

Directional transport of water droplets on superhydrophobic aluminium alloy surface

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The directional transport of water droplets has great potential applications in biochemical analysis. An aluminium (Al) alloy surface with a contact angle (CA) of 154° and a sliding angle of about 3.5° was prepared by the electrochemical etching method, which is eco-friendly and economic. An arc path line with a radius of 50 mm and a width of $400\text{ }\mu\text{m}$ was created on the superhydrophobic surface by means of lithography. CAs of water droplets on the lines exhibit anisotropy and $50\text{ }\mu\text{l}$ water droplets could slide exactly along the created line when the substrate was tilted to about 7° . The anisotropic wettability and mechanism of water droplets transport on the surface was investigated. The surface still has great water transport capability after 8 months, indicating that the water transport property of the patterned surface is stable and persistent. This method combines electrochemical etching and lithography; it is universal and economical, and could be used to build patterns on various substrates to realise the directional transport of water droplets.

1. Introduction: Surfaces with contact angles (CAs) larger than 150° and sliding angles (SAs) less than 10° are deemed to have superhydrophobicity [1]. Lots of plants and animals in nature possess superhydrophobicity. Droplets on their surfaces roll off easily and thereby wash off dust and impurity particles effectively. For example, the lotus has great water repellency due to the randomly distributed micropapillae and waxy branch-like nanostructures [2]; the bristled microstructures endow the water striders with the ability to stand on the water surface easily [3]; and cicada wings show excellent superhydrophobicity due to the hexagonally close-packed nanopillars and waxy coating [4]. Inspired by nature, the applications of superhydrophobic surfaces in industry and agriculture are increasingly being extensively discussed on account of the specific properties of corrosion resistance, drag reduction, anti-oxidation, anti-sticking of snow or ice, anti-fogging, oil–water separation and so on [5–10]. So far, a great variety of methods, such as chemical etching [11, 12], electrochemical etching [13–15], electrochemical deposition [16, 17], electrodeless galvanic deposition [18, 19], anodic oxidation [20, 21], laser microfabrication [22], templating [23] and one-step spray coating [24], have been successfully employed in preparing artificial superhydrophobic surfaces.

Recently, the realising of directional transport of liquid droplets on superhydrophobic surfaces has drawn the interest of researchers for its potential applications in biochemical analysis and medicine [25–28]. Xu *et al.* [25] prepared a superhydrophobic surface with a designed path line created by a sharp blade so that the water droplet would slide exactly along the line. On the basis of ultraviolet-enhanced photodecomposition technology, Seo *et al.* [26] fabricated the hydrophilic patterns on a superhydrophobic Si surface for water droplet transportation. However, Xu's process is less controllable, that is, a precisely defined path could not be obtained easily. Seo's method is inefficient and lacks universality.

In this Letter, a new method is presented to realise the directional transportation of water droplets on the superhydrophobic aluminium (Al) alloy surface. The Al alloy was first electrochemically etched and fluoridised to acquire the superhydrophobic micro/nanostructures. A photoresist line was created by the next lithography process so that the sliding of water droplets on the prepared surface would exactly follow the designed arc. This method can help fabricate various patterns on different surfaces for transporting water droplets directionally. Therefore, this process can be used for applications in biochemical analysis and the optical domain [25, 26].

2. Experiment

2.1. Fabrication of a patterned superhydrophobic surface: The fabrication process consists of three steps: electrochemical etching, surface energy reduction and photolithography (Fig. 1). First, the polished 6061 Al alloys ($35 \times 35 \times 2\text{ mm}$, Dalian Al material manufacturer, China) was electrochemically etched in the 0.1 mol/l NaCl aqueous solution for 8 min at a current density of 500 mA/cm^2 . The etched Al alloy specimen was then ultrasonically rinsed with deionised water, subsequently dried and immersed in a $1.0\text{ wt\%}$ ethanol solution with fluoroalkylsilane ($\text{C}_8\text{F}_{13}\text{H}_4\text{Si}(\text{OCH}_2\text{CH}_3)_3$) for 90 min to lower the surface energy. This process gave an Al alloy specimen with superhydrophobicity. The negative photoresist (BN308-300, Beijing, Kempur Microelectronics Inc.) was spun onto the prepared superhydrophobic Al alloy specimen by using a spin coater (KW-4A, Institute of Microelectronics of Chinese Academy of Sciences) at 500 r/min for 10 s and 2880 r/min for 30 s, and then prebaked at 90°C for 20 min. A film with a pattern of non-opaque arc was affixed onto the prebaked photoresist and after being exposed to ultraviolet rays in a sealed box for 25 s, the specimen was developed and rinsed with negative photoresist developer and negative photoresist rinser (Kempur Microelectronics

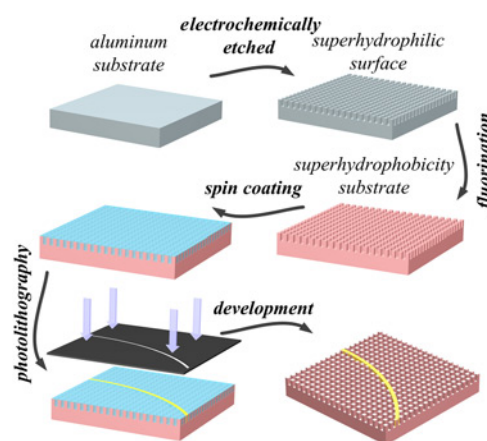


Figure 1 Schematic illustration of the fabrication process of the patterned superhydrophobic surface

Inc., Beijing) for 2 and 1 min, respectively, and finally postbaked at 130°C for 30 min. In this experiment, all chemicals were of analytical grade.

2.2. Specimen characterisation: The surface morphology of the specimens was characterised by a scanning electron microscope (SEM, JSM-6360LV, Japan). Static CAs and SAs were measured at ambient temperature using a CA system, OCA 20 (Dataphysics Instruments GmbH, Germany), with the sessile drop method. To characterise the transportation capability of the water droplets, SAs of water droplets with different volumes were measured on the specimen.

3. Result and discussion: The microstructures of the superhydrophobic Al surface were firstly investigated. Figs. 2a and b are the SEM images of the superhydrophobic surface with 2000× magnification and 5000× magnification. It can be seen that many rectangular-shaped pits with size of a few microns were homogeneously distributed on the surface and therefore, microscale and nanoscale cavities were formed. These hierarchical micro/nanostructures are similar to that of the lotus leaf, which has great static and dynamic superhydrophobicity. Then, the surface was covered with the arc photoresists, forming a line with a width of about 400 µm, a height of 10 µm and a distinct boundary (Fig. 2c, inset of Fig. 2c and inset of Fig. 2d). The morphology of the line was smoother than that of the areas without photoresist.

To evaluate the static and dynamic superhydrophobicities on the unpatterned superhydrophobic surface, the static CA and SA were measured. Water droplets of 5 µl were put on the surface slowly; an average of static CAs measured at five different locations was taken. The static CA on the unpatterned surface was as high as 154° (inset of Fig. 2a). The SA was about 3.5°, indicating that the surface prepared by electrochemical etching has an excellent dynamic superhydrophobicity. After the lithography process, the surface without photoresist still possesses great superhydrophobicity, having a CA as high as 153° and a SA of about 4.2°

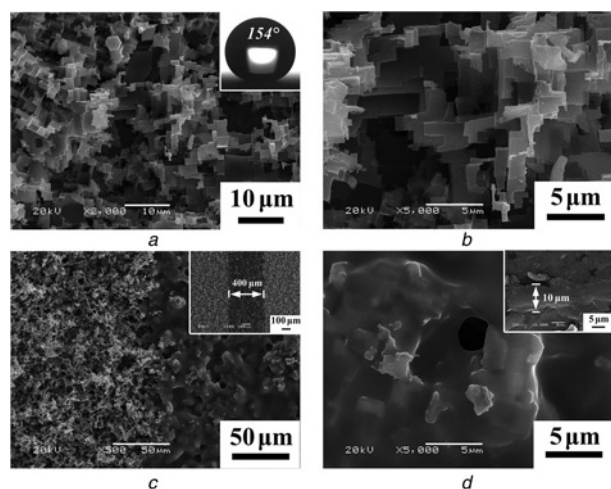


Figure 2 SEM images of unpatterned and patterned superhydrophobic surface on Al substrates

a and b SEM images of unpatterned superhydrophobic surface on the Al substrate with 2000× magnification and 5000× magnification
Inset image of Fig. 2a is the static CA on the unpatterned superhydrophobic Al surface

c SEM images of the boundary between the superhydrophobic surface and the designed photoresist line
Inset image of Fig. 2c is the designed photoresist line on the patterned superhydrophobic Al surface

d Magnified SEM images of the designed photoresist line
Inset of Fig. 2d is the cross section of the designed photoresist line

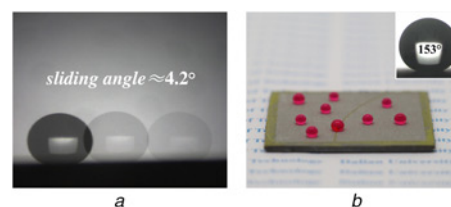


Figure 3 Images of water droplets on sample surfaces

a Image of a water droplet rolling off the superhydrophobic surface without photoresist

b Digital image of water droplets on the sample surface

Inset of Fig. 3b is the CA image of a water droplet on the superhydrophobic surface without photoresist

(Figs. 3a and b and inset of Fig. 3b). This result indicates that the superhydrophobic surface prepared by the electrochemical etching is stable and the lithography process has almost no impact on the superhydrophobicity of the surface. When a water droplet lies on the designed photoresist line, the CAs perpendicular and parallel to the line turn out to be anisotropic. Due to this, the water droplet spreads along the line direction more easily. The static CA perpendicular to the line direction decreased to 98°, compared with 149° along the line direction, as shown in the insets of Figs. 4a and g (the CA was measured by a 20 µl water droplet). To estimate the adhesion between water droplets and the designed line, a water droplet was dragged perpendicular and parallel to the line, respectively, as shown in Fig. 4. When the water droplet was dragged perpendicular to the line, the adhesion force between the water droplet and the needle led to a serious deformation of the water droplet, but could not drag it away from the line (Figs. 4a–f); however, when dragged parallel to the line, the water droplet could slide along the line under the adhesion force (Figs. 4g–l). This experiment suggests that the resistance experienced when water droplets slide along the line is smaller than that perpendicular to the line, and this resistance anisotropy is conducive to transporting water droplets along the line precisely.

Directional sliding processes of the water droplets with different volumes were observed by putting the water droplets on the patterned line slightly and tilting the substrate gradually. A water

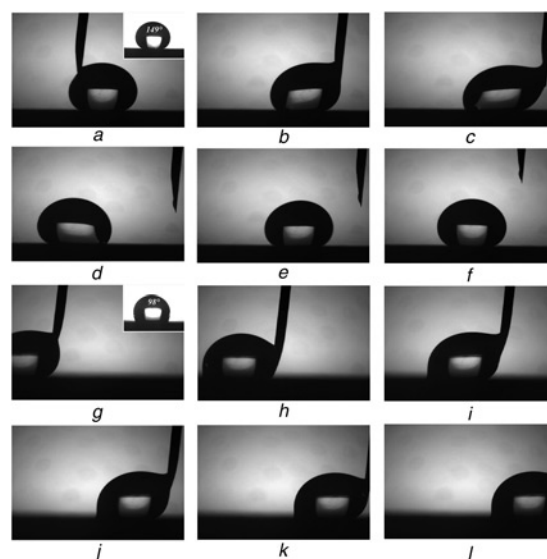


Figure 4 Images of dragging a water droplet on the designed line along two directions

a–f 20 µl water droplet was dragged perpendicular to the designed line

g–l 20 µl water was dragged parallel to the designed line

Insets of Figs. 4a and g are the static CAs parallel and perpendicular to the designed line

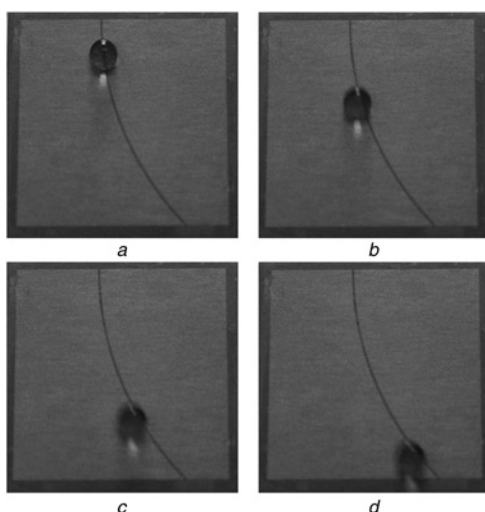


Figure 5 Rolling process of a 50 µl water droplet along the patterned surface

a At the beginning
b After 267 ms
c After 400 ms
d After 467 ms

droplet of 50 µl could slide easily at a SA of about 2° on the etched superhydrophobic surface; this suggests that the adhesion created by the surface is weak. Nevertheless, the same scale water droplet on the patterned line could not roll off at 2°, manifesting a stronger adhesion produced with the assistance of the patterned line. When the substrate was tilted to about 7°, the water droplet started to slide and more importantly, the water droplet was sliding along the designed photoresist line. Figs. 5a–d show the sliding process on the designed photoresist line.

When water droplets rested upon the superhydrophobic surface, air was trapped in the micro/nanostructures, forming an air

cushion. Therefore, water could not penetrate into the structures, which is consistent with the Cassie and Baxter model (Fig. 6a). The air cushion makes the water droplet roll off easily. The adhesion W_{adh} of a liquid on a surface is a function of liquid surface tension γ_{LV} , apparent CA θ_c and the liquid–solid interface area A_{LS} , as given by the Young–Dupre equation [28, 29]

$$W_{adh} = \gamma_{LV}(1 + \cos \theta_c)A_{LS} \quad (1)$$

Using 72.8 mJ/m² as the surface tension of deionised water, liquid–solid contact diameter of about 2.96 mm as measured experimentally with a 50 µl water droplet (Fig. 6c), and a CA of about 154°, the adhesion of the 50 µl water droplet on the superhydrophobic surface was calculated to about 50.67 nJ. However, when a water droplet was dropped on the designed photoresist line, the contact between the water and the surface turned into a composite state, that is, the contact on the line changed into Wenzel status as the hierarchical micro/nanostructures filled with the photoresist, which has a higher surface energy compared with the fluorosilane (Fig. 6b). Water droplets have to overcome the sum of adhesion W_{adh} and W_{ad-adh} to slide down, where W_{ad-adh} is the additional adhesion between the water droplets and the designed photoresist line. Assuming the liquid–solid interface area is an ellipse (Fig. 6d), the overall adhesion $W_{overall}$ can be calculated by the following equation

$$W_{overall} = W_{adh} + W_{ad-adh} \\ = \gamma_{LV}(1 + \cos \theta_c)A_{LS'} + \gamma_{LV}(1 + \cos \theta_c^*)A_{LT} \quad (2)$$

where θ_c^* is the apparent CA on the photoresist, $A_{LS'}$ is the liquid–solid interface area around the line and A_{LT} is the interface area between the liquid and the photoresist line. Using a CA θ_c^* of about 119.5° (as measured experimentally), the overall interaction adhesion of a 50 µl water droplet can be calculated to be 114.9 nJ and is, thus, twice higher than that on the unpatterned superhydrophobic surface. Moreover, the SAs of 50 µl droplets parallel and perpendicular to the designed photoresist line are 7° and 18°, respectively, demonstrating strong anisotropy. The line generated a useful anisotropic force to restrict the movement of water droplets. Therefore, the water droplet could slide directionally along the designed photoresist line.

To characterise the directional transportation property, the sliding processes of water droplets with different volumes were observed. An average of four measurements were taken at each point. As shown in Fig. 7, the SAs decrease with the increasing volume of water droplets. When the water droplets were too small, below 20 µl, they could not overcome the resistance produced by the adhesion; when the water droplets were too large, above 80 µl, they could not slide along the patterned line precisely as the constraining force could not conquer the inertia force produced by the increased mass.

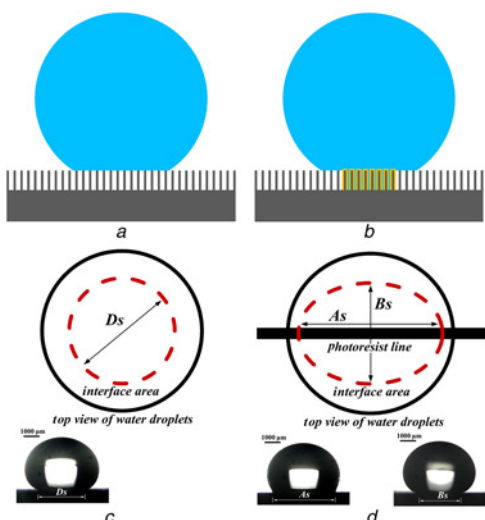


Figure 6 Schematic illustration of water droplet on the superhydrophobic surface and the designed photoresist line

a Schematics of a water droplet on the superhydrophobic surface without the designed photoresist line
b Schematics of a water droplet on the designed photoresist line
c Top view schematics of a water droplet lying on the unpatterned superhydrophobic surface. Liquid–solid interface area is a circle as shown with the red dashed line
d Top view schematics of a water droplet lying on the designed photoresist line. Liquid–solid interface area is an ellipse as shown with the red dashed line

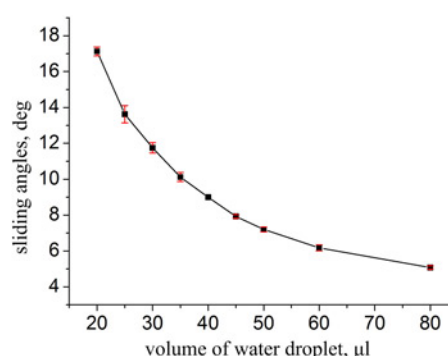


Figure 7 SAs of water droplets with different volumes

The water transport property of the patterned surface is stable and persistent. After being kept for nearly 8 months, the surface still exhibits great water transport capability. A 50 μl water droplet can roll down the line precisely at a high speed.

4. Conclusion: A simple method combining electrochemical etching, fluoridation and lithography is proposed to prepare the designed photoresist line with a width of 400 μm on the superhydrophobic Al surface that exhibits directional transportation capability of water droplets with different volumes. The anisotropic wettability and mechanism of water droplets' transport on the surface was investigated. The patterned surface still has great water transport capability after 8 months, indicating water transport property of the surface is stable and persistent. This Letter provides both a comprehension of the directional transportation behaviour of water droplets and a universal approach to create designed pattern on different superhydrophobic surfaces. This research will have profound effects on potential applications in the biochemical analysis domain and patterned surface modifications.

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6 References

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