Superhydrophobic Films from Raspberry-Like Particles

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Superhydrophobic Films from Raspberry-like Particles

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ABSTRACT

We report a robust procedure for preparing superhydrophobic hybrid films on which the advancing contact angle for water is about 165° and the roll-off angle of a 10-μL water droplet is 3 ± 1°. Dual-size surface roughness, which mimics the surface topology of self-cleaning plant leaves, originates from well-defined silica-based raspberry-like particles that are covalently bonded to an epoxy-based polymer matrix. The roughened surface is chemically modified with a layer of poly(dimethylsiloxane) (PDMS). The robustness and simplicity of this procedure may make widespread applications of so-prepared superhydrophobic films possible.

Mother Nature's elegant self-cleaning surfaces, such as lotus leaves,[1,2] are a combination of low surface-energy species and a peculiar topographic feature based on dual-size roughness: the coarse-scale rough structure is about 10−20 μm, whereas the finer structure on top of the coarse structure is in the range of 100 nm to 1 μm.[3−6] The dual-size structure has proven to be vital in generating the superhydrophobicity of the lotus leaves, especially for obtaining low water roll-off angles. There have been many recent attempts at preparing superhydrophobic surfaces by mimicking, in one way or another, the lotus leaf surface structure.[3,6−11] Porous structures[12−14] and micropatterned structures[15−20] have also been used to prepare superhydrophobic surfaces. Most of the preparations involve strict conditions (such as harsh chemical treatment), expensive materials (e.g., perfluoroalkyl silane, nanotubes), and processing procedures including etching, plasma treatment, chemical vapor deposition, electrodeposition, calcination, and the use of templates. Many of the reported superhydrophobic, polymeric films are composed of uncrosslinked, thermoplastic polymers, and they are often vulnerable to environmental attacks (e.g., solvent, heat). Therefore, the applications of the superhydrophobic films prepared so far have been limited. Apart from using micropatterned templates, it is very difficult to control and reproduce the surface roughness; however, it is also very difficult to generate a structure finer than 100 nm and with dual-size roughness by using templates.

Here we report a simple, yet robust procedure for preparing superhydrophobic films with dual-size hierarchical structure originated from well-defined raspberry-like particles, as illustrated in Scheme 1. First, a conventional cross-linked film based on an epoxy−amine system is prepared with unreacted epoxy groups available for further surface grafting. Second, amine-surface-functionalized raspberry-like silica particles are chemically deposited onto the epoxy films, generating a double-structured roughness. Finally, a layer of monoepoxy-end-capped poly(dimethylsiloxane) (PDMS) is grafted onto the raspberry-like particles to render the film surface hydrophobicity.

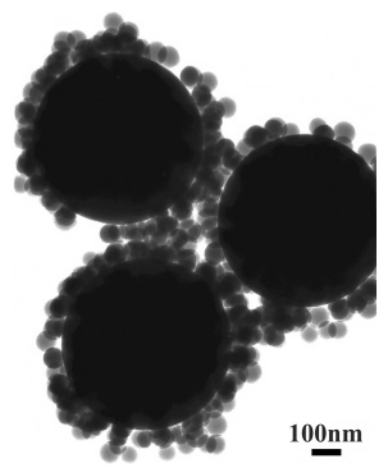

Figure 1. Transmission electron microscopy (TEM) photo of raspberry-like silica particles.

The key to introducing well-adjustable dual-size roughness is the synthesis of well-defined raspberry-like particles. We followed the Stöber method[21] to prepare epoxy-functionalized monodisperse silica particles of about 700 nm and amine-functionalized silica particles of about 70 nm, respectively (see details in the Supporting Information). The small particles were then covalently grafted onto the big ones via the reaction between epoxy and amine groups, leading to raspberry-like silica particles (Figure 1; some loose small particles are still visible, probably because of physical

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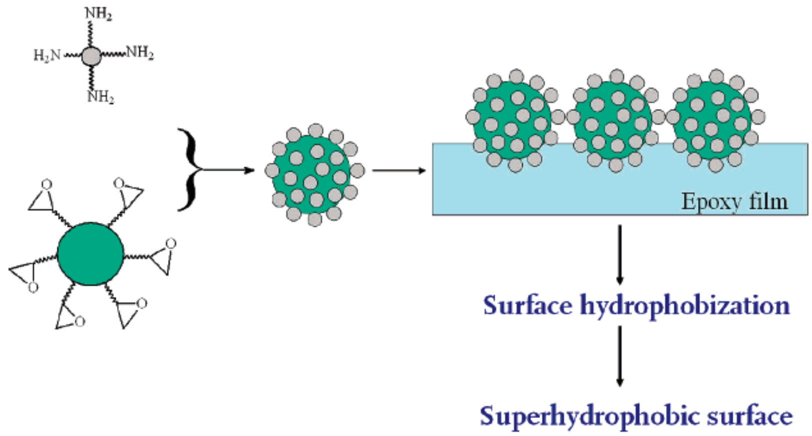
Scheme 1. Preparation of Superhydrophobic Films Based on Raspberry-Like Particles



adsorption) of uniform size with dangling amine groups at surface. By using the Stöber method, it is very convenient to manipulate the particle size while maintaining a narrow size distribution, which enables us to readily adjust the size ratio between the small and large particles and, subsequently, to tune the surface roughness factor at will.

We start the creation of the superhydrophobic films with a conventional polymer film on, for example, aluminum substrates based on thermal curing of a mixture of an epoxy and a diamine with the epoxy in 10% excess (see the Supporting Information). Cross-linked epoxy films offer satisfactory mechanical strength and can be applied easily in various applications. The amine-functionalized raspberry-like particles (dispersed in ethanol) are then deposited on the epoxy film again via epoxy−amine reaction at 75 °C. Loose particles can be flushed away easily with ethanol or water, leaving one layer of the raspberry-like particles covalently bonded to the epoxy-based films. A dual-size-structured surface is now obtained. It should be pointed out here that the particles do not necessarily have only point contact with the epoxy-based film because the epoxy film can be partially cured, which allows the particles to be partially embedded in the film (Scheme 1); after the deposition of the particles, the epoxy can be fully cured. Possible remaining epoxy groups at the surface of the large particles and the epoxy-based films are further reacted with a (bis)amino-functional PDMS. In the end, monoepoxy-end-capped PDMS is grafted to the particles (see the Supporting Information) to bring hydrophobicity to the surface.

The wettability of a film is reflected by the contact angle (CA) of water on the surface. The advancing water CA on a smooth epoxy-based film (surface modified with PDMS) is 107 $\pm$ 2° (an image of a static water droplet on the film surface is shown in Figure 2a), with a CA hysteresis of about 40°. When only large silica particles (~700 nm in diameter) are deposited (surface also modified with PDMS) on the epoxy−amine film, there is an increase of the water advancing CA, reaching 151 $\pm$ 2° (Figure 2b), but at the same time the CA hysteresis also increases significantly to about 57°. Similarly, when only small silica particles (~70 nm) are introduced to the film surface, the advancing/receding CAs are 148°/85°, respectively.

In a sharp contrast, for the film containing raspberry-like particles (surface modified with PDMS), the advancing CA of water further increases to 165 $\pm$ 1° (Figure 2c); the CA hysteresis is shown to be ~2°. More importantly, the roll-off angle of a 10-μL water droplet on the surface is 3 $\pm$ 1° (video clips showing the roll-off of water droplet on the surface are available as Supporting Information). By incorporating raspberry-like particles into the surface modified by PDMS, a conventional, cross-linked epoxy-based film has been turned superhydrophobic easily and successfully. The stability of the superhydrophobic film was tested underwater, and it was found that the immersion of the film in water overnight did not alter the surface wetting property.

It is interesting that if the film containing raspberry-like particles is not surface-modified with a layer of PDMS then the advancing and receding CAs for water on the film are only 22 and 6°, respectively. These values are significantly lower than the water CAs on the corresponding smooth epoxy-based film (advancing/receding CA: 66/30°). This observation clearly indicates that to make a surface super-

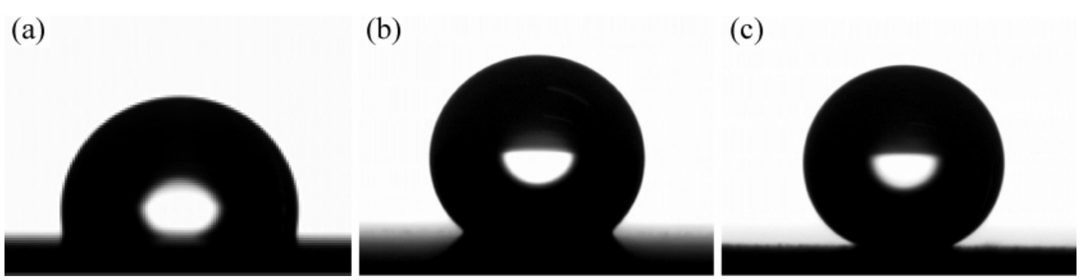


Figure 2. Water droplets of 5 μL on PDMS-covered epoxy-based films containing (a) no particles, (b) large silica particles, and (c) raspberry-like particles.

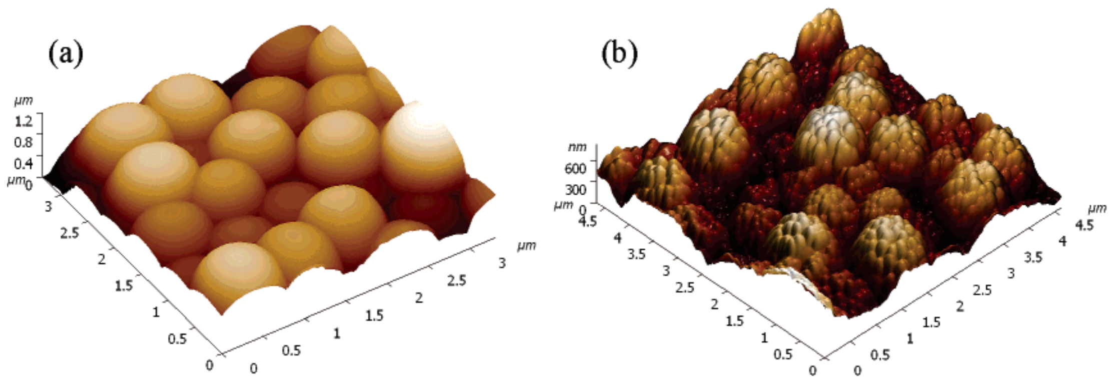


Figure 3. AFM 3D images for PDMS-covered epoxy-based films containing (a) large particles and (b) raspberry-like particles.

hydrophobic it is necessary to combine a proper dual-size surface roughness with enough surface hydrophobicity.

To find out the effect of the surface structure on the film wettability, we use atomic force microscopy (AFM) to examine the films with and without particles. With no particles in the films, the smooth film surface appears to be featureless. With the large particles incorporated into the film, a layer of particles can be observed by AFM (Figure 3a). Apparently, the surface roughness is due to the silica particles. The typical peak−valley distance is ∼400 nm, roughly the radius of a silica particle. When the raspberry-like particles are introduced to the film, the topographic image (Figure 3b) clearly shows a two-level structure: the micrometer-level structure can be ascribed to the large silica particles that are the core of raspberry-like particles, whereas on each of the micrometer-level structures there is a finer structure at a submicrometer (∼70 nm) level. The average peak−valley distance is ∼500 nm. Obviously, the topographic feature of raspberry-like particles is completely preserved in the superhydrophobic film. This dual-size hierarchical structure resembles the surface of a lotus leaf,[1−6] as clearly demonstrated in Figure 3b.

In combination with the CA data, the above AFM analysis unambiguously demonstrates the vital role played by the surface roughness in governing the surface wettability. The surface roughness factor (r) can be defined as the ratio between the actual surface area and the projected surface area.[22,23] It is well known that the surface roughness of a hydrophobic surface enhances its hydrophobicity.[1−3,5,22−28] Two distinct models have been proposed to explain this phenomenon: the Wenzel model[22,23] and the Cassie model.[24] The Wenzel model describes a roughness regime in which both water advancing CA and CA hysteresis increase as r increases (water penetrates into the surface cavity). The Cassie model describes that, as r further increases passing a critical level, the water receding angle also increases dramatically (water does not penetrate into the surface cavity; there is an air pocket between the water droplet and the solid surface), thus minimizing the CA hysteresis.[25,28] At this critical level of surface roughness, there is a transition from the Wenzel regime to the Cassie regime.[21,24] To make a surface superhydrophobic, the advancing water CA should be high enough (>150°) and, more importantly, the CA hysteresis should be very small, leading to a small roll-off angle of the water droplet. In our films containing only large particles, although the surface roughness factor, r, increases significantly as compared to a smooth surface, it is still at a level where the Wenzel regime dominates, resulting in the enlarged CA hysteresis (from 40 to 57°).[25] The surface roughness factor, r, has to surpass a certain level to enter the Cassie regime, at which the difference of advancing and receding CA minimizes. The dual-size surface structure at the lotus leaf surface amplifies the surface roughness factor to reach the Cassie regime. Similarly, in our double-structured films containing raspberry-like particles, the surface roughness factor, r, is also increased by the existence of raspberry-like particles, effectively making our films superhydrophobic and allowing a 10-μL water droplet to roll off of the surface when tilted at an angle of as small as 2°.

Preliminary quantitative analysis on the basis of the AFM images indicates that, for the film containing only big silica particles, the root-mean-square roughness (S_q) is 173 ± 25 nm and $r = 1.45 \pm 0.05$ ($r = 1 + S_{dr}$; S_{dr} is the ratio between the interfacial and project areas[29] and can be obtained directly with the Scanning Probe Image Processor (SPIP) software provided by Image Metrology A/S, Denmark). However, for the film containing raspberry-like particles, $S_q = 185 \pm 20$ nm and $r = 1.54 \pm 0.09$, respectively. The increase in r seems to be small. We believe it is the dual-size surface topology originated from the raspberry-like particle that allows air pockets to exist between the water droplet and the solid surface and turns the film superhydrophobic. A more detailed quantitative investigation of the effects of the surface roughness factor, r, (by varying the size of large and small particles in the raspberry-like particles) on the surface hydrophobicity is under way in our laboratory.

In summary, by employing raspberry-like particles, we successfully developed superhydrophobic films based on conventional silica particles and epoxy polymers in an effort to mimic the two-level surface structure of lotus leaves. It is envisaged that, because of the simplicity and robustness of this procedure, these superhydrophobic surfaces may be useful in a variety of applications.

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Supporting Information Available: Details of experimental procedures, video clips showing continuous roll-off of water droplets on the superhydrophobic film tilted by 3°, and a static water droplet (10 μL) rolling off of the same film when the tilting angle reaches 1.8 ° (the tilting angle is increased gradually from 0 to 1.8 °). This material is available free of charge via the Internet at http://pubs.acs.org.

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