Supplementary Information

An Underwater pH-Responsive Superoleophobic Surface with Reversibly Switchable Oil-Adhesion

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Experimental

Plasma-Induced Graft Polymerization**:** The glass substrates were first cleaned before etching experiment. Then, distilled acrylic acid (AA) was injected into a plasma-induced grafting reactor (Suzhou Omega Machinery Electronic Technology Co., Ltd., DJ-01). Vacuum before switching on the glow discharge was 21 Pa and the working temperature was 20 ^{o}C. In our experiment setup, the argon atmosphere was kept at 50 ± 5 Pa and these conditions would be kept for 15 min. Then, a Start R-F power supply source (Suzhou Omega Machinery Electronic Technology Co., Ltd., DT-01) was applied at 50 W to obtain glow discharge, which was maintained for 30 min. After the glow extinguished, grafting of the AA monomers would take place in the grafting reactor, where a vacuum of 200 ± 10 Pa was maintained for about 30 min. Finally, the chamber was connected with air and the plasma treatment had finished.

Oil contact angle and adhesive force**:** Oil contact angles (OCA) were measured on an OCA20 system (Data-Physics, Germany) at ambient temperature. The samples were placed in a cubic and transparent glass container filled with pH solutions. Oil droplets (1,2-dichloroethane, 2 μL) were syringed out and dropped carefully onto the surfaces in water. The average OCA values were obtained by measuring at five different positions on the same sample. The adhesive forces were measured on a high-sensitivity micro-electromechanical balance system (DCAT 11 system, Data-Physics, Germany). In our experiments, an oil droplet was floating on a metal ring were approached and retracted from the sample surface at a constant speed of 0.05mm s^{-1} at ambient environment. The oil droplet started to move away from the sample surface once contacting, and the balance force would gradually increase, and reached the maximum before the droplet broke away from the surface. The peak data recorded in the force-distance curve was taken as the maximum adhesive force.

Characterization**:** The underwater atomic force microscope (AFM) images were obtained by using a VEECO BioScope Catalyst multi-mode AFM. The PAA-G sample was placed in a sample cell in solution with different pH values.

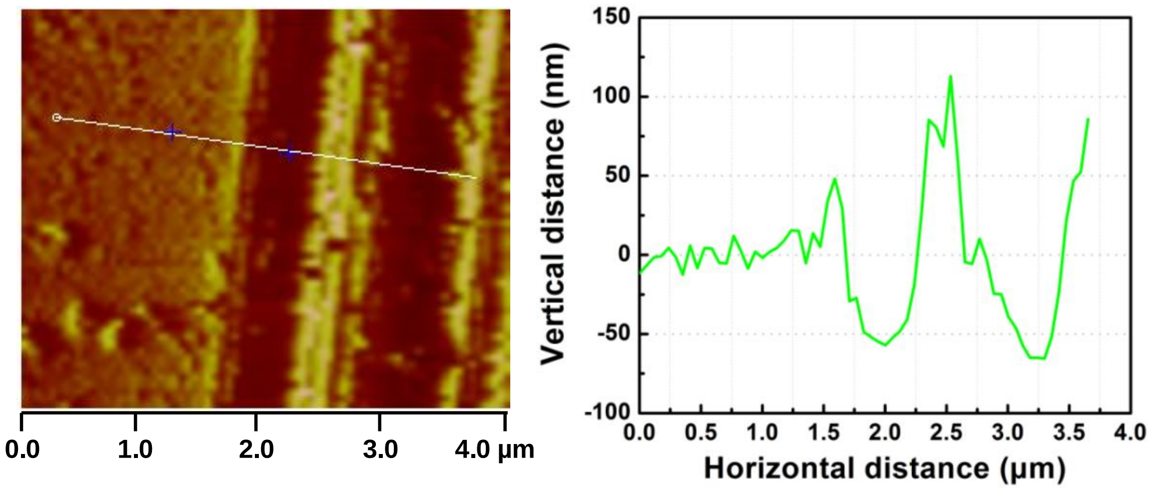

Figure S1. The surface of PAA-glass was scratched and then thickness of PAA grafted on the glass was measured by AFM. The calculated thickness of PAA is about 64.5 ± 9.2 nm.

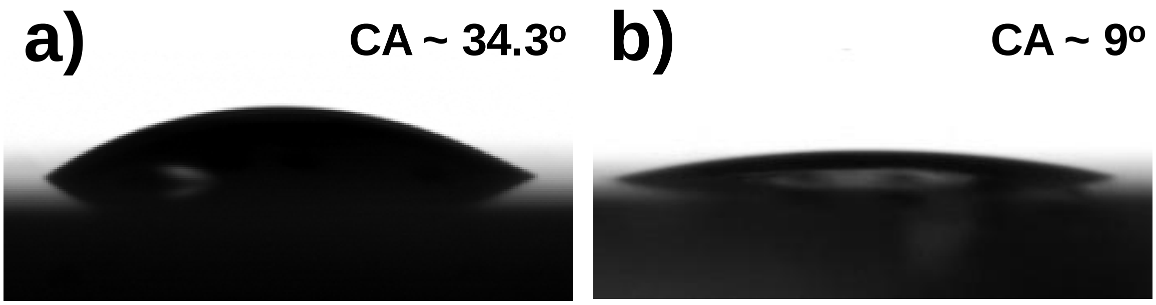

Figure S2. a) The original glass substrate shows hydrophilicity with the contact angle (CA) of 34.3 ± 3.0°.

b) After plasma-induced grafting PAA, the PAA-G shows superhydrophilicity with CA of 9.0 ± 1.5°.

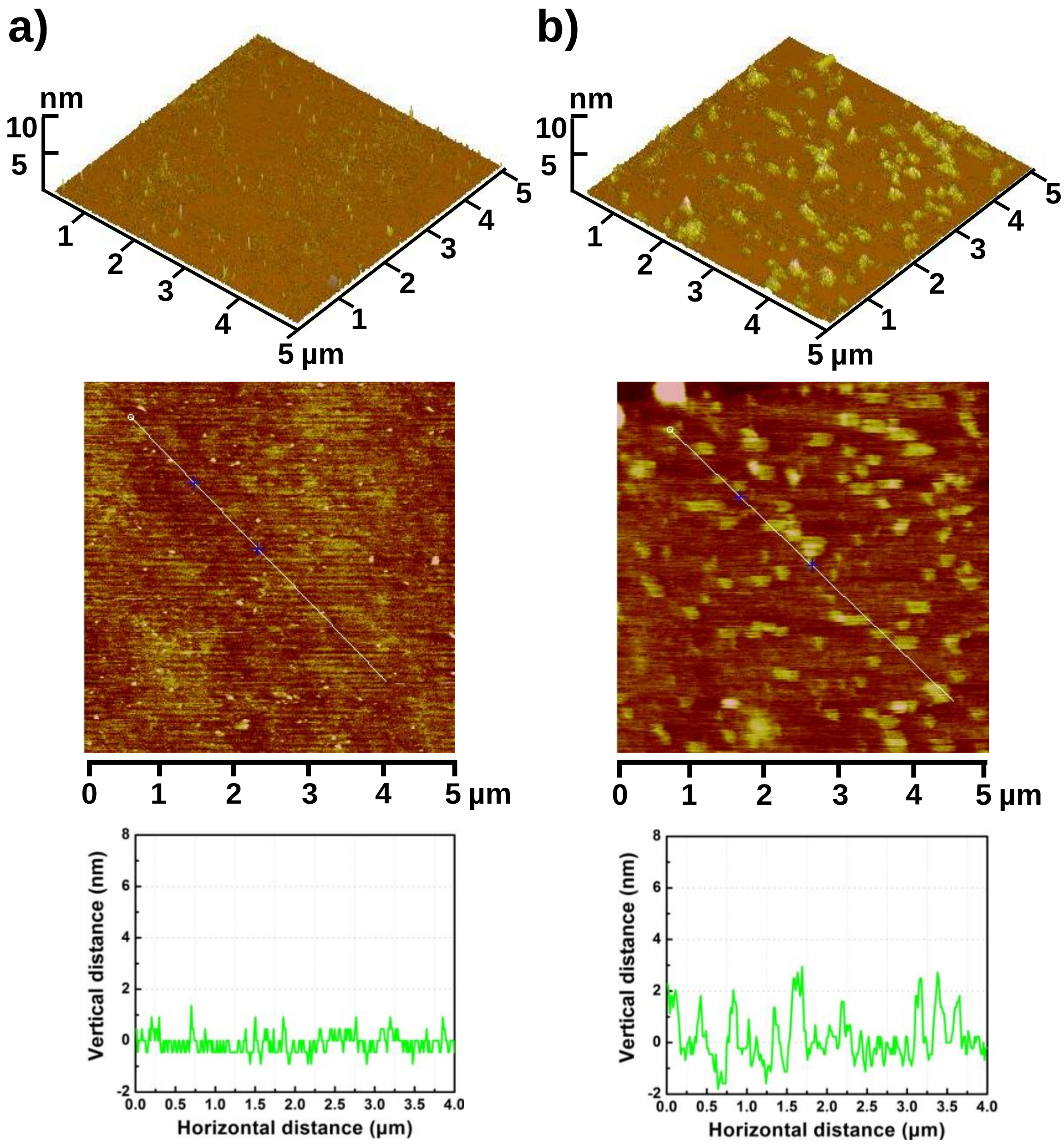

Figure S3. Underwater atomic force microscope (AFM) images of original glass (a) and plasma-treated glass (b) in the deionized water, indicating the roughness increases to about 2 nm from about 0 nm after plasma treated.

In our experiments, an oil droplet was floating on a metal ring and was approached by the sample surface with a constant speed of 0.05mm s^{-1} at ambient environment. When the sample surface contacts the oil droplet, the change in forces on the balance is detected and recorded. The forces on the balance are: F_{total} = wetting force + weight of oil droplet - buoyancy

The wetting force which is defined as: wetting force = γ_{LV}. P . cos θ

where γ_{LV} is the liquid surface tension, P is the perimeter of the cupper holder and θ is the contact angle.

The buoyancy is defined as: buoyancy = ρslg

Where ρ is the density of liquid, s is the cross-area of the cupper holder, l is the depth of cupper holder immersed into liquid and g is the acceleration of gravity. The oil droplet is immersed to contact sample surface and the process is reversed. As the oil droplet retreats from the sample surface, the adhesion force is calculated. The process is illustrated in the following **Figure S4** and the force-distance curve will appear as **Figure 2**. In the process 1 of linear curve: The oil droplet is immersed, buoyant force increases causing a decrease in force on the balance. Forces are measured for advancing angle. When the wetting force is balanced with buoyancy, the force curve will turned flat. In the process 2 of linear curve: After having contacted the oil droplet, the sample is pulled back. Forces are measured for receding angle and adhesive force. In the process 3: When the sample surface leaves the oil droplet, the adhesive force disappeared. The wetting force is balanced with buoyancy, so the curve is flattened.

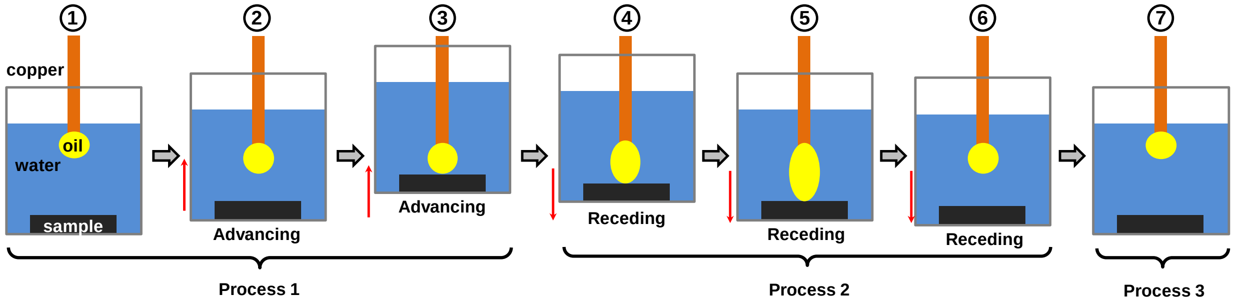

Figure S4. The process of adhesion force testing in water contains three processes: In the process 1, the sample in the water is slowly approaching to the oil droplet held by the cooper ring in the steps from 1 to 3. In the process 2 of steps 4-6, the sample contacts oil droplet and leaves from oil droplet, which results in the shape of the oil droplet changing from spherical to elliptical due to adhesive force. Finally, the sample goes back as showing in the Process 3 of step 7.

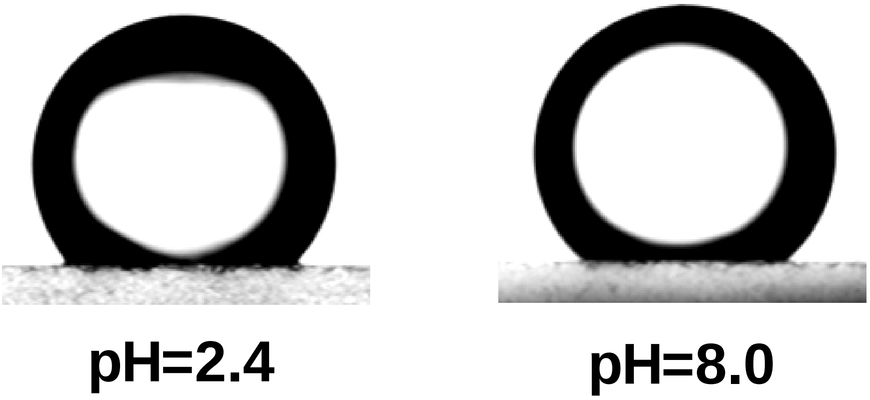

Figure S5. Contact angles of oil droplet (1,2-dichloroethane) on original glass substrate are 132.3 ± 3.8^{o} and 135.9 ± 1.9^{o}, in solution with pH values of 2.4 and 8.0, respectively.

Table S1. The adhesive forces between PAA-G and oils with different surface tensions in the solutions with pH values from 1.0 to 12.0.

Oil	**Surface tension (mNm^{-1})**	**Adhesive force (μN) at different pH values**						
		1.0	**2.4**	**4.0**	**4.6**	**5.0**	**8.0**	**12**
Hexane	18.0	43.4 ± 0.3	33.7 ± 5.1	24.0 ± 6.8	20.4 ± 3.6	5.1 ± 1.3	1.6 ± 0.2	~0
Dichloroethane	24.15	21.6 ± 5.0	16.7 ± 2.1	15.9 ± 3.2	15.0 ±2.9	2.0 ± 0.6	1.5 ± 0.4	~0
Chloroform	28.9	27.8 ± 4.0	22.0 ± 3.0	20.9 ± 4.1	19.3 ± 5.0	5.0 ± 1.5	2.5 ± 0.3	~0
Tetrachloroethane	33.9	22.3 ± 5.9	20.6 ± 7.3	19.6 ± 9.9	18.4 ± 1.8	1.8 ± 0.7	1.6 ± 0.5	~0
Dichlorobenzene	36.7	25.1 ± 4.9	24.0 ± 3.3	23.4 ± 4.4	20.8 ± 3.8	3.0 ± 0.6	1.2 ± 0.4	~0

Table S2. The OCAs of oils with different surface tensions on PAA-G in the solutions with pH values from 1.0 to 12.0.

Oil	**Surface tension (mNm^{-1})**	**Oil contact angle (^{o}) at different pH values**						
		1.0	**2.4**	**4.0**	**4.6**	**5.0**	**8.0**	**12.0**
Dichloroethane	24.15	141.1 ± 2.6	142.3 ± 1.9	144.3 ± 1.6	144.4 ± 1.9	157.2 ± 1.8	165.3 ± 2.3	166.7 ± 1.3
Chloroform	28.9	142.9 ± 1.5	144.6 ± 1.9	145.9 ± 1.7	146.0 ± 2.5	153.1 ± 2.7	157.2 ± 1.6	157.1 ± 0.3
Tetrachloroethane	33.9	142.5 ± 0.4	143.1 ± 0.7	144.9 ± 0.6	146.4 ± 1.2	154.3 ± 1.6	155.7 ± 0.7	155.8 ± 0.7
Dichlorobenzene	36.7	144.0 ± 1.1	146.2 ± 1.1	146.2 ± 0.8	146.8 ± 1.2	158.3 ± 1.7	162.8 ± 1.8	163.5 ± 1.6