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Supporting Information

Hydrophobicity or Superhydrophobicity—Which is Right Choice for Stabilizing Underwater Superoleophilicity?

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Experimental Section:

Materials: Branched polyethyleneimine (BPEI, MW 25 000 Da), tripentaerythritol penta-acrylate (5Acl, MW 524.21 g mol-1), decylamine (DA), dodecylamine (DDA), methylene blue, 1-octadecylamine (ODA) and nile red (Technical grade, Sigma-N3013) were purchased from Sigma Aldrich, Bangalore, India. Ethyl alcohol was purchased from TEDIA Company (United States of America). THF was obtained from RANKEM, Maharashtra, India. Dichloromethane (DCM), dichloroethane (DCE), methanol and sodium chloride (NaCl) were acquired from Merck Life Science Pvt. Ltd., New Delhi, India. Melamine sponge was procured from AR Acoustics LLP, Maharashtra, India.

General Consideration: The glass dipping vials were thoroughly cleaned with ethyl alcohol and acetone prior to preparing respective dipping solutions. Both the water and oil contact angles of the materials were measured at five different positions of each sample using the KRUSS Drop Shape Analyzer-DSA25 instrument at ambient temperature. A dynamic light scattering (DLS) study for determining the change in size of the emulsion droplets was performed using a Zetasizer Nano ZS90 instrument (model no. ZEN3690). All the multilayer coated materials were coated with a thin layer of gold using a gold sputterer prior to obtaining scanning electron microscopic images (SEM) of the multilayers using a Carl Zeiss field emission scanning electron microscope (FESEM). Perkin-Elmer FTIR spectrophotometer was used in recording the Fourier transform infrared spectra of the multilayers at ambient temperature. The digital images were captured using a Nikon COOLPIX B700 digital camera. The oil in water emulsion droplets were characterized with Nikon Eclipse Ts2R (Nikon digital sight DS-U3). 600MHz NMR instrument was used for determining the total organic carbon value of the filtrate after oil-in-water emulsion separation.

Preparation of Superhydrophobic and Hydrophobic Multilayers: Multilayers of polymer and chemically reactive nanocomplex are synthesized following previous reported procedure,1 where two different multilayers were developed in presence and absence of NaCl salt (0.5 mg/ml). Firstly, both 5Acl (265 mg/ml) and BPEI (50 mg/ml) solutions were prepared in salt doped methanol, separately in two glass vials. Then, BPEI and 5Acl solutions were mixed together in 1:0.25 ratio in methanol and the mixture was kept for 5 minutes to initiate the formation of 'reactive' polymeric nanocomplex (NC). Then, a selected substrate (glass or melamine formaldehyde sponge) was simultaneously immersed in two distinct dipping solutions for consecutive 9 times to achieve the multilayers construction through 1, 4-conjugate addition reaction. [1] The 9 bilayers polymeric coating (each BPEI/NC layer pair is further denoted as 'bilayer' in the main text) was embedded with essential hierarchical features to confer superhydrophobicity, after post covalent modification with octadecylamine (ODA in THF; 0.0185 M) for overnight. During the whole layer-by-layer (LbL) deposition process, the concentrations of dipping solutions (BPEI, NC or 5Acl) were maintained by the addition of methanol at regular intervals as needed to compensate the solvent evaporation.

Similarly, hydrophobic multilayers were also constructed—in absence of any salt. The solutions of 5Acl (265 mg ml-1) and BPEI (50 mg ml-1) were prepared in ethanol in two separate glass vials and further this BPEI and 5Acl solutions were mixed together in 1:10 ratio. Then, the mixture was kept for 20 minutes to initiate the formation of the 'reactive' polymeric nanocomplex (NC). The repeated 20 consecutive LbL depositions of 'reactive' NC and BPEI polymer solutions were contributed in formation of porous polymeric multilayer consisting of 20 BPEI/NC layer pairs (each BPEI/NC layer pair is further denoted as 'bilayer' in the main text) on selected substrates (glass or melamine formaldehyde sponge). During the whole LbL deposition process, the concentrations of the polymer (or NC) solutions were maintained by the addition of ethanol as needed after regular intervals to compensate for solvent evaporation. Further, the multilayers consisted of 20 BPEI/NC bilayers were post-modified with different amine containing small molecules i.e. decylamine (DA in THF; 0.055 M), dodecylamine (DDA in THF; 0.054 M) and octadecylamine (ODA in THF; 0.0185 M) for 1 day. Finally, all the multilayers were washed with THF for 3 to 4 times and dried completely in compressed air prior to further essential characterisations.

Separation of Oil/Water Mixtures: The 5% (volume/volume) oil-in-water emulsion solution was prepared by homogeneous mixing of 5 ml DCE in 95 ml of water followed by continuous sonication for 1 hour. Similarly, the emulsions were prepared under different complex chemical environments like extremes of pH (pH 1, pH 12), temperatures (10°C, 70°C), river water and artificial sea water without altering the composition of the emulsion.

The multilayer coated and ODA-modified both hydrophobic and superhydrophobic melamine sponges were placed and fixed inside the bottom of a glass funnel. The emulsion solution was passed through the funnel contained of the hydrophobic and superhydrophobic sponges separately. Under gravity, oil-in water passed through the hydrophobic multilayers coated sponge and provided oil-free aqueous phase at the end, however, superhydrophobic multilayers coated sponge extremely repel the oil-in-water emulsion due to the existence of superhydrophobicity, and whole oil-in-water emulsion remained suspended on top of the superhydrophobic sponge—and passage of any liquid phase was not observed. Similarly, the chemically contaminated emulsions were also separated by using the hydrophobic multilayers coated sponge under vacuum to increase the flux of the separation. The oil-in-water emulsion solution was characterized by DLS study and bright-field optical microscope imaging, before and after performing the filtration based oil/water separation.

The percentage (v/v; %) efficiency of oil separation from oil/water mixtures was calculated by following equation eq S-1, where volume of aqueous phase is measured before and after separation process.

$$\%\,Separation\ Efficiency = \frac{volume\ of\ water\ recovered\ after\ separation\ of\ emulsion}{volume\ of\ water\ present\ in\ emulsion\ solution}\ x\ 100 \qquad \textbf{eq S-1}$$

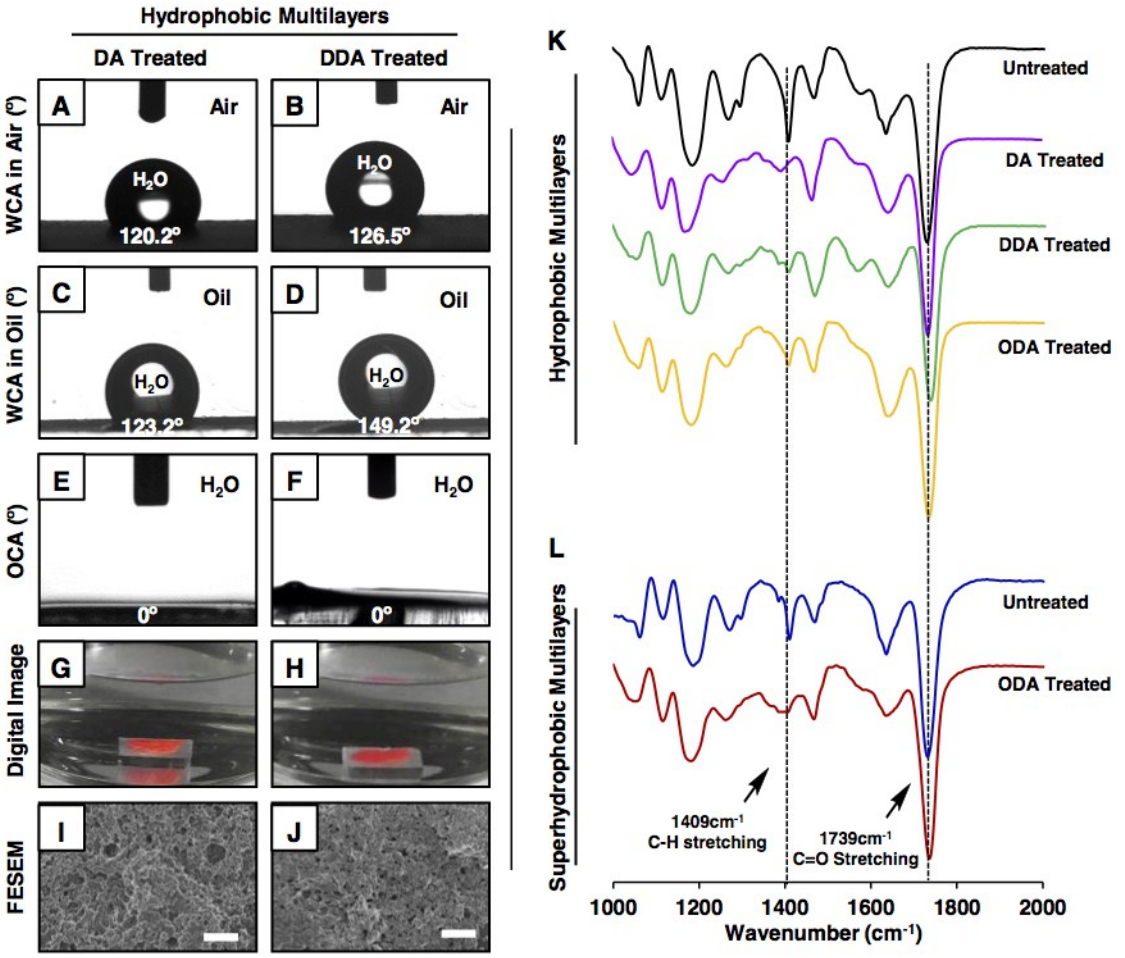

Figure S1. (A-D) Contact angles images of beaded water on decylamine (DA) and dodecylamine (DDA)-treated hydrophobic multilayers (20 bilayers) both in air (A-B) and under oil (C-D). (E-H) Contact angles (E-F) and digital images (G-H) of beaded oil droplet (red color aids visual inspection) on hydrophobic (DA treated: E, G and DDA treated: F, H) multilayers under water. (I-J) FESEM images of the hydrophobic (DA treated: I and DDA treated: J) multilayers (scale bar 6μm). (K-L) FTIR spectra of the 20 bilayers and 9 bilayers multilayers before and after post-modification (untreated; black: hydrophobic, blue: superhydrophobic) and post-modified (treated; DA hydrophobic: purple, DDA hydrophobic: green, ODA hydrophobic: yellow and ODA superhydrophobic: red) multilayers.

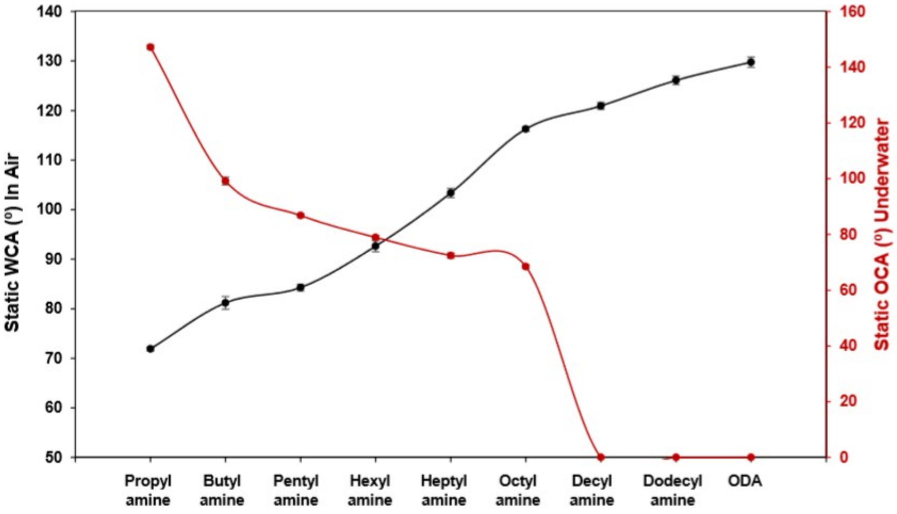

Figure S2. The plot accounting the change in both water contact angle (WCA, in air) and oil contact angle (OCA, underwater) of beaded water and oil droplets on the multilayers coatings after post-modification with various alkyl amines, including propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, decylamine, dodecylamine and Octadecylamine (ODA). The water contact angle (WCA) was gradually increased from ~70° (propyl amine treated) to 130° (ODA treated), superoleophilicity was only observed for hydrophobic multilayers that are post modified with decylamine, dodecylamine and Octadecylamine, and displayed WCA ≥120°.

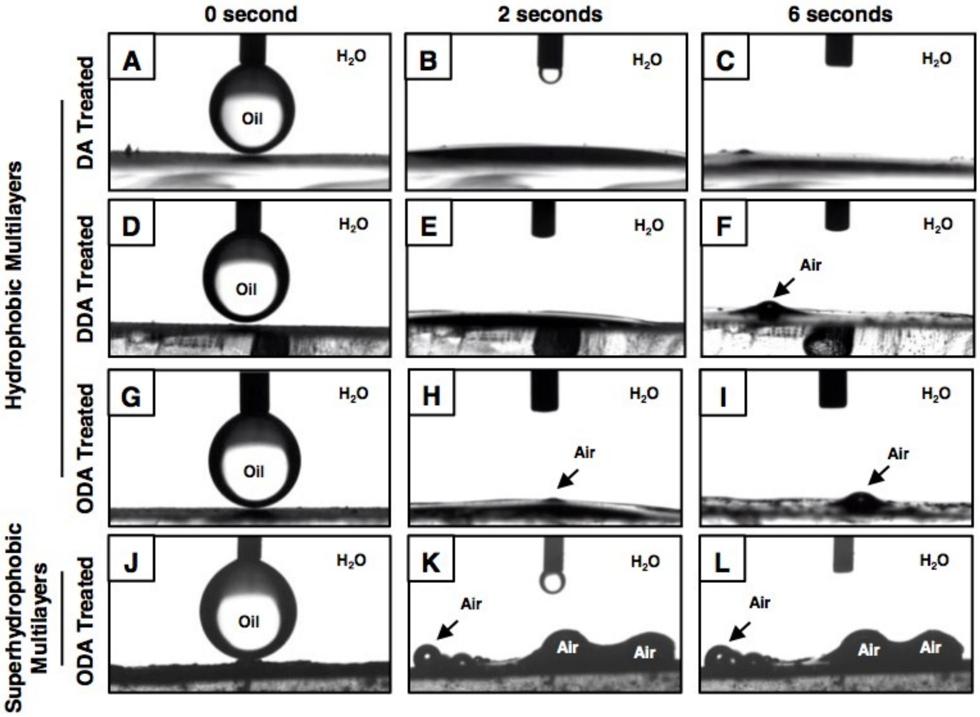

Figure S3. (A-L) Contact angle images comparing the extent of soaking oil droplet on both hydrophobic (DA treated: A-C; DDA treated: D-F and ODA treated: G-I) and superhydrophobic (ODA treated: J-L) multilayers under water.

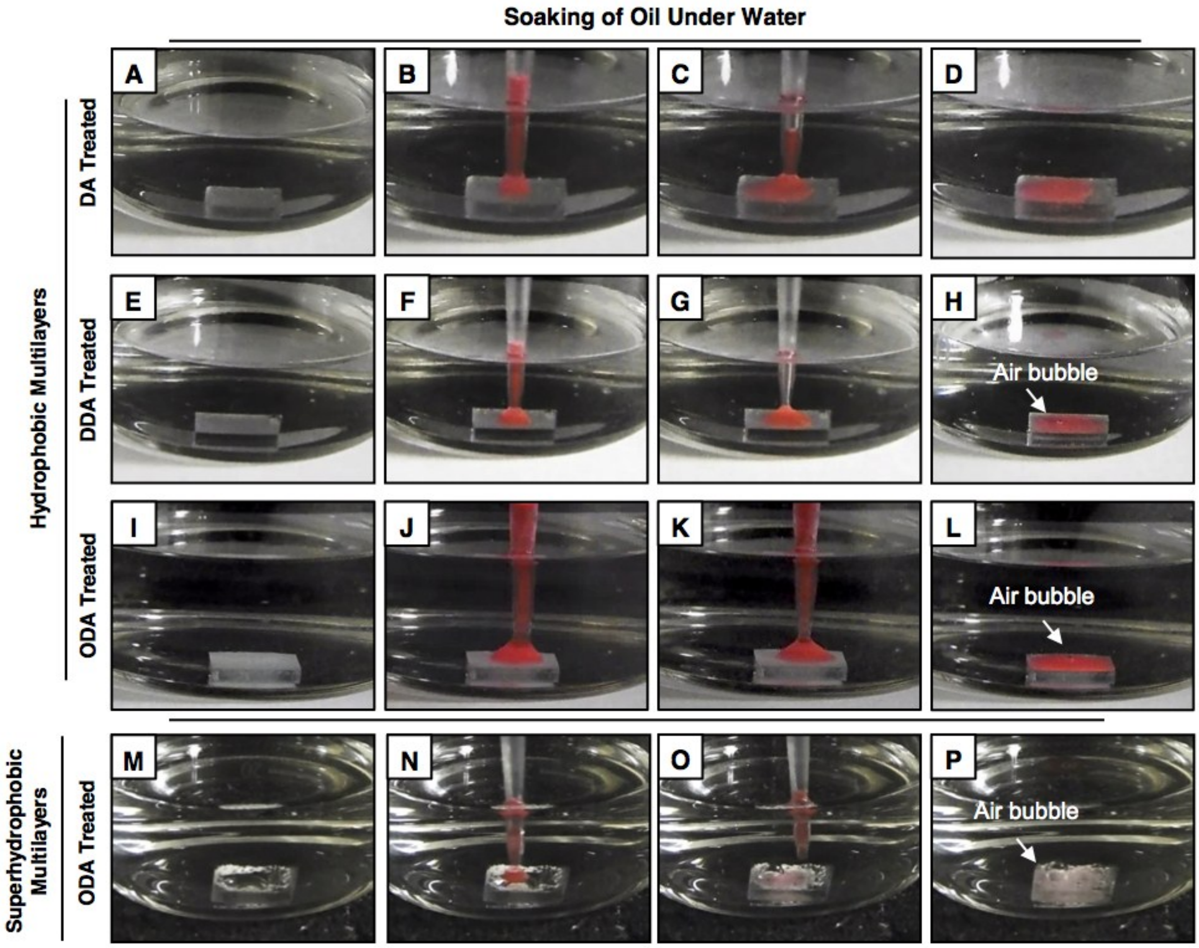

Figure S4. (A-P) Digital images accounting soaking of oil (DCM, dyed with Nile red for visual inspection) phase under water on both hydrophobic (DA treated: A-D; DDA treated: E-H and ODA treated: I-L) and superhydrophobic (ODA treated: M-P) multilayers.

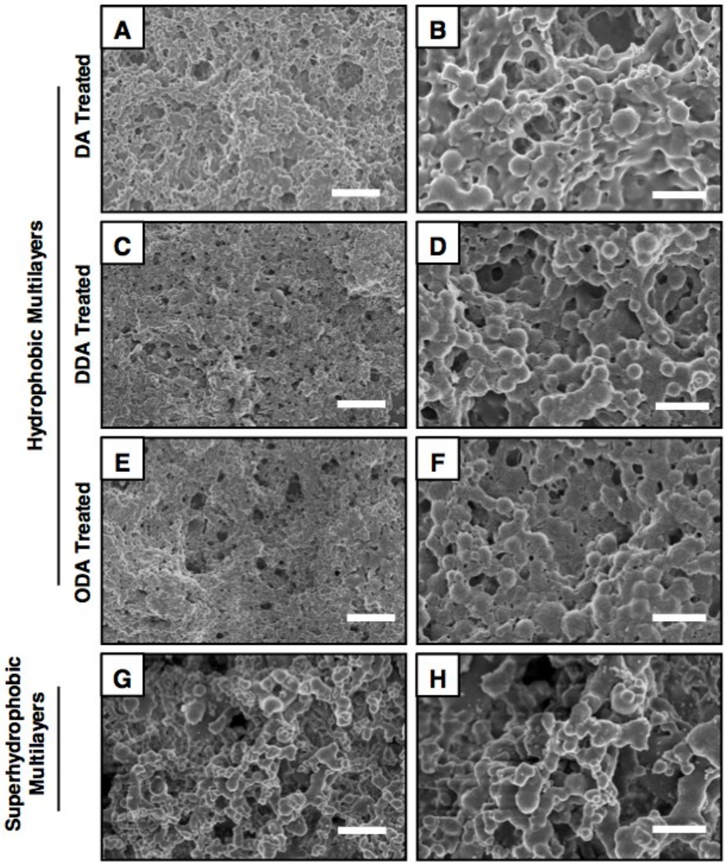

Figure S5. (A-H) FESEM images of hydrophobic (A-F) and superhydrophobic (G-H) multilayers in low (scale bar = 6µm A, C, E, G) and high (scale bar = 2µm B, D, F, H) magnifications.

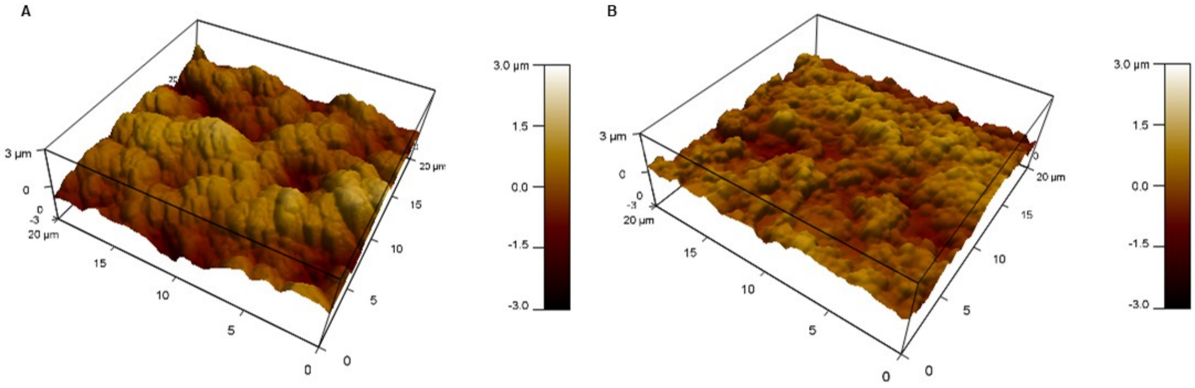

Figure S6. (A-B) Three dimensional AFM images of superhydrophobic (A) and hydrophobic (B) multilayers over a area of 20 µm x 20 µm. Both the images are calibrated at same Z value.

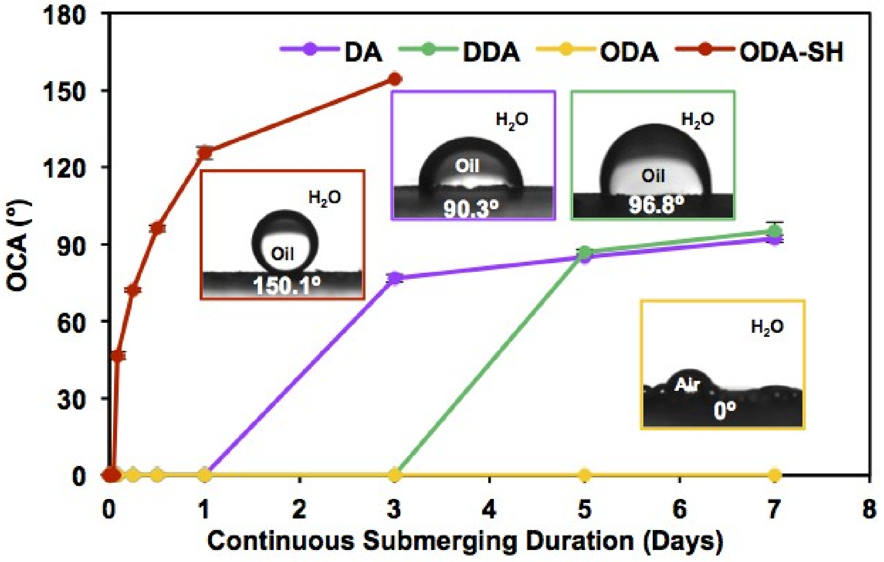

Figure S7. The plot comparing the transition of underwater oil wettability from superoleophilicity to superoleophobicity for hydrophobic (DA treated: purple, DDA treated: green, ODA treated: yellow) and superhydrophobic (ODA treated: red) multilayers, the extreme transition of underwater oil wettability is completed within 2 days for superhydrophobic interface, however ODA-treated superhydrophobic interface keep continued to display underwater superoleophilicity—even after continuous submerging under water for 7 days.

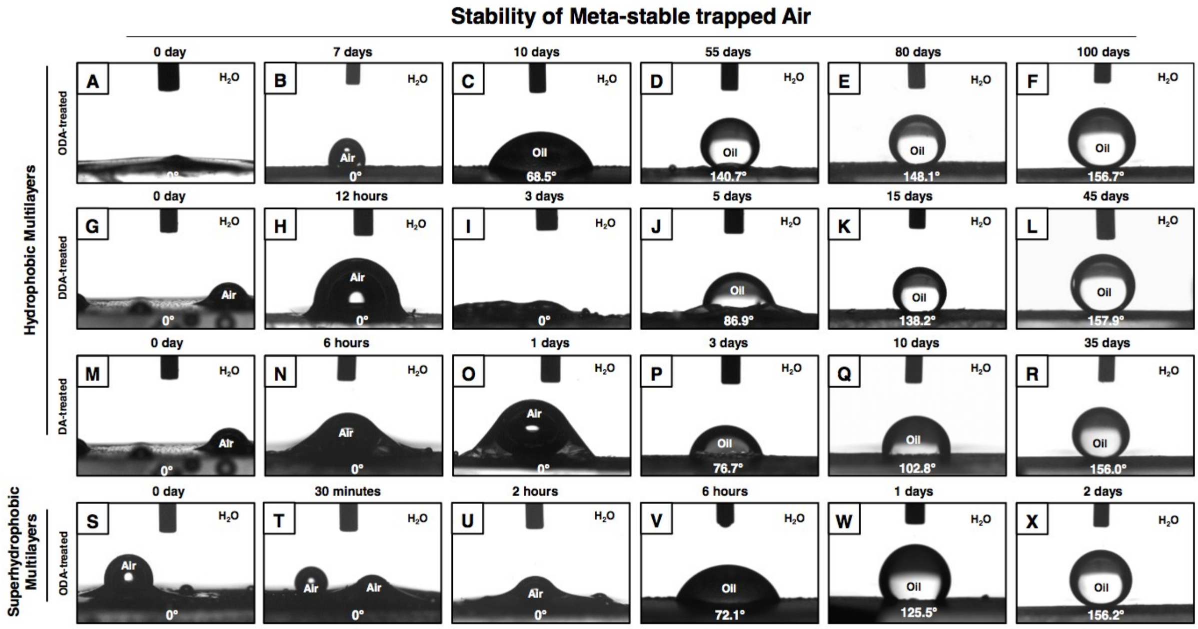

Figure S8. (A-X) Contact angle images illustrating the change of underwater oil wettability for hydrophobic (ODA treated: A-F, DDA treated: G-L, DA treated: M-R) and superhydrophobic (ODA treated: S-X) multilayers with time.

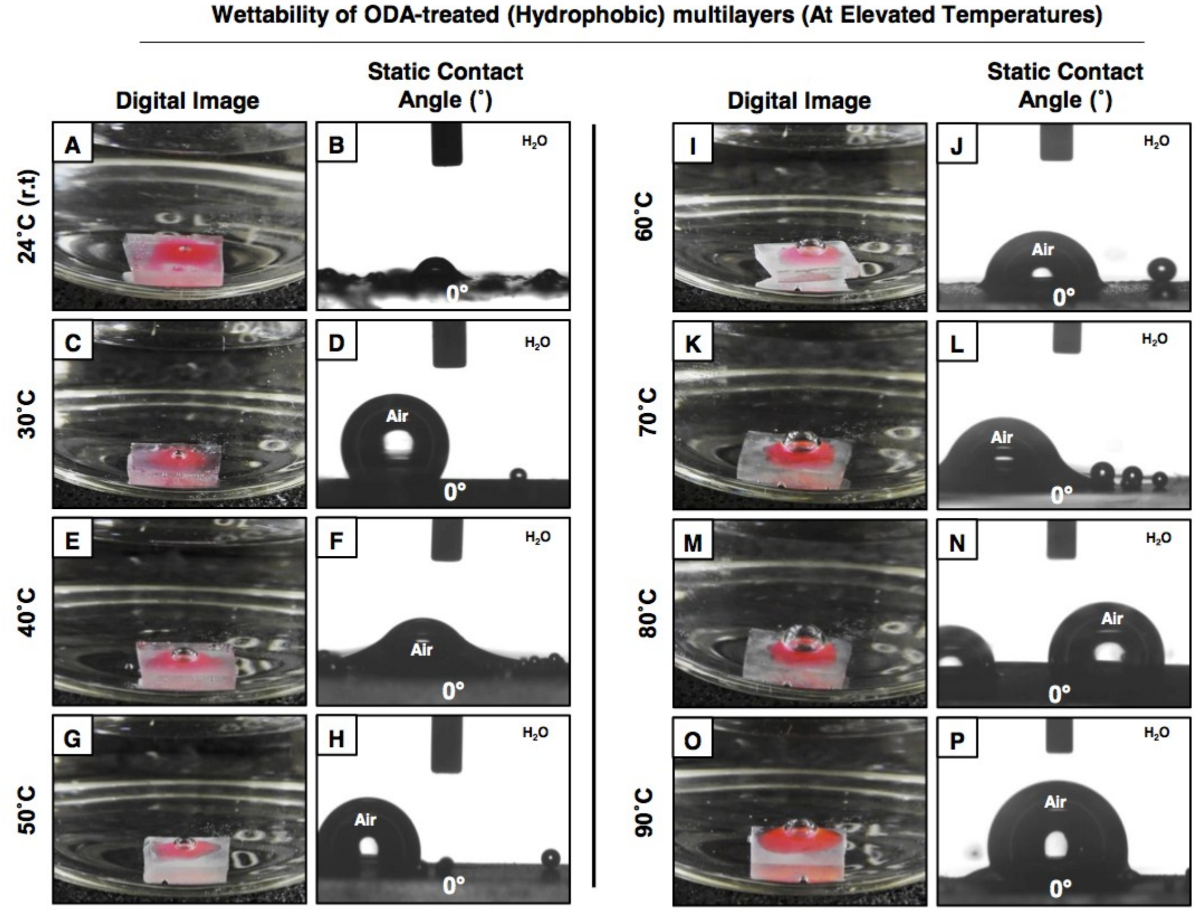

Figure S9. (A-P) Digital (A, C, E, G, I, K, M, O) and contact angle (B, D, F, H, J, L, N, P) images accounting beading of oil (dyed with Nile red) on ODA treated hydrophobic multilayers (20 bilayers) at elevated temperatures starting from room temperature (24°C) to 90°C.

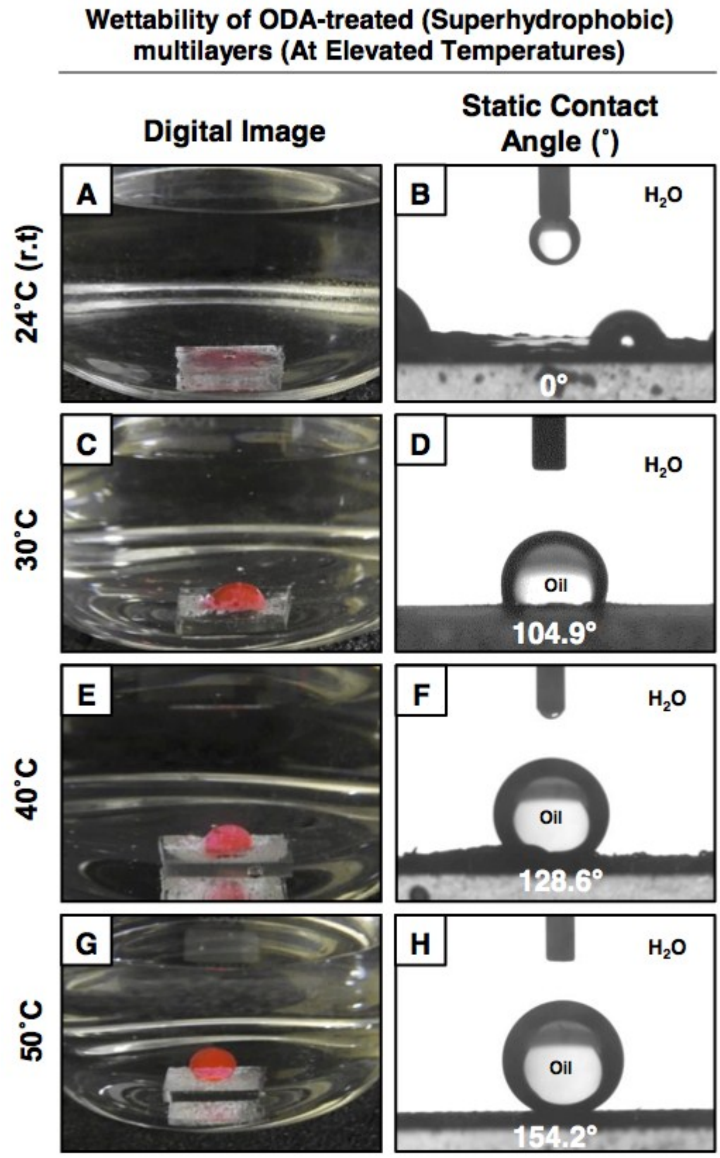

Figure S10. (A-H) Digital (A, C, E, G) and contact angle (B, D, F, H) images illustrating the change in wettability of oil phase (dyed with Nile red) on ODA treated superhydrophobic multilayers (9 bilayers) under water, after exposing to elevated temperatures starting from room temperature (24°C) to 50°C.

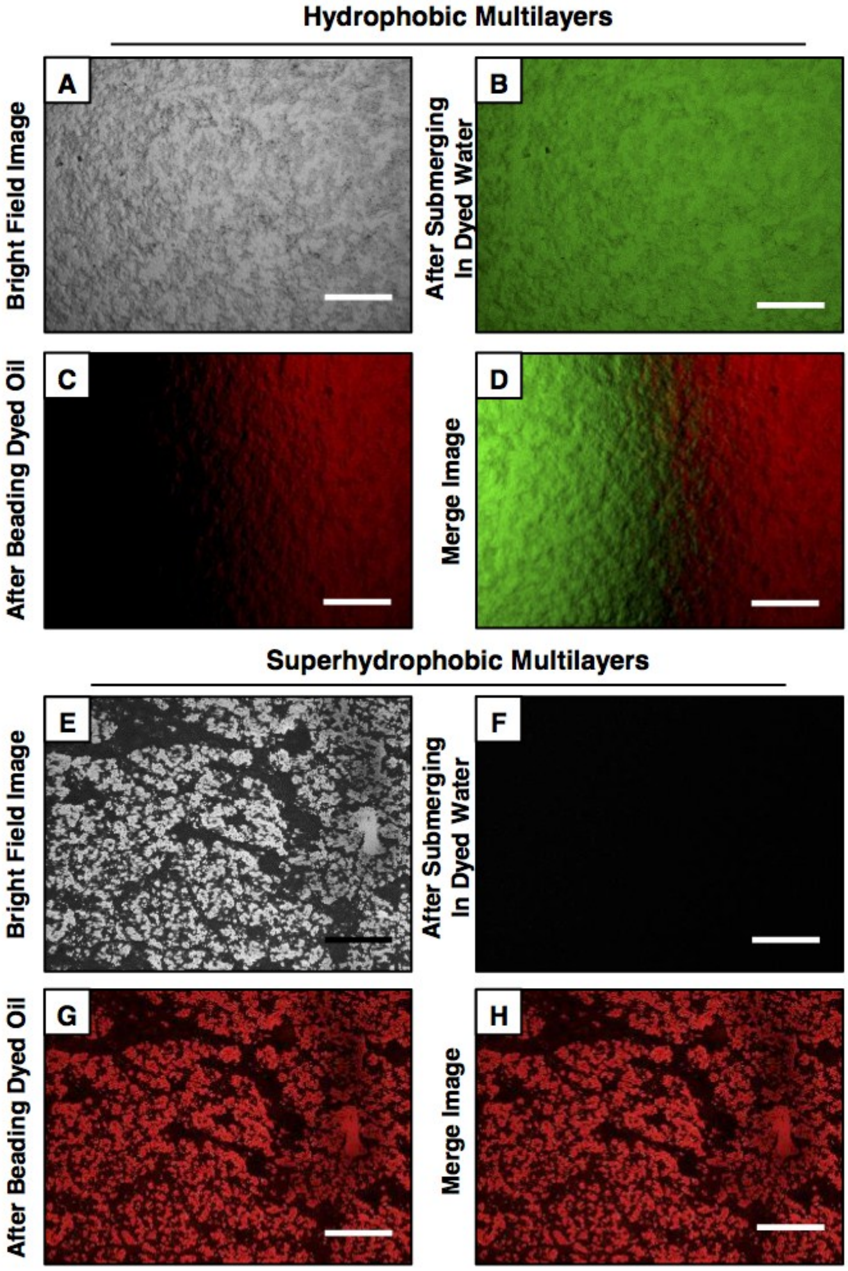

Figure S11. (A-H) Bright field (A, E) and fluorescence (B-D, F-H) images of hydrophobic (A-D) and superhydrophobic (E-H) multilayers after submerging into aqueous phase (dyed with fluorescein; B, F), followed by beading of oil phase (dyed with nile red; hydrophobic: C-D, superhydrophobic: G-H) under water. scale bar 200 µm.

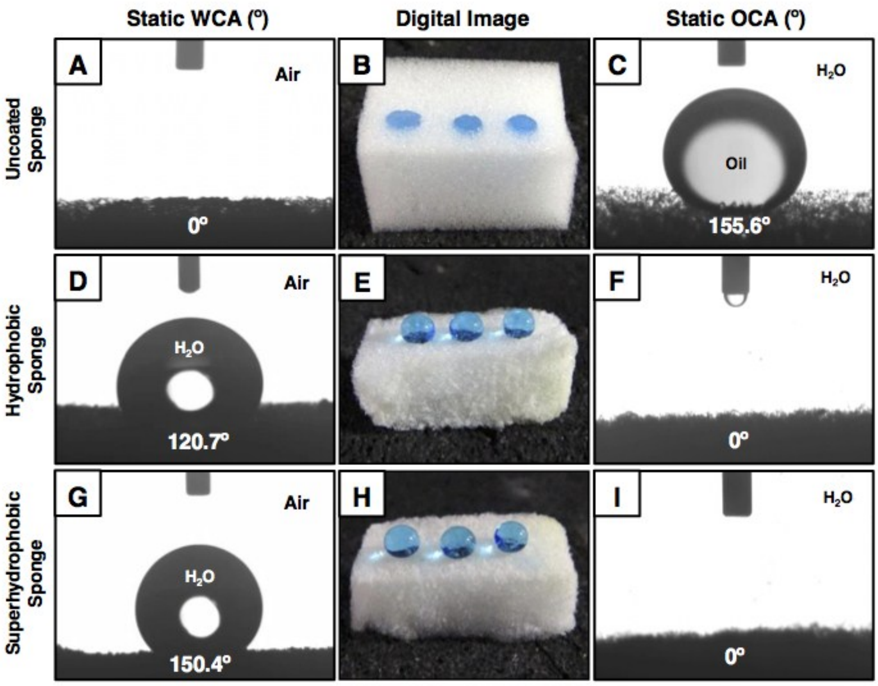

Figure S12. Digital images (A-E) illustrating the process of the separation of oil (DCE) in water emulsion (5%) by exploiting the underwater superoleophobicity of the pH-responsive material at ambient condition. The emulsion separation was performed for consecutive 15 times with a separation efficiency of more than 95% (F) and the complete separation of oil phase from the emulsion was confirmed by the bright field microscopic images (G-H; scale bar 50 µm).

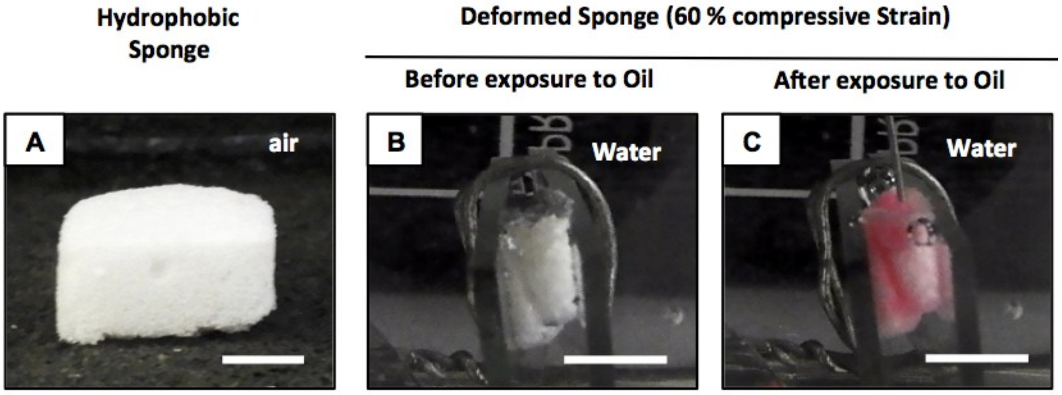

Figure S13. (A-C) Digital images hydrophobic multilayers coated spongy materials before and after incurring 60% compressive strain, followed by exposure to oil phase under water. The compressed hydrophobic sponge readily soaked oil phase (red colour aids visual inspection) under water. Scale bar: 5 mm.

Emulsion Separation of Various Oils/Organic Solvents	Separation Efficiency (%)
Toluene	95.0 ± 0.9
Chloroform	95.0 ± 0.8
Petrol	96.0 ± 1.6
Diesel	95.5 ± 1.0

Table S1. Demonstrating the separation efficiency for oil-in-water emulsion separation for different used oils and water immiscible organic liquids.

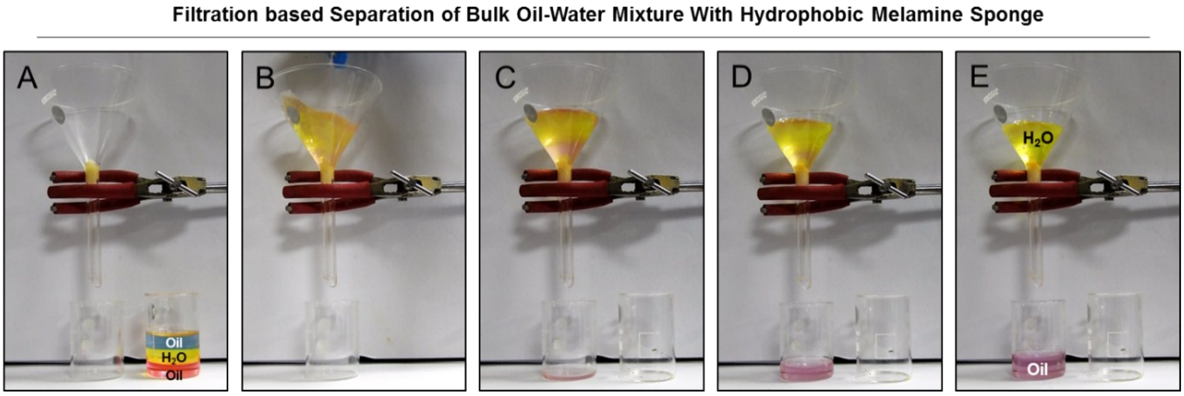

Figure S14. (A-E) Digital images illustrating gravity driven selective filtration of oily phases through hydrophobic multilayers coated sponge that soaked with oil phase. Yellow colour is denoting the aqueous phase, whereas blue and pink colour liquid phase are representing kerosene (floating oil) and dichloromethane (model sediment oil).

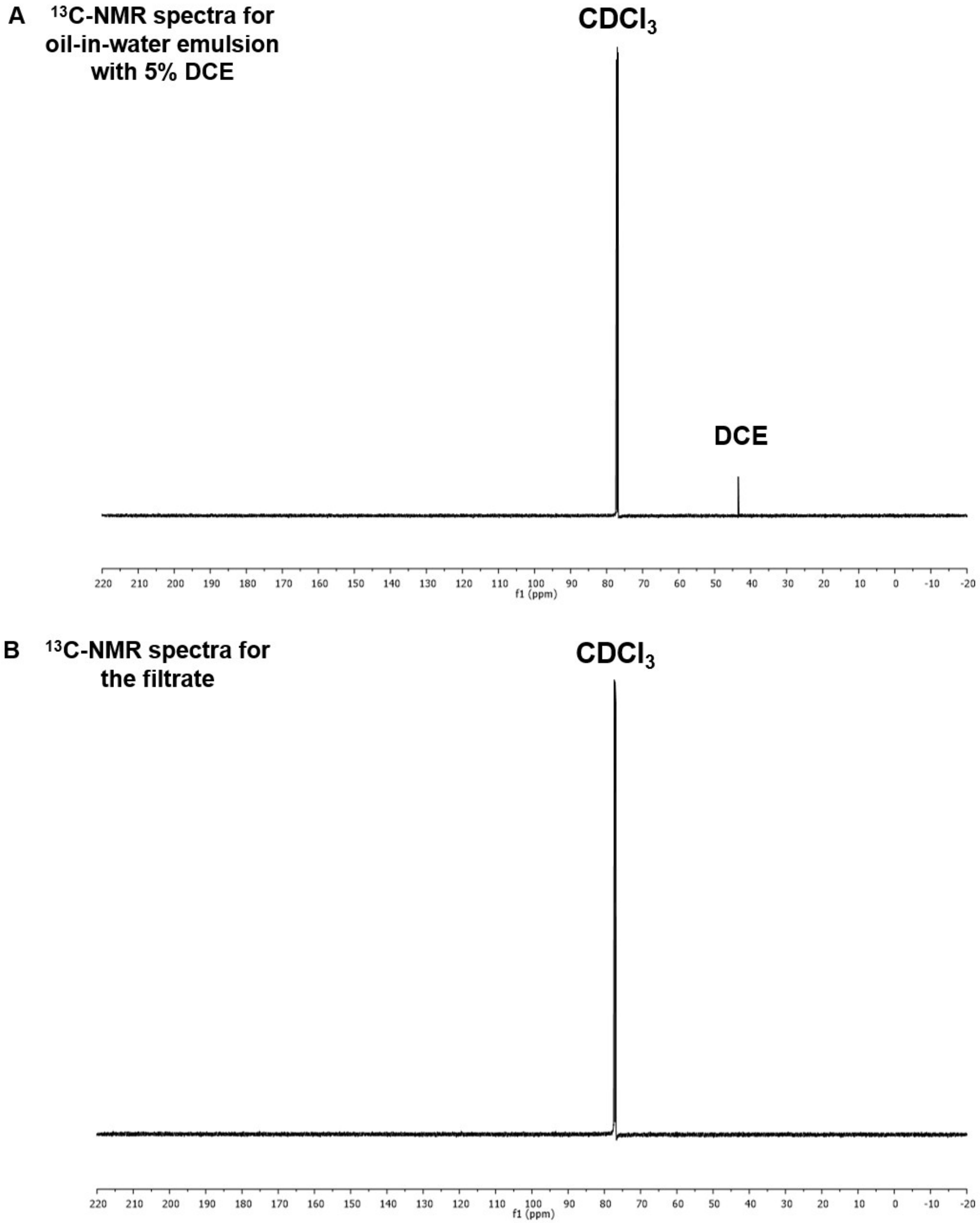

Figure S15. A-B) carbon-13 NMR analysis of the (5% dicloroethane, model oil) oil-in-water emulsion before (A) and after (B) performing separation using hydrophobic multilayers coated sponge. In the ^{13}C-NMR spectrum, No carbon peak at 43.46 ppm for DCE was observed for the filtrated aqueous phase (B).

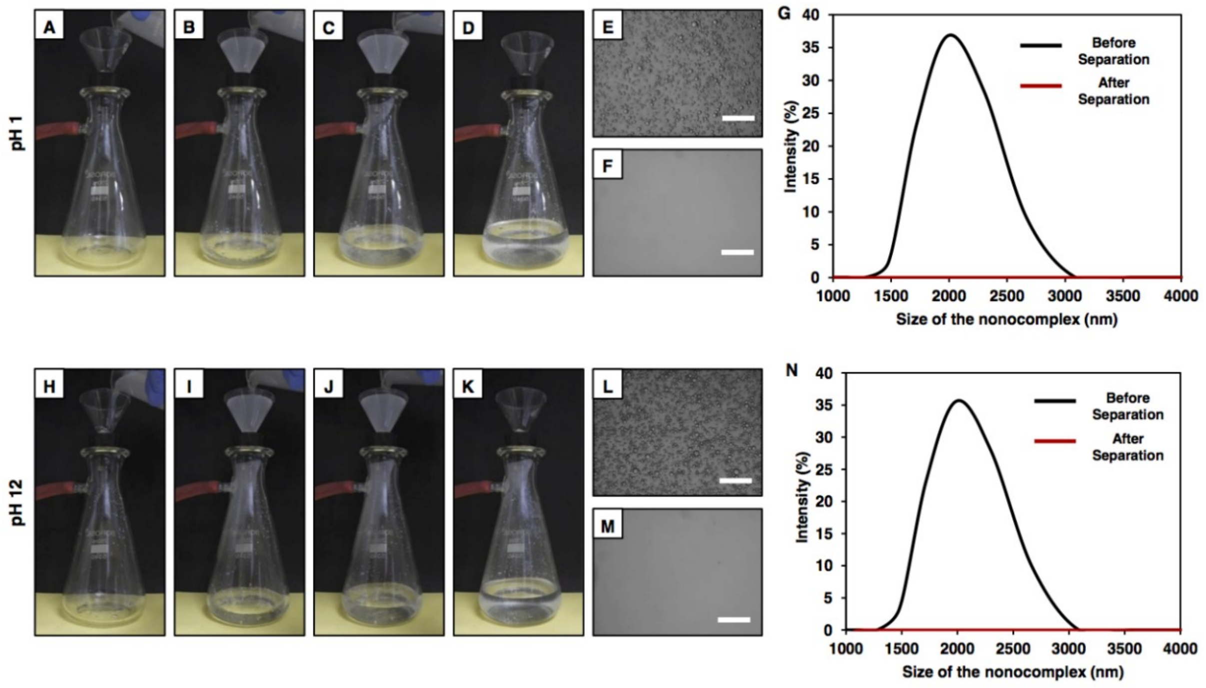

Figure S16. (A-D, H-K) Digital images illustrating the separation of oil-in-water (5%) emulsions by hydrophobic multilayers (ODA treated) coated sponge under extremes of pH (pH 1: A-D, pH 12: H-K), using lab-made prototype. (E-F, L-M) Bright field microscopic images (scale bar: 100µm) of oil-in-water emulsions at extremes of pH (pH 1: E, F and pH 12: L, M) before (E, L) and after (F, M) performing the separation process. (G, N) The DLS study of oil-in-water emulsion—prepared in pH 1 (G) and pH 12 (N), before (black) and after (red) the filtration-based oil/water separation with hydrophobic sponge.

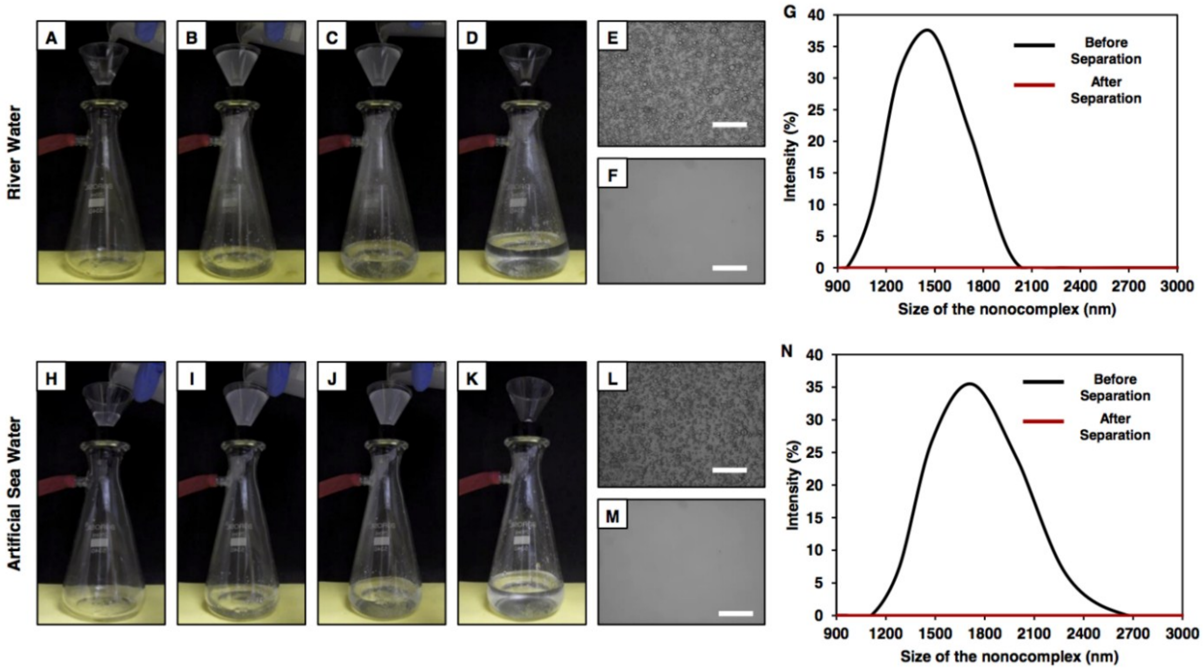

Figure S17. (A-D, H-K) Digital images illustrating the separation of oil-in-water (5%) emulsions, which are prepared with river water (A-D) and artificial sea water (H-K) by hydrophobic multilayers (ODA treated) coated sponge, using lab-made prototype. (E-F, L-M) Bright field microscopic images (scale bar: 100 µm) of oil-in-water emulsions—that are prepared with river water (E-F) and artificial sea water (L-M), before (E, L) and after (F, M) performing the separation process. (G, N) The DLS study of oil-in-water emulsion—prepared with river water (G) and artificial sea water (N), before (black) and after (red) the filtration-based oil/water separation with hydrophobic sponge.

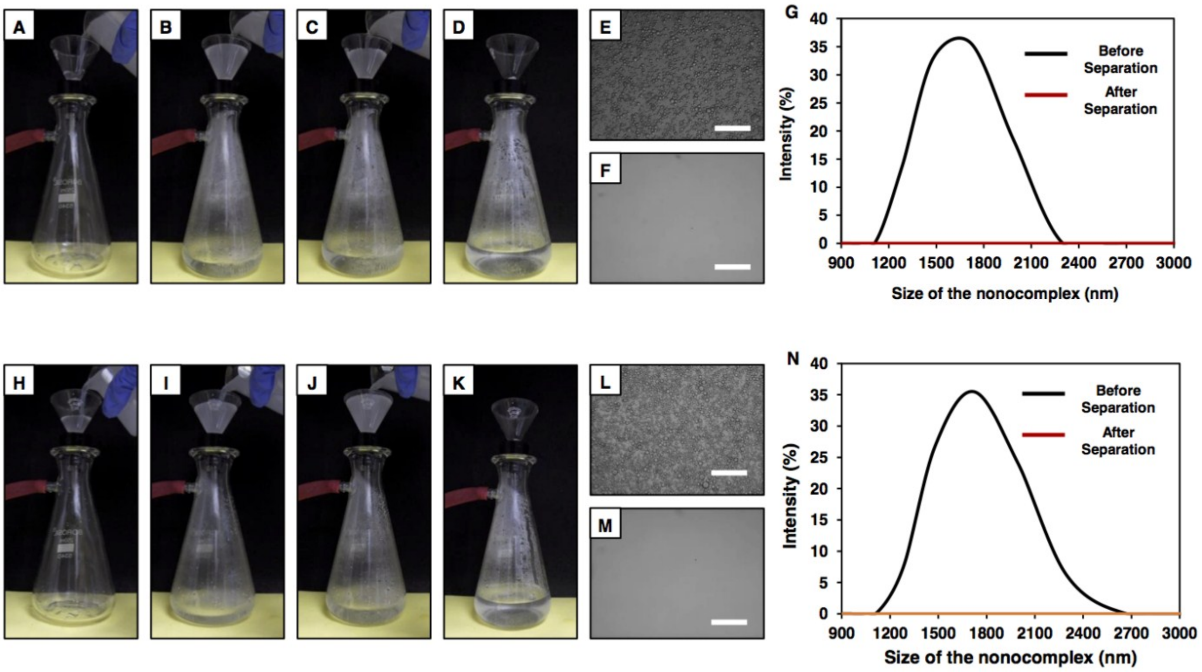

Figure S18. (A-D, H-K) Digital images illustrating the separation of oil-in-water (5%) emulsions by hydrophobic multilayers (ODA treated) coated sponge under extremes of temperatures (10°C: A-D, 70°C: H-K), using lab-made prototype. (E-F, L-M) Bright field microscopic images (scale bar: 100µm) of oil-in-water emulsions at extremes of temperatures (10°C: E, F and 70°C: L, M) before (E, L) and after (F, M) performing the separation process. (G, N) The DLS study of oil-in-water emulsion—prepared in 10°C (G) and 70°C (N), before (black) and after (red) the filtration-based oil/water separation with hydrophobic sponge.