Fabrication of super-hydrophobic film with dual-size roughness by silica sphere assembly

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Abstract

Two simple approaches were developed for the fabrication of super-hydrophobic film with dual-size roughness by taking advantage of assembling silica micro- and nanospheres. Electrostatic adsorbing technique and template-directed self-assembly were used here. The dual-size surface, which mimics the surface topology of lotus leaves, comprises both the micro-scale and nano-scale roughness. After the roughened surface was chemically modified with a layer of fluoroalkylsilane, super-hydrophobicity with a water contact angle higher than 160° and sliding angle as low as 0.5° can be achieved. The simplicity and cheapness of this procedure may make widespread applications of this super-hydrophobic film possible.

Keywords: Hydrophobicity; Surface roughness; Silicon oxide; Adsorption

1. Introduction

Super-hydrophobic surface is very important for both the daily life and industrial application. It can be used for self-cleaning, lossless liquid transfer [1,2], prevention of the snow adhesion [3], antifog and so on. Studies on plants such as lotus leaf suggest that the dual-size structure can contribute to super-hydrophobicity [4,5]. Detailed study revealed that the lotus leaf is covered by many papillae with the diameter in range of 3–10 μm, while these papillae are decorated with smaller protrusions of nanometer size. Water droplets are present on it with a nearly spherical shape and can roll off easily with a slight vibration [6,7]. Enlightened by this phenomenon, artificial dual-size roughness, has been widely used to creating super-hydrophobic surfaces.

A contact angle (CA) θ of a liquid droplet on a flat solid surface is given by the classical Young’s equation [8].

\[
\cos \theta = \frac{\gamma_{SL} - \gamma_{SV}}{\gamma_{LV}}
\]

where \(\gamma_{SL}\), \(\gamma_{SV}\), and \(\gamma_{LV}\) are the interfacial free energies per unit area of the solid–liquid, solid–gas, and liquid–gas interfaces, respectively. Wenzel proposed a theoretical model describing the CA \(\theta_w\) at a rough surface [9]. He modified Young’s equation as follows:

\[
\cos \theta_w = r \left( \frac{\gamma_{SL} - \gamma_{SV}}{\gamma_{LV}} \right) \quad \text{where} \quad \gamma_{LV} = r \cos \theta
\]

where \(r\) is a roughness factor, defined as the ratio of the actual area of a rough surface to the geometric projected area. In contrast, Cassie and Baxter proposed an equation describing the CA \(\theta_c\) at a heterogeneous surface composed of two different materials [10]. When a unit area of the surface has a surface area fraction \(f_1\) with a CA \(\theta_1\) and an area fraction \(f_2\) with a CA \(\theta_2\), the contact angle on the surface can be expressed by the following equation.

\[
\cos \theta_c = f_1 \cos \theta_1 + f_2 \cos \theta_2
\]

They applied this equation to the CA \(\theta_c\) of a rough hydrophobic surface trapping air in the hollows of the rough surface by assuming that the surface is composed of solid and air. When \(f_2\) represents the area fraction of trapped air, Eq. (3) can be modified as follows:

\[
\cos \theta_c = f \cos \theta + (1-f) \cos 180^\circ = f \cos \theta + f - 1
\]

where \(f\) is an area fraction of the solid–liquid interface and \((1-f)\) is that of the solid–air interface. According to Wenzel
and Cassie–Baxter theories, enhancing the ratio of actual area of liquid–solid interface or the air fraction between the liquid and the solid interface is the key factor to create super-hydrophobicity. The combination of the micro- and nanoscaled structure constructs two-level roughness which modify a certain coefficient in Wenzel and Cassie–Baxter equation, thus resulting in the calculated CA value much larger than those only having one level of roughness [11].

By now, a number of techniques including sol–gel method [12], electrospinning [13], chemical vapor deposition [14], solution method [15], template etching [16] and lithography [17] have been used to fabricate dual-size-rough surface. Owing to the complicated procedure and relatively strict conditions, few of them have been applied to the industrial manufacture. Here we report two simple methods to fabricate films with dual-size roughness based on a template of mono-layered silica micron sphere arrays. One approach is depositing sub-micron silica spheres on the template by electrostatic adsorption technique. The other is assembling silica nano-spheres into a structure of a greater order directed by a replication of the template.

2. Experimental details

2.1. Materials and apparatus

Monodisperse silica particles (8 μm, 4 μm, 2 μm, 1 μm, 300 nm and 100 nm in diameters) with the polydispersity of 5% were gained from Catalysts and Chemicals IND.CO., LTD., Kanagawa, Japan. Poly(allylamine hydrochloride) (PAH) was purchased from Aldrich. Fluoroalkylsilane AY43-158E (FAS) was purchased from HONGBIN Chemicals LTD., China. Sodium chloride, acetic acid and hexane were obtained from RONGHA Chemicals CO., China. Dimethylsiloxane (PDMS) (SYLGARD 184) was purchased from Dow Corning CO., Michigan, U.S.A. Scanning Electron Microscopy (SEM) photographs were taken by Scanning Electron Microscopy (HITACHI, S-300N) with an operating voltage of 30 kv. Contact angle of water was measured by Contact Angle Measurement System (KSV Cam-200, KSV instrument LTD.), under a room temperature and a relative humidity of 78%. Water sliding angle was measured by Adjustable Incline Angle Platform (SAIFAN photoelectric instruments CO. China), under the same temperature and humidity as the CA measurement. Muffle Furnace (Isuzu, EPTR-25K) and pH Measurement (6171, YIBO instruments, China) were also used here.

2.2. Preparation of the micron-sphere-array template

The micron-sphere-array template was prepared by a sticky substrate method. An aqueous suspension containing 10 wt.% monodisperse silica spheres with a diameter of 8 μm was deposited on a glass substrate (treated with a solution containing 70% vitriol acid and 30% hydrogen peroxide) for self-assembly. After the sample was completely dried in room temperature, the micro-spheres assembled into close-packed multilayers. Then it was put into a muffle furnace and heated at 630 °C for half an hour. Because the glassy temperature of the glass substrate is around 600 °C while it is around 900 °C for the silica spheres, the surface of the glass substrate became sticky at 630 °C resulting in the bottom layer of the assembled spheres adhering on it. Such an adhesive effect does not occur between the spheres. Finally, the spheres except those adhering on the glass surface were removed by water rinsing.

2.3. Electrostatic adsorption method

In the first method, submicro-spheres were adsorbed onto the template via an electrostatic adsorption, as illustrated in Fig. 1 (A, B, C). The fabrication procedure is as follows: Firstly, the substrate was immerged into an aqueous solution containing 1.0 mg/ml PAH and 0.5 M sodium chloride for an hour. It is known that silica is negatively charged and PAH is positively charged in water. PAH was adsorbed on the micro-/nanoscale silica sphere surface and reversed its surface charge. Then the excessive PAH was removed by water rinsing and calcined at a temperature of 300 °C. Secondly, the substrate was kept in a suspension containing sub-micron silica spheres for 2 h. The negatively charged submicro-spheres adsorbed on the surface of the micron-scaled spheres, which were coated with PAH. Finally, the excessive sub-micron silica spheres were removed by water rinsing. The second step was repeated if multilayered adsorption was necessary. In each cycle, the size of the spheres used for adsorption was reduced.
2.4. Template-directed self-assembly method

In the second method, the micron-sphere-array template was replicated by PDMS, as illustrated in Fig. 1 (A, D, E, F, G). Firstly, the PDMS precursor (Elastomer Base and Curing Agent mixture 10:1) was cast onto the micron-sphere-array template and cured at 60 °C for 45 min. After the PDMS was cured absolutely, the silica template was removed. The topography of the silica template was replicated by the PDMS and a PDMS soft template with honeycomb-like holes on its surface was prepared. Secondly, the as-prepared PDMS soft template was laid on a glass substrate, and then an ethanol suspension of monodisperse silica nano-spheres (5 wt.%, diameter 300 nm) was injected into the gap between the PDMS film and the glass substrate. After the ethanol was completely evaporated in room temperature, the PDMS film was peeled off from the glass substrate. The nano-spheres on the glass substrate replicated the topography of soft-template and a surface with dual-size roughness was presented ultimately.

2.5. Surface modification

In order to render the film with super-hydrophobicity, its surface was modified with FAS. Firstly, 0.8 g FAS was dissolved in 50 g hexane and then 1.0 g distilled water with pH=3, adjusted by acetic acid, was added to the solution. The whole system was churned up over 5 h. Secondly, put the as-prepared film along with a test tube of 2.0 g FAS solution into an airproof system, and then heated at 250 °C for half an hour. When the space was replete with FAS vapor, the surface of the as-prepared substrate was fluoridized. After FAS was tightly coated on the hierarchical surface, super-hydrophobicity was achieved.

3. Results and discussion

Fig. 2a and b shows the scanning electron microscopy (SEM) images of 1 μm and 100 nm silica spheres adsorbed on the micron-sphere-array template, respectively. It was observed that 1 μm spheres congregated disorderly in the void of the three neighboring 8 μm spheres, while the 100 nm spheres were uniformly adsorbed on the template. The weight of the submicro-spheres plays an important role in the adsorbing process. If the weight of the submicro-spheres is comparable with electrostatic force, the adsorption will be influenced by the gravity. Fig. 2c shows SEM image of hexagonally arranged micron-sphere-arrays assembled by silica nano-spheres. The magnified image in Fig. 2d shows that the hexagonal packed micro-spheres were composed of silica nano-spheres with a diameter of 300 nm. Due to the template effect of the PDMS honeycomb, the nano-spheres assembled together in the honeycomb during the evaporation of the ethanol. Because the surface tension of the ethanol-PDMS interface is relatively low, the silica suspension spread uniformly on the surface of PDMS film, which enables the wide-area replication of the PDMS template. In addition, we found that the PDMS film can be easily peeled off without any nano-spheres adhering on it and the dual-size structure was not destroyed after the PDMS was removed, implying that the adhesive force from the PDMS template is weaker than that from the glass substrate. Different from normal self-assembly, disordered arrangement of nano-spheres was found in each micro-unit.
The surface wettability was evaluated by a water CA system. As seen in Fig. 3a, the CA of 4 mg water measured on the as-prepared surface with dual-size roughness, which was assembled by 300 nm silica spheres, was about 161±0.5°. Contrasting to it, the CA on the surface of hexagonal packed 8 μm silica spheres was 115±0.5° while it was 142±0.5° on the surface of randomly deposition of 300 nm silica spheres, as seen in Fig. 3b and c. It suggests that both the two levels of roughness are indispensable to the super-hydrophobicity. Whether a water droplet stably exists in Wenzel state or in Cassie–Baxter state is determined by which state in this situation has a minimum surface free energy. If a Wenzel drop forms, it wets the rough surface absolutely. Comparing with the surface only has micro-level roughness, in a dual-size-rough structure, the nano-scale protrudings enlarge the actual contact area, resulting in a larger value of roughness factor. According to Wenzel equation (Eq. (2)), enhancing the roughness factor brings on an increase of the calculated CA value. Similarly, compared with the surface on which the silica nano-spheres were randomly deposited, the surface with assembled nano-spheres in shape of protuberant micron papillae obviously provides a larger surface area in a three-dimensional way, which enhances the value of roughness factor, so that the CA on the dual-size-rough surface is higher than the one only having nano-level roughness. When a Cassie–Baxter drop is formed, the drop stands on a composite surface of solid protuberance and air. The high CA depends on a high percentage of liquid–solid interface replaced by liquid–gas interface. Obviously, the dual-size-rough surface traps more air fractions than surfaces only having one level of roughness. Besides the surface structure, the effect of the surface chemistry on CA also cannot be neglected. To obtain super-hydrophobic surfaces, coating with low-surface-energy materials such as FAS is often necessary [18]. Surfaces with dual-size roughness made up of silica spheres are not super-hydrophobic if they are not coated with any low-free-energy chemicals.

In order to study the size effect on wettability, several CA values were measured on the template adsorbed with a series of sub-scale silica spheres that vary by an order of diameter. Fig. 4A shows this size effect. It can be observed that when the diameter of the adsorbed sub-scale spheres decreased from 4 μm to 1 μm, the CA increased rapidly from 142±0.5° to 166±0.5°, while it decreased gradually to 148±0.5° when the size of adsorbed sub-scale spheres decreased to 0.1 μm. Such a size effect should come from a structure change of sub-scale spheres adsorbed on the template. For the sub-scale spheres larger than 1 μm, they preferred to existing on the void formed by three neighboring 8 μm spheres, instead of adsorbing uniformly on the surface of 8 μm spheres. That is because the sub-scale spheres for the adsorption are too large and the electrostatic force cannot stabilize the particles on top of the 8 μm spheres. This kind of structure can increase the surface roughness. The situation changes when the adsorbed sub-scale spheres are smaller than 1 μm. These smaller sub-scale spheres form uniform layers on the surface of 8 μm spheres, resulting in that the roughness begins to decreases when the adsorption sub-scale spheres are smaller than 1 μm. Such a

Fig. 3. (a–c) Static behavior of a 4 mg water drop on surfaces of (a) dual-size-rough surface assembled by 300 nm silica spheres, (b) 8 μm silica sphere template and (c) randomly deposition of 300 nm silica spheres. (d) Roll-off behavior of a 4 mg water drop on the surface of dual-size roughened surface fabricated by 100 nm silica spheres electrostatic-adsorbing on 8 μm silica sphere template. The tilting angle of the surface is 0.5°. All of these surfaces were coated with FAS.

Fig. 4. (A) the relationship between CA and the diameters of adsorbed particles. (B) the relationship between SA and the diameters of adsorbed particles. The volume of the water drop used here is 4 μL.
structure change should be responsible for the size effect on the CA. Unexpectedly, an obvious difference in CA measured from samples obtained respectively by the two methods was observed. When the 300 nm spheres were uniformly coating 8 μm spheres, the CA is 148±0.5°. However, when these 300 nm spheres were packed into a PDMS mold forming a micron structure, the CA is 161±0.5°. In the first case, the nano-spheres only existed on the surface of the micro-sphere, while in the other case, the nano-spheres existed not only on the surface of the micro-sphere but also inside the micro-sphere. A solid micro-sphere provided less actual areas of liquid–solid contact or air fraction than a porous sphere.

The static CA alone is insufficient to evaluate hydrophobicity. Sliding angle (SA), which can be expressed by the difference between the advancing and receding contact angle (hysteresis), is another criteria to evaluate the quality of super-hydrophobic surface [19–21]. An absolute super-hydrophobic surface should exhibit both a high CA and a low SA. Fig. 3d shows the sliding behavior of a 4 mg water drop on the film fabricated by adsorbing 100 nm silica spheres on the surface of 8 μm sphere array, modified with FAS. The water drop began to roll off when the film was tilted for only a degree of 0.5°. In most situations, the water drop cannot stand stably on its surface. In a sharp contrast, a 4 mg water drop never moved on the 8 μm silica sphere template which was also modified with FAS, even if the template was laid vertically. It is known that Wenzel Model provides a sticky surface while Cassie–Baxter Model presents a slippy surface. When the surface roughness is replaced by a dual-size structure, the wetting behavior has changed from Wenzel Model to Cassie–Baxter Model. Since SA was mainly determined by the three phase (solid–liquid–gas) contact line, the discrete contact is built up between the solid and liquid surfaces on the dual-size-rough surface, which reduces the length of three phase contact line and enhances the discontinuity of it, consequently leading to the drastic decrease of SA. Fig. 4B shows the dependence of SA on the size of adsorbed particles on 8 μm silica sphere template. Different from CA, the value of SA gradually decreases from 8° to 0.5° along with the decrease of the adsorbed particle size.

4. Conclusions

In summary, two simple methods to fabricate super-hydrophobic films with two-level roughness were presented in this article. Structural effects of dual-size roughness on water wetting behaviors were discussed by measuring the contact angle and sliding angle. As the whole procedure is based on self-assembly of silica spheres which makes the fabrication convenient and inexpensive, wide applications in self-cleaned coating, microfluidic device, thermal transfer apparatus are anticipated.

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References