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# Sprayed superamphiphobic coatings on copper substrate with enhanced corrosive resistance

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ABSTRACT

The oil fouling and limited corrosion resistance problem severely hindered the use of copper, one of important engineering materials, in practical applications. Herein to address this problem, we fabricated a superamphiphobic coating on copper substrate by spray coating. The resulting superamphiphobic surface supports the Cassie–Baxter regime with apparent contact angles of more than 150° and low contact angle hysteresis to water and organic liquids with low surface tension. The resulting superamphiphobic surface also possesses enhanced corrosion resistance, allowing it to exhibit a more positive corrosion potential and a more negative corrosion current density than pristine copper substrate. Moreover, the surface wettability can be tuning by varying the surface composition of the coating. This study represents a key addition to functional superamphiphobic materials.



## 1. Introduction

There has recently been a significant amount of research directed toward producing superhydrophobic surfaces owing to their wide applicability in various fields, including the development of self-cleaning surfaces, anti-fogging films, and anticorrosion coatings [1–5]. Typically, surfaces are considered to be superhydrophobic if they display contact angles > 150° and contact angle hysteresis < 5° with water, and superamphiphobic if they display contact angles > 150° and contact angle hysteresis < 5° with water and oils. To maximize the self-cleaning effect, the coating should not only be able to repel water, but also have the ability to repel organic liquids. The three conventional wetting states described by the Wenzel, Cassie–Baxter, and Cassie-impregnating models are often cited to clarify the superhydrophobic surface. The Wenzel model means a complete wetting state. In the Cassie–Baxter model, liquid droplet only contacts the tips of the surface and trapped large fractions of airs, which generates the non-wetting and easily roll-off properties. Cassie-impregnating model is account for superhydrophobic surface with high adhesive force. Traditional superhydrophobic surfaces are easily fouled by oils and other organic matters, and this susceptibility to oil fouling severely hindered their use in practical applications. Our investigation focuses on the development of surfaces that simultaneously exhibit superhydrophobic and superoleophobic properties; such universally nonwetting surfaces are often referred to as superamphiphobic. However, creating superamphiphobic surfaces has proven to be much more difficult than creating superhydrophobic surfaces, owing to the similarity of the low surface tension of oils to that of the commonly used low energy materials. To address this problem, several studies systematically discussed the impact of surface texture on wettability and demonstrated that the overhang structure or the re-entrant surface curvature was essential to achieve superoleophobicity, besides the roughened texture and low surface energy materials [6–11]. In addition, theoretical analysis has shown that surfaces with two scales of texture can enhance the stability of Cassie–Baxter state by producing re-entrant structure. The re-entrant structures produce the Laplace pressure force ($\Delta P = P - P_0 = -\gamma \cos\left(\theta + \alpha\right)/R - h\tan\alpha$, where $\gamma$ is the surface tension of the liquid, $\theta$ is Young's contact angle of the liquid on a flat surface, $\alpha$ is the inclination angle, $R$ is the half-width between base edges of two adjacent inclined walls, $P$ is the pressure on the liquid side of the meniscus), which can effectively prevent the liquids from penetrating into the texture [12]. The Laplace pressure is important in maintaining a composite interface. This understanding allowed for the possibility of constructing superamphiphobic surfaces, although the pristine surface was hydrophilic and oleophilic, and fabrication methods involved lithography [13–15], deposition [16–18], electrochemical polymerization [19], electrospun method [20,21]. Although targeted superamphiphobic property has

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been achieved [22,23], the fabrication process is usually substrates restricted and time consuming, which limits the application of the obtained surfaces. Thus, seeking a simple way to produce superamphiphobic surfaces became an urgent demand.

As a kind of important engineering materials, copper has widely used in industrial applications, such as aerospace, railway, and automobile. However, the naturally occurring corrosion and oil-fouling properties greatly restricted the scope of its applications. Endowing copper substrate with superamphiphobicity and corrosion resistance may be an alternative way to solve this problem. Here, we developed spraying method to fabricate superamphiphobic coatings based on fluorinated silica and fluoropolymer. Liquids with different surface tension remained spherical on the surface and could roll off the surface easily. The resulting superoleophobic surface also enhanced corrosion resistance, allowing it to exhibit a more positive corrosion potential and a more negative corrosion current density than pristine copper substrate. Tunable surface wettability can be achieved by varying the ratio of fluorinated silica and fluoropolymer.

## 2. Experimental

### 2.1. Materials

Silicon dioxide nanopowder (10–20 nm particle size), poly(vinylidene fluoride-hexafluoro-propylene) (Mw ~ 400,000), Trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane, PFTS, were obtained from Aldrich and used as received. Water (18.2 MΩ cm) was purified with a millipore simplicity system and used for all experiments.

### 2.2. Sample preparation

#### 2.2.1. Preparation of fluorinated silica

0.5 g $SiO_2$ was immersed in piranha solution in 50 °C for 12 h ($H_2SO_4$ and 30 wt% $H_2O_2$ in a 3:2 volume ratio) [24] and washed with distilled water and ethanol until the pH was near 7. After put into a drying cabinet at 60 °C for 3 h, the dried powders were dispersed in 20 mL of toluene using an ultrasonic bath for 20 min to get a homogeneous dispersion. Then added 0.5 ml trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane under stirring at ambient temperature. Keep stirring for 12 h, the resultant suspension was centrifugation at 7500 rpm for 5 min. After discarding the supernatant, the final fluorinated silica was dried 5 h at 60 °C.

#### 2.2.2. Preparation of fluoropolymer/$SiO_2$ coating

Different weight ratio between fluoropolymer and fluorinated silica particles were dispersed in 40 ml acetone, and 0.5 ml trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane was added dropwise under stirring at ambient temperature. The mixture was kept stirring for 3 h, then ultrasonically for 30 min. The suspension was sprayed onto copper with 0.2 MPa nitrogen gas using a spray gun. The coatings were heated in an oven at 155 °C for 2 h.

### 2.3. Characterization

Contact angle (CA) and sliding angle (SA) were measured with approximately 10 μL droplets of water and hexadecane using a Krüss DSA 100 (Krüss Company, Ltd., Germany) apparatus at ambient temperature. X-ray photoelectron spectra (XPS) were obtained on an ESCALAB250xi spectrometer equipped with a focused monochromatic Al X-ray source (1486.6 ev). The morphology of the surface was observed by field-emission scanning electron microscope (JEOL JSM-6701F FESEM). Fourier transform infrared (FTIR) spectra were collected on a Bruker IFS66 V/S spectrometer. The average surface roughness (Ra) was characterized by NanoMap 500LS (America). Potentiodynamic polarization curve measurement was performed on a computer-controlled electrochemical system (CHI600E/700E, Shanghai) in 3.5 wt% NaCl aqueous solution at room temperature. A platinum electrode, superhydrophobic surface/superamphiphobic surface, and a silver/silver chloride (Ag/AgCl) electrode were used as the counter electrode, working electrode, and reference electrode, respectively. The optical images were captured by a digital camera (Canon).

## 3. Results and discussion

Fig. 1a shows the dispersion property of pristine silica, piranha solution treated silica, and fluorinated silica in water. As shown in Fig. 1a, the sedimentation rate of pristine silica was fast in water. After being treated in piranha solution, the silica particle has a good dispersion in water. While for the fluorinated silica, it floats on the surface of water, indicating its repellence to water. The FTIR spectra of pristine silica and fluorinated silica are shown in Fig. 1b. In the spectra of fluorinated silica, the presence of the bands at 1208 and 1132 $cm^{-1}$ is attributed to C-F stretching vibrations, which demonstrates that the fluorinated group was successfully grafted on the silica surface.

The pristine copper was hydrophilic and oleophilic, water (coloured with methylene blue) and hexadecane could wet it easily (see Fig. 2a). After spraying the suspension with molar ratio 1:4 between fluoropolymer and fluorinated silica particle, we obtained a superamphiphobic surface. More importantly, by tuning proportion of fluoropolymer and fluorinated silica to 1:1, we acquired a superhydrophobic surface. As shown in Fig. 2a, to pristine copper, water, and hexadecane droplet spread on the surface, indicating non-water and non-oil repellence. To superamphiphobic surface water droplet appeared to float on the coating surfaces. The bright, reflective surface visible underneath the water droplet is a signature of trapped air and the establishment of a composite solid-liquid-air interface [25]. The formation of this composite state enhanced super-repellence by a high CA (162.9°) and SA (3.7°) for water and CA (158°) and SA (5.1°) for hexadecane (see the Supporting Information, Movie 1 and Movie 2). The water-ethanol mixtures with different surface tension are designed based on a pulished work [26]. Moreover, we obtained a superhydrophobic and oleophobic coating by varying proportion of fluoropolymer and fluorinated silica to 1:1. As shown in Fig. 2a and b, water droplet remained spherical on the surface, but hexadecane penetrated the coating surface, yielding a CA of 158.7° and 94.2° with water and hexadecane, respectively.

In order to thoroughly understand the tunable surface wettability of coatings, the surface morphology and the chemical composition, which are two main factors governing the surface wettability, are considered. Surface morphology of the sprayed coatings with proportion of fluoropolymer and fluorinated silica of 1:4 is not flat (Ra = 679.2 nm) and, large numbers of microscale protrusions were distributed on it, which can trap a large fraction of air (see Fig. 3a and b). Interestingly, the superimposition of protrusions and pores forms re-entrant structures. Based on recent study, when a liquid droplet was placed on this structure, the Laplace pressure force is directed upward, which can effectively prevent the liquid from penetrating into the texture. XPS analysis demonstrated that the elements of coatings surface are carbon, fluorine, oxygen, and silicon, and the content of fluorine element is up to 46.01% (see Fig. 3c). The high concentration of perfluorinated carbons in the alkyl chain leads to an extremely low surface energy for this material and this low surface energy, when combined with the re-entrant surface textures, results in the sprayed coatings surface with superamphiphobicity. As for the sprayed coating with proportion of fluoropolymer and fluorinated silica of 1:1, the content of the