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Article

# Superhydrophobic Al Surfaces with Properties of Anticorrosion and Reparability

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**Supporting Information** 

**ABSTRACT:** Aluminum (Al) is one of the most widely used metals for industry and household applications, but its longevity is limited by its tendency for corrosion. In this work, we report a facile method to fabricate superhydrophobic Al surfaces that have excellent anti-corrosion effect. The surface is obtained by etching Al in CuCl<sub>2</sub> solution to form the micro–nano-pit surface texture followed by lowering its surface energy in an aqueous ethanol solution of stearic acid. The superhydrophobic Al surfaces show water contact angles as high as  $165^{\circ}$ . Electrochemical tests demonstrate that the corrosion rate of the Al surface drops by 94.5% after the superhydrophobic modification (corrosion current density lowers from  $1.11 \times 10^{-4}$  to  $6.10 \times 10^{-6}$  A cm<sup>-2</sup>). We also



show that the superhydrophobic surface will protect the Al from corrosion even under a very harsh environment. In addition, our method is scalable and the superhydrophobic surfaces exhibit excellent flexible and reparable properties. This anti-corrosive superhydrophobic Al surface will prolong Al in its broad usage.

# ■ INTRODUCTION

Throughout the long-term evolution in nature, many organisms developed various characteristics with amazing properties. For instance, one such property is the superhydrophobicity of lotus leaves and water strider legs, which describes the nonwetting characteristics of material surfaces.<sup>1-3</sup> A superhydrophobic surface, normally defined as a surface with a water contact angle (an angle that a liquid makes with a solid) larger than 150°, repels water to form near spherical shapes that do not adhere to them but instead bounce off, which has attracted intensive attention because of its excellent prospects in the fields of self-cleaning, anti-icing, anti-corrosion, and microfluidic devices.<sup>4-14</sup> As a light metal, aluminum (Al) has widely used in general industry as well as in household activities thanks to its excellent heat and electrical conductivities, natural availability, and high mechanical properties.<sup>15</sup> However, these applications are seriously limited because of the easy corrosion or deterioration of Al surfaces. With the extensive nano- and micro-scale surface textures and a layer of air trapped among these structures, a superhydrophobic layer can repel the water and moisture from the surface, which results in a dry and clean surface.<sup>4,16</sup> Consequently, superhydrophobic surfaces can slow down the corrosion or deterioration process on metal surfaces.<sup>7,8,17</sup> It is therefore highly desirable to create a protective superhydrophobic Al surface with large area by facile and costeffective approaches. In this work, we report an easy method to produce superhydrophobic Al surfaces by etching in CuCl<sub>2</sub>

solution to form micro-nano-pit surface textures followed by lowering its surface energy in an aqueous ethanol solution of stearic acid. The fabricated superhydrophobic Al surfaces exhibit excellent properties of anticorrosion, flexibility, and reparability, which have significance to prolong Al materials in its broad usage.

# EXPERIMENTAL SECTION

Al foils (Goodfellow, USA), copper(II) chloride (98%, Alfa Aesar), stearic acid (98%, Alfa Aesar), ethanol (absolute for analysis, Emsure, Merck KGaA, Darmstadt, Germany), sodium chloride (99%, Alfa Aesar), and acetone (99.5%, Alfa Aesar) were used for preparation of the superhydrophobic Al surfaces and characterization of the surface properties.

Al foils with the thickness of ~0.2 mm were degreased in acetone and ethanol by using the ultrasonic method, and cleaned with deionized (DI) water. Then the cleaned Al foils were immersed in CuCl<sub>2</sub> solution (5%) to carry out the etching process. The etching process was stopped when the surface of the Al foil was totally etched (e.g., for an Al foil with a size of about 5 cm<sup>2</sup> in 150 mL CuCl<sub>2</sub> solution, the suitable etching time is about 5 min). During the etching process, ultrasonic was also used to remove the Cu particles aggregated on the Al foils. After the etching process, Al foils were first

Received: October 2, 2018 Accepted: December 6, 2018 Published: December 17, 2018 rinsed with DI water and then ultrasounded with acetone for 10 min to remove the Cu particles finally. Al foils without Cu particles were dried by using nitrogen and immersed in an aqueous ethanol solution of stearic acid (0.01 M) for 10 min. After that, samples are rinsed by pure ethanol and kept in an oven at 60  $^{\circ}$ C for 1 h, and cold in air for using.

Contact angle measurements were done by using a dropshape analyzer (Sl200KB, Kino, USA) with a droplet of distilled water having a drop volume of 0.2  $\mu$ L. The experiments were repeated at five different points on each sample and the average values are calculated. Surface morphologies of samples were examined using scanning electron microscopy (Zeiss-Auriga Germany) and a confocal UV scanning laser microscope (KEYENCE, VK-9700).

To characterize anticorrosion property, the electrochemical measurements were performed by an electrochemical workstation (CHI 680) in 3.5 wt % NaCl solution at the room temperature. The measurements were conducted in a threeelectrode cell with a Ag/AgCl reference electrode and a platinum counter electrode. The sample with an exposed area of 1 cm  $\times$  1 cm serves as the work electrode. Before the electrochemical measurements, all the samples were immersed in the 3.5 wt % NaCl solution for 60 min to obtain a stable open circuit potential (OCP). Polarization curves were obtained for untreated and superhydrophobic Al surfaces by using a scan rate of 1 mV/s in the range of  $\pm$ 100 mV versus the OCP.

## RESULTS AND DISCUSSION

The Al superhydrophobic surfaces are synthesized by two steps: first roughing the surface of a cleaned Al foil by chemical etching in  $CuCl_2$  solution (5%), and then lowering the surface energy of the roughed Al foil by immersing into an aqueous ethanol solution of stearic acid (0.01 M). Detailed fabrication processes are described in the experimental part. Figure 1a,b shows the scanning electron microscope (SEM) images with sample photos (insets) of Al surfaces before and after  $CuCl_2$ 



Figure 1. SEM images and sample photos (insets) of Al surfaces before (a) and after (b)  $CuCl_2$  etching. Contact angle measurement of the Al surface without surface roughness before (c) and after (d) stearic acid modification, and Al surface with surface roughness before (e) and after (f) stearic acid modification.

etching. As can be seen, the chemical etching totally changes the morphologies of Al surfaces, which results in micro-nanopits on the surface of the Al foil. More SEM images with a large area or high magnification are shown in Supporting Information Figure S1. The cross section of laser microscope shown in Figure S2 demonstrate that the height of the micronano-pits variates to about 40  $\mu$ m. The confocal UV laser microscope image of the three-dimensional surface profile can be found in Figure S3. These structures are essential for superhydrophobicity. Without the surface roughness, water static contact angles on the Al surface before and after stearic acid modification are only about 48° and 90°, respectively, as shown in Figure 1c,d. Surface modification by stearic acid solution does not change the morphologies of Al foils, as shown in Figure S4. However, this modification is also very important to obtain the superhydrophobicity. The roughed Al surface without the chemical modification of stearic acid solution is totally hydrophilic. As shown in Figure 1e, water drops disperse immediately on the roughed Al surface upon impact, which makes it difficult to measure the static contact angle. After stearic acid modification on the rough Al surface, water static contact angle is found to be about 165°, as shown in Figure 1f. Surface modification to lower the surface energy with stearic acid solution results in the formation of a spongelike layer on the roughed Al surface due to the process of a carboxyl group that reacts with the Al atom through the following dehydration process:

# $Al^{3+} + 3CH_3(CH_2)_{16}COO^- \rightarrow Al(CH_3(CH_2)_{16}COO)_3$

Bonding of the long nonpositive end of the alkyl to the roughed Al surface creates a low energy surface, which results in the final superhydrophobic property.<sup>15,18</sup> This dehydration process is confirmed by our infrared spectra shown in Figure S5. The roll-off angles for the superhydrophobic surfaces are measured, which are less than 5°. Because of the excellent superhydrophobicity, when a drop of water is released and falls toward the superhydrophobic Al surface, the water droplet is repelled by the Al surface to such a degree that it bounces off the surface, lands again due to gravity, and bounces again and off the surface, as shown in Supporting Information Movie S1. Top- and side-view photos of a water drop locates on the surface of our prepared superhydrophobic Al foil are shown in Figure S6, which is very similar as a water drop on lotus leaves.

For the roughed Al surfaces after modification by stearic acid solution, water droplets could maintain a spherical shape on such surfaces with a water static contact angle of about 165° (Figure 1f). The droplets are repelled by the modified Al surface, and could roll off with a very small angle (Movie S1). Therefore, the Al surface exhibits superhydrophobicity and ultralow adhesion to water droplets. The cooperation between the etching-induced roughness and the low-surface-energy stearic acid layer effectively inhibits the contact between the water droplet and the hierarchical micro- and nano-scale surface. The water droplet is at the Cassie-Baxter contact state.6,7 The water droplet looks like being lifted by the hierarchical micro-nano-structures and touches just the top part of the structures. Therefore, the small contact area between the hierarchical structure and the water droplet leads to the superhydrophobicity of such roughed Al surfaces.

To check the mechanical durability of our superhydrophobic Al surfaces, we carried out the experiment of mechanical abrasion by using sandpaper (grit no. 400). As show in Figure S7, in one abrasion cycle, the Al surface with a weight of 50 g



Figure 2. Tafel plots (a) and Nyquist plots (b) of the untreated Al surface and superhydrophobic Al surface in 3.5 wt % NaCl solution.

Table 1. Corrosion Potential  $(E_{corr})$ , Corrosion Current Density  $(I_{corr})$ , Anodic Slope  $(\beta_a)$  and Cathodic Slope  $(\beta_c)$ , CR and the CIE of the Untreated Al Surface and Superhydrophobic Al Surface

sample	$E_{\rm corr}$ (V)	$I_{\rm corr}$ (A cm <sup>-2</sup> )	$\beta_{\rm a}~({ m mV/dec})$	$\beta_{\rm c}~({\rm mV/dec})$	CR (mm/year)	CIE (%)
untreated Al	-1.52	$1.11 \times 10^{-4}$	208.33	156.25	1.2099	0
superhydrophobic Al	-1.38	$6.10 \times 10^{-6}$	416.67	129.87	0.0665	94.5

was placed face-down to a sandpaper and moved for 10 cm along the ruler; and then the sample was rotated by  $90^{\circ}$  (face to the sandpaper) and moved for 10 cm along the ruler, which guarantees the surface is abraded longitudinally and transversely in each cycle. Our experiment shows that the Al surface can withstand at least 30 cycles of this sandpaper abrasion, which confirmed that the superhydrophobic Al surface has good mechanical durability to some extent.

In order to estimate the anti-corrosion property, Tafel plots were measured for untreated Al surface and superhydrophobic Al surface when the stable OCP was obtained after the samples being immersed into NaCl solution (3.5 wt %) for at least 1 h.<sup>7,8</sup> The measured Tafel plots are shown in Figure 2. On the basis of electrochemical kinetics of corrosion, the corrosion potential  $(E_{corr})$  and corrosion current density  $(I_{corr})$  can be obtained by the extrapolation method in this polarization (Tafel) plots.<sup>9,19–21</sup> The ordinate and the abscissa of the intersection of anodic slope ( $\beta_a$ ) and the cathodic slope ( $\beta_c$ ) represented the  $I_{\rm corr}$  and  $E_{\rm corr}$  values, respectively, as shown in Figure 2. The fitting slopes of the linear parts in the Tafel plots at anodic and cathodic branches are  $\beta_a$  and  $\beta_c$ , as shown in Figure S8. The values of the  $E_{corr}$ ,  $I_{corr}$ ,  $\beta_a$  and  $\beta_c$  derived from Tafel plots are summarized in Table 1. We can find that the  $E_{\rm corr}$  and  $I_{\rm corr}$  of the untreated Al surface are about -1.52 V and  $1.11 \times 10^{-4}$  A cm<sup>-2</sup>, respectively. In comparison to the untreated Al surface, the  $E_{\rm corr}$  and  $I_{\rm corr}$  of the superhydrophobic Al surface reach about -1.38 V and  $6.10 \times 10^{-6}$  A cm<sup>-2</sup>, respectively. On the basis of electrochemical kinetics of corrosion, in such Tafel curves, a more positive  $E_{corr}$ corresponds to a lower corrosion probability, while the  $I_{\rm corr}$ is a measurement of the corrosion rate (CR).<sup>9,19,20</sup> Therefore, this result demonstrates that superhydrophobic modification reduces both the corrosion probability and the CR of the Al surface obviously. The corrosion performance in our system is further evaluated by the electrochemical impedance spectroscopy (EIS) that is a powerful and complementary electrochemical technique.<sup>8</sup> Figure 2b is the EIS spectrum of the untreated Al surface and superhydrophobic Al surface by immersing in 3.5 wt % NaCl solution. It is well known that a large Nyquist loop means a low CR.8 The diameter of the

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Nyquist loop of the superhydrophobic Al surface is significantly larger than that of the normal Al surface, which indicates that the corrosion resistance has been greatly enhanced because of the superhydrophobic treatment.

On the basis of the obtained value of  $I_{corr}$  ( $\mu$ A/cm<sup>2</sup>), we can estimate the CR according to the following equations

$$CR (mm/year) = \frac{3.27 \times 10^{-3} \times I_{corr} \times M}{nd}$$

where *M* is the relative atomic mass of the metal (g/mol), *d* is the density of the metal (g/cm<sup>3</sup>), *n* is the number of electrons required to oxidize an atom of the element in the corrosion process, that is, the valence of the metal, respectively.<sup>21,22</sup> Also the corrosion inhibition efficiency (CIE) can be calculated according to the following equation

$$CIE/\% = \frac{I_{\rm corr} - I_{\rm corr}'}{I_{\rm corr}} \times 100$$

 $I_{\rm corr}$  and  $I'_{\rm corr}$  are the corrosion current densities before and after superhydrophobic modification for our Al surface, respectively.<sup>7</sup> The calculated values of CR and CIE are also summarized on Table 1. These electrochemical values demonstrate that the superhydrophobic modification really protects the surface of Al. The CR drops by 94.5% after the superhydrophobic surface treatment. The trapped air layer on the superhydrophobic surface diminishes the contact of water with the substrate interphase, which results in a barrier for the corrosion ions reaching the Al surface and corroding the metal.<sup>7,8</sup> Furthermore, the trapped air among the hierarchical micro- and nano-structures could repel the corrosion ions due to the Laplace pressure.<sup>7,8</sup> Therefore, superhydrophobic modification can slow down the corrosion or deterioration process in the Al surface.

In order to check the anti-corrosion property of the Al superhydrophobic surface more directly, we tested the untreated Al foil and superhydrophobic Al foil under a harsh environment by using  $CuCl_2$  solution (5%) as etching solution. Figure 3a shows the surfaces of the superhydrophobic and untreated Al foils before the etching test. Because of the strong diffusion of the roughed surface, the superhydrophobic Al foil



**Figure 3.** Photos of a superhydrophobic Al foil (rectangle sample at left side) and an untreated Al foil (round sample at right side) before (a) and after (b) etching by the same  $CuCl_2$  solution (5%) for 65 s, and after (c) pouring off the rest of the etching solution.

looks much darker than the untreated one. After etching by  $CuCl_2$  solutions with the same volume (4 drops) during the same time (65 s), these two Al foils display a totally different appearance. As shown in Figure 3b,c, the superhydrophobic Al surface only shows a very small etched area (the area with light brown color). By contrast, the untreated Al surface is etched seriously. Brown Cu particles are found obviously, which come from the etching of  $CuCl_2$  solution, as shown in Figure 3c. Detailed etching processes for these two foils can be seen clearly in supporting formation Movie S2. This experiment demonstrates undoubtedly that our superhydrophobic Al surface can slow down the corrosion of the Al foil even under a harsh environment.

Furthermore, our superhydrophobic Al surface is scalable. As shown in Figure 4a, it is fast and easy to fabricate such surface with a diameter of 10 cm. In addition, the superhydrophobic Al surfaces exhibit excellent flexible and repairable properties. As can be seen in Figure 4, it still retains the superhydrophobic property after flattening the crumpled Al foil (Figure 4a-d). Also the superhydrophobic property on our Al surface can be repaired. As marked by the red arrows in Figure 4, the sandpaper-abraded areas exhibit obvious hydrophilic property (Figure 4e,f). However, this hydrophilic area can easily be repaired to superhydrophobicity after roughing the surface by CuCl<sub>2</sub> solution etching and then lowering the surface energy by aqueous ethanol solution of stearic acid, which are described in experimental process and shown in Figure 4g-j. It should be noted that, during the surface repairing process, the dropped CuCl<sub>2</sub> solution only locates on the abraded hydrophilic area, as other areas are superhydrophobic (Figure 4h). After lowering the surface energy by dropping stearic acid solution, the superhydrophobic property recovers on these abraded hydrophilic areas (Figure 4i,j). This selectively repairable ability should have important significance for the



**Figure 4.** Photos of a superhydrophobic Al foil before (a) and after (b) crumpling; top-view (c) and side-view (d) photos of the Al foil after flattening with water drops; top-view (e) and side-view (f) photos of the Al foil with water drops and some areas abraded by the sandpaper show hydrophilic property (marked by red arrows); (g) top-view photos of the Al foil without water drops and with some areas abraded by the sandpaper; (h) Al foil with abraded areas that are etching by  $CuCl_2$  solution; and (i) top-view and side-view (j) photos of the Al foil with water drops after superhydrophobic modification again (the repaired areas are marked by red arrows).

practical application of superhydrophobic Al surfaces as touching and damaging the surface is unavoidable in real usage.

# CONCLUSIONS

In summary, superhydrophobic Al surfaces are fabricated by a simple approach, first etching in CuCl<sub>2</sub> solution to form a micro–nano-pits surface texture and then lowering its surface energy in an aqueous ethanol solution of stearic acid. The modified Al surfaces show water contact angles as high as 165°. Electrochemical tests demonstrate that the CR of the Al surface drops by 94.5% after these treatments (corrosion current density lowers from  $1.11 \times 10^{-4}$  to  $6.10 \times 10^{-6}$  A cm<sup>-2</sup>). We also show that the superhydrophobic surface will protect the Al from corrosion even under a very harsh environment. In addition, our method is scalable and the superhydrophobic surfaces exhibit excellent flexible and reparable properties. This anti-corrosive superhydrophobic Al surface will prolong Al in its broad usage.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsome-ga.8b02631.

Additional SEMs, laser microscopy images, photos, Tafel plots, and Movies of samples (PDF)

Release of a drop of water toward the superhydrophobic Al surface which is repelled by the Al surface (AVI) Detailed etching processes for two foils (AVI)

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#### Notes

The authors declare no competing financial interest.

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