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Supporting Information

Aloe Vera Mucilage Derived Highly Tolerant Underwater Superoleophobic Coating

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Movie 1 : Translation of oil droplet on the top surface of AVM under water.

Movie 2: Knife scratch Test performed on AVM coated substrate.

Movie 3: Advancing and receding contact angle on 5Acl treated AVM substrate.

Movie 4: Advancing and receding contact angle on Glu-AVM treated substrate.

Movie 5: Knife scratch test on Glu-AVM coated substrate.

Movie 6: Separation of light oil/water mixture

Movie 7: Separation of heavy oil/water mixture.

Experimental section:

Materials: Dipentaerythritol penta-acrylate (5Acl, MW 524.21g/mol), Silicone oil (CAS No. 63148-58-3), rhodamine-6G (CAS No. 989-38-8) and methylene blue (CAS No. 122965-43-9) were obtained from Sigma Aldrich, (Bangalore, India). Dimethyl sulfoxide (DMSO) was obtained from Fischer Scientific (Mumbai) India. Ethyl Alcohol (CAS No. 64-17-5, Lot No. 17030799) was purchased from TEDIA Company, United States of America. Adhesive Tape was obtained from Jonson tape Ltd Pvt., New Delhi, India. Nile Red (CAS No. 7385-67-3) and D-Glucamine (>95%) were purchased from Tokyo Chemical industry. Dichloroethane (CAS No. 107-06-2ADR) was purchased from Lobo Chemie Pvt. Ltd., Mumbai, India. Fibrous polyurethane (PU) substrate (fabric), vegetable oil and kerosene oil were purchased from a local shop in Guwahati City, Assam, India. Motor oil (Castrol Active 20W-40) was purchased from Castrol India Ltd. Sand was collected from a construction site of IIT, Guwahati.

General Consideration: The glass wares were washed thoroughly with ethyl alcohol and then acetone prior to prepare the desired solutions. Kruss Drop Shape Analyzer-DSA25 instrument with mechanical liquid dispenser was used for contact angle measurements at ambient temperature. Field Emission Scanning Electron Microscope (FESEM) images were obtained using a Carl Zeiss Field Emission Scanning Electron Microscope. FTIR spectra were recorded using a Perkin Elmer Instrument at ambient temperature by preparing KBr pellet with the sample. The digital photographs were captured by Cannon Powershot SX420 IS digital camera for all experimental demonstrations. Labconco FreeZone Freeze Dryer was used for lyophilizing the aloe vera mucilage and leaf.

Lyophilized Aloe Vera Mucilage and Green exterior of Leaf: Both the exterior green peel of the AV leaf and stored mucilage within the Aloe vera AV leaf was lyophilized (Analytical Chemistry, 1973 45, 1296) using Labconco FreeZone Freeze Dryer instrument. This lyophilization process allowed to remove the immobilized water from selected material directly from solid state to gas phase, where the material is exposed first to liquid nitrogen for freezing the liquid water in the material, and then under the applied vacuum (0.310 mbar) (that maintained using automated set up) this frozen aqueous phase is directly converted to gas phase and escape from the material. This approach is highly adopted in drying protein without destroying its structure.

Aloe Vera Mucilage Coating on Fibrous and Stretchable substrate:

In order to coat the stretchable polyurethane fabric (14cm x 14cm) with aloe vera mucilage, the interior of the aloe vera leaf was exposed by peeling off the rind (green portion that acts as a protective layer) and discarding the aloin (yellowish portion). Subsequently, Aloe Vera mucilage weighing 8.5g was squashed manually and coated over an area of 196 cm^2 using a paint brush in to and fro motion to ensure uniform coating on the fabric. The fabric was allowed to air dry overnight and thereafter, the underwater oil wettability was examined using contact angle measurements and digital images.

Chemically Reactive Aloe Vera Mucilage Coating and its Post Modifications:

The Aloe Vera mucilage (AVM) coated fibrous substrates were thereafter treated with 5Acl (1.325g in 10 mL of ethanol) solution for 2 h. Afterwards, it was washed thoroughly in ethanol to remove excess of 5Acl. Then, the 5Acl treated AVM coated substrate was transferred into glucamine (5mg/ml in DMSO) solution for overnight. Next, the coated substrate was washed using DMSO and THF. Then, the fabric was vacuum dried and the oil wettability was examined with contact angle measurements and visual inspections.

Physical and Chemical Durability Tests:

Various practically relevant challenging physical and chemical settings are performed to examine the durability of the AVM derived underwater superoleophobicity in the stretchable membrane. The details of each durability test are accounted in the following section;

Sand Drop Test: 100g of sand was poured from a height of 25cm onto both the AVM and Glu-AVM (2cm x 2cm) coated fibrous substrates (which was titled at an angle of 45^o). The underwater oil wettability after the sand drop test was investigated by measuring the oil contact angles and visual inspections.

Sand Paper Abrasion Test: Sand paper abrasion test was performed by fixing the coated (both AVM and Glu-AVM; 2cm x 2cm) fibrous substrates onto a glass slide and subsequently rubbed a sand paper over it with back and forth motion, and 500g load was applied during this rubbing process. Thereafter, the oil wettability property was examined with contact angle measurements and digital imaging.

Adhesive Tape Test: The AVM derived coated substrates (2cm x 2cm) were brought in contact with a freshly exposed adhesive tape, and an external load of 500g was applied on top for 10 minutes to ensure uniform contact between the respective substrate and the adhesive interface. Thereafter, the fabric was peeled off form the adhesive tape manually and the underwater oil wettability was re-examined by following standard characterization processes.

Physical Manipulations: Both the AVM and Glu-AVM coated substrates were manually bended, creased, twisted and winded without any preference for several times. Subsequently, the digital images were acquired and oil contact angles were measured underwater to examine the impact of these physical manipulations on the embedded underwater superoleophobic property. Manually and gradually tensile strain was applied on both the AVM and Glu-AVM coated substrates and oil wettability under water was examined after regular intervals.

Chemical Durability Tests: The underwater oil wettability on the freshly exposed aloe vera mucilage and its coating on selected substrate were examined separately after exposing them to various chemically harsh aqueous phases—that are artificial sea water, river water, extremes of pH (1 and 12), surfactant contaminated water (SDS, 1mM) for 30 days. The artificial sea water was prepared by mixing $MgCl_2$ (0.226g), $MgSO_4$ (0.325g), NaCl (2.673g) and $CaCl_2$ (0.112g) in 100 mL of de-ionized water in a volumetric flask.

Effect of heating of the oil wettability on Aloe Vera Mucilage:

The Aloe Vera mucilage was cut into a small piece (2cm x 1.5cm x 0.8cm) and carefully fixed onto a glass slide with the rind acting as the base on the glass slide. The Mucilage was subsequently submerged in de-ionized water (40 mL) in a glass beaker. This was again placed on a hot plate, and a mercury thermometer was used for continuous monitoring of the temperature of the system. A droplet of size (15µl) of red colored DCE was placed on the mucilage exposed to water and the temperature of the system was gradually increased up to 100^oC using a hot plate. The effect of this gradual heating of the aqueous phase on the oil wettability of the mucilage was examined by contact angle measurements and digital images.

Gravity-driven Oil/Water Separation:

AVM derived stretchable and durable membrane was exploited in separation of oil/water mixtures. Various heavy and light oils were used in the current demonstration. A lab made prototype was developed using a 50 mL falcon tube wherein the AVM derived stretchable underwater superoleophobic membrane was pre-wetted with water was tied to the opening of the falcon tube and another hole was made near the closed end of the tube in order to pour the mixture of oil/water with the help of a funnel. Water was dyed with Rhodamine-6G and Methylene blue as required and oil was dyed with Nile Red. The water was selectively passed through the oil-repellent membrane and was collected in a beaker.

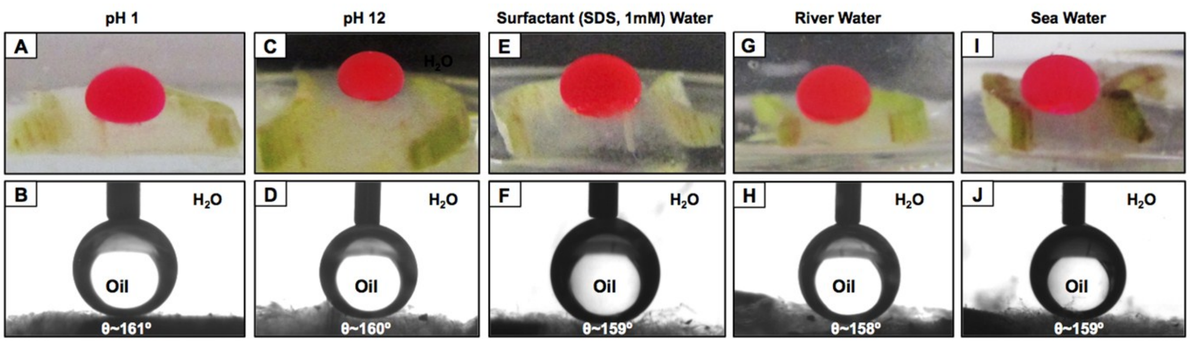

Figure S1. A-J) Digital images (A, C, E, G, I) and oil contact angles (B, D, F, H, J) of beaded oil droplets on AVM after submerging in various complex chemical conditions including pH 1 (A, B), pH 12 (C, D) surfactant (SDS,1mM) water (E, F), river water (G, H) and sea water (I, J) respectively. The oil wettability was examined at regular intervals and nonadhesive underwater superoleophobicity remained intact even after continuous exposure to various chemically challenging settings for 30 days.

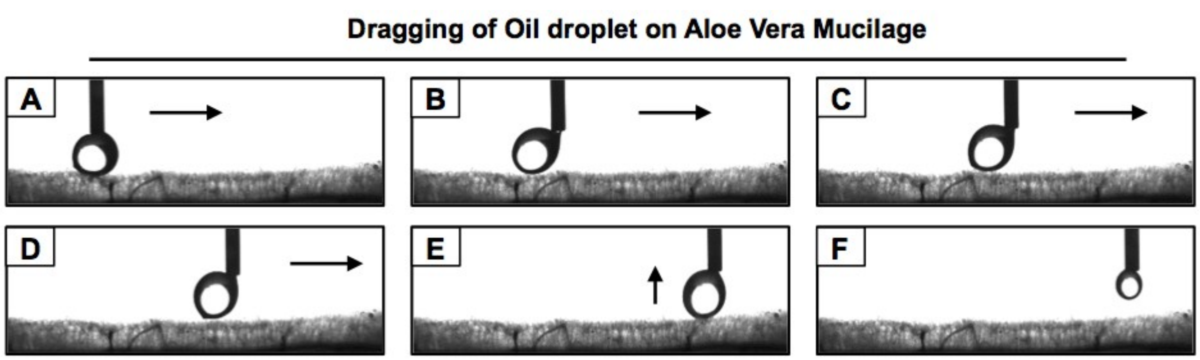

Figure S2. (A-F) Digital images displaying the translation (A-D) of oil droplet on the top surface of AVM under water and receding (E-F) of the beaded oil droplet from AVM surface.

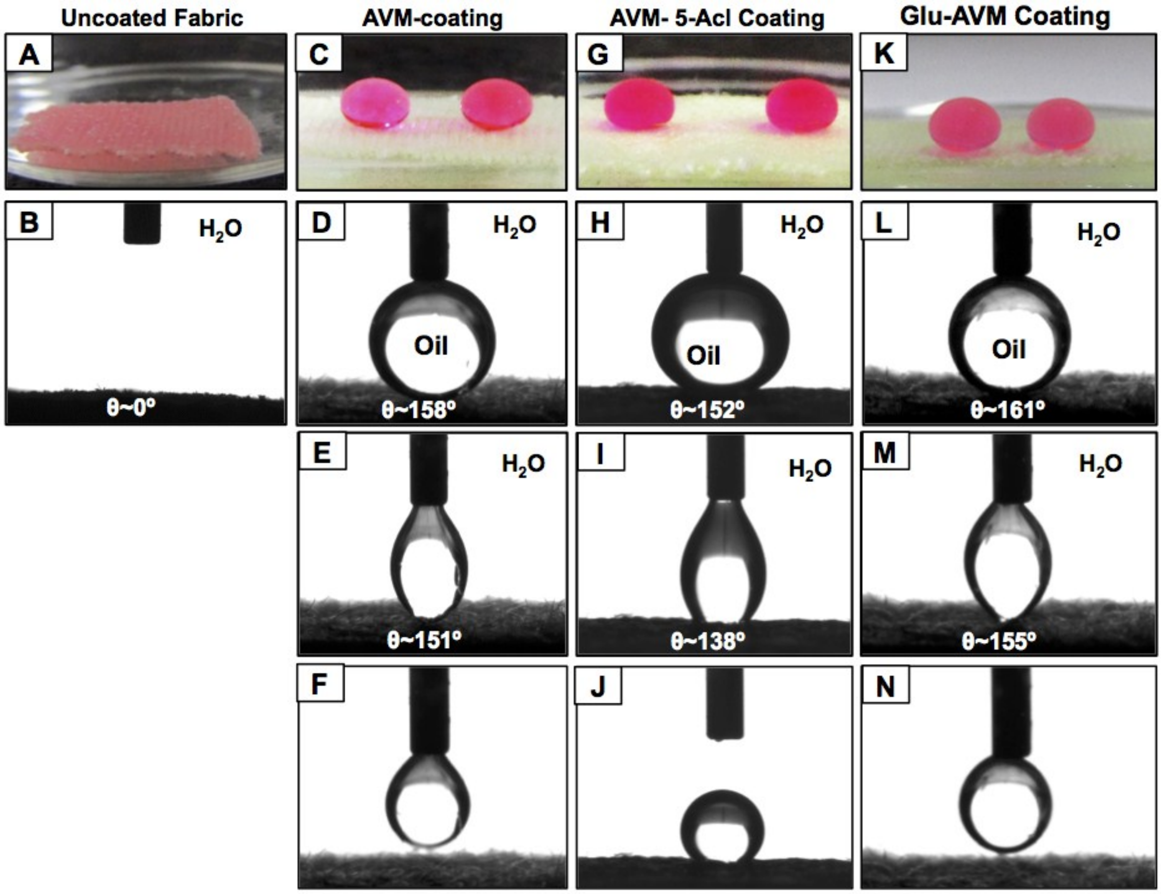

Figure S3. A-K) Digital images (A, C, G, K) and oil contact angles (B, D-F, H-J, L-N) of beaded (D,H,L) and receding (E-F, I-J, M-N) oil droplets on uncoated fibrous substrate (A, B), after AVM coating (C-F), after treatment of AVM coating with 5Acl (AVM-5Acl; G-J) and after the glucamine treatment (K-N) of the AVM-5Acl coating respectively. E-F,I-J,M-N) Contact angle images during receding of the oil droplets from respective interfaces under water.

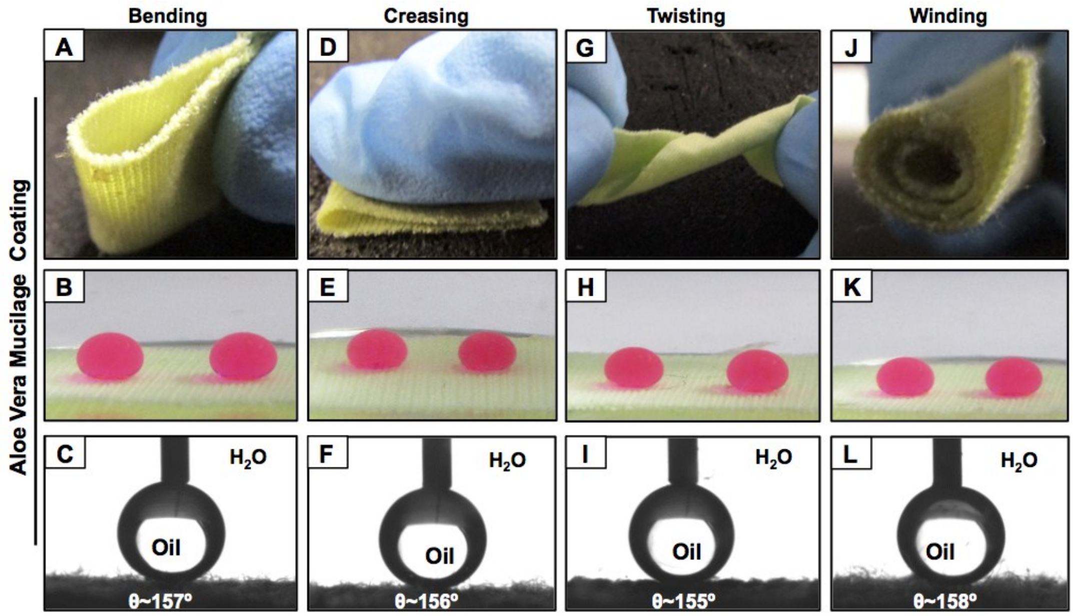

Figure S4. A-L) Digital images (A, B, D, E, G, H, J, K) and oil contact angles (C, F, I, L) of beaded oil droplets on AVM coated membrane after incurring various physical manipulations including bending (A, B, C), creasing (D, E, F), twisting (G, H, I), winding (J, K, L) respectively.

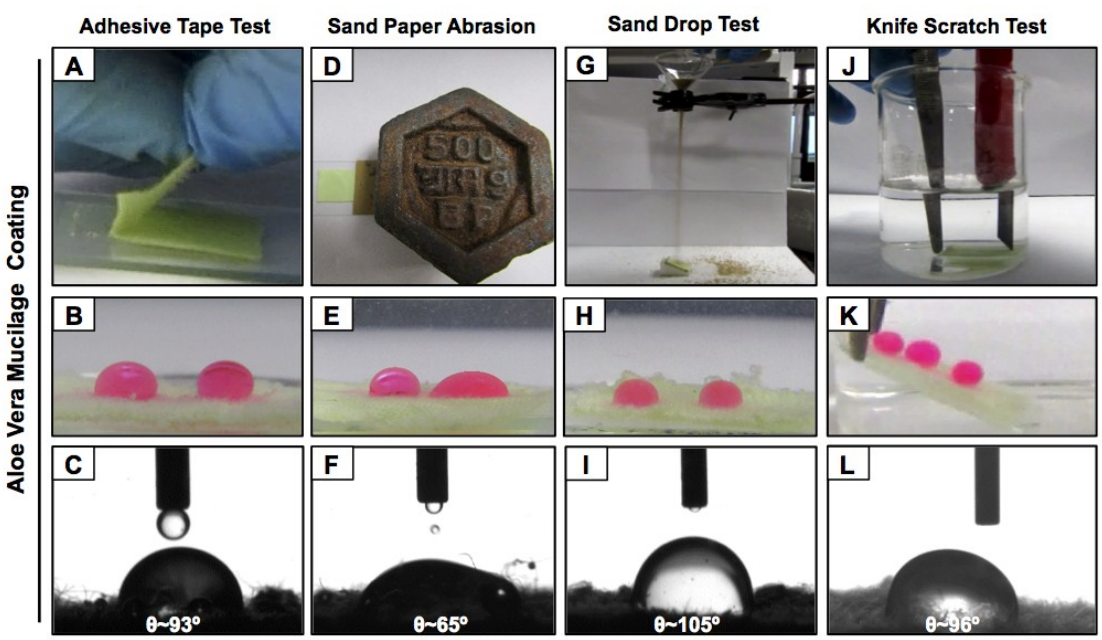

Figure S5. A, D, G, J) Digital images illustrating the set-up for different physical abrasions—including adhesive tape test (A), sand paper test (D), sand drop test (G) and knife scratching (J) test. Digital images (B, E, H, K) and oil contact angles (C, F, I, L) of beaded oil droplets under water on AVM coated fibrous substrate after performing various physical abrasions, including adhesive tape test (A-C), sand paper abrasion (D-F), sand drop test (G-I) and knife scratch test (J-L) respectively.

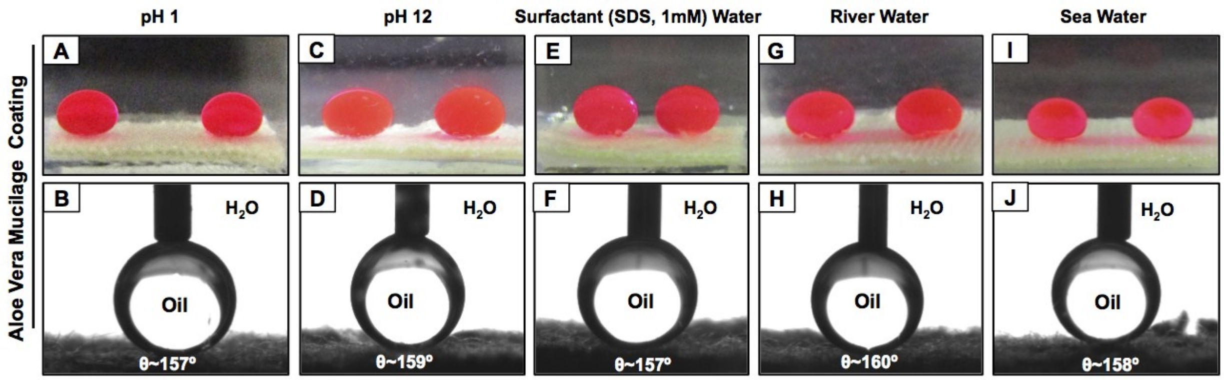

Figure S6. (A-J) Digital images (A, C, E, G, I) and oil contact angles (B, D, F, H, J) of beaded oil droplets under water on AVM coated fibrous substrate after exposing the coating to various chemically harsh aqueous phases including pH 1 (A, B), pH 12 (C, D) surfactant (SDS, 1mM) water (E, F), river water (G, H) and sea water (I, J) for 72 h.

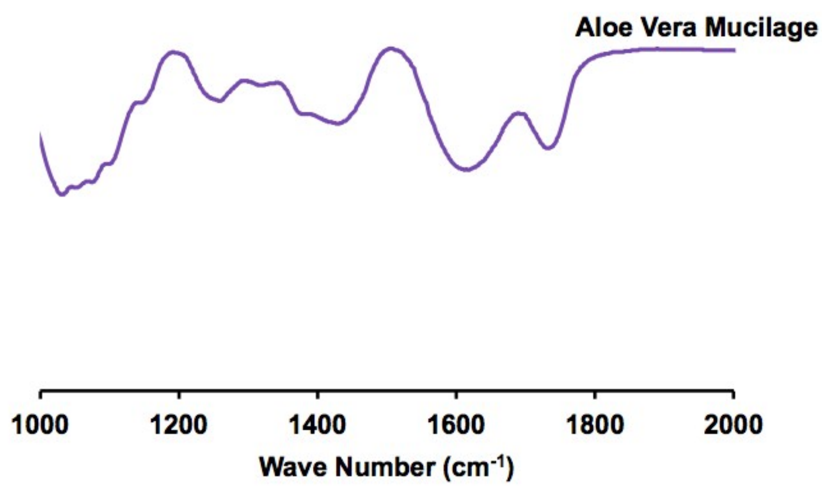

Figure S7. FTIR spectra of AVM. The sharp peak at 1409 cm-1 that signifies the existence of C-H stretching of β carbon of vinyl group is not present in the AVM.

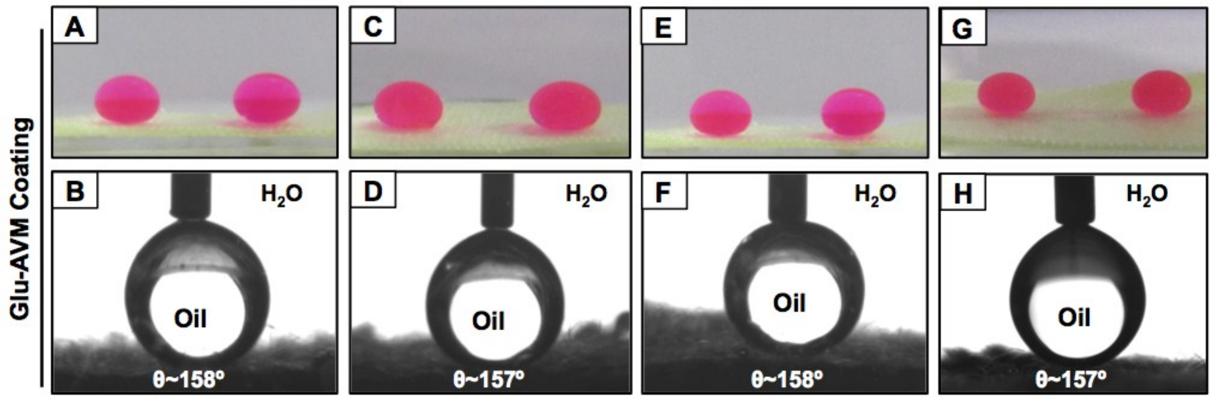

Figure S8. A-H) Digital images (A, C, E, G) and oil contact angles (B, D, F, L) of beaded oil droplets on the Glu-AVM coated fibrous substrate after exposing to various physical manipulations—including bending (A-B), creasing (C-D), twisting (E-F), winding (G-H) respectively.

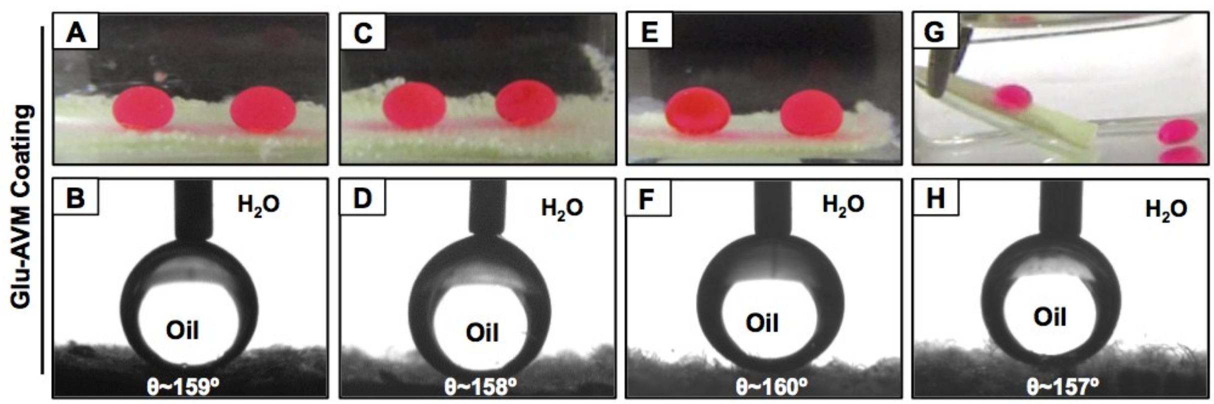

Figure S9. A-H) Digital images (A, C, E, G,) and oil contact angles (B, D, F, H) of beaded oil droplets under water on the Glu-AVM coating after exposing to various physical abrasion tests including adhesive tape test (A-B), sand paper abrasion (C-D), sand drop test (E-F) and knife scratch test (G-H) respectively.

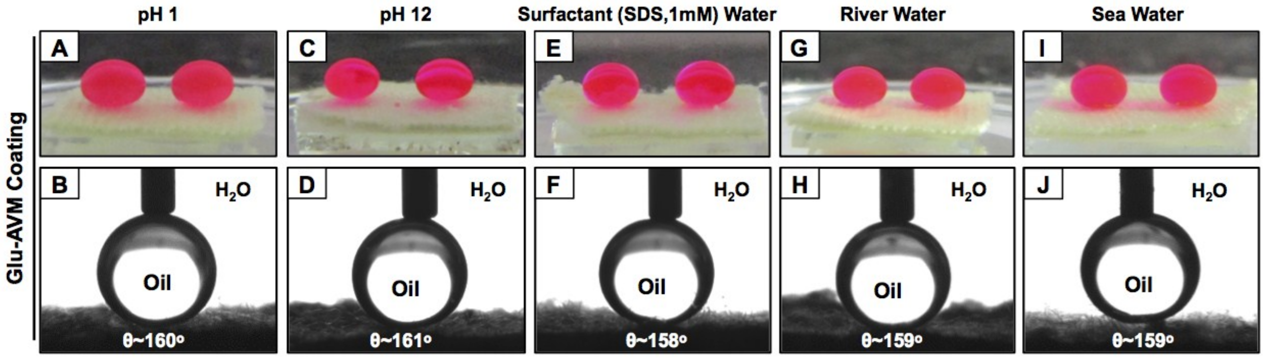

Figure S10. A-J) Digital images (A, C, E, G, I) and oil contact angles (B, D, F, H, J) of beaded oil droplets underwater on the Glu-AVM coated stretchable membrane after submerging it in various harsh chemical media including pH 1 (A-B), pH 12 (C-D) surfactant (SDS,1mM; E-F) water, river water (G-H) and sea water (I-J) for 30 days respectively

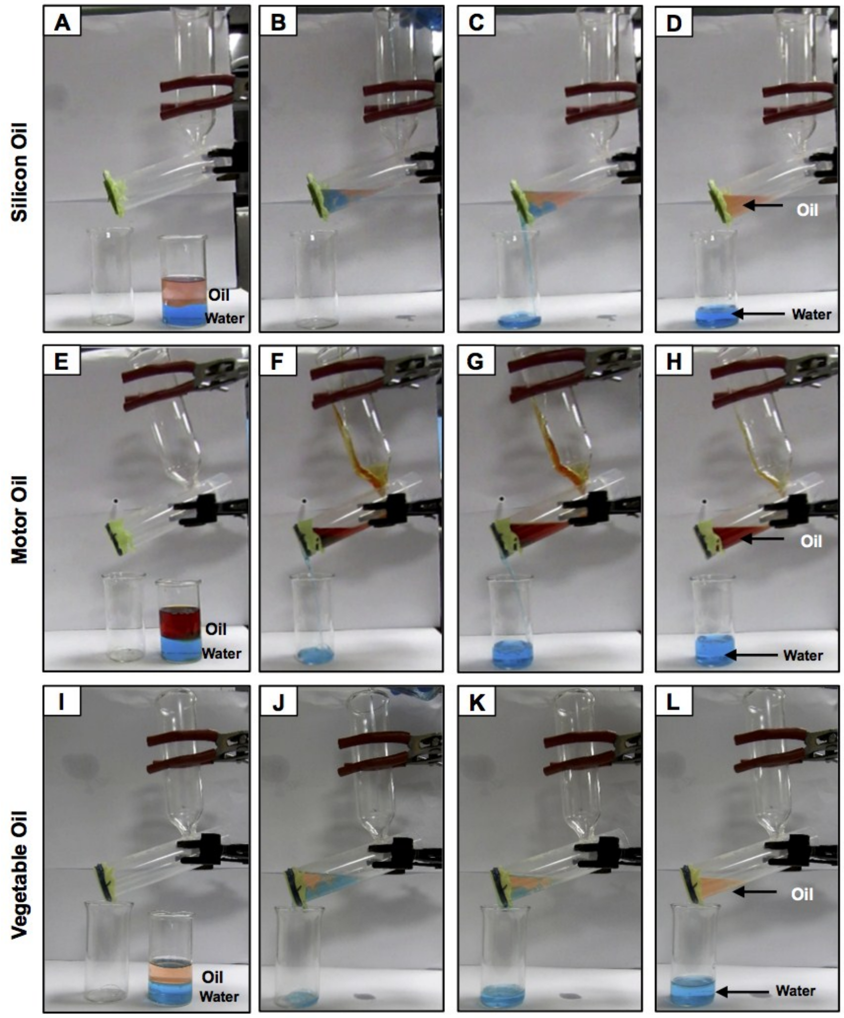

Figure S11. (A-L) Digital images showing the separation of oil/water mixtures for various oils—including silicon oil (A-D), motor oil (E-H) and vegetable oil (I-L). The water phase is colored with blue dye.

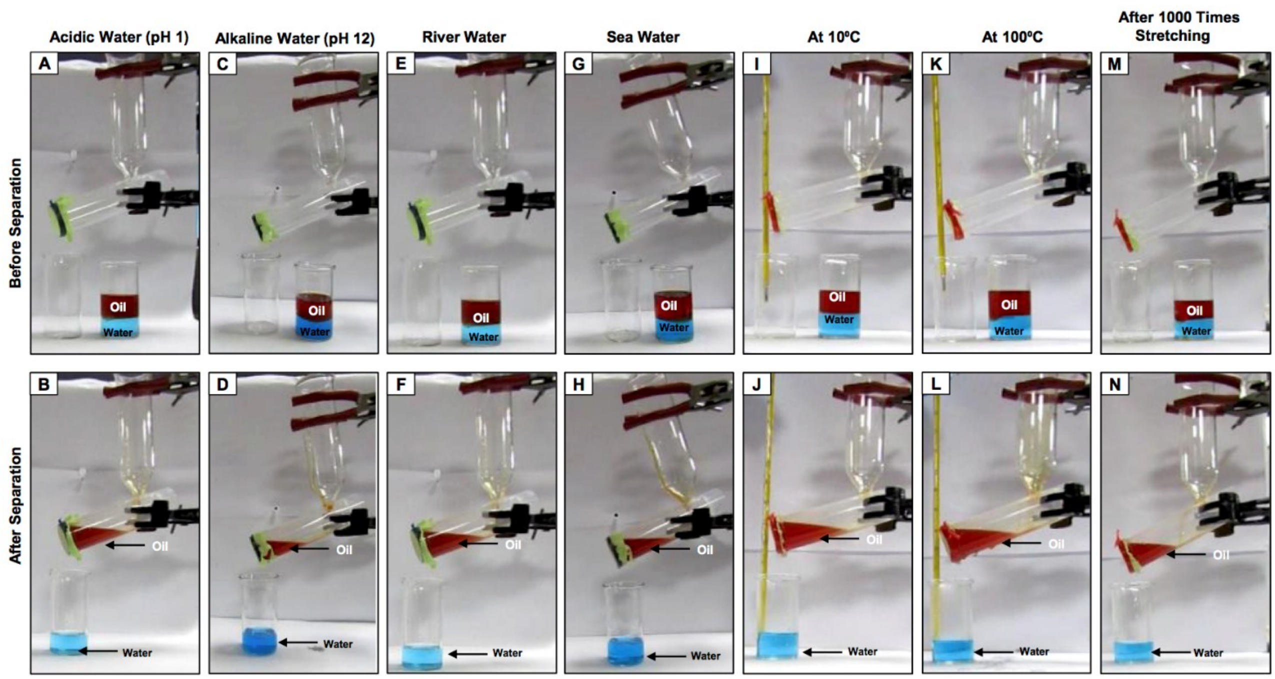

Figure S12. A-N) Digital images showing the separation of oil/water mixtures in various severe practically relevant conditions including pH 1 (A, B), pH 12 (C, D), river water (E, F), sea water (G, H), at 10ºC (I, J), at 100ºC (K, L) and after stretching the biomimicked membrane 1000 times (M, N) respectively.

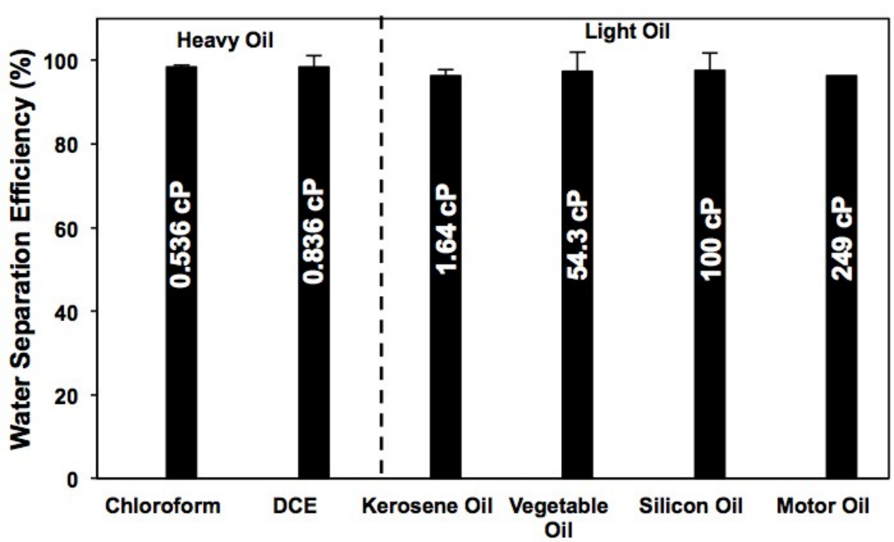

Figure S13. Plot displaying the water separation efficiency of various oil/water mixtures where oils with a wide range of densities and viscosities have been used.