Supporting Information

Sustainable Polymeric Material for Facile and Repetitive Removal of Oil-Spills through Complementary Use of Both Selective-Absorption and Active Filtration Processes

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Experimental section

Materials: Branched poly (ethylenimine) (PEI, MW ~25000), dipentaerythritol penta-/Hexa-acrylate (5Acl, MW 524.21), silicone oil were purchased from Sigma Aldrich (Bangalore, India) and absolute ethyl alcohol (CAS 64-17-5, Lot 1005150) was procured from TEDIA (United States of America). Glass funnel, glass dropper, glass beakers and glass vials were obtained from JSGW (Jain Scientific Glass Works) India. Reagent grade THF was obtained from RANKEM (Maharashtra). Octadecylamine was collected from Alfa Aesar (Hyderabad, India). Rhodamine 6G (Rh6G) was acquired from Labo Chemie (Laboratory Reagents and Fine Chemicals Mumbai, India). Nile red dye was obtained from Sigma-Aldrich (Bangalore, India). NaOH was purchased from Emparta (Merck Specialties Private Limited). Cotton was collected from local medical shop in Guwahati city (Assam, India). Hexane and ethyl acetate was obtained from RANKEM (Maharashtra, India). Hydrochloric acid (Hcl) was purchased from Fisher Scientific (Hyderabad, India). Motor oil was purchased from Castrol India Limited. Dichloromethane (DCM) and chloroform were obtained from Merck Life Science Pvt Ltd (Bangalore, India). Kerosene oil and vegetable oil were purchased from a local shop in Guwahati city (Assam, India).

General considerations: Glass vials that were used for preparing the polymer solutions were thoroughly washed with acetone and ethanol prior to use them in the respective experiments. FTIR spectra were recorded using PerkinElmer instrument at ambient condition and the respective samples are embedded in the KBr pellets before FTIR analysis. Field emission scanning electron microscope (FESEM) images were

obtained using Sigma Carl Zeiss scanning electron microscope. All the samples were coated with gold prior to imaging under FESEM. The contact angle measurements were performed using KRUSS Drop Shape Analyser-DSA25 instrument, where the liquid droplets were dispensed automatically at ambient conditions. Advancing and receding water contact angles were measured using 4µL deionized water droplet at four different locations for each sample. Digital pictures were acquired using a canon power shot SX420 IS digital camera.

Fabrication of superhydrophobic and Superoleophilic cotton

The naturally abundant cotton having both superhydrophobic and superoleophilic in air was prepared using a scalable and eco-friendly dip-coating method. First, cotton was washed with ethanol to remove the undesirable contaminations from the cotton surface. Then the cotton was submerged in BPEI solution (10 mg/mL) for three hours under continuous agitation. Next, the cotton was thoroughly washed with ethanol to remove the loosely bound and unabsorbed BPEI and was kept for drying at ambient condition. After complete evaporation of ethanol solvent, the cotton was transferred to the mixture of 5Acl/BPEI, where the appearance of milky turbid over the duration indicated the formation of nonocomplex. After 1 h, the cotton was removed from the solution, and was thoroughly washed with THF for one hour and was finally transferred into the octadecylamine (ODA, 5 mg/mL of ODA in 10 mL of THF) solution for overnight. Later, the cotton was removed from the ODA solution and was further rinsed successively (five times) with THF, and was finally kept for drying at ambient conditions. Then, the anti-wetting property was examined by beading the liquid water droplets on the synthesized material.

Physical and chemical durability tests on the superhydrophobic cotton

Physical and chemical durability of the embedded superhydrophobicity in the fibrous cotton was examined in detail as follows:

1. **Effect of physical deformation:** In this particular demonstration, the superhydrophobic cotton was manually compressed at various extents. However, after releasing the applied pressure, the material returned to its own shape and size. The cotton (post modified with ODA) was compressed up to 80 %, and the water contact angle was measured before and after releasing the compressive stress on the material (see the main text for more details). Then, the same material was deformed with compressive strain of 80% for 1000 cycles using 500 g load, and the anti-wetting property was examined at regular intervals by accounting the contact angle measurement. The same material was manually bended twisted and even arbitrarily fragmented in multiple parts, and the contact angle of beaded water droplet was measured following the standard process.

2. **Effect of UV exposure**: The superhydrophobic cotton was exposed to ultra-violet (UV) radiations of both shorter (254 nm) as well as longer (365 nm) wavelengths for 240 hours (10 days), and the water wettability in the synthesized material was examined after regular interval by measuring the contact angle of beading water droplet on the material.

3. **Effect of harsh** c**hemical exposures**: The synthesized superhydrophobic cotton was exposed to various severe complex aqueous conditions, including highly acidic (pH 1), alkaline (pH 12), artificial sea-water, and river (Brahmaputra Assam, India) water. The artificial sea water was prepared by mixing $MgSO_4$ (0.325g), $MgCl_2$ (0.226g), $CaCl_2$ (0.112 g) and NaCl (2.673g)) in 100 ml deionized water in volumetric flask. The water wettability on the superhydrophobic cotton was examined, even after continuous exposure to these harsh chemical conditions for 96 hours.

Absorption based separation of Oil and Water

Initially, various light oils (vegetable oil, motor oil, silicon oil etc) were removed using superhydrophobic cotton piece from the oil/water interface. 1 mL of oil (red dyed, for visual inspection) was placed on the air/water interface before bringing the superhydrophobic cotton in contact with the floating oil droplet.

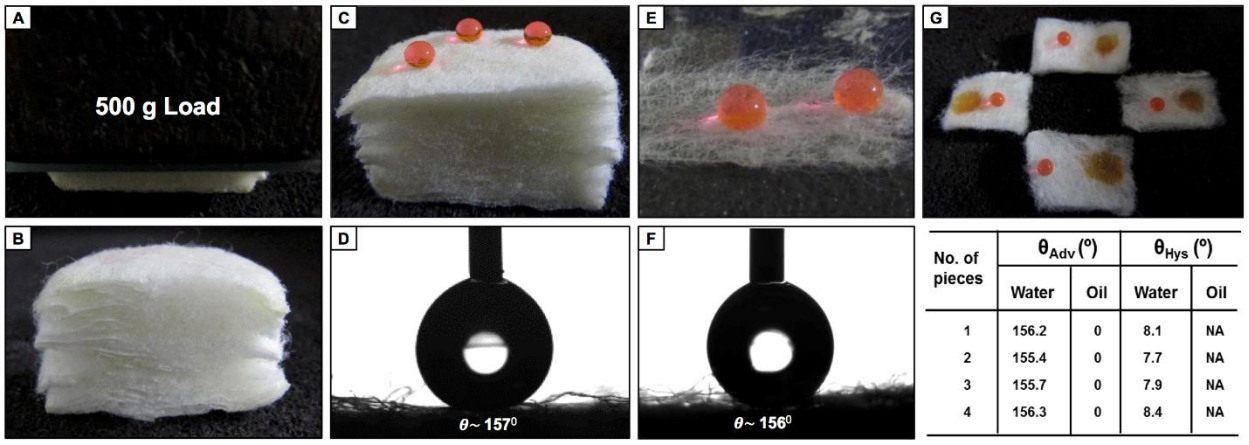
The cotton piece was remained floating on the air water interface and was capable of collecting the floating oil within 30 s. Further, the same experiment was repeated for native cotton, however, the pristine cotton was appeared to be inappropriate in removing oil under same circumstance. Next, superhydrophobic cotton was explored in collection of the bulk oil phase from the oil/water mixtures, irrespective of the location of oils (light and heavy) in the mixture. For early demonstration, single pieces of SHC (0.110 g) were exposed to oil/water mixture that composed of 5 mL of motor oil and 30 mL of water. The oil phase was instantly soaked in the SHC and the separated oil was collected by squeezing the material manually. On the other hand, a piece of SHC was brought in contact with the sediment model (DCM) oil under water, and similar demonstration was also performed with native cotton.

Filtration of oil under water.

To demonstrate active and selective filtration of oil underwater using SHC, a lab-made set up was developed where the large opening of a glass dropper was plugged with. Then, the blocked end of the dropper was brought in contact with the sediment model oil (5 mL of chloroform that was dyed with nil-red for facile visual inspection) under water (see main text for more details). Immediately, the oil phase was selectively passed through the SHC—which was plugged at end of the glass dropper, and was accumulated within the glass dropper. Next, the other opening of dropper was closed with thumb and finally the dropper was taken out from water, and the separated oil was collected in a separate glass vial by opening the end of the glass droper. In this way we have collected all the oil phase from the oil/water mixture with high efficiency. Moreover, the same experiment was extended to separate oil/water mixture from various harsh chemical conditions (acidic, pH 1, alkaline, pH 12, artificial sea water and river (Brahmaputra, Assam India) water.

Gravity-driven filtration:

Another crude prototype was developed in the lab in appropriate combination of falcon tube and glass funnel, where the end of glass funnel was plugged with SHC prior to integrate with falcon tube (see main text for more detail). Then, oil water mixtures that were consisted with two phases or three phases were poured on the prototype. The water in oil emulsion was also separated successfully using this set-up (see movie files for more details). Further, the similar set up was also developed with native cotton to examine the oil/water separation performance.



No. of pieces	θ_{Adv} (°)		θ_{Hys} (°)	
	Water	Oil	Water	Oil
1	156.2	0	8.1	NA
2	155.4	0	7.7	NA
3	155.7	0	7.9	NA
4	156.3	0	8.4	NA

Figure S1. A) Digital image of compressed SHC after application of 500 g load. After releasing the load, the SHC was capable of recovering its native dimension (B). C-D) Digital images (C) and water contact angle (D) of beaded water droplet on SHC, after performing the compression/recovery tests (with 500 g load) for 1000 times. E, F) Digital image (E) and contact angle image (F) of beaded water droplet on SHC after arbitrarily tearing the material using adhesive tape peeling test. G) Digital image of SHC that were manually sliced in four pieces with random preference and both oil and water droplets were beaded on all four pieces of SHC. The detailed oil and water wettability on these four pieces of SHC is given in the table.

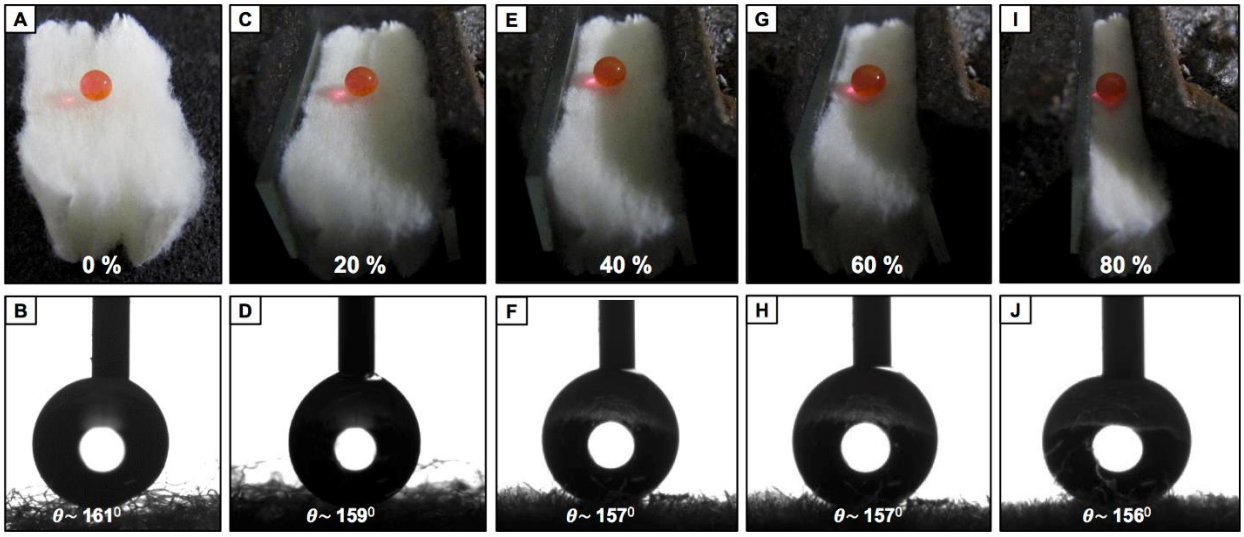


Figure S2. A-J) Digital images (A, C, E, G, I) and water contact angle (B, D, F, H, J) of beaded water droplet on SHC that are deformed with compressive strain of 20 % (C, D), 40 % (E, F), 60 % (G, H) and 80 % (I, J) respectively.

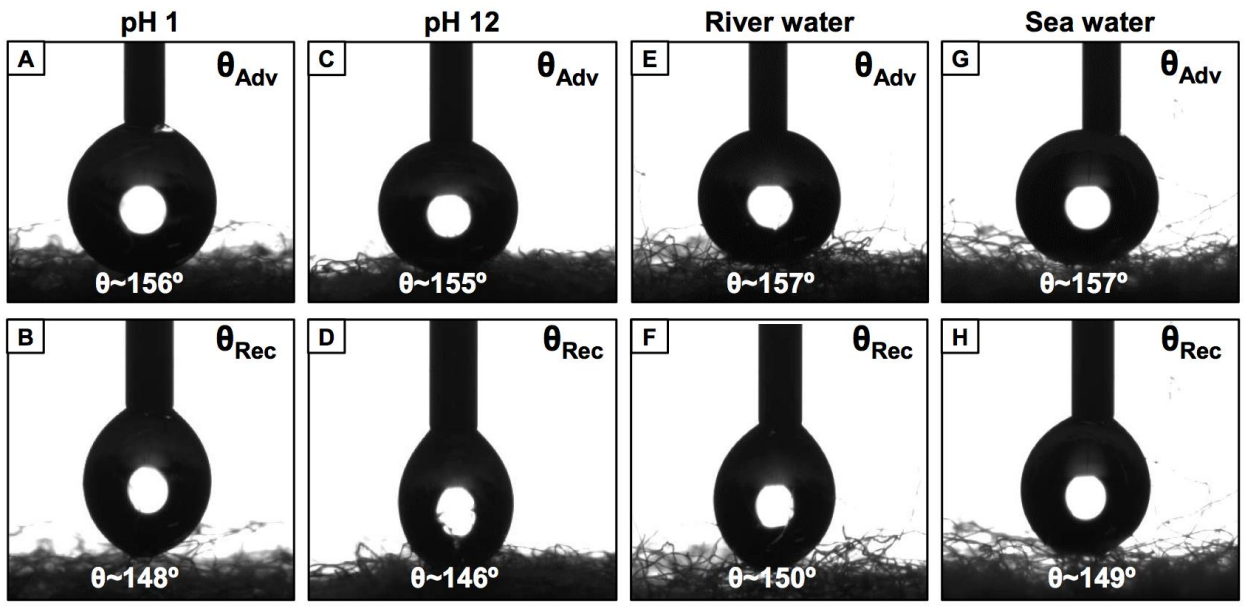


Figure S3. A-H) The advancing (A, C, E, G) and receding (B, D, F, H) water contact angle images of SHC after exposing the material in various complex aqueous mediums including highly acidic medium of pH 1 (A-B), highly alkaline medium of pH 12 (C-D), river (Brahmaputra Assam India) water (E-F) and artificial sea water (G-H) respectively, for 96 hours.

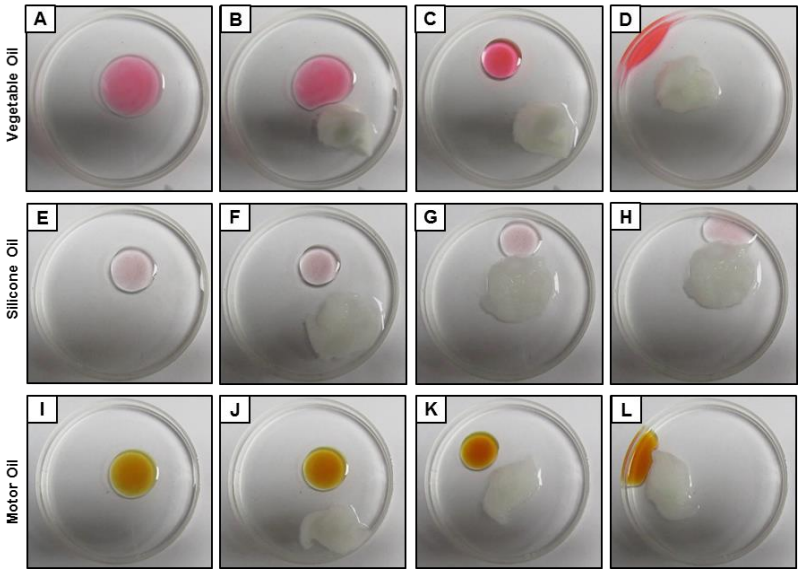


Figure S4. (A-L) Digital images showing the interaction between uncoated cotton and different types of oils including vegetable oil (A-D), silicon oil (E-H) and motor oil (I-L), respectively. Oils are repelled by the native cotton.

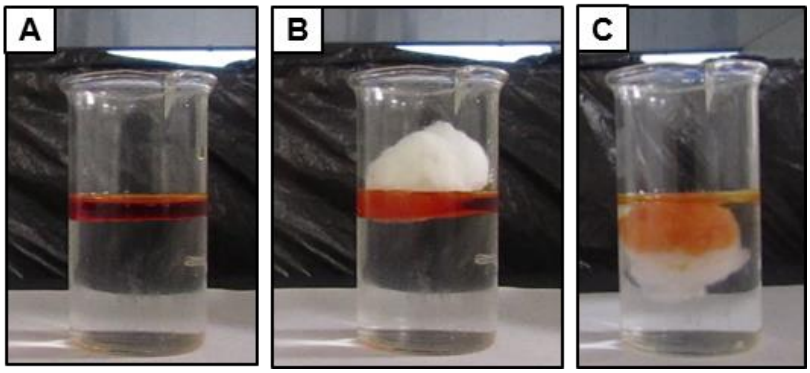


Figure S5. A-C) Digital images illustrating the performance of native cotton in removing the layered motor oils that were floating on aqueous phases.

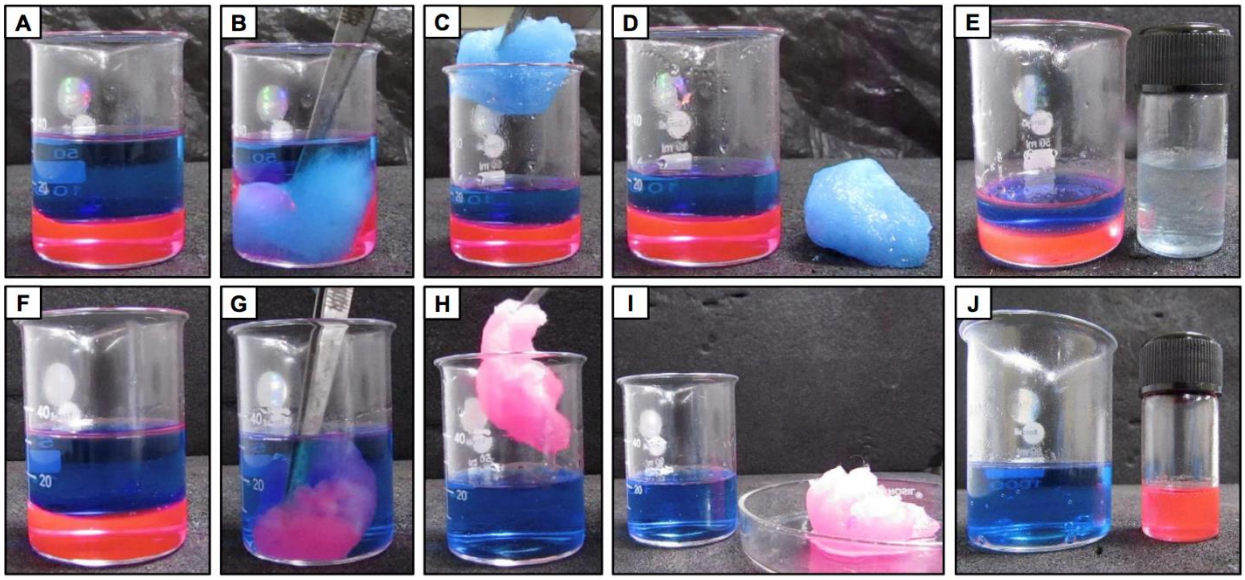


Figure S6. (A-J) Digital images comparing the interaction of native cotton (A-E) and SHC (F-J) with heavy oil (DCM, red color) under water; SHC was noticed to be extremely efficient in separating oil under water and native cotton was completely incapable of removing oil that was settled under water.

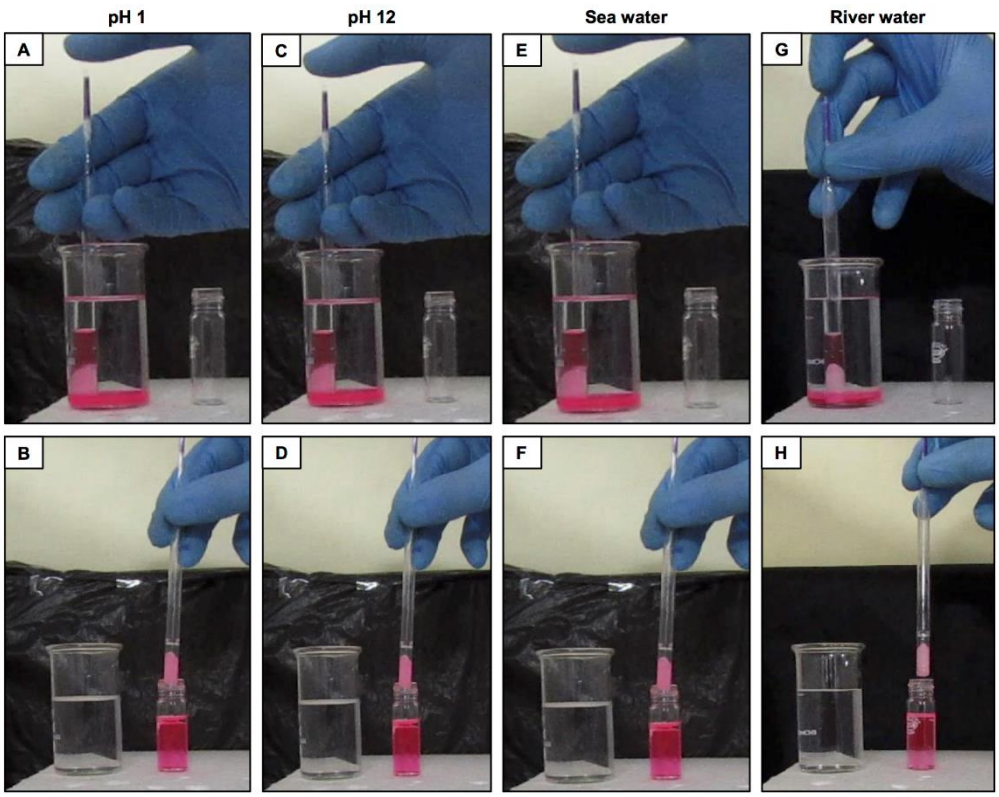


Figure S7. (A-H) Digital images illustrating the collection of sediment oil by filtration through SHC—but against the gravity under various complex aqueous phases including highly acidic medium of pH 1 (A, B), highly alkaline medium of pH 12 (C, D), artificial sea water (E, F) and river (Brahmaputra Assam India) water (G, H).

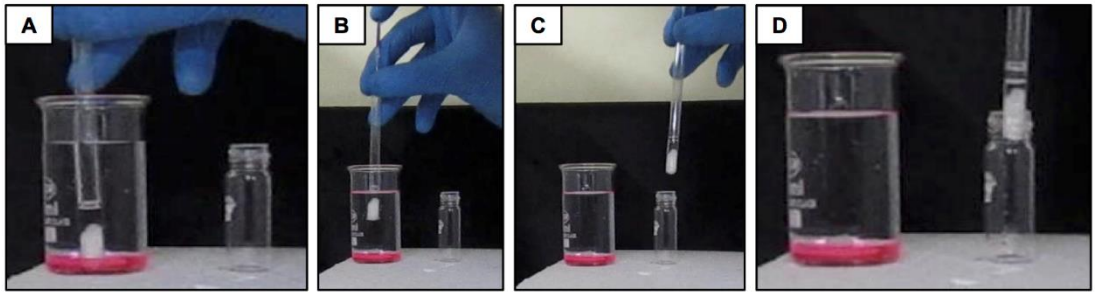


Figure S8. A-D) Digital images illustrating the inability of native cotton in collecting the sediment oil under DI water.

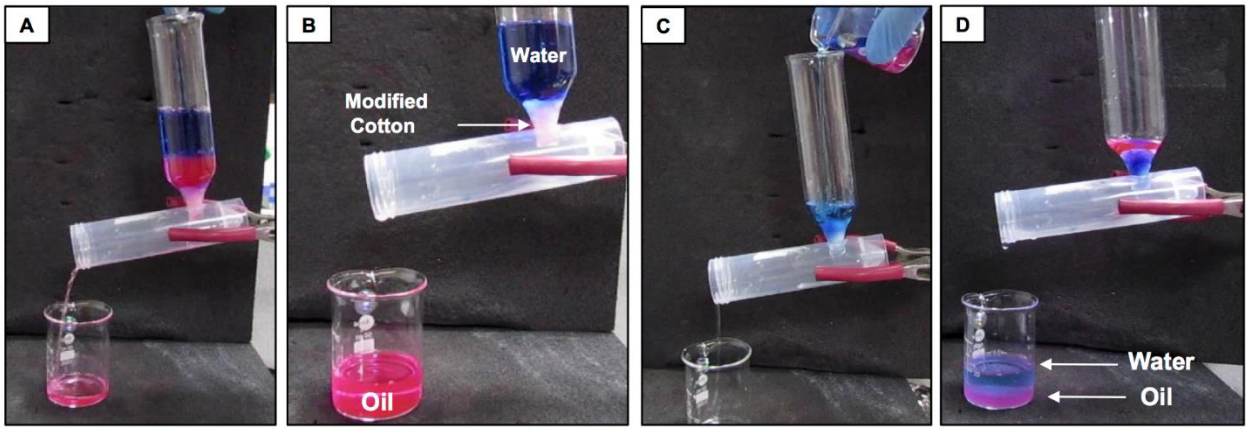


Figure S9. A-D) Digital images are illustrating the ability of both SHC (A-B) and the native cotton (C-D) in the gravity driven separation of oil/water mixture (20 mL DCM and 20 mL of water).

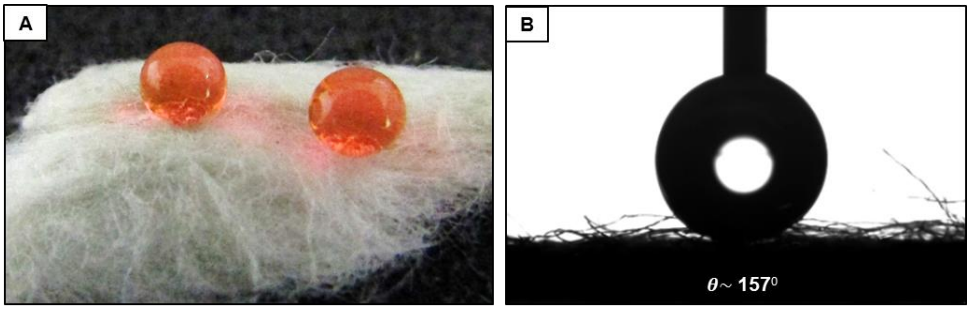


Figure S10. A-B) Digital image (A) and contact angle image (B) of beaded water droplet on SHC after successive (100 times) use in oil/water separation.

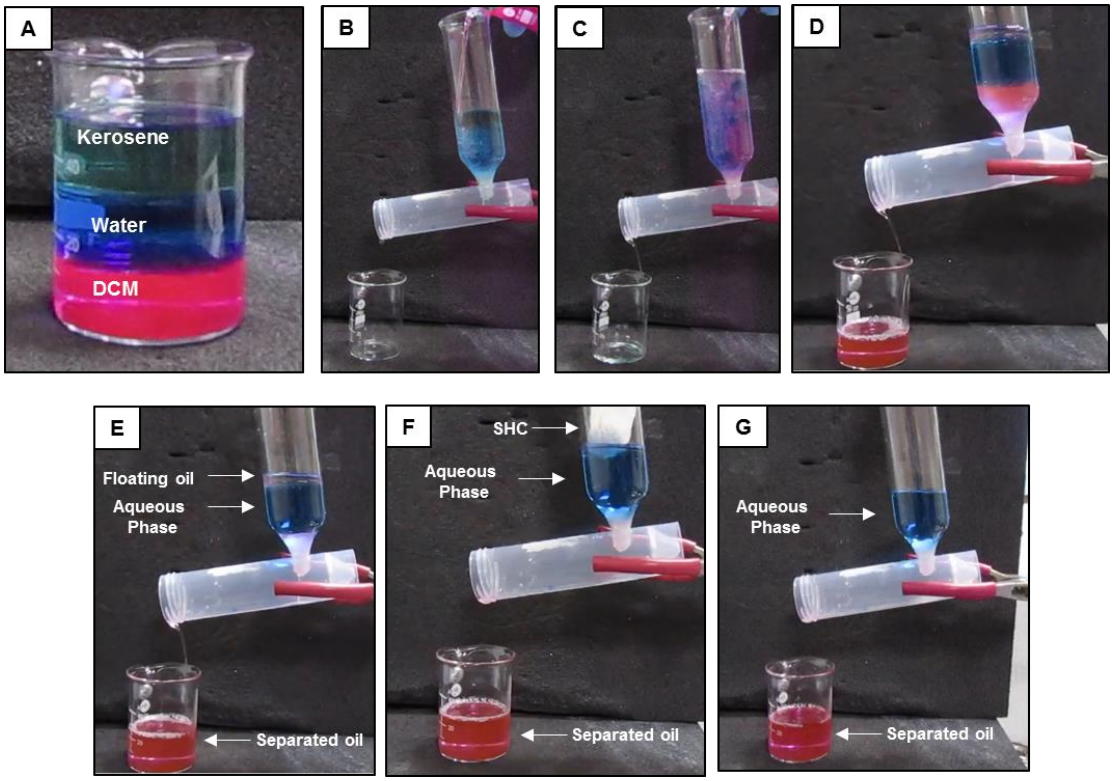


Figure S11. A) Digital image of three phases oil/water mixture that is consisted of kerosene (at top), aqueous phase (at middle) and DCM (model heavy oil, at bottom). B-E) Digital images illustrating the oil/water separation by the gravity driven filtration process, and small fraction of floating oil was finally removed based on absorption process. Pieces of SHC were strategically exploited during complimentary use of both the filtration and absorption processes.

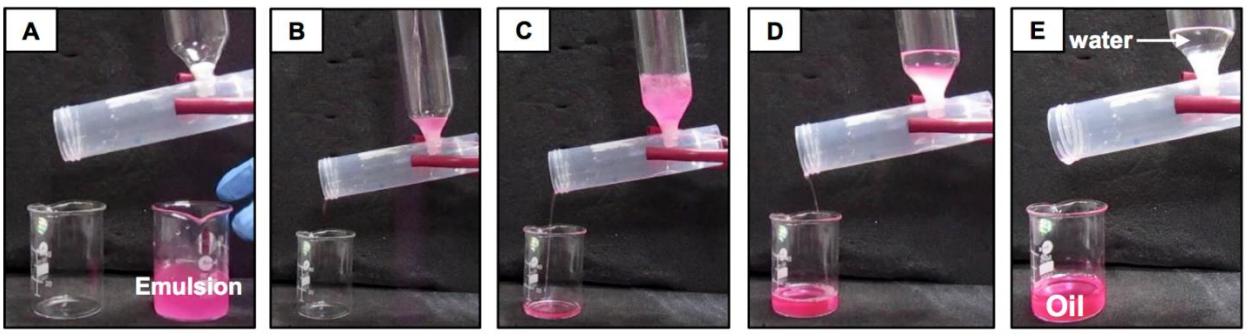


Figure S12. A-E) Digital images are revealing the ability of SHC in gravity driven filtration based emulsion (5 mL of water in 20 mL of DCM) separation.