Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Underwater Superoleophilicity to Superoleophobicity: Role of Trapped Air

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S1: Experimental details.

Preparation of rough-aluminum surfaces: Commercial aluminum surface were cut into smaller 2.0 cm × 2.0 cm squares. Initially, the small aluminum substrates were ultrasonicated for 15 min in a cleanser solution and acetone, respectively. Then rinsed with deionized water several times, and dried in a clean oven at 50 °C for 1 hour, then we obtained the flat aluminum surface. The dry aluminum substrates were then soaked in 4 mol/L hydrochloric acid solution to corrode for 10 minutes. After corroding, the substrates rinsed with deionized water several times after ultrasonicated 30 seconds, and dried in a clean oven at 50 °C for 1 hour.

Modification of FTS: The aluminum surfaces were then immersed into glass vials that contained anhydrous toluene (4 mL), and *FTS* (0.005 mL) was added immediately to the solvent for silanization with a calibrated pipette. The glass vials were closed to the air during the reaction but exposed to the environment during the solution and sample introductions. After the reaction, the substrates underwent a series of rinses with solvents in the following sequence several times: toluene, ethanol, ethanol/water (1/1), and water. Finally, the substrates were dried in an oven at 120 °C for 10 min. The modification of glass surface was same as that of the aluminum surface, but before modification it was hydroxylated by piranha solution.[8]

Measurements: SEM images of the samples were measured with field-emission scanning electron microscope at 3 kV (JSM-6700F, Japan). Contact angles were obtained by using a JC2000D machine (POWEREACH, China) at ambient temperature. The oil droplets were placed carefully onto the surfaces, which were immersed in water. The average contact angle values were obtained by measuring more than five different positions on a same sample.

S2: Digital photos of aluminum plat underwater.

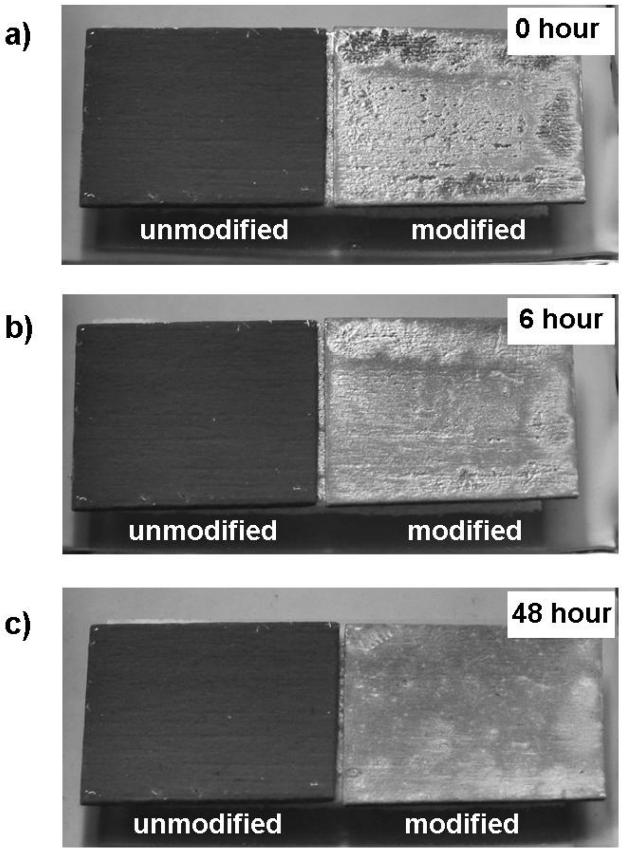

Figure S1. Digital photos of aluminum plat with nanostructures at a depth of 100 cm in water for 0, 6 and 48 hours. FTS-modified (right) and unmodified (left) with 2.0×2.0 cm2 surface area, visualizing the decay of the air layer with time. The dark one on left was used to provide a brightness reference, allowing us to keep the image exposure condition constant.

Figure S1 shows digital photos of unmodified (left) and modified (right) aluminum plat that was taken at different immersing time. The reflection of light from air layer gives samples a silvery appearance, which was observed by a horizontally fixed camera under optimized illumination and exposure conditions. The parameters were kept constant with time. Prior to each experiment the tank was filled with deionized water, keeping the water stationary for the remainder of the experiment. Images of the sample were taken at intervals of 0, 2, 6, 12, 24, 48, 96 and 168 hours, respectively.

Figure S1 shows the digital optical images of 0, 6 and 48 hours. Two kinds of samples showed noticeably different colors when samples were just immerged in water (the left part is unmodified aluminum plat, the right is the modified one). The unmodified aluminum surface shows dark grey, and the modified sample surface shows silvery with a lot of light spots (Figure S1a). With the increasing of the immersing time, the color of the samples changes differently. Figure S1b is a digital photo of the underwater surface after immersed 6 hours, the color of unmodified aluminum surface shows unchanged, while the modified aluminum surface shows a significant reduction in light intensity and start to become grey. After immersed 48 hours, the silver-white part on the modified aluminum surface was reduced significantly and the surface started to show light grey appearance, but the unmodified surface color still shows no change. The color non-uniformity is mainly caused by commercial aluminum surface was not smooth enough. As shown in the figure, unmodified surface showed dark grey, and had no change with immersing time. However, the color of modified surface changed from silvery to grey with immersing time, and the color of two surfaces was not completely consistent even after 7 days.

The FTS-modified rough aluminum plat with nanostructures showed superamphiphobicity in air. In water, the rough structural grooves of surface would be filled with air, and the air in the grooves is reduced accordingly with immersing time. Immersed more than 7 days, unmodified and modified surface color is still not completely consistent, mainly due to the air in the grooves of modified surface has not disappeared entirely. The finally disappeared time of air mainly depends on the nanostructure and porosity size of solid surface.[6]

S3: Explanation of mechanism of wetting property of flat surface underwater.

According to Formula 1 in the text, the surface which is hydrophobic/weak-oleophobic in air ought to be oleophilic ($\gamma_{OA}\cos\theta_O$ - $\gamma_{WA}\cos\theta_W$ >0) underwater. However, uncorroded FTS-modified aluminum surface is oleophobic (110º) in water (Figure S2b). The reasons for that case are as follows.

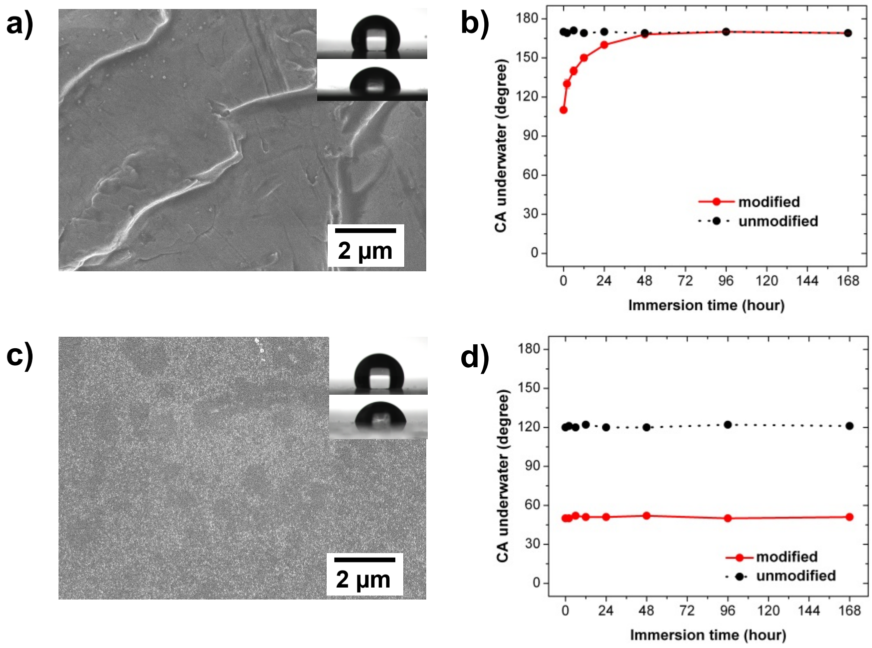

Figure S2. SEM images of flat surfaces. The insets show the morphology of water and oil droplet to the FTS modified surface in air, a) flat aluminum. CAs: 110.7 ± 1.5º/90.7 ± 1.5º, c) flat glass. CAs: 105.6 ± 1.2º/85.2 ± 1.1º. Changes of underwater oil CAs to b) flat aluminum surface and d) flat glass surface with different immersing time at a depth of 100 cm.

From Figure S2a we can see few shallow grooves and nanostructural on the flat aluminum surface. In water, the microstructure on the unmodified flat aluminum surface will be filled with water, resulting in superoleophobic underwater. Grooves on the flat FTS-modified aluminum surface were able to trap a little air, resulting in the reduction of oleophobicity underwater. Along with the increase of immersing time, air disappeared gradually. Finally, the surface turned to be superoleophobic. However, the surface of glass was smooth. The modified surface wouldn't be trapped by air underwater. Thus, its wetting property was changeless. And the wetting properties on modified and unmodified surface meet the underwater Young's equation results (Formula 1 in the text).