



# A electro-deposition process for fabrication of biomimetic super-hydrophobic surface and its corrosion resistance on magnesium alloy



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## ABSTRACT

Super-hydrophobic surface has many special functions that are studied wildly. The ingenious micro-structures of typical plant leaves with super-hydrophobicity enlighten researchers to design and fabricate artificial super-hydrophobic surface. Being the lightest alloy among structural metals materials magnesium alloy was restricted due to its poor corrosion resistance. A super-hydrophobic surface with self-cleaning was successfully deposited on AZ91D magnesium alloy by the nickel plating process. The super-hydrophobic surfaces were covered with cauliflower-like cluster binary micro-nano structural Ni coatings. The procedure was that the samples were processed by plating after pretreatment, finally modified by stearic acid ( $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ ). The surface morphologies, chemical composition, wettability and corrosion resistance are characterized by means of SEM, FT-IR, water contact angle and electrochemical impedance spectroscopy (EIS) measurements. The as-prepared super-hydrophobic surface has a contact angle as high as  $160.8 \pm 1^\circ$  and a SA as low as  $1.8 \pm 1^\circ$ , showing good long-term stability. The super-hydrophobic surface exhibited excellent corrosion resistance property in the 3.5 wt. % NaCl solution. This method could provide a straightforward and effective route to fabricate large-area super-hydrophobic surface with anticorrosion and self-cleaning for a great number of potential applications, and easily extended to other metal materials.

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## 1. Introduction

In recent years, magnesium alloys have been used wildly due to excellent physical and mechanical properties such as low density, metal cutting performance, good electromagnetic shielding, and high strength/weight ratio etc [1,2]. Thus, magnesium alloys have been applied in aircraft, automobile, biological materials [3,4], computer industry and functional materials and so on [5–9]. However, due to low standard potential, magnesium alloy is easily oxidized and corroded, which hinder their large-scale use [10,11].

To improve the corrosion resistance of magnesium alloy, the super-hydrophobic surfaces were fabricated to reduce the expansion of corrosion especially in humid environment. Interestingly, many biological materials exhibit excellent super-hydrophobicity, such as lotus leaves, red rose petals, rice leaves, butterfly wings, mosquito eyes, moth eyes and so on [12–14]. The cooperation of micro and/or nanoscale structure and low surface materials on these natural surface results in the desired wettability, which gives

us inspiration to realize and fabricate super-hydrophobic surface on engineering materials [15–18]. In recent years, various methods have been explored to fabricate the super-hydrophobic surfaces on magnesium alloys such as electrochemical deposition [19–22], chemical etching [23–31], chemical vapor deposition [32], chemical silvering [33], micro-arc oxidation [34], polymer plating [35], phase separation [36] and anodic oxidation [37] etc. Recently, a few electroplate methods have been reported about the fabrication of super-hydrophobic on metal materials surfaces. Some researchers have fabricated stable nanostructured super-hydrophobic surfaces by electroplating on the copper. Kang *et al.* [38] fabricated the super-hydrophobic surface with a distilled water contact angle of  $155^\circ$  on copper surface by polymer plating. Gu *et al.* [39] created the super-hydrophobic surface by using a simple templateless, surfactantless electrochemical technique, and the value of the contact angle was  $154.5 \pm 1.0^\circ$ . Hu *et al.* [40] obtained super-hydrophobic nickel films with micro-nano hierarchical structure by a simple and low cost electrodeposition method, and with a water contact angle of  $154^\circ$ . Other researchers have prepared lotus-like super-hydrophobic surfaces by electroplating on the copper. Xi *et al.* [41] prepared the lotus-like super-hydrophobic surfaces with a distilled water contact angle of  $153.5^\circ$  by electroplating. Chen *et al.* [42,43]

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fabricated cathodic super-hydrophobic surface by one-step electrodeposition process, and the measured maximum contact angle is  $164^\circ$ . From the above, we realized that the super-hydrophobic surface were easily to fabricated on the copper. Compared with other metal materials, however, magnesium alloy substrate fabricated super-hydrophobic surface has rarely been reported due to its high chemical and electrochemical activity. Just like Li *et al.* [44], they fabricated anticorrosion super-hydrophobic surface on magnesium alloy by combining both electrodeposition and chemical modification, and with the contact angle of  $158.5 \pm 0.9^\circ$ . To sum up, compared with other methods, electrodeposition seem to easy to work out, cost less, the surface topography uniform, and very reproducible [45].

In this paper, the super-hydrophobic films were coated on AZ91D magnesium alloy by electroplating, which was processed by pretreatment of sample, electroless nickel plating, electrodeposition of Ni and modification with stearic acid. The micro/nanoscale cauliflower-like cluster binary structure was fabricated. The as-prepared surfaces exhibited super-hydrophobicity with self-cleaning and good long-term stability. Moreover, the anticorrosion behavior of the super-hydrophobic film was described by means of electrochemical measure in detail. Our research is expected to create some ideas from natural enlightenment to improve anti-corrosion property of magnesium alloy while this method can be easily extended to other metal materials.

## 2. Experimental

### 2.1. Materials

AZ91D magnesium alloys (composed: Al of 8.534 wt%, Zn of 0.522 wt%, Mn of 0.208 wt%, Si of 0.016 wt%, Fe of 0.002 wt%, Ni < 0.001 wt%, with balance being Mg) were cut into  $20 \text{ mm} \times 20 \text{ mm} \times 5 \text{ mm}$  as samples in this study. A Ni plate (99.9% purity) was set as the counter electrode in electrodeposition process. The solution of nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) and orthoboric acid ( $\text{H}_3\text{BO}_3$ ) were used as electroplating solution. Absolute ethanol (99.7%, Beijing Chemical Works), distilled water were used in this research.

### 2.2. Pretreatment of Sample

Firstly, the AZ91D samples were polished with SiC paper of successively finer grit down to 2000 grit, ultrasonically degreased 10 min in acetone and dried in air. Secondly, the samples were ultrasonically degreased in an alkaline solution containing 45 g/L NaOH and 10 g/L  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  at  $65^\circ\text{C}$  for 10 min, and then rinsed with deionized water. Thirdly, the samples were immersed in an acid solution containing 125 g/L  $\text{CrO}_3$  and 100 mL/L  $\text{HNO}_3$  (70% V/V) for 30–40s at room temperature, then washed with deionized water. Finally, all samples were dipped in a activation solution containing 350 mL/L HF (40% V/V) for 6–10 min at room temperature, then washed with deionized water and dried in air [20,21].

### 2.3. Electroless Nickel Plating

Because of magnesium alloys exhibiting high activity and easily to be corroded, the samples must be pre-treated before electrodeposition of Ni. The electroless plating was adopted in this study. The samples were immersed in the plating solution containing 15g/L  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , 20g/L  $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ , 25g/L  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ , 40mL/L  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , 18ml/L HF (40% V/V), 10g/L  $\text{NH}_4\text{NF}_2$ , 0.5mg/L thiourea ( $\text{CN}_2\text{H}_4\text{S}$ ), and the pH value of the solution was 5.5–6.5. The electroless plating time was 60min at  $85^\circ\text{C}$ . Then the samples were washed with deionized water, and last dried in air [20,21].

### 2.4. Electrodeposition of Nickel

The obtained samples were used as the cathode, and Ni plates of double size were used as the anode. The optimized bath contained 1.0 mol/L  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and 0.5 mol/L  $\text{H}_3\text{BO}_3$  at  $55^\circ\text{C}$ , and the pH value of the solution was 4.5–5.0 [44]. In the electrodeposition process, a constant current power with current densities about  $15 \text{ mA/cm}^2$  was applied by direct current supply under the different time at for 0, 1, 3, 5, 7 and 10 min. The schematic representation of the experimental setup was shown in Fig. 1.

### 2.5. Modification

The samples were immersed into the stearic acid containing ethanol solution (0.01 mol/L) at room temperature for 60 min.

### 2.6. Sample characterization

The water contact angles (CAs) were measured by a contact angle meter (JC2000A Powereach, China) at room temperature. The average value of five measurements obtained at different positions on sample's surface was adopted as CAs. The surface morphologies of super-hydrophobic were observed by a field emission scanning electron microscope (SEM, EVO 18, ZEISS). The surface chemical constituents were examined by Fourier transform infrared spectrophotometer (FTIR, JACSCO, Japan) and X-ray photoelectron spectroscopy (XPS, SPECS XR50). The corrosion resistance evaluation of the super-hydrophobic surface was measured in 3.5 wt. % NaCl solution for potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) by electrochemical analyzer (GAMRY Reference600, America) at room temperature. A three-electrode configuration was employed in this electrochemical tests, the sample area was exposed  $1 \text{ cm}^2$  as the working electrode, a platinum electrode as the counter electrode and a saturated calomel electrode (SCE) as reference electrode, respectively. The samples were immersed in the NaCl solution for 5 min, allowed the system to be stabilized. The potentiodynamic anodic polarization curves were measured with a sweep rate of  $10 \text{ mV/s}$ . The electrochemical impedance spectroscopic (EIS) measurements were conducted in the frequency ranges between  $10^{-2} \text{ Hz}$  and  $10^5 \text{ Hz}$ , with a sinusoidal signal perturbation of 10 mV and five points per decade.

## 3. Results and discussion

### 3.1. Surface morphology

The process of producing the Ni coating is important, so the electrodeposition time has been investigated in this study. Fig. 2 shows SEM images of sample surfaces under different times for (a) 0, (b) 1, (c) 3, (d) 5, (e) 7 and (f) 10 min, respectively. It is clearly concluded that the surfaces consist of three dimensional microstructures. The samples are covered by a large area of protrusive particles by electroless plating as shown in Fig. 2(a) and the protrusive particles is uniform and tidiness. At 1 min of electrodeposition time, it can be seen clearly that the amount of protrusive particles are increased; at same time more and more particles are packed on surface and formed cauliflower-like clusters as shown in Fig. 2(b). The microstructure of the optimal super-hydrophobic surface [42,43] is shown in Fig. 2(c), and the water contact angles of the sample show the maximum value (in Fig. 6.). It can be seen that the surface is rather rough and covered by particles, and the particles is covered with 1 to  $2 \mu\text{m}$  cauliflower-like clusters. Between the particles, it can be seen that the surfaces are covered with small particles with the diameter of about  $3\text{--}4 \mu\text{m}$ . By this microstructure

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