Microwave-assisted fabrication of superhydrophobic surfaces on aluminium foil and the anti-corrosion properties

Yang Lu[1,2], Lina Huang[1], Xin Xin Cao[1], Libo Wang[1]

[1]School of Materials Science and Engineering, He'nan Polytechnic University, Jiaozuo 454000, People's Republic of China
[2]School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221008, People's Republic of China
E-mail: luyang@hpu.edu.cn

Published in Micro & Nano Letters; Received on 20th September 2015; Revised on 28th October 2015; Accepted on 13th November 2015

Superhydrophobic surface on aluminium (Al) substrate was successfully fabricated via a microwave-assisted process by immersing the clean pure Al substrate into the mixed solution of $Zn(NO_3)_2$ and hexamethylenetetramine, and modified with stearic acid (STA). Surface morphology and composition were characterised by using scanning electron microscopy (SEM), X-ray diffraction and X-ray photoelectron spectroscopy. The wettability and the corrosion resistance properties of the surface modified with STA were characterised. The results show that the sample had a high water contact angle of about 155°. It has good anti-corrosion for alkali and 3.5 wt% sodium chloride solution. From SEM images, it was found that abundant regular micronano sheets distributed on the surface at random and there are large amount of interspace amount the sheets. The special structure and the low surface energy make the Al foil have superhydrophobic surfaces.

1. Introduction: The superhydrophobic performance of material is a common natural phenomenon. Leaves of some plants [1] and wings or legs of some creature [2, 3] show good superhydrophobic properties. The contact angle (CA) on the water is >150°. This unique property possesses potential applicability to drag reduction, self-cleaning, anti-condensation and anti-corrosion in industry and biology [4, 5] and has attracted more and more attention.

The chemical composition and geometrical microstructure of the surface play an important role in building the superhydrophobic property of material [6]. The superhydrophobic surface can be obtained by fabricating the micronano structure and lowering of the surface energy [7]. At present, there are many methods [8–17] of preparing the superhydrophobic surface.

Metal materials are widely used in many fields due to good properties and aluminium (Al) alloys is one of them. However, the corrosion has serious damage on the metal materials. To improve the anti-corrosion and antioxidation performance of material, the surface treatment is very important. The architecture of superhydrophobic surface is an effective method. The chemical etching, anodic oxidation, electrochemical corrosion, laser etching, boiling water immersion and the *sol–gel* method are the most common ways to fabricate superhydrophobic surfaces on Al substrates [18–23].

In this Letter, a microwave-assisted method was used to fabricate superhydrophobic surface on Al substrates. After modified with stearic acid (STA), the as-prepared sample has superhydrophobicity with a high CA of 155° and has good anti-corrosion for alkali and 3.5 wt% sodium chloride (NaCl) solution.

2. Experimental results: Materials hexamethylenetetramine ($C_6H_{12}N_4$, 99%), zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$, 99.5%] and STA ($C_{18}H_{36}O_2$, 99.5%) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Al foils were purchased from Tianjin Chemical Reagent No. 3 Plant. Distilled water was laboratory prepared. All materials were used without further purification. First, Al foils were cleaned ultrasonically for 20 min in acetone, ethanol, and deionised water. Secondly, $C_6H_{12}N_4$ (0.005 mol) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.005 mol) were dissolved in 100 ml distilled water and the cleaned Al foils were immersed in the above mixture solution and kept at 80°C for 60 min by microwave heating and the obtained films were cleaned with distilled water and oven dried at 120°C for 60 min. Finally, the obtained films were placed in 1.0 wt% STA solution of ethyl alcohol and kept for 24 h, then cleaned and oven dried at 80°C for about 4 h.

The morphology of the surface modified with STA was characterised by the JSM-6390LV model scanning electron microscopy (SEM). X-ray diffraction (XRD) pattern was obtained using D8 Advance Bruker X-ray diffractometer equipment with Cu K*a* radiation using Ni-filtered. Highly sensitive X-ray photoelectron spectroscopy (XPS) analysis on the surface was carried out on a PHI-5702 multifunctional X-ray photoelectron spectrometer to obtain useful information about the chemical state of the elements of the film. The CA measurement (POWEREACH, JC2000C1) was used to obtain the wettability of the sample by the measurement of the CA on the surface of Al foil. CA values were measured five times and taken the mean on different areas of the sample.

3. Results and discussion: Fig. 1 shows the morphologies of the surface modified with STA which is characterised by SEM. From Fig. 1*a*, it can be observed that many regular micronano sheets uniformly distributed on the Al substrate randomly. Some large particles on the surface are likely the residues that have not been washed off. Figs. 1*b* and *c* show the high-magnification SEM image of the sample. From this figure, we can estimate roughly that the lamellar thickness is about 50–100 nm. Furthermore, the micronano sheets folded together and resulted in a large amount of the pore space. A lot of the micronano sheets and pore space create a hierarchical and porous structure on the surface of Al substrate which changed the surface properties of Al foil.

To know the surface composition, the sample modified with STA was characterised with XRD. Fig. 2 illustrates the XRD characterisation of the as-prepared sample. The characteristic diffraction peaks with 2θ values at 38.579°, 44.802°, 65.180° and 78.300° can be assigned to the crystal plane (111), (200), (220) and (311) of bare Al substrate. The diffraction peaks with 2θ values at 10.059°, 20.223° and 34.359° correspond to the crystal plane (003), (006) and (012) of hydrotalcite-like compounds, which accorded with the experimental results of ZnAl-LDH reported in the literature [24, 25].

To determine the surface composition of the sample modified with STA, it was characterised by XPS and the survey spectrum

doi: 10.1049/mnl.2015.0369

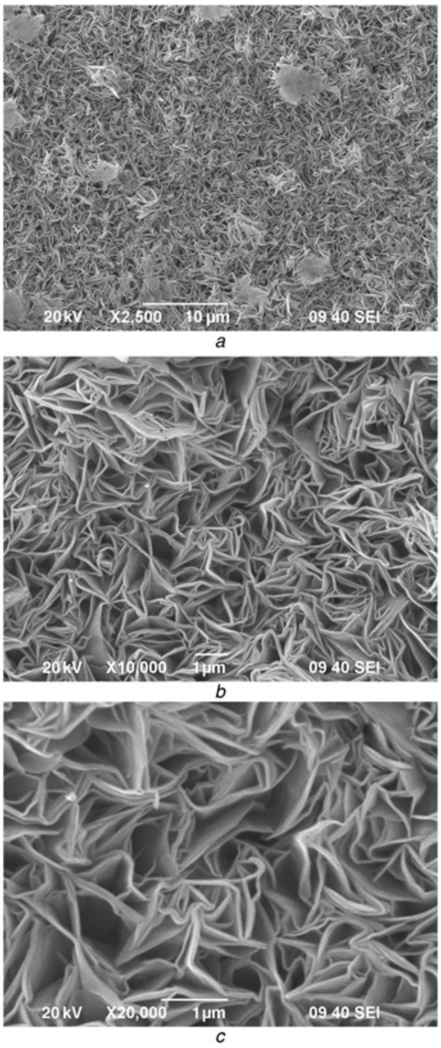

Fig. 1 *SEM images of the surface of sample modified with STA with different magnifications*
a ×2500
b ×10000
c ×20000

and high-resolution XPS spectra of Zn2p, Al2p and O1s were shown in Fig. 3. The results analysis indicated that the superhydrophobic films were composed of element Al, zinc, oxygen, nitrogen and carbon (Fig. 3*a*). The presence of C1s signal probably from the STA ($C_{18}H_{36}O_2$) that adsorbed on the surface of ZnAl-LDH and the adventitious C from exposure to air. The high-resolution XPS spectra for Zn2p, O1s and Al2p are shown in Figs. 3*b–d*, respectively. In Fig. 3*b*, the Zn2p peak at 1021.4 eV is assigned to ZnAl-LDH. In the Al2p spectrum (Fig. 3*c*), the fitting peaks at 74.2, 73.6 and 72.9 eV binding energies are assigned to ZnAl-LDH, Al oxide and Al, respectively. In Fig. 3*d*, the peaks at 531.8 eV can be assigned to the carboxy group (COOH) group of STA [25].

The results of wettability of the sample were shown in Fig. 4. From Figs. 4*a* and *c*, it can be observed that the CA of the ZnAl-LDH film modified with STA as high as 155°, which indicates that the sample modified with STA has superhydrophobicity. By contrast, the CA of the ZnAl-LDH film without STA modification is about 16° (Figs. 4*b* and *c*). The above analysis indicate that

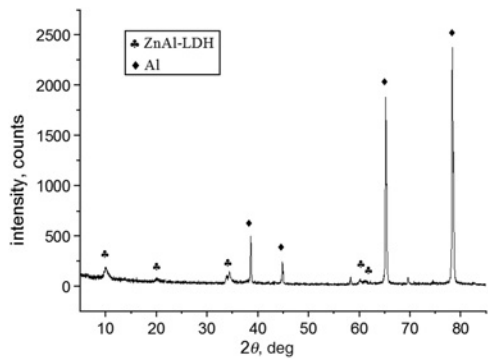

Fig. 2 *XRD pattern of the sample modified with STA*

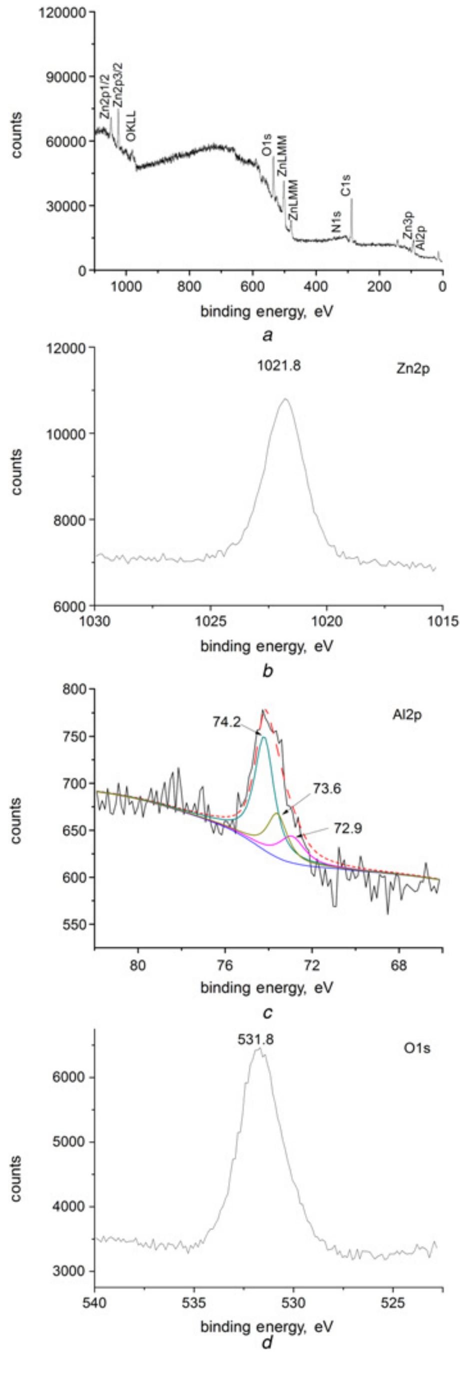

Fig. 3 *High-resolution XPS spectra of Zn2p, Al2p and O1s*
a Survey spectrum
b High-resolution XPS spectra of Zn2p
c Al2p
d O1s of sample modified with STA

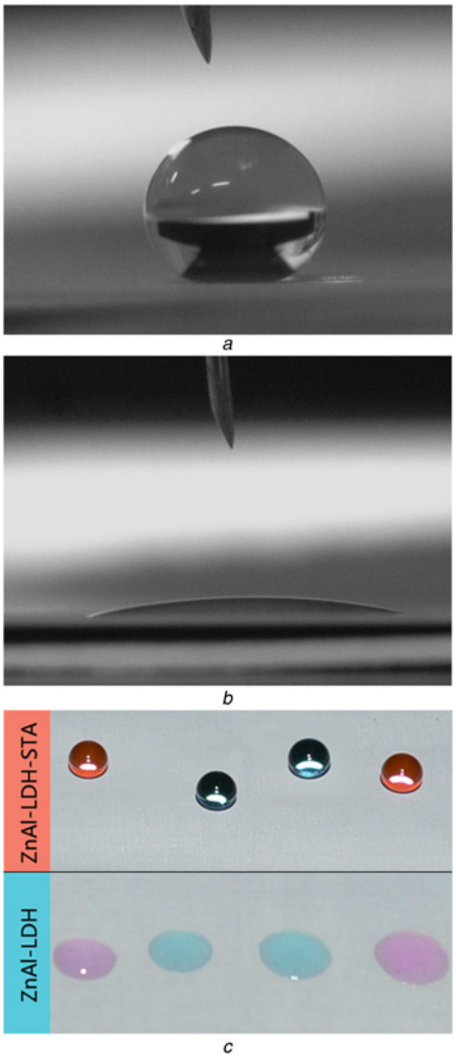

Fig. 4 *CA image of a water droplet on the surface of the ZnAl-LDH film*
a After
b Before chemical modification
c Optical images of water droplets on the film

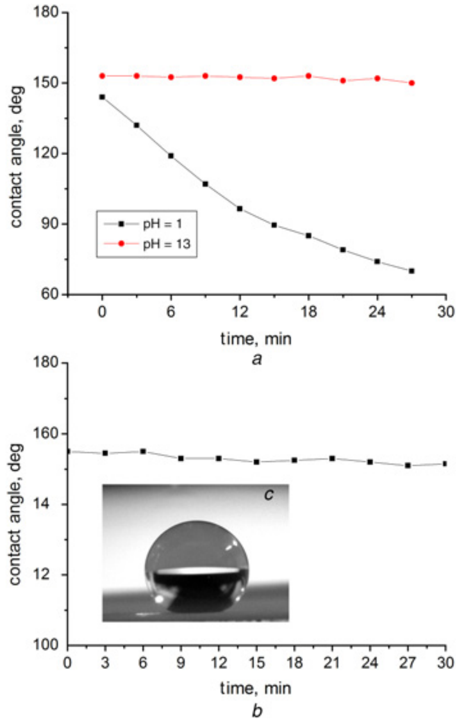

Fig. 5 *Variation of the CA versus time with acid and alkaline droplet deposited over the surface*
a Water CA of superhydrophobic surface versus time with HCl (pH = 1) and NaOH (pH = 13)
b Water CA versus the immersion time in 3.5 wt% NaCl solution
c CA image of a water droplet on the surface after 30 days in 3.5 wt% NaCl solution

the superhydrophobicity behaviour of the sample originated from the synergistic effects of the porous structures and the surface chemical composition.

The corrosion can cause the failure of metal material and lead to the large economic losses. With the development of the scientific technologies, anti-corrosion technology has become an important subject in the industrial fields. Therefore, the protection of metal is intimately involved with the people's livelihood and sustainable development of economy. Therefore, we can prevent the metal corrosion at a certain extent by metal surface treatment.

The corrosion resisting properties of the sample modified with STA in the medium of hydrochloric acid (HCl) (pH = 1) and sodium hydroxide (NaOH) (pH = 13) solution were investigated. Fig. 5*a* discloses the variation of the CA versus time with acid and alkaline droplet deposited over the surface. It can be seen that the sample has the good anti-corrosion properties on alkaline condition, and the CA has not changed with the increasing of time under the alkaline condition, while the water CA with acid droplet decreases quickly with the increasing of contact time. This can be explained by the reaction of hydrogen ion (H^+) and ZnAl-LDH which destroy the surface morphology and results in the loss of the superhydrophobicity property.

In general, seawater corrosion is the main factor that causes serious damages to the surface. In this regard, a diluted NaCl solution (3.5 wt%) was used for seawater simulating test. The superhydrophobic surface was immersed into the solution for 1month and the results are shown in Figs. 5*b* and *c*. The water CA has little changes with extending immersion time for 30 days, which indicates that the superhydrophobic film coating on Al substrate exhibits good stability. This phenomenon also means that there is no change of the surface state and the superhydrophobic structure. The above analysis shows that the superhydrophobic surface has excellent seawater anti-corrosion properties and has a potential application of Al and its alloys as engineering materials.

4. Conclusions: In conclusion, superhydrophobic surface on Al substrate has been successfully fabricated. The SEM results of morphology show that the superhydrophobic surface on Al substrate is fabricated by many regular micronano sheets, the XRD and XPS analyses indicate that the sheets were composed of ZnAl-LDH. The CA of the as-prepared surface is about 155° and the treated surface has good anti-corrosion for alkali and 3.5 wt% NaCl solution.

5. Acknowledgments: This work was supported by the Fundamental Research Funds for the Central Universities (grant no. 2014XT05), Program for Innovative Research Team (in Science and Technology) in the University of Henan Province (grant no. 2012IRTSTHN007), Program for Innovative Research Team of Henan Polytechnic University (grant no. T2013-4) and the Opening Project of Henan Key Discipline Open Laboratory of Mining Engineering Materials (grant no. MEM12-11).

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doi: 10.1049/mnl.2015.0369

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