

DEVELOPMENT OF FRACTAL ULTRA-HYDROPHOBIC COATING FILMS TO PREVENT WATER VAPOR DEWING AND TO DELAY FROSTING

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Abstract

Superhydrophobic films fabricated on copper and aluminum surfaces have potential applications to solve water condensation and frosting problems on chilled ceiling system. The rough surfaces of copper foils obtained by solution immersion method exhibit the existence of fractal structures. The hydrophobicity of copper surfaces is enhanced with fractal structures. The relationship between contact angles (CAs) and the fractal dimensions (FDs) for surface roughness of Cu samples with different etching time is investigated. Moisture condensation and frosting experiments on the two kinds of surfaces are conducted in natural environment under different chilling temperatures. During condensation, micro water condensate droplets drift down the surface like dust floating in the air. Several larger condensate droplets about 1–2 mm appear on the substrates after 3 h condensation. This continuous jumping motion of the condensate will be beneficial in delaying frosting. The results demonstrate that dense nanostructures on copper surfaces are superior to loose lattice-like microstructures on aluminum surfaces for preventing the formation of large droplets condensate and in delaying the icing. The large water droplets

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of 2–3 mm in diameter that would form on a common metal foil are sharply decreased to dozens of microns and small droplets are formed on a modified surface, which will then drift down like a fog.

Keywords: Superhydrophobicity; Surface Roughness; Fractal Dimension; Preventing Droplets Condensate; Delaying Frosting.

1. INTRODUCTION

Recently, chilled ceiling has been widely applied in air conditioning as it has many advantages such as energy savings, thermal comfort and low operation cost.¹ However, moisture condensation on the chilled ceiling surfaces has been the main problem that limits the application and dissemination of this air conditioning system. Water droplets will form when moisture condensates on chilled surfaces. They will grow up and finally drift down the surface leading to the occupant complaining about these large water droplets. The generally adopted method to avoid dew point condensation is to make the cooling ceiling temperature a little bit higher than the dew point. This method will increase the investment that is required to obtain enough cooling capacity. Many researchers had proposed various ways to solve this problem.^{2–5} However, they are complicated and the reliability is questionable.

A novel strategy to delay or prevent the formation of water condensates is to change the wettability of the ceiling surfaces. Superhydrophobic surfaces have attracted large attention for their potential applications in our lives.^{6–8} Dropwise condensation can be realized on superhydrophobic surfaces. This kind of condensation state is superior to filmwise mode. Dropwise condensation enables droplets to fall off from the substrate in smaller sizes⁹ and transfer the majority of heat from surface, leading to a higher heat transfer coefficient.^{10,11} Many factors may affect the mobility of condensate drops. Chen *et al.*⁹ found that superhydrophobic property was retained after condensation on a two-tier texture surface. A rapid removal of condensate droplets was realized in this surface. A surprising out-of-plane jumping motion of the coalesced drops was observed on this surface. The speed of jumping droplet was as high as 1 m/s.¹² Feng *et al.*¹³ investigated the influence of surface roughness and chemical properties on the spontaneous motion of condensate droplets. However, the surface structures such as micro and nanostructures

also have great influence to this motion, which will be discussed in this work.

The self-propelled jumping behavior of condensate droplets also opens up the possibility to fabricate the anti-icing surfaces.^{8,14,15} This will be important to avoid various problems caused by icing. Thus, moisture condensation and frosting experiments are both conducted in our work. Micro/nano structures are necessary to obtain superhydrophobicity. The surfaces showing fractal structures can enhance the water-repellent property.¹⁶ Simple solution immersion methods are adopted to fabricate nanostructures on copper surfaces and microstructures on aluminum alloy surfaces. Fractal patterns form on the surfaces of copper foils after being etched in an acid solution. The hydrophobicity of copper surfaces is enhanced with fractal structures. In this paper, atomic force microscopy (AFM) images are used to obtain power spectral density (PSD) graphs and/or fractal dimension (FD). PSD analysis correlates the vertical amplitude with the spatial frequency of surface features, revealing the characteristics of the surface structure. FD is a dimensionless number that describes the complexity of the object's structure and strongly corresponds to visual perception of roughness.¹⁷ The two parameters are used to describe the morphology characteristics of a solid surface. This method provides an advanced description of surface patterns. The relationship between contact angles (CAs) and FDs for surface roughness of Cu surfaces with different etching time is discussed. Moisture condensation and frosting experiments on copper and aluminum surfaces are carried out in natural environment under different temperatures. Condensate droplets forming on these superhydrophobic surfaces drift down continuously like a fog. The effect of preventing the formation of large condensate droplets is obtained in this paper. The effect of different surface structures on preventing the formation of large condensate droplets and in delaying frosting is investigated. This study will be helpful to design surface structures for anti-condensation and anti-icing.

2. EXPERIMENT SETUP

2.1. Preparation of Nanostructured Superhydrophobic Films on Copper Foils

The details of preparing nanostructures on copper surfaces had been reported in literatures.^{18–20} Copper foils with sizes of 40 mm × 25 mm × 0.1 mm (Sinopharm Chemical Reagent Co. Ltd., Shanghai, P. R. China; purity 99.8%) are immersed in 4 mol/L hydrochloric acid solution for 1 min. They are then ultrasonically cleaned with ethanol for 5 min. The cleaned copper foils are then immersed in 100 mL solution for about 15–120 min in room temperature, which is prepared by mixing 2.5 M NaOH solution with 0.13 M (NH₄)₂S₂O₈ solution. Cu-*x* represents the copper samples with different etch time, where *x* is the etch time. The copper samples are taken out. They are then rinsed with deionized water and dried in air. The superhydrophobic property of copper foils is strengthened by immersing these samples in a 20 g/L ethanol solution of steric acid for 24 h, followed by drying at 60°C for 1 h.

2.2. Preparation of Micro-Structured Superhydrophobic Films on Aluminum Alloy Foils

The details of fabrication of superhydrophobic film on alloy foils can be found elsewhere.²¹ First, the aluminum alloys are immersed in 3.5 M hydrofluoric acid for 10 min to remove the surface oxide layer. They are then cleaned with deionized water and dried in air. These cleaned samples are etched in an acid solution for 2.5 h. The solution is prepared by mixing 0.08 mol/L oxalic acid solution with 1.0 mol/L hydrochloric acid solution with the same volume ratios. After that, these samples are washed with deionized water for several times and dried. Finally, 20 g/L steric acid ethanol solution is used to lower the surface energy of the surface to further strengthen the hydrophobicity of these surfaces.

2.3. Condensation and Frosting Experiments

Moisture condensation on copper and aluminum foils before and after modification is carried out in natural environment with 0°C cooling bath. Frosting experiments are conducted on copper and

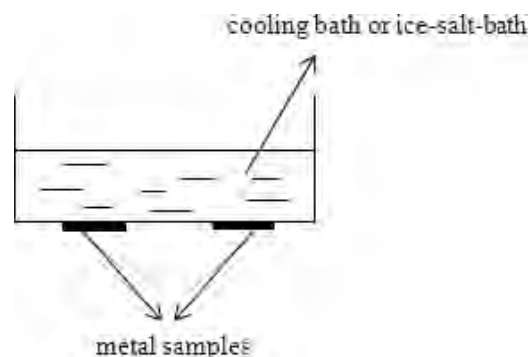


Fig. 1 Schematic of condensation and frosting experiment devices.

aluminum foils under -15°C by ice-salt bath. The condensation and icing situations are recorded at different time intervals. The schematic of experiment devices is shown in Fig. 1.

2.4. Characterization

The wettability of samples is measured by DataPhysics OCA 20 CA system at ambient temperature with a 4 μL droplet. Four different sites are measured on each sample. The mean value is taken as the final result. The surface morphology of prepared samples is observed by scanning electron microscope (SEM, S-3700N, HITACHI, Japan).

AFM images are acquired by standard AFM tapping mode using a commercial AFM probe (Tap 300 Al). The FDs of samples are obtained by analyzing the AFM images of samples. SCPM Imager analysis software is used to obtain the PSD. The SCPM Imager is an image processing software of scanning probe microscope. The software and scanning probe microscope are manufactured by Benyuan Nano-instrument Co., Ltd. The slope of a linear fit through data on a logarithmic plot of PSD versus the spatial frequency is obtained to calculate the FD of each sample according to the following equation: $FD = 0.5 * (7 - \beta)$, where β represents the absolute value of the slope.¹⁷

3. RESULTS AND DISCUSSIONS

3.1. Nanostructures Formed on Copper Surfaces

It is a facile and effective method to fabricate nanostructures on metal surfaces with controllable morphology.¹⁸ The surface structures of copper foils with different reaction time are observed by SEM and presented in Fig. 2. Different morphologies

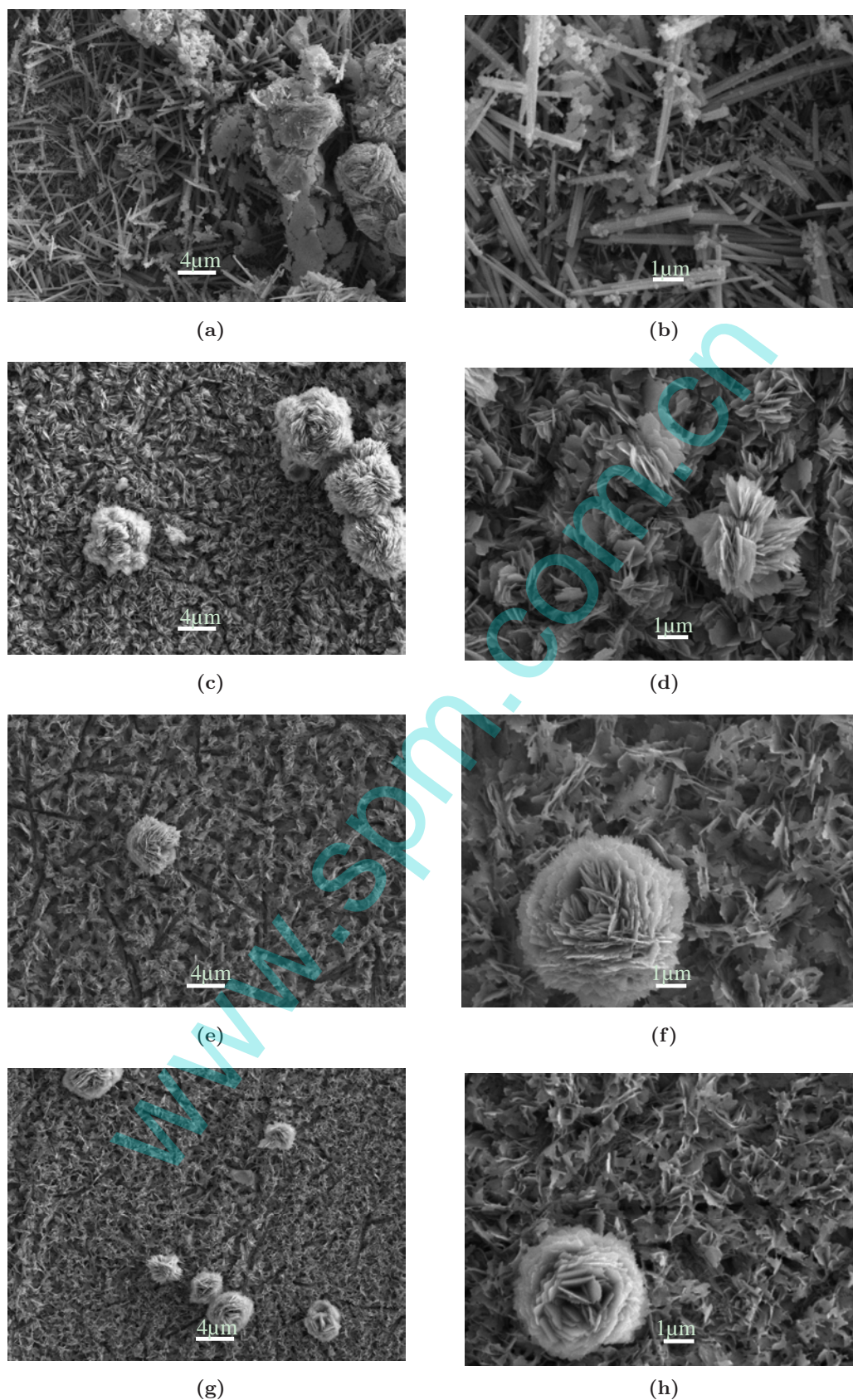


Fig. 2 SEM images of coppers after being immersed in an aqueous solution by mixing 2.5 M NaOH and 0.13 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ for different reaction time: (a), (b) 15 min (Cu-15); (c), (d) 60 min (Cu-60); (e), (f) 90 min (Cu-90); (g), (h) 120 min (Cu-120). (a), (c), (e), (g): Low magnification and (b), (d), (f), (h): high magnification.

including nanorods, nanosheets and microflowers are formed on copper surfaces as immersion time varied. In the early stage, nanorods cover a large area of copper substrate as shown in Figs. 2a and 2b. They then turn to sheet-like structures. When the reaction time is longer than 60 min, these sheets become sharper while their inter-sheets distances are smaller with reaction time (see Figs. 2d and 2f). Microflowers with diameters of 2–8 μm are sparsely distributed in all samples. With a prolonged reaction time of about 2 h, the shapes of these microflowers are maintained. Chen *et al.*²⁰ found that flower-like CuO were formed synchronously during the growth of nanorods. He also found the transition of Cu(OH)₂ nanorods to nanotubes happened when the duration was 60 min. This is markedly different from our experiments. A transition of Cu(OH)₂ nanorods to CuO nanosheets is observed in this work. This is consistent with the literature (when the etch time is 3 h, Cu(OH)₂ nanorods turn to CuO nanoslices).²⁰ The time of transition of nanostructure morphology is shortened (60 min in this paper). One reason is the different reaction temperatures in our experiments. The heat released by the dissolution of sodium hydroxide would increase the temperature of the etching solution. Thus, the initial reaction temperature is about 50°C which is higher than the temperature (room temperature) used by Chen. A high reaction temperature may lead to a different morphological transformation because of the metastable nature of Cu(OH)₂ and CuO nanoribbons.²² The other reason is the higher concentration of ammonium persulfate. The formation of Cu(OH)₂ and CuO nanostructures on copper surfaces involves inorganic polymerization (polycondensation) reactions under alkaline and oxidative conditions. The amount of oxidant (NH₄)₂S₂O₈ has an effect on the structures of products.¹⁸ It can shorten the oxidation time of copper foils.²⁰ No blue region is observed on the sample surface when the duration is 60 min. Thus, the black CuO nanosheets are the main morphology.

3.2. Fractal Features on Superhydrophobic Copper Surfaces

The disordered rough structures of copper surfaces exhibit fractal features. The FD can be evaluated as $D = D_{\text{cross}} + 1$, where D_{cross} is the FD of cross-sectional SEM images by box-counting method.¹⁶

However, the cross sections of copper samples are difficult to obtain without destroying their nanostructures, especially for these pure coppers. They are soft, even in 60° below zero. The liquid nitrogen extraction method is not feasible to obtain the cross sectional structures. Thus, the SEM images are unable to evaluate the FDs.

To solve the problem, AFM images are used in this paper. The FDs of samples are obtained by analyzing the AFM images of samples. The dimension of surface roughness can be determined by the equation: $FD = 0.5 * (7 - \beta)$, β is the slope of a linear fit through data on a logarithmic plot of PSD versus the spatial frequency.¹⁷ The AFM image of Cu-90 (AFM images in Fig. 3c) is used as an example to calculate the FD. The logarithmic plot is plotted in Fig. 4. It should be noted that the relatively good linear relationship between PSD and frequency on the logarithmic scale is only over a limited range of length. The reason is that the pattern in a real surface may not be fractal as a whole. The self-similarity of Cu surface with micro/nano structures is satisfied over a limited range of length. The FD of Cu-90 min is 2.71 with the slope of 1.578 (Fig. 4). The values of FD of other copper foils with changed etching time are listed in Fig. 5.

The CAs and FDs for surface roughness of Cu samples vary with the etching time of Cu samples. The hierarchical structures lead to a robust superhydrophobic property after being modified with steric acid. The wettability of these foils with different durations is evaluated by static water CA. The volume of the water droplet used for CA measurements is 4 μL . Such small droplet can eliminate the measuring deviation of CA caused by gravity deformation. The wettability of the surface changes from hydrophilic to superhydrophobic after chemical etching and modifying with steric acid. When the etching time is 15 min, the nanostructures sparsely distribute on the surface. Some areas may be bare without nanostructures which will lead to a small CA (149.5° in Fig. 5). When the reaction time is longer than 60 min, these sheets become sharper while their inter-sheets distances are smaller with reaction time (Figs. 2d and 2f). The structures capturing more air are beneficial to decrease the rate of liquid and solid contact area. Thus, the CAs of these samples increase when the etching time is prolonged.

FD is a parameter that represents the complexity of structure contour. Overall, the FDs increase as the etch time is longer (Fig. 5, except for the sample

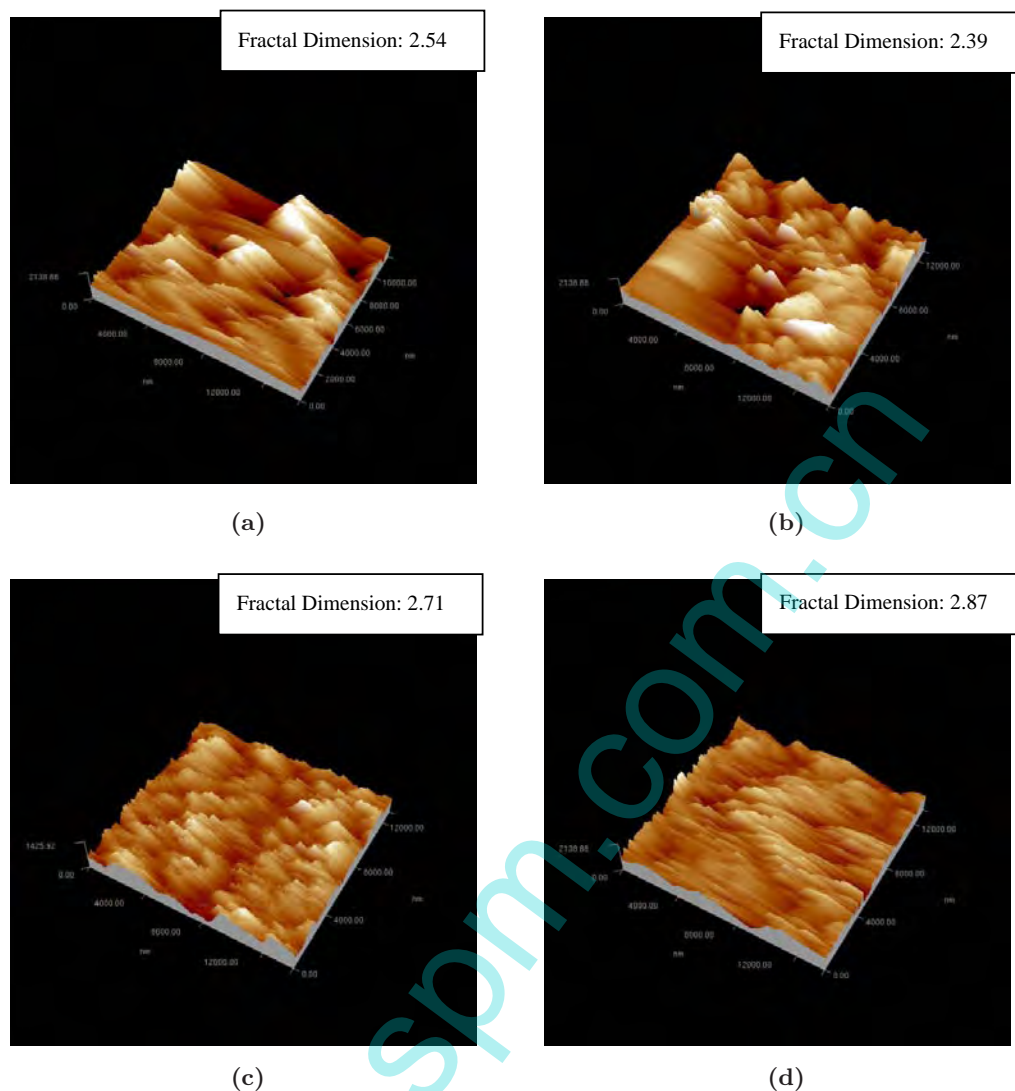


Fig. 3 3D AFM images of coppers after being immersed in an aqueous solution of 2.5 M NaOH and 0.13 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ for different reaction time: (a) 15 min (Cu-15); (b) 60 min (Cu-60); (c) 90 min (Cu-90); (d) 120 min (Cu-120).

of Cu-15). The reason is that the surface structures are more dense and rough as the etching time is prolonged, which can be observed in the SEM images in Fig. 2 (the edges of nanosheets become shattered as etch time prolongs). It is worth noting that the FD of Cu-15 is larger than Cu-60 which can be due to the different surface structures. The surface of Cu-15 consists of unevenly distributed nanorods, microflowers and small needle-like fragments in the bottom of nanorods (Fig. 2b). The richer structure contour leads to a larger FD. When the etching time is longer, the surface morphologies of copper foils become more similar. In addition to the microflower, only sheet-like structures with similar outlines appear in the surfaces (Figs. 2d and 2f). Thus, the DF of Cu-15 is larger than Cu-60.

In a word, the change trends of CA and FD with etching time of copper samples are similar (Fig. 5). When the time is prolonged, the CAs and FDs of surface roughness increase. The hydrophobicity of copper surfaces is enhanced with fractal structures. The larger FD of Cu-15 than Cu-60 may be due to the different nanostructures of the two surfaces.

3.3. Microstructures Formed on Aluminum Alloy Surfaces and Superhydrophobic Property

Aluminum is an active metal. Usually, an oxide layer grows on its surface to prevent further reaction. Hydrofluoric acid is used to remove the oxide

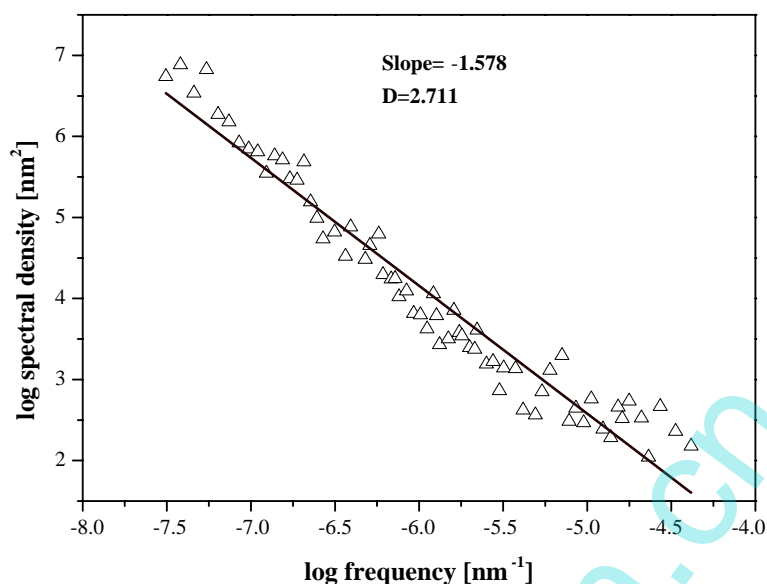


Fig. 4 The PSD analysis for the copper sample with an etching time of 90 min.

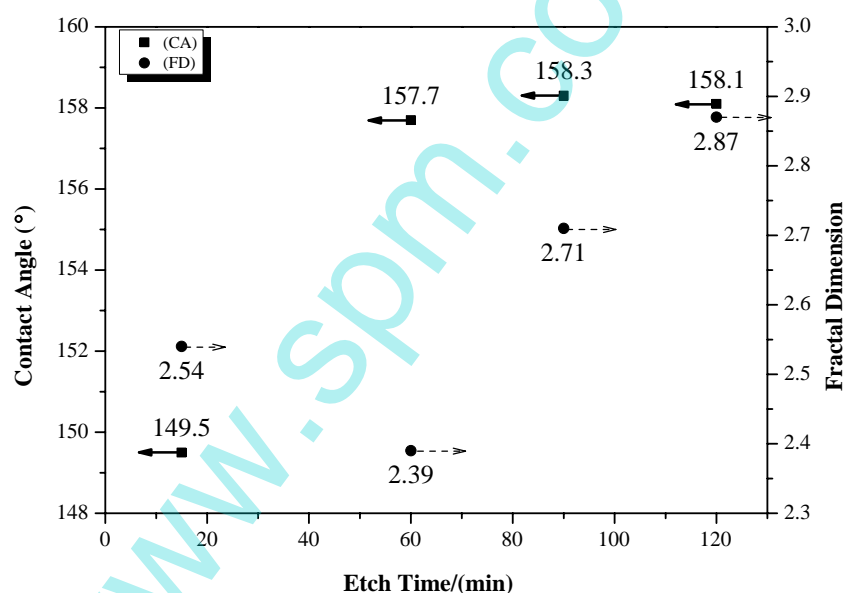


Fig. 5 The relationship between CAs and the FDs for surface roughness of Cu samples with different etching time.

layer before acid etching. Oxalic acid is added to the reaction solution because it is easier to control the morphology of aluminum surface.²¹ Figures 6a and 6b are SEM images at low and high magnification of aluminum alloy after being immersed in the mixture solution of hydrochloric acid and oxalic acid for 2.5 h. The concave-convex lattice-like microstructures distribute on the sample surface. The FD of etched aluminum alloy is 2.69 (Fig. 6e). The microstructures rather than nanostructures formed on aluminum surface may increase

the FDs of samples with larger surface roughness. On the other hand, more dense nanostructures formed on the copper surface as the prolonged etch time will increase the FD. Thus, the FD of aluminum is larger than copper sample Cu-60 and smaller than Cu-90. The CA of the sample is 158.6° after steric acid modification. While flat aluminum alloy without any modification is hydrophilic with a CA of 77.4°. However, the static CAs of modified aluminum and copper surfaces are similar. Two factors influence the superhydrophobicity, namely,

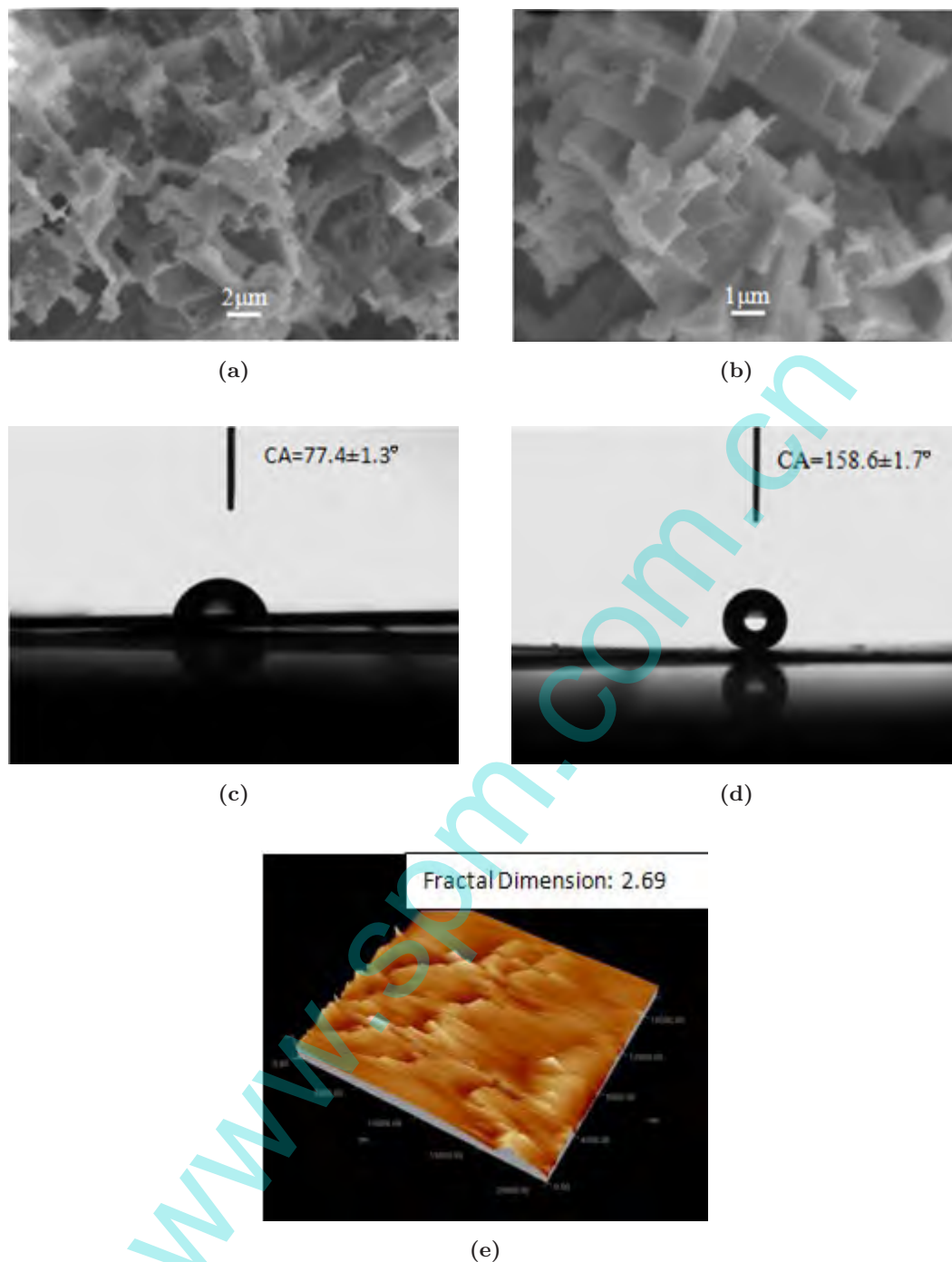


Fig. 6 SEM images at low (a) and high (b) magnification of aluminum alloy after being immersed in the mixture solution of hydrochloric acid and oxalic acid for 2.5 h. (c) CA of aluminum alloy without modification; (d) CA of aluminum alloy after being etched for 2.5 h and modified with steric acid. (e) A 3D AFM image of aluminum alloy after being etched.

surface roughness and surface chemical components. The different orders of magnitude of roughness on copper and aluminum surfaces have no significant influence on CAs. The static angles are measured by a macro droplet of 1.8 mm in diameter. The CAs of copper and aluminum samples are

similar because the CAs are measured by a large droplet (several orders of magnitude larger than roughness). However, the situations of condensation on the two samples will be different because of the small dimension of moisture. This will be discussed later.

3.4. Moisture Condensation on Copper and Aluminum Alloy Substrates

Robust superhydrophobic property will be a key factor to keep dropwise condensation under low temperature. On the copper surface with etching time of 15 min, most condensate droplets are larger than 2 mm after 3 h condensation (Fig. 7b). The effect of preventing the formation of large condensate droplets is not good. Spontaneous movement phenomenon of condensate droplets is observed on copper surfaces with a prolonged etching time. Dust-like condensates drift down the substrates all the time. This phenomenon is related to the self-propelled jumping motion of the coalesced drops. This motion is powered by the surface energy released upon coalescence of drops.¹² Usually, film condensation appears on a raw material copper foil surface because of its hydrophilic property. The condensate droplets grow large (about 3 mm in diameter in Fig. 7a and then drift down in larger size. However, this nanoscaled superhydrophobic copper surface enables these condensate droplets (dozens of microns) to drift down like a fog. This floating behavior will prevent the formation of larger condensate. Figure 7c is a superhydrophobic copper surface with an etching time of 90 min. After 3 h

condensation, several large droplets with diameter of 1–2 mm stay on the substrate. Most of these condensate droplets are difficult to observe with naked eyes (Figs. 7c and 7d). The results demonstrate that it is possible to solve the dewing problem on cooling ceiling surface by superhydrophobic surfaces.

Similar scenarios are observed on superhydrophobic aluminum surface. In the early stage, micro droplets drift down slowly just like the dust floating and moving in the air. As condensation continues, many larger droplets (1–2 mm) appear on the substrate (Fig. 8b). They are much smaller than those on raw material aluminum surface as shown in Fig. 8a. However, larger condensate droplets will form on superhydrophobic aluminum surface compared with that on the copper surface. Larger droplets appear on superhydrophobic aluminum alloy surface because of the surface defects. The stability and uniformity of microstructures are hard to control. In addition, the larger size of lattice-like structures on aluminum surface will generate smaller Laplace pressure. Small condensate droplets easily enter into these cavities because of the small pressure, which will be harmful to keep superhydrophobicity under condensation. The smaller value of FD of aluminum surface resulting from the looser

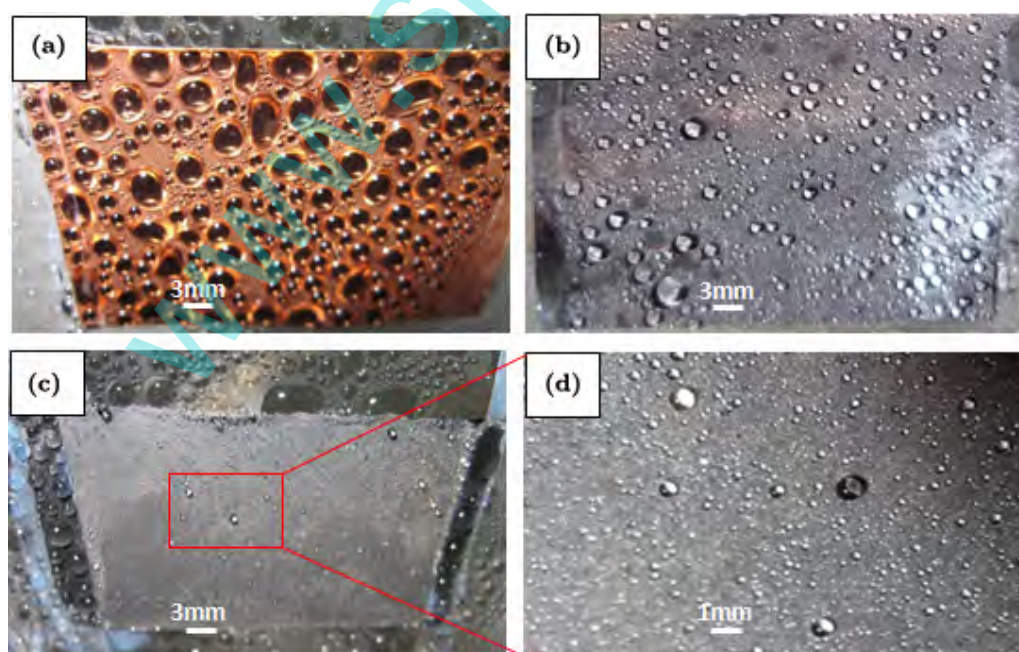


Fig. 7 Moisture condensation on copper foils about 3 h before (a) and after modification. The chilling temperature was 0°C. (b) The copper sample with an etching time of 15 min; (c) the copper sample with an etching time of 90 min and (d) local magnification of (c).

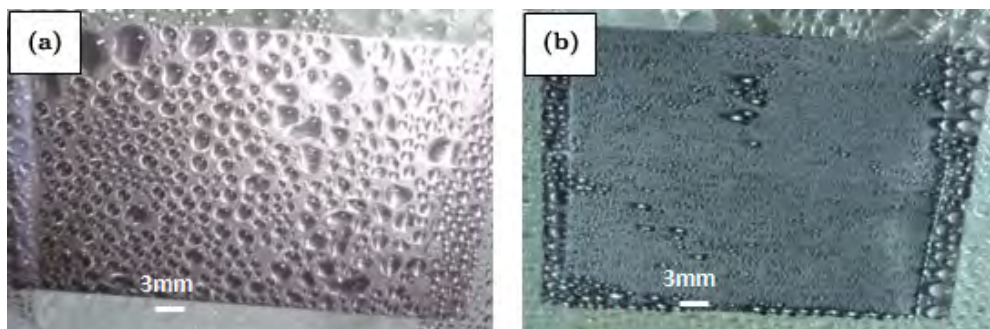


Fig. 8 Moisture condensation on aluminum alloy foils before (a) and after (b) modification. The chilling temperature was 0°C . The condensation time was 3 h.



Fig. 9 Images of frosting experiments on copper (left column) and aluminum (right column) foils under -15°C with different cooling time. The red sample in left column was unmodified copper foil.

structures compared with Cu-90 also improves this point. Feng *et al.*¹³ pointed out that nanostructures facilitated the Wenzel-to-Cassie transition of condensate drops for their sufficiently narrow spacing and higher perpendicularity. A larger Laplace pressure was generated between dense nanosheets which would strengthen the anti-wetting effect of structure surface. Thus, the nanoscaled structures on superhydrophobic surfaces are conducive to prevent the formation of large droplets condensate.

3.5. Frosting Experiments on Copper and Aluminum Alloy Substrates

The frosting experiments on copper and aluminum superhydrophobic surfaces are conducted under -15°C . Copper sample with 90 min etching time is used. Figure 9 shows the images of frosting experiment on copper foils (left column) and aluminum alloy foils (right column) with different cooling time. The unmodified copper foil (the red foil) in left column is completely covered by frost after 40 min. While on superhydrophobic copper surface, the ice mainly forms on outer edges. After 137 min, many liquid droplets instead of frost remain on the center, which demonstrates a markedly anti-icing effect of the nanostructure copper surface. Continuously removing micro condensate droplets should be favored to delay frosting which had been reported in literatures.^{8,23} On the other hand, air existing among nano/micro structures as well as the structures themselves will increase the heat transfer resistance from cooling substrate to condensate.²⁴ Compared with copper sample, the delaying effect of superhydrophobic aluminum surface is not so remarkable. Frost forms on the outer edges of aluminum foil about 37 min and proceeds to grow inward. A large area of aluminum surface is covered by ice in 137 min which is different from copper surface. Thus, the micro-scaled structures of aluminum alloy surface are not ideal to prevent or delay ice formation compared with nanoscaled structures on the copper surface.

In a word, the FD is directly related to the surface roughness. The rougher and denser the surface is, the larger the FD will be. The copper surface with dense nanostructures is more ideal to present the formation of larger water condensate and to delay frosting.

4. CONCLUSIONS

Solution immersion techniques have been used to fabricate rough structures on copper and aluminum alloy surfaces. Superhydrophobic property of these etching surfaces was obtained after modifying with steric acid. Fractal patterns form on the surfaces of copper and aluminium foils after being etched in solutions. The FDs of samples are obtained by the PSD of the AFM images of samples. The FD is directly related to the surface roughness. The relationship between CAs and FDs of Cu surfaces with different etching time is discussed. The change trends of CA and FD with etching time of copper samples are similar. The longer the etching time, the larger the CA and FD. The hydrophobicity of copper surfaces is enhanced with fractal structures.

Moisture condensation and frosting experiments are conducted on copper and aluminum sample surfaces. These superhydrophobic metal surfaces enable condensate droplets with dozens of microns in diameter to drift down like a fog, which successfully prevents the formation of larger condensate droplets. While on a common metal foil, condensate droplets will grow bigger and then drift down when their diameter is close to the capillary length. The rougher and denser the surface is, the larger the FD will be. The copper surface with dense nanostructures is more ideal to present the formation of larger water condensate and to delay frosting. Thus, it will be possible to solve water condensation and frosting problems on chilled ceiling system by fabricating nanoscaled superhydrophobic film on metal surfaces.

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