Petal shaped nanostructures planted on array micro-patterns for superhydrophobicity and anti-icing applications

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Abstract: The aim of this paper is to report a facile strategy of planting a layer of petal shaped nanostructures on the surface of array micro-patterns, and producing the excellent superhydrophobicity and anti-icing property. In this work, the superhydrophobic surfaces were prepared by modifying petal shaped nanostructures (constructed by chemical etching in alkaline solution) planted on array micro-patterns (constructed by lithography process with the electrochemical etching under the neutral solution condition) on aluminum substrate with fluoroalkylsilane (FAS-17). Meanwhile, we further studied the effects of chemical etching process parameters on morphology and superhydrophobicity, and on this basis explored the anti-icing potential under the condition of icing wind tunnel. The results indicated that the process parameters including NaOH concentration of 0.05 M, etching time of 5 min, and the subsequent boiling time of 40 min were of benefit to producing the ideal nanostructure morphology and geometric dimension, and the resultant surface displayed an excellent superhydrophobicity with the apparent contact angle of 165° and the sliding angle being almost equal to zero (cannot be measured). Furthermore, the as-superhydrophobic surface generated a tremendous anti-icing potential, greatly preventing the icing accumulation at -10°C under the condition of icing wind tunnel, and exhibiting a lower ice adhesion strength comparing with a market mature production of superhydrophobic coating.

Keywords: superhydrophobicity; petal-shaped nanostructures; anti-icing; aluminum

1. Introduction

Ice formation and accretion often occur on the surface of aircraft, especially when aircraft encounters supercold and high humidity environments, which will result in the aircraft operating more difficultly, fuel efficiency loss, and even catastrophic events with fatalities [1-3]. Over the past few decades, many efforts have been devoted to combat the effects of ice formation and accretion, and these efforts can be probably divided into two research orientation: active anti-icing techniques and passive anti-icing/deicing techniques [4,5]. Current traditional passive anti-icing/deicing strategies continue to be improved, such as enhancing the electro-thermal efficiency, using new type of anti-icing additive, and mechanically breaking the ice with higher power. Although these ice mitigation methods succeed in reducing the impact and adhesion of ice on the surface of aircrafts, there are inevitable limitations (like non-completely deicing, high energy consumption, and disabled ice detector, etc.) in practical applications especially under a harsh environment [6,7]. With the development of bio-inspired and nanometer techniques, designing and constructing the superhydrophobic surface have aroused much attention from some aviation scientists for expecting to reduce the dependent extent on the traditional passive anti-icing/deicing strategies, even to replace them in future [8-11].

Inspired by bio-mimetic investigations on biological surfaces like lotus leaves, rose petals, butterfly wings, water-strider legs, and mosquito eyes, many researchers discovered that the superhydrophobicity of plant and animals skins comes from the synergistic action of chemical compositions and multi-scale hierarchical structures

[12-16]. Based on this feature, scientists designed and successfully fabricated the superhydrophobic surfaces with a high contact angle of greater than 150° and a sliding angle of less than 10° . Also, some underlying mechanism was revealed that the hierarchical micro-nanostructures can entrap numerous small air-pockets underneath the reference droplet and form an air layer to suspend the droplet [17-19]. Therefore, the hierarchical structure surfaces do not only exhibit excellent superhydrophobicity to repel water, and but also naturally offer the potential of anti-icing applications due to the heat isolation and lubrication of this air layer. Generally, the surface chemical compositions can be easily tailored by the low-surface energy compound (e.g., long-chain fatty acid or fluorosilane). Thus, substantial efforts have been devoted to construct multi-scale hierarchical structures to produce a higher capacity of capturing air-pockets and finally obtain the ideal superhydrophobic surfaces [20,21]. Up to now, researchers have designed a variety of multidimensional micro-nanostructures, such as nanowires [22], nanorods [23], nanopillars [24], nanoflakes [25], nanospike [26], etc.

It was well known that the multi-scale hierarchical structures play an important role in producing the superhydrophobicity. Also, many strategies have been adopted to construct the dual-scale roughness on the aluminum substrates, mainly including micromachining [27], chemical etching [28], plasma etching [29], electrochemical anodization [30], sol-gel technique [31], and physical coating [32]. Yin et al. fabricated a superhydrophobic surface by chemical etching and subsequent surface modification. Also, the prepared superhydrophobic surface exhibits a good

superhydrophobicity with a high apparent contact angle of 161.2° [33]. Zhang et al. combined chemical deposition and fluoroalkylsilane (FAS) modification to tune the wettability of an aluminum substrate, and observed a rapid bouncing behavior of an impact droplets within 12 ms [34]. Furthermore, Cheng et al. successfully fabricated a superhydrophobic surface with a static water contact angle of up to 169° and a sliding angle of approximately 0° via the successive thermal treatment. Moreover, the superhydrophobic surface generated outstanding anti-icing properties under a cold condition of about -15°C [35].

Among these, the chemical etching route is proved to be one of the most promising approaches, because it is convenient, time-saving, and low-cost. Moreover, as a subtractive manufacturing method, the obtained micro-nanotextures possess the strong adhesion strength with substrate, and more importantly it offers a facile and large-area prepared route to effectively control the surface textures by tuning the process parameters. However, the superhydrophobic anti-icing surfaces fabricated by single chemical etching approach are difficult to maintain the high superhydrophobicity and anti-icing property for a long time, especially when encountering the harsh environments [36]. Thus, it is of great scientific significance to plant a layer of nanostructures on the surface of microscale patterns and form a composite hierarchical structures with a robust superhydrophobicity and icephobicity.

In this paper, a facile two-step approach was used to fabricate a superhydrophobic anti-icing surface on aluminum substrate. We planted a layer of petal shaped nanostructures (chemical etching method) on the surface of array micro-patterns

(lithography technique), and gained the superhydrophobicity after the modification of fluoroalkylsilane (FAS-17). Furthermore, the effects of chemical etching process parameters on morphology and superhydrophobicity were systematically investigated, and on this basis we explored the anti-icing potential under the condition of icing wind tunnel, expecting to further promote the application researches of superhydrophobic surface.

2. Experimental Section

2.1. Material

Aluminum foils (99.9%) were obtained from Beijing Nonferrous Metal Research Institute, China, and then were manufactured into small pieces with the size of 15 mm×15 mm and 50 mm×50 mm, respectively. SU-8 photoresist was purchased from the Gersteltec Sarl Co., Ltd., Switzerland. All the other chemicals used in this experiment such as NaOH, NaNO₃, acetone and ethanol were analytical grade and provided by Sinopharm chemical reagent Co., Ltd., China.

2.2. Experimental procedure

Firstly, Al foils were successively ultrasonically cleaned with acetone, alcohol, and deionized water for 15 min to remove surface grease and then dried immediately under the cold wind condition. Secondly, coordinating the mask with a standard UV mask aligner, the photoresist film (thickness of 5 μm) with the exposure area of 130 μm×130 μm as well as the center-to-center spacing distance of 230 μm was obtain. Subsequently, the sample was immersed in 100 mL 10% NaNO₃ aqueous solution for 2 min under 10 V voltage in an open air condition. After stripping and rinsing , the

controllable regular microscale patterns could be obtained. On this basis, we conducted a series of chemical etching experiment to obtain the optimized process parameters for the ideal nanostructure morphologies and superhydrophobicity [37,38]. The chemical etching method to fabricate secondary nanostructures can be divided into three parts: 1) alkaline etching with NaOH solution at 60 °C; 2) boiling treatment; 3) drying treatment to form Al₂O₃. In this exploration, we changed the three etching process parameters, including NaOH concentrations, etching time, and boiling time, respectively. Among these, NaOH concentrations was set at 0.01 M, 0.05 M, 0.10 M, 0.15 M, and 0.20 M. Etching time varied from 1 min to 9 min, and boiling time was divided into from 10 min to 50 min with the interval of 10 min. Finally, the as-prepared micro-nanoscale hierarchical structure surfaces were modified in 1 wt% FAS-17 ethanol solution for 24 h and then dried at 120 °C for 2 h, producing the superhydrophobicity.

2.3. Characterizations and anti-icing measurement in icing wind tunnel

The morphologies of sample surfaces were observed by field emission scanning electron microscopy (FE-SEM; Hitachi S4800, Japan) equipped with an energy dispersive spectroscopy (EDS) instrument under a vacuum environment. Also, the chemical compositions of sample surfaces were recorded by using Fourier Transform Infrared Spectrometer (FT-IR; Nicolet Nexus670, USA). The chemical component of the surfaces was studied by X-ray photoelectron spectroscopy (XPS) using an X-ray photoelectron spectrometer (Kratos AXIS UltraDLD, Japan). Regarding the superhydrophobicity, the apparent water contact angles (CA) of different samples

were measured by a contact angle meter (Kruss DSA100, Germany), yet the sliding angle cannot be measured due to the lower droplet adhesion (the sliding angle is almost equal to zero). Water droplets were placed on sample surfaces with a volume of 5.0 μL , and the data were the average value of at least 5 measurements for each sample.

To further evaluate the anti-icing potential of micro-nanoscale hierarchical structure superhydrophobic surface, the icing wind tunnel measurement was carried out under the condition of $-10\text{ }^{\circ}\text{C}$ working temperature, 20 m/s wind speed, and 3 g/cm^3 liquid water content, and the icing formation and accretion process was also observed using a professional camera. Furthermore, a market mature production of sol-gel superhydrophobic coatings was utilized to make a comparative study for more accurately showing the anti-icing potential (or level) of the micro-nanoscale hierarchical structure superhydrophobic surface.

3. Results and discussion

3.1. Preparation of the superhydrophobic surface

It is well known that the preparation of superhydrophobic surfaces is determined by a synergistic action of low surface energy and geometrical micro-textures [39,40]. Also, the geometrical micro-textures are considered to be a vital role for generating superhydrophobicity. We firstly constructed the array micro-patterns on aluminum substrate through lithography process, and subsequently implemented the chemical etching process to form the micro-nanoscale hierarchical structure. After modifying

with FAS-17, the hierarchical structure surface displays an excellent non-wettability, the schematic diagram of the preparation process is shown in Figure 1.

Figure 2 illustrates the SEM images of the micro-nanoscale hierarchical structure surface (the etching parameters of secondary petal nanostructures are NaOH concentration of 0.05 M, etching time of 5 min, and the subsequent boiling time of 40 min, respectively). It can be seen from Figure 2a that array micro-patterns are evenly distributed on the surface of aluminum substrate, and the depth of each micro-pattern is approximately 37 μm and its width reaches 142 μm . Comparing to the original design of mask with the dimension of 130 $\mu\text{m} \times 130 \mu\text{m}$ and the spacing of 100 μm , the width of the present array micro-patterns gets a little larger owing to the isotropy of etching process. On this basis, a layer of petal shaped nanostructures are planted on the surface of the primary array micro-patterns through the further chemical etching technique (see Figure 2b). The observed results demonstrate that the petal shaped nanostructures completely cover on the internal and external surface of as-constructed array microscale patterns. The dimension of petal shaped nanostructures is approximately 100 nm, and some nanostructures gather and form a series of three-dimensional spherical with diameter of 1 μm dotted on pre-existing petal shaped surface.

According to research results reported by our previous literatures, the secondary nanostructures play a more important role in producing superhydrophobicity especially reducing the droplet adhesion comparing with the primary microstructures. Here the petal shaped nanostructures are formed through the alkalescence etching

treatment, and their underlying formation mechanism can be elucidate below. With the proceeding of chemical reaction in a NaOH solution:

β -Al(OH)₃ precipitation generates slowly and reaches gradually a critical supersaturation point. Comparing with the homogeneous nucleation, heterogeneous nucleation needs less barrier energy, which leads to a heterogeneous nucleation of the β -Al(OH)₃ easily taking place on the aluminum foil [41]. Subsequently, due to the ultra low content of CO₂ product, the continuous consumption of Al(OH)₄⁻, and the generation and accumulation CO₃²⁻ product, the heterogeneous nucleation of β -Al(OH)₃ takes place with a very low reaction speed. Such an low nucleation rate effectively controls the subsequent growth process, and leads to the anisotropic growth of β -Al(OH)₃ nuclei [42]. Furthermore, it is known that the β -Al(OH)₃ is a monoclinic phase with a natural crystalline anisotropy. Thus, the β -Al(OH)₃ grows along its long axis and finally forms the petal shaped nanostructures on the surface of array micro-patterns under the combined action of crystalline anisotropy and quasi equilibrium [43]. After drying treatment, the petal shaped β -Al(OH)₃ occurs the dehydration reaction and transforms into Al₂O₃, (the EDS surface scanning images of elements are shown in Figure 3).

FAS-17 is an ideal selection to change the surface chemical compositions for gaining the superhydrophobicity. Figure 4a shows the FT-IR spectra before and after

the modifying with FAS-17. It can be clearly seen that the hierarchical structure surface modified by FAS-17 shows a remarkable difference with some characteristic absorption peaks appearing at the FT-IR spectra. The bands at 2923.78 cm^{-1} , 2853.31 cm^{-1} correspond to the C-H asymmetric and symmetric stretching vibrations, respectively. Meanwhile, the band at 1630.74 cm^{-1} is ascribed to the C-H stretching vibrations, yet the other two bands at 1401.82 cm^{-1} and 748.42 cm^{-1} are assigned to the C-H in-plane and out-plane flexural vibrations, respectively. The characteristic absorption peak at 1062.91 cm^{-1} belonging to the C-F stretching vibration of the $-\text{CF}_2-$ and $-\text{CF}_3$ groups are clearly visible, indicating that the low surface energy groups has been successfully assembled onto the surface of micro-nanoscale hierarchical structures (the assembled process is shown in Figure 4b), and obtains the superhydrophobicity.

Furthermore, Figure 5 illustrates the surface chemical components of the sample before and after modifying with FAS-17. It can be seen that the sample possesses high intensity peaks of the F1s and FKLL and low intensity peaks of the O1s after modifying with FAS-17. Also, in the high resolution spectrum of C1s, the peaks corresponding to $-\text{CF}_2$ (at 291 eV) and $-\text{CF}_3$ (at 294 eV) are observed, Further indicating the micro-nanoscale hierarchical structures being successfully modified and producing the superhydrophobicity.

3.2. Petal shaped nanostructure morphology and superhydrophobicity

It is well known that chemical etching method is widely used to construct large area of microscale structures or nanostructures, and there is a strong bonding strength

between micro-nanostructure and substrate because of the subtractive manufacturing features. Based on these advantages mentioned above, it is of great significance to concertedly control the three key parameters, including NaOH concentration, etching time, and boiling time, for generating the suitable size and morphology of nanostructures, and finally obtaining the superhydrophobicity.

Figure 6 shows the relationship between the NaOH concentration and the morphology. It can be seen from Figure 6a that the sample being etched in 0.01M NaOH aqueous solution displays a layer of petal shaped nanostructures, yet these nanostructures exist a certain extent of continuity and do not form the complete three-dimensional spherical. While the NaOH concentration increases to 0.05 M, the results reveal that the large numbers of petal shaped nanostructures with the length of ~100 nm evenly distribute on the surface, and some petal shaped nanostructures gather and form a series of three-dimensional spherical bodies with diameter of 1 μm . Furthermore, with the NaOH concentration increasing, the size of petal shaped nanostructures and the size and uniformity of three-dimensional spherical bodies almost remain constant. As a consequence, the sample surfaces exhibit a robust superhydrophobicity with all these apparent contact angles reaching 150° , as depicted in Figure 7. These results indicate the apparent contact angles keep consistent and are up to 165° with the NaOH concentration varying from 0.05 M to 0.2 M, expect the fact that the sample being etched in 0.01 M NaOH solution has the lowest apparent contact angle of 156.08° . Here all these samples exhibit an outstanding superhydrophobicity with a very high contact angle, and also possess a very low

droplet adhesion so that the sliding angle cannot be measured in experiment (almost equal to zero).

Additionally, we furthermore investigate the effect of the etching time on the morphology, and the changes of morphologies are shown in Figure 8. When the chemical etching reactions proceed to 1 min, it can be seen that the chemical etching reaction is uncompleted so that the size of petal shaped nanostructures is very small. As the chemical etching time being prolonged to 3 min, the petal shaped nanostructures exhibit a certain extent of growth, and evenly distribute on the surface of array micro-patterns. Also, the chemical etching reaction time reaches 5 min, even longer, petal shaped nanostructures grow up into stable and suitable size, and form a series of three-dimensional spherical bodies evenly distributing on the surface. In combination with the relationship between the etching time and the superhydrophobicity (see Figure 9), the superhydrophobic surface exerts a lower non-wettability with an apparent contact angle of below 160° , when the etching time is 1 min. As the etching time is prolonged, the results indicate that the apparent contact angles increase greatly, and maintain a high level with the value being up to 161.4° . Thus, considering the whole process, the chemical etching time of 5 min is more rational to induce a suitable morphology and superhydrophobicity.

In order to obtain a perfect petal shaped nanostructures, a boiling treatment is necessary to improve the petal shaped nanostructures, especially the spacing distance of nanostructures. The Effects of boiling time on the surface morphology is described in Figure 10. As the boiling time varies from 10 min to 30 min, it can be easily find

only a large number of petal shaped nanostructures with the length of ~100 nm evenly distribute on the surface. while the boiling time increases to 40 min, some three-dimensional spherical bodies gradually being formed and also evenly distribute on the surface with petal shaped nanostructures. This change mainly attribute to that the boiling treatment benefits to expand the petal shaped nanostructures, and leads to increasing the spacing distance of nanostructures. In this case, some petal shaped nanostructures take place squeezing phenomenon, resulting in appearing some three-dimensional spherical bodies.

Moreover, these three-dimensional spherical bodies gradually grow up with the boiling time increasing. Combining with the resultant superhydrophobicity (Figure 11), when the boiling time is below 40 min, the apparent contact angle sustainably increases with the value from 156° to 164.31° . However, with the boiling time increasing continuously, the apparent contact angle does not increase and drop down to 158° at the boiling time of 50 min.

Here, it can be concluded that the optimal chemical etching time and boiling time are 5 min and 40 min, respectively, at 0.05 M NaOH solution for the as-prepared superhydrophobic sample surface with the suitable morphology and size of petal shaped nanostructures and non-wettability (the apparent contact angle reaching 164.31° , the sliding angle being almost equal to zero).

3.3. Anti-icing potential in icing wind tunnel

It is well known that ice formation and accretion occur easily on the surface of aircraft under a cold nature condition. Thus, we take a evaluation on the anti-potential

of the as-prepared superhydrophobic surface at $-10\text{ }^{\circ}\text{C}$, and also do a comparative investigation with a market mature production of sol-gel superhydrophobic coating (the apparent contact angle of 155° and the sliding angle of 5°). After measured time of 10 min in a icing wind tunnel, we use the high magnification camera to capture the images of these sample surfaces. Figure 12 shows the measured results about the anti-icing property of the as-prepared superhydrophobic surface, and the as-prepared superhydrophobic surfaces are labeled as S1, S2, and S3, simultaneously the market mature production of sol-gel superhydrophobic coatings are labeled as S1', S2', and S3'. It can be easily found that the areas of ice formation and accretion on the surfaces of S1, S2, and S3 are smaller than those on the surfaces of S1', S2', and S3'. Due to the edge effect, some supercooled water droplets after impacting onto the superhydrophobic surfaces prefer to gradually agglomerate into larger ice crystals with some uncovered interspacing. Although some sample surfaces also accumulate a certain extent of ice, the ice adhesion strength is so low that the accumulated ice can be fallen off under a slight force action. However the some ice closely sticks to the surface of the market mature sol-gel superhydrophobic coating in a clear ice form. Thus, it can be drawn a conclusion that comparing with some market mature sol-gel superhydrophobic coatings, the micro-nanoscale hierarchical structure (array micro-patterns and petal shaped nanostructures) superhydrophobic surface generates a tremendous anti-icing potential, greatly preventing the icing accumulation at $-10\text{ }^{\circ}\text{C}$ under the condition of icing wind tunnel, and exhibiting a lower ice adhesion strength.

Conclusion

In summary, we planted a layer of petal shaped nanostructures on array micro-patterns (constructed by lithography process) by means of chemical etching method, finally forming a micro-nanoscale hierarchical structure superhydrophobic surface after modifying with FAS-17. Also, based on the importance of nanostructures to superhydrophobicity, the optimal chemical etching time and boiling time are 5 min and 40 min, respectively, at 0.05 M NaOH solution for the as-prepared superhydrophobic sample surface with the suitable morphology and size of petal shaped nanostructures and non-wettability (the apparent contact angle reaching 164.31° , the sliding angle being almost equal to zero). On this basis, the as-prepared superhydrophobic surface generates a tremendous anti-icing potential, (comparing with a market mature production of sol-gel superhydrophobic coating) greatly preventing the icing accumulation at -10°C under the condition of icing wind tunnel, and exhibiting a lower ice adhesion strength.

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Figure list:

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Figure 12. The measured results about the anti-icing property of the as-prepared superhydrophobic surface, and the as-prepared superhydrophobic surfaces are labeled as S1, S2, and S3, simultaneously the market mature production of sol-gel superhydrophobic coatings are labeled as S1', S2', and S3'. (a) The image of sample surfaces placed in the icing wind tunnel; (b) The image of sample surfaces placed outside the icing wind tunnel.

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