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Opposite and Complementary: A Superhydrophobic-Superhydrophilic Integrated System for High-flux, High-efficiency, Continuous Oil/Water Separation

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Fig. S1 Liquid barriers block the separation of oil/water mixtures. (a,b) The separation of water (dyed with methylene blue) and hexane (dyed with Sudan II) on an anti-water (AW) membrane. The formation of a water barrier blocks the further permeation of hexane, so the separation device is tilted to bring the hexane into contact with the separation membrane, and it can then through completely (b), however, this method is only suitable for small amounts of the liquid mixtures; (c) the superhydrophobic AW membrane cannot bear high water pressure, and water permeates the membrane, suggesting the necessity of reducing the liquid pressure.



Fig. S2 Optical photographs of original copper mesh (400 mesh size) (a); PAM coated copper mesh (b) in the wet state; oxidized copper mesh before (c) and after (d) treatment with PFTS.



Fig. S3 The advancing (ϑ_A) and receding (ϑ_R) contact angles of the AW and AO membranes. (a) Water droplet on AW membrane (in air): $\vartheta_A = 143.6^\circ$; $\vartheta_R = 142.3^\circ$; $\vartheta_A - \vartheta_R = 1.3^\circ$. (b) Oil droplet on AO membrane (in water): $\vartheta_A = 145.0^\circ$; $\vartheta_R = 144.1^\circ$; $\vartheta_A - \vartheta_R = 0.9^\circ$. (c) Water droplet on AW membrane (in oil): $\vartheta_A = 150.8^\circ$; $\vartheta_R = 149.0^\circ$; $\vartheta_A - \vartheta_R = 1.8^\circ$. The difference of the advancing and receding contact angles of both membranes is very low, which exhibits ultra-low affinity of AW membrane for water and AO membrane for oil.



Fig. S4 Schematic diagrams of situations in which the integrated device cannot separate oil/water mixtures due to the formation of a liquid barrier. (a) Water forms a liquid barrier that blocks the further permeation of oil. (b) Oil as a liquid barrier hinders the penetration of water.



Fig. S5 Schematic diagrams of situations that the effective separation areas of both membranes are decreased with respect to the original membrane area. The original separation area is occupied by sacrificed area up to about 50%, and the remaining effective separation area is reduced to about 50% or less, which affect the separation speed directly.

Experimental Section

Materials: Copper mesh (400 mesh, Taitong Metal Mesh Ltd., China). Polyacrylamide (PAM, $M_n \ge 3,000,000$), N,N'-methylenebisacrylamide (BIS), and acrylamide were purchased from Sinopharm Chemical Reagent Co., Ltd. 2,2diethoxyacetophenone (DEOP, Adamas Reagent Co., Ltd. China). 1H,1H,2H,2Hperfluorodecyltriethoxysilane (PFTS, Alfa Aesar). Sodium hydroxide (NaOH), ethanol, acetone, hydrochloric acid (HCl) were purchased from Beijing Chemical Works. Potassium peroxydisulfate (K₂S₂O₈, Xilong Chemicals Co., China). All reagents were analytical grade and used without further purification.

Preparation of superhydrophobic nano-needles copper mesh: The commercial copper mesh was cleaned ultrasonically in acetone, ethanol, distilled water, and HCl, respectively to remove the dirt and oxides on the surface. Then the copper mesh was immersed in a mixed aqueous solution of 2.5 M NaOH and 0.1 M K₂S₂O₈ for 30 min, and washed with distilled water. Subsequently, the oxidized copper mesh was treated with PFTS for 3 h.

Preparation of PAM-hydrogel-coated copper mesh: Acrylamide was added into the distilled water and stirred until dissolved completely. Then, BIS, DEOP, and PAM were added into the solution and stirred for 10 h. The cleaned copper mesh was carefully immersed in the prepared solution, so that the solution adhered uniformly on the surface of mesh. Then, the mesh was drawn out horizontally and exposed to ultraviolet (UV) light (365 nm, 50 W). After 5 min, the membrane was washed with distilled water, and the PAM-hydrogel-coated mesh was obtained.

Instrumentation and Characterization: The surface morphology of the as-prepared membranes was characterized by an environmental scanning electron microscope (SEM, Quanta 250 FEG). The surface chemical composition of the oxidized copper mesh was confirmed by means of X-ray diffraction (XRD, XRD-6000). The wettability of the as-prepared membranes was evaluated by the contact angle on an OCA20 instrument (Data-Physics, Germany) at ambient temperature. (The volume of each tested liquid drop was 4 μ L). The oil concentration of the collected water after the separation process was measured by the infrared spectrometer oil content analyzer (OIL480, China). The residual oil was extracted by CCl₄ from the permeated water before analysis. The water concentration in permeated oil was analyzed directly by a Cou-Lo Aquamax.

Oil/water separation experiments: A separation device was assembled with two separation channels. The two prepared membranes were fixed between two steel flanges and installed on the device with an effective separation area of 4.15 cm², respectively.

(1) $\rho_{oil} < \rho_{water}$: A mixture of water (colored by methylene blue) and light oil was poured into the separation device, and then the separation proceeded. The permeated liquids from both membranes were collected with beakers, respectively.

(2) $\rho_{oil} > \rho_{water}$: The positions of the two membranes were switched and the mixed liquid consisting of water (colored by methylene blue) and heavy oil was separated as in the process described above.