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Superhydrophobic Film on Hot-Dip Galvanized Steel with Corrosion Resistance and Self-Cleaning Properties

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Abstract: Super-hydrophobic film with hierarchical micro/nano structures was prepared by galvanic replacement reaction process on the surface of galvanized steel. The effects of the etching time and copper nitrate concentration on the wetting property of the as-prepared surfaces were studied. Scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and electrochemical technique were employed to characterize the surface morphology, chemical composition, and corrosion resistance. The stability and self-cleaning property of the as-fabricated super-hydrophobic film were also evaluated. The super-hydrophobic film can be obtained within 3 min and possesses a water contact angle of $164.3^{\circ} \pm 2^{\circ}$. Potentiodynamic polarization measurements indicated that the super-hydrophobic film greatly improved the corrosion resistance of the galvanized steel in 3.5 wt % NaCl aqueous solution. The highest inhibition efficiency was estimated to be 96.6%. The obtained super-hydrophobic film showed good stability and self-cleaning property.

Keywords: super-hydrophobic surface; hot-dip galvanized steel; anti-corrosion resistance; self-cleaning

1. Introduction

Galvanizing is recognized as a traditional technology to protect steel free from corrosion. The hot-dipped zinc coating on steel surface can provide both barrier protection and cathodic protection [1]. However, galvanized layers, in highly aggressive environments (such as coastal or marine environments), may suffer atmospheric corrosion. High humidity and salt spray ingress can accelerate the corrosion process, which makes it unable to provide adequate corrosion protection to ensure long-term service life for steel substrate [2]. Chromium-containing passivation has been extensively employed as an effective method to inhibit corrosion of zinc layer. However, now it has been restricted due to its adverse effects on human health and environmental. To suppress this issue, a few techniques have been developed to mitigate the corrosion process of galvanized layer, such as corrosion inhibitors [3], graphene based coatings [4], sol-gel protective coatings [5–7], silicon protective coatings [8], and so on.

Nowadays, with the advances of non-wetting bio-inspired materials the technology of corrosion resistant for metals has been broadened [9–13]. Super-hydrophobic surfaces (water contact angle larger than 150° and contact angle hysteresis less than 10°), which exhibit excellent self-cleaning, water repulsion, anti-icing, and corrosion resistance characteristics, have drawn much attention both



in scientific research and practical applications. Super-hydrophobic film keeps corrosion at coastal areas by not allowing a large volume of corrosive liquids to interact with the active surface. It has shown great potential for corrosion control [14].

To fabricate super-hydrophobic surfaces, modifying a rough surface with low energy materials and roughing low surface materials are the most commonly used methods. Techniques such as chemical etching [15], layer by layer deposition [16], sol-gel [17], electrochemical reaction and deposition [18,19], spray [20], solution-immersion method [21], and laser etching [22] have been used to create rough surfaces with multiple scales structures. Up to now, many super-hydrophobic surfaces have been created based on various substrates such as polymers [23], glasses [24], metals [25–27], fabrics [28], etc. Among these, fabrication of super-hydrophobic surfaces on metallic materials play a significant role in considerable industries due to its water-repel and self-cleaning properties.

To date, super-hydrophobic films have been made on various engineering materials such as aluminum, copper, magnesium, zinc, titanium, and stainless steel to improve their anti-corrosion properties [27,29–31]. However, most of the fabrication methods for super-hydrophobic surfaces are relatively complex, require special equipment, high cost and time-consuming, which greatly restrict its application in industries. Galvanizing is one of the most popular methods used to protect steel substrate in engineering and industry. Therefore, incorporate super-hydrophobic films into the design of steel products that can not only improve the corrosion resistance of the galvanized parts, but also decrease maintenance costs over the life of structure. Nevertheless, there are few reports focusing on the application of super-hydrophobic surfaces on hot-dip galvanized steel [32]. It is, therefore, important to develop a simple, environmental, and cost-effect way for large-scale fabrication of super-hydrophobic surfaces based on galvanized substrates. Numerous studies have confirmed that chemical etching is a facile way to create hierarchical structures on metallic substrates. However, the long time needed for the etching process ranged from 2 h to 24 h [33-35], which restrict its extensive application for large-scale preparation in real industry. Recently, a few facile methods was reported to fabricate super-hydrophobic surface on metals. Song et al. [36] reported a simple and highly effective method of fabricating super-hydrophobic surface on Al plates within several seconds by immersing the Cu coating Al plate in ethanol solution of fluoroalkylsilane. Cao et al. [37] developed a simple preparation method for super-hydrophobic surface on zinc within 5 min through a displacement reaction between a zinc plate and an acidic SnCl₂ solution without surface modification. However, most of the researches focused on the preparation methods [38–40], and there is a lack of in-depth study of its formation mechanism and coating properties.

In our present work, we report a simple and fast method, which is inspired by Song et al., for constructing a super-hydrophobic film with hierarchical structure on galvanized steel surface. The super-hydrophobic film can be fabricated within 3 min. In addition, the formation mechanism of the super-hydrophobic process was investigated. The corrosion resistance, stability, and self-cleaning properties of the as-fabricated super-hydrophobic film was also evaluated in this study. From a viewpoint of industry application, the presented method is more facile and cost-effective than the works reported before, which can be potentially used for the large-scale preparation of super-hydrophobic surfaces based on galvanized steel.

2. Experiment

2.1. Materials

Commercially available Q235 steel plates were purchased from Tianjin YiChi Steel sale Co., Ltd., Tianjin, China. Zinc ingot (99.995%) were purchased from Zhuzhou Smelter Group Co., Ltd., Zhuzhou, China. Cupric hydrate, acetone, anhydrous ethanol, and stearic acid were obtained from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd., Tianjin, China. All the reagents used were analytical-grade and used as received without further purification.

2.2. Sample Preparation

Q235 steel plates specimens, with a size of $3.5 \text{ cm} \times 5 \text{ cm} \times 0.25 \text{ cm}$, were pretreated by degreasing, pickling, fluxing processes to ensure a clean steel surface. Then the steel articles were immersed in a bath of molten zinc (\approx 450 °C; zinc \geq 99.995%). The as-fabricated galvanized steel samples were ultrasonically degreased with acetone and ethanol for 10 min respectively. Then the specimens were rinsed with deionized water three times. After that, the galvanized steel samples were immersed vertically in a 50 mL cupric hydrate solution (with Cu²⁺ concentration ranging from 0.05 M to 0.2 M) for different time at ambient temperature. Hereafter, the immersed substrates were rinsed with deionized water to remove the residual salts and dried under a stream of hot air. Finally, the samples were immersed in a 0.05 M stearic acid (STA, with low surface energy of about 30.03 mJ/m² [41]) ethanol solution for different time, rinsed with anhydrous ethanol, and then dried under a heat airflow at a temperature about 80 °C for 10–20 s. The schematic fabrication process is shown in Figure 1. For ease of understanding, Table 1 shows the details of each sample prepared.



Figure 1. Schematic fabrication process of super-hydrophobic galvanized steel sheet.

Table 1. Details of	the samples prepared.
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Sample	Details	
Blank sample	Samples without any treatment	
Stearic acid (STA) modified sample	Samples only modified with stearic acid (STA)	
Etched sample	Samples after immersion in Cu(NO ₃) ₂ aqueous solution without STA modification	
Super-hydrophobic sample (SHS)	Samples etched by $Cu(NO_3)_2$ at optimum conditions and followed by STA modification	

2.3. Characterization of Super-Hydrophobic Film

Static water contact angles (WCA) were measured by DAS30 contact angle measurement system (KRUSS, Hamburg, Germany) at room temperature. The volume of deionized water used for the WCA measurement was 10 μ L. The average WCA values were obtained by measuring five different positions of the same sample. Surface morphology of the steel surface was observed by scanning electron microscope (SEM/EDS, Quanta 450 FEG, Hillsboro, OR, USA) operating at 20 kV. X-ray diffraction (XRD) was carried out to determine the phase structure of the super-hydrophobic film on galvanized steel. Chemical composition of the super-hydrophobic film was detected by X-ray photoelectron spectrometer (XPS), using the Al K α as the excitation source. All binding energies in the spectra were corrected using standard binding energy of C1s peak (284.6 eV) as reference. The functional groups

of super-hydrophobic film was identified by Fourier transform IR (FTIR) spectroscopy (V80, Bruker, Karlsruhe, Germany).

2.4. Electrochemical Test

Electrochemical tests were performed on the CHI660E electrochemical workstation using an three-electrode electrochemical system (Shanghai Chenhua Instrument, Shanghai, China), where 3.5 wt % NaCl aqueous solution was used as electrolyte at room temperature. The samples with different treatments were used as the working electrode with an area of 1 cm², a platinum plate, and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. Before measurement, the working electrode was immersed in the electrolyte until the open circuit potential (E_{oc}) reached a steady state (fluctuation less than 10 mV). The potentiodynamic polarization curves were carried out at a scanning rate of 1 mV/s raging from -0.2 V (vs. E_{oc}) to +0.2 V (vs. E_{oc}). The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined by the resultant polarization curve. Each test was repeated at least three times to verify the repeatability of the results.

2.5. Self-Cleaning Test

The self-cleaning test was carried out in a glass petri dish, where the samples were placed at an inclination about 10° . Graphite powder (~40 μ m), which acted as contaminant, were spread over the sample surface. Self-cleaning behavior via rolling droplets of water were recorded by a high definition video camera.

3. Results and Discussion

3.1. Surface Wettability

Surface wettability of the samples were characterized by the static water contact angle system. Figure 2 shows the static WCA on different surfaces, which presents the changes of wettability during the super-hydrophobic process. As shown in Figure 2, WCA of the blank sample (initial galvanized steel sheet) is $72 \pm 2^{\circ}$, indicating that its surface is hydrophilic. WCA of the sample modified by STA only increases to $119 \pm 2^{\circ}$. This is because the STA molecules on the surface of the galvanized steel lowered its surface free energy, making the sample hydrophobic. After immersion into 0.1 M Cu(NO₃)₂ aqueous solution, the WCA of the etched sample decreases drastically to $9 \pm 2^{\circ}$, and its surface is completely wetted by water droplet. This may attribute to the Cu film coated on the surface of galvanized steel that enhance its roughness leading to the completely wetting behavior. However, after it was modified by STA, the Cu coated sample successfully transforms from super-hydrophilicity to super-hydrophobic surface (SHS) without any adhesion. By this etching process, as well as low surface energy passivation process, the super-hydrophobic film can be prepared successfully on the surface of galvanized steel.



Figure 2. Static water contact angles (WCA) of the samples with different treatment process.

The immersion process mentioned above was further optimized by varying immersion time and $Cu(NO_3)_2$ concentration. The effect of immersion time on WCA at different copper nitrite concentrations were shown in Figure 3. All the samples were modified with STA prior to measuring the static contact angle. The WCA of STA-modified sample is $119 \pm 2^{\circ}$, and this point is given as a reference point at time zero. The dotted line in Figure 3 corresponds to a contact angle of 150°. When the contact angle was larger than 150°, the surface was consider as superhydrophobic. When the Cu(NO₃)₂ concentration is 0.05 M, the WCA of the samples increases fast after etching for 5 s and fluctuate at about 140° as immersion time increases. However, the WCA cannot meet the requirements of super-hydrophobicity. The increase of $Cu(NO_3)_2$ concentration enhanced the hydrophobicity of the coatings. As Figure 3 shows that when the $Cu(NO_3)_2$ concentration is 0.1 M, WCA of the samples reach a super-hydrophobic level after etching for 5 s and slightly fluctuate as etching time increases. When the concentration of copper nitrite is 0.15 M and 0.2 M, a similar trend can be found as the etching time increases. It can be seen from Figure 3 that the WCA reaches a maximum value of $164.3 \pm 2^{\circ}$ when the copper nitrate concentration is 0.1 M and the optimal immersion time is 15 s. Therefore, superhydrophobic samples fabricated under this processing conditions were used for further studies.



Figure 3. Effect of immersion time and copper nitrite concentration on WCA.

3.2. Surface Morphology

The surface morphology of different treated samples were characterized by SEM. Figure 4 shows the SEM images of (a) blank sample; (b) etched sample; (c) super-hydrophobic sample, respectively; and (d–f) are the corresponding high magnification images. It can be found from Figure 4a,d that the initial galvanized steel surface is relatively flat, except for some scratches. Figure 4b shows the surface morphology of the sample after etching with 0.1 M copper nitrate solution for 15 s. There are a large amount of tiny spherical particles, with an average diameter of 3 μ m, on the surface of the galvanized sheet. It can be further seen from Figure 4e that the tiny spherical particles are composed of hierarchical micro/nano structures. This hierarchical structure improves the surface roughness, which is helpful to enhance the super-hydrophilic property. Figure 4c,f show the surface morphology of the etched sample modified by stearic acid. From the images we can see that the hierarchical micro/nano structures become more distinct, and the pompom-like structures are filmed on the surface of galvanized. It is these pompom-like hierarchical micro/nano structures that endow super-hydrophobic and rolling off properties to galvanized plate surfaces.



Figure 4. SEM images of (**a**) blank sample; (**b**) etched sample; (**c**) super-hydrophobic sample, respectively; and (d-f) are the corresponding high magnification images, respectively.

3.3. Surface Composition Analysis

3.3.1. EDS Analysis

Figure 5 shows the surface elemental composition of (a) blank sample; (b) etched sample; (c) super-hydrophobic sample, respectively. The illustrations are physical topographies of the sample surfaces. The EDS analysis results confirm that the surface of initial galvanized sheet (Figure 5a) is mainly composed of Zn (99.84%) element. As can be seen from Figure 5b, the etched sample surface consists of Zn, Cu, O, N, and Fe. The micro/nano structures on the etched sample surface can be attributed to the galvanic replacement deposition between Zn and Cu(NO₃)₂, which can be explained by the following reaction:

$$\operatorname{Zn} + \operatorname{Cu}^{2+} \longrightarrow \operatorname{Cu} + \operatorname{Zn}^{2+}$$

The appearance of N and parts of O may ascribe to the residual from the solution. Since the basic substrate is steel, the element Fe can be ascribe to the steel substrate. The increase of oxygen

content suggests that more oxygen is brought into the etched sample surface, and might generate metal oxides [42]. Furthermore, a large amount of Zn element is detected on the deposited particles, which demonstrate that the Zn²⁺ not completely enter into the solution but remains at the reaction interface. The super-hydrophobic sample surface consists of C, O, Zn, Cu, and Fe, as shown in Figure 5c. The new peak due to C (51.73%) appeared in Figure 5c, while the N element disappeared and the content of Zn, Cu, and O decreased significantly. These variations indicate that the STA is grafted on the surface of the etched sample, which has a significant impact to its wettability.



Figure 5. EDS spectra of (a) blank sample; (b) etched sample; (c) super-hydrophobic sample.

3.3.2. XRD Analysis

The X-ray diffraction (XRD) was carried out to further determine the phase structure of the super-hydrophobic film on galvanized steel. Figure 6 illustrates the X-ray diffraction and results of the prepared samples. The low angle X-ray diffraction (Figure 6a) results demonstrates that two distinct peaks at 6.57° , 9.15° was observed on the superhydrophobic sample surface, which corresponds to Zinc stearate (Zn[CH₃ (CH₂)₁₆ COO]₂, abbreviated as Zn(SA)₂). It should be noted that no characteristic peaks has been found on the blank sample and etched sample surfaces. Meanwhile, some weak peaks that corresponds to ZnO were detected on the etched sample, demonstrating the oxidation of Zinc.

Besides, some characteristic peaks at 36.3°, 39.2°, 43.5°, 70.8° in Figure 6b,c and 77.1° in Figure 6d, respectively, which are in good agreement with the characteristic peaks of Zn(002), (100), (101), (103), and (004). This arises from the galvanized zinc layer.



Figure 6. X-ray diffraction results of the prepared samples: (**a**) the low angle X-ray diffraction; (**b**) blank sample; (**c**) etched sample; (**d**) super-hydrophobic sample.

3.3.3. FTIR Analysis

FTIR spectra was employed to study the functional group of the as-prepared superhydrophobic film. Figure 7 shows the FTIR spectra results of stearic acid and the compound scratched from the superhydrophobic film, respectively. It can be seen that the characteristic peaks related to alkyl chain, such as asymmetric vibrations of $-CH_3(2953 \text{ cm}^{-1})$, asymmetric and symmetric vibrations of $-CH_2$ (2846 cm⁻¹, 2918 cm⁻¹) can be found in the high frequency region of both stearic acid and superhydrophobic film [26]. It is well known that the carboxyl group (COO-) from stearic acid appears at 1702 cm⁻¹. However, it was nearly disappeared in the superhydrophobic film exhibit some newly formed adsorption peaks at 1539 cm⁻¹, 1461 cm⁻¹, and 1398 cm⁻¹, which correspond to asymmetric and symmetric stretches of COO- group [43]. Thus based on the FTIR analysis, we can deduce that the stearic acid is not physically absorbed on the film, but instead reacts chemically with the particles on the surface of galvanized steel, and Zn stearate (Zn[CH₃ (CH₂)₁₆ COO]₂) with low surface energy is most likely formed on the superhydrophobic surface.



Figure 7. FTIR spectra of stearic acid and superhydrophobic film.

3.3.4. XPS Analysis

The formation mechanism was further confirmed with XPS measurements, as shown in Figure 8. The curves labeled with (A) and (B) in Figure 8a are Cu coated sample and super-hydrophobic sample, respectively. The survey region shown in Figure 8a indicates that Zn, O, C, and Cu are main components on the sample surface. Figure 8b shows the high resolution core level spectra of the copper element. The peaks at binding energies of 963.2 eV ($Cu2p_{1/2}$) and 952.3 ($Cu2p_{1/2}$) are attributed to the Cu2p region of metallic copper [21], indicating that copper was deposited on the galvanized steel surface. The other two peaks located at 934.8 eV ($Cu2p_{3/2}$) and 932.7 ($Cu2p_{3/2}$), which can be implied to the oxidation of the deposited copper particles after drying process, should be assigned to the copper element in Cu-O. However, nearly all the Cu2p spectra peaks disappeared after modified by STA, indicating that a layer of stearic acid film was absorbed on the surface of the micro-copper particles on the surface of the galvanized steel plate. Since no other carbon-containing substances was introduced during the etching process. Therefore, the weak carbon peak in Figure 8c-A is most likely due to the intervention of air. As can be seen from Figure 8c-B, a strong peak of carbon element at binding energy of 285.0 eV was detected. The high-resolution core level of C1s after STA modification is resolved into two components: 288.8 eV and 284.75 eV. The peak located at 288.8 eV can be attributed to the carbon element in the carbonyl bonds (-COO-), while the peak at 284.75 is attributed to the C-C and C-H functional group [27]. This is in good accordance with the results of FTIR. Figure 8d depicts the Zn2p high resolution of the sample before (black) and after STA modification (red). It is found that the spectra intensity of the sample without STA modification are stronger than the SHS one. The binding energy of Zn2p_{3/2} and Zn2p_{1/2} peaks are centered at around 1022.1 eV and 1045.2 eV, respectively with a spin-energy separation of about 23 eV. This results suggests that the zinc element exists in its ionic form (Zn^{2+}) consistent with Wertheim's results [44] and the XRD results where ZnO phases and Zn(SA)₂ were detected before and after STA modification, respectively.

296

292

290



Figure 8. XPS spectra of (A) Cu coated sample and (B) super-hydrophobic sample: (a) survey region; (**b**) Cu2p; (**c**) C1s; (**d**) Zn2p.

282

3.4. Theoretical Formation Mechanism for Super-Hydrophobic Surface

288

Binding energy (eV)

286

The formation mechanism of the super-hydrophobic process has been studied in this paper. Based on the comprehensive analysis results (SEM/EDS, FT-IR, XRD, XPS), we proposed a possible schematic model to illustrate the formation mechanism of the super-hydrophobic surfaces, as shown in Figure 9. When the Galvanized steel substrate was immersed in the copper nitrate solution, a galvanic replacement reaction between Zn and $Cu(NO_3)_2$ occurred (Equation (1)). Zinc ions (Zn²⁺) were forced to release from the galvanized zinc layer, meanwhile the copper ions(Cu^{2+}) get electrons to form copper and deposited on the substrate. Interestingly, both EDS and XPS results indicate that a large amount of Zn element is detected on the deposited particles. Therefore, we infer that the Zn^{2+} not completely enter into the solution but remains at the reaction interface between Zn layer and aqueous solution (as shown in Figure 9a). After the galvanic reaction process, the obtained surfaces exhibit super-hydrophilic property, where the water can completely spread (as shown in Figure 9a). When the above-obtained surfaces were modified with STA, the STA molecules combined with the composite particles (Cu/Zn²⁺), generating zinc stearate (Zn[CH₃ (CH₂)₁₆ COO]₂) and copper stearate(Cu[CH₃ (CH₂)₁₆ COO]₂). In addition, some STA molecules can be attached to the surface of composite particles by physical adsorption (as shown in Figure 9b). Thus the super-hydrophobic surface with micro/nano structures was formed. The detailed reaction equations are described as follows [43]:

$$Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$$
(1)

$$Zn \longrightarrow Zn^{2+} + 2e^{-}$$
 (2)

Binding energy (eV)

$$2Zn + O_2 \longrightarrow 2ZnO$$
 (3)

$$2Cu + O_2 \longrightarrow 2CuO$$
 (4)

$$Zn^{2+} + CH_3 (CH_2)_{16} COOH \longrightarrow Zn[CH_3 (CH_2)_{16} COO]_2 + 2H^+$$
 (5)

$$\operatorname{Cu}^{2+} + \operatorname{CH}_3(\operatorname{CH}_2)_{16}\operatorname{COOH} \longrightarrow \operatorname{Cu}[\operatorname{CH}_3(\operatorname{CH}_2)_{16}\operatorname{COO}]_2 + 2\operatorname{H}^+$$
(6)

It is well known that hierarchical micro/nano structures play an important role in the wettability of a solid surface. A large amount of air can be trapped in the interspace of the hierarchical structures, which can lead to the larger CA and smaller SA according to the Cassie–Baxter equation [45,46]:

$$\cos\theta = f \cdot \cos\theta_0 + f - 1 \tag{7}$$

where *f* is the area fraction of liquid–solid interface and θ and θ_0 represent the WCA of the composite hierarchical structures surface and the smooth surfaces, respectively. Herein, it was calculated from the obtained data that *f* = 0.03, demonstrating that the contact-area fraction of the water-air interface is 0.97. The results demonstrate that the air occupies about 97% of the contact area between super-hydrophobic galvanized substrate and water droplet. It reveals that the hierarchical micro/nano structures with low surface energy keep corrosion at corrosive areas by not allowing a large volume of corrosive liquids to interact with the active surface, which have showed great potential for corrosion control.



Figure 9. Schematic illustration of the formation mechanism for super-hydrophobic film: (**a**) etching process and wettability; (**b**) STA modification process and wettability.

3.5. Corrosion Resistance of Super-Hydrophobic Film

A comparative study on the corrosion resistance of the galvanized steel plates with different wetting properties was conducted using electrochemical method. Figure 10 shows the potentiodynamic polarization curves of the galvanized steel plates with different wetting properties in 3.5 wt % NaCl solution. The corrosion potential E_{corr} and the corrosion current density i_{corr} from the Tafel polarization curves are tabulated in Table 2 for the ease of comparison. As can be clearly seen from Figure 10 and Table 2, the super-hydrophobic sample positively increases from -1.096 V to -0.844 V, which exhibits significantly higher potential compared to that of blank sample. Accordingly, the super-hydrophobic sample shows an appreciable reduction in corrosion current density (1.632×10^{-6} A/cm²) in comparison to the corrosion current density of the blank sample (4.802×10^{-5} A/cm²).



Figure 10. Potentiodynamic polarization curves of the galvanized steel plates with different wetting properties in 3.5 wt % NaCl solution.

Table 2. Corrosion potential (E_{corr}) and corrosion current density (i_{corr}) of galvanized steel samples with different wetting properties in 3.5 wt % NaCl solution.

Sample	E_{corr} (V)	<i>i_{corr}</i> (A/cm ²)	η (%)
Blank sample	-1.096 ± 0.01	$4.802 imes 10^{-5}$	-
Hydrophobic	-1.095 ± 0.02	$1.615 imes10^{-5}$	66.4
Super-hydrophilic	-1.089 ± 0.02	$7.652 imes 10^{-5}$	-
Super-hydrophobic	-0.844 ± 0.03	$1.632 imes 10^{-6}$	96.6

Futhermore, the corrosion current density of the super-hydrophilic sample shown in Table 2 has nearly doubled, which may be attributed to the rough surface structure on the sample. This causes an enhanced adsorption of corrosive electrolytes, making it more susceptible to corrosion. As is known to us that a higher corrosion potential or a lower corrosion current density corresponds to a lower corrosion rate and a better corrosion resistance. Therefore, the increasing of E_{corr} and the decreasing of i_{corr} indicate that the super-hydrophobic sample possesses a better corrosion resistance. This may be attributed to the formation of air layer on the super-hydrophobic sample surface that acts as a corrosion barrier to inhibit the electrons and ions transfer between substrate and electrolyte. The inhibition efficiency (η) of the samples was calculated using the following equation [47]:

$$\eta = \frac{[i_{B-corr} - i_{S-corr}]}{i_{B-corr}} \times 100\%$$
(8)

where i_{B-corr} and i_{s-corr} are the corrosion current density of bare sample and super-hydrophobic sample, respectively. The highest inhibition efficiency was estimated to be 96.6% for the super-hydrophobic sample.

3.6. Stability and Self-Cleaning Properties

The chemical stability of the as-fabricated super-hydrophobic surfaces is a critical factor to determine the feasibility for practical applications. In this study, the stability of the super-hydrophobic surfaces were examined by exposure to the outdoor environment for about 6 months. Figure 11 shows the results of WCA before and after exposure for 6 months. The results indicate that the WCA angle and roll-off property has nearly no variation for long-time exposure, and show good stability in air.



Figure 11. WCA image for stability (a) initial state; (b) after exposure for 6 months.

Besides, the self-cleaning property of super-hydrophobic surfaces also plays an important role in its practical applications. Figure 12 shows the process of the self-cleaning behavior of the as-prepared super-hydrophobic surface in comparison to the control surface. The samples were placed in a glass petri dish at a slope angle of about 10° and subjected to continuously falling droplets. Graphite powders (~40 µm) as contaminants were spread over the sample surfaces. As can be seen from Figure 12(b1–b5) the as-prepared super-hydrophobic galvanized steel plate showed excellent self-cleaning action by allowing the water droplet carry the contamination away from its rolling and bouncing process. However, this is not the case for the control sample as shown in Figure 12(a1–a5), where the contaminants remains. The results indicate that the as-fabricated super-hydrophobic galvanized steel surface has a low-adhesion to the contaminants and can be easily taken away by the rolling-off water droplets. The super-hydrophobic surface exhibits excellent self-cleaning property, which can protect the steel surface free from adhering by pollutants in practical application.



Figure 12. Photographs of the self-cleaning behavior process: (**a**) the control surface; (**b**) the super-hydrophobic surface.

4. Conclusions

In summary, super-hydrophobic galvanized steel surfaces were successfully fabricated by a facile galvanic replacement reaction and STA modification. The super-hydrophobic surface can be obtained within 3 min. The as-fabricated super-hydrophobic surface is mainly composed of Zinc stearate covered copper agglomerate particles with hierarchical micro/nano structures and has a maximum WCA of 164.3°. The as-prepared super-hydrophobic surface show excellent performance of corrosion resistance in 3.5 wt % NaCl aqueous solution by not allowing a large volume of corrosive liquids to interact with the galvanized surface. The formation of air layer on the super-hydrophobic surface that

acts as a corrosion barrier to inhibit the electron and ion transfer between substrate and electrolyte. The highest inhibition efficiency was estimated to be 96.6%. Furthermore, the as-fabricated film show good chemical stability and long-term durability in air and also exhibit excellent self-cleaning property. This method may provide a fast, green, and cost-effective way to realize the long-term corrosion control for galvanized steel.

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