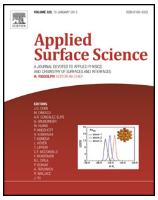
Applied Surface Science 325 (2015) 151–159

Contents lists available at ScienceDirect

Applied Surface Science

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



Fabrication of hierarchical structures for stable superhydrophobicity on metallic planar and cylindrical inner surfaces

Xiuqing Hao[a,b,*], Li Wang[a,*], Danhui Lv[a], Quandai Wang[c], Liang Li[b], Ning He[b], Bingheng Lu[a]

[a] State Key Laboratory for Manufacturing Systems Engineering, School of Mechanical Engineering, Xi'an Jiaotong University, Xi'an 710054, China
[b] College of Mechanical and Electrical Engineering, Nanjing University of Aeronautics & Astronautics, Nanjing 210016, China
[c] School of Mechanical and Precision Instrument Engineering, Xi'an University of Technology, Xi'an 710048, China

ARTICLE INFO

Article history:
Received 22 August 2014
Received in revised form 27 October 2014
Accepted 3 November 2014
Available online 18 November 2014

PACS:
42.82.Cr
81.65.Cf

Keywords:
Superhydrophobic
Electrochemical micromachining
ZnO
Droplet bouncing
Cylindrical inner surface

ABSTRACT

Recently, the construction of stable superhydrophobicity on metallic wetting surfaces has gained increasing attention due to its potential wide applications. In this paper, we propose an economic fabricating method, which not only is suitable for metallic planar surfaces, but also could be applied onto cylindrical inner surfaces. It mainly involves two steps: etching micro-concaves by a movable mask electrochemical micromachining (EMM) technique and fabricating nanopillars of ZnO by a hydrothermal method. Then the influences of surface morphology on the static and dynamic behaviors of water droplets are investigated. The energy loss during impact on the surfaces is quantified in terms of the restitution coefficient for droplets bouncing off the surfaces. For hierarchical structures with excellent superhydrophobicity (contact angle ≈180° and sliding angle ≤1°), the droplet bounces off the surface several times, superior to the droplet's response on single nanopillars (contact angle ≈165.8° and sliding angle ≈6.29°) where droplet bounces off only for limited a number of times, and even far better than the dynamics of a liquid droplet impinging on microstructures (contact angle ≈132.1° and sliding angle >90°) where droplet does not rebound and remains pinned. The highest elasticity is obtained on the hierarchical surface, where the restitution coefficient can be as large as 0.94. The fabricating method is then applied onto the cylindrical inner surface and the wetting behavior is confirmed to be consistent with the planar surface. This method, which can be generalized to any kind of solid electroconductive metal or other surfaces with different shapes, could find wide practical applications in self-cleaning surfaces, chemical industry, microfluidic devices, mechanical engineering and aviation.

1. Introduction

Superhydrophobicity, implying extreme water repellency with contact angle (CA) over 150° and sliding angle (SA) less than 10° [1], is a distinctive characteristic of surface structure. The representative superhydrophobic surface is Lotus Leaf, which was discovered in 1997. There have been many efforts in understanding Lotus effect, which is jointly contributed by the dual scale hierarchical structure of papillose epidermal cells and the additional layer of epicuticular waxes. Recently, mimicking nature in producing superhydrophobic surfaces has been undertaken by increasing researchers in the lab and industry [2] due to its potential practical applications, including self-cleaning windows [3,4], water-proofing cloths and textiles [5–7], windshield, roof tiles, and antibiofouling surfaces [8–11]. The wettability of a solid surface is governed by surface chemical properties and its roughness [12,13]. Combining chemical modification with surface structuring can realize specific wettability on functional surfaces, which may bring an advance in a wide variety of applications [14]. Several different techniques have been employed to modify a surface's morphology and chemistry [15–21]. One typical way to realize superhydrophobicity is by introducing surface topology and controlling the area ratio of the top pillar surface to the total base surface in order to offer plenty of air pockets between solid and liquid and maintain the droplet in Cassie–Baxter state [22–24].

Many researchers have investigated the effect of surface morphology on the wetting behavior and bounce ability of a

---

* Corresponding authors at: State Key Laboratory for Manufacturing Systems Engineering, School of Mechanical Engineering, Xi'an Jiaotong University, Xi'an 710054, China. Tel: +86-29-83395021; Fax: +86-29-83399512.
E-mail addresses: xiuqing.hao@gmail.com (X. Hao), wanglime@mail.xjtu.edu.cn (L. Wang).

http://dx.doi.org/10.1016/j.apsusc.2014.11.014
0169-4332/© 2014 Elsevier B.V. All rights reserved.

water droplet [25–30]. Jung and Bhushan [26] demonstrate that hierarchical surfaces have better water repellency as compared to single-roughness (SR) elements. Based on the Laplace pressure and Bernoulli pressure, they formulate an expression for the critical velocity of a droplet on textured surfaces beyond which it would convert to a Wenzel state. Richard et al. [31], Bartolo et al. [32] and Reyssat et al. [33] show that the transition can occur on the patterned surface at a critical geometric parameter. Malouin et al. [29] extend advances in the understanding of a droplet rebound on both uniform and non-uniform textured surfaces, and show that the droplet rebound trajectory could be tuned by surface roughness gradients. It is noted that the most studies focus mainly on the single-tier surface structures with spacing sizes in two extreme ranges (the micro-posts arrays with micro-spacing and the nano-pillars arrays with nano-spacing) [34], while the dynamic behaviors of water droplet impacting on multi-level hierarchical structures and the effects of the geometrical dimensions and morphologies of the different level structures are not involved in the above studies. Furthermore, most studies are conducted on the surfaces with raised posts, few have been reported concerning the dynamic response of a droplet impinging on the hierarchical surface with concave microstructures.

The construction of superhydrophobic surface on metal substrates is of great interest to extend their applications [35,36]. For example, cuprum and its alloys (such as brass and bronze) are considered as one of the most widely used engineering materials, possessing important applications in aviation, aerospace, automotive, machinery manufacture, shipbuilding, and chemical industries because of their superior physical and mechanical properties, such as high plasticity, easy processing, and good corrosion resistance. Various fabrication techniques have been used to obtain textured superhydrophobic surfaces, including both physical and chemical methods [36–42]. Examples of fabrication processes include lithography, chemical vapor deposition, sol–gel and dry etching. Although every technique has its own specialities and advantages, only few methods are suitable to be applied onto the metallic cylindrical inner surface, such as transmission pipe and hydrodynamic bearing. For instance, the texture of planar metallic surface could be obtained by the conventional photolithography followed by chemical etching or electrochemical micromachining (EMM) technique. However, this method is not fit for cylindrical inner surface because of the difficulties in fabricating the patterned mask. In addition, the chemical etching and EMM method are generally just able to get the microstructures with low aspect ratio (ratio of the height and diameter), which does not benefit to obtain stable superhydrophobicity [47]. Another typical way to obtain texture on metallic substrates is by laser technique [43] which could get different texture conveniently. However, it belongs to serial processing method and usually demands long time for large-area fabrication, and in principle, does not have the ability of inner surface structure fabrication. Meanwhile, it is worthy to note that the introduction of the hydrophobicity into the pipe or sliding bearing system has strong potential for drag reduction and energy consumption [44,45]. Therefore, developing more convenient and cost-effective methods for fabricating micro/nano or hierarchical structures over large areas on the surface with different shapes and suitable for various metallic substrates is necessary and imperative.

In this study, an efficient method, combining EMM and hydrothermal process, is reported to prepare stable superhydrophobic and highly water repellent surfaces for metallic materials. The dynamics of drop impact on hierarchical structures, along with single-tiered microcrater and ZnO nanopillar jungles, are investigated. The aim is to compare the impact behaviors upon various types of hydrophobic surfaces and to examine the effect of different roughness. Moreover, complementary to recent studies of drop impact using superhydrophobic surfaces, the structure could find many potential applications in our daily life and industrial fields.

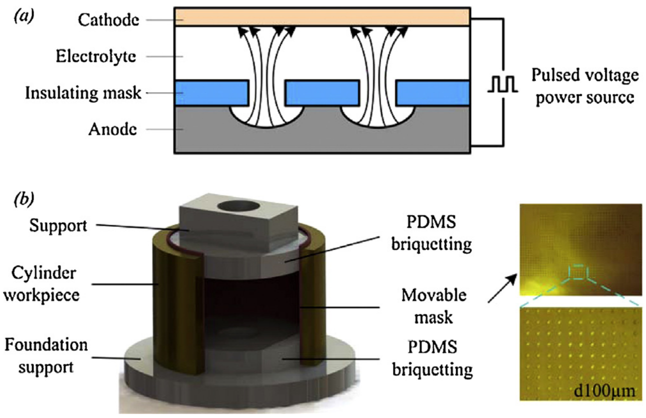


Fig. 1. The schematic diagram of the movable mask EMM for the cylindrical inner surface: (a) the principle of the movable mask EMM; (b) the texture fabricating setup and the image of the movable mask.

2. Experimental details

2.1. Materials and surface texture fabrication

Tin-bronze (ZQSn6.5-0.1), an important material of hybrid bearing in engineering, is selected as the object material. A movable mask EMM method and a hydrothermal process of ZnO are introduced to obtain micro-concaves and nano-pillars, respectively. The fabricating details of surface texture are as follows.

All the samples are cleaned in ultrasonic baths of acetone (10 min), ethanol (10 min) and deionized (DI) water (5 min). After drying with pure nitrogen, dehydrating in a hot plate (100 °C) and cooling, the surfaces are well prepared.

2.1.1. Single-tier microtextured surface (STMS)

The microstructures are obtained by a movable mask EMM method. The schematic diagram of the movable mask EMM for the cylindrical inner surface is shown in Fig. 1. Fig. 1(a) gives the principle of the movable mask EMM method, which is achieved by putting a layer of patterned insulating mask on the anode surface to confine the current distribution. The texture fabricating setup and the image of the movable mask are displayed in Fig. 1(b). The PDMS briquetting is used to provide a press pressure and to fit the mask with the cylinder inner surface. The mask is a flexible polyimide film and etched with femtosecond laser to obtain the perforated patterns.

During EMM, the metallic workpiece serves as anode and an aluminum plate is used as cathode. A pulsed voltage of 10 V with the frequency of 100 kHz and the pulse-on time of 480 ns is applied between the anode and cathode during the whole etching process. Both electrodes are facing each other with a gap of 20 mm in the electrolyte which is a neutral salt solution with the compositions of 10 wt% $NaNO_3$ + 10 wt% NaCl (details of the optimization of electrolyte could be referred to previously published paper [46–48]). The solution is stirred with an ultrasonic agitator during etching, which facilitates the concentration gradient alleviation and continuous renewal of the electrolyte at the critical dissolution areas. The etching velocity is about 0.4 μm/min under these conditions.

2.1.2. Single-tier nanotextured surface (STNS)

The fabrication of well-aligned ZnO nanopillars mainly involves three steps. First, the ZnO seed crystal solution is prepared by a colloid method. In details, zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$)