# Supporting Information

# Biodegradable Polymer Based Common Chemical Avenue for Optimizing Switchable, Chemically Reactive and Tunable Adhesive Superhydrophobicity

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## Experimental section

**Materials:** Chitosan (low molecular weight; product # 448869) was procured from Sigma Aldrich, Bangalore. Dipentaerythritol penta-/hexaacrylate (5Acl, MW ~ 524.21 g/mol), Decanoyl chloride (DC), tetramethylrhodamine isothiocyanate (TRITC), fluoresceinamine, Nile red (Technical grade, Sigma-N3013), butylamine (98%), hexylamine (99%), octylamine (99%), decylamine (99%), sodium dodecyl sulfate (SDS, ≥99%), dodecyltrimethylammonium bromide (DTAB) (99%) and methylene blue were purchased from Sigma-Aldrich, Bangalore, India. Bromothymol blue had been procured from HiMedia Laboratories Pvt. Ltd, Mumbai, India. Dichloromethane (DCM) was acquired from Finar Chemicals, Gujarat, India. Whatman42 filter paper (diameter 12mm) was purchased from GE Healthcare Life Sciences. Rhodamine 6G was purchased from Labo Chemie, Mumbai, India. Conc. hydrochloric acid was obtained from Fischer Scientific, Mumbai, India. Sodium hydroxide, acetic acid and ammonia were purchased from Merck Specialties Private Limited, India. Tetrahydrofuran (THF) and Sodium chloride (NaCl) were obtained from RANKEM, Maharashtra, India. Sandpaper (grit no. 400) was purchased from Million International, India. Glass slides (Boroleb, India), and adhesive tape (Jonson tape Ltd. India) were acquired from different sources. Sand was collected from a construction site at IIT-Guwahati, Assam. This sand was used in experimental demonstrations after thorough washing with water. For all the experiments deionized water was used unless not specified otherwise.

**General considerations:** Dynamic light scattering (DLS) measurements were taken by using a Zetasizer Nano ZS90 (model no ZEN3690) instrument. FTIR spectra for the samples were collected employing a PerkinElmer instrument, where samples were first embedded in a KBr pellet following the standard protocol. Liquid water contact angles (WCA) on the materials were estimated using a KRUSS Drop Shape Analyzer DSA25 instrument at ambient temperature and 5 µL of deionized (DI) water droplets were used for both the static and dynamic contact angle measurements. Scanning electron microscopy (SEM) images were obtained using a Carl Zeiss field emission scanning electron microscope where all nonconductive polymeric samples were gold-sputtered under vacuum to achieve a thin layer of conductive gold coating on the polymeric samples prior to scanning under FESEM. All digital pictures were taken with a canon power shot SX420 IS digital camera.

**Preparation of Chitosan Particles:** Chitosan particles were prepared by de-solvation method, where a 80 mg of chitosan was dissolved in 40 mL of 0.1 (M) acetic acid to achieve a final concentration of 2 mg/mL. The solution was sonicated for 5 minutes for uniform dissolution and stirred for 1 hour at 500 rpm to get a homogeneous acidic solution of chitosan. Then, a 40 mL of ethanol (EtOH) was dropwise added into the solution of chitosan with contineous agitation. After that, the whole solution was centrifuged for 5 minutes at 3000 rpm and top liquid portion was decanted giving a transparent semisolid mass. The residue was dispersed in 10 mL of ethanol (EtOH) that doped with 6 mg of NaCl and whole solution was sonicated for 30 minutes, to get an uniform dispersion of chitosan nanoparticles. This dispersion was finally used for preparing chemically reactive gel.

**Fabrication of Chemically 'Reactive' Polymeric Gel Material:** The chitosan particles contributed in formation of polymeric gel material through 1, 4-conjugate addition reaction with 5Acl molecules. 1.325 g of 5Acl was dissolved in 10 mL ethanol by sonication. Then 5 mL of this solution was added to 3 mL of chitosan dispersion followed by addition of 500 microliters of 25% ammonia solution to make the solution alkaline. The mixture was kept on shaker plate for vigorous shaking till the solution became completely turbid and the appearance of turbidity took around 3 hours. Finally, the mixture was moulded in any desired shape by transferring and keeping the mixture to that particular mould for 3 hours without any disturbance. The self-standing gel was washed thoroughly with THF for removal of unreacted loosely bound reactants.

**Post Chemical Modifications:** For achieving 1,4 conjugated addition reaction-based post chemical modifications, the prepared polymeric material was exposed to different amine-containing small molecules e.g. butylamine (35.23 mg/mL, in THF), hexylamine (36.6 mg/mL, in THF), octylamine (37.23 mg/mL, in THF), decylamine (37.47 mg/mL, in THF) and octadecylamine solution (35 mg/mL, in THF) for 24 hours at ambient condition. After the post-chemical modification, the material was washed with THF for multiple times to get rid of loosely bound selected small molecules.

For modifying the material through nucleophilic substitution reaction, a freshly prepared polymeric material was treated with acid chloride group (DC; 40 µL/mL in DCM) for 24 hours with addition of small amount of triehtylamine at low temperature (0°C to 5°C) to achieve 'chemically-reactive' adhesive superhydrophobicity. After taking out the sample from the DC solution, it was washed with DCM, THF and water to remove all the loosely adhered DC molecules.

In case of dual chemical modification of the chitosan-based material, a freshly prepared gel was first treated with acid chloride (DC; 40 µL/mL in DCM) for 24 hours with addition of small amount of triehtylamine at same reaction condition and after washing with DCM and THF, the material was then treated with octadecylamine (35 mg/mL, in THF) for another 24 hours at ambient condition followed by washing with THF and water. After the dual-modification with acid chloride and ODA molecules, the material was able to exhibit non-adhesive superhydrophobicity.

Besides, the dual treated and DC-treated material was transferred to the TRITC (1 mg/10 mL of EtOH) and fluoresceinamine solution (1 mg/10 mL of EtOH) and the treatment was continued for 24 hours. After the treatment, the samples were washed several times with THF and EtOH to remove all the unreacted dye molecules.

**Chemical Durability**

The dual functionalized material (ODA/DC treated) was exposed to different chemically harsh aqueous conditions—including extremely acidic water (pH 1), basic water (pH 12), artificial sea water, river water and surfactant-contaminated water (SDS: 1mM, DTAB: 1mM) for a duration of 15 days for examining chemical durability of the embedded non-adhesive superhydrophobic property. Finally, the samples were taken out and washed thoroughly with ethanol followed by air drying. The water wettability was examined by measuring the contact angle of beaded water droplets.

**Physical Durability**

The physical durability of the non-adhesive superhydrophobic material was investigated by adopting some standard durability tests, including adhesive tape test, sand paper abrasion test and sand drop test. Further, the material was exposed to UV-radiation for 30 days and finally the wettability property of the materials was examined by contact angle measurements after each and every physical durability tests.

*Adhesive tape test:* The surface of the material was bought in contact with adhesive tape surface and 250 g of load was applied on top of it to ensure a uniform and homogeneous contact between the sample and the adhesive tape. After 10 minutes, the tape was manually peeled off, which resulted in random fracture of the top surface of the material.

*Sand paper abrasion test:* Sand paper (grid no. 400) was used for this test. The sand paper was placed onto the material with an applied load of 250 g on the top for achieving uniform contact between the material and the sand paper. The sand paper with applied load was rubbed back and forth for 10 times continuously for abrading the top-most surface of the material resulting in transfer of some powdery material to the sand paper. The anti-wetting property of both the sand paper and the powdery material were tested under contact angle instrument along with their digital images.

*Sand drop test*: 250 g of sand grains was poured onto the sample from a height of 25 cm. The impact due to the granular sands appeared to be minimal as the embedded superhydrophobicity remained unperturbed, which was examined with CA data and digital image analysis.

**Patterning on pH-responsive Superhydrophobic Surface:**

*Paper-based printing:* Whatman42 filter paper was cut into 'triangle' shape for paper-based printing on pH-responsive superhydrophobic surface. First, the triangular shaped filter paper was inked with acidic (pH 1) solution of dyed (Rhodamine 6G). The wet paper was placed onto the material for 30 seconds, and then, this filter paper was gently taken out from polymeric interface. The contact of wet paper on the polymeric interface facilitates the rapid transfer of acidic aqueous solution of dye to the material provided, and eventually provided the desired 'triangle' print. Additional 50 µL of acidic solution of the same dye was added for achieving the three dimensional pattern with triangular shape. The patterned material was then kept in open air for drying.

*Stamp-based printing:* An 'IIT' (Indian Institute of Technology)-stamp was designed by cutting the matchsticks in particular shape and arranged them on a glass slide to develop the stamp. Then, the stamp was immersed in pH 1 solution dyed with Rhodamine 6G for 30 seconds prior to printing on the pH-responsive superhydrophobic surface. Printing procedure was done by placing the stamp onto the material surface and was taken out after 30 seconds. The acidic (pH 1) solution of the dye was transferred to the material and provided the desired 'IIT' print. The patterned material was then kept for air drying.

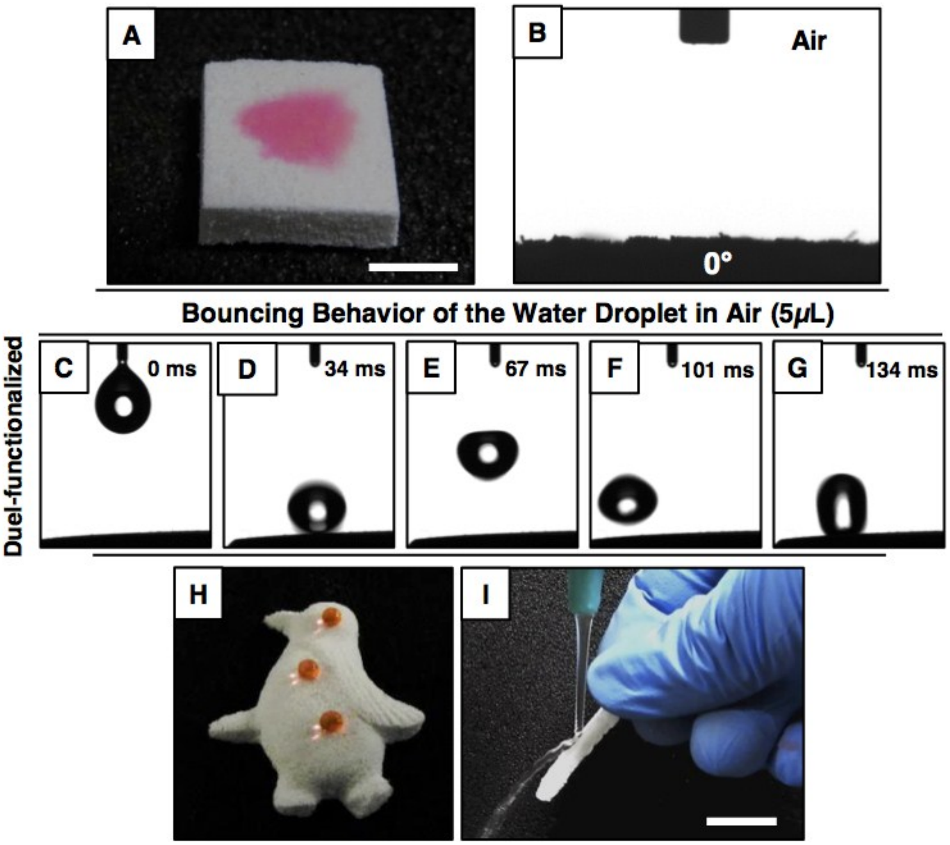

**Figure S1:** A-B) Digital image (A) and contact angle (B) of the water droplet on untreated polymeric material. (C-G) Contact angle images of the bouncing behavior of a water droplet (5 µL) on the dual-functionalized material. (H)The chitosan based superhydrophobic material molded in a shape of penguin. (J) Water stream bounces away when falls on the surface of the dual treated material.

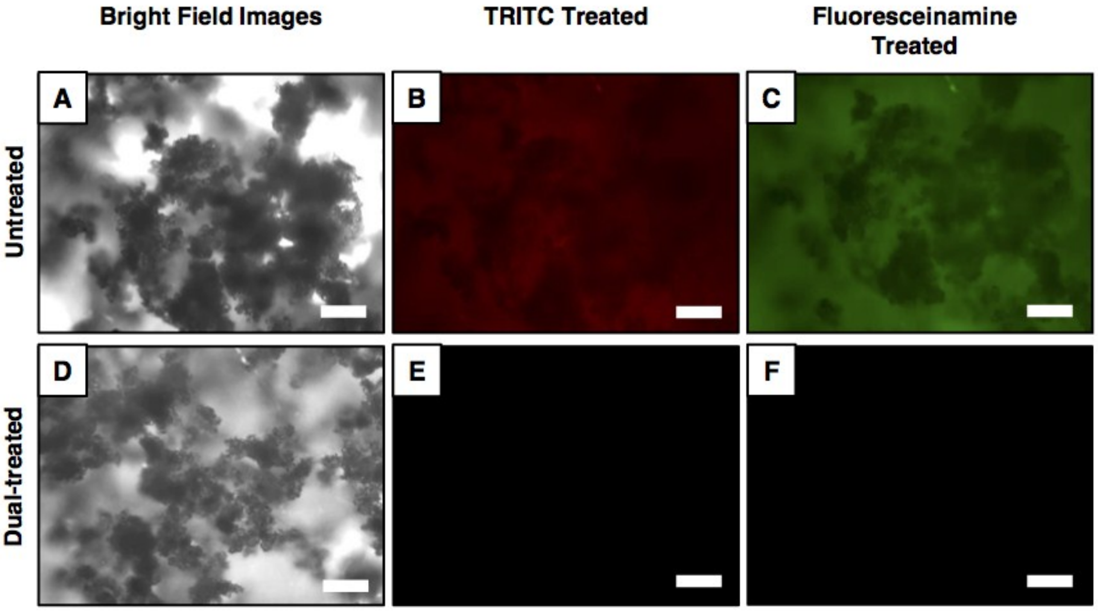

**Figure S2:** A-F) Bright field and fluorescent microscopic images (scale bar-100µm) of untreated (A-C) and dual-functionalized (ODA/DC modified) (D-F) material after post-modification with both TRITC (B,E) and fluoresceinamine (C,F) dyes.

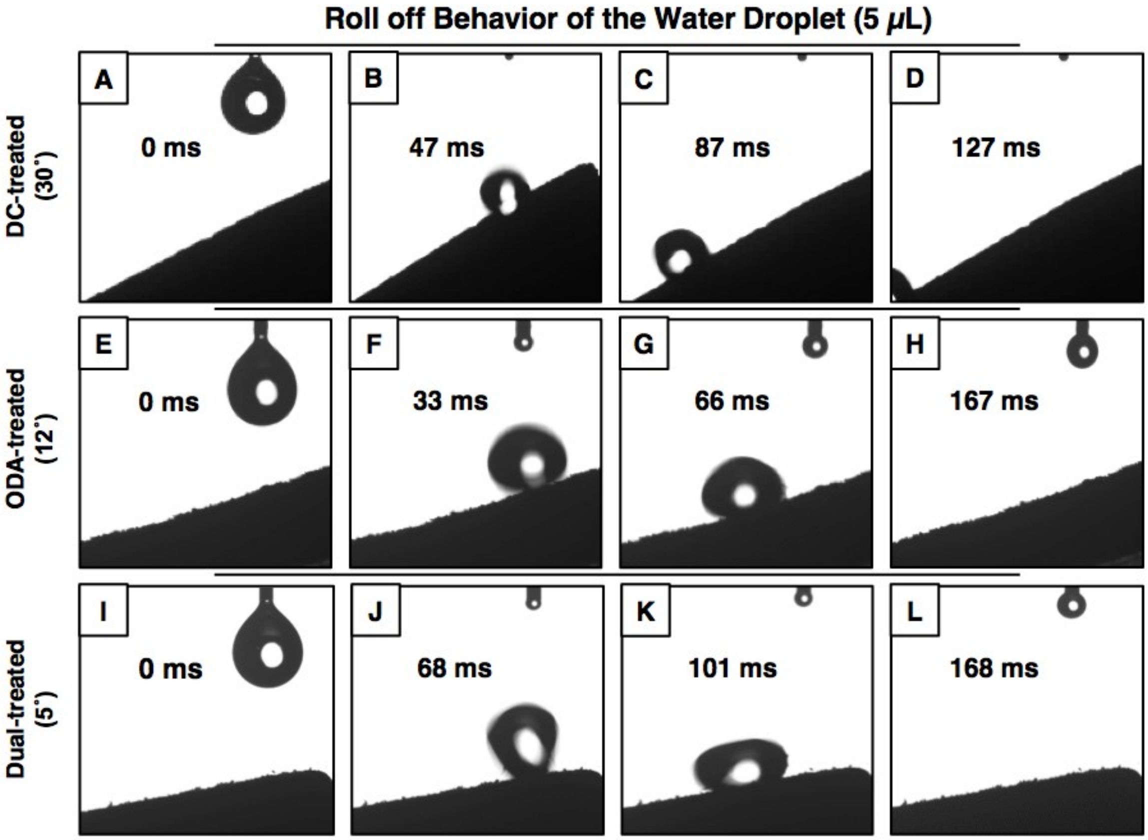

**Figure S3:** A-L) Contact angle images illustrating the rolling off phenomena of the beaded water droplets on both mono-functionalized (DC-treated (A-D) and ODA-treated (E-H)) and dual-functionalized (ODA/DC modified; I-L) materials that are kept tilted with 30˚, 12˚ and 5˚ respectively.

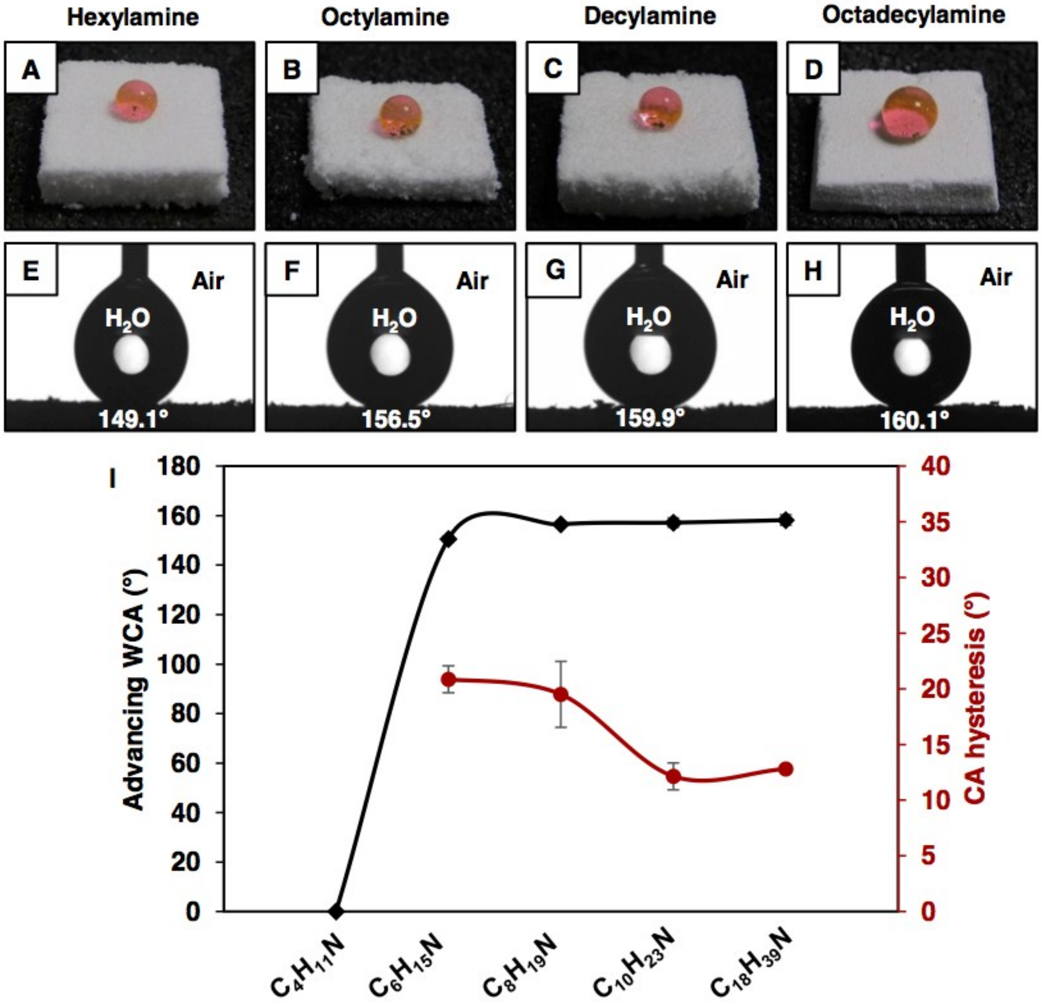

**Figure S4:** A-H) Digital images (A-D) and contact angle measurements (E-H) of the beaded water droplet (red color aids visual inspection) on different amine-modified (hexylamine: A,E; octylamine: B,F; decylamine: C,G; octadecylamine: D,H) chitosan based material. (I) The graphical representation of the variation of advancing WCA (black) and CA hysteresis (red) with the change in the length of hydrocarbon in the selected amine-containing small molecules.

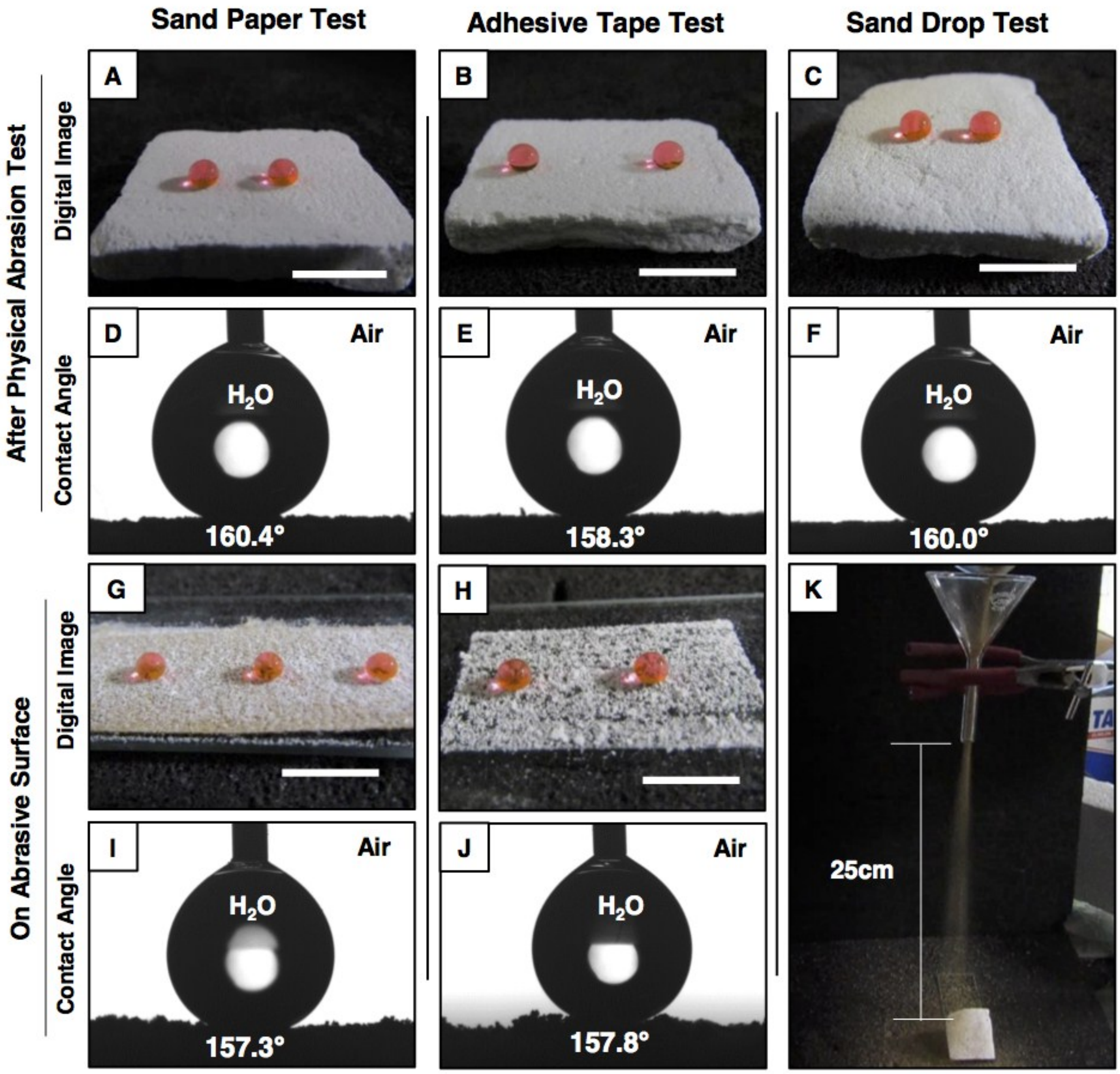

**Figure S5:** A-F) Digital images (A-C) and advancing contact angle measurements (D-F) of the dual-functionalized polymeric material after different physical abrasion tests, i.e. sand paper test (A,D), adhesive tape test (B,E), and sand drop test (C,F). (G-J) The abraded portions of the material adhere to the abrasive surfaces (sand paper: G,I and adhesive tape: H,J) are also capable of showing superhydrophobicity as confirmed by the digital images (G-H) and contact angle measurements (I-J). (K) Digital image of the experimental set-up for the sand drop test.

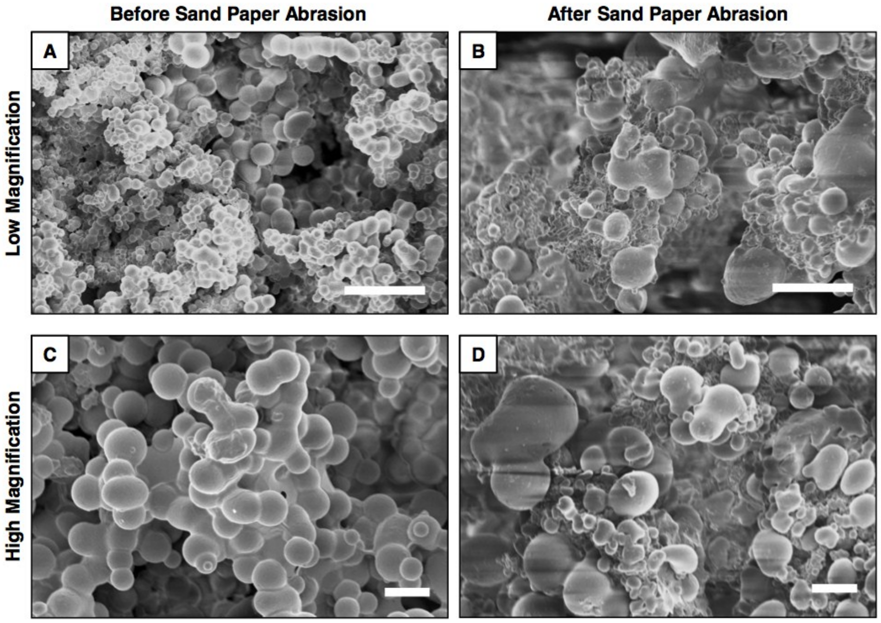

**Figure S6:** A-D) FESEM images of the dual-functionalized material before (A,C) and after (B,D) sand paper abrasion test at low (A-B; scale bar: 40 µm) and high (C-D; scale bar: 6 µm) magnifications.

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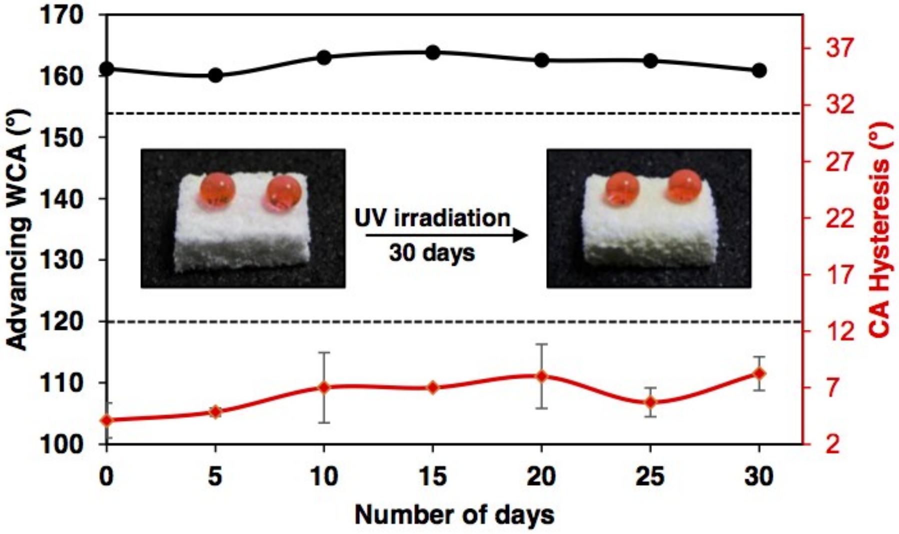

**Figure S7:** The anti-wettability of the non-adhesive superhydrophobic material (dual-functionalized) is retained even after UV-irradiation for 30 days.