Electrolytic colouring method for preparing robust coloured superhydrophobic surfaces with good corrosion resistance

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Achieving diverse colours in superhydrophobic surfaces is of interest in academic research and industrial applications. The current methods used to prepare coloured surfaces tend to be complicated, expensive or difficult to control the coloured areas and tune the colours. The study reports an efficient and low-cost electrolytic colouring method for the preparation of robust coloured superhydrophobic Al surfaces. The surfaces are firstly electrochemically etched and anodised before electrolytic colouring is performed. Colours of the superhydrophobic surfaces can be easily tuned by adjusting the anodisation time, and the colouring areas can be well controlled with the combination of mask technology. The corrosion behaviour and abrasion resistance of the coloured superhydrophobic surfaces are characterised by polarisation curves and abrasion tests. The results demonstrate that the coloured superhydrophobic surfaces possess excellent corrosion and abrasion resistances, indicating their application potential in industrial fields.

1. Introduction: Surfaces with a contact angle >150° and a sliding angle of <10° are defined as superhydrophobic (SH) surfaces [1–3]. The special water wettability has significant application values in different fields such as self-cleaning [4, 5], oil/water separation [4, 5], antifogging [6, 7], corrosion resistance [8, 9] etc. The preparation of SH surfaces generally involves two steps: fabricating micro/nanostructures followed by low-surface energy modification [10]. Thanks to its excellent properties including lightness and high specific strength, aluminium and its alloys have been widely used in aerospace field and industries, and the preparation of SH aluminium surfaces is therefore of great importance [11–14]. To date, there have been a few research studies focusing on the fabrication of SH aluminium surfaces by various methods including chemical method [15–17], ultraviolet irradiation [18, 19], plasma modification [20–23], and laser processing [24, 25].

The aforementioned method used to obtain SH aluminium surfaces has provided insights for future research efforts. However, the mechanical strength of these prepared surfaces is not enough for practical applications. The coating method has been proposed to overcome this problem, which could obtain robust SH surfaces on various substrates [26], but the involved chemical reagents tend to be dangerous and might pose a threat to the environment. Therefore, it is meaningful to develop an efficient and environmental-friendly method to prepare robust SH aluminium surfaces.

On the other hand, although there has been a lot of research employing various technologies to prepare SH surfaces, the diverse colours of these surfaces are seldom studied. Since coloured aluminium surfaces have wide applications in construction, transportation, shipbuilding and electronics fields, the preparation of robust coloured SH aluminium surfaces has good practical application prospects. Recently, researchers have attempted to prepare coloured SH surfaces by spray-coating and grafting [26].

However, the colour-tuning processes in these methods tend to be relatively complicated [27, 28]. Furthermore, the processing area cannot be easily controlled in these methods, which might restrain their further applications such as preparing coloured SH patterns. In this study, we firstly employ a simple electrolytic colouring method to prepare robust coloured SH surfaces and patterns with the assistance of mask technology. The aluminium surfaces are first electrochemically etched and anodised. The coloured surfaces can then be obtained by performing electrolytic colouring for just 6 min. The colours of the surfaces can be easily tuned by adjusting the anodisation time. Finally, SH surfaces with different colours can be obtained by treatment with a fluoroalkylsilane ethanol solution. We investigate water wettability, corrosion behaviour and abrasion resistance of the obtained SH surfaces using contact angle measuring instrument, electrochemical workstation, and load-sandpaper test. According to the results, the prepared SH coloured surfaces show excellent water repellence with good corrosion and abrasion resistances.

2. Experimental

2.1. Materials: 6061 Aluminium sheets (50 mm × 50 mm × 2 mm) were purchased from Dalian Al material Manufacturer (China). Sodium chloride (NaCl), oxalic acid, aluminium oxide, sulphuric acid and potassium permanganate ($KMnO_4$) were purchased from Tianjin Damo Manufacturer (China). Fluoroalkylsilane was purchased from Deguassa Co. (Germany). All chemicals were analytically pure and used as received.

2.2. Preparation of coloured SH surfaces: Shown in Fig. 1 is the preparation process of coloured SH aluminium surfaces. Aluminium sheets were first polished using abrasive papers to

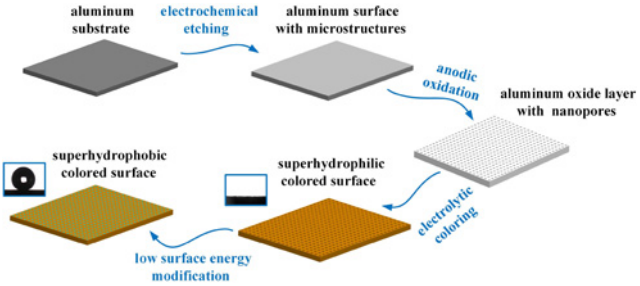


Fig. 1 *Preparation process of coloured SH surfaces*

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remove the oxide layers. Then, to construct microstructures that are necessary for superhydrophobicity, the polished sheets were electrochemically etched in 0.1 M NaCl solution with 0.5 A/cm^2 for 8 min. The etched surfaces were then anodised in 0.3 M oxalic acid solution for different times (3, 6, 9, 12, 15 min) under 60 V. After that, electrolytic colouring was performed in an aqueous mixture of 0.1 M Al_2O_3, 0.25 M H_2SO_4 and 0.06 M $KMnO_4$ for 6 min

Finally, coloured SH aluminium surfaces can be obtained after modified by fluoroalkylsilane ethanol solution for 30 min followed by 20 min heating in a thermostat with a temperature of 120°C.

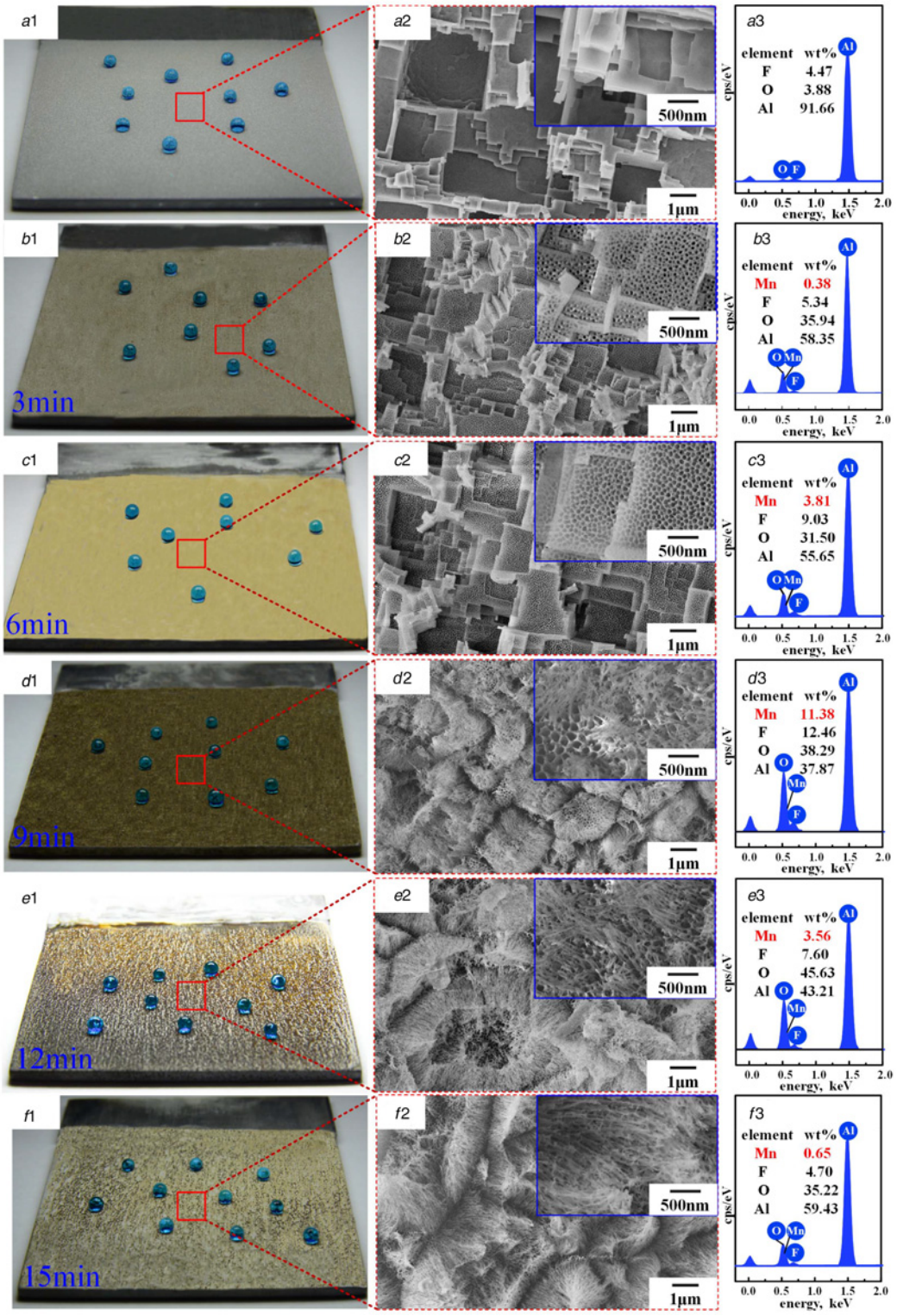


Fig. 2 *Pictures, SEM images and EDS spectra of different surfaces*
*a*1–*f*1 Pictures of Al surfaces anodised for a different time followed by electrolytic colouring
*a*2–*f*2 Scanning electron microscopy images of Al surfaces anodised for a different time followed by electrolytic colouring
*a*3–*f*3 EDS spectra of Al surfaces anodised for different times followed by electrolytic colouring

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2.3. Characterisation: The surface morphology and composition were characterised using a scanning electron microscope (SEM, SUPRA 55 SAPPHIRE, Germany). Chemical compositions of the samples were investigated by using an energy-dispersive X-ray spectroscope (EDS, INCA Energy, Oxford Instruments). Contact angles and sliding angles were investigated using 5 µl droplets by a contact angle measuring instrument (DSA 100, Krüss, Germany). The values were measured five times at five different locations on the samples surfaces. Corrosion resistance of the coloured SH surfaces was investigated by an electrochemical workstation (REFERENCE 600, Gamry, USA). The electrolytic cell used a three-electrode system: the platinum electrode was used as the counter electrode, the saturated calomel electrode was used as the auxiliary electrode, and the sample with an exposed area of 1 cm^2 was used as the working electrode. 3.5% NaCl solution (pH = 6.0) was used as the corrosion medium, and the samples were immersed in the corrosion medium for 1 h before measurement to ensure stable open circuit potential (OCP). Electrochemical impedance spectra (EIS) tests were performed at frequencies ranging from 10^5 to 1 Hz at OCP with amplitude of perturbation voltage of 10 mV.

3. Results and discussion: As shown in Fig. 2, SH surfaces of different colours can be obtained by adjusting anodisation time. The etched SH surface without anodisation was grey after electrolytic colouring. With the increase of anodisation time, the colours of the anodised surfaces firstly became gradually darker (Figs. 2*a*1–*d*1), and then became lighter (Figs. 2*e*1–*f*1). The different colours of SH surfaces are induced by the deposition of the Mn ion from $KMnO_4$ solution onto the nanoholes on the anodic oxide film, as shown in Fig. 3*a*. The deposition process of elemental Mn can be certified by the X-ray diffraction (XRD) image of the coloured SH Al surface, as shown in Fig. 3*b*. The peak at 40.4° is attributed to the characteristic peak of Mn(400), which could confirm the change of Mn^{7+} to Mn. Therefore, the deposition mechanism can be briefly expressed by the following reactions:

The deposition reaction of the metal ions on the cathode

$$Mn^{7+} + 7e^- \rightarrow Mn.$$

The discharge reaction of the hydrogen ion on the cathode

$$2H^+ + 2e^- \rightarrow H_2.$$

The anodic film on SH surfaces thus has specific colours due to the diffuse reflection of the deposited metal ions with different concentrations. As shown in Figs. 2(*a*3–*f*3), no Mn element could be detected on the electrolytic-coloured SH surface without anodisation; while the electrolytic-coloured surfaces after anodising for 3, 6 and 9 min had Mn contents of 0.38, 3.81 and 11.38%, respectively. When the anodisation time was >9 min, the Mn content decreased with the increase of time, and the Mn content of the electrolytic-coloured surface after anodised for 15 min was just 0.65%. Therefore, the colours of the SH surfaces are closely related to the Mn content of these surfaces, which are indeed adjusted by controlling anodisation time to obtain different micro/nanostructures. The etched surface without anodisation mainly consisted of step-like microstructures with pits and protrusions but no nanoholes. As a result, it was quite difficult for Mn to deposit on the surface during the electrolytic-colouring process, and the surface colour was not obviously changed after colouring. During the anodisation process, a lot of nanoscale holes appeared on the step-like microstructures, and the scale of the holes became gradually larger. This, in turn, permitted a higher concentration of Mn to deposit during electrolytic colouring leading to darker colours. However, when the anodisation time was more than 12 min, the walls of the nanoholes were broken, and the nanoholes gradually became nanowire forests. Therefore, the Mn content decreased during electrolytic colouring and the surface colour became much lighter.

To investigate the water wettability of the prepared SH surfaces with different colours, we measured the contact angle and sliding angle of these surfaces. As shown in Fig. 4, the surfaces exhibit good superhydrophobicity, with a contact angle and sliding angle being >155° and <10°, respectively. Therefore, we could successfully tune the colours of the surfaces without affecting their good superhydrophobicity after modification just by adjusting anodisation time.

Corrosion resistance is an important factor in terms of the practical application of SH surfaces [29]. Here, we investigated the corrosion resistance of the coloured SH Al surface by electrochemical measurement. The potentiodynamic polarisation curves of the coloured SH Al surface, untreated bare Al surface and coloured but unmodified superhydrophilic (SL) Al surface is shown in Fig. 5. For a typical polarisation curve of a tested surface, the higher corrosion potential (E) and lower corrosion current density (I) generally demonstrate the better corrosion resistance. Therefore, it can be seen in Fig. 5 that the coloured SH Al surface had much more excellent corrosion resistance compared with the bare Al surface and the coloured SL Al surface. The corrosion potential of the coloured SH Al surface increased by 0.126 V, and its corrosion current density decreased by three

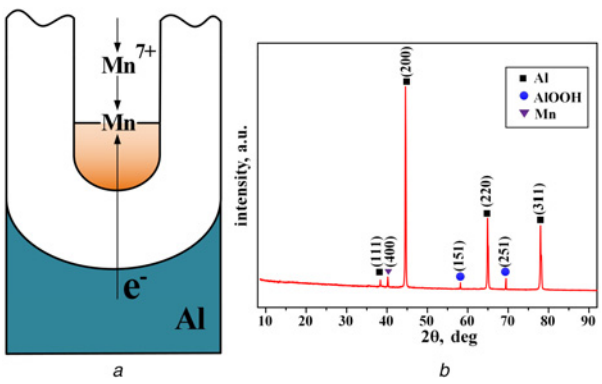


Fig. 3 *Schematic diagram and XRD image*
a Schematic diagram of electrolytic colouring
b XRD image of coloured SH Al surface

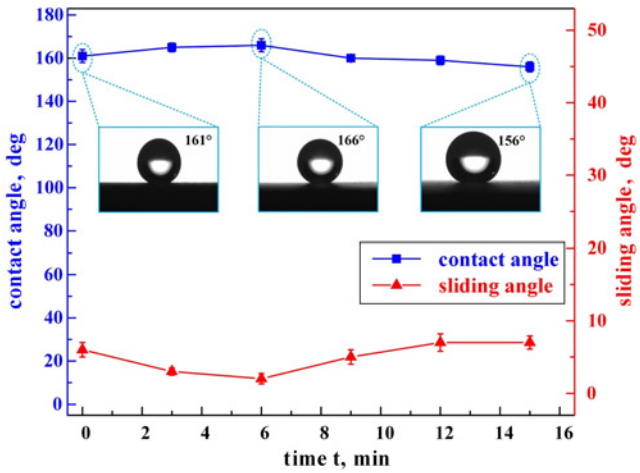


Fig. 4 *Wettability of SH Al surfaces with different colours*

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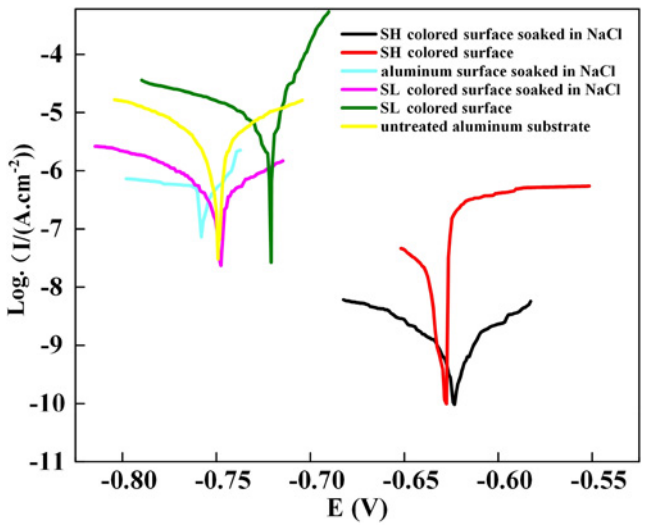


Fig. 5 *Polarisation curves of different Al surfaces*

orders compared with that of the bare Al surface. After immersing in 3.5 wt% NaCl solution for 72 h, the corrosion potential and corrosion current density of the bare Al surface and coloured SL surface changed obviously, while those of the coloured SH surface were not apparently affected. To further explore the corrosion resistance capability of the three surfaces, their EIS was measured by an electrochemical method. As shown in Fig. 6*a*, the Nyquist and Bode plots of the as-prepared samples were tested after immersing in NaCl solution. The impedance hemicycle diameter of the coloured SL Al surface and the untreated Al surface was hundreds of kΩ cm^2. The impedance spectra of the coloured SH Al surface showed a large impedance hemicycle whose diameter was around several thousands of kΩ cm^2, showing better corrosion resistance. After immersing in NaCl solution for 72 h, the hemicycle diameter of the impedance spectra reduced gradually, as shown in Fig. 6*b*. The coloured SH Al surface still showed a large impedance hemicycle with a diameter of hundreds of kΩ cm^2, which was two orders and one order of magnitude larger than that of the untreated Al surface and SL Al surface, respectively. Therefore, we believe that the prepared coloured SH Al surfaces possess good corrosion resistance, paving the way for their application in industrial fields.

Fig. 7*a* shows the abrasion test process of the coloured SH surfaces. 100 g load was fixed on the back of the coloured SH surface, which was placed face-down on the sandpaper (1000#) [29]. The SH surface was then moved back-and-forth for 10 cm as a cycle. The contact and sliding angles were investigated on five different abrased areas to test the wettability change of the whole area. As shown in Fig. 7*b*, after 40 abrasion cycles, the SH surfaces still exhibited superhydrophobicity with a contact angle being 156°–165° and a sliding angle being 1°–3°, indicating its relatively good abrasion resistance.

Combining with mask technology, the processing area of electrolytic colouring could be well controlled. The whole surface was firstly electrochemically etched and then anodised for 9 min; after that, patterned masks fabricated by a micro-milling machine were used to cover specific areas of the anodised surfaces during the electrolytic colouring process. After colouring, the colours of the exposed areas were well tuned, while the colours of the covered areas were not affected. As a result, the coloured SH patterns could be prepared, as shown in Fig. 8. The excellent controllability of the electrolytic colouring method we propose is expected to promote its practical application in different fields; especially those require different colours on one substrate.

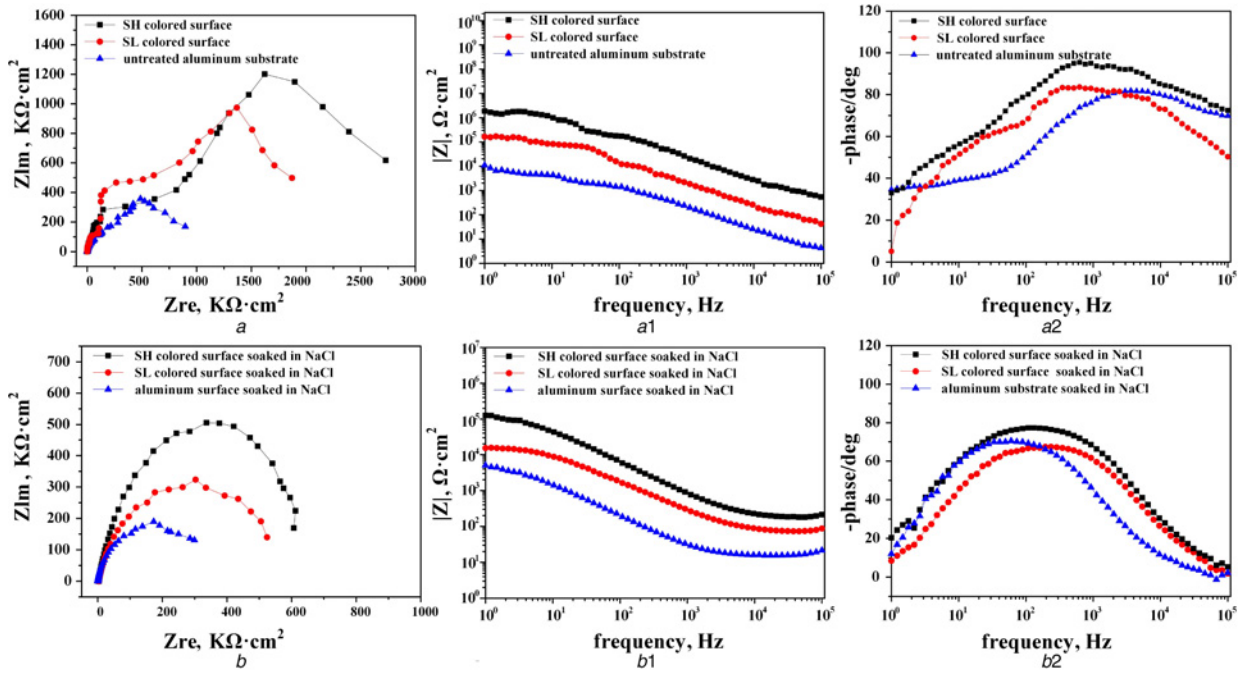


Fig. 6 *EIS results of different surfaces*
a EIS results of untreated Al, SH Al and SL Al surface after immersion in 3.5% NaCl solution for 1 h
a_1 Bode plots of $|Z|$ versus frequency
a_2 Bode plots of phase angle versus frequency
b EIS results of untreated Al, SH Al and SL Al surface after immersing in 3.5% NaCl solution for 72 h
b_1 Bode plots of $|Z|$ versus frequency
b_2 Bode plots of phase angle versus frequency

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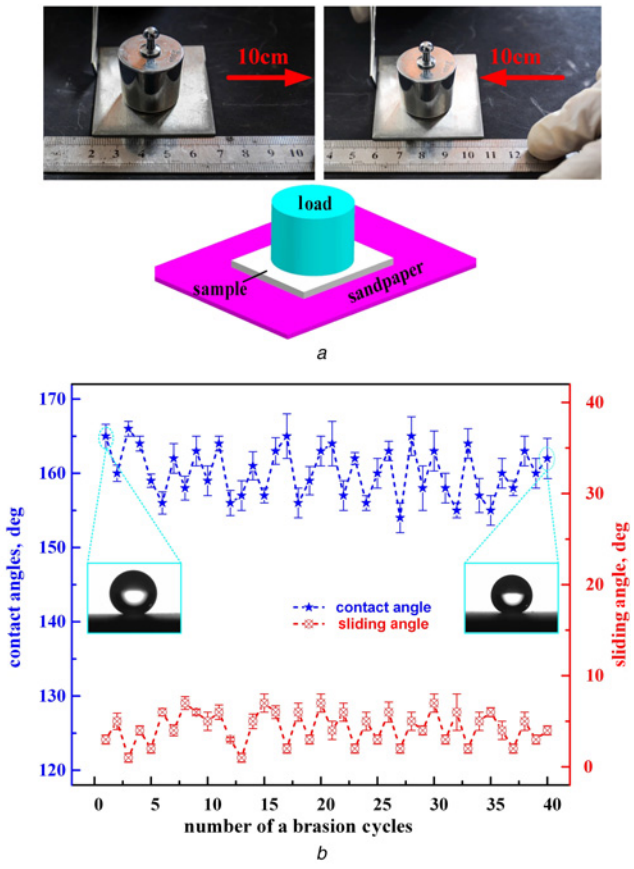


Fig. 7 *Abrasion test of coloured SH surfaces*
a Picture and schematic diagram of the test process
b wettability of coloured SH surfaces after abrasion

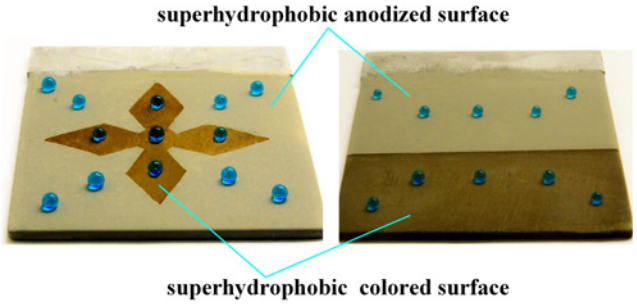


Fig. 8 *Coloured SH patterns*

4. Conclusion: In summary, we have demonstrated a new method combining electrochemical etching, anodisation, and electrolytic colouring to efficiently prepare robust coloured SH aluminium surfaces. The colours of the SH surfaces could be easily tuned by adjusting the anodisation time. When the anodisation time was 9 min, the prepared SH surface had relatively darker colour; while further increasing the anodisation time would result in the loss of nanoholes and the lighter colour of the surface. The results of electrochemical measurements and abrasion tests indicated that the prepared coloured SH surfaces had excellent corrosion and abrasion resistances. The coloured areas could be easily controlled by employing mask technique and coloured SH patterns could be thereby prepared. We think that the low-cost and efficient method presented here could provide a valid strategy and have potential practical applications for fabricating coloured SH metal surfaces and patterns.

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