

Supporting Information

Green and Rapid Synthesis of Durable and Super-Oil (under water) and Water (in Air) Repellent Interfaces

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Experimental section

Materials: Branched poly (ethyleneimine) (BPEI, MW~25000), dipentaerythritol penta/Hexaacrylate (5Acl, MW~ 524.21) were obtained from Sigma Aldrich (Bangalore India). Reagent grade THF was purchased from RANKEM (Maharashtra, India). Propylamine, pentylamine, hexylamine, octylamine, decylamine and octadecylamine were procured from Sigma Aldrich (Bangalore India). Microscopic glass slides were obtained from JSGW (Jain Scientific Glass Works) India. Plastic and card board were obtained from local shop in Guwahati city (Assam India). Dichloromethane (DCM) was purchased from Merck Life Science Private Limited Mumbai India. Whatman filter paper was purchased from GE Healthcare Services (Bangalore India). Aluminum foil was obtained from Parekh Aluminex Limited (PAL) Maharashtra India. Adhesive tape was obtained from Jonson Tapes (India). Rhodamine-6G was purchased from Labo Chemie (Laboratory Reagents and Fine Chemicals Mumbai India). Nile red was obtained from Sigma Aldrich (Bangalore India). HCl was purchased from Fischer Scientific Mumbai India. NaOH was obtained from Emparta (Merck Specialties Private Limited). Brahmaputra River water was collected from Guwahati (Assam India). Wood and Sand grains were collected from a local construction site in IIT Guwahati campus and was rinsed thoroughly prior to use. All material were used as obtained without any further purification.

General considerations: Glass vials that are used in performing various experiments, were thoroughly washed with acetone and ethanol prior to use. Field emission scanning electron microscope (FESEM) images were acquired using Sigma Carl Zeiss Scanning electron microscope and the samples were sputtered with conducting gold layer prior to imaging. FTIR spectra were recorded at ambient conditions using PerkinElmer instrument and samples were mixed uniformly with KBr before giving the shape of pellets. The contact angles were acquired using Kruss Drop Shape Analyser-DSA-25 instrument at ambient conditions. Advancing and receding contact angles were measured using deionized water droplet at four different locations for each sample. Digital images were acquired using a canon power shot SX420 IS digital camera.

Preparation of Solvent Free ‘Reactive’ Polymeric Gel and Post-Chemical Modifications:

Branched poly (ethylenimine) (BPEI) and dipentaerythritol Penta/Hexaacrylate (5Acl) were mixed in a single container with desired molar ratio. The mixture instantly turns into semisolid gel and finally forms a solid gel within 30 seconds, then the solid gel was taken out and was subsequently rinsed with THF for removing the unreacted reactants. Afterwards the gel was transferred in the solutions of selected small molecules (having primary amine groups) including propylamine (30mg/mL), pentylamine (30mg/mL), hexylamine (30mg/mL), heptylamine (30mg/mL), octylamine (30mg/mL), decylamine (30mg/mL) and octadecylamine (5mg/mL) respectively for overnight. Then, samples were further rinsed with THF for one hour to remove the unreacted and loosely bound small molecules and were kept for drying at ambient conditions. Afterwards the change in wettability was examined with digital images and contact angle measurements. To achieve underwater superoleophobicity, the synthesized ‘reactive’ polymeric gel was post modified with glucamine (5mg of glucamine/mL of DMSO) for overnight. Then the gel material was thoroughly washed with DMSO to remove the unadhered glucamine and was subsequently washed with THF for fast drying at ambient conditions.

Coating on Various Substrates: The reactive polymeric composite films were fabricated by placing the chemically ‘reactive’ gel on the cleaned surface of various selected substrates including glass, wood, plastic, whatman filter paper, aluminum foil, card board, where the polymeric gel was uniformly spread out using microscopic glass slide. Then the coated substrates were washed thoroughly for removing unreacted reactants. Later, the substrates were modified with selected small molecules (e.g.; ODA and glucamine molecules) for embedding the material with desired biomimicked wettability—including superhydrophobicity in air and superoleophobicity under water.

Physical and Chemical Durability Tests: Various physical and chemical durability tests were performed on the ‘reactive’ polymeric gel coated substrates (that are post modified with ODA molecules), and the detailed descriptions are provided below;

1. Adhesive Tape Test: The stability of the coated film on the selected substrates and the durability of embedded special wettability of the coating were qualitatively examined with standard adhesive tape peeling test—which is widely used before in literature. The fresh adhesive surface of the tape was brought in contact with the surface of coated film on the arbitrarily selected substrates (e.g.; glass, filter paper and Al foil) and 100 g load was applied for

improving the contact of adhesive surface on coated film. Then, the adhesive tape was manually peeled off, and some top portion of the coating was transfer to the adhesive tape. Afterwards, the water wettability was examined in details on the defected region of the coated substrates (see main text for more details).

2. Sand Drop Test: In this standard durability test, coated glass substrate (post functionalized with ODA) was placed with tilting angle of 45° . Then, 100g of sand was poured on the coated substrate from a height of 15 cm with continuous flow. The physical integrity as well as the antiwetting property of the coated substrate remains intact.

3. UV-Exposure: The effect of UV light irradiation on the stability of embedded antiwetting property in the polymeric coating was examined in details. The polymeric coating on glass substrate (post modified with ODA) was exposed to UV radiations of both the short (254nm) and longer (365nm) wavelengths for 5 days (120 hours). The antiwetting property of the resulting polymeric coating was measured after each 24 hour period with digital images and contact angle measurements.

4. Chemical Durability Test: The stability of the embedded superhydrophobicity in the polymer coating on glass substrate (post modified with ODA) was examined in the presence of complex and severe aqueous phases. Before performing the experiment, the artificial sea water was prepared by mixing following salts (with appropriate compositions): MgCl_2 (0.2265g), MgSO_4 (0.325g), NaCl (2.673g) and CaCl_2 (0.112g) in 100 mL of deionized water. Afterwards, the coated substrate was exposed to various harsh aqueous chemical condition such as extremes of pH (1, 12), high ionic strength (artificial sea water), and river (Brahmaputra, Assam India) water. Then, the antiwetting property was examined with visual inspections and contact angle measurements.

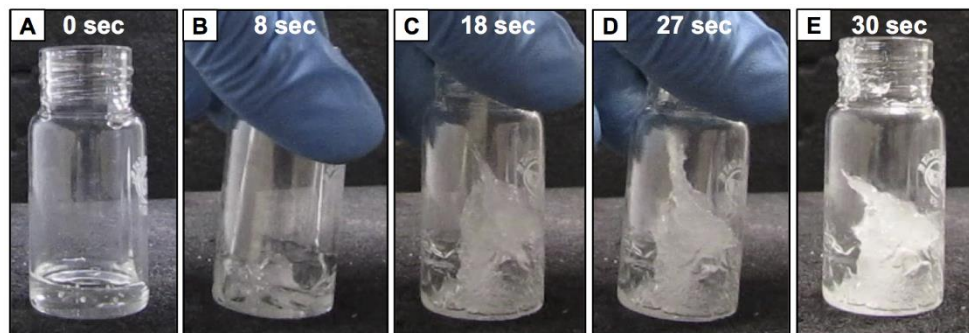


Figure S1. A-D) Digital images are illustrating the process of gel formation on continuous mixing of BPEI and 5-Acl, where optically transparent mixture (A) of liquid reactants are transformed into opaque gel within 30 seconds (E).

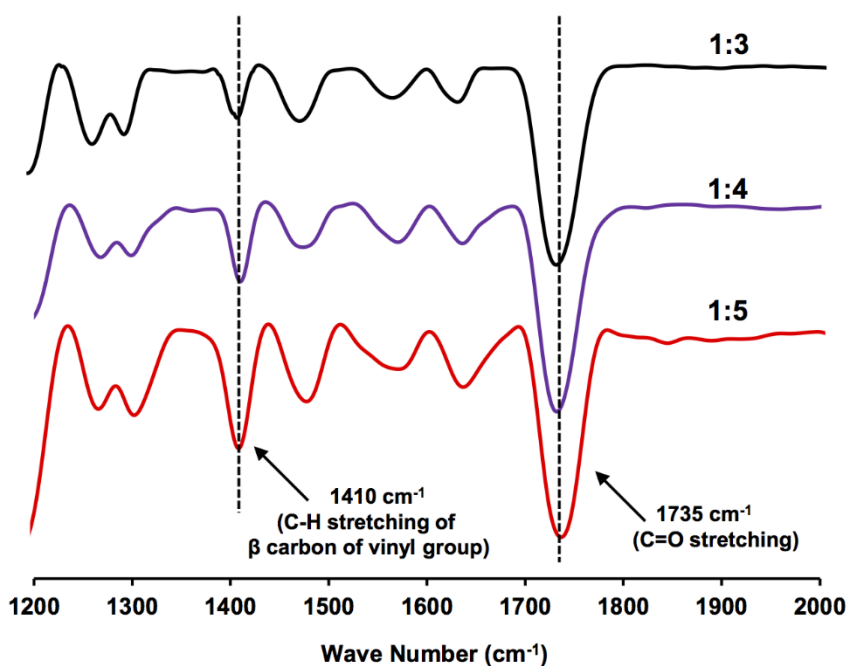


Figure S2. FTIR spectra of reactive polymeric gels that are synthesized by changing composition (molar ratio) of the reactants (BPEI/5-Acl) including 1:3 (black), 1:4 (violet), and 1:5 (red)) in the reaction mixtures. The IR peaks at 1736 cm^{-1} and 1410 cm^{-1} denoting the carbonyl stretching and symmetric deformation of C—H bond for β -carbon of vinyl groups.

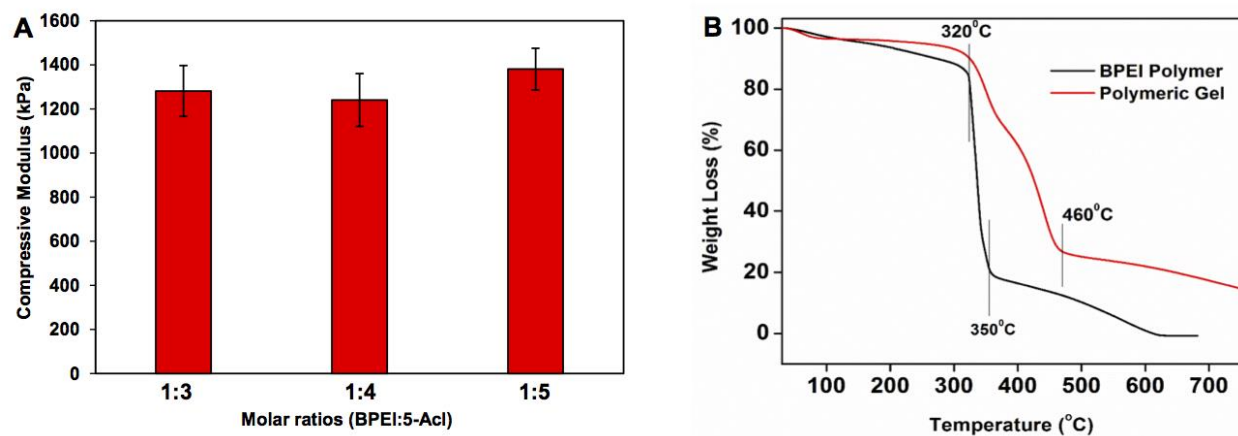


Figure S3. A) Accounting compressive modulus of polymeric gels that are synthesized by changing composition (molar ratio) of the reactants (BPEI/5-Acl) including 1:3, 1:4, and 1:5, in the external solvent less reaction mixtures. B) Illustrating % of weight loss of the synthesized material (red) and native BPEI polymer (black) with increasing the temperature.

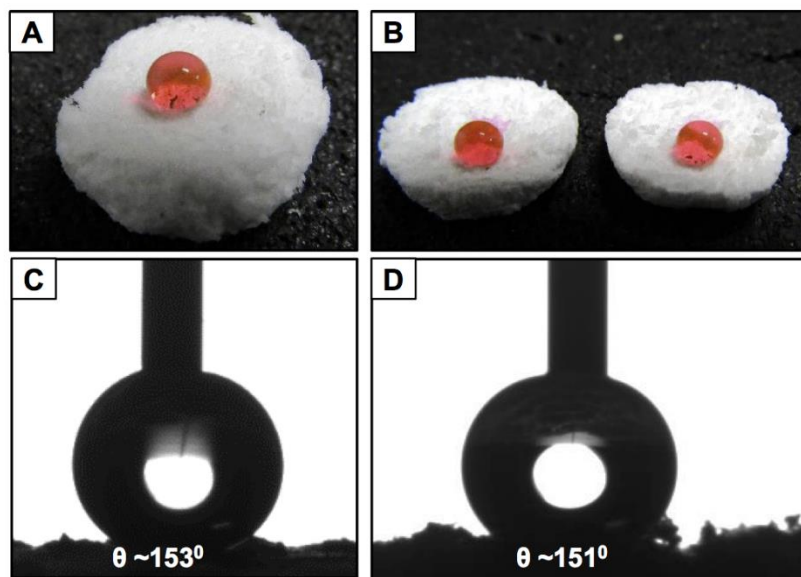


Figure S4. A-D) Digital images (A, B) and water contact angle images (C, D) of beaded water droplet on the synthesized polymeric gel after post modification with ODA before (A, C) and after (B, D) exposing the interiors of the material.

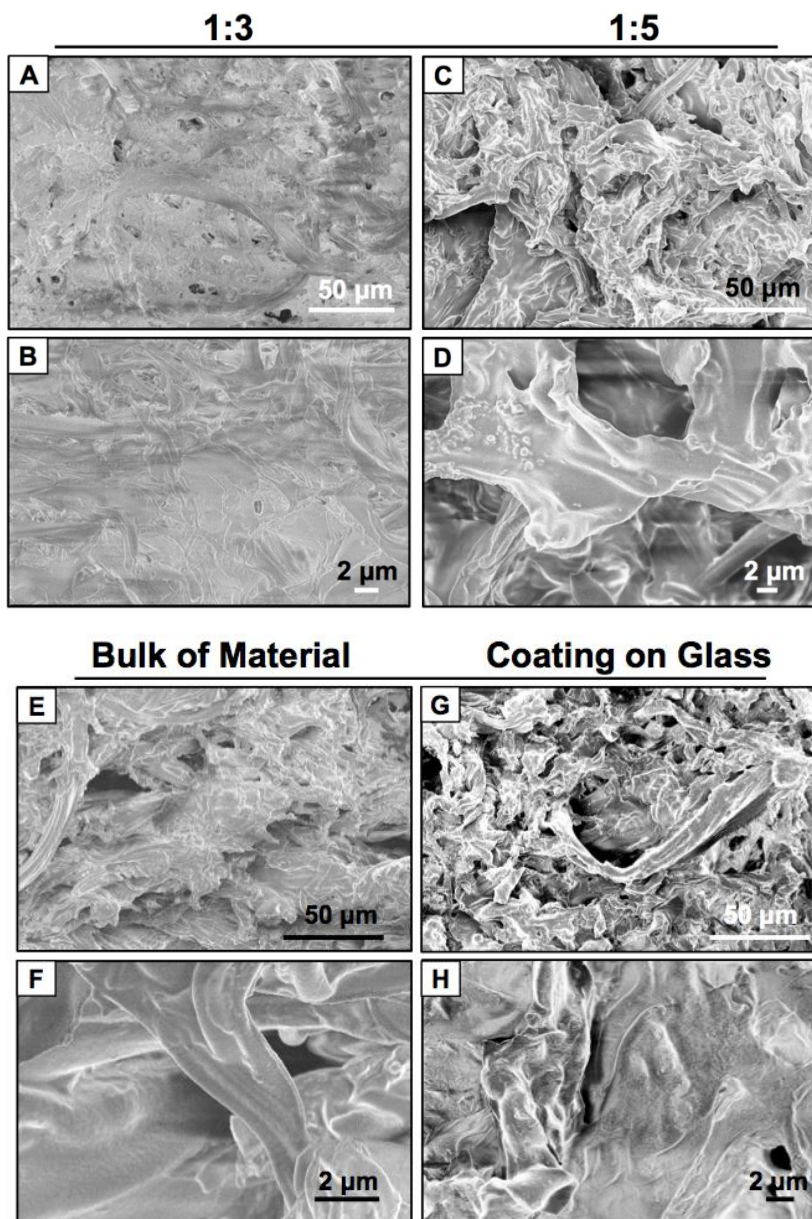


Figure S5. A-D) FESEM images of solvent free polymeric gels (that are prepared with BPEI/5-Acl molar ratio of 1:3 (A-B) and 1:5 (C-D) after washing thoroughly with THF, both in lower (A, C) and higher (B, D) magnifications. E-H) FESEM images of the interior (bulk) of the polymeric gel (E-F; that are prepared with BPEI/5-Acl molar ratio of 1:5) and coated interface (G-H) on the glass substrate.

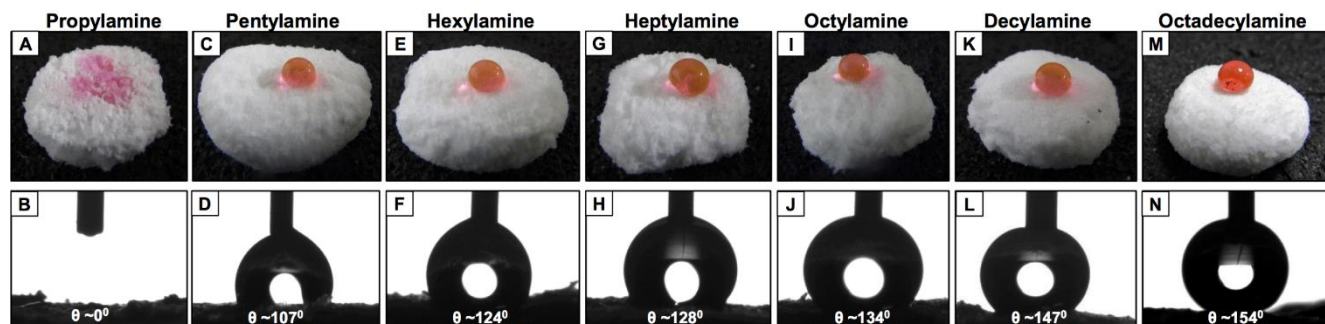


Figure S6. A-N) Digital images (A, C, E, G, I, K, M) and water contact angle images (B, D, F, H, J, L, N) of the beaded aqueous (red color aids visual inspections) droplets on solvent free polymeric gel (molar ratio of BPEI and 5Acl is 1:5) after post modification with various amine containing small molecules including propylamine (A-B), pentylamine (C-D), hexylamine (E-F) heptylamine (G-H), octylamine (I-J), decylamine (K-L) and octadecylamine (M-N) respectively.

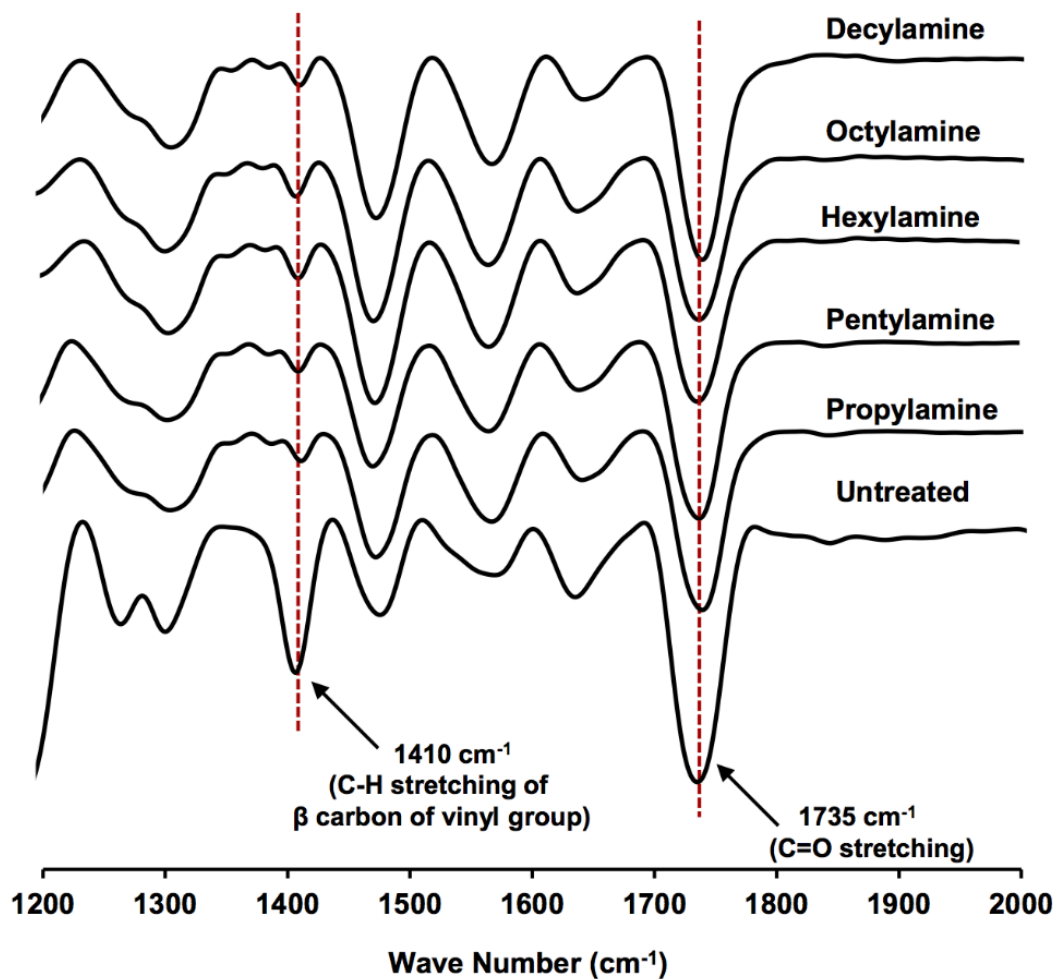


Figure S7. FTIR spectra of the solvent free and ‘reactive’ polymeric gel before and after post modification with various amine containing small molecules including propylamine, pentylamine, hexylamine, octylamine and decylamine respectively. The IR peaks at 1736 cm^{-1} and 1410 cm^{-1} are referring to the carbonyl stretching and C-H stretching of vinyl moiety (β -carbon) of acrylate group, and the significant depletion of the IR peak intensity at 1410 cm^{-1} with respect to the another IR peak at 1736 cm^{-1} denoted the mutual reaction between residual acrylate groups and amine containing small molecules.

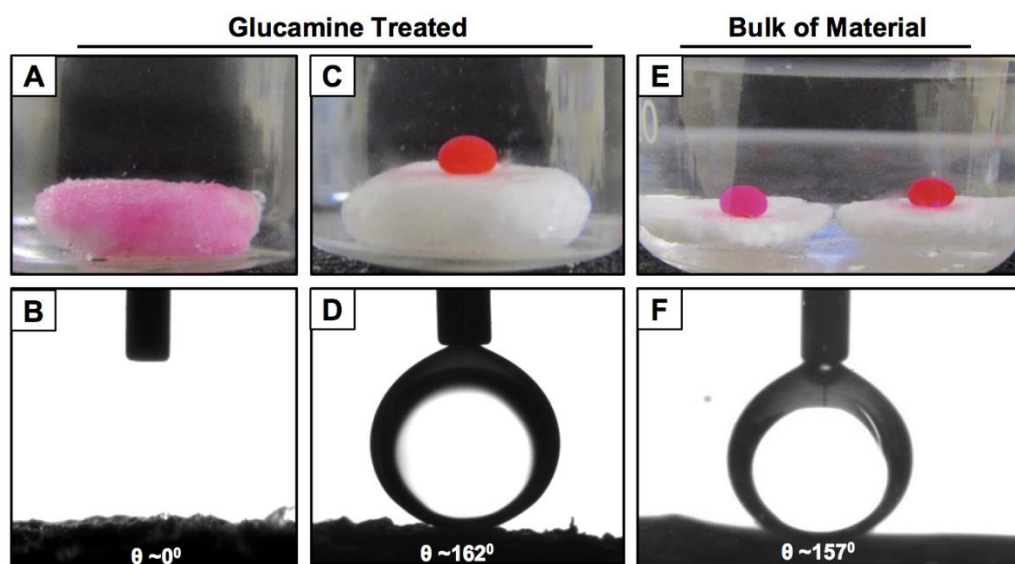


Figure S8. A-F) Digital images (A, C, E) and contact angle images (B, D, F,) of the beaded oil droplet under water on the polymeric gel before (A-B) and after (C-D) post functionalization with glucamine molecule, respectively. E-F) Digital image (E) and underwater oil contact angle image (F) of beaded oil droplet under water on the freshly exposed interior of the polymeric gel.

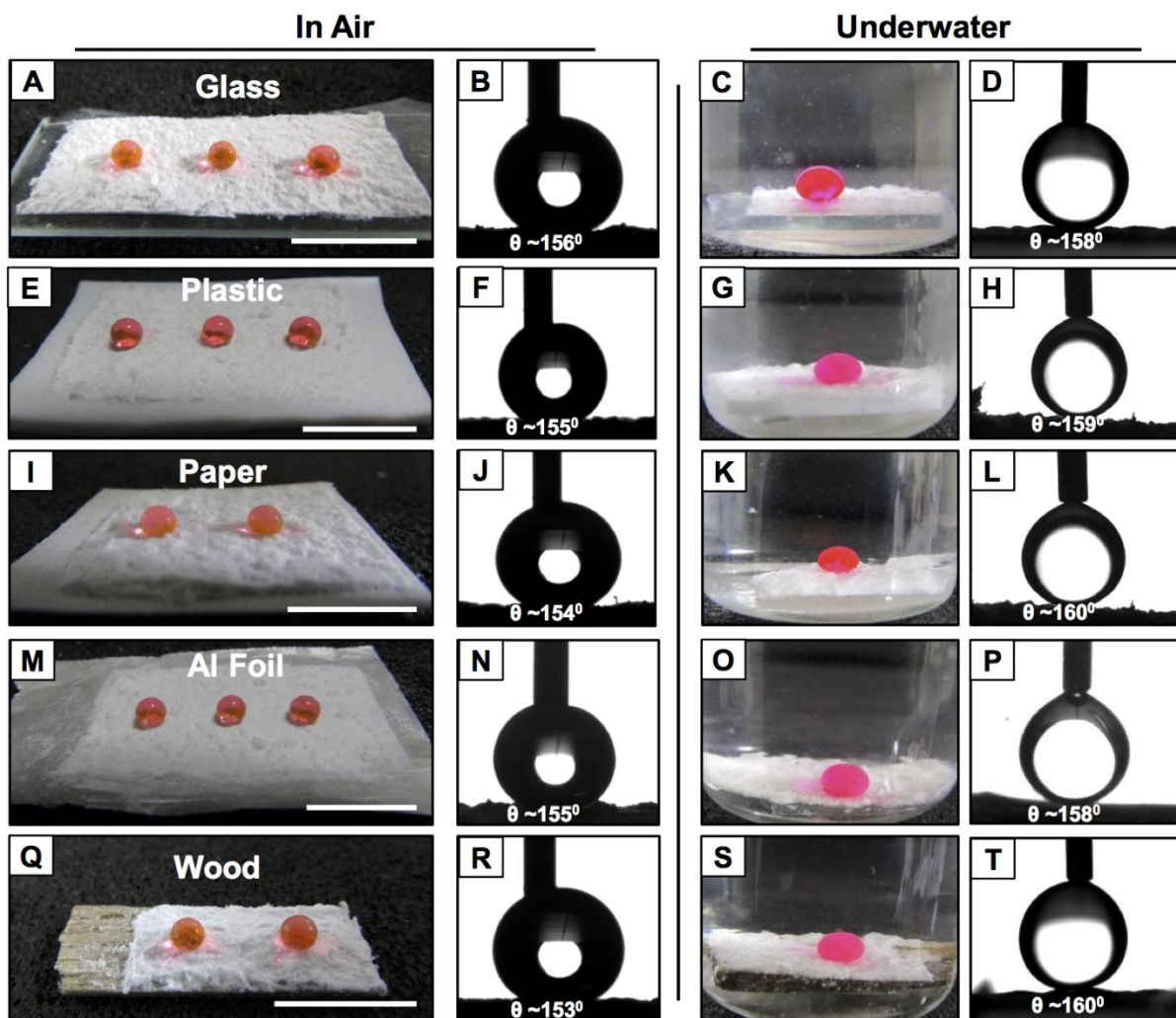


Figure S9. A-T) Digital images (A, C, E, G, I, K, M, O, Q, S) and contact angle images (B, D, F, H, J, L, N, P, R, T) of beaded water (in air; A-B, E-F, I-J, M-N, Q-R) and oil (under water; C-D, G-H, K-L, O-P, S-T) droplets on the solvent free polymeric coatings on the various substrates, including glass (A-D), plastic (E-H), filter paper (I-L), aluminum foil (M-P), wood (Q-T). (Scale bar; 1 cm).

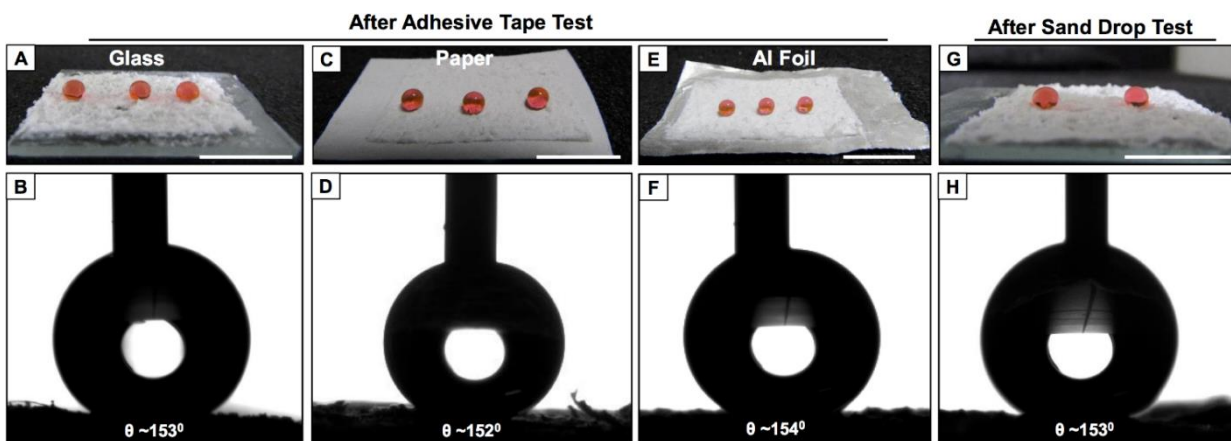


Figure S10. A-F) Digital images (A,C, E) and water contact angle images (B, D, F) of beaded water droplets on the ODA modified polymeric coatings on various substrates—including glass (A, B), filter paper (C, D), aluminum foil (E, F), after performing the adhesive tape test. G-H) Digital image (G) and contact angle image (H) of water droplet that is beaded on the polymeric coating after the sand drop test. (Scale bar: 1 cm).

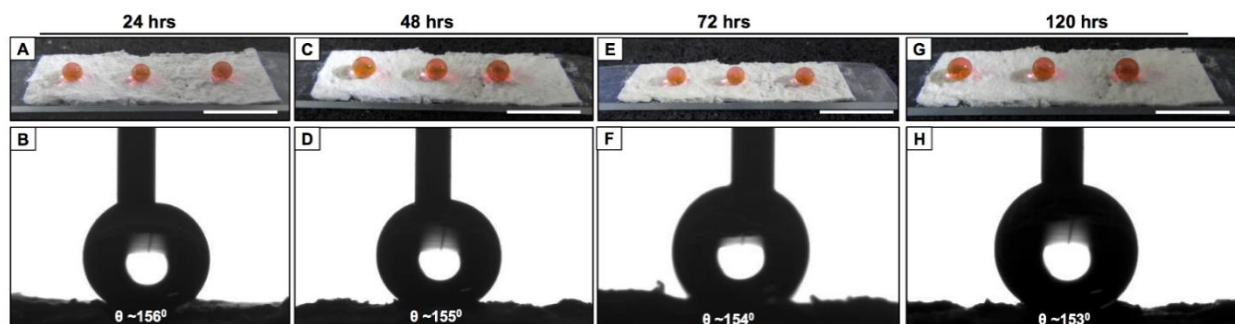


Figure S11. (A-H) Digital images (A, C, E, G) and contact angle images (B, D, F, H) of beaded water droplet on the solvent free polymeric coating (post modified with ODA) on glass substrate after continuous exposure to UV radiations of short (254nm) and long (365nm) wavelengths for 24 hours (A, B), 48 hours (C, D), 72 hours (E, F) and 120 hours (G, H) respectively. (Scale bar: 1 cm).

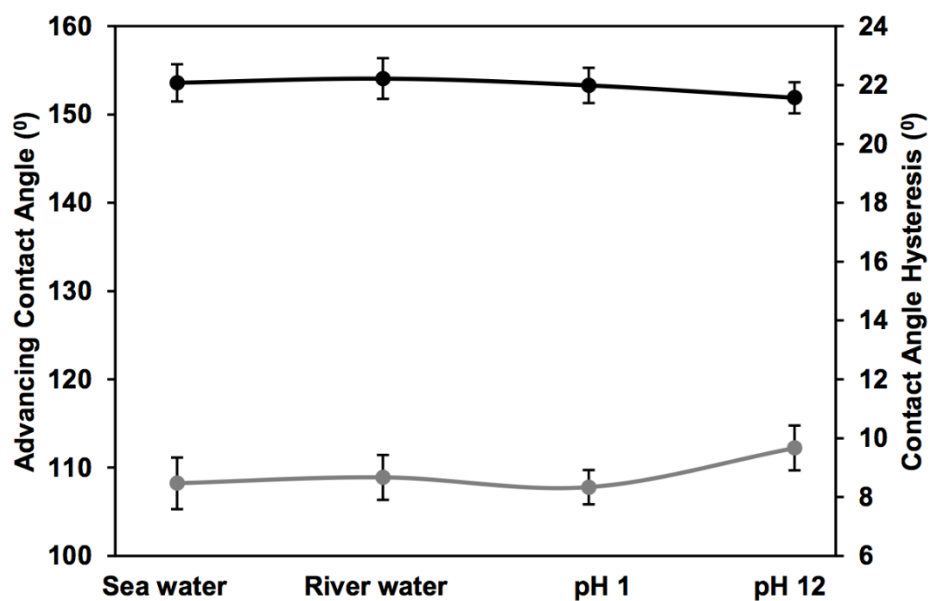


Figure S12. The plot accounting the advancing contact angle (black) and contact angle hysteresis (grey) of beaded harsh aqueous phases—including extremes of pH (1, 12), high ionic strength (artificial sea water) and river (Brahmaputra, Assam, India) on the solvent free polymeric coating (post modified with ODA).