Materials Letters 196 (2017) 115-118

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Combination of chemical etching and electrophoretic deposition for the fabrication of multi-scale superhydrophobic Al films



materials letters

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ARTICLE INFO

Article history: Received 6 December 2016 Received in revised form 2 March 2017 Accepted 4 March 2017 Available online 6 March 2017

Keywords: Multi-scale Nanoparticles Electrophoretic deposition Superhydrophobicity Mechanical durability

ABSTRACT

In this study, we reported a new method to fabricate superhydrophobic Al films by combination of HCl/ H_2O_2 etching and electrophoretic deposition process. Through this two-step method, multi-scale hierarchical structures were successfully introduced on the surface. After hydrophobization, the resultant surface showed an excellent superhydrophobicity with a water contact angle of 169.6° and a sliding angle of ca. 1°. Furthermore, the surface exhibited excellent mechanical durability and could withstand abrasion tests under 8 kPa for 60 cm without losing superhydrophobicity. It also maintained superhydrophobicity when exposed to air or water for a long-term period. This work provides a cost efficient method to prepare mechanically robust and stable superhydrophobic Al alloy surface.

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1. Introduction

Superhydrophobic surface with a water contact angle (CA) over150° are often presented in nature, such as lotus leaf, rose petal and water strider legs [1]. Inspired by the hydrophobic biological nature, considerable efforts have been devoted to preparing artificial superhydrophobic surfaces on different substrates with the properties of self-cleaning, corrosion resistance, water-oil separation and anti-icing [2,3]. Although the fabrication methods of superhydrophobic surfaces are various, few products are available for real application due to their poor mechanical durability and short-term stability. Recently, some studies revealed that it is preferable to introduce micro and nanoscale hierarchical structures onto the substrates to ensure superhydrophobicity after surface wear [4,5]. Al is an important engineering material and widely used in various industrial areas. Thus, it is highly desirable to coat Al films with hierarchical structures for increased long-term stability and mechanical durability. Several novel strategies were developed to create multi-scale hierarchical structures on Al substrates by chemical etching-anodic oxidation method [6] and acid etchingboiling water immersion method [7] to generate superhydrophobicity with excellent robustness.

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In this study, we reported a new method to fabricate superhydrophobic Al films by combination of HCl/H₂O₂ etching and electrophoretic deposition (EPD) process. Through this two-step method, multi-scale hierarchical structures were successfully introduced on the surface. After hydrophobization by 1H,1H,2H,2 H-Perfluorodecyltriethoxysilane (FAS), the resultant surface displaying superhydrophobicity with CA of 169.6° and a water sliding angle (SA) of ca. 1°. Furthermore, the surface shows excellent superhydrophobicity when exposed to air or water for a longterm period. It can also withstand abrasion tests under 8 kPa for 60 cm without losing superamphiphobicity, demonstrating excellent mechanical durability.

2. Experimental

First, Al alloy substrate was mechanically polished using 1500# sandpaper and ultrasonically cleaned with ethanol and deionized water. The cleaned Al plates were then etched in a solution that contains $1.5 \text{ mol} \cdot \text{L}^{-1}$ HCl and $1.5 \text{ mol} \cdot \text{L}^{-1}$ H₂O₂ solution for 5 min to obtain a microstructured surface. Subsequently, 0.1 g Al nanoparticles (80 nm, Aladdin Industrial Inc., Shanghai, China) were added into a suspension (100 mL) of acetyl acetone and ethanol (vol. = 1:1), followed by ultrasonication for 20 min. Then, a pair of the microstructured Al plates were vertically immersed in the suspension with the distance of 1 cm and a 10 V DC was applied at room temperature for 3 min. Finally, the as-prepared sample



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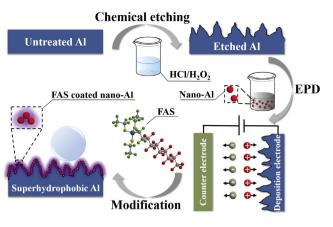


Fig. 1. Schematic illustration of the fabrication process.

was dipped in a 2 wt.% ethanol solution of FAS (Aladdin Industrial Inc., Shanghai, China) for 1.5 h and subsequently dried at 100 °C for 15 min. The schematic of fabrication route is shown in Fig. 1.

The morphologies of samples were characterized using a field emission scanning electron microscope (FESEM, JSM-7800F, Japan) and atomic force microscopy (AFM, MPF-3D-BIO, USA). The surface chemical composition was characterized by a powder X-ray diffraction (XRD, ZD-3AX, Japan), energy-dispersive X-ray spectroscope (EDS) and Fourier transform infrared spectrophotometer (FTIR, Nicolet iN10, USA). The CAs and SAs measurements were performed using an optical contact angle meter (HARKESPCA, China). The impact dynamics of drop was recorded by a high speed-video camera (Phantom V7.3, USA) at a rate of 2000 fps.

3. Results and discussion

To better understand the effect of the combination of etching and EPD on the Al surface morphology, we characterized the sample with SEM and AFM (Fig. 2). Under SEM, the panoramic morphology of the substrate shows micron-sized caverns and protrusions existed (Fig. 2a). This protrusion is composed of stepshaped microplateau (Fig. 2b). With further observation, this irregular microplateau structure are composed of Al nanoparticles with average diameter of 80 nm (Fig. 2c). This rough morphology is quite different from the Al structure obtained through a single etching process (Fig. 2d). In addition, the AMF images further confirmed the introduction of the nanostructure on the etched surface of irregular microplateau structure by the following EPD process (Fig. 2e and f). After the deposition of Al nanoparticles, the CA was increased from 161° (Fig. 2d) to 169.6° (Fig. 2b). This is mainly because of the micro- and nanoscale roughness and the high curvature of the convex nanoparticles on the surface after EPD process [8]. We also found increased EPD process results in decreased roughness of the substrate. When the EPD was longer than 3 min, over deposition of Al nanoparticle masked the Al microplateau substrate, resulting in a less rough morphology and slightly decreased CA (Fig. S1. Supporting information). By the combination of chemical etching and EPD process, we successfully fabricated a

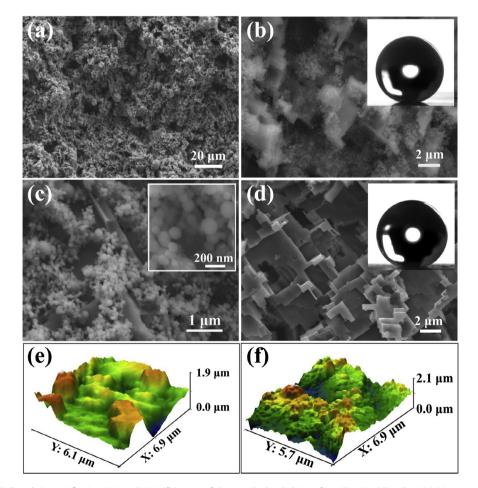


Fig. 2. The low (a) and high (b and c) magnification SEM and AFM (f) images of the superhydrophobic surface. The SEM (d) and AFM (e) images of the etched Al surface. The insets (in b and d) are the respective droplet images.

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