Supporting Information

Wettability manipulation of overflow behavior *via* vesicle surfactant for water-proof surface cleaning

Ting Wang, Yifan Si, Siqi Luo, Zhichao Dong, and Lei Jiang**

Supplementary Materials:

Experimental Section
Figure S1-S14
Table S1
Caption for Movie S1

Experimental section

Fabrication of the setup of overflow experiment: As shown in Fig.1, the setup consisted of aluminum round plate with superhydrophobic margin, a nozzle with liquid pipe and an electrical gear pump. Liquid transported out of the nozzle on the downside margin of round plate and flowed along/out the margin of round plate. The flow velocity was controlled by rear pump. A high-speed camera captured the whole process of flow behavior from side view.

Modifying the margin of Aluminum round plate with superhydrophobicity: Aluminum round plate with a diameter of about 20 mm was fabricated by mechanical cutting. Two methods were used to fabricate the superhydrophobic margin. The first one: Aluminum round plate was immersed in a 70℃ water bath for 10 min to obtain the nanostructures on the surface. Then, the nanostructured plate was modified with stearic acid to achieve the superhydrophobicity (Fig.1). The second one: firstly, the superhydrophobic polymer-particle dispensed solution was prepared by adding 1.0 g of hydrophobic fumed silica nanoparticles and 3 mL of ST-200 solution in to 17 mL of acetone. Then, aluminum round plate dipped into superhydrophobic polymer-particle solution at a speed of 40 mm/s and immersion depth of 15 mm, held for 30 s and pulled up at speed of 40 mm/s by a WPTL dip coater (MIT Co.) at 30℃. Finally. The coated aluminum round plate dried in air surrounding.

Instruments and characterization. SEM images were captured with a filed-emission scanning electron microscope at 10 KV (Hitachi S-4800, Japan). Cryo-TEM images were obtained with FEI Tecnai Spirit BioTwin TEMs. Cryo-transfer holders were used to ensure low-temperature transfer and observation of frozen hydrated specimens. *LEXT* Nano Research Microscope (OLS4500) was used to characterize the morphology of superhydrophobic surface and AOT washed surface. 2D Diffusion-Ordered Spectroscopy (DOSY NMR) and Spin-spin relaxation time (T_2) measurement NMR spectra were carried out at 25 ℃ on a Bruker Avance 600 spectrometer. 2D DOSY NMR spectra was used to test the diffusion speed of SDS and AOT molecules at liquid-liquid interface with a concentration of 0.01 wt%, respectively. Spin-spin relaxation time (T_2) was used to characterize the average molecular motion at liquid-solid interface. The molecular motions at AOT and SDS mixture aqueous solution were firstly tested. After adding some superhydrophobic solid surface in the mixture solution, the molecular motions were then tested. The difference of relaxation time (ΔT_2) in two systems indicated the influence of superhydrophobic solid surface on diffusion of molecules. The larger of ΔT_2 value indicated the faster diffusion speed at solid-liquid interface. Contact angles were measured on OCA 20, DataPhysics (Germany) with water droplets of 5μL, at ambient temperature. The CA values of various surfactants were obtained by measuring more than five different positions on the superhydrophobic substrate. Dynamic surface tension of surfactants with different concentrations were measured by bubble pressure tensiometer, KRUSS BP100, and the diffusion coefficient speed at liquid-air interface was simulated during the measurement process. Liquid flow behaviors were recorded by high-speed camera, i-SPPED 3 at frame rate of 2000 fps, from side views. The flowing velocity was controlled by Harvard gear pump from 20 mL/min to 100 mL/min. The inside diameter of nozzle is about 0.51 mm. Therefore, the velocity of liquid is controlled from 1.0 m/s to 6.0 m/s.

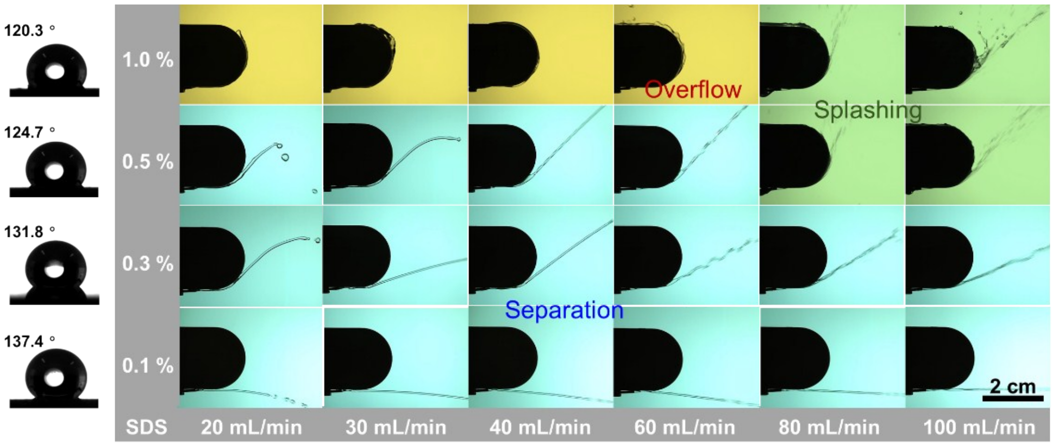

Figure S1. Snapshot diagram of upward flow behavior of SDS surfactant solution with concentrations varying from 0.1% to 1.0% and velocities changing from 20 to 100 mL/min. The left side contact angle is tested by the corresponding SDS concentration on the superhydrophobic coating surface. As the concentration of SDS increases, overflow behavior tends to occur. The fluid flow behavior changes from separation (the blue part) to complete overflow (the yellow part) or even splashing (the green part).

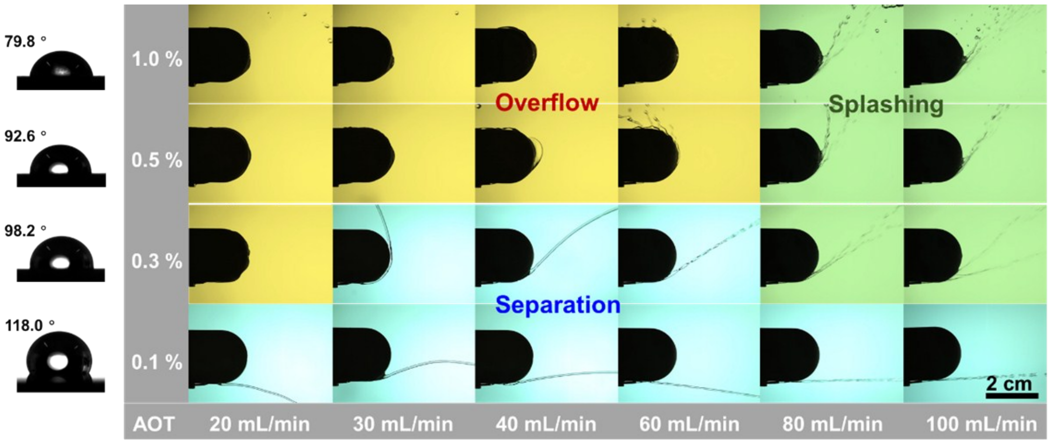

Figure S2. Snapshot diagram of upward flow behavior of AOT surfactant solution with concentrations varying from 0.1% to 1.0% and velocities changing from 20 to 100 mL/min. The left side contact angle is tested by the corresponding AOT concentration solution on the superhydrophobic coating surface. The decrease of contact angle follows by the increase of surfactant concentration. Flow behavior of surfactant solution changes from separation flow to completely overflow, as the increase of concentration. Reducing flow velocity provides a relatively longer contact time for vesicles surfactant solutions on the superhydrophobic curve surface, thus promoting overflow behavior. In addition, higher concentration of the surfactant increases vesicles to aggregate at the newly created interface. An overflow behavior is achieved. Splashing (the green part) often occurs at higher flow speed. At this moment, liquid flow tends to keep a stable state (low-energy state), thus, breaking into small droplets under high velocity, finally showing as splashing.

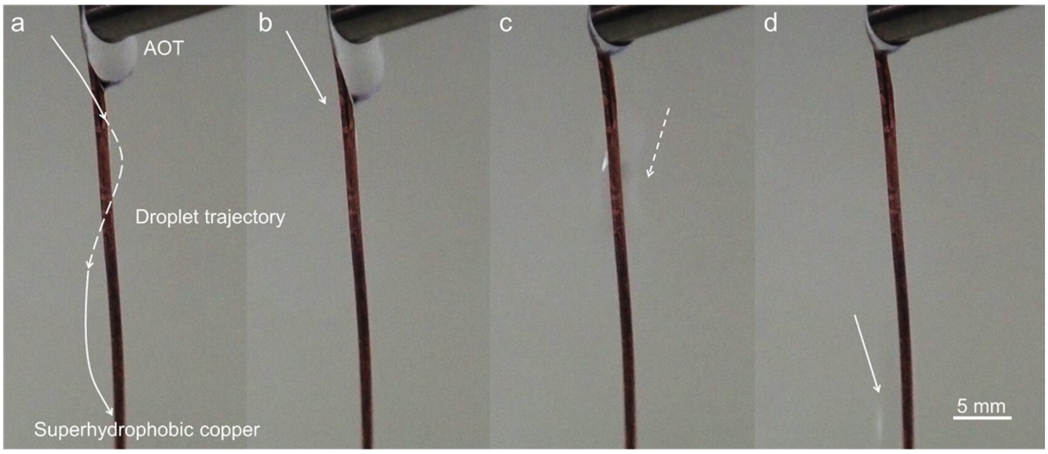

Figure S3. AOT aqueous solution overflow around copper fiber.

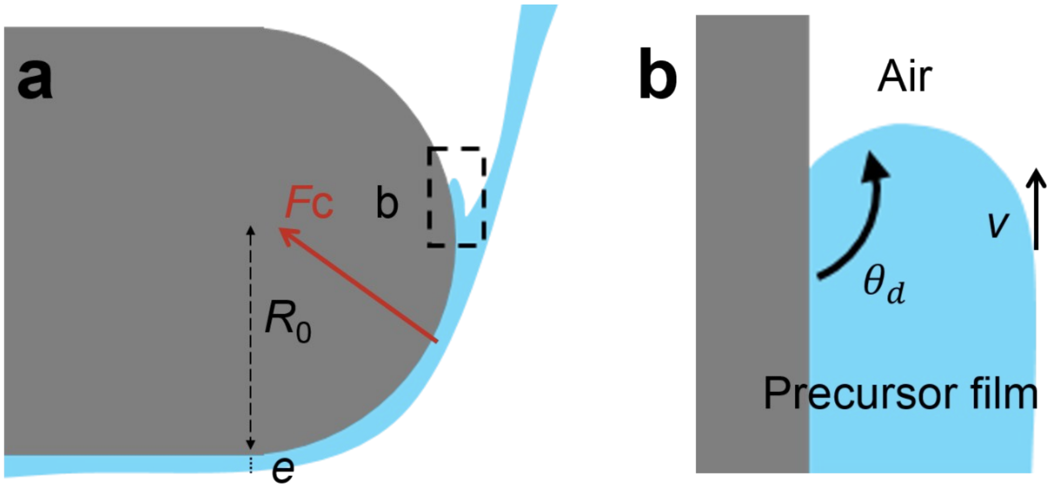

Figure S4. Force analysis of flow behavior. **a,** Diagram of the upward overflow around superhydrophobic curve edge. The centripetal force, as the driving force, demonstrates as: $F_c = \frac{\rho e S v^2}{R_0}$, where ρ is the mass density of the liquid, v is the linear flow velocity, S is the wetted area, e is the thickness of liquid layer as it travels on the curved surface, and R_0 is the outer radius of curvature (the sum of $e/2$ and R, the plate's radius of curvature). **b,** Magnification of the triple-line region. θ_d is the dynamic contact angle, which is larger than the static contact angle θ_0 for a moving triple line (with velocity v). The threshold velocity is reached as the contact line is no longer stable, which occurs as $\theta_d \rightarrow 180°$.

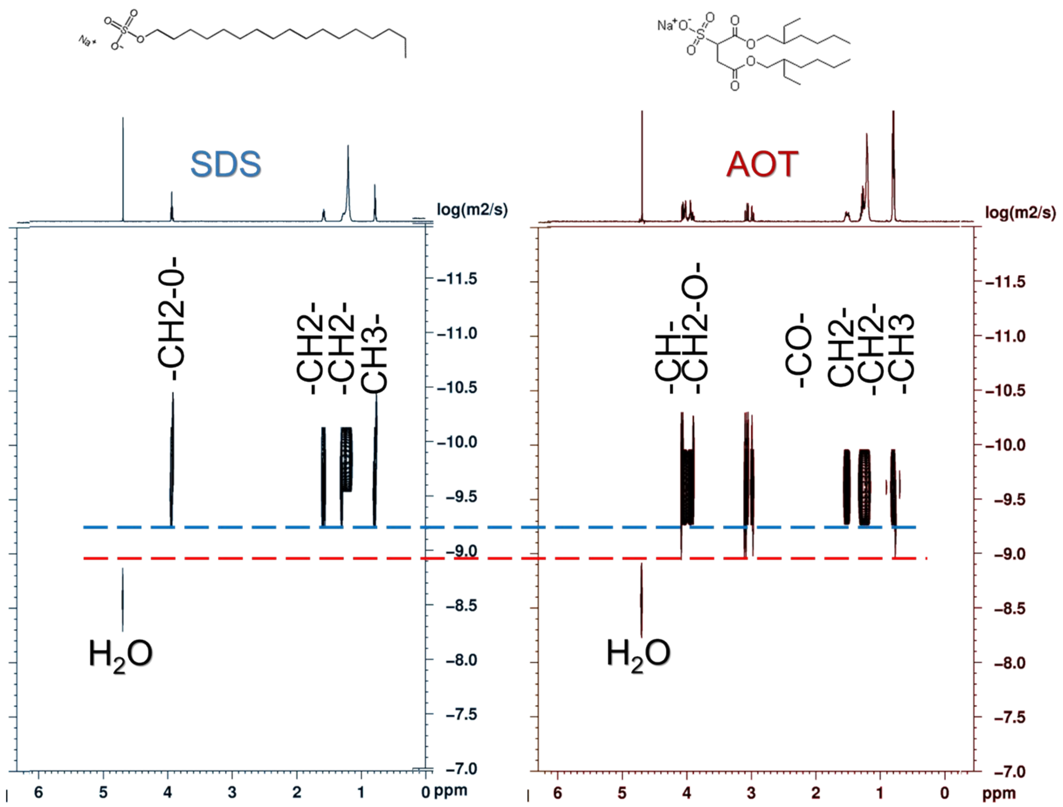

Figure S5. Diffusion coefficients (diffusion speed) of SDS (0.01%), and AOT (0.01%) derived from [1]H NMR. The average diffusion coefficients of SDS and AOT are measured to be 1.178 × 10^{-10} m^2/s, and 1.392 × 10^{-10} m^2/s, respectively. AOT has a relatively faster diffusion speed at liquid-liquid interface.

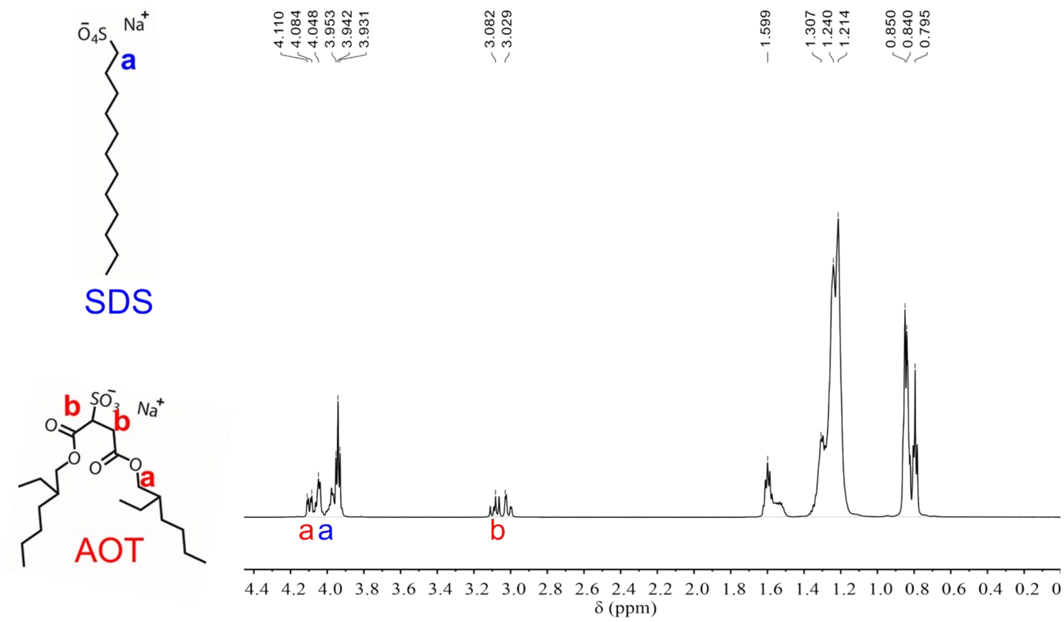

Figure S6. [1]H NMR spectra and proton assignments of SDS and AOT in D2O at 0.1 wt%.

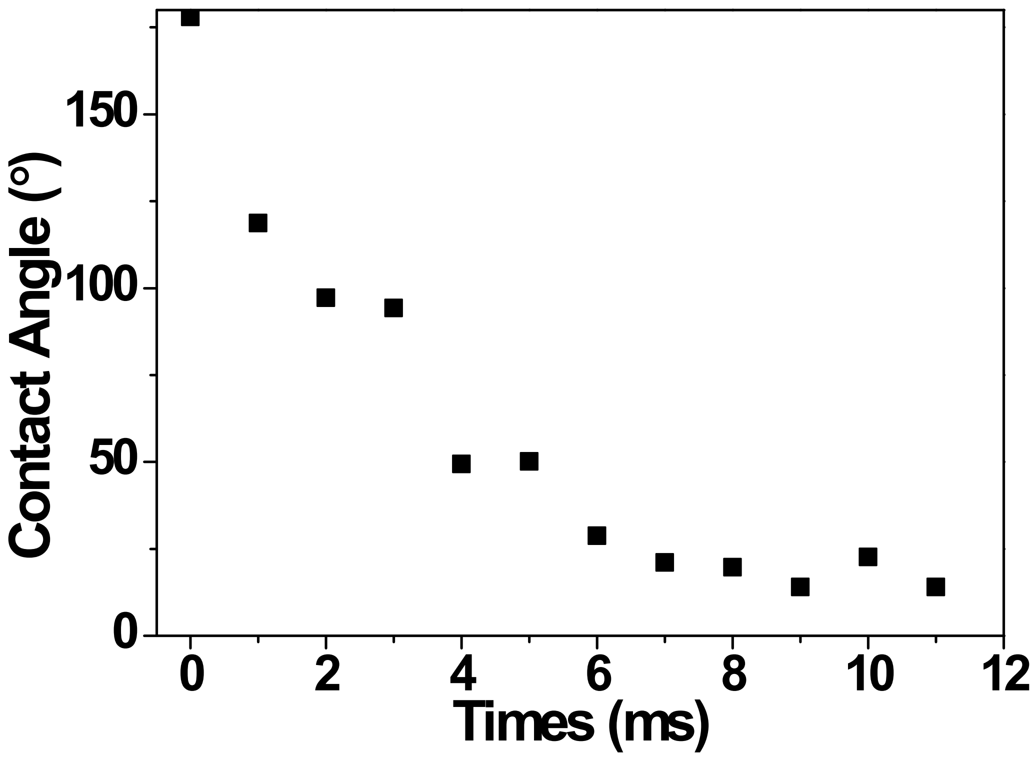

Figure S7. Contact angle of AOT solution on superhydrophobic substrate varies with contact time. The dynamic contact angle decreases sharply from nearly 160° to about 20° within 8 ms.

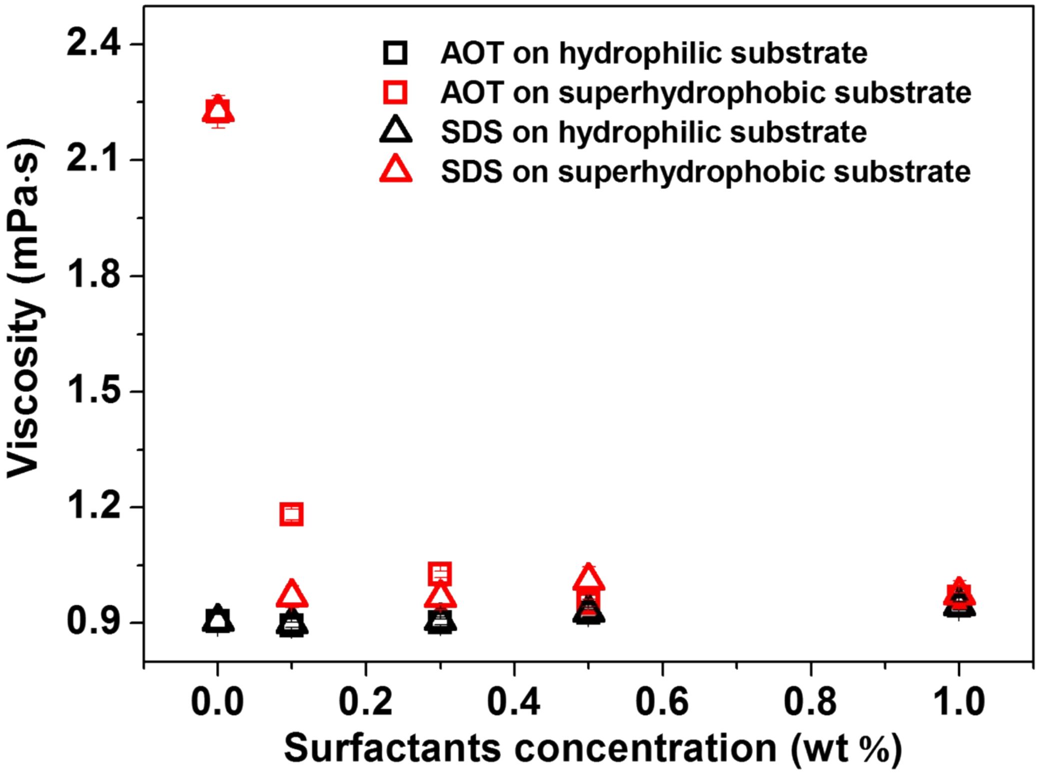

Figure S8. Viscosity of surfactants on substrate with different wettability varies concentrations. The viscosity of AOT solution decreases sharply with the increase of surfactants concentrations. The viscosity value of 0.5% AOT solution is similar with that of 0.5% SDS solution.

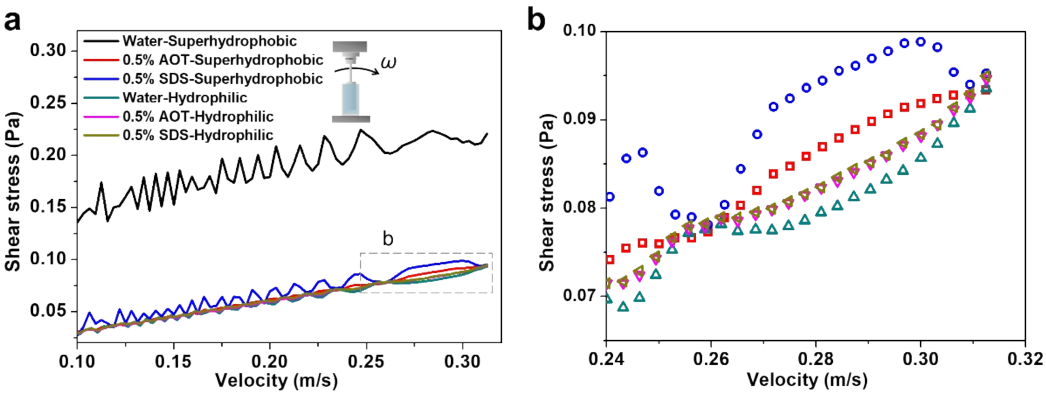

Figure S9. Shear stress of surfactants on substrate with different wettability varies with velocity. The shear stress of liquid on superhydrophobic surface is larger than that on hydrophilic surface. The shear stress of AOT solution on superhydrophobic surface is smaller than that of SDS solution.

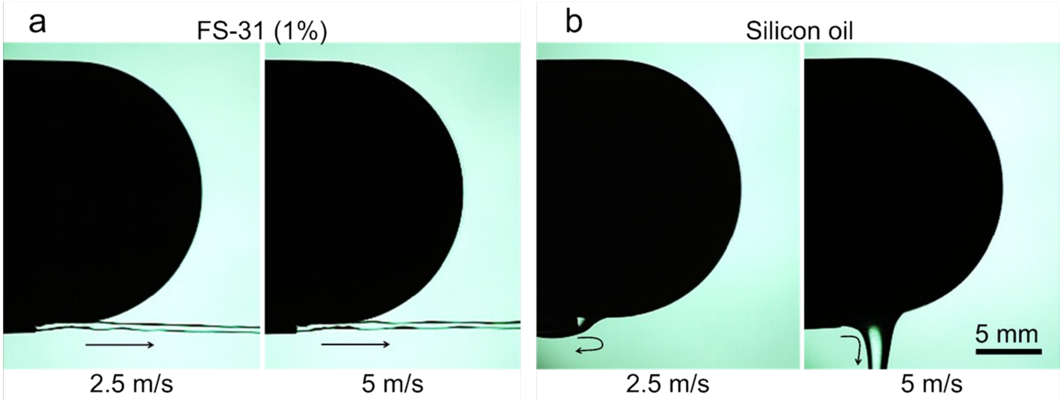

Figure S10. Separation flow behaviors of low surface tension liquids (FS-31, silicon oil) at both low and high flow velocities.

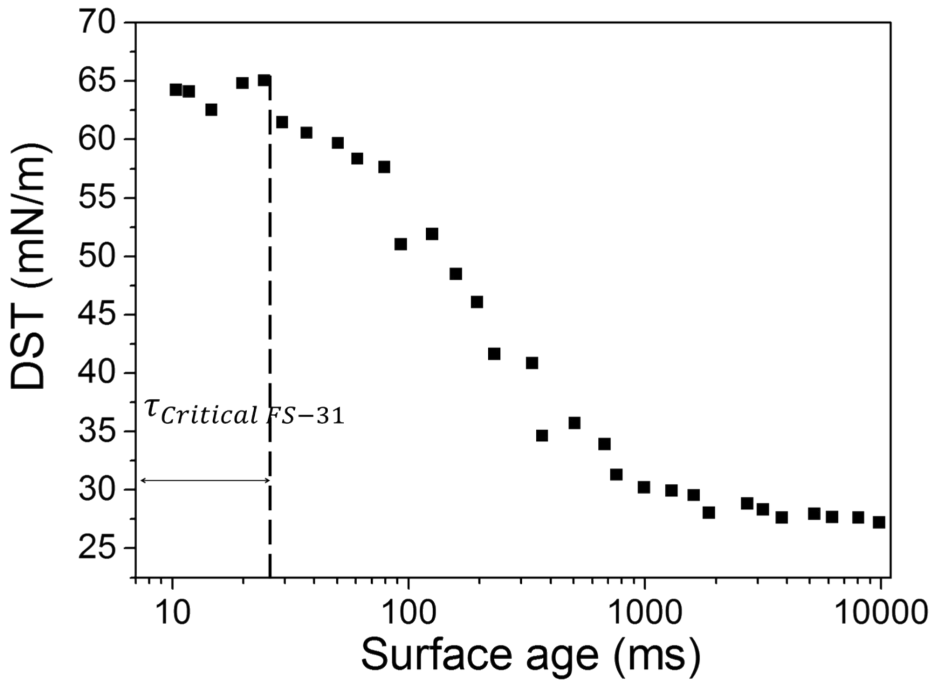

Figure S11. Dynamic surface tension of FS-31 aqueous with a concentration of 0.5 wt%. FS-31 has a critical response time to the decrease of dynamic surface tension of about 24.5 ms. The response time is nearly 3.06 folded longer than that of AOT. Even though FS-31 and AOT have similar stable surface tension, for the critical response time of wettability change and the decreasing rate of the change of surface tension, AOT shows much smarter dynamic property than FS-31, resulting in the fast wettability change and overflow behavior of AOT on superhydrophobic surface.

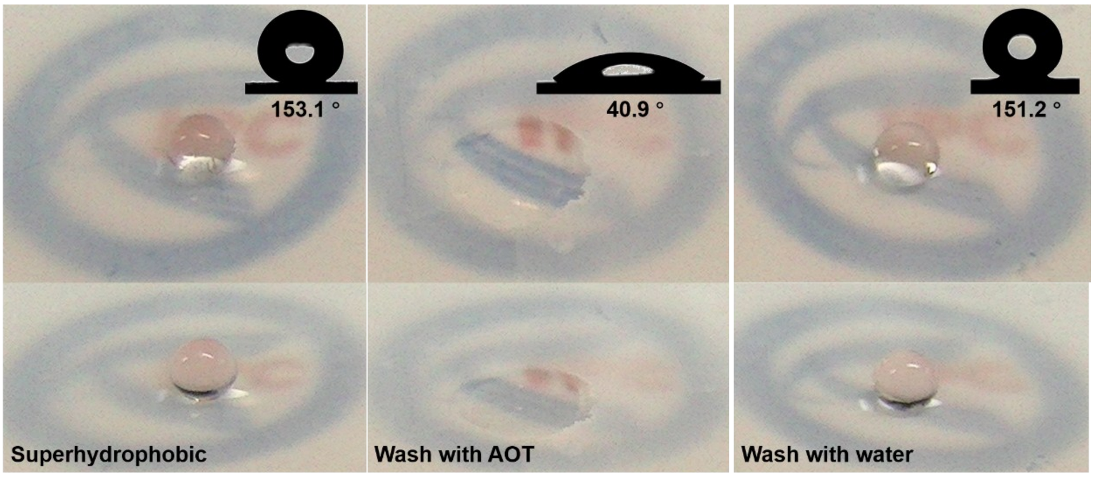

Figure S12. Wettability transition of superhydrophobic substrate *via* wash with AOT and wash with water. After many rounds of wash process, surface superhydrophobicity keeps stable.

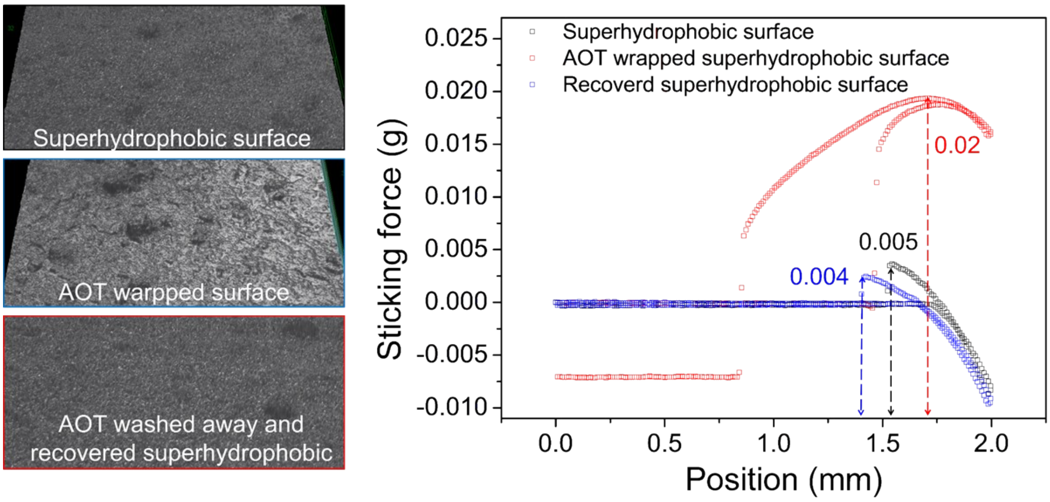

Figure S13. Low AOT surfactant retention after washing process, measured by the morphology and sticking force of washed surface *via* Nano Research Microscope and Dynamic Contact Angle. As the photos show, superhydrophobic surface has clear micro-nanostructures, while AOT warped superhydrophobic surface has relatively smooth surface. After AOT washes away, superhydrophobic surface recovers. The sticking forces perfectly demonstrate the low sticking force of recovered superhydrophobic surface. Both the microscope photos and sticking forces indicate that AOT has been cleaned out and superhydrophobicity recovers.

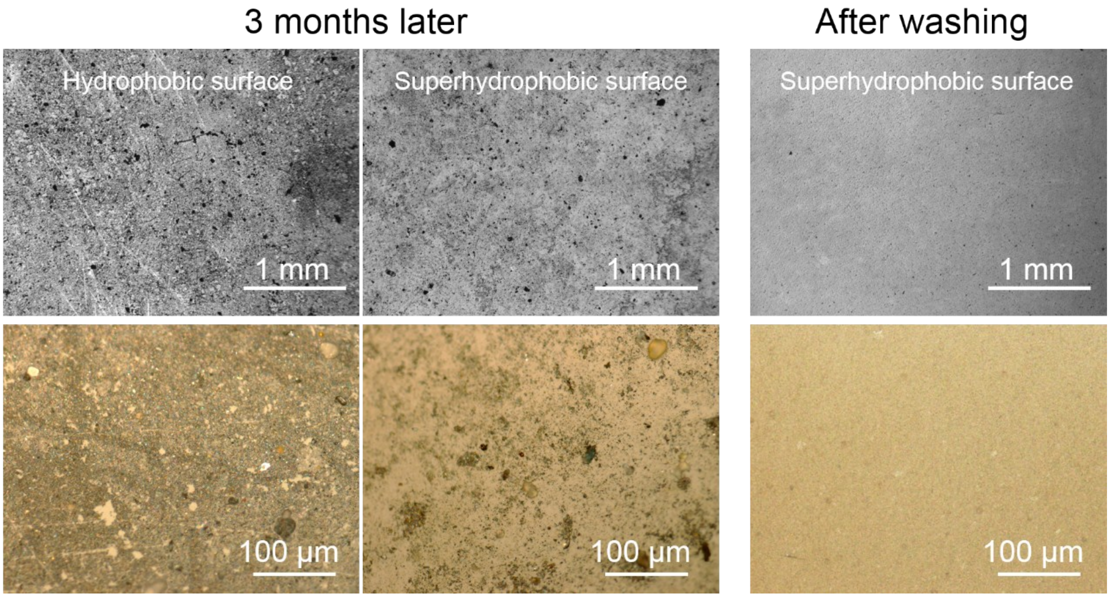

Figure S14. Wash effect of contaminated superhydrophobic surface, measured by optical microscope. Under 3 months of deposition of dirt, Superhydrophobic and hydrophobic surfaces have been contaminated by air. After flushing with AOT surfactant solution and water, surface superhydrophobicity recovers.

Table S1 : Different types of diffusion coefficient of AOT and SDS surfactant aqueous			
Test method	Diffusion coefficient type	AOT	SDS
Maximum bubble method	Diffusion coefficient for liquid/air interface (m^2/s)	2.58×10^{-10}	1.39×10^{-11}
2D DOSY NMR spectra	Diffusion coefficient for liquid/liquid interface (m^2/s)	1.392×10^{-10}	1.178×10^{-10}
Spin-Spin Relaxation Time (T_2)	The increment of Liquid/solid diffusion compared with liquid/liquid diffusion ΔT_2 (ms)	1147.58	134.65

Table S1. Different types of diffusion coefficients of AOT and SDS molecules, measured by different methods. The average diffusion speeds of AOT at liquid-air, liquid-liquid and liquid-solid interfaces are faster than those of SDS.

Caption for Movie

Movie S1. Wettability manipulation of overflow behavior *via* vesicle surfactant. Upward overflow behavior of surfactant solutions around superhydrophobic margin. Washing away absorbed surfactants with water.