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Fabrication of flexible superhydrophobic films by lift-up soft-lithography and decoration with Ag nanoparticles

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Abstract

Superhydrophobic films with excellent flexibility have been fabricated by combining the lift-up soft-lithography technique and chemical reduction of $[\text{Ag}(\text{NH}_3)_2]^+$ ions to Ag nanoparticles (NPs) on the surface of silica spheres which are patterned on the polydimethylsiloxane (PDMS) films. Scanning electron microscopy (SEM) images reveal the presence of raspberry-like hierarchical structures on the PDMS films. The influence of the amount of Ag NPs and the size of the silica spheres on the wettability of the soft films is investigated carefully. Because PDMS films are elastomeric materials, our superhydrophobic films offer great flexibility. The resulting films can be easily transferred from one substrate surface to another without destroying their superhydrophobicity. These flexible and superhydrophobic films can be used repeatedly to satisfy a wide range of applications.

 Supplementary data are available from stacks.iop.org/Nano/20/065304

1. Introduction

The wettability of solid surfaces is an important property, studied and widely used, from fundamental material research to many practical applications [1, 2]. The slippery superhydrophobic surface refers to that on which the water contact angle (CA) is larger than 150° and the sliding angle (SA) is less than 10° [3]. In recent years, such superhydrophobic surfaces have been widely used in many fields, for instance, in the areas of surface self-cleaning [4], marine coating [5], preventing the adhesion of snow, fog and raindrops to window surfaces and reducing flow resistance in microfluidic channels [6, 7]. The superhydrophobic surface originated from the famous lotus effect of some natural leaves, which was first demonstrated by Barthlott and Neinhuis [8]. Further study revealed that the wettability of a surface was governed mainly by its chemical composition and geometrical structure [9]. Accordingly, superhydrophobic surfaces have

been constructed usually based on two essential concerns: (i) micro- and nanoscale hierarchical structures to increase the roughness of a surface [10] and (ii) chemical modification to reduce the surface energy of a rough surface [11]. Based on these two principles, various techniques have been established to engineer superhydrophobic surfaces, with notable examples including lithographic patterning [12], layer-by-layer techniques [13, 14], electrochemical deposition [15], sol-gel approach [16], electrospinning and plasma etching/deposition [17–21]. Through these approaches, lots of superhydrophobic materials have been fabricated. For example, Jiang and co-workers have fabricated a series of superhydrophobic structures inspired by the superhydrophobic living organisms in nature, such as the eyes of mosquitoes, the legs of water striders, and rambutans [22–24]. Seeger and co-workers have reported a general method of growing silicone nanofilaments onto various materials to obtain superhydrophobic surfaces [25]. The recent development on superhydrophobic surfaces has been reported in several reviews [3, 26–28].

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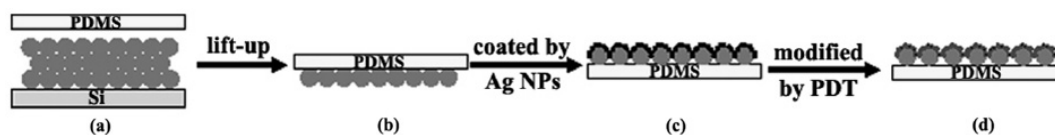


Figure 1. Schematic illustration of the fabrication procedure of a flexible superhydrophobic film.

To date, the efforts on fabrication of superhydrophobic surfaces focus mainly on the formation of hierarchical structures on rigid substrate surfaces [29, 30]. For many applications, there is an outstanding requirement for superhydrophobic films with flexibility that can be folded and transferred among a number of surfaces with different curvatures [31, 32].

Here, we report a straightforward procedure to obtain hierarchical structures on soft poly(dimethylsiloxane) (PDMS) films by lift-up soft-lithography and post-decoration with Ag nanoparticles (NPs) to render the superhydrophobic surfaces. During the past decade, soft-lithography has been well developed as a new micro-fabrication method to prepare various patterned surfaces by using elastomeric stamps, molds and masks. Compared with other approaches, soft-lithography is relatively inexpensive with simple procedures and does not demand special instruments [33]. Obviously, the reported approach is low-cost and easy to handle. The advantages of our soft superhydrophobic films are appreciable: (i) they can be reused, and hence minimize material waste; (ii) various smooth surfaces can become superhydrophobic via ready coating with these films, especially for those hydrophilic materials which can hardly exhibit superhydrophobicity.

2. Experimental details

2.1. Materials

PDMS elastomer kits (Sylgard 184) were purchased from Dow Corning (Midland, MI). 1H, 1H, 2H, 2H-perfluorodecanethiol (PDT) was obtained from Aldrich. (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane (HTTS) was obtained from ABCR GmbH & Co. KG. Silver nitrate (AgNO_3), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25 wt% in water), tetraethyl orthosilicate (TEOS), isopropanol and glucose were analytical grade and used as received. In all preparations, absolute ethanol and deionized water were used.

2.2. Preparation of superhydrophobic film

Monodisperse silica spheres were synthesized according to the well-known Stöber method [34]. Afterwards, the resulting silica spheres were centrifuged and redispersed in ethanol.

Figure 1 outlines our procedures for the preparation of a superhydrophobic film, which begins with the assembly of monodisperse silica spheres on the surface of a silicon wafer by the evaporation of a suspension of silica spheres in ethanol (figure 1(a)) [35]. With soft-lithography, a single layer of close-packed spheres is transferred to the surface of the PDMS film (figure 1(b)) [36]. Next, Ag NPs are deposited onto the silica spheres (figure 1(c)) [37]. Generally, the PDMS film containing the transferred silica spheres was immersed in a 0.5 M $[\text{Ag}(\text{NH}_3)_2]^+$ ion solution for four hours and dried under

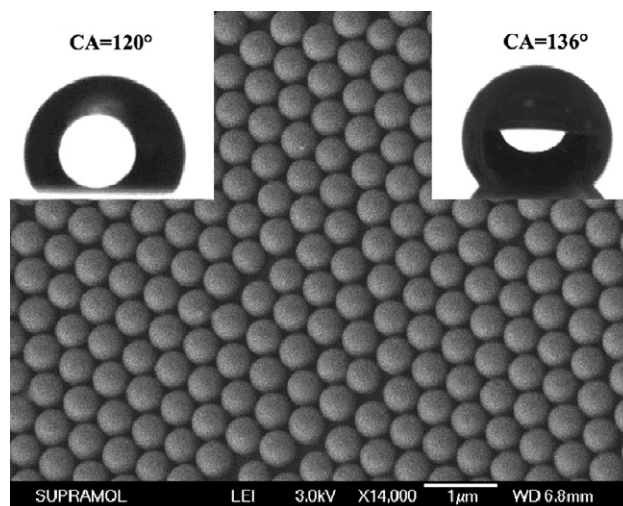


Figure 2. SEM image of a hexagonal close-packed silica array on the surface of a PDMS film; the diameter of the silica spheres is about 520 nm. The insets on the left and right top are the water droplets before and after the HTTS modification. The water CA before and after the surface modification is 120° and 136°, respectively.

the flow of nitrogen. The substrate was then immersed in a 0.5 M glucose solution for six hours at room temperature to reduce the $[\text{Ag}(\text{NH}_3)_2]^+$ ions to Ag NPs on the surface of the silica spheres arranged in an ordered array. Finally, the surface of the as-prepared sample is chemically modified with 2 mM PDT solution in ethanol for one hour to reduce the surface energy (figure 1(d)).

2.3. Characterization

The morphologies of the silica spheres on the surface of PDMS films and Ag NPs coated on the periodic silica spheres were investigated with a JEOL JEM-6700F field emission scanning electron microscope (SEM) with primary electron energy of 3 kV, and the samples were sputtered with a layer of Pt (ca. 2 nm thick) prior to imaging to improve conductivity. Water contact angle measurements were performed at room temperature using a drop-shape analysis system (DSA 10 MK2, KRÜSS). A 2.0 μl droplet of deionized water was dropped onto the samples and the average of at least five measurements taken at different positions on each sample was adopted as static CAs. X-ray diffraction (XRD) data were collected on a Siemens D-5005 x-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$).

3. Results and discussion

Figure 2 displays an SEM image of the ordered silica spheres which are pressed and sunk on the surface of the PDMS film.

Table 1. Water CAs before and after hydrophobic modification of PDMS surfaces at different steps of the fabrication process.

Fabrication step	PDMS + Ag NPs	PDMS + SiO ₂	PDMS + SiO ₂ + Ag NPs
CA (before modification)	116°	120°	115°
CA (after modification)	140°	136°	152°

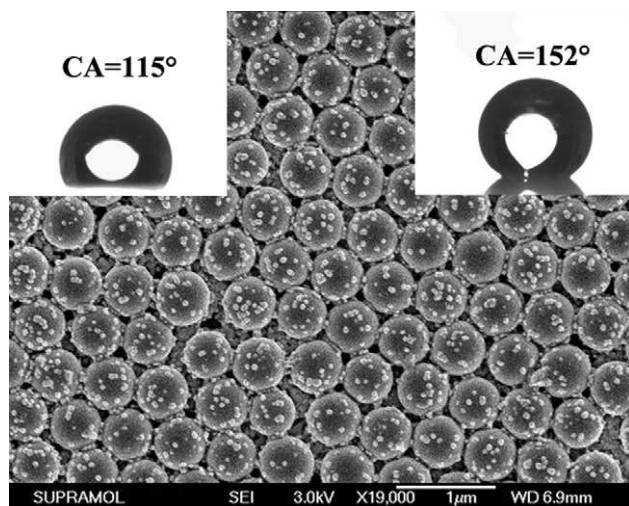


Figure 3. SEM image of silica spheres coated with Ag NPs whose diameters range from 30 to 40 nm; the silica spheres are pressed to sink partially into a PDMS film with a hexagonal array. The insets on the left and right top are the water droplets before and after the PDT modification. The water CA before and after the surface modification is 115° and 152°, respectively.

Table 1 lists the water CAs before and after modification by a grafting agent with low surface energy at different fabrication steps. The ordered silica spheres with a hexagonal close-packed array were transferred by lift-up soft-lithography onto the hydrophobic PDMS film (the CA of the flat hydrophobic PDMS film was about 114°). The average diameter of the silica spheres is about 520 nm and the PDMS film containing silica spheres shows hydrophobicity with a CA of 120° (as shown in the left inset of figure 2, table 1). After modification by HTTS, the CA of the silica pattern increases to 136° (as shown in the right inset of figure 2, table 1) [13].

Figure 3 is the SEM image of the ordered silica spheres on the PDMS film but coated with Ag NPs. These silica spheres are uniformly coated with Ag NPs and also adopt an ordered hexagonal array. Therefore, the silica spheres on the PDMS film are robust, as their ordered structure is perfectly preserved during the entire chemical reduction procedure. It is easy to understand that there is a small portion of each sphere embedded in the PDMS film via the soft-lithography procedure, and the $[\text{Ag}(\text{NH}_3)_2]^+$ ions are likely to locate on the surface of the spheres left outside, resulting in the occurrence of Ag NPs on the silica spheres during the chemical reduction. Figure 3 clearly illustrates the existence of Ag NPs on the silica spheres leading to a raspberry-like structure, which is hierarchical. The diameter of the Ag NPs ranges from 30 to 40 nm. The water CA on this surface is about 115° (as shown in the left inset of figure 3, table 1), which is a little smaller than that of the corresponding silica array

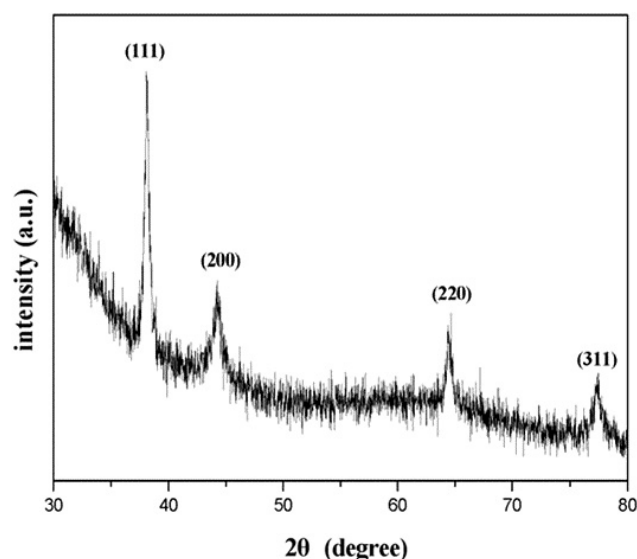


Figure 4. XRD pattern of the Ag NPs on the surface of silica spheres sunk partially into a PDMS film.

(as shown in the left inset of figure 2). This hierarchical surface is still hydrophobic. Moreover, the wettability of the structure changes from hydrophobicity to superhydrophobicity after surface modification with PDT, which is a chemical agent with low surface energy. The water CA increases significantly to 152° (as shown in the right inset of figure 3, table 1). In addition, the modified surface exhibits a small SA of about 4°, suggesting that the water droplet on the surface is not stable and easily rolls off (see figure S1 in supplementary information, available at stacks.iop.org/Nano/20/065304).

The XRD pattern of the sample in figure 4 shows four diffraction peaks corresponding to (111), (200), (220) and (311) Bragg reflection of silver, which is in good agreement with those reported for Ag NPs [38].

Let us turn our attention to surface roughness. For the PDMS film shown in figure 2 with silica spheres arranged in an ordered array, its surface roughness only comes from the presence of silica spheres. For the PDMS film shown in figure 3 with a raspberry-like surface, its surface roughness comes from the presence of both silica spheres and Ag NPs. Such a two-level structure is worthy of notice: the large silica spheres represent a micrometer-level structure and the Ag NPs symbolize a nanometer-level structure. Obviously, the raspberry-like structure was completely preserved during the fabrication of the superhydrophobic film. With the dual-size hierarchical structure, this superhydrophobic film resembled the surface of a lotus leaf.

The superhydrophobicity of the hierarchical structure could be explained with the modified Cassie–Baxter

Table 2. Water CAs before and after hydrophobic modification of PDMS surfaces coated with silica spheres of various sizes.

Diameter of silica spheres (nm)	520	650	700	850	1100
CA (before modification by PDT)	115°	113°	114°	116°	116°
CA (after modification by PDT)	152°	153°	154°	156°	154°

equation [39–42]:

$$\cos \theta_{n+1} = (1 - \omega_n) \cos \theta_n - \omega_n, \quad (1)$$

where n is the generation number of the hierarchical structure and θ_n is the contact angle on a surface of the n th generation. In our case, the first generation structure corresponded to the PDMS surface decorated with the Ag NPs. After hydrophobic modification, on such a surface, the CA was about 140° (see figure S2 in supplementary information (available at stacks.iop.org/Nano/20/065304), table 1). The second generation structure consisted of the PDMS surface coated with silica spheres and decorated with Ag NPs. After hydrophobic modification on such a surface, the water CA was about 152° (as shown in the right inset of figure 3). Using the measured values of the water CA, we can estimate a value for ω in equation (1), the fraction of the surface in contact with the droplet, equal to 0.5. This value is indicative of water droplets in contact with a part of the silica sphere surface corresponding to an angle of 45°. This is reasonable for droplet sizes much bigger than the silica spheres, which further indicates that our fabricated surfaces are in agreement with the modified Cassie–Baxter equation on a structure of dual-scale topography.

For the present methodology, the number of Ag NPs on the silica spheres could be controlled by the concentration of $[\text{Ag}(\text{NH}_3)_2]^+$ ions. The lower the concentration of $[\text{Ag}(\text{NH}_3)_2]^+$ ions, the less the number of Ag NPs on the silica spheres. Such a relationship is due to the fact that lower $[\text{Ag}(\text{NH}_3)_2]^+$ ion concentration led to less $[\text{Ag}(\text{NH}_3)_2]^+$ ions on the silica spheres. Figure 5 shows the relationship between the water CA and the concentration of $[\text{Ag}(\text{NH}_3)_2]^+$ ions. The water CA increases with the increase of the concentration of $[\text{Ag}(\text{NH}_3)_2]^+$ ions. When the $[\text{Ag}(\text{NH}_3)_2]^+$ ion concentration is low, only small parts of the surface of silica spheres were decorated with Ag NPs, leading to small surface roughness and low water CA. As shown in figure 5, the concentration of the glucose is fixed at 0.5 M. When the concentration of $[\text{Ag}(\text{NH}_3)_2]^+$ ions is 0.1 M, the water CA of the film is about 125° after the PDT modification. This film does not achieve superhydrophobicity. When the concentration of $[\text{Ag}(\text{NH}_3)_2]^+$ ions reaches 0.5 M, the surface of the silica spheres is nearly completely coated by Ag NPs. Therefore, even if the concentration of $[\text{Ag}(\text{NH}_3)_2]^+$ ions further increases, the water CA changes little.

The relationship between the size of the silica spheres and the wettability was also investigated. The concentrations of $[\text{Ag}(\text{NH}_3)_2]^+$ ions and glucose were fixed at 0.5 M, and we investigated the wettability of the raspberry-like surfaces. Figure 6 shows the SEM images of our four raspberry-like surfaces with different silica spheres, whose average diameters are 650 (figure 6(a)), 700 (figure 6(b)), 850 (figure 6(c)) and 1100 nm (figure 6(d)), respectively. The hexagonal

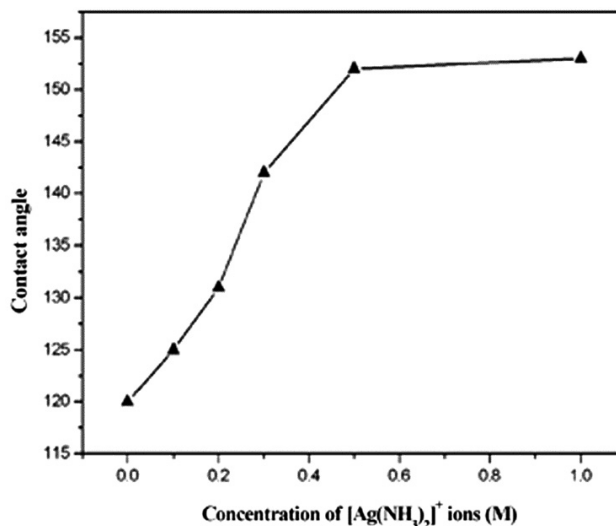


Figure 5. The effect of the concentration of $[\text{Ag}(\text{NH}_3)_2]^+$ ions, ranging from 0.0 to 1.0 M, on the water CA. The concentration of glucose is 0.5 M and the diameter of the silica spheres is 520 nm.

arrangement of the silica spheres and the diameters of the silica spheres can be distinguished clearly. Moreover, Ag NPs with diameters ranging from 30 to 40 nm distribute randomly on the surface of the silica spheres. Table 2 shows the relationship between the silica diameter and water CA of the film before and after the PDT modification. It demonstrates that the size of the silica spheres has little effect on the wettability of the resulting film. Namely, the dimensional change of the micrometer-level structure, ranging from 500 to 1100 nm, has little effect on the wettability of the hierarchical structure, whereas the amount of nanometer-level objects on the microstructures dominates the wettability of the hierarchical structure.

In our study, the silica spheres on the PDMS film were mechanically stable, because they sank into the polymeric film during the lift-up soft-lithography process (see figure S3 in supplementary information, available at stacks.iop.org/Nano/20/065304) [43, 44]. The PDMS film is a soft material that could be easily rolled, stretched and folded. Accordingly, the superhydrophobic film could be easily peeled away from one substrate and then transferred to another one. During the transfer process, silica spheres with Ag NPs coating remained intact on the surface of the PDMS film. Thus, the superhydrophobicity of the film was preserved.

Figure 7(a) shows the optical image of a superhydrophobic film. The array of the silica spheres decorated by the Ag NPs is presented in the center of the transparent PDMS film. The color of the pattern is brown, which is the feature color of Ag NPs. The dimensional size of the trapezium superhydrophobic film presented in figure 7(a) is $(2.0 + 3.5) \times 2.5 \text{ cm}^2$. The film can firmly stick on the flat glass without any glue, and it does not

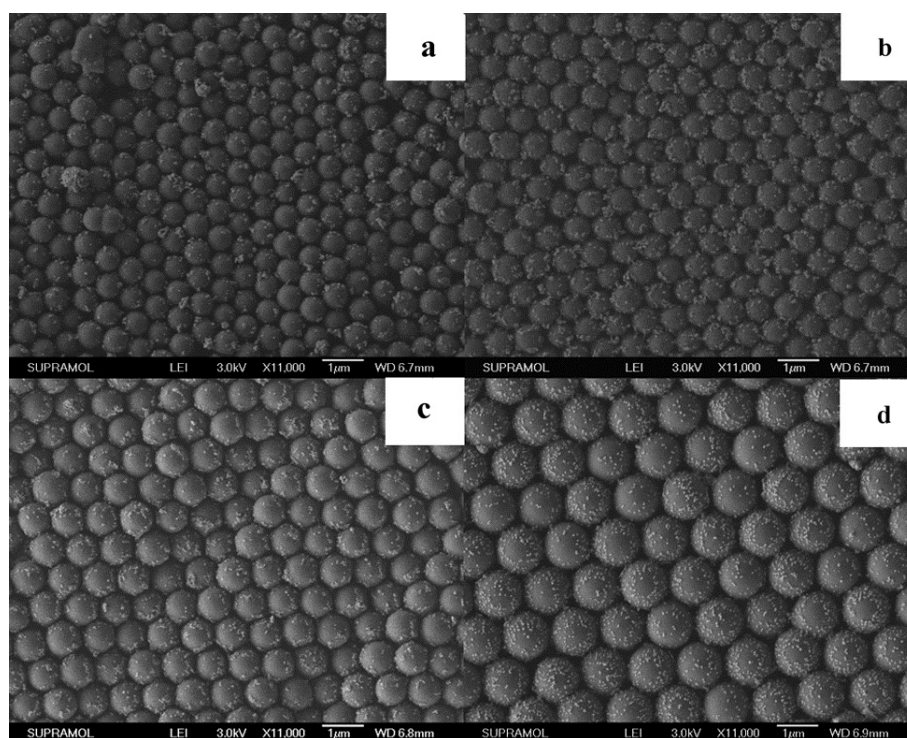


Figure 6. SEM images of the silica arrays on PDMS films; the diameter of the silica spheres is (a) 650 nm; (b) 700 nm; (c) 850 nm and (d) 1100 nm. The surface of the silica spheres is decorated with Ag NPs.

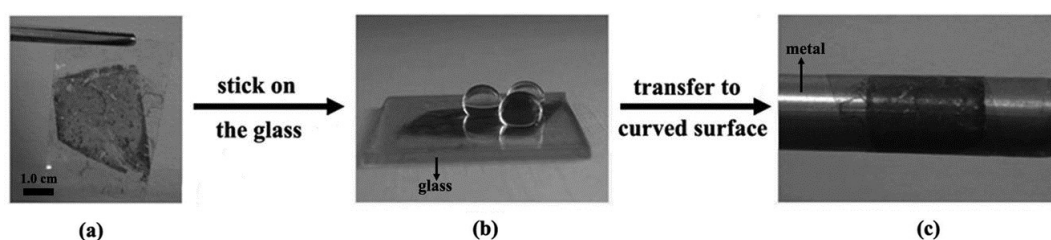


Figure 7. Optical images of (a) a superhydrophobic film; the transparent margin is the PDMS film, and the silica spheres coated with Ag NPs are located in the center. (b) The water droplets, with a volume of 50 μl each, on a superhydrophobic film which is stuck on a glass substrate; the shape of the droplet is nearly spherical. (c) The film peels away from the glass and transfers onto the curved hydrophilic metal surface.

fall off from the substrate even inverted 180°. Figure 7(b) is a direct optical image of water droplets on the superhydrophobic film. The volume of every droplet is 50 μl . From the image we can see that the shape of the droplets is nearly spherical, indicating the film exhibits a good superhydrophobic property. When superhydrophobicity is demanded on a curved surface, the substrate can be dipped into ethanol where the PDMS film can be peeled away from the glass substrate; then the film is transferred carefully to the smooth, curved surface. As shown in figure 7(c), the film is coated on a curved and hydrophilic metal surface. A water droplet rolls down easily due to the small sliding angle of the superhydrophobic film. Consequently, a photo of the droplet on a curved surface could not be taken.

4. Conclusions

In summary, we have successfully fabricated a flexible superhydrophobic surface with a micrometer-level and

nanometer-level hierarchical structure on PDMS films. Lift-up soft-lithography and chemical reduction led to the presence of a raspberry-like structure on the PDMS films; the hierarchical structure originated from coating ordered silica spheres with Ag NPs. SEM images have been used to evaluate the roughness of the PDMS films patterned with silica spheres which were decorated with Ag NPs. The effects of the amount of Ag NPs and the size of silica spheres on the wettability of the PDMS films have been investigated: the former played a major role on the wettability. Our superhydrophobic films could be easily transferred to a number of smooth substrates with different curvatures. During the transfer process, the superhydrophobicity remained intact. Thus, our flexible superhydrophobic films could be used many times to satisfy a wide range of applications.

Acknowledgments

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