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PAPER

Fabrication of hybrid nanostructured arrays using a PDMS/PDMS replication process

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In the study, a novel and low cost nanofabrication process is proposed for producing hybrid polydimethylsiloxane (PDMS) nanostructured arrays. The proposed process involves monolayer self-assembly of polystyrene (PS) spheres, PDMS nanoreplication, thin film coating, and PDMS to PDMS (PDMS/PDMS) replication. A self-assembled monolayer of PS spheres is used as the first template. Second, a PDMS template is achieved by replica moulding. Third, the PDMS template is coated with a platinum or gold layer. Finally, a PDMS nanostructured array is developed by casting PDMS slurry on top of the coated PDMS. The cured PDMS is peeled off and used as a replica surface. In this study, the influences of the coating on the PDMS topography, contact angle of the PDMS slurry and the peeling off ability are discussed in detail. From experimental evaluation, a thickness of at least 20 nm gold layer or 40 nm platinum layer on the surface of the PDMS template improves the contact angle and eases peeling off. The coated PDMS surface is successfully used as a template to achieve the replica with a uniform array *via* PDMS/PDMS replication process. Both the PDMS template and the replica are free of defects and also undistorted after demoulding with a highly ordered hexagonal arrangement. In addition, the geometry of the nanostructured PDMS can be controlled by changing the thickness of the deposited layer. The simplicity and the controllability of the process show great promise as a robust nanoreplication method for functional applications.

I. Introduction

Fabrication processes of ordered nanostructure arrays have recently attracted a vast amount of research attention for being applied to many functional applications, such as surface plasmonics,[1–3] high density data storage,[4,5] photonic devices,[6] nano-filtration,[7] and chemical and biological sensors.[8,9] Standard lithography techniques such as X-ray, E-beam and focused ion beam lithography are methods used to fabricate high-resolution nanostructured arrays. However, their low productivity and high cost are barriers to pattern such structures.[10–13]

Among the many fabrication techniques developed for producing nanopatterned surfaces, soft lithography using PDMS has been extensively employed as a robust, inexpensive, and simple method to replicate nano/micro structures.[14] In recent years, soft lithography has emerged as promising and inexpensive technique to pattern functional, metallic, ceramic and polymeric structures with a good pattern transfer between the mould and patterned structures.[15–18]

PDMS nanostructured arrays can be obtained by replica moulding on a master template, which can be fabricated either by using conventional lithography techniques or through utilizing alternative methods like self-assembly and electroforming.[19–22]

Using PDMS as a master template in a PDMS/PDMS replica moulding process has been recognized as having the potential to replace conventional solid templates such as SU-8 and silicon based stamps. The PDMS casting process is principally dependent on the surface characteristics of the master mould. Surface treatments of the PDMS master template using oxygen plasma and surfactants treatment have been investigated as a means to alter the surface characteristics and to reduce the adhesion between the two PDMS layers. Hassanin and co-workers reported an approach by surface treatment of the PDMS structures using diluted ceramic surfactant solutions prior to the replication process. In addition, Gitlin and co-workers used a PDMS mould treated with hydroxypropyl-methylcellulose (HPMC) in the replication process.[23,24] However, those results were limited to only pattern micro structures. Tooley and co-workers presented a replication process of nanopost arrays using PDMS/PDMS. In their study, plasma and silanized treatments were used to modify PDMS surface properties. They observed cracks and broken posts in the PDMS surface due to the mismatch in the coefficient of thermal expansion of PDMS and its oxidized surface layer.[25] Ng and

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co-workers described a PDMS nanoreplication process of nano arrays using ultrathin layer-mediated processes. They used conventional lithographic techniques and micromachining to fabricate the master mould. Afterwards, a PDMS template was treated using direct write patterning of titanium by focused ion beam.[26] Although the latest aforementioned techniques produce nanoscale patterns, they are either not cost effective and time efficient for preparation of the master mould, or they are not yet developed enough to prevent imperfections in the replica mould.

The proposed process in this research is based on the following considerations: 1) Monolayer self-assembly, as a productive technique, has been used to develop nanoparticle arrays on a large scale with a low cost and controlled arrangement; 2) PDMS replication process, as a traditional method, has been widely used in the fabrication of replica nanostructured arrays; 3) Surface modification, as an effective approach, has been applied to alter the PDMS surface properties by bringing desirable characteristics despite the ones originally found on the PDMS surface. The use of Au and Pt sputtered on the PDMS surface in the PDMS/PDMS nanoreplication process have been introduced.

This research introduces a low cost process for patterning large area PDMS hybrid nanostructure arrays using a novel PDMS/PDMS replication process. Specifically, we replicate the surface patterns of hybrid nanostructured arrays into another PDMS surface. We first fabricate the PS sphere template by using a micropipette to deposit spheres onto a silicon substrate. Next, a PDMS template is produced using replica moulding of the assembled PS template followed by a sputtering coating process. Furthermore, the effects of both gold and platinum thin films on the contact angle between the PDMS topography and the PDMS slurry, peeling off ability and surface topography of the two PDMS pairs have been studied. Based on the surface modification altered by the deposited film, we were able to transfer the patterns of the PDMS template onto PDMS replica using a PDMS/PDMS replication process.

II. Experimental

1. Fabrication procedure

The presented replication process is schematically depicted in Fig. 1. First, a PS template consisting of a monolayer of PS spheres is formed on a silicon substrate Fig. 1(a, b). This template is used for the first replica moulding process, which leads to the formation of a PDMS soft template with a highly ordered hybrid nanopattern on its top surface, as shown in

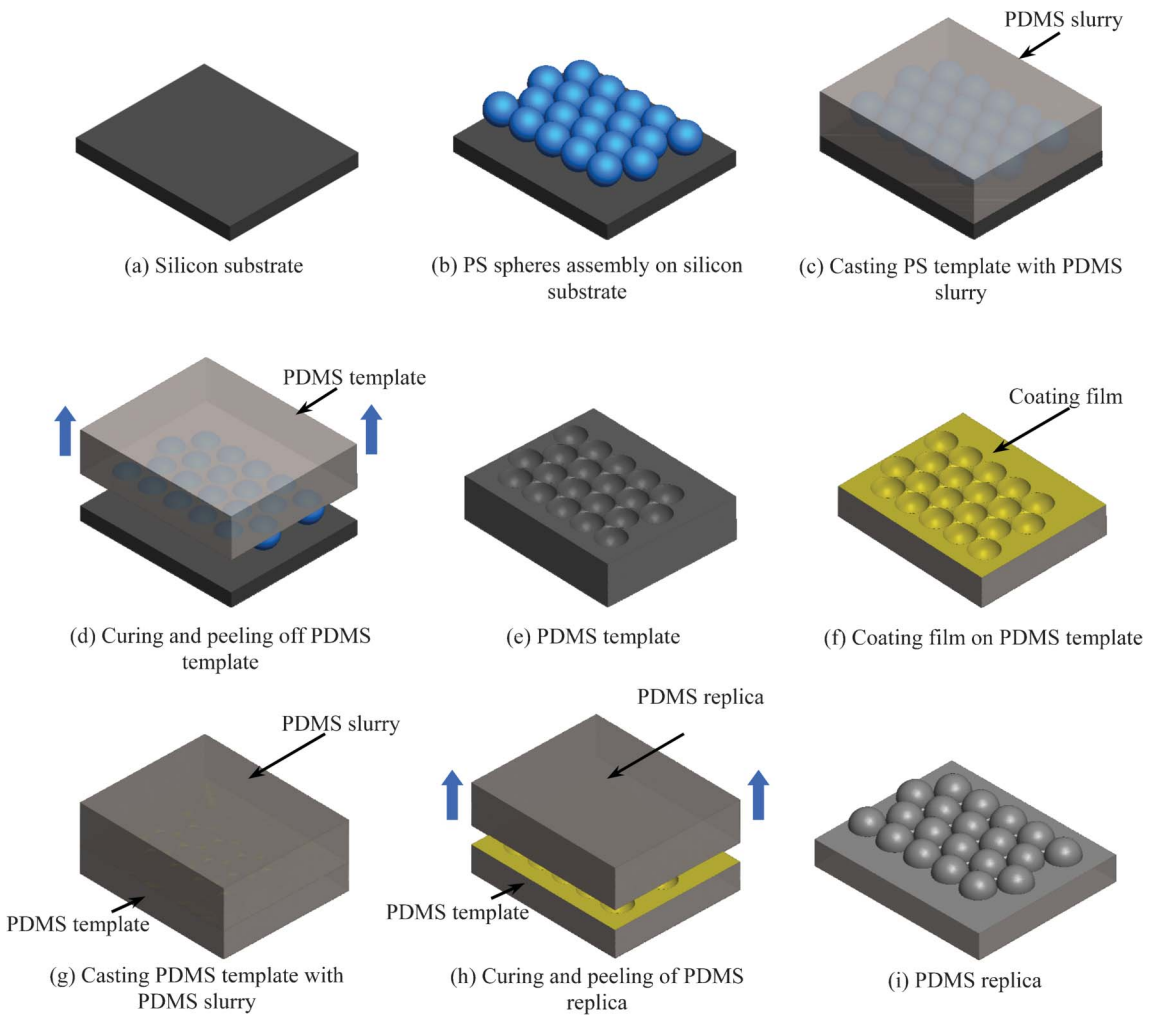

Fig. 1 A schematic diagram of the proposed nanoreplication process.

Fig. 1(c, d, e). Next, a metal film is sputtered onto the top surface of the PDMS mould, Fig. 1 (f). Then, another replica moulding soft lithography process is performed to replicate the PDMS template, Fig. 1(g, h). Finally, the cured PDMS mould is peeled off from the PDMS template and the replicated PDMS mould is obtained, Fig. 1(i).

2. Preparation of PS pattern template

Preparation of a PS pattern template is the first step of the experimental work which is described here. The PS pattern template was prepared by the formation of uniformed PS arrays on a Si substrate using a micropipette. Single side polished silicon wafer (100) was firstly cut into 1.5 cm × 1.5 cm pieces and cleaned with acetone. Next, the cleaned substrate was treated by piranha solution (1 : 3, H_2O_2 : H_2SO_4) at 80 °C for 30 min. Once cooled, the substrate was rinsed with copious amounts of distilled water. The substrate was sonicated in solution (1 : 1 : 5, NH_3 : H_2O_2 : H_2O) for 40 min to increase the hydrophilicity of the surface and followed by rinsing repeatedly with distilled water again and dried with nitrogen stream. Then, a micropipette was used to drop 10 μl of 1 wt% diluted aqueous suspensions of polystyrene spheres with a mean diameter of 1.1 μm and a size distribution of 3% (Duke Scientific Corporation, USA).

The PS microspheres were drop coated using a micropipette.[27] This is a facile method of achieving distribution of the droplet. The quality of the results strongly depends on the latex/water proportion, the properties of the substrate, and the homogeneity of the solvent evaporation. The latex/water proportion was estimated by considering that a monolayer of microspheres should cover the area of substrate thoroughly. Micro/nano-spheres evenly spread out across the surface of substrate due to the columbic repulsion in between the particles. The relative humidity in the clean room was 49% at 21 °C and the self-assembly process was undertaken in a 100 ml Petri dish under the aforementioned conditions to slow down the evaporation process. The drop was spread evenly and a single layer of spheres was formed and used as the master template.

3. Preparation of PDMS template

The PDMS template with the inverted PS pattern was prepared using a replica moulding process. The required thickness of the template is about 2 mm. Sylgard 184 (Dow Chemical Co.) prepolymer was used in the experiments and the preparation steps are reported here. PDMS monomer and cross-linking agent were thoroughly mixed in 10 : 1 (weight ratio) by mechanical stirrer for 15 min and was de-aired in a vacuum chamber for 30 min to remove air bubbles in the mixture. The mixture was then cast onto the PS master mould. Next, the mould was put into a vacuum chamber for another hour to de-air the bubbles on the pattern interface and the PDMS slurry. The PDMS was cured at 60 °C for 2 h followed by cooling. Subsequently, the PDMS replica was gently peeled away from the PS template. The fabricated PDMS template was then sonicated in an acetone bath to clear off any residual colloidal spheres followed by drying using a nitrogen stream. This soft mould was used as a template to replicate the desired PDMS array and is explained in the next section.

4. Coating and nanoreplication process

The PDMS template was reinforced by the adhesion of a glass or plastic plate into the PDMS template. The supported PDMS template was coated with a gold or platinum film using sputter coater at 0.1 Torr and 20 °C with 20 mA current in an argon atmosphere. Coating PDMS with gold and platinum in the PDMS/PDMS replication process has not yet been explored. Therefore, the effect of sputtering coating on the surface topography is essential before performing the PDMS/PDMS replication process. Different coating thicknesses were applied to the PDMS template samples and the surfaces were examined. The thickness of the deposited layer was tuned directly from the sputter coater by controlling deposition duration. After coating, the PDMS slurry was poured on the PDMS template and placed in a vacuum chamber for 5 h. A long vacuum duration is needed to ensure that the PDMS patterns are filled with the PDMS slurry. The desired PDMS replica was cured at 60 °C for 2 h and then demoulded from the PDMS template by peeling off the replica with the aid of a razor blade.

5. Surface characterisation

Two challenges need to be addressed in developing a PDMS/PDMS replication process. One is to improve the surface wettability nature. A conformal contact between the PDMS slurry and the PDMS master template is necessary to achieve nanopattern transfer. The other challenge is to improve the peeling off ability and to introduce a clean demoulding process. With respect to the first challenge, the flatter the PDMS slurry drop shape (low contact angle), the better the wetting of the nanopattern interface. As for the second challenge, it is important to reduce the adhesion between the PDMS template and its replica after curing and to keep them undamaged during demoulding.

The contact angle, peeling ability, and surface topography of the surfaces of PDMS samples were studied to characterise the replication process. Eight sets of PDMS/PDMS replication experiments were grouped according to their surface nature. Firstly, in set A, PDMS template surfaces were left unpatterned and uncoated. Secondly, in set B, sample surfaces were nanopatterned and uncoated. Then, in set C, sample surfaces were left unpatterned and coated with a 20 nm platinum film. In set D, sample surfaces were left unpatterned and coated with a 20 nm gold film. In set E, sample surfaces were nanopatterned and coated with a 20 nm platinum film. In set F, sample surfaces were nanopatterned and coated with a 20 nm gold film. In set G, sample surfaces were nanopatterned and coated with a 40 nm platinum film. Finally, in set F, sample surfaces were nanopatterned and coated with a 40 nm gold film.

The aim of studying contact angle is to investigate the wettability of the PDMS template by the PDMS slurry. An average of ten contact angle readings was taken. The peeling off ability was performed after the pair of contacted PDMS samples are cooled down to room temperature to allow a similar curing condition. In the experiments, two PDMS pairs were peeled off manually and the sample quality were visually inspected. When each of the two PDMS pairs, the template and the replica, are complete and not damaged after peeling off the process is recorded as being successful, otherwise it is recorded as

unsuccessful. At least ten samples were made on each set. The peeling off ability is defined as follows.

$$\text{Peeling of fability} = \frac{\text{Number of undamged samples}}{\text{Total number of samples}} \quad (1)$$

Both the contact angle and the peeling off ability experiments were carried out in a clean environment to avoid contamination of particles in the air. Surface topography, size uniformity and periodicity of all samples were observed using Jeol 7000 scanning electron microscope (SEM) operated with an acceleration voltage of 20 kV. The SEM samples were prepared by attaching the prepared samples to an aluminium stub using conductive adhesive tape. To prevent a build-up of surface charge during image acquisition, the samples were then sputtered with a thin gold layer prior to SEM examination.

III. Results and discussion

The SEM images of the PS template are shown in Fig. 2(a, b). A monolayer of self-assembled 1.1 μm PS spheres is on top of a silicon substrate, forming a closely packed hexagonal array. After pouring the PDMS slurry onto the PS spheres and peeling off the cured PDMS mould, we obtained a PDMS hybrid nanostructured array replica template, as shown in Fig. 2(c, d). It can be clearly observed that the patterned hemispherical nanobowl structures are uniformly patterned with a smooth concave surface. In addition, triangular shaped nanopillars are located at the junction of the bowls. Both the bowls and nanopillars are highly ordered, preserving the PS template surface topography.

The obtained PDMS template was coated with either a gold or platinum layer. The deposited layer of the gold on the surface of PDMS replica was assumed to be uniform in simulation. In particular, the film thickness was assumed constant throughout the topography of the PDMS template. Experimental validation was performed by generating various thicknesses of the deposited layer. Fig. 3 and 4 show the simulation and experimental results at various deposition thicknesses. It can be clearly seen that the thickness of the deposited layer significantly affects the PDMS template topography. The higher the deposited thickness, the lower the bowls diameter and the higher the nanopillars diameter. The depth of the nanobowls remains

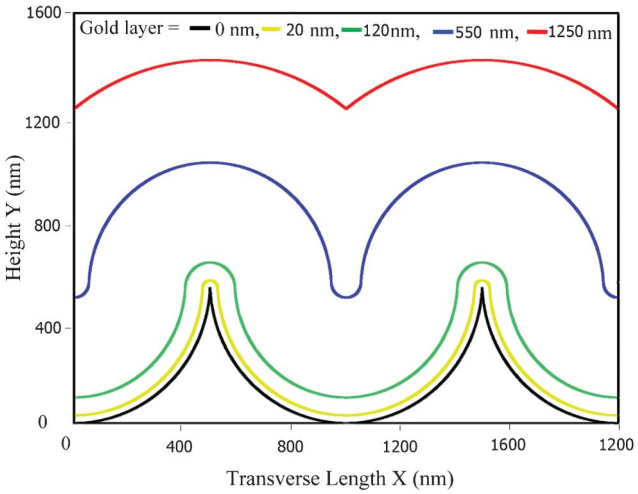

Fig. 3 PDMS surface topography as a function of deposited layer.

constant when the layer thickness is less than or equal to 550 nm, which is the radius of the PS spheres. In addition, the geometry of the bowls changes gradually from nearly hemisphere to conical, with inward curvature increasing with the deposited thickness. By further increasing the layer thickness, the bowls and the nanopillars become shallower. Thus, the variation of the coating thickness can be used together with the size of PS spheres to tune the nanostructures PDMS template. The simulation and experimental analysis prove the assumption of a uniformed deposition.

Contact angle measurement and peeling off ability results *versus* samples are listed in Table 1. In addition, photos of the contact angle measurement are shown in Fig. 5. The average contact angle of a PDMS slurry drop on unpatterned and uncoated PDMS surface is 14°. The low contact angle indicates a good wetting property between PDMS plain surface and the PDMS slurry, unlike the hydrophobic behaviour of the PDMS surface when contacted with water where the contact angle ranges from 89°–120°.[28] No samples were successfully demoulded, and the peeling off ability is 0%.

With the presence of nanopatterns on the PDMS surface, the surface wetting properties are degraded where the average value of the contact angle is 31°. This may be attributed to the specific

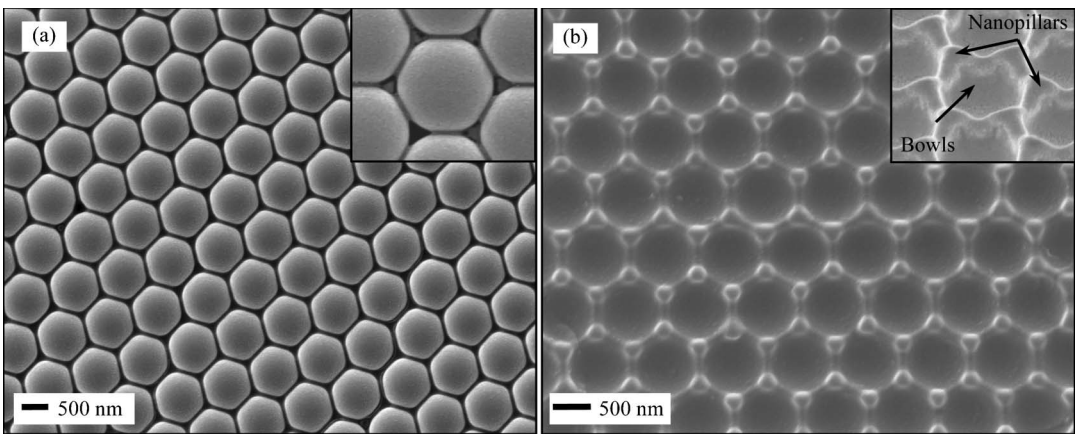

Fig. 2 SEM images of (a) self-assembled PS spheres on silicon substrate, (b) PDMS nanostructures template.

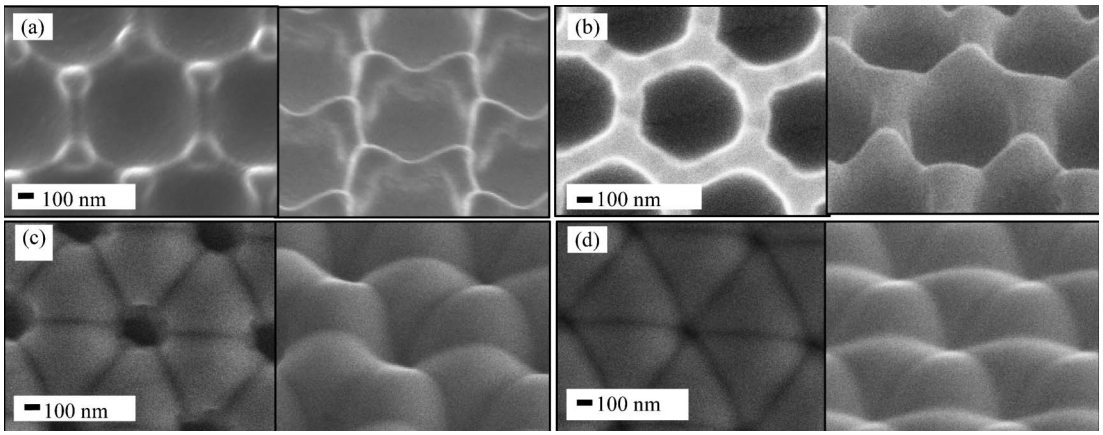

Fig. 4 SEM images of PDMS nanostructures template topography coated with (a) 20 nm, (b) 120 nm, (c) 550 nm, (d) 1250 nm gold layer.

Table 1 Contact angle and peeling off ability of the replication process

Group	Description	PDMS contact angle	Peeling off ability
A	unpatterned and uncoated	14°	0%
B	nanopatterned and uncoated	31°	0%
C	unpatterned and 20 nm platinum coated	10°	80%
D	unpatterned and 20 nm gold coated	6°	100%
E	nanopatterned and 20 nm platinum coated	12°	60%
F	nanopatterned and 20 nm gold coated	8°	100%
G	nanopatterned and 40 nm platinum coated	12°	100%
H	nanopatterned and 40 nm gold coated	8°	100%

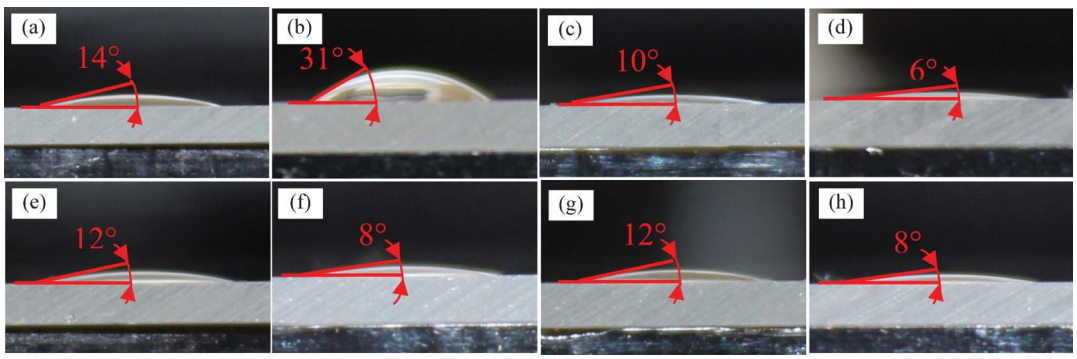

Fig. 5 Contact angle images for sets (a) A, (b) B, (c) C, (d) D, (e) E, (f) F, (g) G, (h) H.

characteristics of nanotopography. The nanopatterned surfaces of the untreated PDMS resisted the outward spread of PDMS slurry and helped to maintain a higher contact angle. These results are similar to those in the literature,[28] where the presence of patterned structures has been proven to enhance the hydrophobic nature. On the other hand, the peeling off ability remains at 0%. All the peeling attempts failed with uncoated PDMS samples due to the high bonding force between the PDMS pair impeding demoulding associated with the adhesive interaction between the PDMS slurry and the PDMS template during the curing step.

For the unpatterned and coated samples in groups C and D, the decrease of the contact angle and the increase in the peeling off ability is abrupt when the samples are coated with either a gold or platinum layer. The best results are for samples coated with gold where the contact angle is decreased to about 6° and the peeling off ability is improved to about 100%, while samples coated with platinum have a contact angle of 10° and peeling off ability of about 80%.

Similarly, in set E, where samples are nanopatterned and coated with 20 nm platinum, the contact angle is decreased to about 12° and hence the surface wetting properties are improved. On the other hand, the peeling off ability is only about 60%. SEM images of set E topography are shown in Fig. 6. It can be noted that the pattern of the PDMS template is partially transferred to the PDMS replica. The bowls can be identified in the PDMS template with notable distortion. In addition, the nanopillar pattern cannot be identified on the PDMS template and are presented on the surface of PDMS replica. On the other hand, the bump arrays on the PDMS replica are visually distinguished.

In set F, as shown in Fig. 7, where samples are coated with a 20 nm gold layer, the surface wetting properties of the

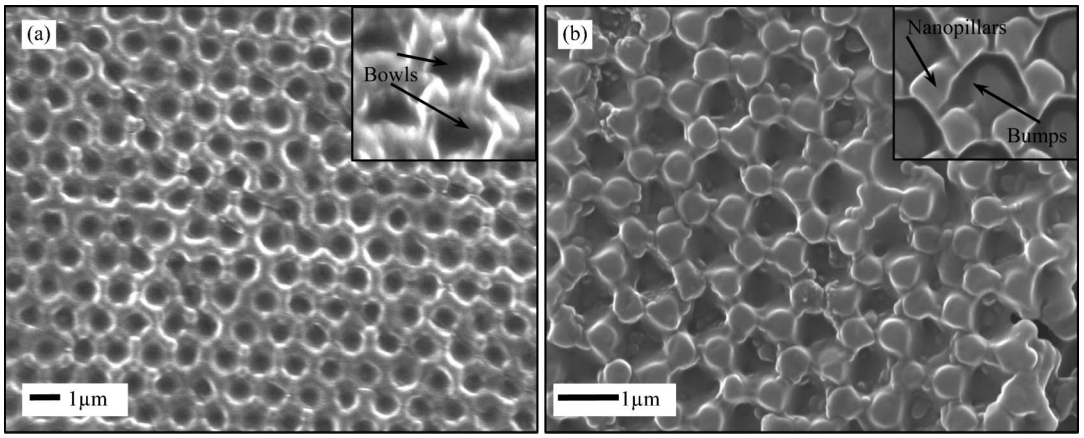

Fig. 6 SEM images of PDMS nanopatterned after peeling off for set E coated with a 20 nm platinum layer (a) PDMS template, (b) PDMS replica.

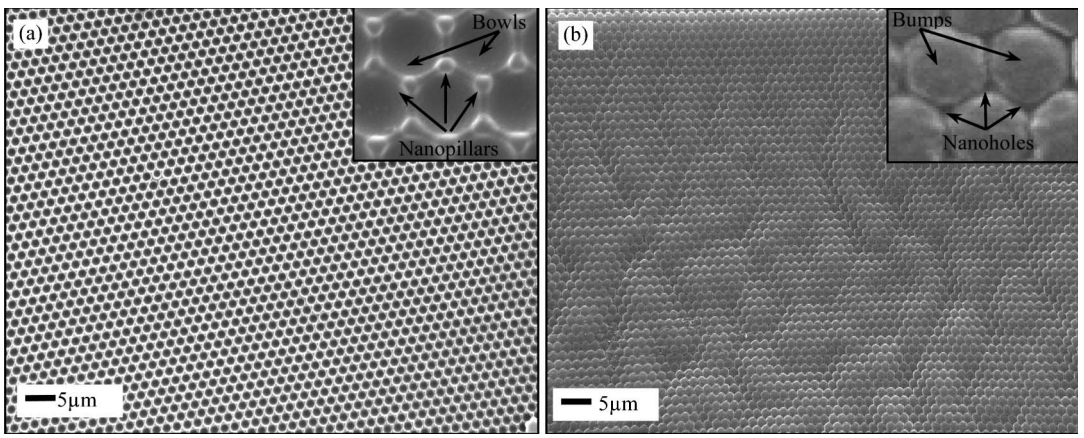

Fig. 7 SEM images of PDMS nanopatterned after peeling off for set F coated with a 20 nm gold layer (a) PDMS template, (b) PDMS replica.

nanopatterned PDMS template were significantly improved. The average value of the contact angle decreased to about 8° while the peeling off ability of the samples is significantly improved to 100%. All samples were demoulded easily and both the original and the copy were remained intact. Samples coated with 20 nm gold not only had improved wetting properties against PDMS slurry, but also reduced the molecular adsorption to PDMS surfaces, which enhanced the peeling off ability. SEM images of the gold-coated template and the replica are shown in Fig. 7. Contrary to set E, the PDMS replica shows complete and uniformly patterned bump arrays. In addition, the bowls and nanopillars of the template are kept intact after demoulding.

The influence of deposited average thickness on the wetting behaviour of sample surface and the peeling off ability was studied experimentally for sets G and H. SEM images of the PDMS topography of the samples are shown in Fig. 8 and Fig. 9.

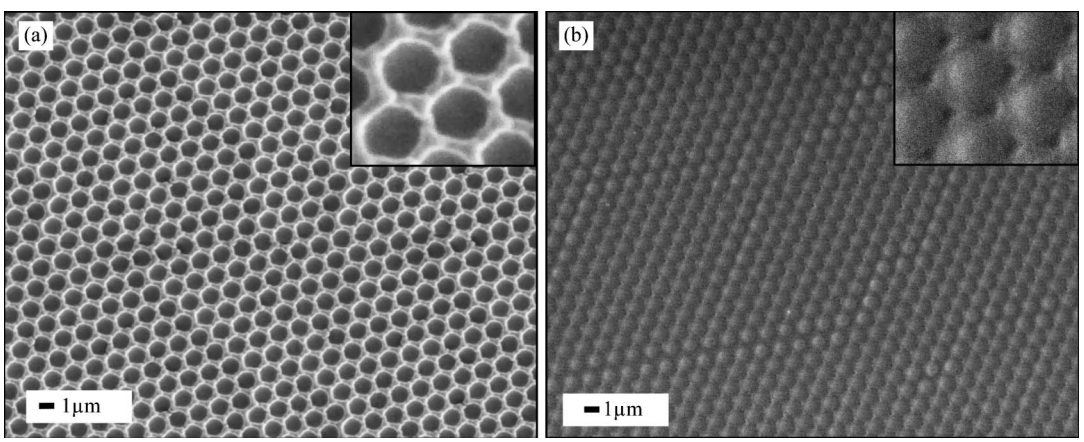

Fig. 8 SEM images of PDMS nanopatterned after peeling off for set G (a) PDMS template, (b) PDMS replica.

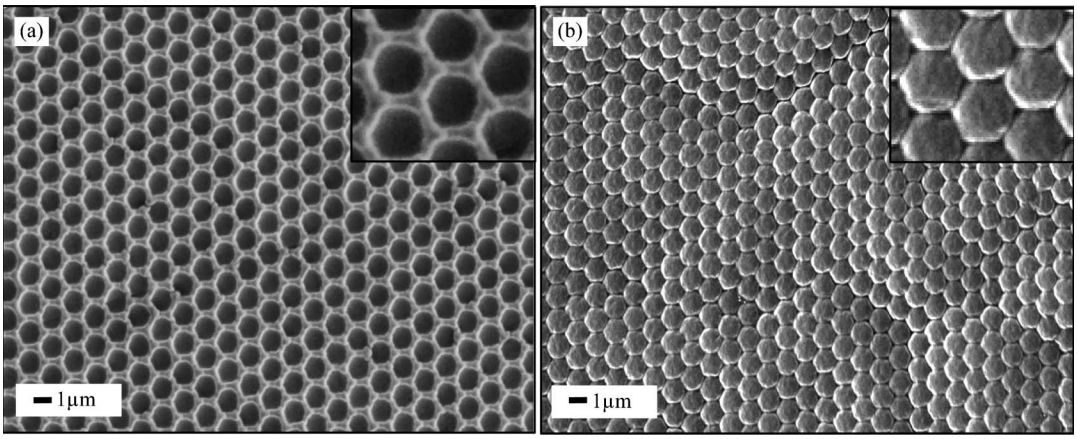

Fig. 9 SEM images of PDMS nanopatterned after peeling off for set H (a) PDMS template, (b) PDMS replica.

With further increasing platinum thickness from 20 nm to 40 nm, the average value of the contact angle remained unchanged at 12°, while the peeling off ability of the samples improved from 60% to 100%. Both the template and the replica were demoulded without distortion, as shown in Fig. 8. On the other hand, when the gold thickness increased from 20 nm to 40 nm, both the contact angle and the peeling off ability remained unchanged. Fig. 9 shows the results of both the PDMS template and the replica of set H that are similar to those found in Fig. 7. A slight decrease in the diameter of the bowls and increase in the nanopillar thickness can be noticed when compared to results obtained using 20 nm layer thicknesses.

By comparing Fig. 6 and Fig. 8, for samples coated with 20 nm and 40 nm platinum layers, it can be noted that the replication process is significantly improved and the results similar to those of the gold-coated samples. A schematic explanation of the peeling off mechanism for samples E and F is illustrated in Fig. 10(a, b), respectively. It can be concluded that when the average thickness of the platinum is close to 20 nm, Pt formed on the PDMS topography may not be able to cover the entire surface of the nanopillar tips of the PDMS replica. This results in an adhesion between these tips in the template and the PDMS replica during curing. Afterwards, the nanopillars were broken from the template and attached to the replica during peeling off. Consequently, the PDMS template contains only the bowl pattern and does not contain any of the nanopillars, see Fig. 6. The nanoreplication process was significantly improved with further increasing of the platinum layer to about 40 nm. At such high deposition thickness, the platinum particles were able to form on all the PDMS topography including the tips of the nanopillars, which eases the peeling off ability and hence improves the perfection of the resultant nanostructures.

Conclusions

A nanofabrication process is proposed for producing hybrid nanostructured arrays based on coated PDMS nanostructure surface and a novel PDMS/PDMS replication process. Our study shows that a thickness of at least a 20 nm gold layer or 40 nm platinum layer on the nanostructured PDMS template works best as a release layer in comparison with uncoated plain PDMS surfaces, uncoated but nanostructured surfaces, and 20 nm Pt coated nanostructured surfaces. The contact angles of the PDMS slurry were decreased from 31° to 8° and 12° when the

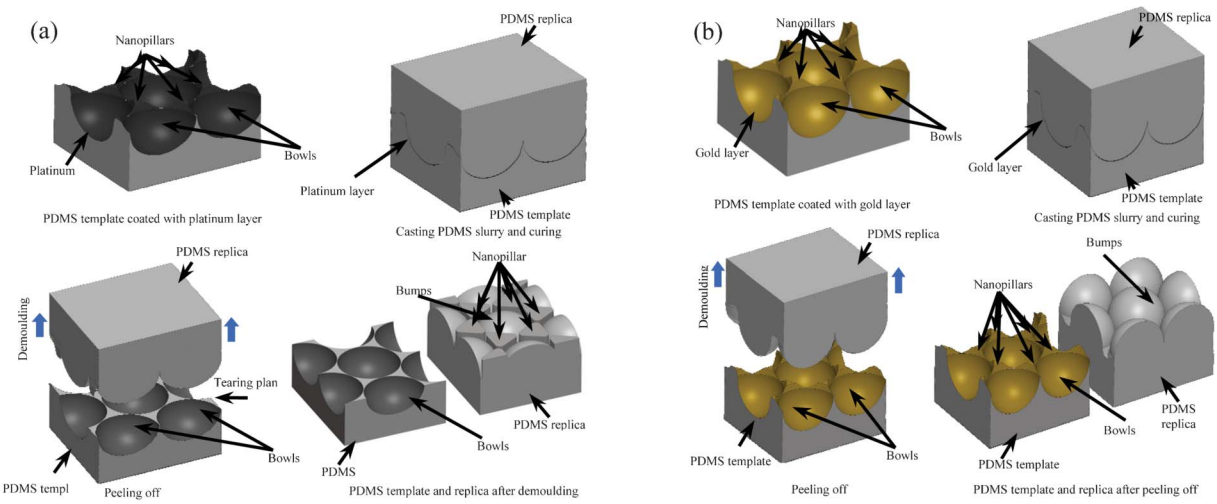

Fig. 10 A schematic explanation of the peeling off mechanism of samples E, and F, respectively.

nanostructured PDMS samples were coated with a 20 nm gold layer or a 40 nm platinum layer, respectively. In addition, the peeling off ability improved from 0% to 100%. The combinational enhancement of both the contact angle and the peeling off ability leads to a conformal contact during filling and an easy peeling off after curing. Experimental and simulation results of the coating process show that the gold sputtering coating produces uniform film coating. Various geometries and sizes of the coated PDMS nanostructure arrays were obtained by controlling the thickness of the deposited layer on top of the PDMS nanostructure template. The synthetic strategy provides a versatile way of developing a functional PDMS substrate. Consequently, not only can the nanostructured arrays be successfully patterned, but also the two PDMS pairs, although composed of the same material, can be easily detached from each other using simple processes, which make the fabrication process simple and convenient without the need for expensive or sophisticated patterning instruments.

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