

Supporting Information

Synergistic Chemical Pattern on Hydrophilic Slippery Liquid Infused Porous Surface (SLIPS) for Water Harvesting Application

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Experimental section

Materials: Branched poly(ethyleneimine) (BPEI, MW ~ 25 000 Da), dipentaerythritolpenta-acrylate (5-Acl, MW ~ 524.21 g mol⁻¹), octadecyl acrylate, rhodamine cadaverine (Rh-NH₂), fluorescein isothiocyanate (FITC) purchased from Sigma-Aldrich, Bangalore, India. D-glucamine (>95%) was obtained from TCI (Tokyo Chemical Industry). Krytox Oil (Dupont KrytoxR GPL 103) was procured from H Costenoble GmbH & Co. KG (Eschborn, Germany). Pentanol procured from Alfa Aesar. Ethanol, THF were procured from Merck Specialties Private Limited, India. A-4 sized printing paper was acquired from J K Copier. Spray bottles (100 mL capacity, nozzle diameter 400 mm) and ultrasonic cool mist humidifier (Crane, EE-5301) were obtained from Amazon India. Sandpaper (grit no. 400) was purchased from Million International, India. Olive oil (Borges Extra Virgin Olive Oil), Fountain Pen (Legend Executive Fountain Pen), Glass slides (Boroleb, India) and adhesive tape (Jonson tape Ltd. India) were acquired from different local sources. The sand was thoroughly washed with water before the experimental use.

General considerations: All ATR-IR spectra were recorded using PerkinElmer UATR Two at ambient conditions. The contact angles, roll-off angles, sliding angles were obtained from Kruss drop-Shape Analyser-DSA25 instrument at laboratory temperature (~25°C). The FESEM images were acquired using Sigma Carl Zeiss scanning electron microscope (each sample was coated with a conducting gold layer prior to imaging). All fluorescence microscopic images were captured using a ZEISS Axio Vert.A1 inverted microscope with 10X objective. The contact angles were taken using 5 µl water droplets at four different locations of the same synthesized interface. The Fog harvesting was carried out by using an ultrasonic cool mist humidifier (Crane, EE-5301). The Digital images and videos were captured using a Nikon Coolpix b-700 digital camera.

Fabrication of Dual Chemically Reactive Porous Polymeric Interface (DCRPPI): The DCRPPI was prepared following the previously reported method. In brief, the reactive reaction mixture was prepared by mixing 10 mL 5Acl solution (0.252M in pentanol) and 3 mL BPEI solution (0.105M in pentanol with respect to the polymer repeat unit). The reaction mixture agitated vigorously for 5 minutes, which yielded a milky turbid solution. Then, the turbid reaction mixture (13 mL) was sprayed uniformly onto the A4 Size paper at an angle of nearly 90° over a 623.7 cm² area from a distance of 15 cm using a commercially available spraying

bottle. Then, the coated substrates kept in air overnight for solvent evaporation. The coated paper was washed thoroughly with THF for 15 minutes and kept it in the air for drying.

Post Covalent Modification of DCRPPI: The dual residual chemical reactivities of DCRPPI were strategically exploited for post covalent modifications—which were essential to achieve various bio-inspired wettability. For example, SHI was prepared through the post chemical modification of DCRPPI with octadecyl acrylate (ODAC), where residual amine of DCRPPI readily reacted with acrylate group of ODAC through 1,4-conjugate addition reaction at ambient condition. Firstly, the chemically reactive interface (DCRPPI) submerged in a THF solution of octadecyl acrylate (5 mg/mL) for 12 h followed by washing the coated substrate thoroughly with fresh THF multiple times to remove excess and loosely deposited octadecyl acrylate. Finally, the post modified coating was kept in a vacuum for drying. The octadecyl acrylate treatments provided the desired superhydrophobicity. Further, treatment of this ODAC-treated coating with D-glucamine yielded a hydrophilic interface, where residual acrylate groups of DCRPPI readily reacted with primary amines of D-glucamine through 1,4-conjugate addition reaction. An ODAC-treated coating was subsequently treated with the solution of D-glucamine (5 mg/ml) in 25% ethanol solution for dual post covalent modification. A similar protocol was followed for single and dual post-modification of DCRPPI with Rh-NH₂ and FITC.

Fabrication of chemically patterned superhydrophobic interface (CP-SHI): At first, the desired pattern was printed on a paper prior to deposit a chemically reactive superhydrophobic coating, where the DCRPPI on the pre-printed substrate (which contains an array of black dots aligned with the certain spacing) was treated with ODAC and the residual acrylate groups was exploited to develop spatially selected chemical modulation with D-glucamine. The chemically reactive SHI interface was fabricated on a preprinted paper. The pre-printed each black spot guided to transfer the solution of D-glucamine (5 mg/mL in 25 % ethanol solution) on the SHI using a fountain pen, and kept the interface as it was for 6 h. After that, substrates were washed thoroughly with ethanol for 1 h and kept it in the air for drying. The spatially selected chemical modification with D-glucamine provided the hydrophilic patterns on the superhydrophobic interface—which was denoted as CP-SHI.

Fabrication of HL-SLIPS, HB-SLIPS, CP-HL-SLIPS and CP-HB-SLIPS: HL-SLIPS, CP-HL-SLIPS were prepared through the infusion of olive oil to the SHI and CP-SHI respectively. Similarly, HB-SLIPS, CP-HB-SLIPS were fabricated through the infusion of synthetic krytox oil to the SHI and CP-SHI respectively. In brief, 20 μ L of lubricant spread on the respective polymeric coating using a tracing paper over an area of 6 cm², and the excess lubricant was removed by vertically placing the substrates for 10 min.

Fog Harvesting Set-up: An ultrasonic cool mist humidifier (Crane, EE-5301) with a flow rate of 100 mL/h was used for the fog harvesting set up to evaluate the water harvesting performance of i) superhydrophobic interface (SHI), ii) hydrophobic-SLIPS (HB-SLIPS) and iii) hydrophilic-SLIPS (HL-SLIPS), iv) chemically patterned superhydrophobic interface (CP-SHI), and further, the selection of appropriate lubrication yielded v) chemically patterned hydrophobic-SLIPS (CP-HB-SLIPS) and vi) chemically patterned hydrophilic-SLIPS (CP-HL-SLIPS). All above mentioned interfaces were placed at a fixed distance (5 cm) from the outlet of the humidifier and the bio-inspired interfaces were kept with a tilting angle $\sim 45^\circ$ from the horizontal plane. A clean and dry beaker was placed under the bio-mimicked interfaces at a distance

of 10 cm for collecting the water droplets from the bio-inspired interface. The weight of the collected water droplets was measured after every certain interval of time. The experimental temperature was maintained at $25 \pm 2^\circ\text{C}$. The water collection efficiency (WCE) was calculated using the formula: $\text{WCE} = w/A.t$ where w is the weight of collected water in mg, A is the fog capture area in cm^2 , and t is the collection time in h. The entire set up was covered with a wooden box.

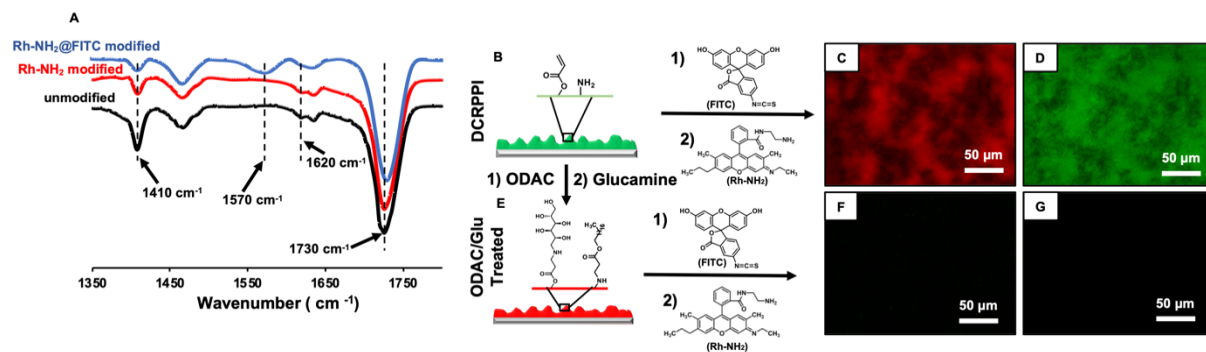


Figure S1. A) The ATR-IR spectra before (black) and after single (with Rh-NH₂; red) and dual (successive treatments with Rh-NH₂ and FITC; blue) post-modifications of dual chemically reactive porous polymeric coating (DCRPPI), where the characteristic IR peaks at 1730 cm^{-1} and 1410 cm^{-1} were corresponded to the carbonyl stretching and symmetric deformation of the C–H bond for the β carbon of the vinyl group, respectively. Further, the appearance of IR peak at 1570 cm^{-1} confirms the mutual chemical reaction between isothiocyanate group of FITC and residual amine of DCRPPI. B,E) Schematic representation of DCRPPI before (B) and after (E) consecutive treatments with both ODAC and D-glucamine (denoted as Glu). C,D) Fluorescence images of the DCRPPI after the sequential treatments with both Rh-NH₂ and FITC. F,G) Fluorescence images of the DCRPPI that was pre-treated with ODAC and Glu, prior to treatment with both Rh-NH₂ and FITC. The pre-modification of DCRPPI with ODAC and D-glucamine, consumed all the residual reactivates and it failed to react with both Rh-NH₂ and FITC. Eventually, no fluorescence signal was noted.

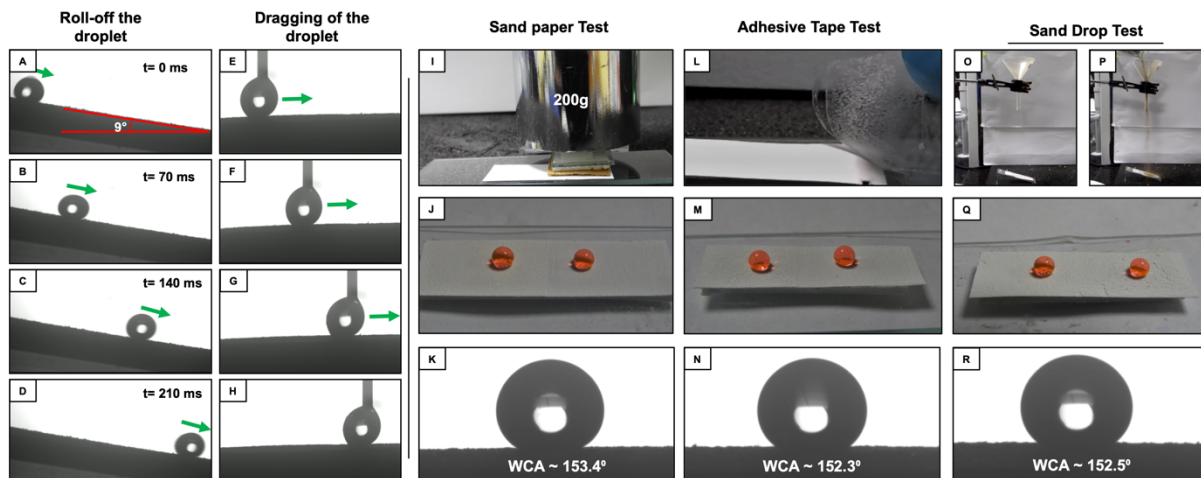


Figure S2. A-D) Contact angle images depicting the rolling of the beaded water droplet on titled (9°) SHI. E-H) Contact angle images illustrating dragging of the water droplet on SHI without breaking the beaded water droplet. I,L,O,P) Digital images describing the process of sand-paper abrasions test (I), adhesive tape test (L) and the sand drop test (O,P). J-K, M-N, Q-R) Digital (J,M,Q) and contact angle (K,N,R) images of beaded water droplets (red color aids visual investigation) on SHI after incurring different abrasive exposures (sand paper abrasion: J,K ; adhesive tape test: M,N; sand drop test: Q,R).

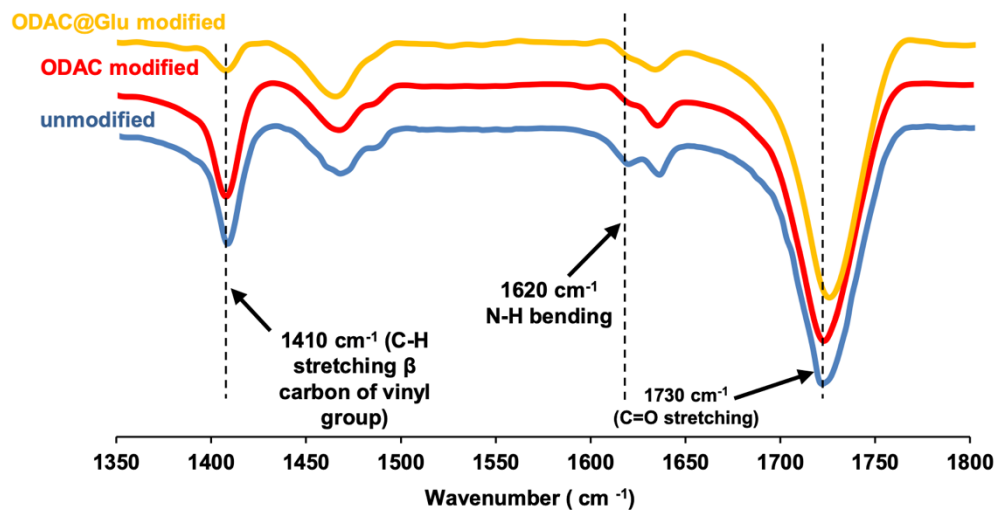


Figure S3. ATR-IR spectra of dual chemically reactive porous polymeric coating (DCRPPI) before (blue) and after single (ODAC ; red) & dual (successive treatments with both ODAC and D-glucamine; yellow) post covalent modifications. The IR peaks at 1410 cm^{-1} , 1620 cm^{-1} and 1730 cm^{-1} appeared due to symmetric deformation of the C-H stretching of β -carbon of the vinyl group, primary N-H bending of the residual amine and stretching of the carbonyl groups respectively.

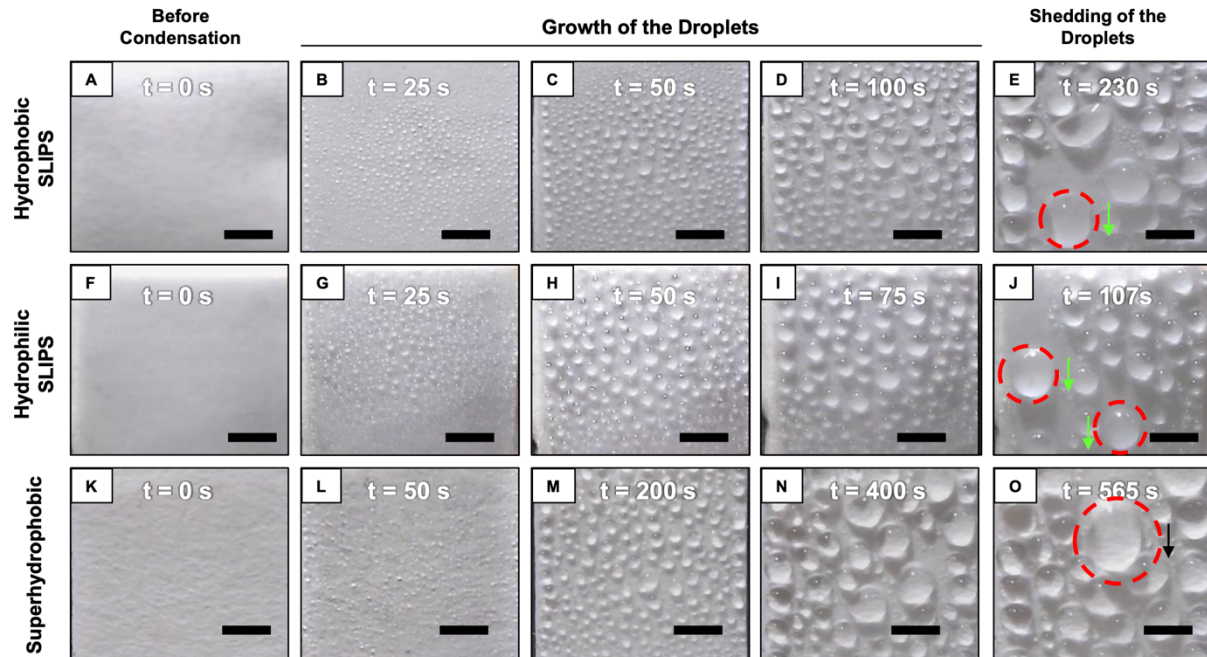


Figure S4. A-O) Digital images illustrating the process of water harvesting on hydrophobic-SLIPS (HB-SLIPS; A-E, scale: 3 mm), hydrophilic-SLIPS (HL-SLIPS; F-J, scale: 3 mm) and superhydrophobic interface (SHI; K-O, scale: 3 mm).

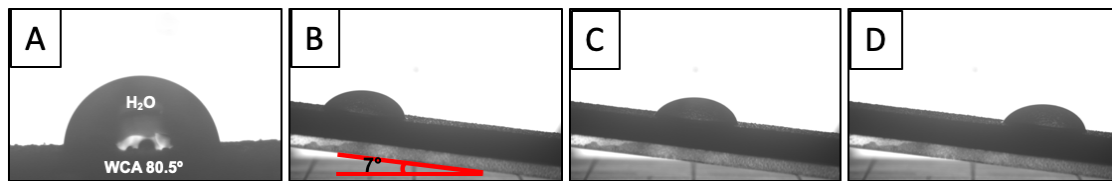


Figure S5. A-D) The contact angle images depicting the static water contact angle and slipping of beaded water droplet on hydrophilic SLIPS after fog collection.

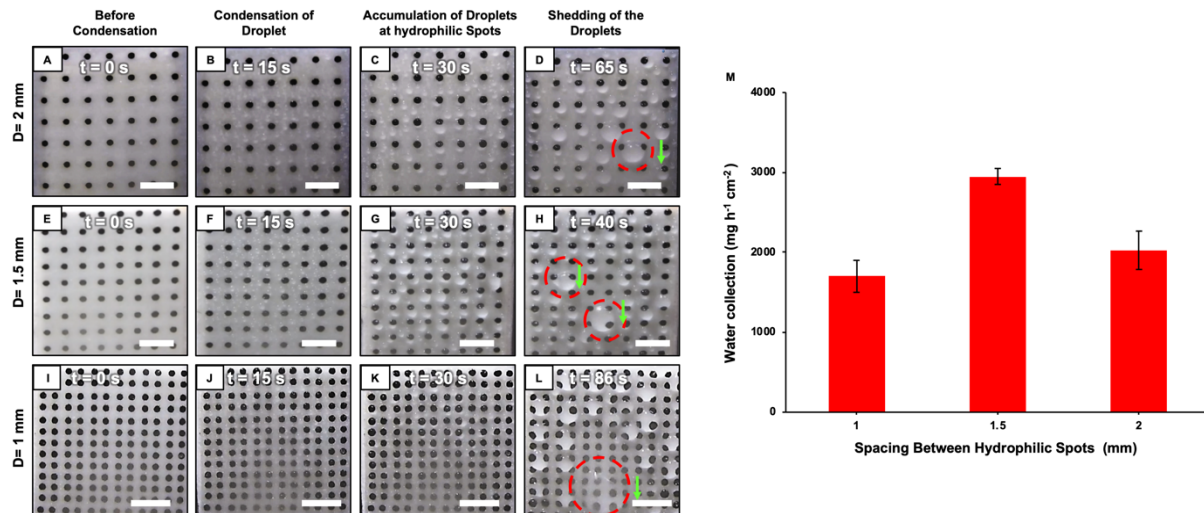


Figure S6. A-L) Digital images describing the process of water harvesting on CP-HL-SLIPS, where the spacing between the hydrophilic spots was varied from 1 mm to 2 mm (D=2 mm, A-D; D= 1.5 mm, E-H; D=1 mm, I-L, scale: 3 mm). M) A plot accounting the impact of change in the spacing between hydrophilic spots of CP-HL-SLIPS on the water harvesting ability.

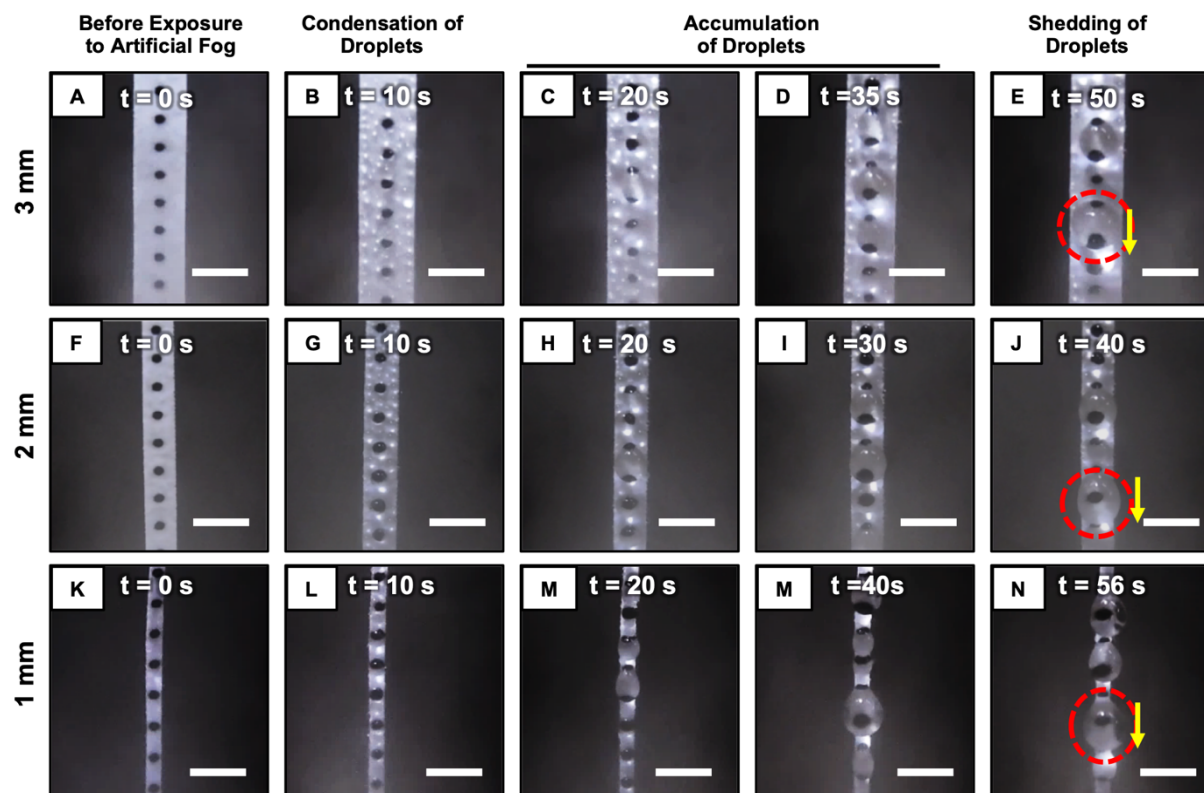


Figure S7. A-N) Digital images accounting the impact of physical confinement of CP-HB-SLIPS on the water harvesting ability, where the edge to edge distances (3 mm, A-E; 2 mm, F-J; 1 mm, K-N, scale: 3 mm) of CP-HB-SLIPS were gradually varied from 1 mm to 3 mm with interval of 1mm.

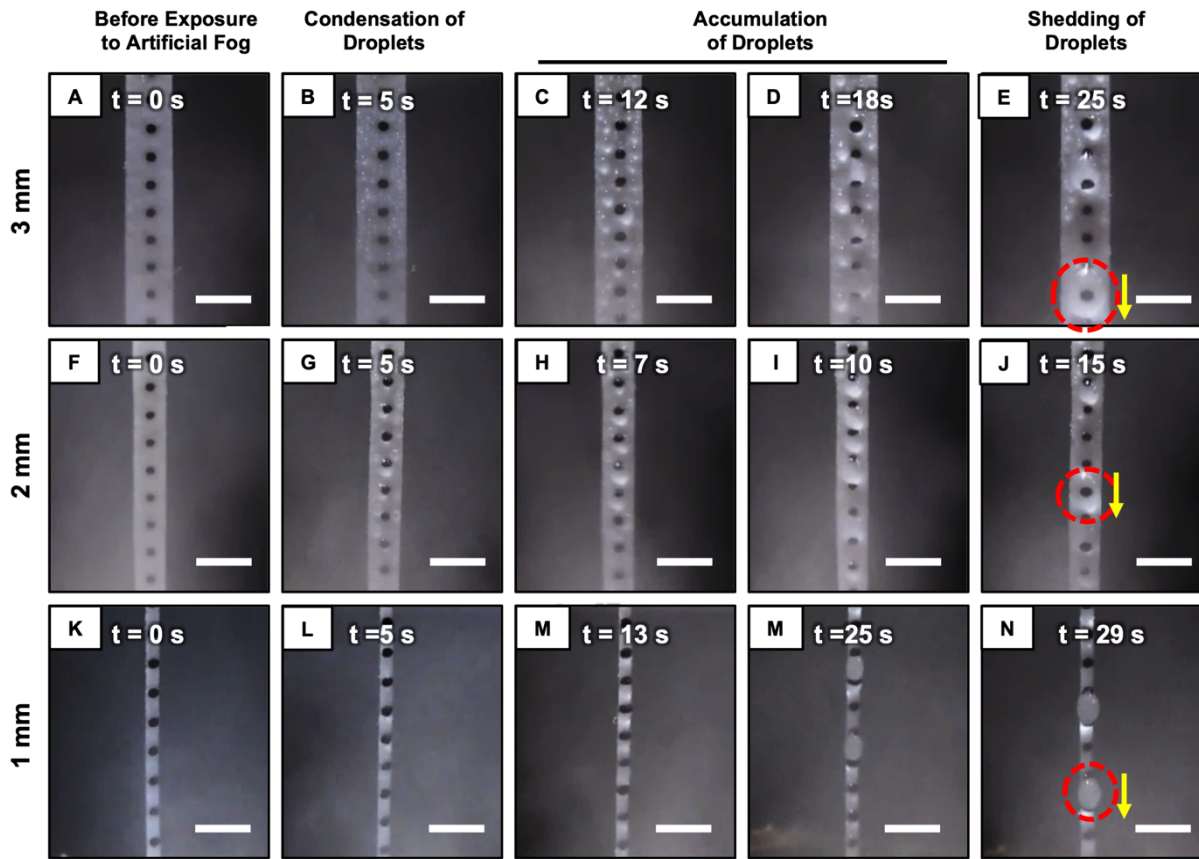


Figure S8. A-N) Digital images accounting the impact of physical confinement of CP-HL-SLIPS on the water harvesting ability, where the edge to edge distances (3 mm, A-E; 2 mm, F-J; 1 mm, K-N, scale: 3 mm) of CP-HL-SLIPS were gradually changed from 1 mm to 3 mm .

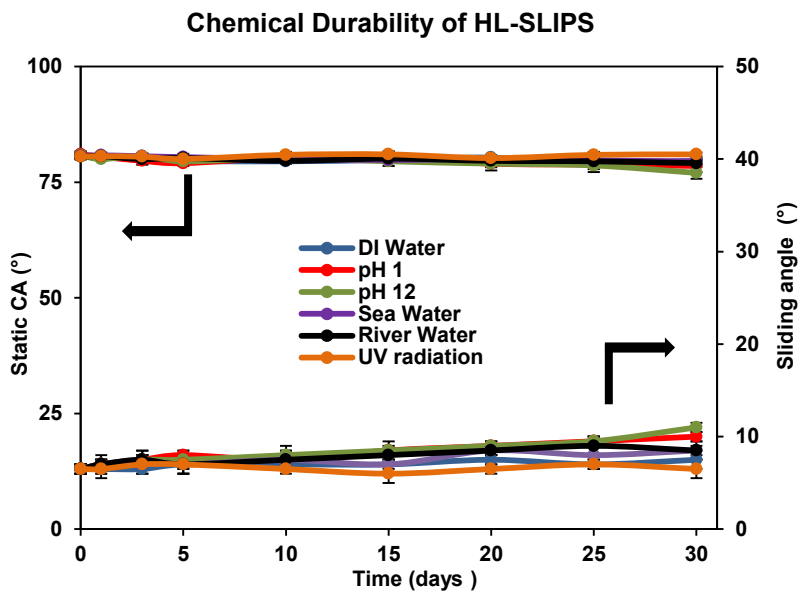


Figure S9. The plot illustrating the durability of hydrophilic SLIPS. The synthesized polymeric coating survived the exposures of various and severe chemical exposures including extremes of pH (1 and 12), artificial sea water and river (Brahmaputra, Guwahati, India) water, UV-light (at short range: 254 nm and long range: 365 nm) for 30 days. The lubricated (olive oil) interface displayed uninterrupted slippery property with low ($\sim 10^\circ$) slipping angle of beaded water droplets.