Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

'Fish-Scale' Mimicked Stretchable and Robust Oil-Wettability That Perform in Practically Relevant Various Physically/Chemically Severe Scenarios

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Movie 1: Accounting the super-oil-repellence of the synthesized material after performing the adhesive tape peeling test

Movie2: Illustrating the knife test on biomimicked interfaces under water.

Movie 3: Demonstrating the light-oil/water separation performance through biomimicked interfaces.

Movie 4: Demonstrating the heavy model-oil (DCE)/water separation performance through biomimicked interfaces.

Movie 5: Illustrating the filtration based oil/water separation through synthesised special interfaces at high temperature (100°C).

Movie 6: Illustrating the filtration based oil/water separation through synthesised special interfaces at low temperature (10°C).

Experimental Section:

Materials: Branched polyethyleneimine (BPEI, MW~ 25000), dipentaerythitol penta-acrylate (5-Acl, MW~ 524.21g/mol), Nile red (Technical grade, Sigma-N3013) were purchased from Sigma Aldrich, Bangalore, India. Dimethyl sulfoxide (DMSO) were purchased from Fischer Scientific, Mumbai, India. Ethyl alcohol (CAS Registry No. 64-17-5, Lot 1005150) was purchased from TEDIA Company (United States of America). Adhesive tape (Jonson tape Ltd. India) were purchased from local sources. THF was obtained from RANKEM, Maharastra, India. Dichloromethane (DCM), dichloroethane (DCE) were acquired from Merck Life Science

Pvt. Ltd., New Delhi, India. D-glucamine (>95%) was purchased from Tokyo chemical industry. Fibrous polyurethane (PU) substrate (fabric), soybean oil (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 the construction site of IIT Guwahati.

General Consideration: The glass vials were washed thoroughly with ethyl alcohol and then acetone in prior to begin solution-preparation. KRUSS Drop Shape Analyzer-DSA25 instrument with mechanical liquid dispenser was accounted for contact angle measurements at ambient temperature. The size of the nano-complex was quantitatively determined by Dynamic light scattering (DLS) study using Zetasizer Nano ZS90 instrument (model no. ZEN3690). Scanning electron microscopic (SEM) images were acquired using a Carl Zeiss field emission scanning electron microscope (FESEM). The FTIR spectra were recorded using a Perkin-Elmer instrument at ambient temperature by incorporating the polymeric matrix to the KBr pallet. The digital photographs were captured by Canon Power Shot SX420 IS digital camera for all the experimental demonstrations. The oil in water emulsion droplets are characterized with Nikon Eclipse Ts2R (Nikon digital sight DS-U3).

Construction of Reactive Multilayers on Stretchable Fibrous Substrate and Post Covalent Modification of Multilayers: First, solutions of BPEI (265 mg/mL) and 5Acl (50mg/mL) are prepared in ethanol. Then, 5 mL of 5Acl was mixed with 500 µL of BPEI and kept the reaction mixture for 20 minutes with continuous agitation. Next, this mixture of BPEI/5Acl having polymeric nano-complex (NC) was used in layer-by-layer deposition through mutual covalent reaction with another dipping solution—that is BPEI polymer. The construction of multilayers of NC/BPEI on the selected fibrous substrate was as follows; i) stretchable fibrous substrate was dipped in BPEI solution for 10 s; ii) the fibrous substrate was removed from the polymeric dipping solution and rinsed twice with ethanol bath for 10s each time; iii) the fibrous substrate was placed in reaction mixture of BPEI/5Acl for 10s; iv) the substrate was removed and rinsed repeatedly by following the step ii). This cycle was repeated for 20 times to develop appropriate hierarchical topography on the selected fibrous substrate. Next, the covalently cross-linked polymeric multilayers on stretchable substrate was post modified with primary amine containing appropriate hydrophilic small molecules (e.g., glucamine) to make polymeric coating highly water compatible. The coated fibrous substrate was submerged into the solution of glucamine (5 mg/mL; DMSO) for overnight. After treatment, the excess glucamine solution was washed thoroughly with THF and dried completely under stream of cold air.

Physical and Chemical Durability of the Bio-mimicked Wettability:

Physical Durability Test:

1. *Sand drop test:* A stream of sand grain (100 gm) was dropped on the stretchable 'fish-scale' mimicked interface (1cm × 2cm) that was kept tilted with 45°, and the sand grain was poured from a height of 25 cm. The underwater oil wettability was examined by measuring the oil contact angles and visual inspections.

2. *Sand paper abrasion test:* The abrasive sand paper was rubbed on the artificial bio-mimicked interfaces with applied load of 700 g over 2 cm^2 area. The external applied load is strategically used for improving the contact between the abrasive rough surface and the synthesized polymeric coatings on fibrous substrate. Finally, the oil wettability property was investigated with contact angle measurements and visual inspections.

3. *Adhesive Tape Test:* First, the synthesized bio-mimicked interface was brought in contact with freshly exposed adhesive tape (1cm×2cm), and a load of 700gm was applied on it, to ensure the uniform contact between the matrix and the adhesive surface of the tape. After 5min, the tape was manually peeled off, and the underwater oil wettability was re-examined by measuring the oil contact angle and visual inspections.

4. *Bending, creasing, twisting, and wending of bio-mimicked interfaces:* The synthesized 'fish scale' mimicked wettability was exposed to common practiced various physical manipulations—including bending, creasing, twisting and wending. The stretchable bio-mimicked substrate was manually bended, creased, twisted and wended with random preference for several times. Thereafter, the oil contact angles were measured under water to examine the impact of these physical manipulations on the embedded bio-mimicked wettability.

Chemical Durability Tests: The under-water superoleophobic interfaces were exposed to various chemically harsh aqueous phases—including artificial sea water, river water, extremes of pH (1 & 12), surfactant (SDS solution (1mM), DTAB solution (1mM)) and protein (BSA solution (5 weight %)) contaminated water etc. for 10 days yet the property was unaltered which was confirmed by contact angle measurements. 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 100ml of deionized water in a volumetric flask.

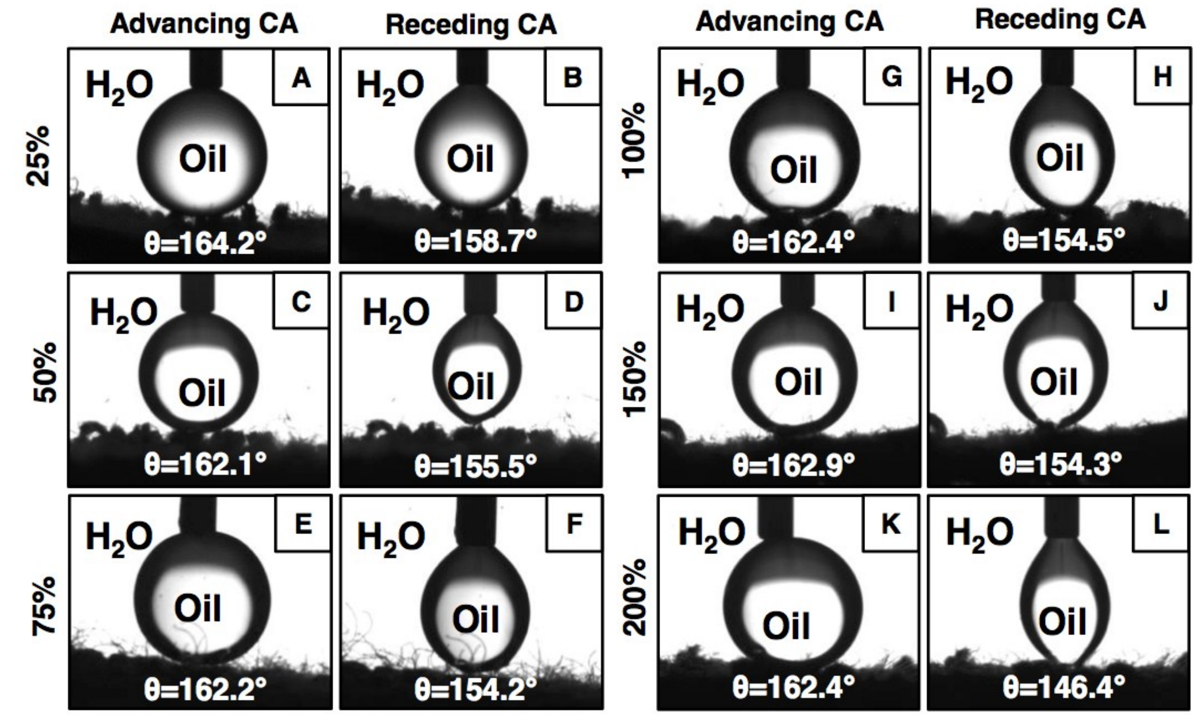

Figure S1. A-L) Advancing (A,C,E,G,I,K) and receding (B,D,F,H,J,L) contact angle images of beaded oil droplet under water on the biomimicked special interfaces after incurring tensile deformations with strains of 25% (A-B), 50% (C-D), 75% (E-F), 100% (G-H), 150% (I-J) and 200% (K-L) respectively.

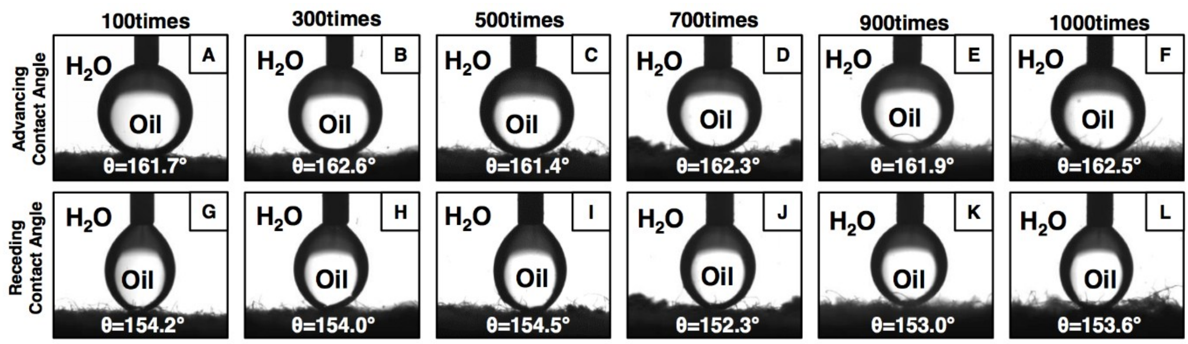

Figure S2. A-R) Advancing (A-F) and receding (G-L) contact angle images of beaded oil droplets under water on the biomimicked interfaces after incurring successive physical deformations for 100 (A,G), 300 (B,H), 500 (C,I), 700 (D,J), 900 (E,K), 1000 (F,L) times with 150 % of tensile strain.

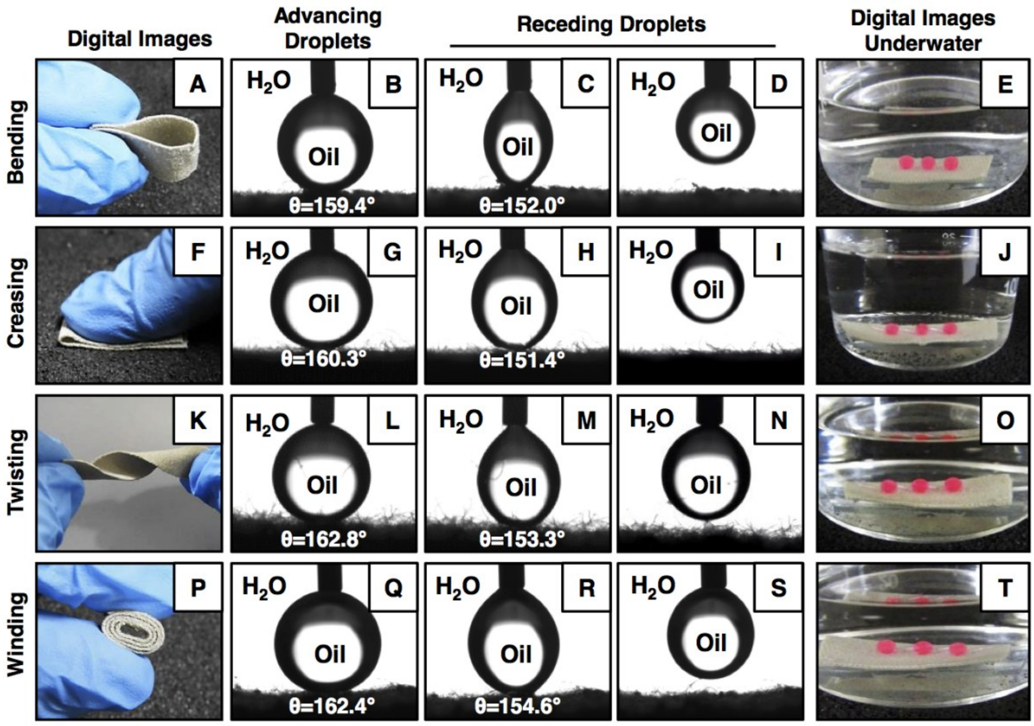

Figure S3. A,F,K,P) Digital images of the various physically manipulated biomimicked special interfaces. B-D,G-I, L-N, Q-S) Advancing (B,G,L,Q) and receding (C-D,H-I,M-N,R-S) contact angle images of beaded oil droplet on the physically manipulated (bended (B-D), creased (G-I), twisted (L-N), winded (Q-S)) biomimicked interfaces under water. E,J,O,T) Digital images of beaded oil droplets on the biomimicked interfaces after performing various physical manipulations—including bending (E), creasing (J), twisting (O) and winding (T) .

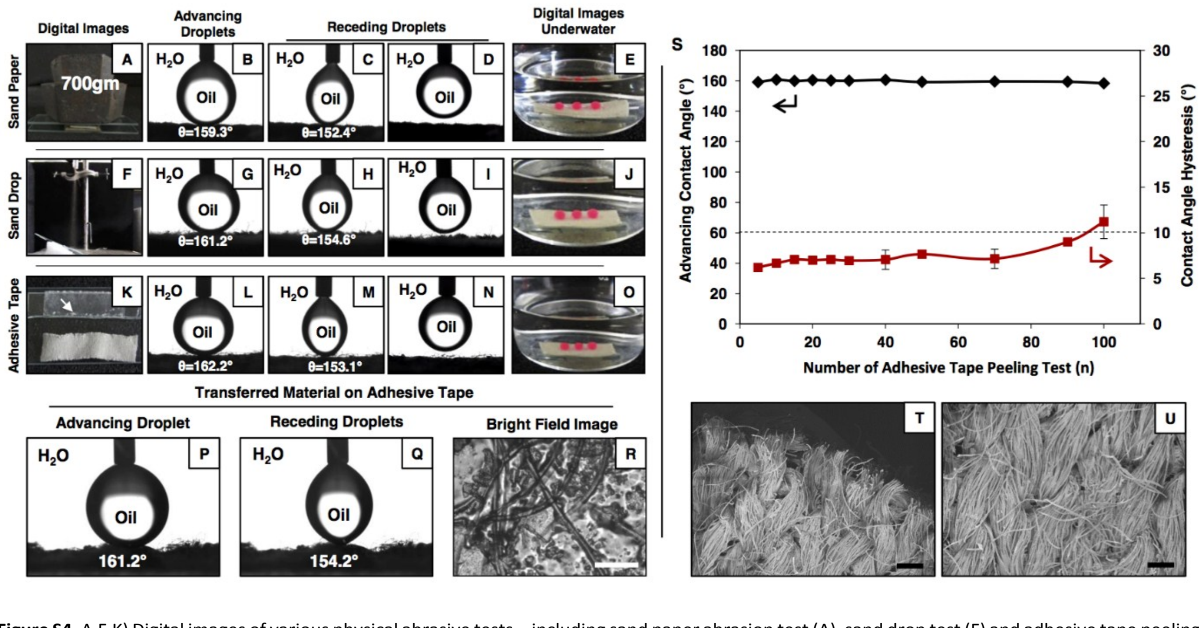

Figure S4. A,F,K) Digital images of various physical abrasive tests—including sand paper abrasion test (A), sand drop test (F) and adhesive tape peeling test (K), on the synthesised underwater super-oil-repellent interfaces. B-D,G-I,L-N) Advancing (B,G,L) and (C-D,H-I,M-N) receding contact angle images of beaded oil droplet on the synthesized special interfaces after conducting the sand paper abrasion test (B-D), sand drop test (G-I) and adhesive tape peeling test (L-N). E, J, O) Digital images of beaded oil droplets under water on the artificial biomimicked interfaces after the performance of various abrasive tests—including sand paper abrasion test (E), sand drop test (J) and adhesive tape peeling test (O). P-Q) Advancing (P) and receding (Q) oil contact angle (OCA) images on the transferred material that adhered on the adhesive tape. R) Bright field optical image of the transferred material on adhesive tape (scale bar=100μm). Q) The plot accounts the change in advancing and receding OCA with successive adhesive tape peeling tests on the same biomimicked interface, the dotted line indicates the upper limit of non-adhesive superoleophobicity under water. R-S) FESEM images of the stretchable biomimicked material (edge (R) and center (S)) after performing adhesive tape peeling test (scale bar=200μm).

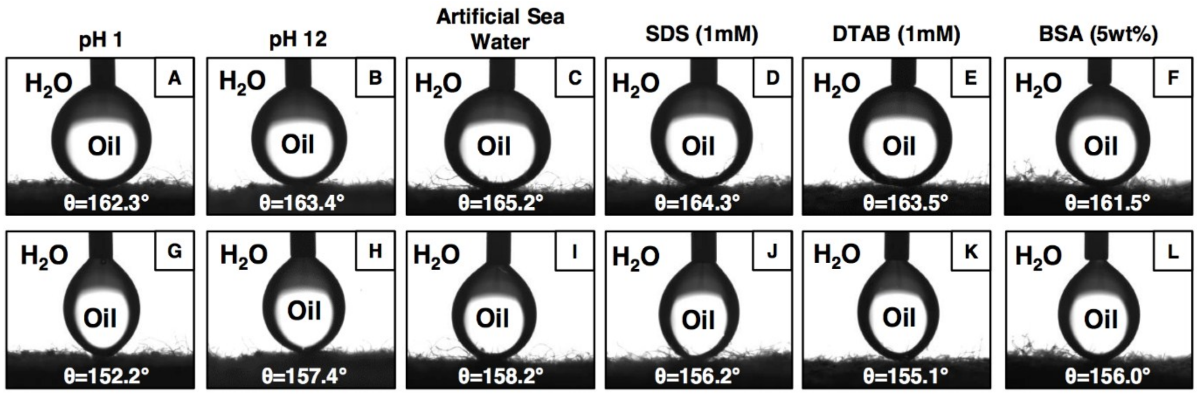

Figure S5. A-L) Advancing (A-F) and receding (G-L) contact angle images of beaded oil droplets on the biomimicked super-oil-repellent interfaces—which was continuously exposed to different chemically complexes harsh environments—including highly acidic (pH1, A, G) water, highly alkaline (pH12, B, H) water, artificial sea water (C, I), SDS (D, J) and DTAB (E, K) contaminated (1 mM) water and BSA protein (F, L) contaminated water (5wt%) for 10 days.

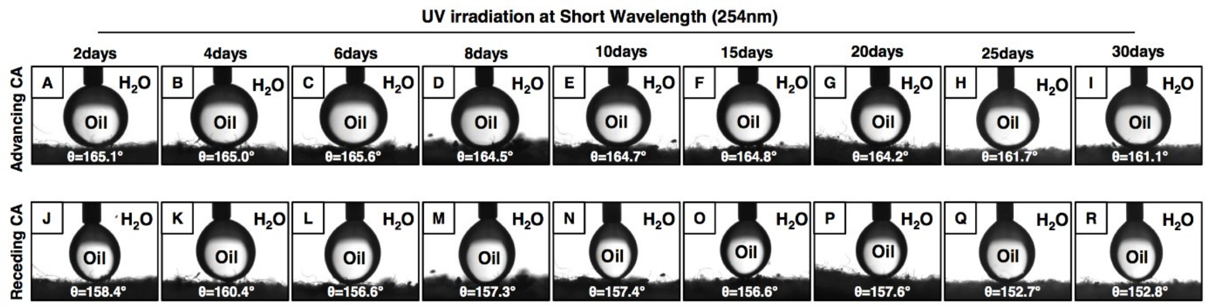

Figure S6. A-R) Advancing (A-I) and receding (J-R) contact angle images of beaded oil droplets under water on the artificial super-oil-repellent interfaces that are exposed prolonged (30 days) UV irradiation at 254nm wavelength.

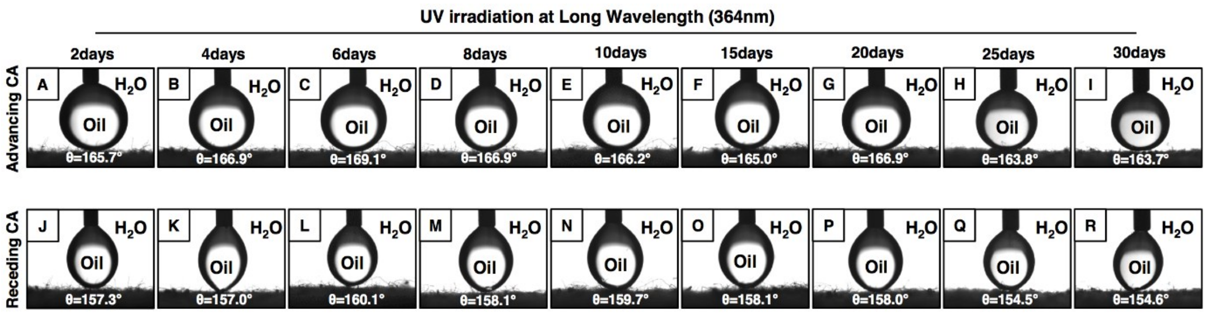

Figure S7. A-R) Advancing (A-I) and receding (J-R) contact angle images of beaded oil droplets on synthesized oil-repellent interfaces under water, after exposing the biomimicked interface to UV irradiation at 364nm wavelength for 2days (A,J), 4days (B,K), 6days (C,L), 8days (D,M), 10days (E,N), 15days (F,O), 20days (G,P), 25days (H,Q), 30days (I,R).

Table S1: Accounting the Effect of Tensile Deformation of the *Physically/Chemically Abraded Biomimicked Material on its Oil-Wettability Under Water*

Physical Insults	% Strain	$\theta_{adv.}$ (°)	$\theta_{hys.}$ (°)
Bending	150	159.3° ± 0.1	7.8° ± 0.8
Creasing	150	159.6° ± 0.4	8.8° ± 1.1
Twisting	150	160.4° ± 1.2	8.0° ± 0.2
Rolling	150	160.3° ± 0.4	6.3° ± 1.5
Sand Paper	150	159.9° ± 0.8	6.1° ± 1.5
Sand Drop	150	159.3° ± 0.1	5.8° ± 0.4
Adhesive Tape	150	160.7° ± 1.1	7.2° ± 0.8
Acidic Water (pH=1)	150	159.4° ± 0.2	8.9° ± 0.9
Basic Water (pH=12)	150	159.2° ± 0.1	6.1° ± 0.4
Artificial Sea Water	150	160.5° ± 0.2	7.3° ± 0.0
SDS Water	150	160.1° ± 0.2	7.0° ± 0.5
DTAB Water	150	159.7° ± 0.6	6.3° ± 0.7
BSA (5 wt%) Water	150	159.2° ± 0.5	7.8° ± 0.1

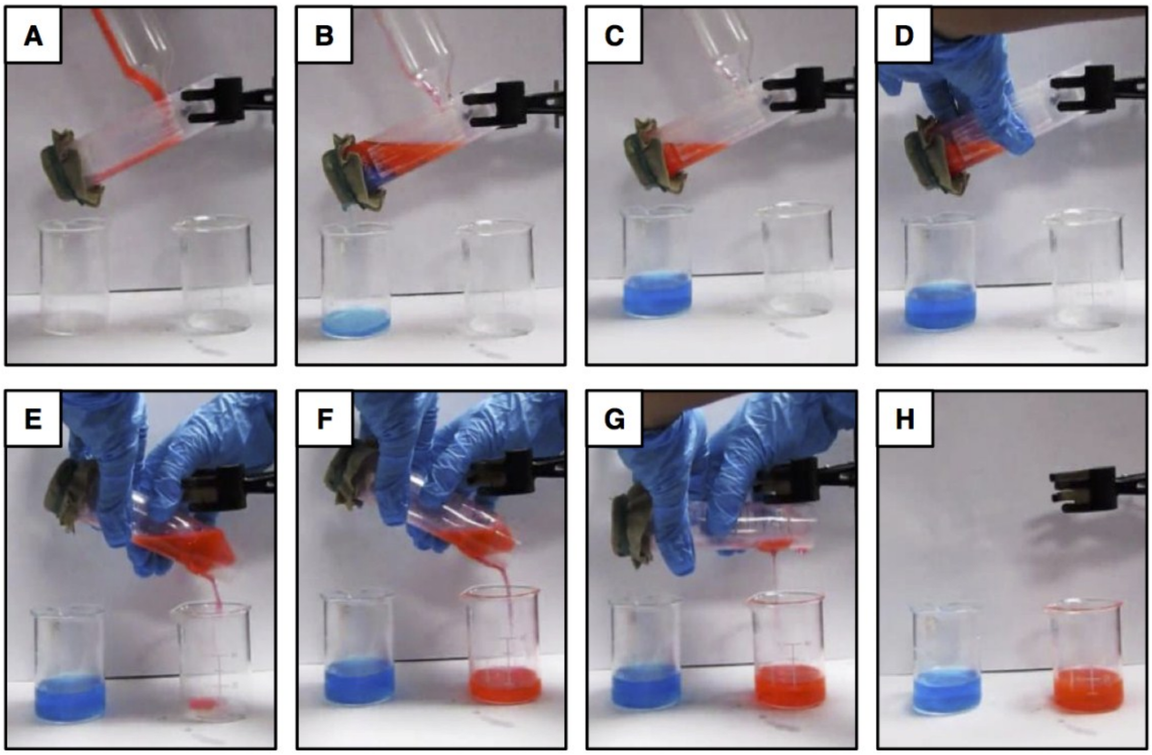

Figure S8. A-H) Digital images of the selective filtration/collection (A-C) of aqueous phase (added methylene blue dye facilitates visual inspection) from oil (soybean oil, Nile red dye aids visual inspection)/water mixture. D-H) Digital images illustrating the collection of water free residual oil phase in separate container through the side hole of the prototype.

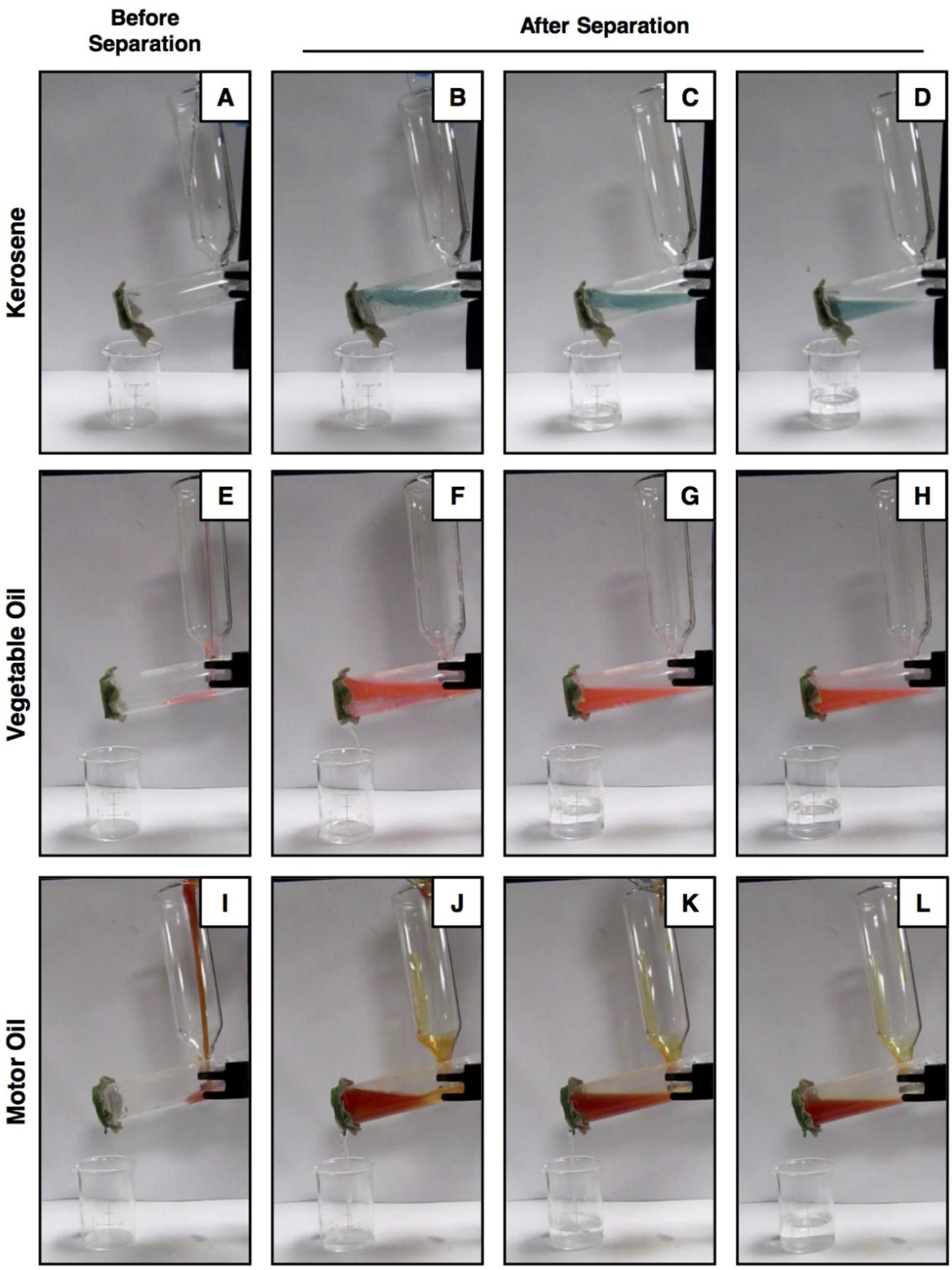

Figure S9. A-L) Digital images illustrating the separation of oil/water mixture, where various oils (kerosene, vegetable oil and motor oil) with different viscosities are used in preparation of the oil/water mixtures.

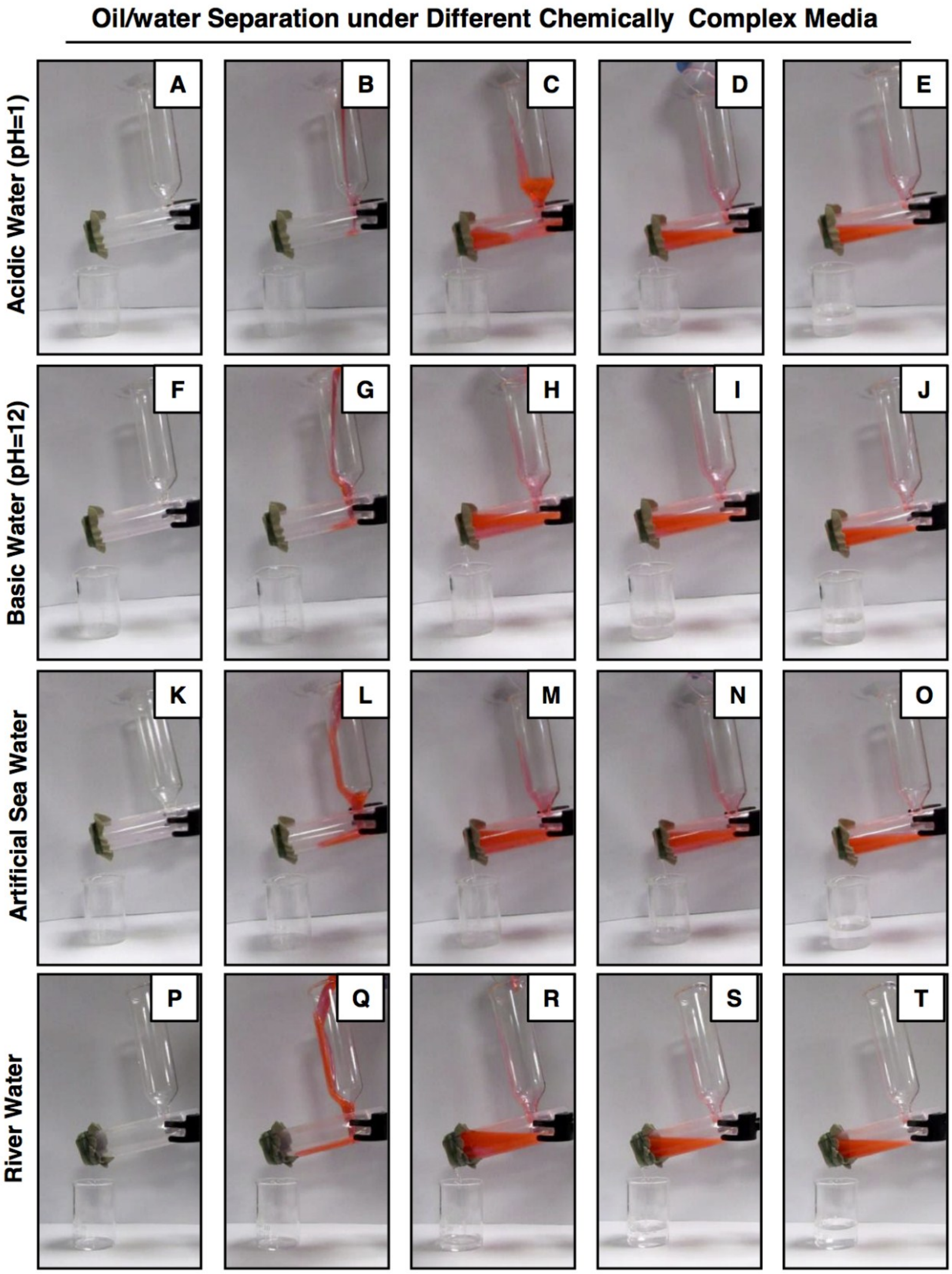

Figure S10. A-T) Digital images demonstrating the oil/water separation performance under different chemically complex scenarios—including highly acidic water (pH1), highly basic water (pH12), artificial sea water and river water.

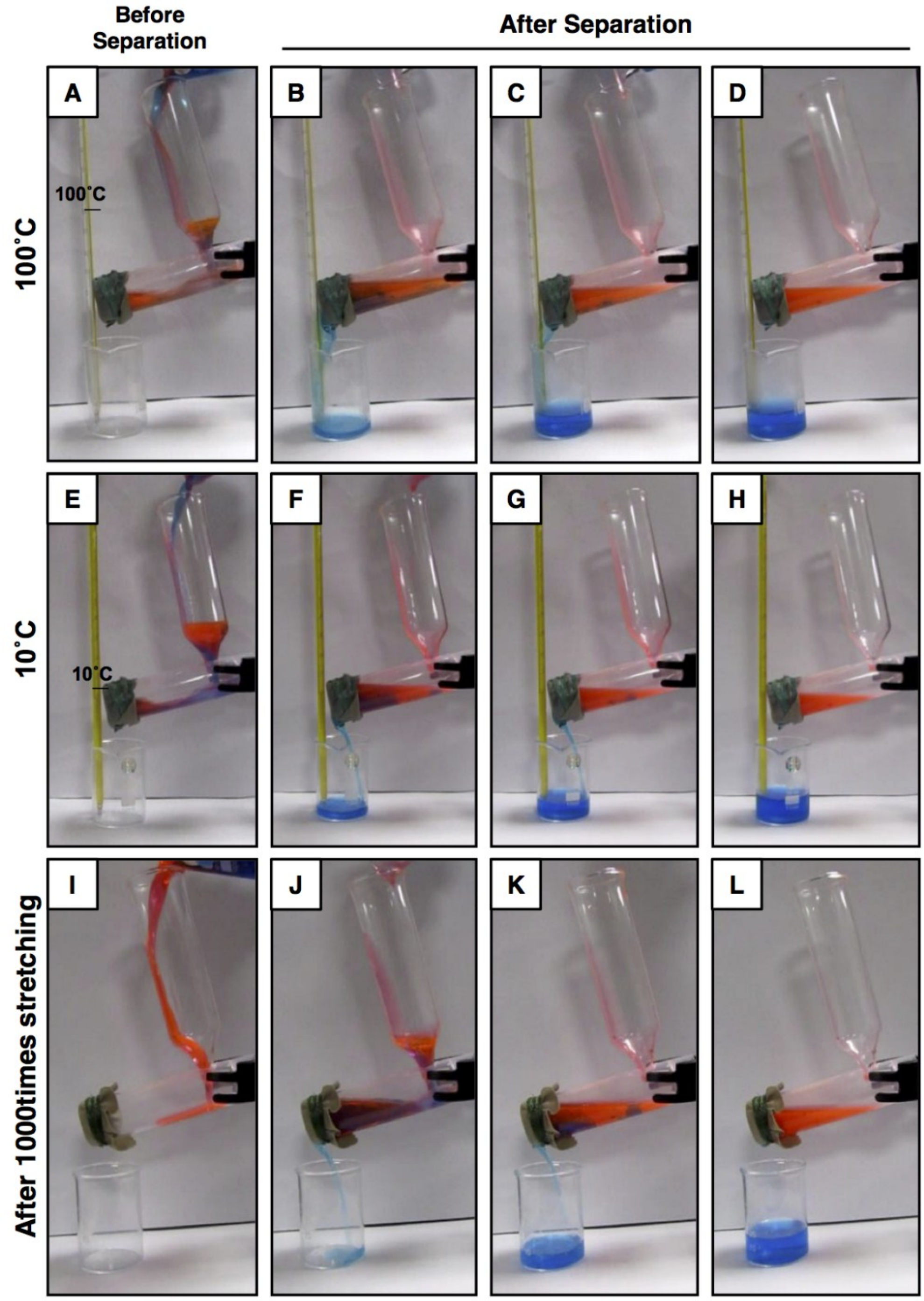

Figure S11. A-L) Digital images illustrating the successful and selective filtration of aqueous phases from oil/water at high temperature (A-D; 100°C), low temperature (E-H; 10°C) through biomimicked interfaces, even after exposing the biomimicked interface to successive tensile deformation (150 %) for 1000times.

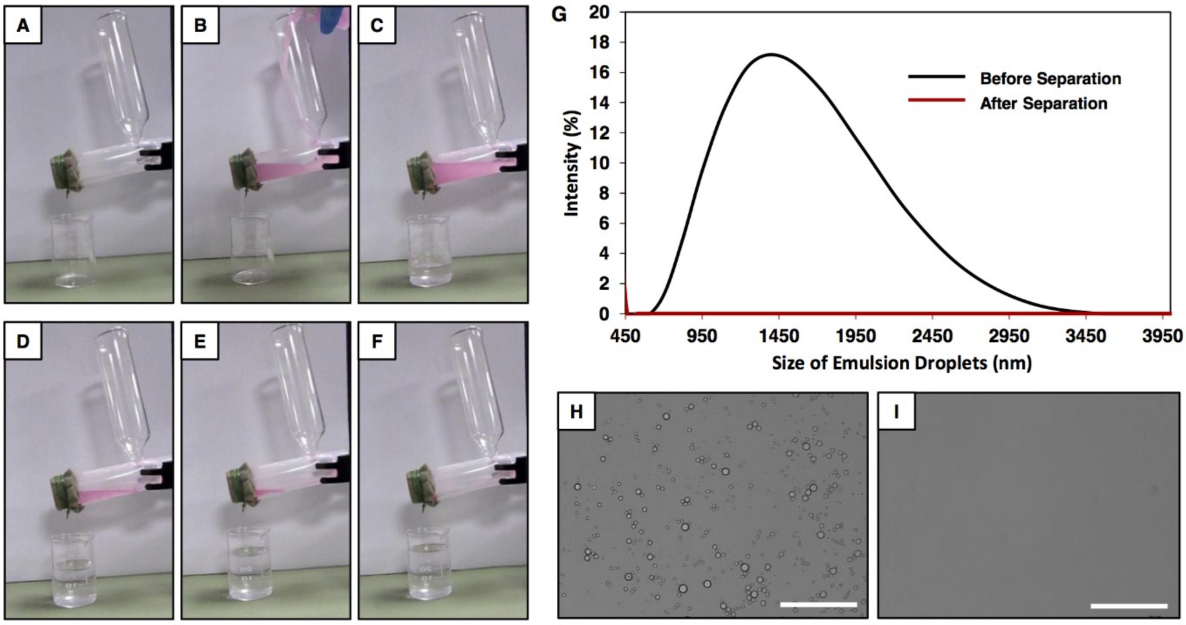

Figure S12. A-F) Digital images demonstrating the selective water separation performance from oil-in-water emulsion solutions, where water insoluble Nile red dye is added in oil phase to improve the visual inspection. G) DLS profile of oil-in-water emulsion solutions before (black) and after (red) filtration process. H-I) Bright field microscopic images (scale bar- 100μm) of the oil-in-water emulsion solution before (H) and after (I) separation performance through biomimicked interfaces.