Supporting Information

Reduction of Imine Based Cross-linkages to Achieve Sustainable Underwater Superoleophobicity That Performs at Challenging Conditions

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Movie 1: Illustrating Sand Paper Abrasion test followed by examination of the embedded oil repellence underwater

Movie 2: Illustrating the Adhesive Tape Test and investigation of the oil repellence after this harsh exposure

Movie 3: Analysis of the embedded super-oil-repellence after performing the Knife scratch test

Movie 4: Demonstration of gravity-driven filtration based Crude Oil/water separation

Movie 5: Demonstration of gravity-driven filtration-based crude oil/water separation, where the bio-mimicked interface is pre-exposed to the crude oil phase.

Movie 6: Demonstration of gravity-driven filtration-based kerosene oil/water separation, where the bio-mimicked interface is pre-exposed to the kerosene oil phase.

Experimental Section:

Materials: Bovine Serum Albumin (M_W ~ 66.5kDa, Faction V), Silicone oil (CAS No. 63148-58-3), sodium dodecyl sulfate (SDS), dodecyl trimethyl ammonium chloride (DTAB) were purchased from Sigma-Aldrich. Glutaraldehyde (25% aqueous solution) was purchased from Merck, India. Nile Red (CAS No. 7385-67-3) was purchased from Tokyo Chemical Industry. Absolute ethyl alcohol (CAS No. 64-17-5) was purchased from TEDIA Company (United States of America). Sodium Chloride, magnesium chloride, calcium chloride, magnesium sulphate, sodium hydroxide was purchased from Merck Specialties Private Limited. Hydrochloric acid was purchased from Fischer Scientific (Hyderababd, India). Chloroform and dichloromethane were purchased from FINAR. Petroleum ether and ethylacetate RANKEM (Maharashtra, India). Polyurethane fabric, calibration weights, vegetable oil were procured from Amazon, India. Sand Paper, Adhesive Tape was procured from local stationary shop. Crude Oil was obtained from Oil India Refinery, Assam. Kerosene, petrol, diesel, motor oil, was procured from Indian Oil Petrol Pump. Sand was collected from a local construction site in IIT Guwahati and rinsed with water, dried before use.

General Considerations: The glass wares were washed with acetone and water thoroughly prior to use. Kruss Drop Shape Analyzer-DSA25 instrument with automatic liquid dispenser was used

for contact angle measurements. The contact angles were measured using 5µL dichloromethane droplet at four different locations of each sample. Field Emission Scanning Electron Microscope (FESEM) images were obtained using a Carl Zeiss Field Emission Scanning Electron Microscope. The samples were sputtered with gold coating prior to analysis. UV spectra was obtained using the Perkin-Elmer Lambda 750 (UV/Vis/NIR Spectrometer). Digital images were captured using a Canon Powershot SX420 IS digital camera. Phase contrast and fluorescence microscopic images were obtained using a ZEISS Axio Vert.A1 inverted microscope. Milli-Q grade water was used for all experiments.

Synthesis of Durable Underwater Protein Derived Superoleophobicity:

Briefly, 1mL aqueous solution of 40 mg/mL bovine serum albumin (pH adjusted to 8.0 with 0.1 N NaOH) was taken in a beaker. To this solution of BSA, 7 ml of ethanol was added at a rate of 1 mL/min under continuous stirring at room temperature till faint turbidity was observed. Thereafter, a commercially available polyurethane based fibrous substrate (3 cm x 3 cm) was placed in the beaker to ensure the deposition of BSA followed by 'in-situ' addition of 200 µl of 8% aqueous solution of glutaraldehyde (GA) to induce imine-based cross-linking in the freshly deposited BSA protein. The reaction was kept undisturbed for 12 hours under constant stirring. Subsequently, the deposited imine (brown turbid solution) based cross-linked BSA coating was subjected to reduction by addition of 25 mL of aqueous solution (70 mg/mL) sodium borohydride and kept unperturbed for 6 hours. During this reduction process, the brown turbid solution became colorless. Thereafter, the fabric was taken out and washed thoroughly with water and the embedded underwater superoleophobic property was examined through contact angle measurements and digital images. To verify the process of cross-linking and reduction, the as obtained de-solvated BSA, GA-crosslinked BSA and after reduction of GA-crosslinked BSA were subjected to centrifugation at 12000 rpm for 15 mins to collect the sediments, which were further washed thoroughly thrice with water prior to record the UV spectrum. Moreover, the morphology of the fabric was examined using Carl Zeiss Field Emission Scanning Electron Microscope.

Physical and Chemical Durability Tests: To examine the robustness of the embedded oil repellent property, various practically relevant and harsh physical and chemical durability tests were carried out on the protein derived underwater oil repellent fibrous substrate.

Sand Paper Abrasion: In sand paper abrasion, an abrasive sand paper was manually rubbed across the protein derived underwater oil repellent fibrous substrate for ~50 cycles with 700 g load on top at a sliding speed of 4 cm/sec. Thereafter, the durability of the embedded oil repellent property was examined via contact angle measurements and digital images.

Adhesive Tape Test: The protein derived underwater oil repellent membrane was placed on an adhesive tape with 700 g load on top to ensure uniform contact between the membrane and adhesive tape. Subsequently, the membrane was peeled off from the surface of the adhesive tape and the freshly exposed surface of the protein derived underwater oil repellent membrane was examined using contact angle measurements and digital images.

Sand Drop Test: In this particular test, 150 g of sand was poured from a height of 25 cm on the reduced-BSA coated fibrous substrate which was pre-tilted at an angle of 45°. After performing sand drop test, the underwater oil repellency was examined by measuring the underwater oil contact angles and the digital images.

Knife Scratch Test: Random scratches were made on the reduced-BSA coated fibrous substrate in all possible directions using a sharp-edged knife for multiple times and thereafter, the oil repellency was examined via contact angle measurements and digital images.

Physical Manipulations: The amine based (after reduction of imine) crosslinked BSA coated fibrous substrate was manually bended, creased, twisted and winded for 25 times with arbitrary preferences. Thereafter, the digital images were acquired, and the underwater oil contact angles were measured to examine the impact of these physical manipulations on the embedded underwater superoleophobicity. The protein-based fibrous substrate was also subjected to 150% tensile strain for 1000 cycles and subsequently, the digital images and oil contact angles were measured at regular intervals.

UV irradiation: The protein derived underwater superoleophobic fibrous interface was exposed to both short (254 nm) and long (365 nm) wavelength UV irradiation for 30 days. The embedded oil repellency was examined at regular intervals by measuring the oil contact angles and acquiring digital images.

Chemical Durability: The underwater extreme oil repellency on the reduced-BSA coated fibrous substrate was examined at regular intervals after exposure to different chemically harsh aqueous conditions i.e. acidic water (pH 1), basic water (pH 12), surfactant contaminated water (SDS, 1 mM and DTAB, 1 mM), river water (Brahmaputra river, Assam, India) and seawater for 30 days. Artificial seawater was prepared by mixing $MgCl_2$ (0.226 g), $MgSO_4$ (0.325 g), NaCl (2.673 g) and $CaCl_2$ (0.112 g) in 100 mL of de-ionized water in a volumetric flask.

Gravity-Driven Filtration Based Oil/Water Separation: The protein derived highly durable underwater superoleophobic fibrous substrate was extended for oil/water separation. A lab made prototype was developed using a 50 mL falcon tube in which one end of the tube was tied with the pre-wetted protein derived underwater superoleophobic membrane. Another hole that made at the closed end of tube allowed to pour the respective oil/water mixture in the lab-made prototype. In the first demonstration, an equal amount of crude oil/water (20 mL/20 mL) mixture

was poured through the prototype for selective filtration of the water phase. Similar experiment was also carried out for kerosene/water mixture. In another set of demonstration, the prototype was filled with 35 mL of crude oil to contaminate the underwater superoleophobic interface with crude oil, and thereafter, water was continuously poured via the open hole with the help of a funnel. It resulted selective permeation of only the water phase through the underwater superoleophobic membrane. Similar demonstration was carried out using kerosene. The water collection efficiency was calculated following the widely used formula given below;

$$\eta = \{(V_f)/(V_i)\} \text{ X } 100$$

Where, η is the water collection efficiency (%), V_i is the initial volume of water taken before separation and V_f is the final volume of water obtained after separation through the underwater superoleophobic membrane.

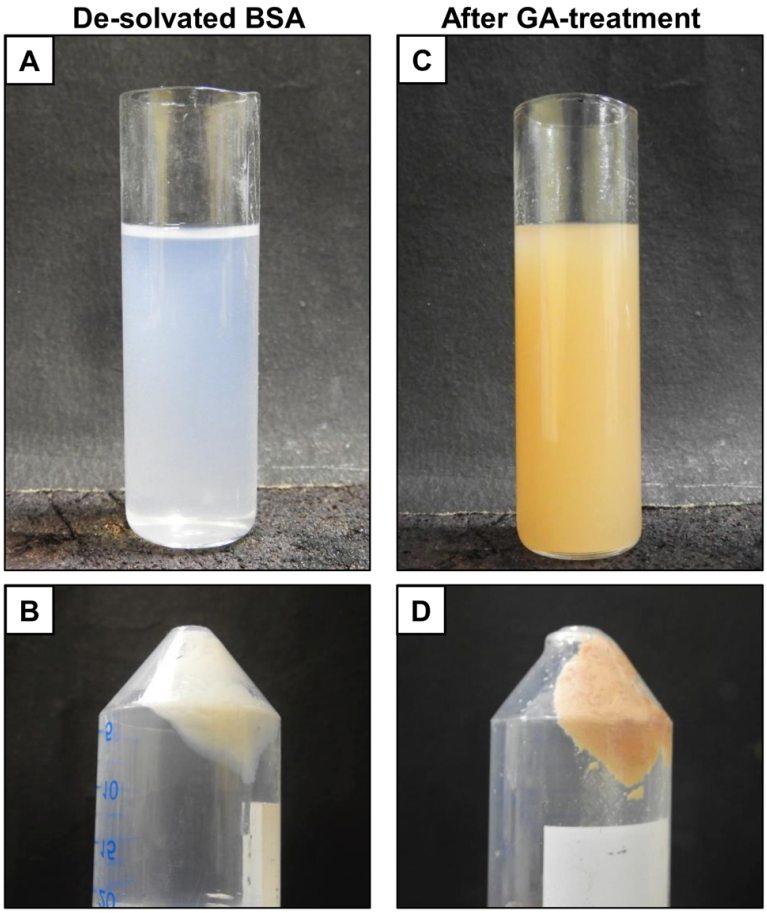

Figure S1. A) Digital image of faintly turbid solution (A) and sediment (B) of BSA protein after de-solvating with ethanol, where the de-solvated BSA residue was centrifuged, washed and collected (B). C-D) Digital image of yellow colored solution (C) and sediment (D) of GA-crosslinked BSA protein (de-solvated), where the GA-crosslinked BSA protein residue was centrifuged, washed and collected (D).

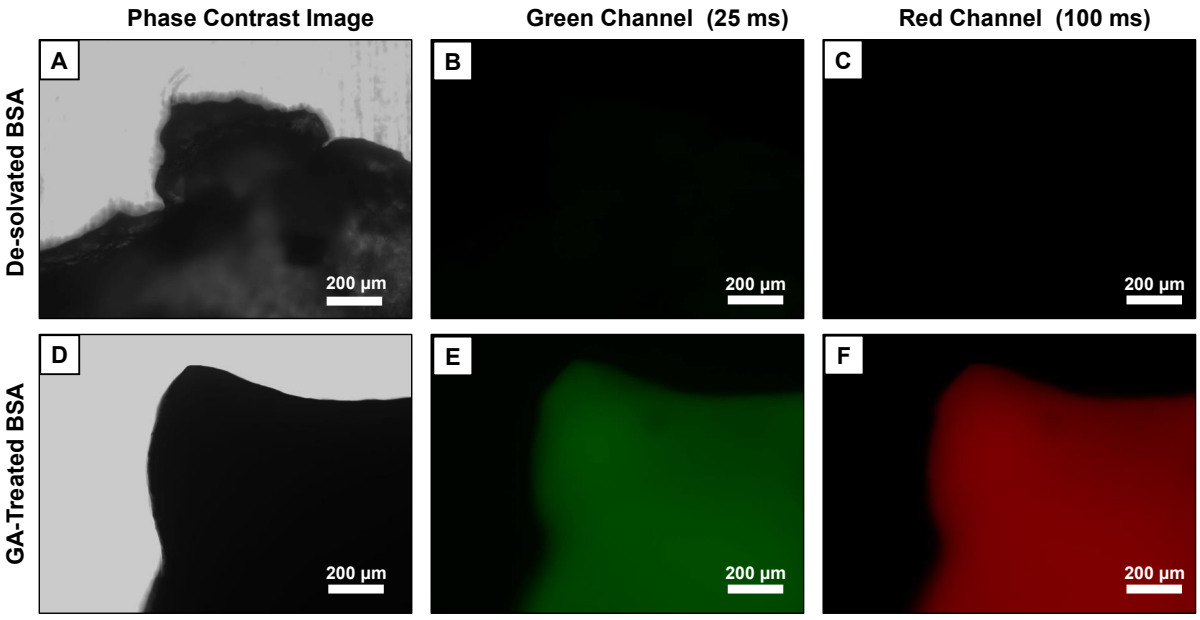

Figure S2. A-C) Phase contrast image (A) and fluorescence microscope images (B-C) of de-solvated BSA protein residues collected by centrifugation. D-F) Phase contrast image (D) and fluorescence microscope images (E-F) of GA-crosslinked BSA protein (collected by centrifugation).

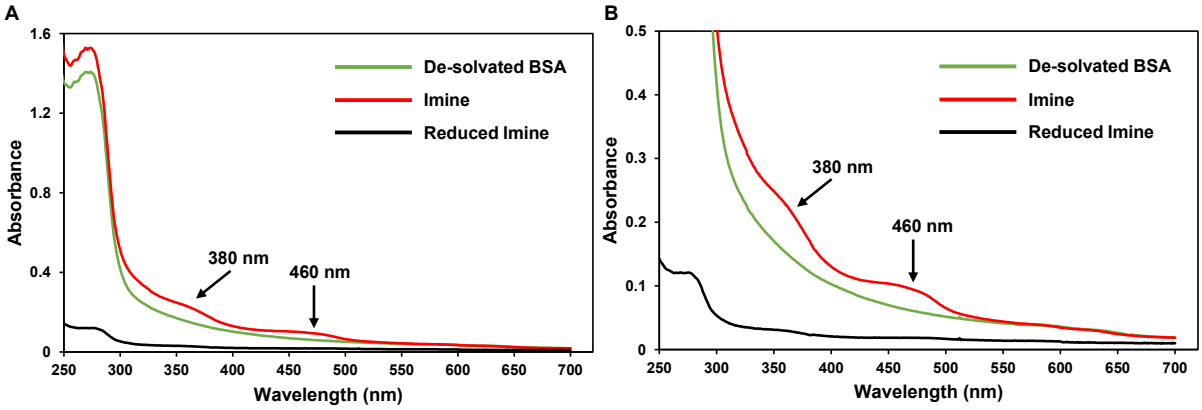

Figure S3. A-B) UV spectral of desolvated BSA before (green) and after (red) tretment with glutaraldehyde in low (A) and high (B) magnifications. The peaks at 380 nm and 460 nm are characteristic peaks for the imine and the peak at 280nm is characteristic of BSA protein. On reduction of the GA-crosslinked BSA protein with sodium borohydride, the peaks corresponding to imine disappear confirming the successful reduction process (black).

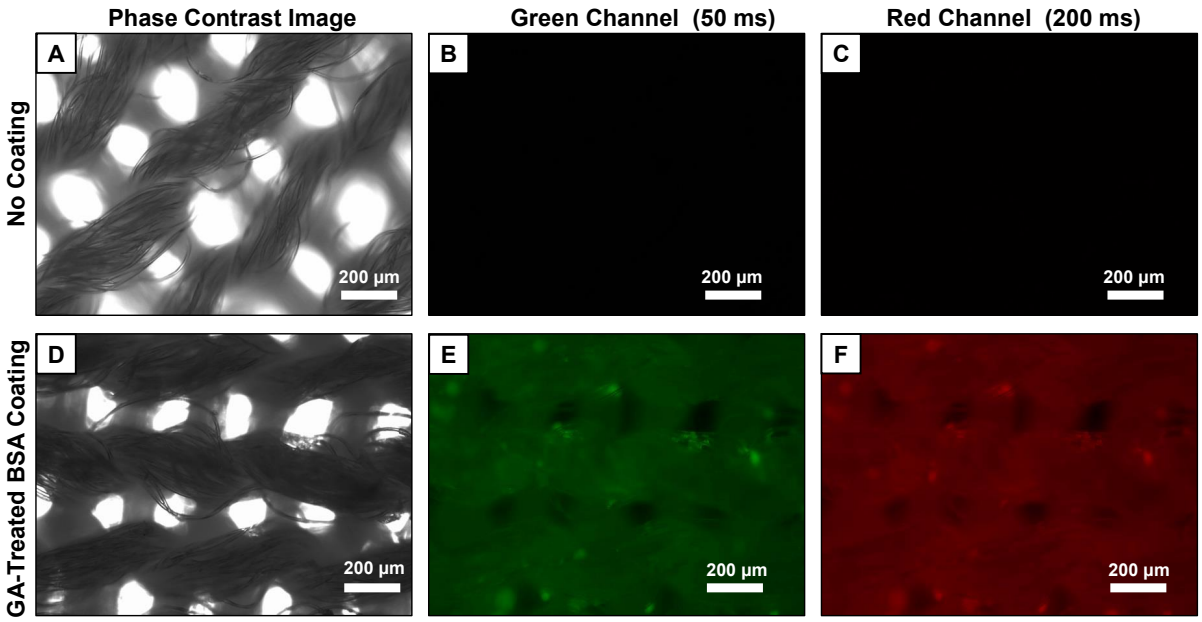

Figure S4. A-F) Phase contrast image (A,D) and fluorescence microscope images (B-C, E-F) of fibrous substrate before (A-C) and after (D-F) depostion of GA-crosslinked BSA protein.

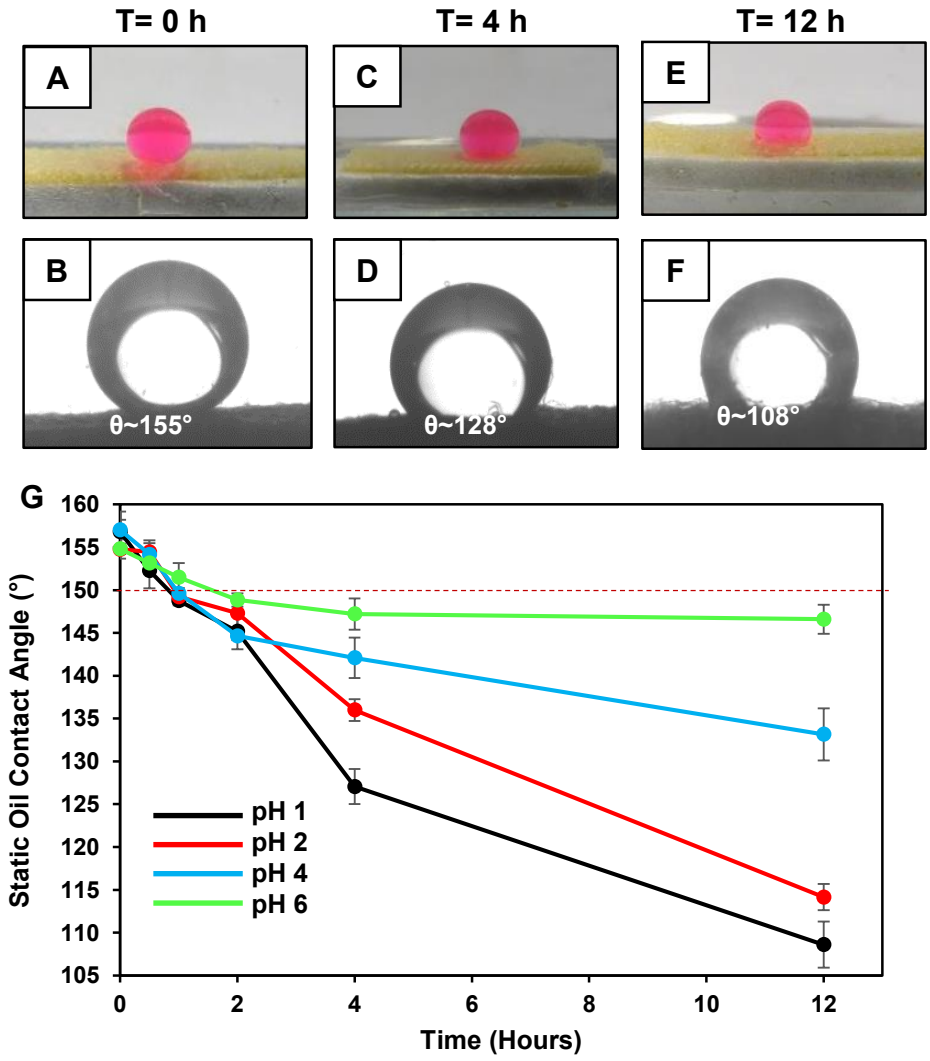

Figure S5. A-F) Digital images (A,C,E) and contact angle images (B,D,F) of the beaded oil droplet (underwater) on the fibrous substrate coated with GA-crosslinked BSA—after the exposure to acidic water (pH 1) at t= 0 h (A-B), t= 4 h (C-D) and t= 12 h (E-F). G) Plot accounting for the change in underwater oil contact angle with time on the GA-crosslinked BSA coating after exposure to different acidic media i.e. pH 1 (black), pH 2 (red), pH 4 (blue) and pH 6 (green).

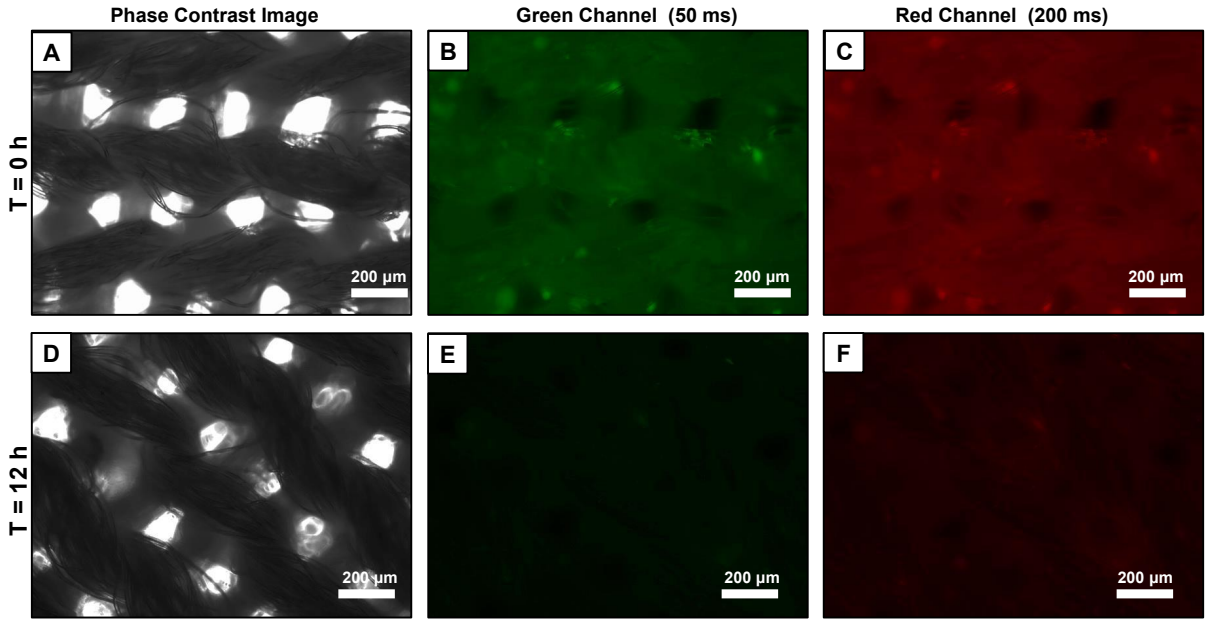

Figure S6. A-F) Phase contrast images (A,D) and fluorescence microscope images (B-C, E-F) of the fibrous substrate coated with GA-crosllinked BSA before (A-C) and after (D-F) exposure to acidic media (pH 1) for 12 h.

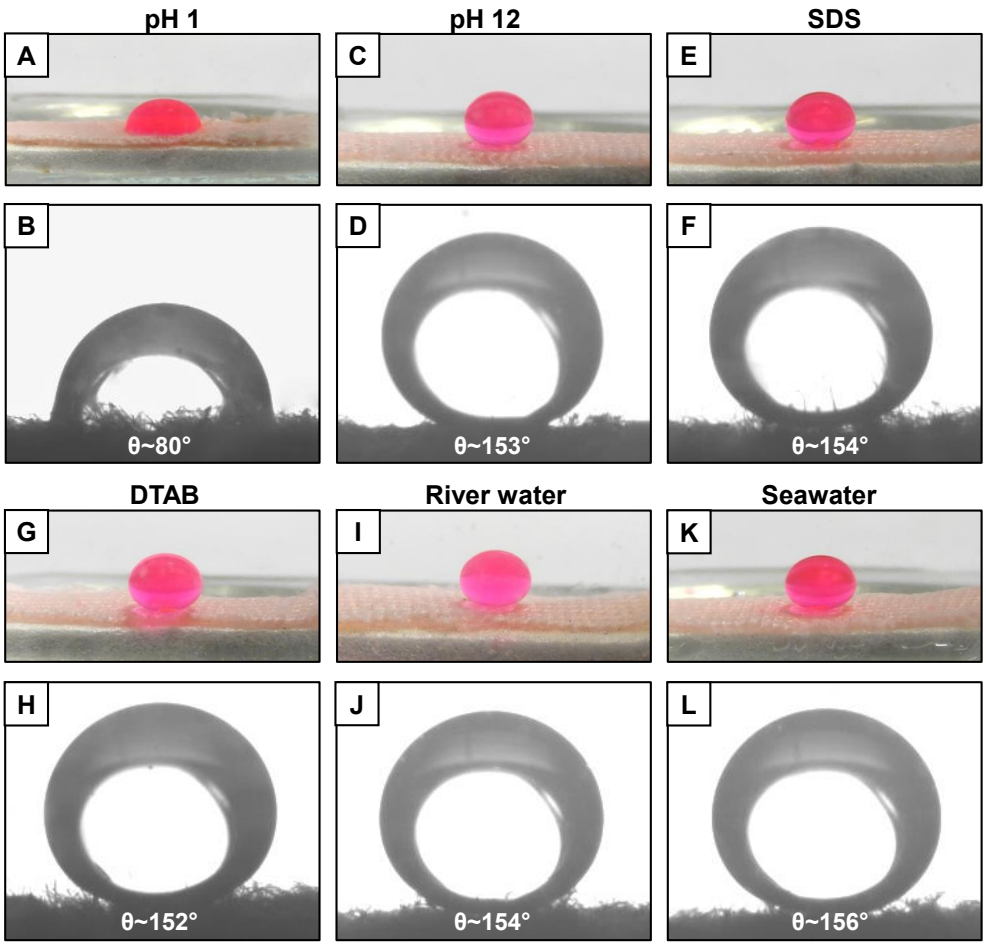

Figure S7. A-L) Digital images (A,C,E,G,I,K) and contact angle images (B,D,F,H,J,L) of the beaded oil droplet (underwater) on the fibrous substrate coated with GA-crosslinked BSA after exposure to various chemically harsh aqueous media including acidic water (pH 1), basic water (pH 12),surfactant contaminated water (SDS, DTAB), river water and seawater for 30 days.

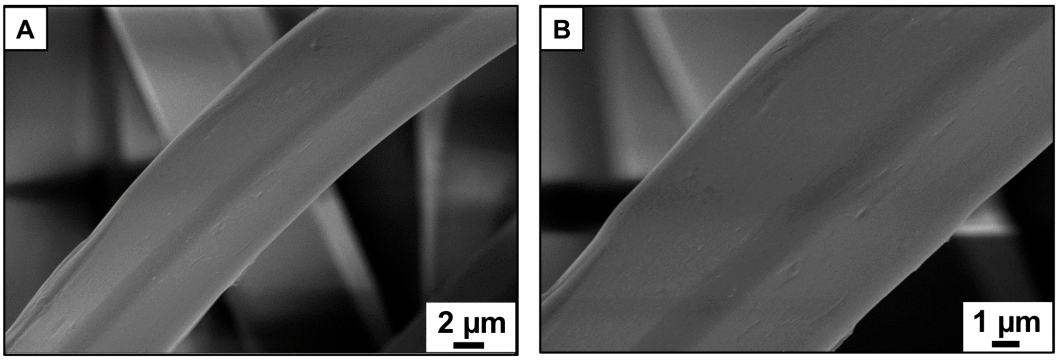

Figure S8. A-B) FESEM images of uncoated fibrous substrate at lower (A) and higher magnifications (B).

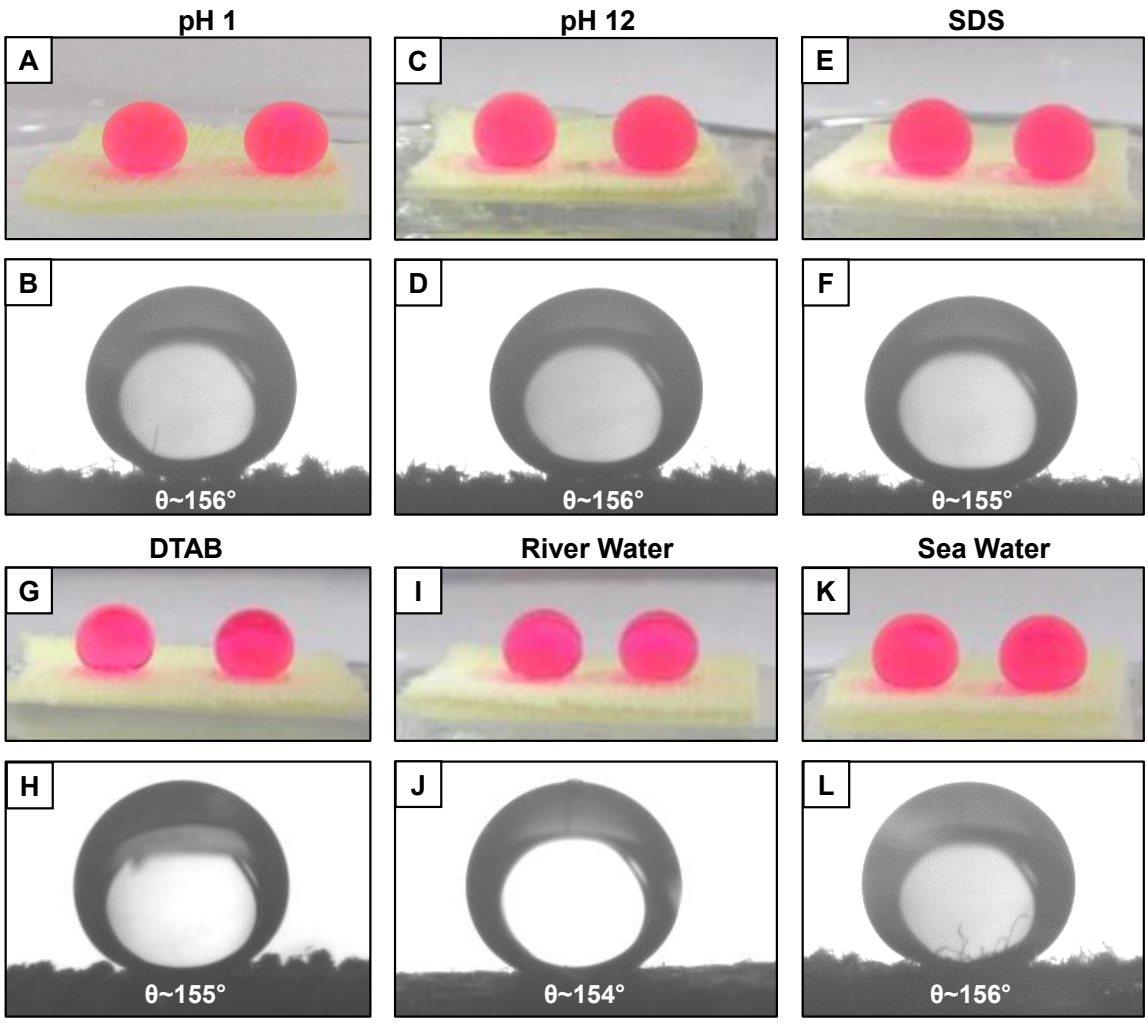

Figure S9. A-L) Digital images (A,C,E,G,I,K) and contact angle images (B,D,F,H,J,L) of the beaded oil droplet (underwater) on the fibrous substrate that coated with GA-crosslinked BSA and followed by treated with sodium borohydride, where the coated substrte was exposed to various chemically harsh aqueous media including acidic water (pH 1), basic water (pH 12),surfactant contaminated water (SDS, DTAB), river water and seawater for 30 days, prior to investigate the underwater oil wettability.

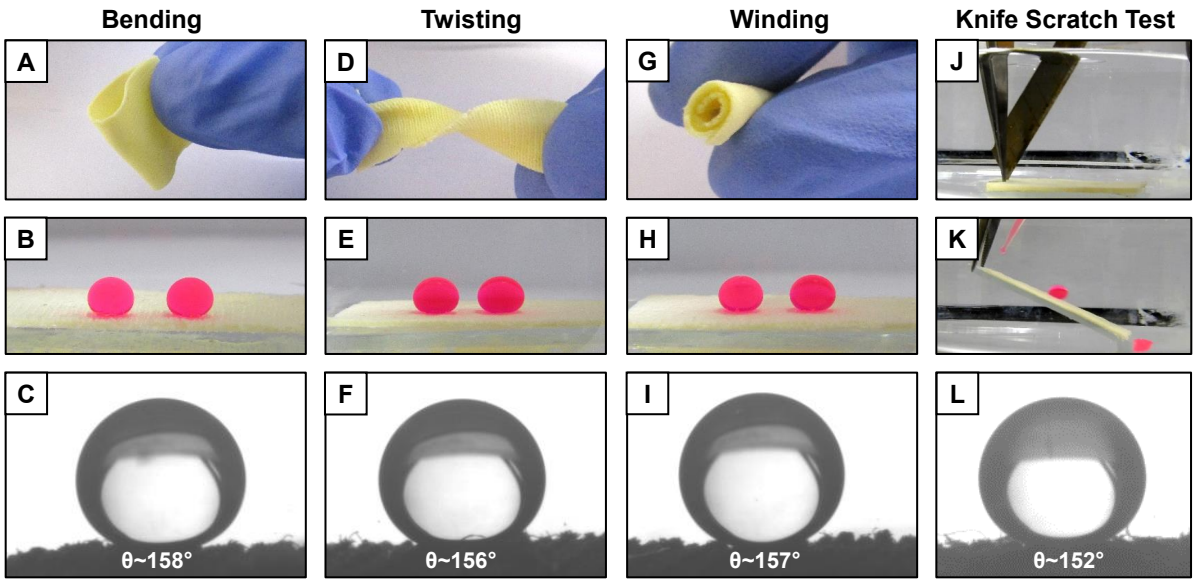

Figure S10. A-L) Digital images (A-B,D-E,G-H,J-K) and contact angle images (C,F,I,L) of the beaded oil droplet (underwater) on the fibrous substrate that coated with stable crosslinked BSA (treated with sodium borohydride), after performing various physical manipulations including bending (A-C), twisting (D-F), winding (G-I) and severe physical abrasion i.e. knife scratch test (J-L).

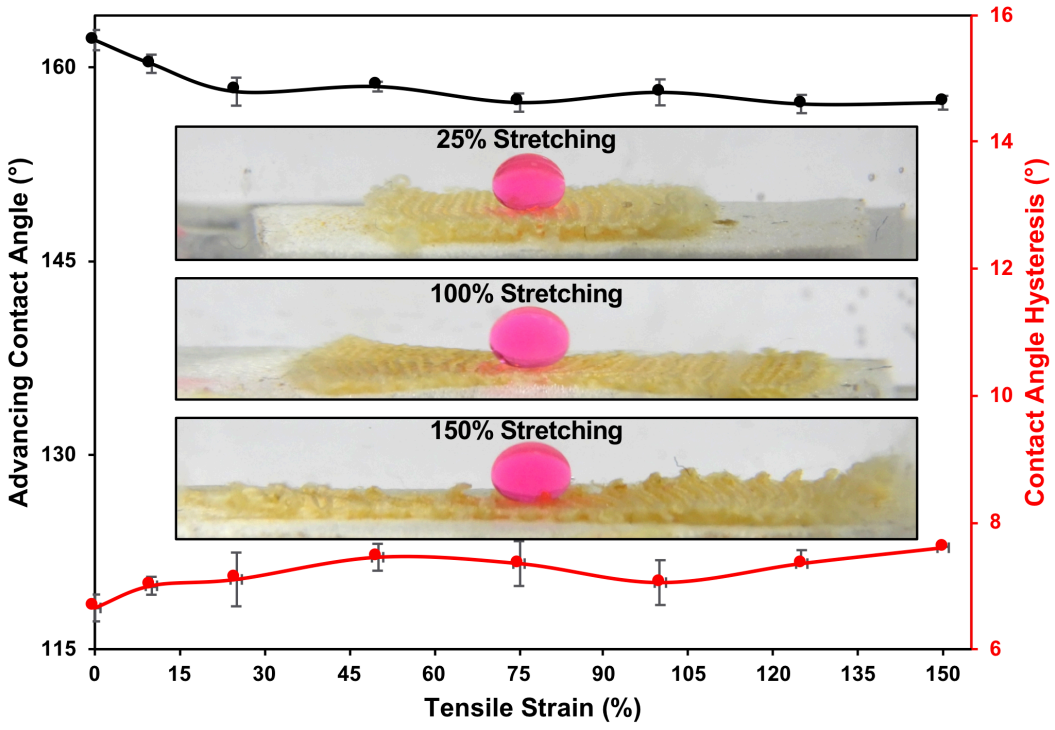

Figure S11. The Plot accounting for the change in oil wettability on the stretchable underwater superoleophobic interface after subjecting to different percentage of tensile strain ranging from 0% to 150%.

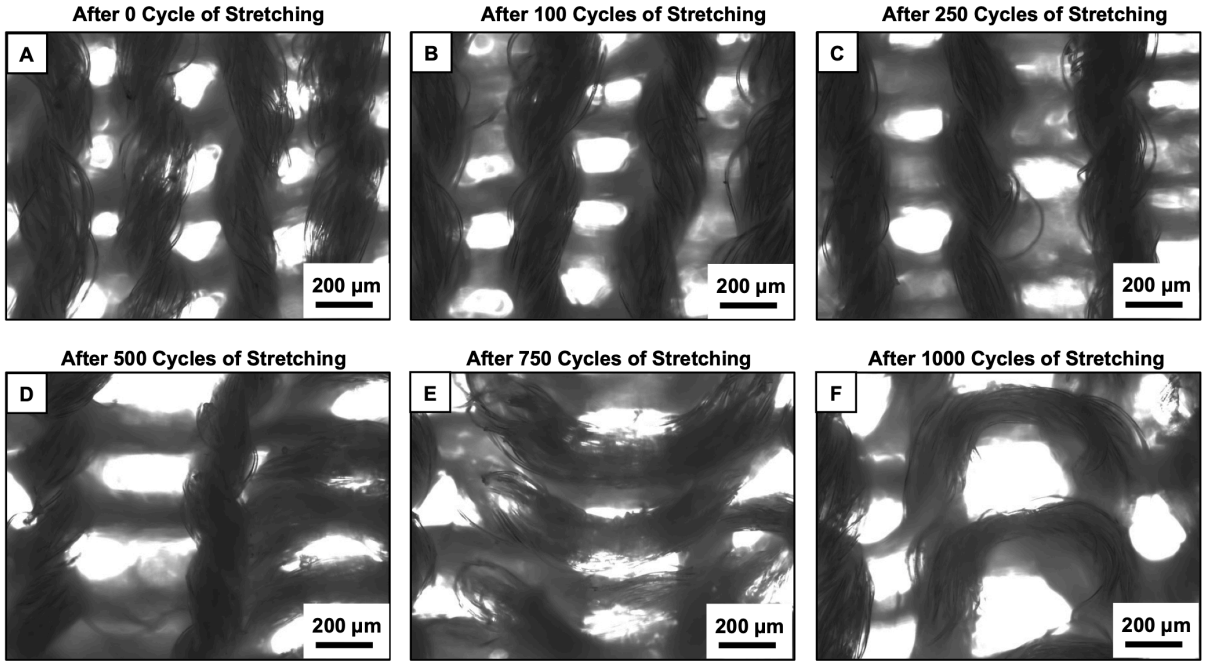

Figure S12. A-F) Microscopic bright field images illustrating the change in the fibrous network of the used substrate after subjecting to repeatative 150% tensile deformation for 1000 cycles. With Increasing the deformation cycle, the arrangement of fibres is observed to change.

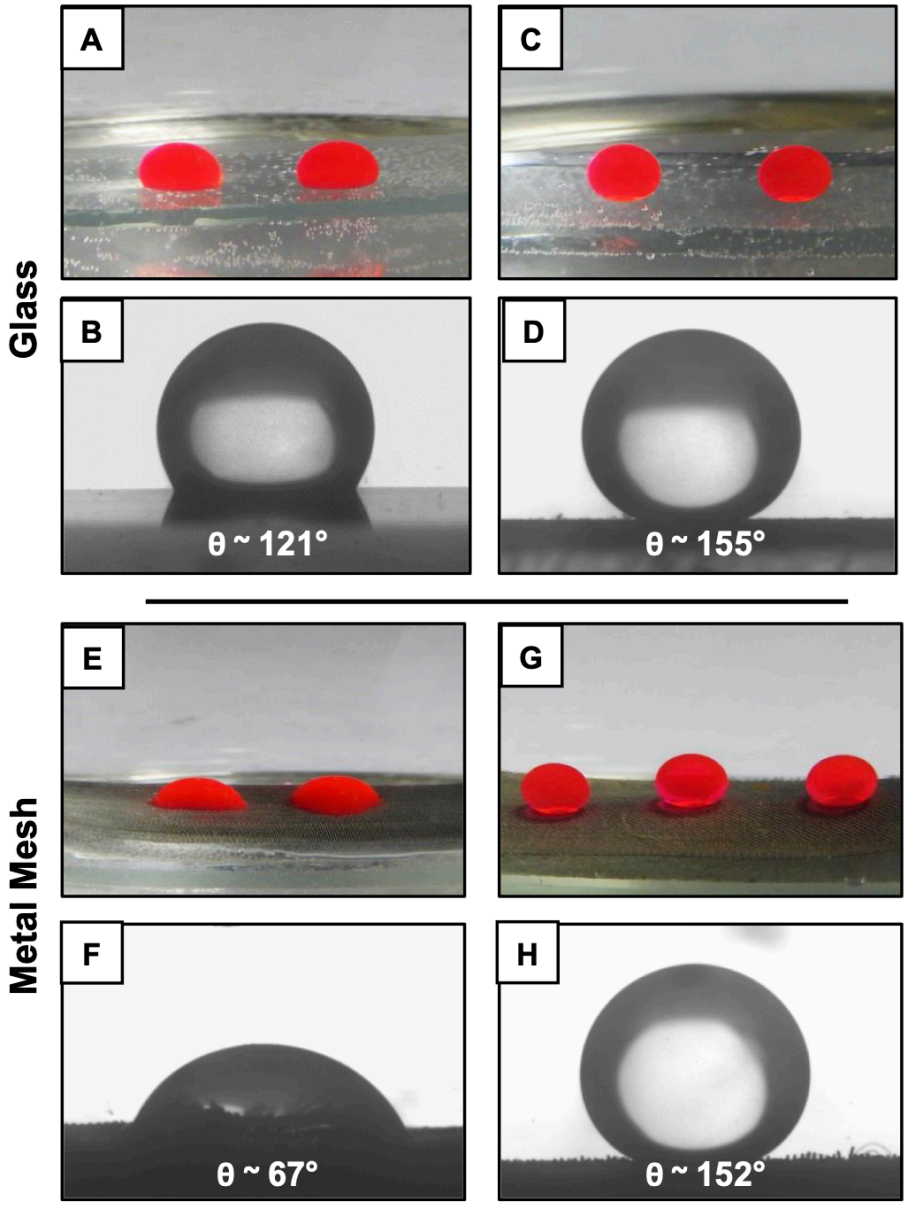

Figure S13. A-D) Digital images (A,C,E,G) and contact angle images (B,D,F,H) of beaded oil droplet underwater on the uncoated (A-B, E-F) and reduced-imine based BSA-coated (C-D, G-H) glass slide (A-D) and metal mesh (E-H).

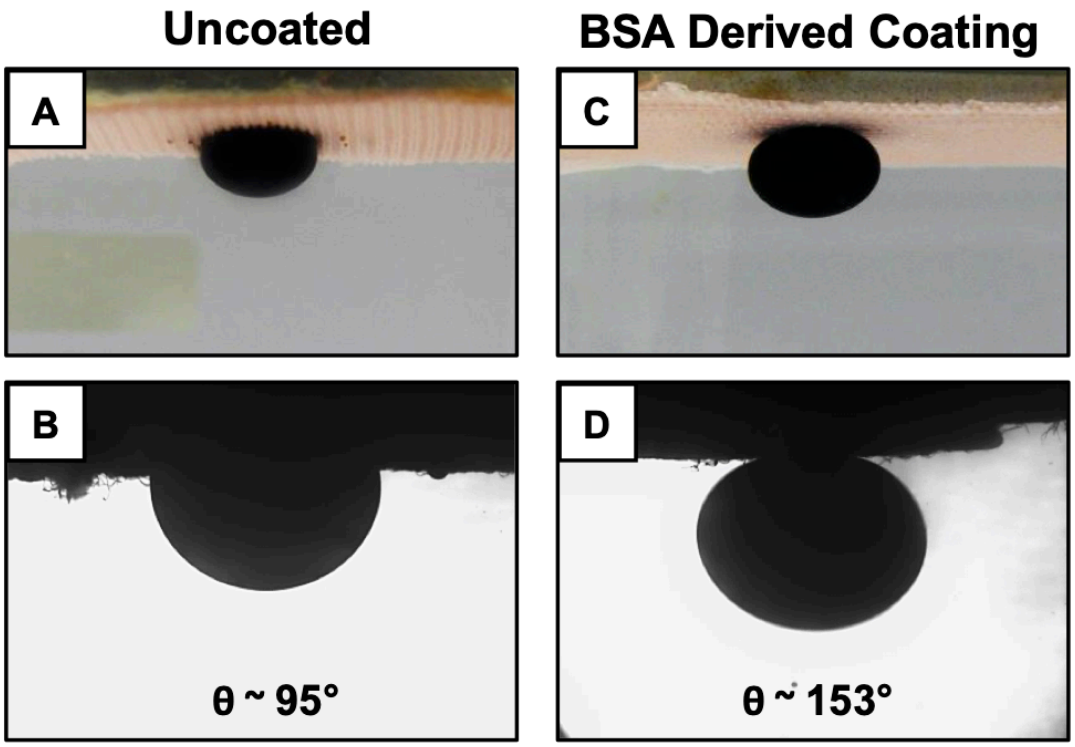

Figure S14. A-D) Digital images (A,C) and contact angle (B,D) images of crude oil droplet underwater on the uncoated (A-B) and reduced-imine based BSA coated fibrous substrate (C-D).

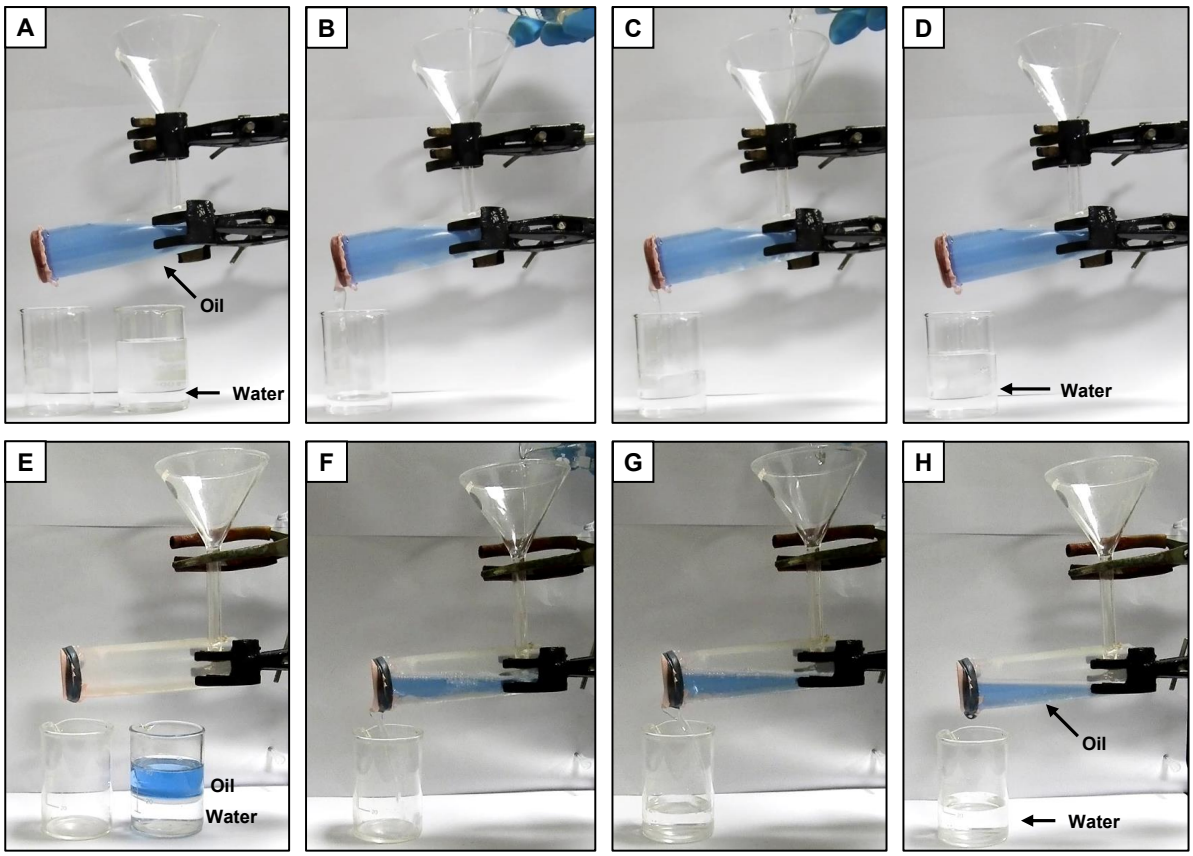

Figure S15. A) Digital images illustrating the lab made prototype, where superoleophobic membrane was completely exposed to kerosene (A). Thereafter, when water was poured through the funnel (B), only the water phase selectively permeated through the membrane under the gravity (C-D). E-H) Digital images illustrating the gravity-driven filtration based separation of kerosene oil/water mixture through the underwater superoleophobic membrane where oil/water mixture was poured through the funnel and the water selectively passes while the oil phase remains suspended on top of the membrane (H).