



# Super-hydrophobic film fabricated on aluminium surface as a barrier to atmospheric corrosion in a marine environment



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## ABSTRACT

Super-hydrophobic aluminium oxide layers were fabricated on aluminium surface with a simple anodisation method followed by fluorination treatment. It is proven that deliquesced NaCl particle can easily slip off the as-fabricated super-hydrophobic layer with low inclination angle for its low attraction to the layer. The super-hydrophobic layer can reduce corrosion of aluminium with an inhibition efficiency of 99.99%. Scotch tape test and Scratch test results indicated that the super-hydrophobic layers show good adherence to the substrate and abrasion resistance. These results demonstrate the advantages of the as-fabricated super-hydrophobic layer as a barrier to marine atmospheric corrosion.

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## 1. Introduction

In open air, especially in the coast or harbour [1], salt particles usually drop on material surfaces and transform into water droplets or films, which provide conditions essential for electrochemical reactions, thereby promoting corrosion of the underlying substrate [2]. Deliquescence of salt particle is regarded as an important factor that induces corrosion in marine atmosphere.

Inspired by the surface phenomenon “lotus effect”, artificial super-hydrophobic surface has been attracting tremendous interests for its potential application in corrosion protection [3–6]. Super-hydrophobic films have been proven to inhibit the corrosion of metal in aqueous solutions because of the presence of air between the super-hydrophobic film and the corrosive medium [7–11]. Low contact angle hysteresis is a typical characteristic of super-hydrophobic surface. When a water drop forms on a super-hydrophobic surface with low inclination angle, it can easily roll off the surface [12,13]. Therefore, salt particles can possibly be removed from a super-hydrophobic film after they transform into a saline solution droplet, and this behaviour can prevent the erosion of the saline solution droplet to the underlying substrate in marine atmospheric environment.

Rough micro/nanostructure and low surface energy are required for the fabrication of super-hydrophobic films [14–18]. Numerous micro- and nanofabrication techniques have been introduced to create super-hydrophobic surfaces over aluminium [19–21]. However,

specific equipment and complicated processes are required for these fabrication methods, thereby limiting the practical application of engineered super-hydrophobic surfaces [21,22]. By comparison, anodisation is considered one of the most promising methods in generating self-ordered nanostructures over large surface areas [23–26]. Simple electrolytic passivation process is employed to grow an oxide layer, and it does not require complicated fabrication facilities or manufacturing equipment. In addition, the insulated oxide film formed generally shows better adherence performance than most other types of paint and metal plating [27,28]. This property is very important for its application in industry.

In this work, a simple anodisation method combined with fluorination treatment was developed to fabricate a super-hydrophobic layer on aluminium surface. The slipping behaviour of deliquesced NaCl particle on the inclined super-hydrophobic layer was examined and analysed, and the corrosion resistance of the super-hydrophobic layer to the substrate was tested with electrochemical measurement. The adherence performance of super-hydrophobic layer to aluminium substrate and its abrasion resistance were evaluated with Scotch tape test and Scratch test methods, respectively. This work demonstrates the advantage of as-fabricated super-hydrophobic layer as a barrier to marine atmospheric corrosion.

## 2. Experimental

### 2.1. Material and reagents

Aluminium (>99.99 wt.%) foil was purchased from Beijing Cuibolin Nin-ferrous Technology Developing Co., Ltd. Other reagents,

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including phosphoric acid (>85 wt.%, chemical reagent), sodium chloride (analytical reagent), perchloric acid (>70 wt.%, chemical reagent) and ethanol (analytical reagent), were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received.

## 2.2. Fabrication of super-hydrophobic surface

### 2.2.1. Electro-polishing

Aluminium foil (1.2 cm × 2 cm × 0.2 cm) was used in the anodisation experiment without an annealing step. Before anodisation, aluminium substrates were electrochemically polished in a 30 mL mixture of perchloric acid and ethanol (HClO<sub>4</sub>:C<sub>2</sub>H<sub>5</sub>OH = 1:4 in volumetric ratio, 5 °C). The electro-polishing process was carried out with 20 V applied potential between aluminium and a counter electrode (stainless steel) for 3 min. The distance between the two electrodes is 2 cm. The electrolyte was vigorously stirred during the electro-polishing process.

### 2.2.2. Anodising of aluminium

The polished aluminium foil was then applied to form a rough microstructure in a two-electrode cell, in which, aluminium substrate was used as working electrode and a stainless steel electrode was employed as counter electrode. The distance between the two electrodes is 2 cm. The aluminium substrate was anodised in 25 mL aqueous solution of 0.2 M phosphoric acid under 120 V anodising voltage. The initial anodisation temperature was 50 °C, and the anodisation time was varied from 1 min to 20 min.

### 2.2.3. Surface modification

The aluminium samples after anodisation were coated with a self-assembled monolayer of silane (1H,1H,2H,2H-perfluorodecyltrichoxysilane, Aldrich Inc.). Briefly, the samples after anodisation were washed with ethanol to replace the water on their surface. After that, they were immersed into 1 vol.% silane/ethanol solution for 5 min at room temperature, and then taken out and heated at 120 °C in an oven for 10 min. After this procedure, a self-assembled monolayer of silane can form over sample surface.

## 2.3. Characterisation of the super-hydrophobic surface

The morphology of the super-hydrophobic surface was characterised with FE-SEM (JSM-6700F). The water contact angle of the surface was measured with a contact-angle meter (JC2000C1, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd.) at room temperature. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo ESCALAB 250 photoelectron spectrometer equipped with an Al-anode at a total power dissipation of 150 W (15 kV, 10 mA). A take-off angle of 45° from the surface was employed. All the analyses were performed at a pressure below  $1 \times 10^{-8}$  Torr. Survey spectra were recorded in the kinetic energy range of 0–1000 eV by 1.0 eV step, and high resolution scans with 0.1 eV step were conducted over the regions of interest: Al 2p, C 1s, F 1s, and Si 2p.

Adherence performance and abrasion resistance of super-hydrophobic layer were evaluated with Scotch tape test and Scratch test, respectively. Scotch tape test was carried out according to ASTM D3359-02. A piece of tape was firmly pressed against the as-fabricated super-hydrophobic layer and then peeled off at 180° angle. The contact angle of the sample is tested after each peeling attempt to determine the adherence performance of the super-hydrophobic layer. Scratch test was carried out according to Refs. [29,30], using a home-made scratch tester. Sandpaper (800 mesh, SiC as abrasive material with average particle diameter of 31.8 μm) was used as an abrasion surface, with the super-hydrophobic layer to be tested facing the abrasion material. As a Scratch test cycle, a pressure (36–108 kPa) was applied to the super-hydrophobic layer, and the

layer was dragged in one direction with a speed and abrasion length of 2 cm/s and 20 cm, respectively. Water contact angle was tested after each abrasion cycle, and the average value was determined by measuring the same sample at five different positions.

## 2.4. Monitoring of NaCl deliquescence process

A simulated marine atmospheric condition was created in a conditioning chamber, wherein the relative humidity (RH) was controlled using aqueous glycerine solution according to Standard ASTM D 5032-97 (Reapproved in 2003). In the conditioning chamber, the sample was placed above the aqueous glycerine solution, and a single NaCl particle with 200–300 μm diameter was gently transferred onto the sample surface without affecting the microstructure of the substrate. Subsequently, the transformation process from a NaCl particle to a saline droplet caused by deliquescence was recorded using a CCD camera, which operates at a speed of 25 frames/s.

## 2.5. Electrochemical test

The corrosion resistance of the aluminium sample was determined by electrochemical impedance spectroscopy (EIS), which was performed in 3.5 wt.% NaCl aqueous solution at room temperature using a computer-controlled electrochemical system (CHI 604C, CH Instruments Inc.). The test was performed in a standard three-electrode system with Ag/AgCl (3 M KCl) as reference electrode, a platinum mesh as counter electrode, and the aluminium sample as working electrode. EIS experiments were carried out at frequency range of 10<sup>5</sup> Hz to 10<sup>-2</sup> Hz at open circuit potential with amplitude of perturbation voltage ± mV. Before EIS measurement, the sample was immersed in test solution for about 30 min until the primary corrosion potential reached a steady state. Each result was repeated for at least 5 times. EIS results were analysed by fitting data with Zsimpwin software.

## 3. Results and discussion

### 3.1. Composition of super-hydrophobic layer

Fig. 1 shows the XPS spectra of the aluminium foil surface after anodisation and surface modification with fluorosilane. The XPS survey spectrum shown in Fig. 1a reveals the presence of Al, C, F, O and Si on the sample surface. As shown in the Al 2p core-level spectrum (Fig. 1b), the binding energy of the Al 2p peak is 74.2 eV, which is assigned to O–Al–O (Al<sub>2</sub>O<sub>3</sub>) bonding [31]. The layer after anodisation is proven to be mainly composed of Al<sub>2</sub>O<sub>3</sub>. From the high-resolution C 1s core-level spectrum (Fig. 1c), three components, namely, –CF<sub>3</sub> group at 292.7 eV, –CF<sub>2</sub>– group at 290.7 eV and C–C bonds at 284.1 eV [32], can be identified. From the F 1s core-level spectrum shown in Fig. 1d, the main peak can be found at approximately 687.7 eV, and it is attributed to F–C covalent bond [33]. Furthermore, an intensified peak exists at the binding energy of 101.6 eV in the high-resolution Si 2p core-level spectrum (Fig. 1e), and it can be assigned to the bonding of Si to O in fluorosilane molecules [31]. These results prove that fluorosilane is grafted on the aluminium oxide surface, and the outermost surface is mainly composed of low-surface energy –CF<sub>3</sub> and –CF<sub>2</sub>– components, which contribute to the super-hydrophobic property.

### 3.2. Microstructure and wettability

Fig. 2 shows the microstructure of the aluminium oxide layer fabricated with varying anodisation time from 1 min to 20 min. A schematic diagram is shown to illustrate the morphology evolution

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