Wetting behaviour and **drag** reduction of superhydrophobic layered double hydroxides films on aluminum

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Abstract:

We present a novel method to fabricate Zn-Al LDH (layered double hydroxides) film with 3D flower-like micro-and nanostructure on the aluminum foil. The wettability of the Zn-Al LDH film can be easily changed from superhydrophilic to superhydrophobic with a simple chemical modification. The as-prepared superhydrophobic surfaces have water CAs (contact angles) of $165\pm 2^\circ$. In order to estimate the drag reduction property of the surface with different adhesion properties, the experimental setup of the liquid/solid friction drag is proposed. The drag reduction ratio for the as-prepared superhydrophobic sample is 20~30% at low velocity. Bearing this in mind, we construct superhydrophobic surfaces that have numerous technical applications in **drag** reduction field.

1. Introduction

In nature, the lotus surface is constituted of micro/nano scale binary structures, which are covered by epicuticular wax [1-6]. The combination results in the superhydrophobic properties. In addition, some parts of many insects also possess superhydrophobicity, such as the legs of the water strider, the wings of the butterfly and cicadas [7, 8]. These surfaces with superhydrophobicity have attracted great attention because of their potential use in fundamental researches and industrial applications, such as self-cleaning, fluid drag reduction, anti-frosting, oil/water separation, corrosion resistance and drag reduction of the steamship[9-11]. Therefore, in the past decades, artificial fabricating these fascinating surfaces has been one of the most active research topics and it has been reviewed in a number of publications [12,13]. Superhydrophobic surfaces have been manufactured mainly by two methodologies: creating micro/nanostructures on hydrophobic substrates, or chemically modifying a micro/nanostructured surface with materials of low surface free energy [14-17].

Layered double hydroxides (LDH), are a class of synthetic anionic clays that consist of positively charged layers containing alternatively distributed divalent and trivalent cations in the sheets and charge balancing anions between the layers [18]. The composition of LDH can be represented by the general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where the metal cations M^{2+} and M^{3+} occupy the octahedral holes in a brucite-like layer and anion A^{n-} locate in the hydrated galleries between the layers. Based on their anion-exchange capability and compositional flexibility, LDH materials have received a great deal of attention due to

their widespread applications as flame retardants [19], catalysts or catalyst precursors [20], adsorbents [21], drug delivery [22], magnetic devices [23] and anticorrosion coatings[24]. Recently, LDH materials can be used to fabricate superhydrophobic surface, because LDH films are easy to form high porosity and roughness.

The superhydrophobic surfaces can retain an air film between water and the solid surface. The surface minimizes the water-solid contact area, significantly reducing the frictional drag between water and the solid. Therefore, the surprising performance of the superhydrophobic surface can be widely used in drag reduction field. Aluminum is widely used in various industrial fields as a basic material for numerous mechanical components. The fabrications of the superhydrophobic surfaces on aluminum and its alloys have attracted more and more attention from many researchers. Some works have been reported on designing rough superhydrophobic surfaces on aluminum, which include the conventional electrochemical machining [25-27] and chemical etching method [28,29]. However, the electrochemical machining and chemical etching methods require the acid corrosive procedure, while sulfuric acid, oxalic acid, and phosphoric acid are often used. These acids have certain hazards to the environment and the health of the operator. Herein, we present a novel method to fabricate the superhydrophobic surface with 3D flower-like micro-and nanostructure on an aluminum foil under a mild condition. Zn-Al LDH film is prepared in situ on anodized aluminum substrate using hydrothermal method, and we study the drag reduction characteristics of the as-prepared surfaces. The design of superhydrophobic

surfaces with long term stability by means of a simple and inexpensive method is reported here.

2. Experimental

2.1 Anodizing process

Industrial grade aluminum foil (1 mm thickness, 99.5% purity, AA1050) was cut into $2 \times 4 \text{ cm}^2$ pieces, then polished mechanically, and cleaned ultrasonically with acetone and ethanol in sequence to remove grease. Anodizing was carried out in a 0.10 M NaCl aqueous solution, with aluminum foil as anode and a graphite plate as cathode. A 25 mA cm^{-2} processing current density was applied and the anodizing time was 120 min at room temperature. Then, anodized samples (sample 1) were totally rinsed and dried in the cold air.

2.2 In situ growth of Zn-Al LDH films on aluminum foil

To fabricate Zn-Al LDH, 100 mL of an aqueous solution (Volume ratio 1:1) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (50 mM), hexamethylenetetramine (HMTA, $\text{C}_6\text{H}_{12}\text{N}_4$, 50 mM) was introduced into a Pyrex1 bottle. Etched samples were vertically immersed into the bottle which were then closed and kept in an oven at 95°C for 3 hours (sample 2). The sample 2 was introduced into new solution baths, and continue to grow the Zn-Al LDH film (sample 3) at 95°C for 3 h. After film deposition, samples were washed with deionized water and dried at room temperature.

2.3 Surface modification

Because fluoroalkyl silane (FAS) have good hydrophobic property (the water contact angle on a smooth FAS film is 110°) and the FAS molecules are easily modified on the surface of hydroxyl rich films, so we chose fluoroalkyl silane (FAS) as surface functionalization reagent in this study. Finally, the samples were immersed in an ethanol solution containing 0.5 wt.% FAS (1H,1H,2H,2H-perfluorooctadecyltrichlorosilane) for 60 min at room temperature and subsequently heated at 120°C for 2 h. A superhydrophobic surface was obtained.

2.4 Characterization

The surface morphologies were observed using a field-emission scanning electron microscope (FE-SEM, TESCAN VEGA), and the corresponding element distributions were determined by energy-dispersive X-ray spectroscopy (EDS). The XPS was collected on an axis ultra X-ray photoelectron spectrometer, using Mg K α X-ray as the excitation sources. The contact angles (CAs) and sliding angle (SA) of water droplets were measured by an optical contact-angle meter system (Data Physics Instrument GmbH, Germany) at ambient temperature. The water CA and SA reported were the mean values measured with 5 μL of water droplets at five different positions on each test surface. The drag reduction efficiency was measured by a self-designed water spraying system.

3. Results and discussion

3.1 surface composition

The corresponding element distributions are determined by energy-dispersive X-ray spectroscopy (EDS). The phase structures of the products are measured by powder X-ray diffraction (XRD) experiments.

Fig.1 (a) and Fig (b) are the EDS spectrums of the untreated aluminum and etched aluminum, respectively. From the Figure we can see that there are only Al element on these samples. Fig.1 (c) and Fig.1 (d) are the XRD patterns of resultant sample 2 and sample 3, respectively. As shown in Fig. 1(c), the pattern of Zn-Al LDH prepared on the sample 2 exhibits three peaks locating at 11° , 23° and 34° , respectively, corresponding to (003), (006) and (012) planes[30,31] . This is the typical reflection characteristic of a Zn-Al LDH structure with intercalated anion of NO_3^- , and the calculated interplanar spacing is 0.823 nm. XRD analysis is utilized to confirm the formation and characteristics of ZnO nanorods grown on the sample 3 surface, as shown in Fig.1 (d). The sharp XRD peaks exhibited the hexagonal wurtzite phase, which corresponds to the (100), (002), (101) planes of ZnO [32-34].

3.2 Surface morphology

The surface morphology of the untreated aluminum surfaces and electrochemically etched aluminum surfaces obtained at the 25 mA cm^{-2} processing current density and 120 min processing time have been observed carefully with SEM (Fig.2). Prior to electrochemical etching, the aluminum surfaces are relatively smooth. Only several scratches and pits generated by polishing are present on the surfaces. After electrochemical etching, the whole aluminum surfaces becomes coarse with the presences of hierarchical rough structures composed of micrometer-scale pits,

protrusions, rectangular-shaped plateaus, smaller step-like structures and particles(Fig. 2a). Many rectangular-shaped plateaus with sizes of 2-5 μm are distributed homogeneously on the pits and protrusions. A large-scale SEM image (Fig.2(b)) shows that some smaller step-like structures and particles are distributed on the aforementioned micrometer-scale plateaus. Hierarchical rough structures composed of micrometer-scale pits, protrusions, rectangular-shaped plateaus, and smaller step-like structures and particles are therefore fabricated on the aluminum surfaces after electrochemical etching.

After insitu growth of Zn-Al LDH films on the etched samples, the surface morphology of aluminum foil has obviously changes. Fig. 2(c) and Fig. 2(d) shows the SEM images of Zn-Al LDH film on Al substrate with different magnifications. From Fig. 2(c), it can be seen that there are two different morphologies: one is 3D flowerlike microspheres with the diameters ranging from 10 to 30 μm , the other is nanowall-like structure. The curly nanowalls with the thickness of 80nm nanometers are uniformly crooked and assemble into the surface, which is revealed by the magnified image (Fig. 2(d)). Fig. 2(d) shows a single flower-like microsphere. It is clear that the single microsphere consists of numerous petal-like lamellas with the thickness of 80 nm. From the large-scale SEM image, we can see that these neighboring lamellas overlap and join each other, forming the complex micro/nanostructures (Fig. 2(d)). The sample 2 was introduced into new solution baths, and continue to grow the Zn-Al LDH film (sample 3) at 95 $^{\circ}\text{C}$ for 3 h. The

SEM images of the as-prepared is shown in Fig. 2 (e). From the large-scale SEM image (Fig.2(f)), ZnO nanorods are grown on the sample 2 surface.

3.3 The surface wettability and adhesion properties

The wettability of the resultant surface is characterized in detail by means of static water CA measurements. To evaluate the wettability of the as-prepared samples, contact angle measurements are conducted by using a water droplet of 4-5 μL . Before chemical modification, the sample 2 shows hydrophilic with a water contact angle of only 0° , as shown in Fig. 3(a). However, after simple chemical modification with silane, the water CA of as-prepared surface is larger than 150° , showing superhydrophobicity. The water CA tests on the three surfaces are measured and the results are presented in Fig. 3. The measured CAs are 153° and 165° for silane modified sample 2 and sample 3, respectively. After hydrophobic treatment with silane the wettability of Zn-Al LDH films is greatly improved.

These surfaces modified with fluorinated silane display excellent superhydrophobic property. That is because the oriented and hierarchical micro/nanostructure provides sufficient roughness and with the presence of fluorinated silane, a large fraction of air could be trapped within the structure. The trapped air can change the contact state from liquid-solid to liquid-air-solid and prohibit water penetrating the grooves of the surface. Thus, ZnO nanorods and nanoflower layer of the sample 3 surfaces are prone to trap larger amount of air and show higher water CA than the sample 2 films.

The adhesion properties of the superhydrophobic surface is also characterized (Fig. 4). we can see that the water droplets stay still even when modified sample 1 is tilted vertically (90°) or even turned upside down(180°), demonstrating a strong water adhesion ability. This case is well explained by the Wenzel model[24], the electrochemically etched aluminum surface has only sub-microstructure, the bottom of water droplets tends to penetrate into the rough grooves, resulting in a larger rolling angle. The water droplets pin the surface tightly, thus form a high contact angle hysteresis. From the Fig. 4(b) and 4(c), many water droplets (15-20 μ L) present round shapes with large CAs on the fluorinated silane modified Zn-Al LDH film. We find that the suspending droplet is difficult to be pulled down to the Zn-Al LDH film in all cases; that is, the surface has almost no apparent water adhesion to the suspending droplet. The resulting surface is so hydrophobic that water droplets form almost perfect spheres on the surface

3.4 Cassie–Baxter and Wenzel regime transition

A stable composite interface is essential for successful design of superhydrophobic surfaces. However, the composite interface is fragile, and it may transform into the homogeneous interface. In this subsection, we study the condition under which the air water interface (meniscus) may transition from the nonwetted state (Cassie state) to the wetted state (Wenzel state). This is important in practical applications related to submerged bodies because once the thin gas layer is replaced by liquid, none of the beneficial effects remain. Bhushan and Jung [35,36] investigated the effect of droplet curvature on the Cassie–Baxter and Wenzel regime transition as shown in Fig.5. First,

they considered a small water droplet suspended on a superhydrophobic surface consisting of a regular array of circular pillars with diameter D , height H , and pitch L , as shown in Fig. 5[37]. The maximum droop of the droplet (δ) in the recessed region can be found in the middle of two diagonal pillars. If the droop δ is greater than the depth of the cavity, then the droplet will just contact the bottom of the cavities between pillars. If it is much greater, transition from the Cassie–Baxter to Wenzel regime occurs.

$$\frac{(\sqrt{2}L - D)^2}{R} \geq H \quad (1)$$

In order to investigate the stability of the composite interface, Lee and Kim adopted the latter approach to develop an equation to determine the maximum allowable hydrostatic pressure in terms of the surface microstructure [38]:

$$P_{\max} \phi_g \leq \frac{-2\gamma \sqrt{\pi(1 - \phi_g) \cos \theta}}{L} \quad (2)$$

where $P_{\max}$ is the maximum allowable pressure without transition, ϕ_g is the gas fraction, γ is the surface tension of the liquid (72×10^{-3} N m in the case of water), θ is the contact angle, and L is the pitch (distance between two posts). Fig. 5(b) schematically shows the microscopic contact state of the superhydrophobic surface underwater when the hydraulic pressure is less than the critical value P_c . Water is suspended on the top of the pillar and the space among pillar formed an air layer, indicating an air/water/ pillar (A/W/P) interface underwater. On the other hand, after the hydraulic pressure exceeds the critical value P_c , the water penetrates into the spaces within the pillar, and the A/W/P interface in this situation does not exist.

Moreover, the existence of a multi-scale pillar increased the contact area between the water and solide surface, enhancing the total adhesion between the water and solide surface based on smooth solid/liquid interface theory. Further, the pressure provides additional energy to eliminate the air layer. Therefore, the critical pressure P_c is a key factor affecting air layers in underwater superhydrophobic surfaces.

3.5 Testing the liquid/solid friction drag

In order to estimate the drag reduction property of the as-prepared surfaces, an experimental setup of the liquid/solid friction drag is reported[39]. Fig. 6(a) shows the schematic for testing the drag reduction efficiency of the as-prepared surfaces. A force sensor was introduced between the two sliding pairs to measure the friction drag between the flat flow and the fixed superhydrophobic surface. The samples to be tested are cut into a size of $1.5 \times 1.0 \text{ cm}^2$ and fixed at the bottom of the force sensor. The copper nozzle with a caliber of $1.5 \times 1.0 \text{ cm}^2$ was used to release flat flow, which was provided by a water pump. The flowmeter was introduced to adjust the flow rate. The friction drag of the solid-liquid interface was transformed into an electric signal and collected by an external data acquisition system and then computed by a computer.

The drag reduction properties of the different surface were measured for 3 times with the same flow rate. The average values were ultimately selected as the friction drag of the corresponding surface. Moreover, the friction drag was also measured under different flow rate to investigate the influence of the flow rate on the drag

reduction performance. As shown in Fig.6(b), the sample 3 possesses a lowest friction drag. The drag reduction ratio for the sample 3 is 20~30% at low velocity. When the flow velocity is at about 4.5 m s^{-1} , the drag reduction ratio of the sample 3 reduces to 10~20%. These results suggest that flow velocity can affect the effect of the drag reduction. The sample 1 has an obvious effect of drag increase when comparing with untreated aluminum foil. The modified sample 3, that is, the drag reduction ratio are the highest among three samples. This phenomenon can be aptly explained by that the sample 3 surface can be maintained stable Cassie state. The magnitude of hydrodynamic slippage which characterizes the anti-drag performance is closely linked to the wettability of a special structured surface. Qualitatively, for The modified sample 3, there is a large but not continuous liquid-air contact layer which prevents the interaction of liquid and solid surface. Thus it is extremely hard for liquid momentum parallel to the interface to transfer, and as a consequence, a long slip length is generated. While for the modified sample 1 which exhibits pretty high adhesion ability, most of the momentum wastes at the interface, resulting in a slippage which is too short to be taken into account. Wetting may lead to the formation of menisci at the interface between solid bodies during sliding contact, which increases adhesion and friction.

4. Conclusion

In this work, Self-assembled Zn-Al LDH film has been developed using a liquid-phase chemical process under a mild condition. The Zn-Al LDH film has a nanoflower structures. Specially, the modified self-assembled hierarchical alumina

surfaces exhibit excellent anti-adhesion to water droplets, automatically repelling water properties. The modified Zn-Al LDH surface has a lower adhesion ability than modified electrochemically etched Al surface. The drag reduction ratio for the modified Zn-Al LDH film is 20~30% at low velocity. These properties are favorable for the potential applications of aluminum materials for various industrial items such as no-loss transportation, drag reduction and energy conversion.

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References

- [1] W. Barthlott, C. Neinhuis, D. Cutler, F. Ditsch, I. Meusel, I. Theisen, H. Wilhelmi, Classification and terminology of plant epicuticular waxes, Bot. J. Linn. Soc. 126 (1998) 237-260.
- [2] K. Koch, B. Bhushan, Y. Jung, W. Barthlott, Fabrication of artificial Lotus leaves and significance of hierarchical structure for superhydrophobicity and low adhesion, Soft Matter. 5 (2009) 1386-1393.

- [3] C. Neinhuis, W. Barthlott, Characterization and distribution of water-repellent, self-cleaning plant surfaces, *Ann. Bot.* 79 (1997) 667-677.
- [4] K. Koch, B. Bhushan, W. Barthlott, Multifunctional surface structures of plants: an inspiration for biomimetics, *Prog. Mater. Sci.* 54 (2009) 137-178.
- [5] K. Koch, B. Bhushan, W. Barthlott, Diversity of structure, morphology, and wetting of plant surfaces, *Soft Matter.* 4 (2008) 1943-1963.
- [6] Z. Guo, W. Liu, Biomimic from the superhydrophobic plant leaves in nature: binary structure and unitary structure, *Plant Sci.* 172(2007)1103-1112.
- [7] X.F. Gao, L. Jiang, Biophysics: water-repellent legs of water striders. *Nature* 432 (2004) 36.
- [8] G. Sun, Y. Fang, Q. Cong, L. Ren, Anisotropism of the non-smooth surface of butterfly wing. *J Bionic Eng.* 6 (2009) 71-76.
- [9] Y. Wu, Q. Wei, M. Cai, F. Zhou, Interfacial Friction Control, *Adv. Mater. Inter.* 2 (2015) 1400392.
- [10] J. Yuan, R. Jin, Water motion and movement without sticking, weight loss and cross-contaminant in superhydrophobic glass tube, *Nanotechnology* 21 (2010) 065704.
- [11] M. Cheng, M. Song, H. Dong, F. Shi, Surface Adhesive Forces: A Metric Describing the Drag-Reducing Effects of Superhydrophobic Coatings, *Small* 11 (2015) 1665-1671.

- [12] F. Guo, X. Su, G. Hou, P. Li, Bioinspired fabrication of stable and robust superhydrophobic steel surface with hierarchical flowerlike structure, *Colloids Surf. A* 401 (2012) 61-67.
- [13] Y. Liu, S. Li, J. Zhang, Y. Wang, Z. Han, L. Ren, Fabrication of biomimetic superhydrophobic surface with controlled adhesion by electrodeposition, *Chem. Eng. J.* 248 (2014) 440-447.
- [14] L. Yao, M. Zheng, L. Ma, W. Li, M. Li, W. Li, M. Li, W. Shen, Self-assembly of diverse alumina architectures and their morphology-dependent wettability, *Mater. Res. Bull.* 46 (2011) 1403-1408.
- [15] S. Wang, L. Jiang , Definition of superhydrophobic states, *Adv. Mater.* 19 (2007) 3423-3424.
- [16] B. Park, W. Lee, J. Kim, K. Lee, Superhydrophobic fabrication of anodic aluminum oxide with durable and pitch-controlled nanostructure, *Colloid Surf. A.* 370 (2010) 15-19.
- [17] B. Su, S. Wang, J. Ma, Y. Wu, X. Chen, Y. Song, L. Jiang, Elaborate positioning of nanowire arrays contributed by highly adhesive superhydrophobic pillar-structured substrates, *Adv. Mater.* 24 (2012) 559-564.
- [18] X. Li, J. Liu, X. Ji, J. Jiang, R. Ding, Y. Hu, A. Hu, X. Huang, Ni/Al layered double hydroxide nanosheet film grown directly on Ti substrate and its application for a nonenzymatic glucose sensor, *Sens. Actuators B* 147(2010) 241-247.

- [19] B. Du, Z. Guo, Z. Fang, Effects of organo-clay and sodium dodecyl sulfonate intercalated layered double hydroxide on thermal and flame behaviour of intumescent flame retarded polypropylene, *Polym. Degrad. Stab.* 94(2009) 1979-1985.
- [20] M. Halma, K. Castro, C. Taviot-Gueho, V. Prévot, C. Forano, F. Wypych, S. Nakagaki, Synthesis, characterization, and catalytic activity of anionic iron(III) porphyrins intercalated into layered double hydroxides, *J. Catal.* 257 (2008) 233-243.
- [21] I. Pavlovic, M.R. Pérez, C. Barriga, M.A. Ulibarri, Adsorption of Cu^{2+} , Cd^{2+} and Pb^{2+} ions by layered double hydroxides intercalated with the chelating agents diethylenetriaminepentaacetate and meso-2, 3-dimercaptosuccinate, *Appl. Clay Sci.* 43(2009) 125-129.
- [22] L. Tammara, U. Costantino, M. Nocchetti, V. Vittoria, Incorporation of active nano-hybrids into poly([epsilon]-caprolactone) for local controlled release: antifibrinolytic drug, *Appl. Clay Sci.* 43 (2009) 350-356.
- [23] D. Yan, J. Lu, M. Wei, J. Han, J. Ma, F. Li, D. G. Evans, X. Duan, Ordered Poly(p-phenylene)/Layered Double Hydroxide Ultrathin Films with Blue Luminescence by Layer-by-Layer Assembly, *Angew. Chem.* 121 (2009) 3119-3122.
- [24] X. Guo, S. Xu, L. Zhao, W. Lu, F. Zhang, D. Evans, X. Duan, One-step hydrothermal crystallization of a layered double hydroxide/alumina bilayerfilm

on aluminum and its corrosion resistance properties, *Langmuir* 25 (2009) 9894-9897.

- [25] H. Wang, D. Dai, X. Wu, Fabrication of superhydrophobic surfaces on aluminum, *Appl. Surf. Sci.* 254 (2008) 5599-5601.
- [26] W. Wu, X. Wang, D. Wang, M. Chen, F. Zhou, W. Liu, Q. Xue, Alumina nanowire forests via unconventional anodization and super-repellency plus low adhesion to diverse liquids, *Chem. Commun.* 9 (2009) 1043-1045.
- [27] C. Jeong, C.H Choi, Single-step direct fabrication of pillar-on-pore hybrid nanostructures in anodizing aluminum for superior superhydrophobic efficiency, *ACS Appl. Mater. Interfaces* 4 (2012) 842-848.
- [28] B. Qian, Z. Shen, Fabrication of superhydrophobic surfaces by dislocation-selective chemical etching on aluminum, copper, and zinc substrates, *Langmuir* 21 (2005) 9007-9009
- [29] Z. Guo, F. Zhou, J. Hao, W. Liu, Stable biomimetic super-hydrophobic engineering materials, *J. Am. Chem. Soc.* 127 (2005) 15670-15671
- [30] X. Guo, S. Xu, L. Zhao, W. Lu, F. Zhang, DG. Evans, X. Duan, One-step hydrothermal crystallization of a layered double hydroxide/alumina bilayer film on aluminum and its corrosion resistance properties, *Langmuir* 25,(2009) 9894-9897.
- [31] Y. Li, S. Li, Y. Zhang, M. Yu, J. Liu, Enhanced protective Zn-Al layered double hydroxide film fabricated on anodized 2198 aluminum alloy, *J. Alloys Compd.* 630 (2015) 29-36.

- [32] M. Zhou, X. Pang, L. Wei, K. Gao, Insitu grown superhydrophobic Zn-Al layered double hydroxides films on magnesium alloy to improve corrosion properties, *Appl. Surf. Sci.* 337 (2015) 172-177
- [33] A. Rodrigues, M C. M. Alves, J. Morais, Self-assembled nanocolumnar ZnO films chemically deposited on stainless steel with controlled morphology and thickness, *Mater. Lett.* 114 (2014) 122-125.
- [34] H. Xu, W. Liu, L. Cao, G. Su, R. Duan, Preparation of porous TiO₂/ZnO composite film and its photocathodic protection properties for 304 stainless steel, *Appl. Surf. Sci.* 301 (2014) 508-514.
- [35] B. Bhushan, Y. Jung, Wetting study of patterned surfaces for superhydrophobicity, *Ultramicroscopy* 107 (2007) 1033-1041.
- [36] Y. Jung, B. Bhushan, Dynamic effects of bouncing water droplets on superhydrophobic surfaces, *Langmuir* 24 (2008) 6262-6269
- [37] Y. C. Jung, B. Bhushan, Wetting transition of water droplets on superhydrophobic patterned surfaces, *Scr. Mater.* 57 (2007) 1057-1060
- [38] C. Lee and C. Kim, Maximizing the giant liquid slip on superhydrophobic microstructures by nanostructuring their sidewalls, *Langmuir* 25 (2009) 12812-12818
- [39] Y. Wang, X. Liu, H. Zhang, Z. Zhou, Superhydrophobic surfaces created by a one-step solution-immersion process and their drag-reduction effect on water, *RSC Adv.* 5 (2015) 18909-18914.

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Fig.2 SEM images of different samples with different magnifications (a and b) sample 1, (c and d) sample 2, and (e and f) sample 3

Fig.3 (a) Unmodified sample 2, (b) and (c) fluorinated silane modified sample 2 and sample 3, respectively.

Fig.4 Photograph of water droplets on the different sample (a) Sample 1 (electrochemically etched aluminum) (b) sample 2 (the Zn-Al LDH film prepared at 95 °C for 3 h) (c) sample 3 (the sample B continues to grow films introducing new solution at 95 °C for 3 h)

Fig. 5 A liquid droplet suspended on a superhydrophobic surface consisting of a regular array of circular pillars. (a) Plan view: the maximum droop of the droplet occurs at the center of the square formed by four pillars. (b) Side view in section A-A. The maximum droop of the droplet (δ) can be found equidistant between two diagonal pillars.

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