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A green one-step fabrication of superhydrophobic metallic surfaces of aluminum and zinc

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ABSTRACT

Superhydrophobic surfaces on metal materials play a significant role in considerable industries because of its eminent water-repel and anti-pollutant ability. A facile green methodology is proposed to in situ fabricate superhydrophobic surface on aluminum surface by simply immersing the plate in an aqueous mixture solution of HCl and stearic acid. Sample possesses high contact angle (150°) and low roll-off angle (8°), because the surface simultaneously combines rough structure with low surface energy. SEM images and contact angle measurements directly show the rough structures and contact angles. It did not require any toxic chemical agents, sophisticated techniques or equipments. The surface modification and ligand bonding of stearic acid on aluminum surface were characterized by Raman spectroscopy and X-ray photoelectron spectroscopy. More importantly, the obtained superhydrophobic surfaces show remarkable stability in acidic and alkaline conditions, and the contact angle can stay above 150° without apparent fluctuation for water droplet with pH value ranging from 1 to 14. A prominent enhancement on the corrosion resistance capacity of the aluminum and zinc plates was achieved after the superhydrophobic treatment.

1. Introduction

Nature is a talented magician, which endows each organism with unique merits. A burst of research activities about surfaces with fascinating wetting properties has been carried out [1], such as cicada's wings [2], nepenthes, geckos' feet, and the best-known lotus leaves [3]. These surfaces are able to repel water and possess excellent superhydrophobic (SH) ability [4–8]. Meanwhile, SH surfaces play an important role in several domains, such as self-cleaning, water-repellence, corrosion resistance, drag-reduction and biomedical applications [9–12]. Investigation on morphology structure reveals that high roughness on micro/nanostructure surface and low surface energy (epicuticular wax crystalloids) are two significant factors in realizing the wettability of the lotus leaf. Therefore, two alternative procedures are inevitable to obtain superhydrophobic surface, i.e. creating rough structure on a low surface energy material surface or modifying rough substrate with a low surface energy material [13].

Up to now, many investigations have been performed on fabricating superhydrophobic surface by various methods, such as electrochemical reaction and deposition, electro-spinning, hydrothermal synthesis, sol-gel process, chemical etching, the self-assembly technique, layer-by-layer deposition and so forth [14–20]. These substrate materials, such as glasses, polymers, semiconductors, carbon nanotubes, cotton wires, metals, and metal meshes, have been sufficiently investigated. Aluminum (Al) and Zinc (Zn) are two kinds of metallic materials with highly controllable morphologies and excellent mechanical properties. They play important role in engineering materials, including military, aerospace, cooler air-conditioner and aerospace [21–26].

Heretofore, plentiful superhydrophobic surfaces have been fabricated on these two metal substrates via traditional two-step process and some complex one-step process. Xie etched the Al alloy by immersing it into a boiling aqueous solution of NaOH for 5 min, then modified it with an ethanol solution of lauric acid for

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30 min to lower the surface tension [27]. Xu adopted an ion exchange deposition process to fabricate superhydrophobic surfaces on Zn substrate and applied octadecyl mercaptan as the modified material [28]. Meanwhile, some relative facile methods have been reported. Saleema created a rough micro nanostructure on Al alloy surface by immersing the substrates in an aqueous solution containing sodium hydroxide and fluoroalkyl-silane (FAS-17) [29]. Song presented a method to render superhydrophobic by one-step electrochemical machining using the sodium chloride aqueous solution containing fluoroalkylsilane as the electrolyte [30]. Nevertheless, these reported processes are still confined by certain drawbacks, such as expensive materials, time-consuming process, and poisonous reagents. Beyond that, most of these methods can be merely effective to a specific metal.

Herein, a facile green one-step hydrothermal process for constructing an environmental stable SH coating on both Al and Zn substrates was presented. In the experiment, aqueous solution containing HCl and stearic acid was used to create micronanoscale structure on Al surface directly. This is the first attempt to construct a superhydrophobic surface in this way. First of all, considering the time-costing of separated steps, our one-step method is quite advantageous. Secondly, experimental intervals or accidents may pollute the samples' surface, which may lead to the destruction of SH surface. Besides, this method is facile to operate compared with the previous approaches, only limited factors deserve researchers' mention [31–33]. As we all know, complex toxic chemical solution is dangerous to operators and contaminative to environment, and is hard to decompose or clear away. The procedure did not require any complex toxic chemical agent. It is deionized water not complex organic solution that was utilized as the solvent. Apart from that, no other sophisticated techniques or equipments were required during the whole experiment. Furthermore, the products are environmentally friendly and would not cause pollution. That is why we comment it as green. Moreover, the procedure is time-saving, and SH surfaces can be obtained within 2 h. Encouragingly, the method can also be applied to Zn substrate. A series of experiments demonstrates that the coating obtained presents many promising properties such as delaying on condensation and frosting and enhancing the resistance against electrochemical etching. It is expected that this facile and inexpensive technique will promote the large-scale production of superhydrophobic engineering materials and will be widely utilized in industrial production area.

2. Experimental details

2.1. Materials

Al foil (99.0%, 0.2 mm thick), Zn sheet (99.9%, 0.25 mm thick), ethanol (C_2H_5OH, 99.0%), acetone (C_3H_6O, 99.0%), hydrochloric acid (HCl, 36.0–38.0 wt%), stearic acid were used as the starting material in the experiment. All regents were analytically pure, purchased from Sinopharm Chemical Regent Co. Ltd. (Shanghai, China) and used without further purification. Deionized water with resistivity of 18.25 M Ω was used in the whole experiment process.

2.2. Preparation of SH films with hierarchical composite structure

The main experimental process was depicted in Fig. 1. In a typical process, Al foils with the size of $1.5 \times 1.5 \times 0.01$ cm^3 were ultrasonically degreased with acetone, ethanol and deionized water for 10 min respectively. Next, the cleaned specimens were dried with a stream of nitrogen. After that, 75 mg stearic acid were added into a weighing bottle which contains 20 mL water. The bottle was then put into a water bath kettle (the temperature was kept constantly at 75 °C) for 15 min to dissolve the stearic acid. Afterwards, 500 μL 0.3 M HCl were added into the bottle, and an Al foil (Zn sheets) was soaked into the solution immediately. The duration ranged from 15 min to 90 min for Al (for Zn it was set for 75 min). After etching procedure, the samples were immediately rinsed with ethanol and then dried under heat airflow at a temperature of about 70 °C for 10 s.

2.3. Characterization

Morphologies and surface structure of the samples were observed using field emission scanning electron microscopy (FESEM, JSM-6700F), and the operating voltage was 5 KV. Surface chemical components were analysed via an X-ray photoelectron spectroscope (XPS) (THERMO Corp., ESCALAB250) equipped with standard monochromatic Al-Kα radiation (hν = 8047.8 eV). The test depth was 3 nm. Raman spectral data were recorded at room

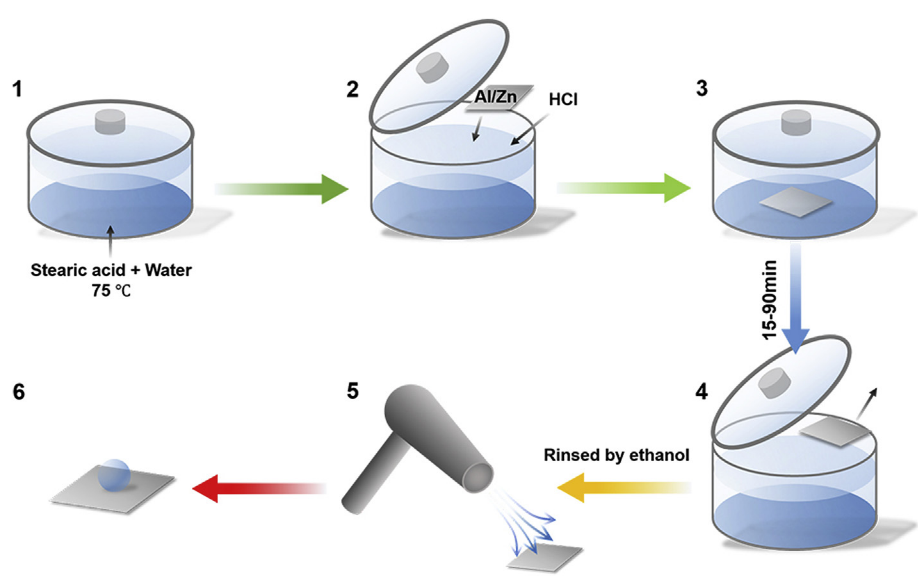

Fig. 1. A main experimental process.