

One-step modification method to fabricate wettability patterns on aluminium substrate

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Published in Micro & Nano Letters; Received on 13th April 2016; Revised on 27th June 2016; Accepted on 29th June 2016

Since there is currently no method to selectively fabricate superhydrophobic regions on superhydrophilic surfaces of metal substrates, wettability patterns on metal substrates are prepared via the three-step technique including superhydrophilic, superhydrophobic and selectively superhydrophilic modifications. Here, an innovative method that can selectively lower surface energy of superhydrophilic surfaces, and thereby makes it more convenient to fabricate the wettability patterns, is proposed. Chemical etching is used to formulate micro/nanoscale rough structures and fabricate superhydrophilic aluminium (Al) surface, which is then covered by patterned mask whose main composition is siloxane. Removing the mask after 80°C water bath heating for 20 s, the covered Al surface has been modified to become superhydrophobic (contact angles $>165^\circ$, sliding angles $<1.5^\circ$), while the uncovered region is still superhydrophilic, and wettability patterns are therefore obtained. Fourier transform infrared spectrophotometer and Raman spectra indicate that the change of wettability is induced by hydrophobic groups on the modified surfaces. The superhydrophobic surfaces fabricated by this method have excellent high-temperature resistance. The method proposed is simple, rapid and environmental-friendly.

1. Introduction: The extreme wettability surfaces refer to surfaces whose water contact angles (WCAs) are less than 10° or larger than 150° [1], and have great application potential in terms of self-cleaning [2], antifogging [3], metal corrosion resisting [4], antiicing and antifrosting [5] and so on. Wettability patterns mean that there are both superhydrophobic (WCAs larger than 150°) and superhydrophilic (WCAs less than 10°) regions on one surface, and have great application value in many fields, such as biochemistry, micro-fluidic chips and liquid transportation [6, 7].

The promising application values of wettability patterns have attracted much attention. Recently, much effort has been dedicated to prepare the wettability patterns. Franssila and co-workers [8] used plasma jet to process superhydrophobic silicon surfaces and fabricate superhydrophilic patterns on superhydrophobic surfaces. Seo *et al.* [9] immersed silicon wafer in dodecyltrichlorosilane to fabricate superhydrophobic surface, and successfully obtained a superhydrophilic track on the superhydrophobic surface by ultraviolet irradiation. Yang *et al.* [10] first prepared superhydrophobic aluminium (Al) surfaces and then obtained hydrophilic patterns by micro milling. Hess and co-workers [11] utilised black phase ink to print hydrophilic patterns on superhydrophobic papers. These developed preparation methods are meaningful and should have promising application prospects. However, the preparation processes of these methods are quite complicated. To date, to the best of our knowledge, selective low energy surface modification has rarely been reported. As a result, the present methods to prepare the patterns involve two-step surface modification: superhydrophobisation of superhydrophilic surfaces followed by selective hydrophilisation of superhydrophobic surfaces. Since the superhydrophobisation was generally realised by immersion of low energy substances, it tended to be high-cost and low-efficient. On the other hand, hydrophilisation methods like plasma treatment [12, 13], ultraviolet irradiation [14] do not have ideal time stability. Consequently, the aforementioned methods to fabricate wettability patterns by two surface modifications are not favourable for batch preparation or practical application, which would regretfully restrain further application of these patterns. It should be significant to study a high-efficient and simpler preparation method of wettability patterns with ideal time stability.

This Letter here proposes a new method to selectively lower surface energy of superhydrophilic surfaces and fabricate wettability

patterns on superhydrophilic surfaces by one step. The superhydrophobic surfaces fabricated by this method had a relatively low sensitivity to temperature, and the superhydrophobicity is relatively more durable. As a result, it should have great application potential in fields like self-cleaning, directional transportation, micro-fluidic chips and biomedical detection.

2. Materials and methods: Shown in Fig. 1 is the preparation process of wettability pattern. Al plate ($40 \times 40 \times 2$ mm, Dalian Al material manufacturer, China) was first polished by abrasive paper to remove oxide surface and then ultrasonically cleaned. After drying, the plate was immersed in 1 mol/l CuCl_2 solution for 15 s followed by ultrasonic cleaning to remove the adhesive Cu layer [15]. The etched plate was then dried and covered by the siloxane containing mask (Kapton tape, Shenzhen Aidacom Techlonogy Co., Ltd., China) whose pattern was manufactured by our laser engraving machine. Then, the sheet covered by mask was immersed into boiling deionised water for 20 s. After removing the mask, the wettability pattern could be obtained.

Surface morphology of samples was observed by a scanning electron microscope (SEM, JSM-6360LV, Japan). Surface chemistry of the samples was analysed by an energy-dispersive X-ray spectroscopy (EDS, INCA Energy, Oxford Ins.), a Fourier transform infrared spectrophotometer (FTIR, EQUINOX55 Germany) and a Raman spectrometer (DXR Microscope Thermo Fisher America). Contact angle (CA) measurements were carried out using optical contact angle meter (DSA100, Krüss, Germany) at ambient temperature. A 5 μl injector was used to dispense the water droplets.

3. Results and discussion

3.1. Analysis of the mask: Since the mask has never been used in surface modification, its surface composition was first investigated via FTIR and EDS spectra. Fig. 2 shows the FTIR spectrum of the mask surface. The peaks at 1100 and 1011 cm^{-1} are attributed to three-dimensional (3D) Si–O–Si bonds and 2D Si–O–Si bonds, respectively [16, 17]. The peaks at 800 , 1257 and 1411 cm^{-1} are assigned to the Si–CH₃ bonds [18]. The absorptions at 850 and 2960 cm^{-1} result from Si–OH bonds and C–H bonds, respectively. It could be seen from the EDS spectrum (the insert image of Fig. 2) that the mask is composed

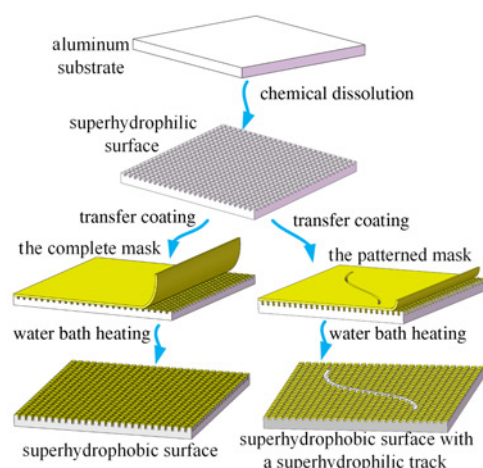


Fig. 1 Preparation process of superhydrophobic surface

of Si, C and O elements (hydrogen cannot be detected), which is consistent with the result of FTIR spectrum.

3.2. Analysis of the micro/nanoscale structures: The etched Al surface had many irregular rectangular pits and bosses with size between 1 and 5 μm , and there were some dual-scale bosses whose dimensions were 100–400 nm on them, as shown in Figs. 3*b* and *c*. After modifying by the mask, the microstructures of Al surface were almost unchanged (Figs. 3*e* and *f*), therefore indicating that this low energy modification method did not cause structure damage of Al surface.

Fig. 4 shows FTIR spectrum of surfaces before and after low surface energy modification. Compared with superhydrophilic Al surface, the superhydrophobic one shows five more typical peaks, which are corresponding to FTIR spectrum of the mask (Fig. 2). The peaks at 1100 and 1011 cm^{-1} are attributed to Si–O–Si bonds, while the absorptions at 1267 and 805 cm^{-1} are attributed to Si–CH₃ bonds. The absorption at 2960 cm^{-1} results from C–H bonds. The laser Raman investigation was used to improve the accuracy of surface characterisation. Fig. 5 shows Raman spectrum of surfaces before and after low surface energy modification by siloxane containing mask. The absorption at 488 cm^{-1} results from stretching vibration of Si–O–Si bonds, while the characteristic peaks at 613 and 708 cm^{-1} are assigned to symmetric stretching vibration of Si–C bonds [19]. The peaks at 862, 1266 and 1411 cm^{-1} are attributed to symmetric rocking vibration, symmetric bending vibration and asymmetric bending vibration of CH₃ groups, respectively.

Since the hydrogen atom of CH₃ groups and that of water repulse each other, it is difficult for water to approach and then wet the surfaces. Moreover, the siloxane molecule has a spiral structure, and

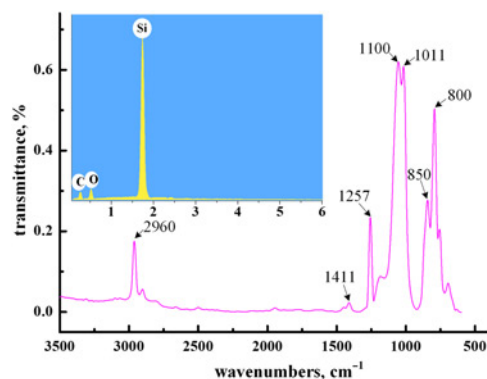


Fig. 2 FTIR and EDS spectra of the surfaces of mask

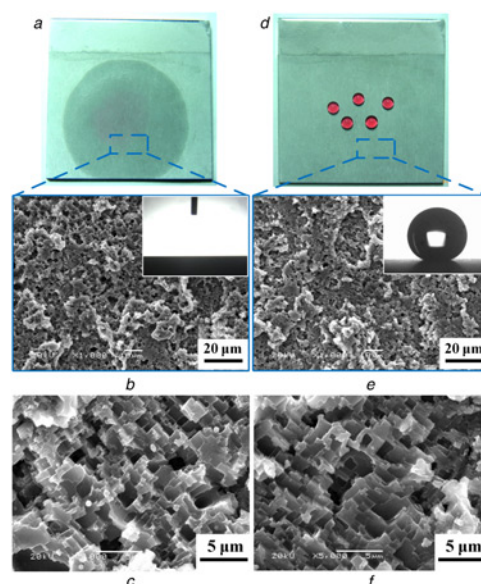


Fig. 3 Surface characterisations

a Image of superhydrophilic Al surface
b, c SEM images of superhydrophilic Al surface
d Image of superhydrophobic Al surface
e, f SEM images of superhydrophobic Al surface

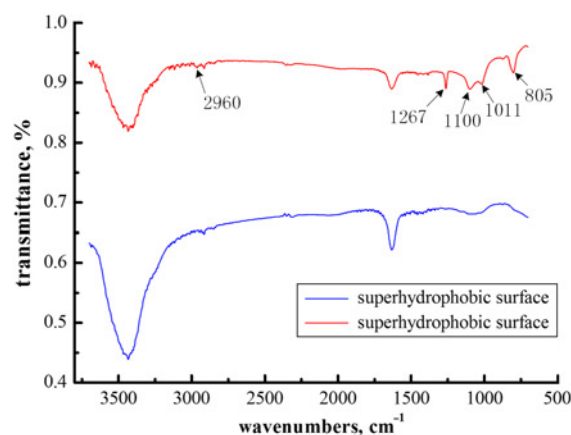


Fig. 4 FTIR spectrum of surfaces

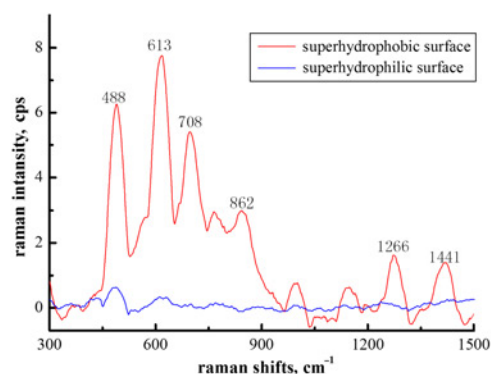


Fig. 5 Raman spectrum of surfaces

the Si–O bonds are towards the spiral axis; while the CH₃ groups face outside and shield the Si–O bonds. The bond angle of Si–O bonds is close to 150°, and the bonds are consequently prone to

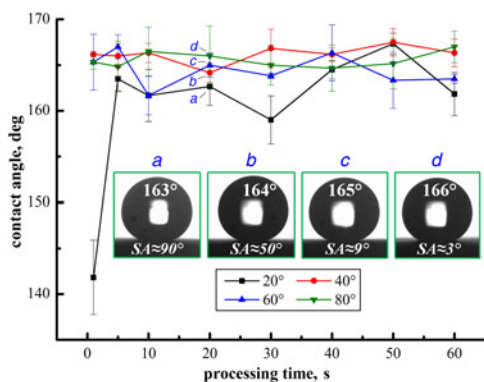


Fig. 6 Variation of WCAs with processing conditions
a–d Contact states of water droplets on surfaces treated for 20 s under different temperatures

become inner spiral [20], resulting in the increase of WCAs. Therefore, the rough surface induced by the 3D Si–O–Si bonds and the hydrophobic organic CH₃ groups on the inorganic rough surface contribute to the wettability variation from superhydrophilicity to superhydrophobicity.

According to FTIR and Raman spectra of the superhydrophobic and superhydrophilic Al surfaces, there are some new hydrophobic groups on the superhydrophobic surface, while adhesive components of the mask cannot be found. Therefore, the modification of superhydrophilic Al surfaces should be realised by chemical reactions between the hydrophobic groups and Al surfaces.

3.3. Wettability of the Al surface: The Al surfaces etched by aqueous CuCl₂ solution for 15 s were superhydrophilic. Water droplets rapidly spread after contacting with the surfaces and the WCAs of these surfaces were 0° (Figs. 3a and b). After low surface energy modification, the superhydrophilic surfaces became superhydrophobic, with the WCAs in excess of 168° and the WSAs less than 3°, as shown in Figs. 3d and e.

Fig. 6 shows influences of different modification conditions on the wettability of modified Al surfaces. Surfaces with WCAs over 150° could be obtained as long as the modifying temperature and the treatment time were more than 20°C and 5 s, respectively. When the modifying temperature was <60°C, although surfaces with WCAs over 150° could still be prepared, their WSAs were more than 90°, and there was some residual liquid after water droplets rolling off. This phenomenon can be explained by Wenzel model shown in Fig. 7a and the following Wenzel equation [21, 22]:

$$\cos\theta_w = \frac{r(\gamma_{SG} - \gamma_{SL})}{\gamma_{LG}} = r\cos\theta \quad (1)$$

where r is the roughness factor, whose value is the ratio of actual solid–liquid contact area to apparent contact area; θ_w refers to apparent CAs of liquids on rough surfaces; and θ denotes the eigen CAs of liquids on smooth surfaces. The solid–liquid contact area in Wenzel state is relatively larger and the adhesive forces between liquids and solid surfaces are therefore greater, resulting in the larger sliding angles. When the temperature was lower, only could the top surface react with the modifying materials and generate low surface energy substances. As a result, the solid–liquid contact area was larger. The contact model between droplets and superhydrophobic surfaces was Wenzel model, and the WSAs were consequently larger.

The WSAs of prepared surfaces were less than 10° when the modifying temperature was more than 60°C, and were below 3° as the temperature was over 80°C (Fig. 6). The lower WSAs can be explained by Cassie–Baxter model depicted in Fig. 7b and

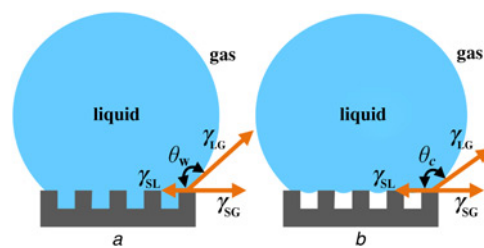


Fig. 7 Models of droplets on superhydrophobic surfaces
a Wenzel model
b Cassie–Baxter model

Cassie–Baxter equation [23]

$$\cos\theta_c = \frac{f_1(\gamma_{SG} - \gamma_{SL})}{\gamma_{LG} - f_2} = f_1\cos\theta - f_2 \quad (2)$$

where θ_c denotes apparent CAs of droplets on rough surfaces; θ refers to eigen CAs of droplets on smooth surfaces; f_1 and f_2 are the proportions of solid–liquid interface and gas–liquid interface in the composite interfaces, respectively ($f_1 + f_2 = 1$). According to (2), for surfaces whose θ_c is over 90°, θ_c increases as f_1 decreases. Therefore, the superhydrophobic surfaces ($\theta_c > 150^\circ$) in this state have a quite small f_1 , namely, a quite small proportion of solid–liquid interface in composite surface. The adhesive forces between liquids and solid surfaces are relatively lower, and sliding angles on the surfaces are consequently smaller. When the temperature was higher, the whole surface reacted with modifying materials and generated low energy substances. The grooves on rough surfaces were filled with air instead of droplets, and there were both air and solid existing under the droplets. Therefore, the apparent solid–liquid interface was indeed composed of solid–liquid interface and gas–liquid interface. Droplet and superhydrophobic surface were in Cassie–Baxter state, and the WSAs were consequently smaller.

3.4. Analysis of stability: Superhydrophilic Al surfaces fabricated under the same etching condition were modified by 0.05 mol/l stearic acid ethanol solution, 0.01 mol/l fluorosilane ethanol solution and the siloxane containing mask, and all modified surfaces became superhydrophobic. Then, variations of their superhydrophobicity with storage temperature and time were investigated. As shown in Fig. 8, with the temperature changing from 20 to 200°C, WCAs of the superhydrophobic surface modified by the mask varied very little and were always more than 150°, whereas WCAs of the surface modified by stearic acid showed obvious fluctuation and were <150° when temperature

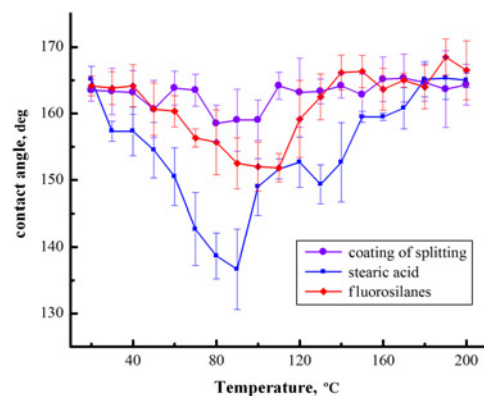


Fig. 8 Investigation on temperature stability of superhydrophobic surfaces modified by different methods

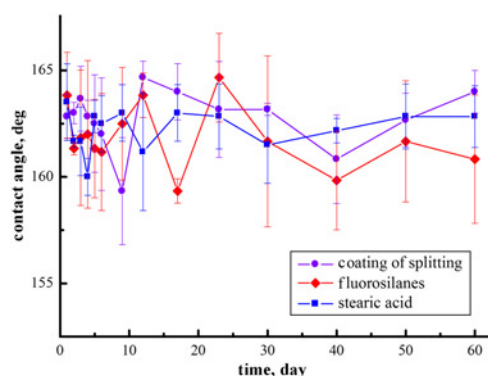


Fig. 9 Investigation on time stability of superhydrophobic surfaces modified by different methods

was between 60 and 100°C, indicating the loss of superhydrophobicity. On the other hand, WCAs of superhydrophobic surfaces modified by different materials were all in excess of 150° after 40 days of storage at room temperature (Fig. 9). Therefore, the superhydrophobic surfaces prepared by our method are less sensitive to temperature and have a good stability over time.

To investigate repeatability of the mask, one mask was repeatedly used to modify different superhydrophilic sheets. As shown in Fig. 10, after used for 15 times, the mask was still capable of modifying the sheets to be superhydrophobic.

4. Application

4.1. Patterned surfaces: Superhydrophilic patterning on superhydrophobic surfaces has great application potential in fields like biomedical detection and micro-fluidic chips. As our method can selectively lower surface energy, it is possible to directly fabricate superhydrophobic regions on superhydrophilic surfaces to obtain the patterned surfaces. The etched superhydrophilic surfaces were covered by patterned masks whose hollow patterns were manufactured by laser engraving machine. After 80°C water bath heating for 20 s and removing the masks, the regional and arrayed patterns could be obtained (Fig. 11a).

4.2. Directional transportation: It is currently a research focus in the droplet control field to fabricate superhydrophilic tracks on superhydrophobic surfaces and thereby realise directional transportation of droplets on the tracks, which can be simply and rapidly achieved by our method. As shown in Fig. 11b, hollow pattern with a 500 µm wide curve was manufactured on the mask. After covering masks, water bath heating and removing masks, superhydrophilic curves could be prepared on superhydrophobic

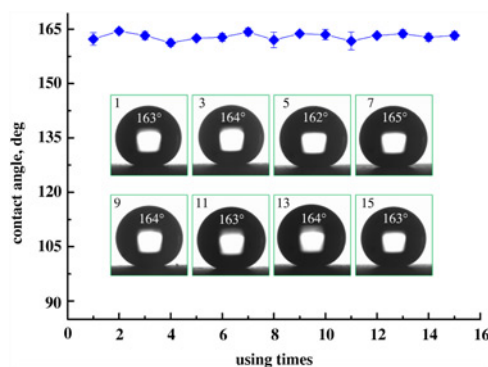


Fig. 10 Superhydrophobicity modified by one mask after used different times

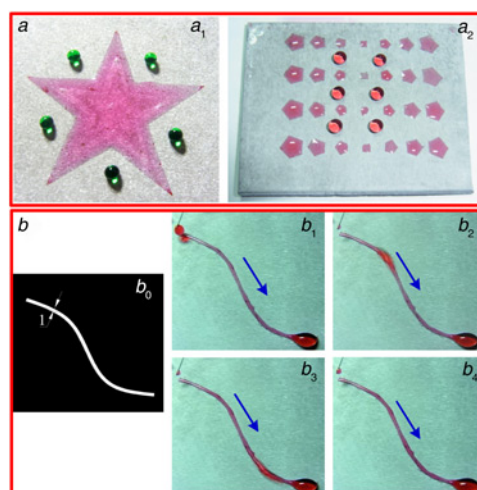


Fig. 11 Images of patterned surfaces and directional transportation process

a₁, a₂ Images of patterned surfaces
b₀ Schematic of the directional transportation track
b₁–b₄ Images of the transportation process

surfaces. Tilting the processed surfaces, water droplets of 20 µl could rapidly roll along the curved tracks to the lowest part.

4.3. Confluence and diffuence of droplets: Superhydrophilic tracks were designed as specific shapes shown in Figs. 11a₀ and b₀. Since the wedge angle structures of these tracks could generate axial Laplace force and capillary force, the spontaneous movement of the droplets could be realised. Fig. 12a shows wettability pattern for droplet confluence. Four identical structures made water droplets move from four corners to the centre driven by Laplace force and capillary force. This pattern can serve as the mixing reaction platform for different solutions, being simple and easy to operate. Shown in Fig. 12b is a wettability pattern for droplet diffuence. Driven by gravity, droplets dripped on the top could roll along the curved track and fully mix. When droplets reached the bifurcation point, they would be averagely distributed by three identical tracks, and the droplet diffuence could be thereby

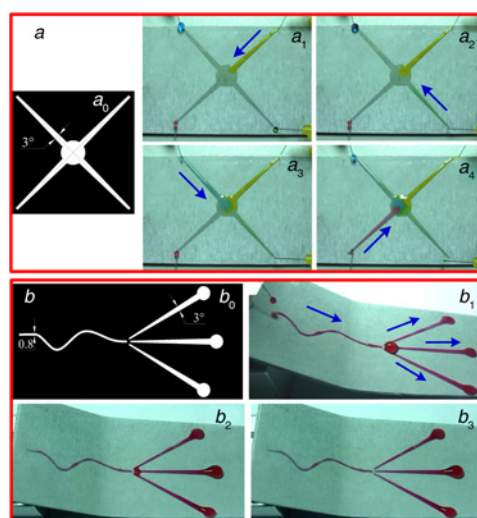


Fig. 12 Images of confluence and diffuence of droplets

a₀ Schematic of the confluence track
a₁–a₄ Images of the confluence process
b₀ Schematic of the diffuence track
b₁–b₄ Images of the diffuence process

achieved. This diffuent model can be applied in distributing solutions and cutting droplets and so on.

5. Conclusion: This Letter proposes a new modification method to lower surface energy. Metal surfaces with micro/nanoscale structures were covered by siloxane containing mask. After water bath heating and removing the mask, the regions covered by mask showed excellent superhydrophobicity. This method does not change microstructures of metal surfaces and can rapidly prepare wettability patterns by just one modification. The superhydrophobic surfaces fabricated via this method have excellent temperature resistance and good stability over time. Since the method can selectively prepare superhydrophobic regions on superhydrophilic surfaces, applications like patterning, directional transportation, droplet confluence and diffuence can be easily realised, which shows great application potential in terms of biomedical detection, micro-fluidic chips and so on.

6. Acknowledgements: This work was financially supported by the National Natural Science Foundation of China (NSFC, grant nos. 51275072 and 51305060) and the National Basic Research Program of China (973 Program, grant no. 2015CB057304).

7 References

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