FULL PAPER

Transferable Crack-Free Colloidal Crystals on an Elastomeric Matrix with Surface Relief

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Crack-free three-dimensional (3D) colloidal silica crystals are fabricated on an elastomeric polydimethylsiloxane (PDMS) stamp via the lift-up method. A surface relief structure is fabricated on the PDMS substrate to enable the formation of colloidal crystal assemblies that cannot be achieved on a plane PDMS substrate owing to the hydrophobic nature of its surface. Four samples of uniform silica particles having different sizes are prepared for colloidal crystal assembly on PDMS substrates with various relief patterns. This strategy not only provides a means for the assembly of crack-free colloidal crystals on a soft hydrophobic surface via the lift-up method but enables the transfer of the crack-free colloidal crystals onto a curved surface.

1. Introduction

Three-dimensional (3D) colloidal photonic crystals have attracted considerable attention owing to their promising applications in the fields of optics, sensors, solar cells, and display devices.[1–4] These applications utilize the unique ability of colloidal crystals to interact with electromagnetic radiation via periodic modulation of their refractive index in three spatial dimensions.[5] The fundamental advantage of colloidal crystals is the size of their structural features, which makes them amenable to interact with visible light. A control of the stop-band of colloidal crystals leads to interesting effects, such as the demonstration of structural colors or enhancement of light harvesting through reflection, which are of special importance in energy and display applications. Generally, these interesting phenomena are predicated on the availability of large and uniformly coated areas of colloidal photonic crystals. However, such wide-area assemblies of 3D colloidal crystals suffer from the formation of cracks that may deteriorate the performance of the system.

Cracks in the organization of colloidal crystals are mainly caused by tensile stresses generated during their self-assembly process. In a typical fabrication process, colloidal crystals are grown by drying a layer of colloidal suspension on a substrate. This layer is usually formed by dipping and removing a substrate from a colloidal suspension. As the solvent in the colloidal suspension evaporates, the volume fraction of the colloidal particles increases. Once the volume fraction reaches 0.54, the colloidal particles tend to form a crystalline phase. On subsequent drying, the particles self-assemble into other close packed structures, ceasing at the face-centered-cubic structures, when their volume fraction reaches 0.74.[6] The progressive changes in the crystal arrangement driven by evaporation leads to stresses in the structure. Moreover, stresses are also imposed owing to the shrinkage of the colloidal particles while drying and constraints on the shrinkage inflicted by a rigid substrate.[7,8] To obtain crack-free assemblies of colloidal crystals, many different approaches have been explored, such as preshrinking of colloidal spheres before assembly,[9] use of liquid substrate or a topologically patterned substrate,[10,11] formation of crystal structures having low-stacking density or multicoating,[12] and addition of monomers in a colloid suspension for polymerization during the assembly process.[13] However, these approaches are impractical because they are either costly or require poisonous substrate, or they are limited in scalability. Therefore, a fabrication process that alleviates these problems to form crack-free colloidal crystals needs to be developed. In addition, it will also be very useful to assemble crack-free colloidal crystals on a transferable substrate, which can be re-used after the colloidal crystals are transferred onto other flexible or curved substrates.

Presently, a polydimethylsiloxane (PDMS) elastomeric substrate has been recognized as the best transferable substrate because of its mechanical flexibility, optical transparency, molding capacity at nanometer resolution, conformal contact, good release characteristics, and low material cost.[14,15] Owing to these advantages, PDMS has been explored for use as replica molds for colloidal crystal assembly and formation of 2D patterned arrays by micro-contact printing processes that are based on soft lithography.[16,17] Among the fabrication methods to obtain a colloidal crystal assembly layer, dip-coating is considered as an inexpensive method to form reasonable uniform coatings of colloidal assemblies on relatively large areas

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(square-centimeter scale). This method offers the advantage of quick fabrication with precise control of the film thickness by adjusting the concentration of colloidal particles in the suspension and by regulating the substrate lifting speed, which does not cause any change in the particle concentration during the film formation.[18] Unfortunately, it is a challenge to directly assemble crack-free 3D colloidal crystals on a transferable PDMS substrate using the lift-up method, and no one has ever succeeded. This is probably because of the low surface energy of PDMS, which can hinder the pinning process of colloidal particles at the substrate-colloidal suspension-air interface.

Here, we devised a transferable PDMS substrate with a surface relief structure to aid the assembly of colloidal particles and successfully demonstrated the formation of crack-free 3D colloidal crystals. Furthermore, we could transfer the crack-free 3D colloidal crystals on the PDMS substrate onto a flat or a curved substrate.

2. Results and Discussion

When a wettable substrate such as glass or silicon wafer is dipped in a colloidal solution, the colloidal particles move toward the contact line at the substrate-colloidal suspension-air interface, because the rate of evaporation of the solvent is the highest there. At the same time, if the colloidal particles transported to the contact line have sufficient attractive (adhesive) interaction with the substrate, the colloidal particles can be stuck at the contact line (pinning process). The colloidal particles pinned at the contact line fix it and prevent it from moving downward on further evaporation of the solvent in colloidal solution during the lift-up process. The colloidal particles assemble into an ordered structure along the contact line by lateral capillary forces; the fixation of the contact line by pinned colloidal particles causes further influx of solvent toward the contact line. Therefore, the colloidal particles are continuously transported toward the pinned contact line and consequently assembled into a 3D colloidal crystal on continuous evaporation of the solvent. On the other hand, a non-wettable substrate such as PDMS or Teflon does not allow any 3D colloidal crystals to assemble because the pinning process is very difficult to occur on its surface. The contact angle of water on the PDMS substrate was 107° (see Supporting Information Figure S1). Therefore, colloidal particles in water cannot form colloidal crystals on the PDMS substrate because the evaporation rate of water would not be the highest at the contact line, and as a result, the colloidal particles cannot be pinned at the contact line. Hence, in this work, we dispersed colloidal silica particles in ethanol in order to reduce the contact angle to below 90°. Although the contact angle of ethanol on PDMS was measured as 40°, the flat PDMS substrate could not assemble 3D colloidal silica crystals on its surface (see Supporting Information Figure S2). This might be due to the weak adhesion between the colloidal silica particles and PDMS because of the very low surface energy of PDMS. As schematically illustrated in **Figure 1**a, the colloidal silica particles dispersed in ethanol are not pinned at the PDMS-colloidal silica suspension-air interface (contact line), and consequently, the colloidal suspension slips downward on further evaporation of ethanol. The adhesion

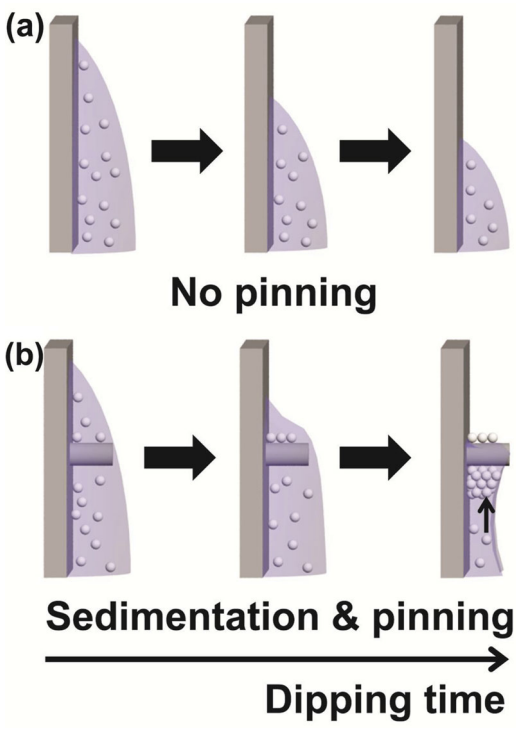

Figure 1. Schematic illustration of expected colloidal assembly on a) flat PDMS and b) PDMS with a surface relief structure.

between PDMS and colloidal silica particles is weak because the surface of PDMS is hydrophobic, while the colloidal silica particles are hydrophilic in nature. As a result, there are no suitable pinning sites for silica particles available on PDMS. Therefore, we devised the strategy of preparing a PDMS substrate with a surface relief structure that can fixate the colloidal silica particles on the surface relief structure during the lift-up process. The colloidal silica particles, which get sedimented on the surface relief structure, further fix the contact line, allowing the formation of 3D colloidal crystals along the contact line as illustrated in Figure 1b.

In this work, we designed transferable PDMS substrates with three different surface relief patterns (see Figure S3 for a detailed description of the pattern dimensions). We fixed the height of all of the patterns to 10 μm in order to compare the effect of the pattern structure. The scanning electron microscopy (SEM) images of the transferable PDMS substrates with different surface reliefs are shown in **Figure 2**a–c. To provide pinning sites on the PDMS substrate for colloidal silica particles, we used cylindrical, cross-shaped, and long rectangular relief patterns. Surprisingly, all of the transferable PDMS substrates with surface relief could form crack-free 3D colloidal silica crystals on their surface, as shown in Figure 2d–f. The successful formation of colloidal crystals can be attributed to the surface relief structure, which provided pinning sites for the colloidal particles; for instance, silica particles could easily sediment on the wall surface of the cylindrical rod structures aligned vertically on the PDMS substrate. This simple approach

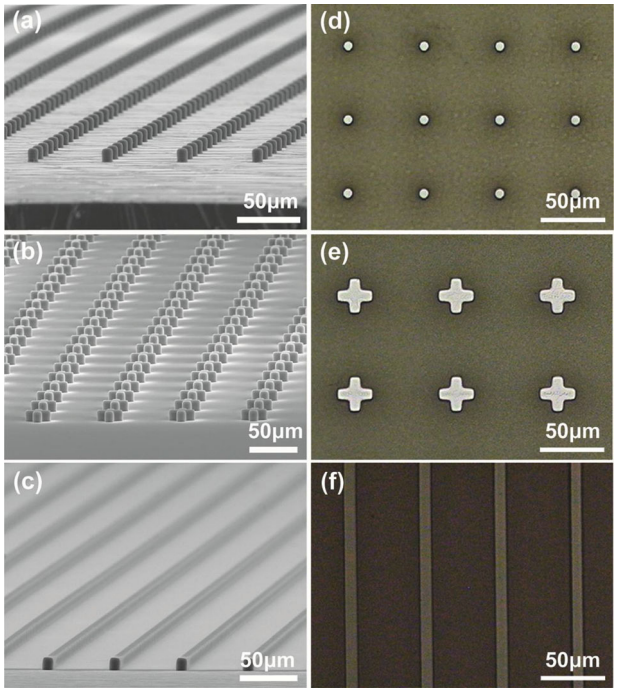

Figure 2. a–c) SEM images of PDMS stamps with different surface reliefs, and d–f) OM images of crack-free silica particle assemblies on corresponding PDMS stamps.

has important implications because it provides facile method for the fabrication of crack-free colloidal crystal assembly layers and mitigates the problems associated with cracks limiting the applications of colloidal crystals. This approach can be applied to double-sided assembly of colloidal crystals provided the PDMS substrate has surface relief patterns on either side of its surface.

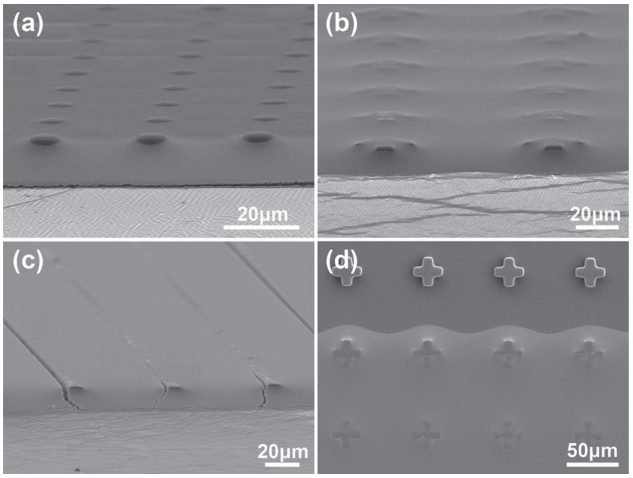

Figure 3. Pinning of colloidal assembly layer at the contact line of PDMS stamps with a) cylindrical, b) cross, and c) long rectangular surface reliefs. d) PDMS stamp with cross surface relief which were partially dipped into silica particle suspension resulting in a contact line formation starting from the dipped region.

To elucidate the underpinnings of the assembly of 3D colloidal crystals on a transferable PDMS substrate with surface relief, we carefully investigated the morphology of the crystals at the contact line, as shown in **Figure 3**. As illustrated in Figure 1b, the silica colloidal particles were pinned at the surface relief on the PDMS substrate and the pinned colloidal particles held the contact line from slipping down on further evaporation of the solvent. As expected, the assembled colloidal particles exhibited the shape of a capillary between two cylindrical posts on the PDMS substrate. The magnified SEM images clearly confirm that some colloidal particles were stacked on the wall surface cylindrical relief structure.

SEM images of the colloidal assembly at different surface reliefs are shown in **Figure 4**. The SEM and photo images (see Supporting Information Figure S4 and Figure S5) clearly show that with the help from the surface relief structure, colloidal assembly layer can be formed on the PDMS substrate using a lift-up method. It is interesting to observe that the colloidal assembly adjacent to the relief wall (Figure 4b,c) appears darker in the SEM image. Since the brightness reflects the electron density in a SEM image, the darker part of colloidal could be due to the compact packing of silica particles as compared to the outer region. This implies that the colloidal assembly is formed by capillary forces generated by the meniscus on the relief walls (see Supporting Information Figure S5). In this aspect, our approach differs from those of the template-directed[19–21] or microchannel-based colloidal crystallization,[22] because our process utilizes the interaction at the surface relief wall rather than ordering an assembly in conformance of the patterns on the substrate.

We used a syringe pump for the lift-up procedure as shown in **Figure 5**a. This configuration not only enables control of the lifting rate but also allows for the lift-up of multiple-samples at a time. We measured and calibrated the lift-up rate ($\mu m \cdot s^{-1}$) by varying the rate of movement ($mL \cdot h^{-1}$) of the syringe pump (see Supporting Information Figure S6). We optimized the concentration of silica particles and lift-up rate to obtain a flat colloidal assembly layer between the reliefs (Figure 5b,c). The thickness of the colloidal crystal layer obtained using lift-up process can be determined by Equation 1, as follows:

$$t \sim \beta L j_e \phi / 0.605 v d (1 - \phi) \quad (1)$$

where t is the thickness of the colloidal crystal, β is the ratio of the velocity of the particles in the suspension to the velocity of the suspension, L is the length of meniscus, j_e is the evaporation rate of the solvent, ϕ is the volume fraction of the particles in colloidal suspension, d is the diameter of the colloidal particles, and v is the lift-up speed of the PDMS substrate.[23,24]

The concentration of silica particles was gradually increased from 1 wt% at a fixed lift-up rate of 1.1 $\mu m \cdot s^{-1}$ until a uniform thickness of the colloidal crystal layer was obtained. It was also observed that the lift-up rate influenced the thickness of the colloidal crystal layer between the reliefs. The thickness of the colloidal assembly remained unchanged with changes in the size of the particles used in this work. Finally, the concentration of the silica particles in the suspension and the lift-up rate were fixed at 10 wt% and 1.1 $\mu m \cdot s^{-1}$, respectively.

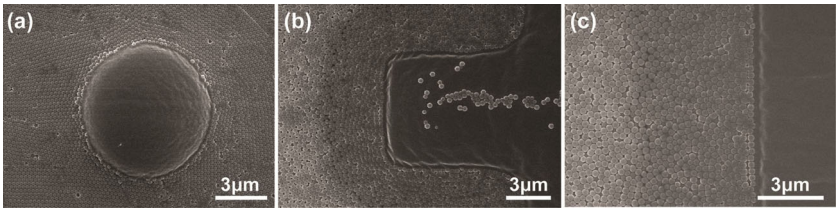

Figure 4. SEM image of crack-free 225 nm colloidal silica crystal assemblies near the surface relief wall of PDMS stamps with a) cylindrical, b) cross, and c) long rectangular surface reliefs.

As shown in Figure 4, a wrinkling effect can be seen in the colloidal crystal layer, which could have been induced by the swelling of ethanol owing to its moderate affinity for PDMS.[25] Surface reliefs on a PDMS substrate make it even more hydrophobic in nature (Supporting Information Figure S1). In consideration of the requirement for a substrate to be hydrophilic to promote the assembly of colloidal particles, which are also hydrophilic, the heightened hydrophobic property of the substrate should prevent the formation of any colloidal crystal. However, the results are quite the contrary; the surface relief enhanced the formation of the colloidal crystal. This is a remarkable result and substantiates the importance of reliefs in the formation of colloidal crystals.

The colloidal assembly layers on PDMS demonstrated different structural colors depending on the size of the particles used. The position of the reflectance peak shifted to longer wavelengths as the particle size increased (**Figure 6**). The colors matched with those determined by theoretical calculations based on the size of the particles. Exception was observed for the colloidal particles of size 300 nm which exhibited a pinkish color rather than red color, which can be predicted by Bragg's equation (Equation 2).

$$\lambda = 1.633 d n_{average} \quad (2)$$

where d is the center-to-center distance between two neighboring spherical particles and $n_{average}$ is the average refractive index of a silica nanoparticle (=1.34).[26,27]

Since light is also scattered owing to inhomogeneities in the colloidal packing, a whitish appearance owing to inhomogeneities combined by the red color from the colloidal assembly resulted in a pinkish appearance of the 300 nm colloidal particle layer. In the structural colors observed in nature, the whitish appearance is removed by an appropriate dye, which absorbs the diffuse lights to form a brilliant and non-whitish color.[28] It is expected that introduction of an appropriate dye may improve color appearance for 300 nm colloidal layer.

PDMS is a flexible elastomer, which has an excellent release behavior that enables the feasible transfer of a coated region. As we could successfully obtain a crack-free colloidal crystal assembly on a PDMS substrate with surface relief, we investigated the possibility of transferring a crack-free colloidal assembly from the PDMS substrate onto a curved surface (see **Figure 7** and also the movie file in the Supporting Information).

The crack-free assembly of colloidal silica particles on an elastomeric stamp (Figure 7a) was successfully transferred to a double-sided adhesive tape on the curvature (radius = 4.25 cm) of a cup (Figure 7b). The transferred colloidal assembly also showed its intrinsic color. The SEM images (Figure 7d–f) of the transferred colloidal crystal assembly layers were analyzed. Except for some cracks that could be observed at the edges of the layers and the assembly on the cross-pattern surface relief, we could transfer the crack-free colloidal assembly layers onto a double-sided tape. Although the assembly layer on the cross-pattern surface relief exhibited the same structural color as the other layers, cracks extending from each side of the wall were observed during the transfer.

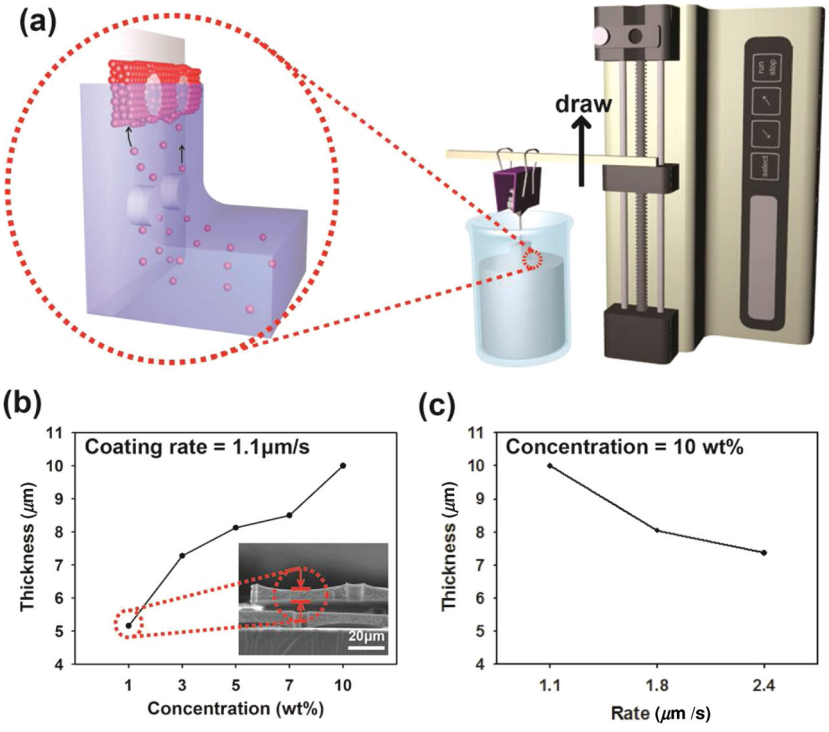

Figure 5. a) Outline of colloidal assembly layer fabrication. Lift-up rate of the PDMS stamp was precisely controlled by a programmable syringe pump. Thickness of the colloidal assembly layer between the reliefs by varying the b) silica particle concentration in suspension and c) lift-up rate. The thickness was measured at the thinnest region of the colloidal assembly layer.

3. Conclusions

We have proposed a facile fabrication method for the crack-free assembly of colloidal crystals on a PDMS substrate with surface relief. With this method, a 10 μm thick layer of colloidal crystals could be assembled on a square-centimeter-scale area of the elastomeric substrate. This fabrication method

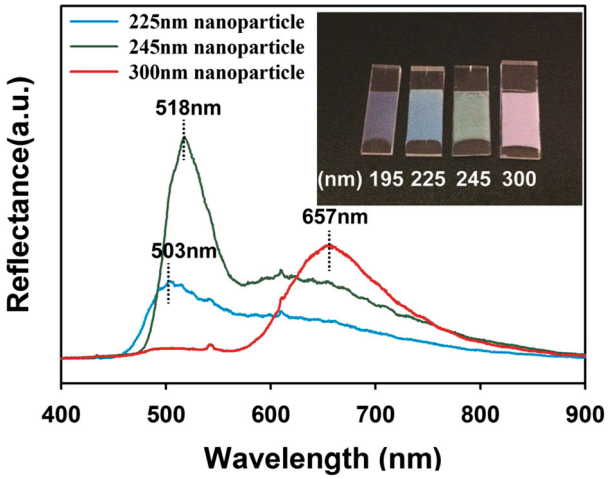

Figure 6. Reflection spectra of different colloidal assembly layers made of differently sized silica particles on PDMS stamps with a cylindrical surface relief.

provides an important insight for realizing crack-free coating of colloidal crystals on flat or curved areas.

4. Experimental Section

Synthesis of Uniformly-Sized Silica Particles: Monodisperse silica spheres were synthesized using the sol–gel method. The following reagents were used; ethanol (≥99.5%, Sigma-Aldrich), ammonium hydroxide solution (NH_4OH, 28.0-30.0%, Sigma-Aldrich), L-arginine (≥98%, Sigma-Aldrich), triple distilled water, and tetraethylorthosilicate (TEOS, 98%, Aldrich). The average diameter of the silica particles was varied from 195 nm to 300 nm by decreasing the amount of ammonium hydroxide (see Figure S7 in the Supporting Information). The first seed particles were prepared in a 20 mL vial. First, L-arginine (9.1 mg) was added to water (6.9 mL) under ambient conditions. After thoroughly mixing the solution, cyclohexane (0.45 mL) was added and the vial was heated to 60 °C in an oil bath under magnetic stirring. Then, TEOS (0.55 mL) was added to the solution, which was kept at 60 °C for 20 h. The second seed particles were prepared in a vessel. First, L-arginine (3 mg) was added to water (18 mL) under ambient conditions. After thoroughly mixing the solution, prepared first seed particles solution (5 mL) and cyclohexane (0.45 mL) were added and the vessel was heated to 60 °C in an oil bath under magnetic stirring. Then, TEOS (1.76 mL) was added to the solution, which was kept at 60 °C for 20 h. The third seed particles were prepared in a vessel. First, L-arginine (22.5mg) was added to water (82.5 mL) under ambient conditions. After thoroughly mixing the solution, prepared second seed particles solution (15 mL) and cyclohexane (7.25 mL) were added and the vessel was heated to 60 °C in an oil bath under magnetic stirring. Then, TEOS (7.515 mL) was added to the solution, which was kept at 60 °C for 20 h.[29] In a typical regrowth reaction, the seed particles, ethanol, distilled water, and ammonium hydroxide solution were mixed using a magnetic stirrer. After mixing, TEOS was added using a syringe pump (KDS 100, KD Scientific) at the rate of 0.8 $mL \cdot h^{-1}$. The synthesized silica particles were washed with ethanol before use.

Fabrication of PDMS Stamps with Specific Surface Relief: PDMS stamps with surface patterns of cylinder, straight line, and cross were prepared from a commercially available liquid prepolymer mixture of a silicon elastomer base and curing agent (Sylgard 184, Dow Corning). A mixture of the elastomer base and curing agent (91/9 w/w) was vigorously stirred at 350 rpm for 40 min. Any bubbles generated during mixing were removed by repeatedly evacuating and purging the mixtures in a vacuum oven. PDMS stamps with the requisite surface patterns were obtained by thermal curing of the prepolymer mixture on a respective photoresist master at 80 °C for 5 h. The cured PDMS was then peeled off from the master.

Characterization: Colloidal assembly of silica particles was observed using OM (BX41, Olympus) and SEM (MIRA LMH, TESCAN, and Hitachi S-4800). For SEM, an accelerating voltage of 30 kV was used and the samples were not overlaid by a conductive coating. The average size and the standard deviation of size were determined from the SEM images by averaging diameters of more than 100 particles. A UV-vis spectrometer (QE 65000 fiber-optic, Ocean Optics) was used to monitor the reflection from the colloidal silica assembly. Contact angles of water and ethanol on flat PDMS and patterned PDMS samples were measured using a contact angle analyzer (Phoenix 300 Plus, SEO, Korea).

Colloidal Silica Assembly on PDMS Stamps: The PDMS stamps with surface patterns were dipped into a silica particles/ethanol suspension

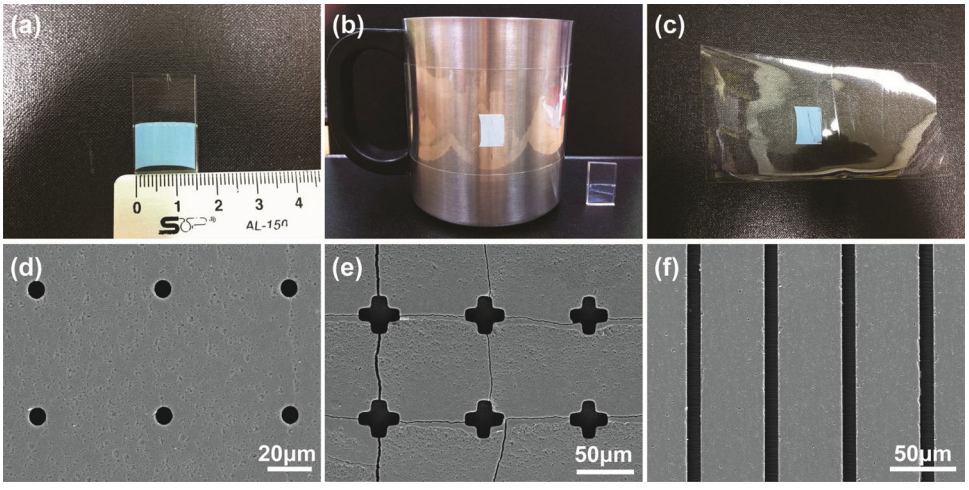

Figure 7. Photoimages of a) crack-free colloidal assembly layer on PDMS (1.5 cm × 1.5 cm), b) transferred colloidal assembly layer on a double-sided tape placed on curved surface, and c) detached double-sided tape. d–e) SEM images of colloidal assembly layers transferred to a curved surface using molds shown in Figure 2a–c, respectively.

(10 wt%). Then the PDMS stamps were withdrawn from the suspension at a rate of 1.1 $\mu m \cdot s^{-1}$ using a syringe pump (KDS 100, KD Scientific). Silica particles aligned from the side-wall of the surface. After drying in air, the colloidal assembly on the PDMS exhibited colors corresponding to the size of particles used.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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