Supporting Information

S1 Materials

Perfluorooctanoic acid (A-PFO; 90%), perfluorododecanoic acid (A-PFD; 92%), sodium hydroxide (NaOH; 97%; granulated), polyvinylpyrrolidone (PVP; K13-18), acetic acid (CH3COOH; 99.5%), ammonia solution (NH3·H2O; 25-28%), copper chloride (CuCl2; 98%), titanium oxide nanoparticles (99.8%; 5-10nm; anatase, hydrophilic) were obtained from Aladdin, used as recieved Spray-Mount Artist's Adhesive 6065 was ordered form Minnesota Mining and Manufacturing Company (3M).

S2 Preparations of samples

S 2.1 Preparation of the mixture of A-PFO and S-PFO solutions

4.60 g A-PFO was dissolved in absolute ethyl alcohol to obtain 100 mL 0.1 M A-PFO/ ethyl alcohol solution. 0.10 g PVP was then added in order to form films better when sprayed onto solid subtracts. The solution was divided into two parts equally, then 0.2 g sodium hydroxide was added into one of the two parts to form 50 mL 0.1 M S-PFO solution. Then the A-PFO and S-PFO solution were mixed with different ratio from 0:10 to 10:0, forming eleven different mixture solutions (5 mL).

S 2.2 Fabrication of A-PFO/S-PFO coated flat surfaces

Glass slides were cleaned in a sonication bath in acetone, ethyl alcohol and deionized water for 10 min successively, then dried at room temperature for 24 h after rinsed by deionized water for 15 s. 1 mL of each solution with different ratio of A-PFO and S-PFO was sprayed on a cleaned slide by an airbrush at a working distance of 15 cm with 0.2 MPa air, respectively. Then the coated slides were kept in enclosure space for 24 h to allow solvent to evaporate completely.

S 2.3 Fabrication of A-PFO/S-PFO coated nano-structured rough surfaces

0.40 g TiO2 nanoparticles (P5~10) were dispersed in 4 mL of each prepared solution by a magnetic stirrer at a revolving speed of proximately 1000 rpm for 10 mins. Then these mixtures were sprayed onto cleaned and dried glass slides immediately by an airbrush at a working distance of 15 cm with 0.2 MPa air, respectively. The coated samples were kept in enclosure space for 24 h to allow solvent to evaporate completely. **S 2.4 Preparation of sodium acetate**

10 g sodium hydroxide (NaOH) was dissolved in deionized water to make 50 ml aqueous solution. 15 mL acetic acid (CH₃COOH) was added into this solution. The fully acted solution was heated by an alcohol burner to get sodium acetate trihydrate (CH₃COONa \cdot 3H₂O) crystals. Then these crystals were put into a vacuum drying oven dried in vacuum situation at 125°C for 30 min, after which sodium acetate anhydrous (CH₃COONa) was obtained.

S 2.5 Preparation of copper acetate

17 g copper chloride (CuCl₂) was dissolved in deionized water to make 50 mL aqueous solution. 40 mL ammonia solution (NH3·H2O) was added into this solution, then copper hydroxide (CuOH) deposit was made after filtration. The filtered deposit

was rinsed by deionized water for 3 time. Then the deposit was put into 50 mL deionized water, after which 15 mL acetic acid (CH₃COOH) was added into this mixture to dissolve the CuOH. The fully acted solution was heated by an alcohol burner till crystals appeared. Then more copper acetate hydrate ((CH₃COO)₂Cu·H₂O) crystals were get after the condensed was cooled. These crystals were filtered and rinsed by 30% acetum. Then these crystals were put into a vacuum drying oven dried in vacuum situation at 105°C for 30 min, after which sodium acetate anhydrous (CH₃COONa) was obtained. Fabrication of copper perfluorododecanate S 2.6 (C-PFD), copper perfluorooctoate (C-PFO), sodium perfluorododecanate (S-PFD) and sodium perfluorooctoate (S-PFO) coated nano-structured rough surfaces

Sodium acetate and copper acetate are synthesized from sodium hydroxide, copper chloride and acetic acid. 0.82 g sodium acetate was dissolved in absolute ethyl alcohol to prepare 100mL 0.1M sodium acetate/alcohol solution, and 0.91 g copper acetate was dissolved in absolute ethyl alcohol to prepare 100 mL 0.05M copper acetate/alcohol solution., Four solutions (C-PFD, C-PFO, S-PFD and S-PFO) were obtained through combining one fluorocarbon (0.67 g A-PFD or 0.46 g A-PFO) with one acetate solution (10 mL copper acetate solution or 10 mL sodium acetate solution). 1.0 g TiO2 nanoparticles (P5~10) were dispersed into each solution by a magnetic stirrer at a revolving speed of proximately 1000 rpm for 10 min. These mixtures were sprayed onto cleaned glass slides immediately by an airbrush at a working distance of 15 cm with 0.2 MPa air, respectively. Then the slides with coatings were kept in enclosure space for 24 h to allow solvent to evaporate completely.

S 2.7 Fabrication of the oil-water separation mesh with S-PFO

A piece of 300 mesh wired steel mesh ($5 \times 5 \text{ cm}2$) was exposed in spray gel fog for about 1 s, by which a glue film was form on the mesh surface. Then 5 mL S-PFO solution with 0.50 g well dispersed TiO2 nanoparticles was sprayed onto the mesh at a working distance of 15 cm with 0.2MPa air. This process was repeated 6 times. The mesh was then dried at room temperature for 24 h.

S 3 Oil/Water Separation

The constitution of oil/water separation device is shown in Fig S1, a separation mesh coated with S-PFO superhydrophilic/superoleophobic coating is sandwiched between a 20 cm long glass pipe (25 mm in diameter with a glass flange of 50 mm diameter and 5 mm thickness at one end) and a 5 cm long glass pipe (25 mm in diameter with a glass flange of 50 mm diameter and 5 mm thickness at one end). The junction was sealed with silicon cement.

The sealed separation device was dried in ambient environment for 24 h before using. The oil/water mixture containing 50 mL water and 50 mL soybean oil was poured into the separation device directly, and the separation process was drove only by gravity, as is shown in Fig S2 and Movie S4. Finally, 50 mL water and 50 mL soybean oil were obtained with no obvious water-in-oil or oil-in-water impurities, as is shown in Fig S3.

To calculate water flux and separation efficiency, four kinds of oil/water mixtures with 50 mL oil and 50 mL water, which were diesel/water (DSL/W), soybean oil/water (SBN/W), lubricating oil/water (LB/W) and hexadecane/water (HDC/W), were

separated by using the prepared membranes. The oil contents in water after separation were measured by total organic carbon analyzer (TOC, ANALYTIKJENA Multi N/C, Germany).



Figure S1 Oil/Water Separation Device



Figure S2 Oil/Water Separation Process



Figure S3 Separated oil and water

Movies Catalogue

Movie S1 Water Penetrating Fast on Superhydrophilic Surfaces Movie S2 Water Droplet Formed a 85° Contact Angle before Spreading out Movie S3 Soybean Oil Droplet Touching and Leaving C-SPFO Surface Movie S4 Oil/Water Separation with S-PFO Coatings