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Wetting behavior of superhydrophobic surface in the liquid influenced by the existing of air layer

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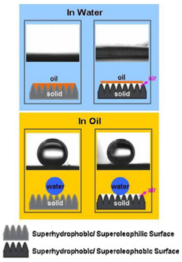
HIGHLIGHTS

- The oil wettability in water and water wettability in oil is studied.
- The oil contact angle in water on the surface is about 0°.
- The water contact angle in oil on the surface is 180°.
- The wettability in liquid accord with liquid spreading in air.

GRAPHICAL ABSTRACT

The oil-wetting behavior in water and water-wetting behavior in oil on superhydrophobic/superoleophilic surface and superhydrophobic/superoleophobic surface have been investigated. Two superhydrophobic surfaces both present an oil contact angle of about 0° in water, but show a water contact angle around 180° in oil. The oil can crowd out the air and seep into the grooves on superhydrophobic/superoleophilic surface when oil drops drip on the surface due to the surface superoleophilicity. In oil, the rough grooves of superhydrophobic/superoleophilic surface fill with oil, but the superhydrophobic/superoleophobic surface keeps a layer of air on its grooves. The air layer makes the rough surface forming a continuous liquid/air interface in liquid. When the other liquid droplet drips on the surface, it will be a contact with liquid/air interface which accord with liquid spreading at liquid/air interface in air.



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ABSTRACT

The oil-wetting behavior in water and water-wetting behavior in oil on superhydrophobic/superoleophilic surface and superhydrophobic/superoleophobic surface have been investigated. Two superhydrophobic surfaces both present an oil contact angle of about 0° in water, but show a water contact angle around 180° in oil. When two superhydrophobic surfaces are immersed in water, both of them retain a layer of air on the surface. The oil can crowd out the air and seep into the grooves on superhydrophobic/superoleophilic surface when oil droplet drips on the surface, but it will not occur on superhydrophobic/superoleophobic surface because of surface superoleophobicity. In oil, the rough grooves of superhydrophobic/superoleophilic surface fill with oil, but the superhydrophobic/superoleophobic surface keeps a layer of air on its grooves. The air layer makes the rough surface forming a continuous liquid/air interface in liquid. When the other liquid droplet drips on the surface, it will be a contact with liquid/air interface which accord with liquid spreading happening at liquid/air interface in air. And the situation and the shape of the other liquid droplet on the surface were also as same as it at liquid/air interface in air.

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1. Introduction

It is widely known that when quantitative liquid is put on the other incompatible liquid, two situations may happen: one is that the liquid spread out on the incompatible liquid, the other is not. That is all decided by spreading coefficient [1]. Not only is the liquid spreading situation extremely significant to prepare monomolecular film, such as well-known LB film [2]. But also the liquid not spreading condition can be used preparing synthetic liquid-repellency surface. Recently, Aizenberg et al. have reported slippery liquid-infused porous surfaces (SLIPS) with pressure-stable omniphobicity using nano/microstructured substrates to lock in place the infused lubricating fluid [3]. In recent years, underwater special wetting behavior on solid surface has attracted a number of researchers' attention [4]. Because it has lots of promising application, such as marine antifouling [5], anti-drag [6] and so on [7]. It is known that the superhydrophobic surface can tap air in its rough grooves under water [8]. The trapped air makes the underwater oil wetting behavior on superhydrophobic surface to be a complex oil/water/air/solid multi-phase interface. Hejazi et al. have studied the wetting of rough surface with four-phase interface and found that the air bubbles present on the surface inside crevices made the surface in water to be a discontinuous water/air/solid composite interface [9]. In a previous paper, we reported an underwater superoleophilic surface with oil capture ability and found that the trapped continuous air layer play an important role in superhydrophobic surface underwater superoleophilicity [10a]. Moreover, we have found that the break of the continuity of trapped air layer on superhydrophobic/superhyoleophobic surface can cause a significant change of three-phase contact line, which can tune the surface underwater wettability changing from superoleophilic to superoleophobic [10b].

In this contribution, superhydrophobic/superoleophilic surface and superhydrophobic/superoleophobic surface will be prepared on corroded rough aluminum plate by modifying methyltrichlorosilane (MTS) and 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane (FTS). And the oil-wetting behavior in water and water-wetting behavior in oil on two prepared surfaces will be studied. Furthermore, we will explore the role of continuous trapped air layer on the superhydrophobic surface wetting behavior with the other liquid in liquid.

2. Experimental

2.1. The process of preparing hydrophobic surfaces

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 h, 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 min. After corroding, the substrates rinsed with deionized water several times after ultrasonicated 30 s, and dried in a clean oven at 50 °C for 1 h.

Modification organosilane: The aluminum surfaces were then immersed into glass vials that contained anhydrous toluene (4 mL), and organosilane (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 1 h 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 surfaces were dried in an oven at 120 °C for 10 min.

2.2. Measurements of surface topography and wetting behavior

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 (1,2-dichloroethane) droplets or water droplets were placed carefully onto the surfaces, which were immersed in water or oil. The average contact angle values were obtained by measuring more than five different positions on a same sample.

3. Results and discussion

Two kinds of used liquid in the study are deionized water and 1,2-dichloroethane. Their spreading situation on each other surface in air is showing in Fig. 1. Oil droplets rapidly spread out the whole water surface once they were dripped on water (Fig. 1a). But it can be clearly seen in Fig. 1b that water droplets did not spread and showed spherical suspending on oil. And only small part of water droplet exposed above oil surface. Based the spreading coefficient $S_{2/1}$ of liquid spreading at liquid/air interface in air, defined as [1]:

$$S_{2/1} = \gamma_1 - \gamma_2 - \gamma_{1/2} \tag{1}$$

where $S_{2/1}$ is the free energy variation of liquid 2 on liquid 1, called spreading coefficient of liquid 2 on liquid 1; γ_1, γ_2, $\gamma_{1/2}$ are the interface tension of liquid 1 and air, liquid 2 and air, liquid 1 and liquid 2, respectively. When $S_{2/1}$ is positive, liquid 2 can spread out on liquid 1. On the contrary, liquid 2 will not spread when $S_{2/1}$ is negative. In air, water surface tension (γ_W) is 72.0 mN m^{-1} and 1,2-dichloroethane surface tension (γ_O) is 24.15 mN m^{-1} [11]. The 1,2-dichloroethane/water interfacial tension ($\gamma_{O/W}$) is 28.3 mN m^{-1} [12]. Therefore, $S_{O/W} = 19.55$ mN m$^{-1} > 0$, and $S_{W/O} = -76.15$ mN m$^{-1} < 0$, indicating that oil (1,2-dichloroethane) can spread out on water but water cannot spread out on oil. The calculation outcome is consistent with the experiments.

From the scanning electron microscope (SEM) image (Fig. 2a), we can clearly see that the flat aluminum plate before modification is relative smooth and has few shallow grooves on the surface. The rough aluminum plate after corrosion before modification had nanostructures on the surface (Fig. 2b). Fig. 2c–f shows the water and oil static contact angles in air of prepared surfaces. MTS modified flat surfaces were hydrophobic and oleophilic (Fig. 2c), and FTS modified flat surfaces showed hydropbobicity and oleophobicity (Fig. 2d). MTS modified rough surfaces were superhydrophobic and superoleophilic (Fig. 2e), and FTS modified rough surfaces approached superhydrophobic and superoleophobic (Fig. 2f).

To study the wettability of prepared surfaces in liquid, we measured the surfaces' oil contact angle in water and water contact angle in oil (Fig. 3). The oil contact angles of two flat modified surfaces in water were 51.4 ± 1.4° and 46.3 ± 1.5°, respectively (Fig. 3a and c), showing oleophility under water. However, in oil, their water contact angles were both proximity 180° (Fig. 3e and g). For two kinds of prepared rough surface, their oil contact angles were about 0° in water (Fig. 3b and d). Whereas it can be seen clearly in measuring process that air bubbles were squeezed out on the MTS modified superhydrophobic/superoloephilic surface when oil droplet dripped on the surface, but this phenomenon had not been observed on FTS modified superhydrophobic/superoleophobic surface. Nevertheless, the water drops on these two rough surfaces were appearing spherical in oil (Fig. 3f and h).

The wetting behavior of modified flat surfaces in water and oil can be explained by a formula for calculating the contact angle of