Applied Surface Science 393 (2017) 449–456

Contents lists available at ScienceDirect

Applied Surface Science

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

Full length article

Facile and cost-effective fabrication of patternable superhydrophobic surfaces via salt dissolution assisted etching

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ARTICLE INFO

Article history:
Received 28 July 2016
Received in revised form 7 October 2016
Accepted 9 October 2016
Available online 11 October 2016

Keywords:
Superhydrophobic surface
Polydimethylsiloxane
Cost-effective fabrication
Salt-dissolution-assisted etching

ABSTRACT

Superhydrophobic surfaces with extremely low wettability have attracted attention globally along with their remarkable characteristics such as anti-icing, anti-sticking, and self-cleaning. In this study, a facile and cost-effective approach of fabricating patternable superhydrophobic surfaces, which can be applied on various substrates (including large area and 3D curvilinear substrates), is proposed with a salt-dissolution-assisted etching process. This novel proposal is environmentally benign (entirely water-based and fluorine-free process). The only required ingredients to realize superhydrophobic surfaces are commercially available salt particles, polydimethylsiloxane (PDMS), and water. No expensive equipment or complex process control is needed. The fabricated superhydrophobic surface shows high static contact angle (~151°) and a low sliding angle (~6°), which correspond to the standards of superhydrophobicity. This surface also shows corrosive liquids (acid/alkali)-resistant characteristics. Moreover, the self-cleaning ability of the fabricated surfaces is explored. As a proof-of-concept application of the present approach, the spatially controllable superhydrophobic patterns on flat/curvilinear substrates are directly drawn with a minimum feature size of 500 μm without the use of expensive tooling, dies, or lithographic masks.

1. Introduction

Superhydrophobic surfaces, which present a static contact angle of water close to or higher than 150°, have drawn worldwide attention both in the academy and industry because of their remarkable characteristics such as anti-icing, anti-sticking, anti-contamination, and self-cleaning [1–5]. Taking the self-cleaning effect as an example, particulate contaminants or dusts located on the solid surface can be easily removed by rolling the water droplets off the surface [6,7]. With this benefit, a superhydrophobic property has been applied in various products such as paints, solar cells, shoes, windshields, and textiles [1–4,8–10]. In nature, many surfaces show superhydrophobic property; examples of these surfaces are lotus leaf, rose petal, and water strider's leg [11–15]. The superhydrophobic property in these surfaces is mainly due to the cooperative effect of the roughness with micro/nano-hierarchical topography and low-surface energy waxy coating. From the above understanding, constructing micro/nano-sized structures on the surface and reducing the surface energy are considered essential steps to realize the superhydrophobic surface. With increasing efforts devoted to realize the superhydrophobic surface, various approaches have been suggested and developed using lithography, plasma etching, micro-machining, self-assembling, electrochemical etching, sol-gel method, phase separation, and chemical vapor deposition [1–3,8,16–25]. Despite the great technological advancements on fabrication of superhydrophobic surfaces with the abovementioned methods, several strategies still require special equipment, complex process control, expensive ingredients, and post-chemical treatments with fluorinated compounds [1–4,8,9,26,27]. Recently, approaches relying on a fluorinated compound involving an organic solvent, which enables facile realization of superhydrophobicity with the help of its extremely low surface energy, have attracted attention as environmentally detrimental methods because of their adverse effects on human beings and the environment [28–31]. In this sense, the development of a simple, cost effective and environment friendly method to fabricate superhydrophobic surfaces would be advantageous in practice.

Polydimethylsiloxane (PDMS) is a well-known inexpensive elastomeric silicon-based material with plenty of advantages such as deformability, biocompatibility, thermal stability, and non-toxicity [32–35]. Given these benefits, PDMS is widely used from biomedicine to microfluidics and lab-on-a-chip applications [32,36–38]. PDMS is fluorine-free but hydrophobic with relatively

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http://dx.doi.org/10.1016/j.apsusc.2016.10.057
0169-4332/

low surface energy; the well-known resistance of PDMS elastomers to wetting is an advantage for applications such as coatings [39–43]. From this viewpoint, PDMS can exhibit superhydrophobicity by roughening its surface [3,9,44]. To date, various superhydrophobic PDMS surfaces have been successfully fabricated by methods employing laser etching, plasma etching, templating, and phase separation; PDMS has received much attention as a suitable material to realize superhydrophobic surfaces [3,8,45]. However, many approaches involve the utilization of expensive equipment and complex process control, which hinder their practical utilization. In this study, a facile and cost-effective approach to realize a fluorine-free superhydrophobic PDMS surface is proposed with a salt-dissolution-assisted etching process. This novel process is based on the exposure of a salt-particle-embedded PDMS surface to an aqueous environment, resulting in dissolution of salt particles. The remaining PDMS surface becomes roughened with micro/nano-hierarchical topography depending on the size of salt particles. Thus, the process is called salt-dissolution-assisted etching. Notably, the proposed process is different from the conventional salt-leaching technique, which is often employed to fabricate porous materials. Considering that the conventional salt-leaching technique fabricates porous bulk materials, all salt particles inside a material should be interconnected to those on the surface for its exposure onto solvents, such as water. For its implementation, the particles and the surrounding material should be uniformly mixed and the ratio between them is crucial and demanding. Also, Pretreatments such as particle compaction should be performed for the interconnection of particles. Unlike the conventional salt-leaching technique, the proposed process only requires surface modification of the material, avoiding its bulk modification. Therefore, the process can be easily achieved by simply introducing the particles onto the material surface, thereby enabling facile and fast fabrication of a superhydrophobic surface without additional steps. The fabricated surface shows a high static contact angle (~151°) and a low sliding angle (~6°), which satisfy the standards of superhydrophobic surfaces [2,3]. It is experimentally shown that the fabricated superhydrophobic PDMS surface has corrosive liquids (acid/alkali)-resistant characteristics with the help of the intrinsic property of PDMS and hierarchical rough structures on its surface resulting in the reduced contact surface area compared with the flat surface. Given that the whole process to realize the superhydrophobic surface is 1) entirely based on water (without the use of volatile organic solvents) and 2) the only required ingredients are commercially available salt particles and PDMS, avoiding the use of expensive materials and equipment, the present fabrication approach can be regarded as cost effective, facile, and environmentally benign. The superhydrophobic surfaces on a large-area substrate as well as 3D curvilinear substrates are successfully fabricated, and their self-cleaning abilities are demonstrated. By employing the proposed approach, spatially controllable superhydrophobic patterns, which offer a means for controlling the wetting behavior of aqueous solutions, are directly drawn onto flat/curvilinear substrates without the use of expensive tooling, dies, or lithographic masks.

2. Material and methods

2.1. Materials

PDMS (Silicone Elastomer-184, Dow-Corning) mixed with curing agent (curing agent-184, Dow-Corning) in a 10:1 wt. ratio and NaCl (+80 mesh particle size, Sigma) are utilized to fabricate the superhydrophobic PDMS surface. KOH (45%, JT Baker) and HCl (37 wt%, Aldrich) are diluted with deionized water (Samchun Chemical) to regulate the pH of the solution. KCl (Sigma) is used to investigate the effect of electrolyte concentration. Carbon nanopowder (12 nm flake, Graphene Supermarket) is utilized as dust in the self-cleaning experiment.

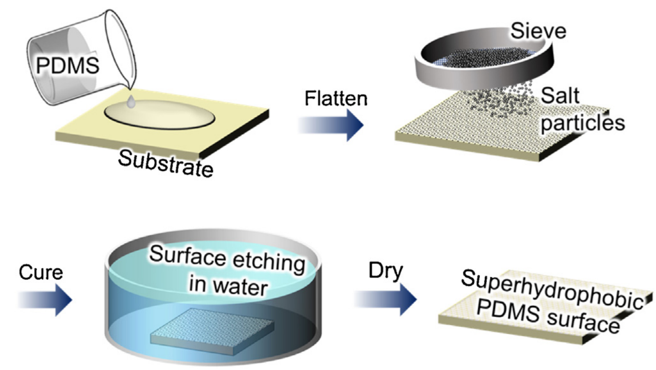

Fig. 1. Schematic diagram to fabricate superhydrophobic PDMS surface with the help of a salt-dissolution assisted etching process.

2.2. Fabrication of the superhydrophobic surface

First, PDMS mixed with curing agent is poured onto the substrate. To flatten PDMS, PDMS is spin-coated onto a flat substrate. In the case of 3D curvilinear substrates, PDMS onto the substrate is self-leveled and flattened by exposing it to an ambient temperature for about 5 mins. After introducing salt particles onto PDMS, the salt particle embedded PDMS is cured on a hot plate (180 °C) for 10 min. The result confirmed that curing of PDMS can be achieved in an oven (65 °C) for 4 h. After the curing process, the sample is dipped into the water bath and then sonicated for 10 min to completely dissolute the salt particles.

3. Results and discussion

3.1. Fabrication of superhydrophobic surfaces through salt-dissolution-assisted etching

Fig. 1 shows a schematic of the fabrication of superhydrophobic PDMS surface with the help of a salt-dissolution-assisted etching process. First, uncured PDMS mixed with curing agent is poured onto the substrate. After flattening uncured PDMS, salt particles are introduced onto the top surface of uncured PDMS, and then it is cured and dipped into water to implement the salt-dissolution-assisted etching process. In this step, only salt particles are selectively etched by exposure to the aqueous environment, and the cured PDMS is kept onto the surface resulting in micro/nano-hierarchical topography. Given that the topography is highly dependent on the size of the salt particles, and it directly influences the roughness and concomitant hydrophobicity of the surface, the maximum size of the salt particles is controlled by the sieve (mesh size of 63 μm). Detailed information about the fabrication procedures including process condition are in the materials and methods section. In this paper, stainless steel and aluminum are exclusively utilized as substrate materials with their enough adhesion on PDMS [43,46]. Notably, although no limitation exists on the material selection regarding the substrate, the adhesion between PDMS and the substrate should be confirmed to realize of a durable superhydrophobic surface. If the substrate presents poor adhesion to PDMS, applying pre-treatment (such as oxygen plasma treatment or adhesion promotor coating) to the substrate by modifying the surface chemistry would be helpful to enhance the adhesion [47].