A simple way to fabricate an aluminum sheet with superhydrophobic and self-cleaning properties*

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A superhydrophobic aluminum sheet is fabricated via a hot water immersing process and subsequently surface modification with heptadecafluorodecyltrimethoxy-silane (HTMS). As revealed by the scan electron microscopy (SEM), X-ray diffraction (XRD), and Fourier-transform infrared spectrophotometer (FTIR) results, a rough pseudoboehmite film is formed on the aluminum sheet, and HTMS molecules are grafted on the film surface successfully. These two factors make the treated aluminum sheet present superhydrophobicity with a water contact angle larger than 160° and sliding angle less than 5°, and possess a self-cleaning property. Furthermore, the flexible superhydrophobic aluminum sheet could be pasted to a cylinder surface without destroying its superhydrophobicity. At the end, the effect of hot water treatment time on superhydrophobicity is investigated.

Keywords: superhydrophobic, self-cleaning, surface modification

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1. Introduction

Superhydrophobicity is a special wettability of a solid surface. One of the most perfect examples in nature is the lotus leaf, which shows good self-cleaning and water-repellent properties. Due to the potential applications, such as self-cleaning,[1,2] anti-fog,[3] corrosion barrier, and so on,[4–6] superhydrophobicity has aroused a lot of interest among researchers from the circles of fundamental science and industry. It has been realized that surface roughness and surface energy are two important factors affecting the wettability. To be superhydrophobic, a surface should have both high surface roughness and low surface energy.[2,7] Surface roughening and modification with low surface energy material are basic routes to fabricate superhydrophobic surfaces.[1–3,8,9]

Aluminum and its alloys are important engineering materials. They have been widely used in marine, airplane, power line and building construction, etc. It is believed that the superhydrophobic surfaces will not only endow these engineering materials with self-cleaning properties, but also enhance their anti-corrosion/icing abilities.[4–6,10–14] Recently, a number of studies, focusing on fabricating superhydrophobic surfaces on these engineering materials, have been conducted. For example, Guo *et al.*[15] have fabricated a superhydrophobic surface on aluminum and its alloy by a chemical etching method, Meng *et al.*[12] and Xi *et al.*[16] have reported on a general approach to fabricating the superhydrophobic surfaces on engineering materials by immersing them in perfluorocarboxylic acid for a couple of days or putting them into an electrodeposition system containing perfluorocarboxylic acid. Cho *et al.*[17] have constructed a superhydrophobic surface on aluminum foil by anodic oxidation method. These studies have paved the way for fabricating a superhydrophobic surface on engineering materials. However, there are some disadvantages which need to be overcome, such as time consumption and the safety of the chemical etching process.

In this paper, we bring a simpler way to prepare an aluminum sheet with superhydrophobicity and self-cleaning properties. As shown in Fig. 1, the fabrication process includes two convenient steps: hot water immersing treatment and low surface energy material modification. After water treatment for 2 h and surface modification, the aluminum sheet shows good su-

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perhydrophobicity with water contact angle (WCA) greater than 160° and water sliding angle (WSA) less than 5° for 8-μL water droplet. It also shows perfect self-cleaning property. When the water droplet is dropped on the treated aluminum sheet covered with soil mesh, it rolls off the surface and carries soil mesh away. Additionally, the flexible superhydrophobic aluminum sheet could be easily pasted to cylinder substrates without destroying its superhydrophobicity. Finally, the effect of hot water treatment time on the aluminum superhydrophobicity is also investigated.

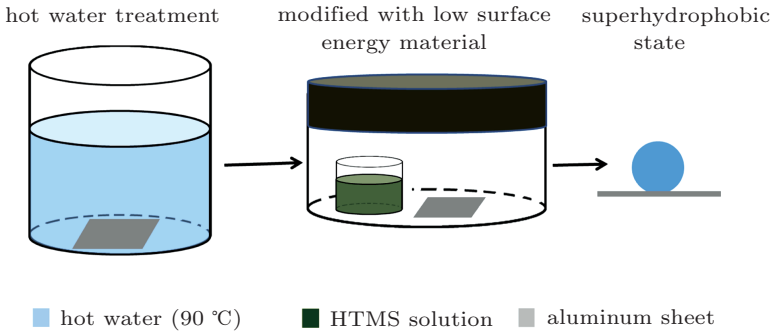


Fig. 1. (colour online) Schematic illustration of the experimental process to fabricate a superhydrophobic aluminum sheet.

2. Experiment

2.1. Materials

Aluminum foil (99.0%, 0.1-mm thick), ethanol (C_2H_5OH, 99.0%), acetone (C_3H_6O, 99.0%), and Toluene (C_7H_8, 98.5%) are purchased from Sinopharm Chemical Regent Co. Ltd. (Shanghai, China). Heptadecafluorodecyltrimethoxy-silane (HTMS) is bought from Dow Corning Co. (USA). Deionized water with resistance as high as 18.25 MΩ·cm was used in the whole experimental process.

2.2. Sample preparation

The main process to fabricate a superhydrophobic aluminum sheet is shown in Fig. 1. The details are as follows. Firstly, the aluminum sheets were ultrasonically treated successively in acetone and ethanol for 5 min. The cleaned specimens were dried by N_2 flow. Secondly, the specimens were immersed into hot water (90 °C) for a certain time as shown in Table 1. Then, the samples were taken out and rinsed with water. After being dried in air, the treated aluminum sheets and 1-mL HTMS toluene solution (5 V%) were sealed in a weight bottle, and placed in an oven at 80 °C for 3 h to reduce the surface energy of the aluminum sheet. Then the samples were taken out and cooled down to room temperature in the fuming hood.

Table 1. Experimental and superhydrophobicity parameters of the samples.

Sample name	Water temperature/°C	Immersion time/h	WCA/(°)	WSA/(°)
90-0.5	90	0.5	165.6	3.0
90-1	90	1	165.9	3.1
90-1.5	90	1.5	166.6	4.7
90-2	90	2	165.1	4.9
90-4	90	4	158.6	7.7

2.3. Characterization

The morphologies of the as-prepared samples were investigated by using a scanning electron microscope (SEM, JSM-5600LV, JEOL Ltd, Japan). Water contact and sliding angles were characterized by the CAST2.0 contact angle analysis system (Solon Information Technology Co. Ltd., Shanghai, China) in am-

bient atmosphere at room temperature. An 8-μL water droplet was dropped on the aluminum sheet to test static contact angle and the sliding angle. The water contact angle and sliding angle measurements were repeated five times for each sample, and the mean values were reported. The X-ray diffraction (XRD, MXPAHF, MAC Ltd., Japan) test was carried out with Cu Kα radiation ($\lambda = 1.54506$ Å, 1 Å=0.1 nm). Fourier-transform infrared spectrometer (FTIR, 8700, Thermo Nicolet Co. USA) was used to characterize the surface chemistry.

3. Result and discussion

3.1. Morphology and crystal phase

Figure 2 shows the scanning electron microscopy (SEM) images of an untreated aluminum sheet (Fig. 2(a)) and the sample 90-2 at different magnifications (Figs. 2(b)–2(d)). It could be clearly seen from Figs. 2(b)–2(d)) that three types of structures are formed on the aluminum sheet: (i) nano-sheets, (ii) embossments and holes covered by nano-sheets, (iii) micro-rods. The sheet is uniformly covered by the nano-sheets, which are all about 30-nm thick and about 500-nm wide, as shown in Fig. 2(d). As the nano-sheets intersect with each other, forming the cauliflower-like structure, a lot of air pockets were formed between the nano-sheets. This will increase the surface roughness of the aluminum sheet, and reduce the solid fraction of the surface. The formation of air pockets should benefit the superhydrophobic property of the treated aluminum sheet.

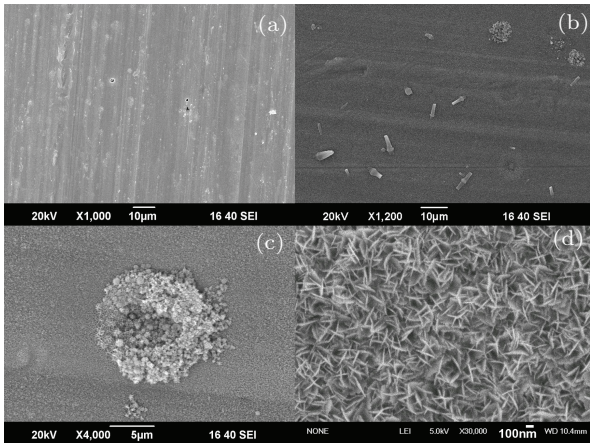


Fig. 2. The SEM images of the untreated aluminum sheet (a), the sample 90-2 at different magnifications ((b), (c), and (d)).

Comparing the two curves in Fig. 3, it could be clearly found that there are two new tiny peaks in curve *b*. The two peaks centre at 28.21° and 48.94° corresponding to a boehmite phase (JCPDS NO. 83-2385). Broadening of the XRD peaks and low intensity indicate that the film formed on the aluminum sheet is pseduoboehmite.[18,19] The pseudoboehmite phase is poor crystalline boehmite, and has a general formula of $Al_2O_3{\cdot}xH_2O$, $1 < x < 2.1$. As seen from Fig. 4, it could be also confirmed that the rough film formed on the aluminum surface is in pseudoboehmite phase, as the FTIR absorption bands at 3280, 3090, and 1090 cm^{-1} are due to the pseudoboehmite.[20]

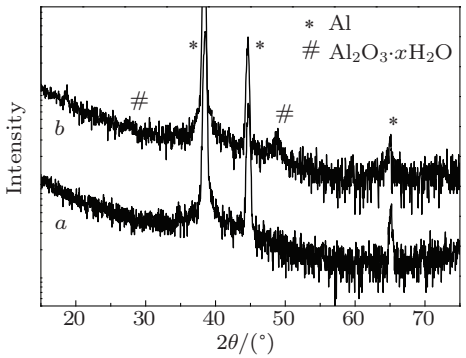


Fig. 3. The X-ray diffraction patterns of the untreated aluminum sheet curve *a* and the sample 90-2 curve *b*.

According to the previous report of Vedder and Vermilye,[20] the nano-sheets covered on the aluminum sheet are the products of the reaction between hot water and the amorphous oxide layer of the aluminum sheet. Firstly, the oxide layer is dissolved in hot water. Then, vertical pseudoboehmite nano-sheets grow on the aluminum sheet. As shown in Fig. 2(a), some holes and embossments exist on the aluminum sheet. During the hot water treatment, the nano-sheets are formed on the surface of holes and embossments, just as they are formed on the flat aluminum sheet. As a result, the embossments and holes covered by nano-sheets are formed on the aluminum sheet surface.

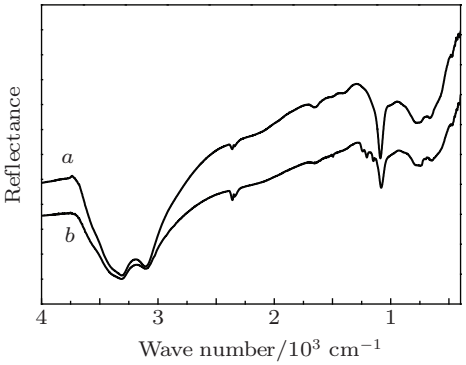


Fig. 4. The FTIR spectra of the as-prepared sample 90-2 curve *a* and the after modification with HTMS curve *b*.

3.2. Wettability of the treated aluminum sheets

Comparison between the FTIR spectra in Fig. 4 shows new absorption peaks between 1120 cm^{-1} and 1350 cm^{-1} are present in the modified sample. These peaks arise from the C–F stretching vibration of $–CF_2$- group.[21] This result indicates that the HTMS molecules are adsorbed on the sample successfully. It coincides with the different wettabilities of the modified and unmodified samples as shown in Fig. 5. Both the untreated aluminum sheet and sample 90-2 show different wettabilities before and after surface modification: the untreated aluminum sheet changes from hydrophilicity (WCA 80°, Fig. 5(a)) to hydrophobicity (WCA 113°, Fig. 5(c)), while sample 90-2 changes to superhydrophobicity (WCA 165.1° and WSA 4.9°, Fig. 5(d)) from superhydrophilicity (WCA close to 0°, Fig. 5(b)). Additionally, there are some differences in wettability between the untreated aluminum sheet and sample 90-2. These differences can be ascribed to their different surface structures.

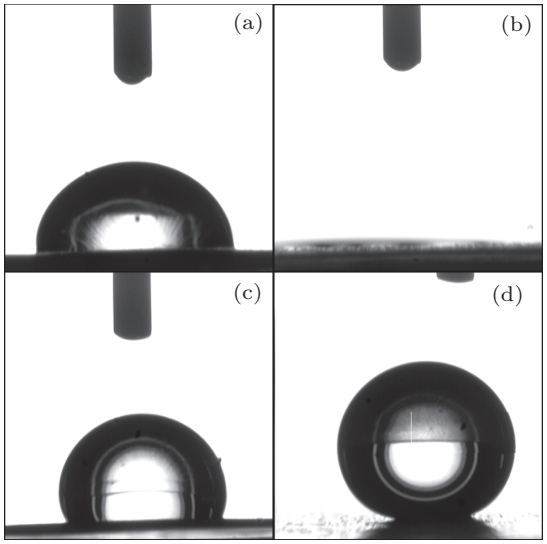


Fig. 5. Optical pictures of a water droplet contacting aluminum sheet (a), sample 90-2 (b), HTMS modified aluminum sheet (c), and HTMS modified sample 90-2 (d).

According to Wenzel model[22]

$$\cos\theta_{\rm r} = r\cos\theta_{\rm s}, \tag{1}$$

in which $\theta_{\rm r}$ is the apparent WCA on a rough surface, while $\theta_{\rm s}$ is the intrinsic WCA on a flat surface, and r is the surface roughness factor. Because r is always larger than 1, it could be calculated from Wenzel model that increasing surface roughness can enhance both the hydrophilicity and the hydrophobicity of the surfaces depending on the intrinsic wettability of the surface. After immersing the sample 90-2 in hot water, a lot of nano-sheets were formed on the sample 90-2 surface (Fig. 2(d)). Compared with the surface roughness of the untreated aluminum sheet, the surface roughness of sample 90-2 is increased. As the pseudoboehmite is intrinsically hydrophilic, the sample 90-2 presents a superhydrophilic property.

After modification with HTMS, sample 90-2 has the self-cleaning properties with high WCA and low WSA. This property could be explained by using the Cassie–Baxter model,[23,24]

$$\cos\theta_{\rm r} = f(\cos\theta_{\rm s} + 1) - 1, \tag{2}$$

where $\theta_{\rm r}$ is the apparent WCA on the heterogeneous surface, $\theta_{\rm s}$ is the WCA on the flat surface coated with HTMS ($\theta_{\rm s} = 114°$ in this experiment as reported by Gong),[25] and f is solid (water–solid contact) fraction of the surface. It could be deduced from the Cassie–Baxter model that reducing (increasing) water–solid contact fraction of the surface (f) will make the contact angle increase (decrease). As the nano-sheets vertically grew on the aluminum sheet, a lot of air pockets were formed. That means that the solid fraction of sample 90-2 surface was reduced. Consequently, the hydrophobicity of the sample 90-2, which has been grafted with HTMS molecules, should be enhanced. The experimental data accord well with the deduction as the sample 90-2 shows superhydrophobicity with WCA 165.1° and WSA 4.9°. It also could be calculated from Eq. (2) that the water–solid contact fraction of sample 90-2 surface is 5.7%. This result indicates that 94.3% of the contact area between water and sample 90-2 is air. That implies that the water droplet just suspends on the air film trapped between the nano-sheets. As a result, the water droplet minimizes its surface tension and interfacial energy by keeping a sphere-like configuration.

3.3. Effect of immersion time on the wettability of the aluminum sheet

The samples, which were immersed in hot water for different times, exhibit similar morphologies. The surfaces of different samples are all covered with three types of structures similar to that of sample 90-2. However, the numbers of microrods covering their surfaces are different. As shown in Fig. 6, all the samples are covered by the pseudoboehmite nano-sheets. But the number of microrods on the surfaces is increased

with increasing immersion time. There are just a few microrods on the sample 90-0.5, but a lot of microrods on the sample 90-4. In some parts of the surface covered by the microrods, the contact area between the water droplet and the sample will increase, which, as deduced from the Cassie–Baxter model, will result in the decrease of the contact angle.

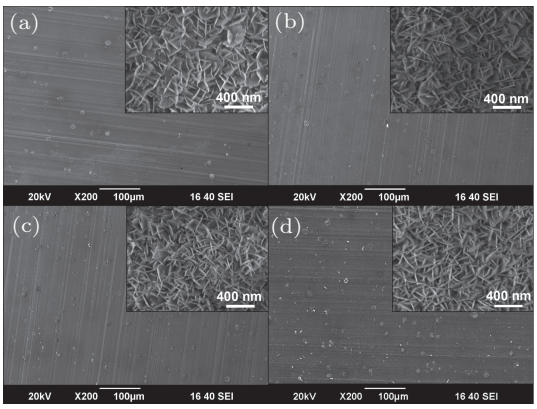


Fig. 6. The SEM images of samples 90-0.5 (a), 90-1 (b), 90-1.5 (c), and 90-4 (d), with the insets showing the enlarged part of the picture of each of the samples.

Figure 7 shows the effect of immersion time on the wettability of the sample. When the immersion time is less than 1.5 h, the samples show similar superhydrophobicities with WCA around 166°, WSA less than 5°. Then, the WCA will decrease with prolonging the immersion time. As the immersion time increases to 4 h, the WCA of sample 90-4 decreases to 158.6° and WSA increases to 7.7°. This phenomenon could be explained as illustrated in Fig. 8, and should be related to the microrod coverage.

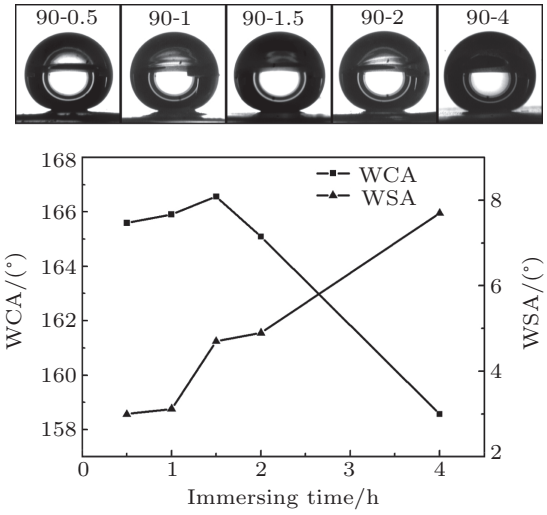


Fig. 7. Plots of immersion time-dependent WCA and WSA values.

By comparing Figs. 8 (a) and 8(b), it can be clearly seen that the microrods covering the sample surface will increase the solid-water contact fraction of surface (f). As the other conditions are not changed, this will result in the reduction of the WCA as deduced from the Cassie–Baxter model. At the same time, the increasing contact area between water and solid surface will enhance the attraction between the water droplet and the surface, which will result in bigger WSA.[26–28] When the immersion time is less than 2 h, there are no remarkable differences among the samples. So they could show similar superhydrophobicities. However, when the immersion time increases to 4 h, the surface of the sample changes a lot by the microrods. It can be seen from Fig. 7 that the water droplet on sample 90-4 has a bigger contact area than others. As mentioned above, bigger f will affect the superhydrophobicity of the surface, and makes the WCS decrease to 158.6° and the WSA increase to 7.7°. The experimental phenomenon coincides well with the Cassie–Baxter model. To obtain the best superhydrophobic aluminum sheet, the immersion time of the aluminum in hot water should be less than 2 h.

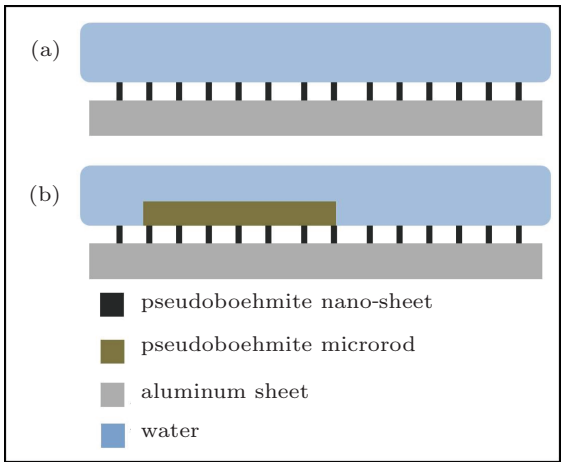


Fig. 8. (colour online) Schematic illustration of the effect of the microrod on wettability (the partial pictures of the water droplet contacting the treated aluminum sheets): (a) without and (b) with microrods covering the aluminum sheet. The coverage of microrods on aluminum sheet will increase the contact area between water and the aluminum sheet.

3.4. Self-cleaning properties

The samples also show great self-cleaning property. As shown in Figs. 9(a) and 9(b), a layer of soil mesh was sprinkled on treated aluminum sheet surface. Then a water droplet was dropped on the sample surface. When the water droplet contacted the sample, it just rolled off and carried the soil meshes

away, leaving a clean surface. Additionally, the aluminum sheet is very flexible and can be pasted to other substrates without destroying its superhydrophobicity. As shown in Fig. 9(c), the water droplets just bounced up as they rushed onto the treated aluminum sheet, which covered a measuring cylinder surface. That means the treated aluminum sheet could be used on non-flat object surfaces.

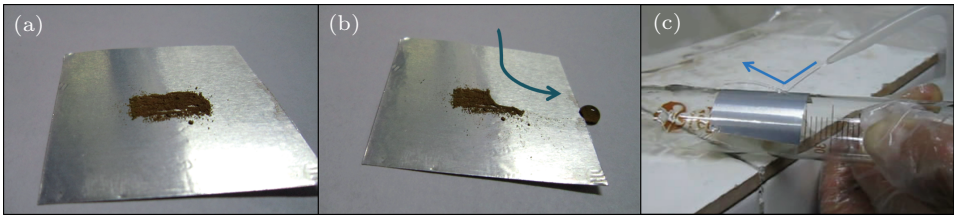


Fig. 9. (colour online) Optical pictures of the soil mesh on the treated aluminum sheet before (a) and after (b) a water droplet has passed by, and (c) the aluminum sheet pasted to graduated cylinder without destroying its superhydrophobicity.

4. Conclusion

We demonstrated a simple method to fabricate a superhydrophobic surface on an aluminum sheet by immersing it into hot water and subsequently surface modification. The treated aluminum sheets showed great superhydrophobic and self-cleaning properties. To produce the treated aluminum sheets with the best superhydrophobicity, the immersion time of the aluminum sheet in hot water should be less than 2 h. The whole fabricating process is not only easy to control, but also time saving. At the same time, the treated aluminum sheet could keep its superhydrophobicity after being bent. This property will expand the usage of the treated aluminum sheet to non-flat objects. These great properties make this method an excellent candidate to fabricate a superhydrophobic surface on an aluminum sheet for large scale application.

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