Supporting Information

A General and Facile Chemical Avenue for Controlled and Extreme Regulation of Water-Wettability in Air and Oil-Wettability Under Water

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***Experimental section*:**

Materials: Dipentaerythitol penta-acrylate (5Acl), branched polyethyleneimine (BPEI, MW~ 25000), propylamine, hexylamine, octylamine, decylamine, sodium dodecyl sulfate (SDS) and Nile red (Technical grade, Sigma-N3013) were aquired from Sigma Aldrich, Bangalore, India. . n-butylamine was bought from Spectrochem Pvt. Ltd., Mumbai, India. HCl and Dimethyl sulfoxide (DMSO) were obtained from Fischer Scientific, Mumbai, India. 1-pentylamine, heptylamine, and 1-octadecylamine were purchased from Alfa-Aesar and ethyl alcohol was purchased from TEDIA Company (United States of America). THF was obtained from RANKEM, Maharashtra, India. Sand paper (grit no. 400) was acquired from Million International, India. Microscopic glass slides were obtained from JSGW (Jain Scientific Glass Works, India), aluminium foil (Parekh Aluminex Ltd., India), and adhesive tape (Jonson tape Ltd. India) were obtained from local sources. Dichloromethane (DCM) and methanol was acquired from Merck Life Science Pvt. Ltd., New Delhi, India. D-glucamine (>95%) was purchased from TCI (Tokyo Chemical Industry). Sand and wood was collected from a construction site at IIT-Guwahati, Assam.

General Consideration: The glass vials, which were used for the preparation of solutions were washed thoroughly with ethyl alcohol followed by acetone prior to using them in LbL deposition process, and compressed air was used to dry the synthesized multilayers of both the polymeric nano-complexes (NC) and BPEI. The dynamic light scattering (DLS) measurements were performed with Zetasizer Nano ZS90 instrument (model no. ZEN3690) for examining the growth of the NC in BPEI/5Acl solution during LbL deposition process both in presence and absence of NaCl salt. The available chemical functionalities both

in the growing NC and its multilayers constructions were investigated using a Perkin-Elmer Fourier transform infrared (FTIR) spectrophotometer at ambient temperature, where the polymeric samples were appropriately mixed up with KBR prior to form the KBr pallet. Contact angles of both oil (under water) and water (in air) were measured at five different locations for each sample using KRUSS Drop Shape Analyzer-DSA25 instrument with automatic liquid dispenser at ambient temperature by exerting the sessile drop measurement method. The advancing angle that was measured just after bringing the respective liquid droplet (4.5µl) to the polymeric coating, and the receding contact angle was taken just before either breaking of the droplet or detaching the droplet from the polymeric coating. All the contact angles were fitted with ellipse-(tangent) fitting method and the contact angle hysteresis was measured by subtracting the receding contact angle from advancing contact angle of the respective liquid. A Carl Zeiss field emission scanning electron microscope (FESEM) was used to characterize the topography of the multilayers coatings of NC and polymer (BPEI), and all the samples were coated with a thin layer of gold using a gold sputterer prior to characterizing the samples. The digital images were acquired with a Canon Power Shot SX420 IS digital camera. The optical transparency of the coating under water was estimated using Perkin-Elmer Lambda 750 (UV/VIS/NIR Spectrometer). The thickness of the multilayers coatings were measured using Veeco Dektak 150 surface profilometer.

Preparation of 'Reactive' Layer by Layer (LBL) Assembly: The solutions of 5Acl (265 mg/mL) and BPEI (50mg/mL) were prepared first in methanol—which was doped with NaCl salt (0.5mg/ml), separately in two glass vials. Then, 1250µL of BPEI was mixed with 5 ml of 5Acl solution in methanol and the mixture was kept for 5 minutes to initiate the formation of 'reactive' polymeric nano-complex (NC) (see text for more details). Then, a glass substrate (5.5 cm x 1 cm) was selected for constructing multilayers coatings of both NC and polymer (BPEI) by exploiting a covalent LbL deposition process. The multilayers coatings of NC was prepared by consecutive dipping of glass substrates in the respective dipping vials for regular deposition of BPEI and NC on the planar glass substrate following the general approach, where the glass

substrate was stepwise dipped (i) into BPEI solution (with or without salt doping) of methanol for 10 s and followed by (ii) two consecutive washing with methanol solution for 10 s, next (iii) the substrate was placed in solution of NC (mixture of BPEI/5Acl) for another 10 s, then, (iv) the substrate was again exposed to two consecutive methanol bath, each for 10 seconds just to wash out the unabsorbed or loosely absorbed molecules. This whole deposition cycle was repeated for desired times and then either immediately used in other relevant studies or kept in vacuum desiccator. Same protocol was adopted for synthesis of multilayers of BPEI polymer, where solution of NC was replaced with solution of 5Acl. During the whole 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.

Post-Modification with Desired Amine-Containing Small Molecules: The 'reactive' multilayers coatings that are either consisted with BPEI and NC (in presence/absence of salt) or consisted with BPEI and 5Acl was chemically post-modified with strategically selected amine containing small molecules including propylamine (34.23mg/ml, in THF), butylamine (35.23mg/ml, in THF), pentylamine (35.95mg/ml, in THF), hexylamine (36.6mg/ml, in THF), heptylamine (37mg/ml, in THF), octylamine (37.23mg/ml, in THF), decylamine (37.47mg/ml, in THF), octadecylamine (35mg/ml, in Ethanol) and glucamine (2.5mg/ml, in DMSO) following our previous reported procedures through 1,4 conjugate addition reaction by exploiting the residual acrylate groups in the multilayers. After exposing the multilayers in the corresponding amine-containing small molecule solutions for overnight, each modified material was thoroughly washed with ethyl alcohol/THF, and finally dried in compressed air, prior to further essential characterization or other relevant proof of concept demonstrations.

Physical and Chemical Durability of the Anti-Fouling Properties:

Physical durability:

1. Sand drop test: The 'reactive' multilayers coated glass slides (1cm x1 cm) that were post-functionalized with hydrophilic (glucamine) and highly hydrophobic (octadecylamine) small molecules respectively, were immobilized on a ~45° tilted surface using an adhesive tape in air, and a continuous stream of sand grains (60 g) was poured from a height of 20 cm using a funnel over the slide. Anti-wetting properties of the material was examined by taking contact angles and digital images before and after performing the sand drop test.

2. Adhesive Tape Test: Initially, one adhesive surface of a double sided adhesive tape (1cm×1cm) was exposed to the microscopic glass slide prior to bringing the appropriately (glucamine/ODA) post-functionalized multilayer coatings in contact with another adhesive surface of the tape, and a 50g load was placed over the system further to facilitate a uniform contact of the polymeric coating against the adhesive surface. After 15 minutes, the polymeric multilayer coated glass slides were manually peeled off from the adhesive surface, and the morphology of the coating and the anti-wetting properties in the coatings were investigated in detail. (See the main text for more detail).

Chemical Durability: The multilayer coatings of NC, which were post functionalized with glucamine and ODA, and were able to display anti-liquid (water/oil) wettability properties both in air and under water, were exposed to different harsh and chemically complex conditions like alkaline solution (0.1M NH_3; pH 11), acidic solution (0.1M HCl; pH 1), SDS solution (1mM), river water and artificial sea-water. The artificial sea-water was prepared by mixing $MgCl_2$ (0.226g), $MgSO_4$ (0.325g), NaCl (2.673g) and $CaCl_2$ (0.112g) in 100ml of deionized water in a volumetric flask. The water and oil wettability both in air and under water respectively in the respective materials were examined with visual inspections and contact angle measurements after exposures to mentioned chemically harsh media.

***Coating on Various Substrate*:** Both the water and oil wettability, respectively in air and under water was examined for selected bare substrates including cotton-fabric, aluminium foil and wood. Then, all the

substrates were coated with multilayers (9 bilayers) of NC (in presence of salt) following the previously mentioned procedure, and were post chemically functionalized with glucamine and ODA molecules. Finally, the desired anti-liquid (water/oil)-fouling properties were characterized with visual inspections and contact angle measurements.

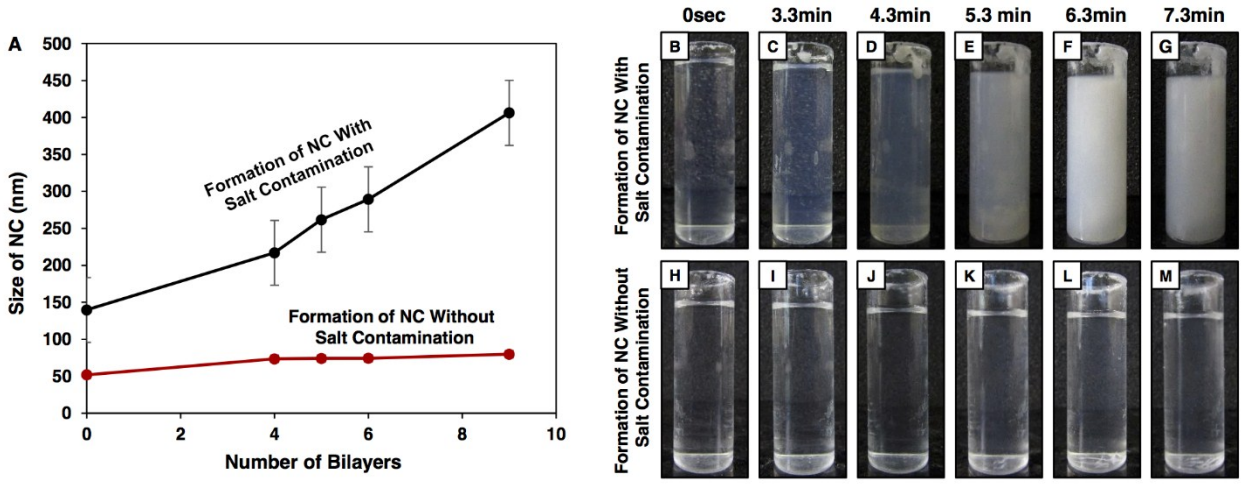

Fig. S1. A) The DLS plot compares the growth of NC in the dipping solution (BPEI/5Acl mixture in methanol) that are prepared in presence (black) and absence (red) of salt (NaCl) during consecutive LbL deposition process. B-M) Digital images showing the change in visual appearance in the solution (dipping solution) of BPEI/5Acl mixture in methanol both in presence (B-G) and absence (H-M) of salt with time, during the multilayer construction.

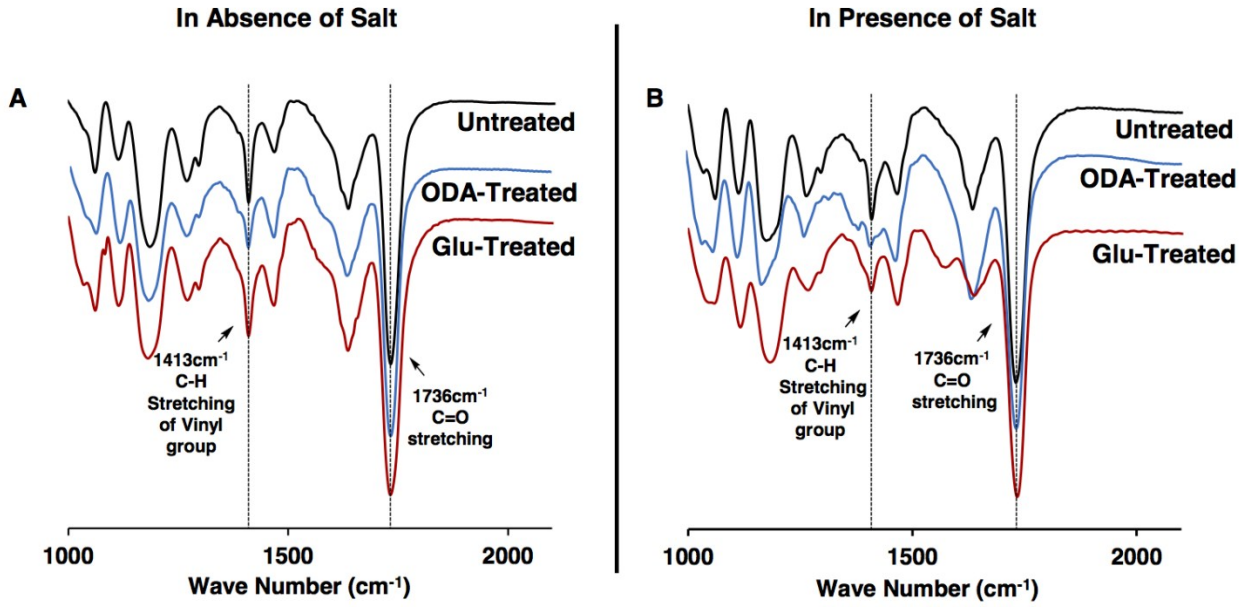

Fig. S2. A-B) FTIR spectra of multilayers of NC, which were synthesized both in absence (A) and presence (B) of salt, before (black) and after post chemical treatments with small molecules including ODA (blue) and glucamine (red).

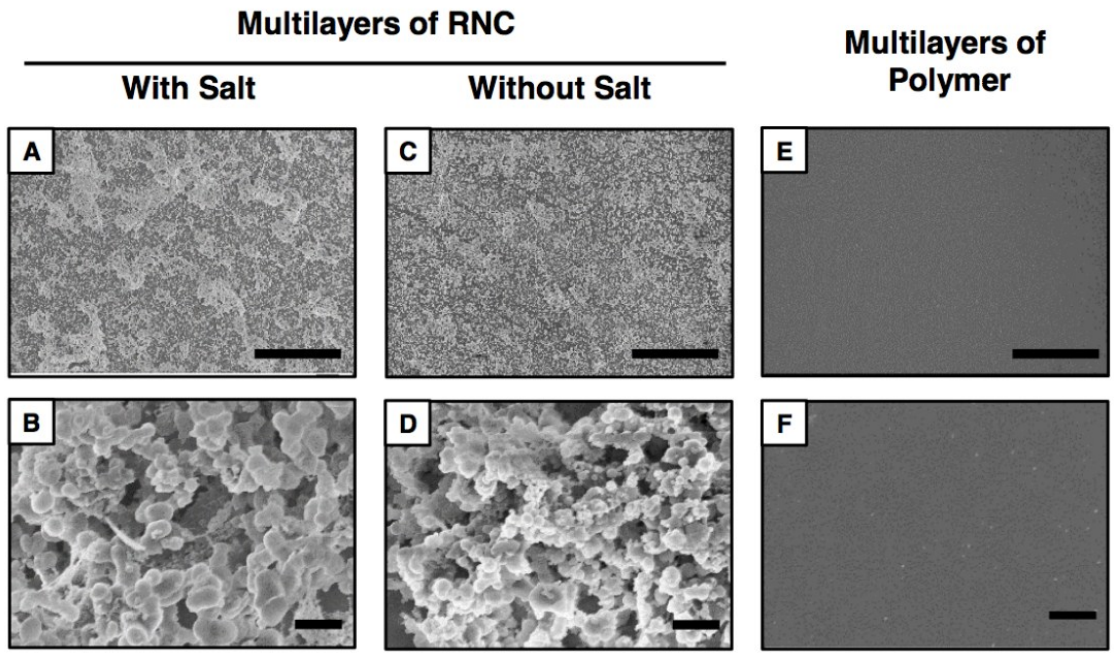

Fig. S3. A-D) FESEM images (in low (A, C; scale bar = 20 µm) and high (B, D; scale bar = 500 nm) magnifications) of multilayers of NC that are prepared in presence (A-B) and absence (C-D) of salt. E-F) FESEM images of multilayers coating of BPEI (prepared in presence of salt) in low (E, scale bar = 20 µm) and high (F, scale bar = 500 nm) magnifications.

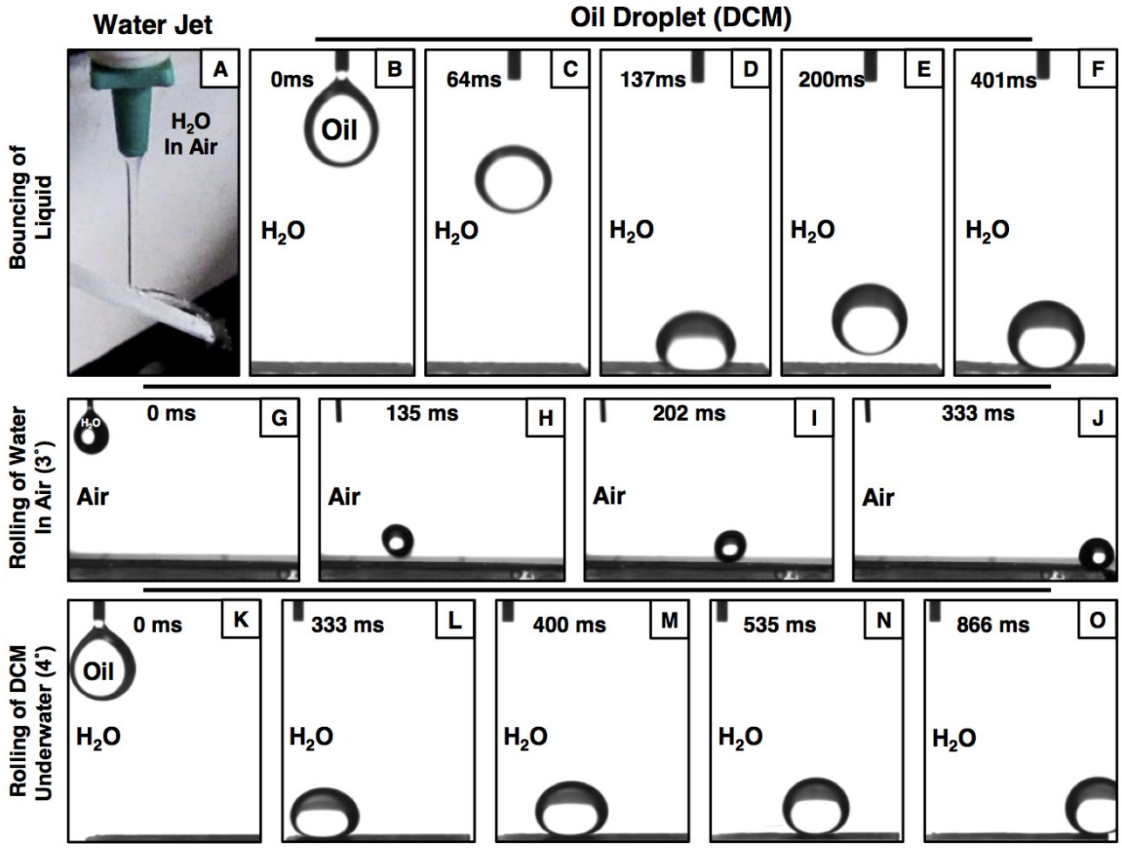

Figure S4. A) Digital image of bouncing water jet on the superhydrophobic multilayers coating in air. B-F) Contact angle images illustrating the bouncing of oil droplet under-water. G-O) Accounting the rolling of a water droplet (5µL) in air (G-J) and an oil droplet (11 µL) under water (K-O), where the multilayers of NC that are post modified with ODA (G-J) and glucamine (K-O), were tilted with 3˚ and 4˚ respectively.

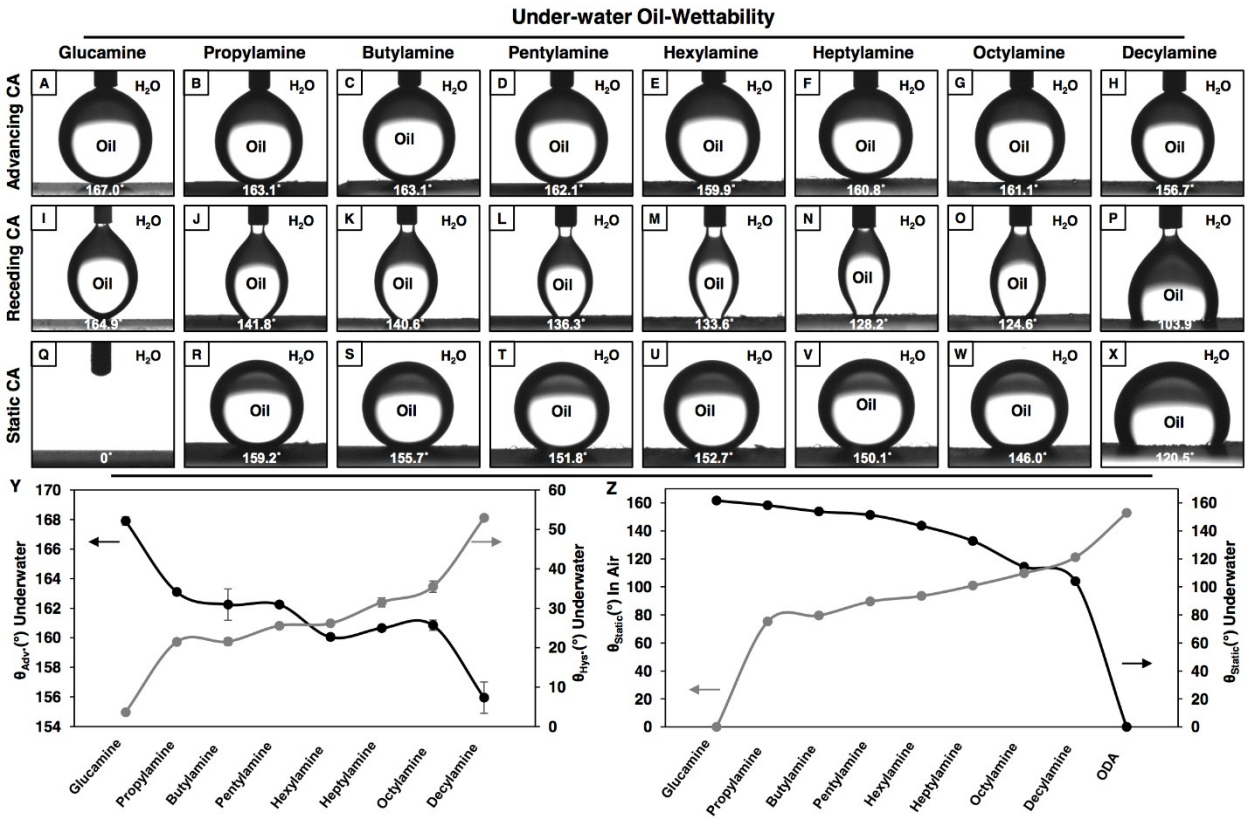

Figure S5. A-X) Advancing (A-H), receding (I-P) and static (Q-X) oil contact angle images on the multilayers of NC, which were synthesized in presence of salt and post functionalized with glucamine (A, I, Q), propylamine (B, J, R), butylamine (C, K, S), pentylamine (D, L, T), hexylamine (E, M, U), heptylamine (F, N, V), octylamine (G, O, W) and decylamine (H, P, X), under water. Y) Plots are accounting the change in the oil-wettability (advancing CA, contact angle hysteresis) under water, Z) Comparative change in wettability of both oil (black) and water (grey) on multilayers of NC with change in chemical functionality in the multilayers coatings.

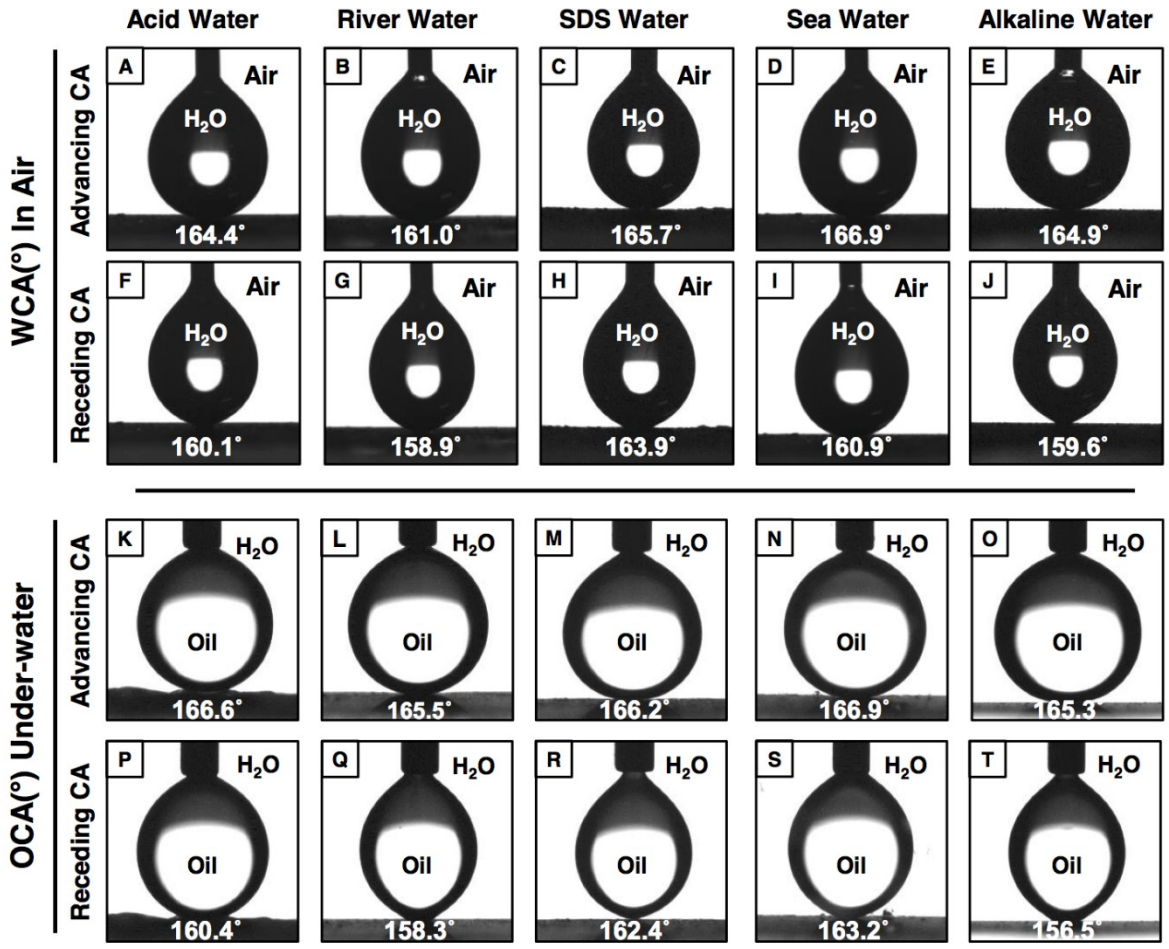

Figure S6. A-T) Advancing (A-E, K-O) and receding (F-J, P-T) contact angle images of water (A-J, in air) and oil (K-T, under water) after exposing the multilayers of NC that are treated with ODA (A-J) and glucamine (K-T) in harsh chemical environments including acidic water(pH=1; A,F,K,P), river water (B,G,L,Q), SDS water (1mM; C,H,M,R), Sea water (D,I,N,S) and alkaline water (pH=11; E,J,O,T).

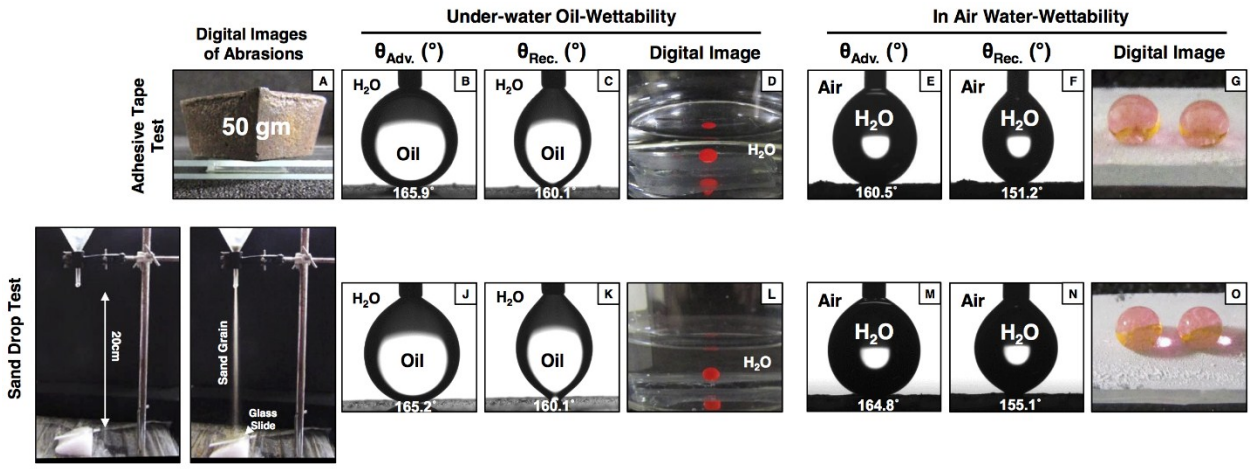

Figure S7. A-G) Digital images (A,D,G) and contact angle images (B-C, E-F) of beaded oil (under water; B-D) and water (in air, E-G) droplets on the glucamine (B-D) and ODA (E-G) treated multilayer of NC (9 bilayers) after performing the adhesive tape test (A). H-I) Digital images of sand drop test. J-O) Contact angle (J-K, M-N) and digital (L, O) images of the beaded oil (J-L) and water (M-O) droplets underwater and in air respectively on the respective (glucamine (J-L) and ODA (M-O) modified) multilayers of NC after carrying out the sand drop test (H-I).