 mg/mL, with 1.0 M NaCl present) and PMSS (1.0 mg/mL, with 1.0 M NaCl present, pH=10.6) aqueous solutions. Each dipping was followed by a copious water rinse. At 2.5 deposition cycles, the final dipping is in PAH solution. For ion exchange of the outermost PEM counterion, corresponding to the PAH capping layer, the as-formed PEM was immersed in aqueous sodium decanoate (0.01 M) for 5 min, removed, rinsed with copious water, and dried in a stream of nitrogen.

**Characterization.** Micrographs of meshes were acquired with a FEI XL30 field-emission scanning electron microscope, and X-ray photoelectron (XPS) spectra were obtained by a Thermo-electron ESCALAB250 spectrometer equipped with a monochromatic Al X-ray source (1486.6 eV). XPS spectra were recorded at a 90° takeoff angle (angle between the sample surface and the detector) with 20 eV pass energy. Water contact angles (WCA) and oil contact

angles (OCA) were measured on a Ramé-Hart 200-F1 standard goniometer at room temperature using as probe fluids ultrapure water (5  $\mu$ L), and 1,2-dichloroethane (3  $\mu$ L in air, 5  $\mu$ L in water). A sample was either mounted directly on the sample stage (for in-air measurements) or fixed horizontally in a glass vessel filled with water placed on the stage (for underwater measurements) of the goniometer, and a drop of the probe fluid was carefully placed onto the mesh with a micro-syringe. A digital image of the probe liquid on the sample was captured with a camera and the contact angle was measured from the image. Each reported contact angle is an average of at least five independent measurements. Liquid purity was analyzed with a Thermo Scientific TRACE Gas Chromatograph Ultra AI1310 equipped with a thermal conductivity detector. For the water-removing mode, the separation efficiency is calculated by oil rejection coefficient (R (%)),<sup>3</sup>

$$R(\%) = (1 - C_p/C_o) \times 100$$

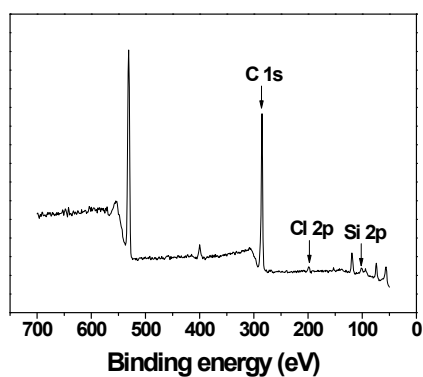
where  $C_o$  and  $C_p$  is the oil content in the original oil/water mixture and in the water permeated, respectively. Analogously, in oil-removing mode the separation efficiency is defined as water rejection coefficient and is calculated from water contents in the mixture and in the oil permeated.



**Figure S1.** Water contact angle measured in air as a function of the number of bilayers of the (PAH/PMSS)<sub>n</sub> PEM carrying decanoate counterion.



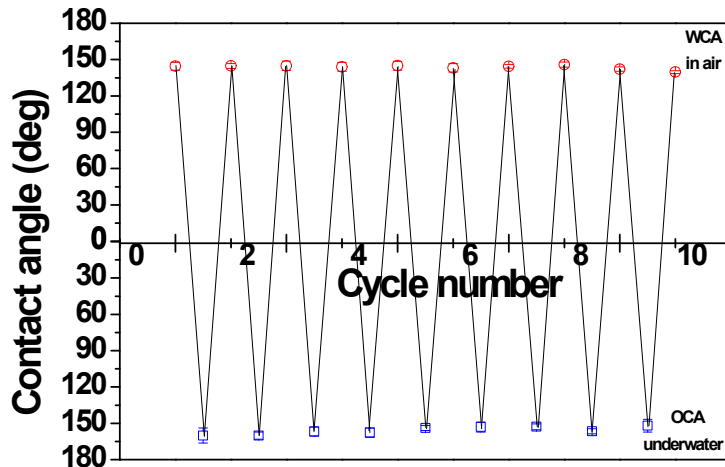
**Figure S2.** Contact angle of 1,2-dichloroethane in air on the PEM-C<sub>10</sub>-mesh of lower than 5°.



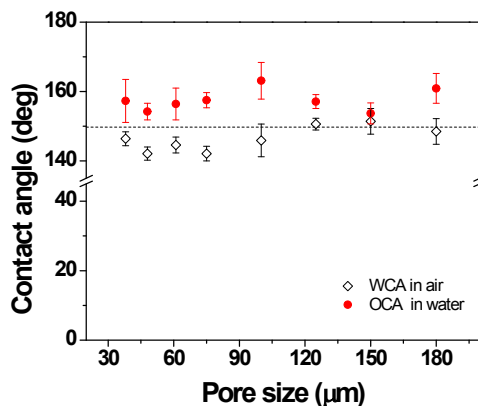
**Figure S3.** XPS survey spectrum of the PEM after the counterion is exchanged with chloride.



**Figure S4.** PEM carrying chloride counterions exhibits hydrophilicity with a WCA of 35°.



**Figure S5.** Switches of the mesh in between oil-removing (red circles) and water-removing (blue squares) modes, showing excellent switch reversibility and robustness of the PEM.



**Figure S6.** WCA in air and OCA underwater as functions of the pore size of the mesh.

Despite lack of previous comment, the mesh pore size plays a key role in the oil/water separations described, with two concerns most obvious. First, the pore size could impact the relevant contact angle, WCA in air for PEM-Cl-mesh and OCA under water for PEM-Cl-mesh. Figure S6, which demonstrates that these contact angles are independent of pore size over the range of accessible pore sizes, puts this first concern to rest. Second, the mesh pore size impacts liquid permeation in at least two ways. If the pore size is too large, under pressure, the liquid mixture simply breaks through the mesh, transporting both oil and water indiscriminately. In the tests reported in Figures 3 and 4, the liquid pressure applied at the mesh is just the hydrostatic

pressure of the liquid mixture, corresponding to a liquid height of a few centimeters. If the pore size is too small, however, the permeate is transported across the mesh slowly, increasing the separation time. The selected pore size, 61  $\mu\text{m}$ , provides a reasonable balance, precluding break through and passing the permeate at a reasonable rate.

## References

- 1 K. Tadanaga, N. Katata and T. Minami, *J. Am. Ceram. Soc.*, 1997, **80**, 1040.
- 2 L. Feng, Z. Zhang, Z. Mai, Y. Ma, B. Liu, L. Jiang and D. Zhu, *Angew. Chem. Int. Ed.*, 2004, **43**, 2012.
- 3 Z. Xue, S. Wang, L. Lin, L. Chen, M. Liu, L. Feng, L. Jiang, *Adv. Mater.*, 2011, **23**, 4270.