Micropatterns of colloidal assembly on chemically patterned surface

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Abstract

Micropatterns of colloidal assembly were fabricated by the wetting/dewetting of suspensions on chemically patterned polydimethylsiloxane (PDMS). With the aid of plasma oxidation using screen masks, we fabricated the hydrophilic/hydrophobic patterns on the PDMS surface and dropped the suspensions of colloidal particles (210 or 410 nm diameter particles on such patterned substrate). In the evaporation process, the colloidal suspensions were split and drawn from the hydrophobic domains to the hydrophilic domains via the wetting/dewetting process, and wetted only the hydrophilic domains to form an ordered colloidal assembly. In our experimental, the aqueous suspension with ethanol offered better results of the microarrays of colloidal assembly with ordered microstructures because of the low surface tension and fast evaporation rate of ethanol. The proposed method was applied to fabricate the micropatterns of colloidal assembly with various size of colloidal particles and patterned domains.

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1. Introduction

Ordered arrays of colloidal sphere particles have generated significant interest because of their potential application as template from porous materials (that can act as catalysts in chemical and biological process), mask for nonlithographic patterning, sensor arrays, and photonic crystal devices [1–3]. For the practical applications, it is of great interest to selectively position the colloidal particles on surface to obtain superstructures with specific geometries. Various approaches have been reported to control the selective deposition of colloidal particles onto patterned surfaces; electrostatic forces [4,5], spatial confinement with topographical structures of surface [6–8], and wettability differences [9–11]. The methods using electrostatic forces introduced surfaces with positive/negative or charged/neutral monolayer patterns onto which charged colloidal particles are selectively attached. High selectivity of the colloidal particles is shown with this approach, but only disordered colloidal layers are generated. The methods with spatial confinement produced ordered colloidal layers with good control. Recently, several methods based on micromolding and template-directed approaches [12–14] have been reported to create the architecture of colloidal crystals, and different opal structures were obtained. In these processes, well defined microstructures of colloidal crystals could be fabricated; however, they require a sequence of complex manufacturing processes to fabricate the surface structures. Also, the methods using the wettability of colloidal suspension onto the substrate surface created the chemically patterned surface using microcontact printing and lithographic techniques, and the colloidal particles are assembled via the absorption affinity to the hydrophilic surface. These methods were also used to inset vacancy defects in colloidal crystals.

Here, we report on an alternative technique for the micropatterns of self-assembly of polystyrene (PS) colloidal particles on the patterned polydimethylsiloxane (PDMS) substrate via selective plasma oxidation. In the proposed method, we place the masks onto the surface of PDMS substrate to prepare chemically patterned surface. This simple method is based on the selective wetting of a colloidal suspension on the hydrophilic regions of patterned surface. Once the aqueous suspension of colloidal particles was deposited on the chemically patterned surface of PDMS, the suspension wetted only the hydrophilic domains by the wetting/dewetting process, and the colloidal crystals settled.
down through the evaporation of aqueous suspensions. Compared to other techniques, this method could offer the simple method to fabricate the patterned PDMS surface in a one-step process to control the wettability of surface. Moreover, the size and geometry of the corresponding colloidal particle assembly can be easily varied with ranging from a few micrometers up to several millimeters by using commercially available transmission electron microscopy grids (TEM grids) as masks. Thus, this method involves no investment in lithographic equipment and can be rapidly applied to pattern surface.

2. Experiments

PS submicron-sized colloidal particles were synthesized by emulsifier-free emulsion polymerization. Deionized water (450 g) was poured into a reactor and the corresponding water was kept at a temperature of 80 °C and was stirred at 350 rpm. Sodium styrene sulfonate (0.3 g) as emulsifier and sodium hydrogen carbonate (0.25 g) as buffer were added to the corresponding water. After 10 min, styrene monomer (50 g) was inserted in the corresponding solution. After 1 h, potassium persulfate (0.25 g) was introduced as initiator into the corresponding solution. Finally, polymerization was performed under nitrogen atmosphere for 18 h. The effective diameter of the prepared PS colloidal particles measured by Zeta Plus (Brookhaven Ins. Corp.) is 210 and 440 nm, and polydispersity of those is 0.005. PS colloidal particles measured by Zeta Plus (Brookhaven Ins. Corp.) is 210 and 440 nm, and polydispersity of those is 0.005. PS colloidal particles were suspended in deionized water with various volume ratio, and it was sonicated for 5 min before use.

Flat PDMS substrates were formed by curing Sylgard 184 (Dow Corning) on planar silicon wafer for 80 min at 70 °C, and PDMS substrates were cleaned with ethanol using sonication for 5 min. To pattern the selective oxidation of PDMS surfaces, different pattern and mesh size TEM-grids (Gilder Grids) was used as masks to cover the surface of PDMS. The grids were placed, and they were pressed and firmly adhered on the PDMS surface using the slide glass. Then, the masked PDMS substrate was placed for 3 min into a plasma cleaner (Plasmatic System Inc.). After plasma oxidation and removal of grids, the PDMS surface is not noticeably deformed. A small droplet of PS colloidal suspension was put onto the patterned PDMS surface, and the evaporation of the colloidal suspensions was performed at 25 °C with 20% relative humidity. The schematic of micropatterning PS colloidal particles is shown in Fig. 1.

The surfaces were imaged with scanning electron microscopy (SEM, JEOL). Thin gold layer with a thickness of 5 nm was deposited on the samples. The evaporation of suspension was observed with optical microscopy (OM, Kodak).

3. Results and discussions

In this work, we laterally control the surface chemistry of PDMS by partially covering a hydrophobic PDMS substrate with suitable masks. The surface properties of PDMS have a strong hydrophobic nature (∼SiCH₃ terminated surface) and a low interfacial free energy (ca. 21.6 × 10⁻³ J m⁻²); however, under appropriate plasma oxidation conditions, the surface of PDMS substrate is partitioned into the hydrophilic SO₃⁻ surface as shown in Fig. 1. The hydrophobic regions are those parts of the substrate that were covered by the mask during plasma oxidation, while the hydrophilic regions correspond to the location of the holes of the mask. The region that is fully shadowed by the mask reject the wetting of PS colloidal suspensions, and the region that is fully oxidized allows the formation of colloidal assembly. Contact angle measurements provide a direct evidence of the PDMS surface chemistry and formation of the colloidal assembly; the contact angle of the surface treated with plasma oxidation was 14° with a water-based suspension, whereas that of covered regions was 72°.

When a drop of colloidal suspension was placed on the patterned PDMS substrate, it first formed a hemisphere shape wetting the only patterned PDMS surface as shown in Fig. 2a, since the colloidal suspension faced with the outer hydrophobic region. However, after the time of evaporation, as the meniscus of suspension moved inward the patterned area, the contact angle of the drop of suspension decreases apparently. We observed this wetting/dewetting process of colloidal suspension on the patterned area using optical microscope (OM), as seen in Fig. 2b (where the dark area is the colloidal suspension). Once the meniscus of suspension met the patterned regions, it split at the interface of the hydrophilic/hydrophobic area, and receded from the hydrophobic regions into the hydrophilic regions. It was clearly observed that the suspension was placed only on the hydrophilic square domains as the meniscus of suspension moved inward during the evaporation. After the suspensions wetted the hydrophilic regions, PS colloidal particles then settled down and formed self-assembly of colloidal particles on the hydrophilic regions through the evaporation of water in suspensions.

Fig. 3 shows the micropatterns of PS particles assembly using the proposed technique on the PDMS surface patterned by...
plasma oxidation with a screen mask of 20 μm squares. Fig. 3a is the scanning electron microscopy (SEM) image showing that 0.5 vol.% aqueous suspensions of 410 nm PS spheres are selectively deposited to form the colloidal assembly on the 20 μm hydrophilic squares nearly free of particles on the hydrophobic regions covered by the masks. However, as the magnified image of PS colloidal assembly in Fig. 3b, it is observed that an incompletely ordered layer formed on each hydrophilic domain, and that the colloidal particles were not deposited evenly over the patterned domain. Moreover, many particles were deposited around the bulk suspension droplet and formed thick colloidal layers ring like ‘coffee stains’ (Fig. 4). These thick ring layers are normally found when a suspension droplet simply evaporates due to the contact line pinning [16]. However, when the aqueous suspension with 10 vol.% of ethanol was dropped on the patterned PDMS surface, micropatterns of the PS colloidal assembly were produced with good quality over the patterned squares compared with no ethanol used, as shown in Fig. 3c and d. Furthermore, the particles were uniformly deposited over the square patterns with ordered structures over a large patterned area. Because the suspensions added ethanol had a lower surface tension than that of pure water-based suspen-
Fig. 3. Micropatterns of colloidal assembly from (a) the water-based suspension of 410 nm PS particles, and (b) its magnification, from (c) the suspension added 10 vol.% ethanol of the same particles, and (d) its magnification.

Fig. 4. SEM image of the aggregation of colloidal crystals around TEM grid patterns after the evaporation of pure water-based colloidal suspension.

sion, the pinning phenomenon of suspension meniscus was not considerably occurred rather than the pure water-based suspension during the evaporation of suspension [17]. Thus, the wetting/dewetting process was well realized at the interface of the hydrophobic/hydrophilic patterns, which was crucial to fabricate the micropatterns of colloidal assembly. Moreover, the higher vapor pressure of ethanol caused a faster evaporation rate, and higher dispersibility of the colloidal particles. Higher vapor pressure of ethanol added suspension caused a convective flow in the suspension, and the higher dispersibility of particles, which is also an important factor in the formation of an ordered structure of colloidal assembly. Therefore, colloidal particles were uniformly deposited and formed an ordered structure on the patterned hydrophilic domain using the ethanol added suspension. However, the colloidal suspension with the excess amount of ethanol over 30 vol.% created disordered deposition without micropatterns, since the rapid evaporation rate of ethanol and the good wettability with a bare PDMS hindered the wetting/dewetting process at the patterned surface.

Other experiments were performed with the different size of colloidal particles and patterned domains. As shown in Fig. 5a and b, the suspension of 410 nm colloidal particles (1.0 vol.%) with 10 vol.% of ethanol was dropped on 50 μm line type and 50 μm hexagonally patterned domains, respectively. PS colloidal assemblies were formed on the patterned line with three-dimensional ordered microstructures. Fig. 5c shows the results of the suspension of 220 nm PS particles (1.0 vol.%) on 10 μm squares pattern. Likewise with above results, colloidal particles were nicely deposited with three-dimensional microstructure, and micropatterns of PS colloidal assembly were fabricated over a large area. These results show that the various sizes of the colloidal particle and patterned domains were applied for the creation of the microrrays of colloidal crystals through the wetting/dewetting process of suspensions using the proposed method.
4. Conclusions

We have proposed a simple and robust self-assembly process to create micropatterns of ordered PS colloidal particles on the patterned PDMS surface through the wetting/dewetting process of colloidal suspension. We prepared the hydrophobic/hydrophilic surface patterns on the PDMS substrate in one-step process using plasma oxidation with masks, which is a simple and efficient method, and a versatile route for tailoring the geometry of particles deposition sites to control the wettability. In our experiments, when we used the ethanol added suspensions rather than using a pure water-based suspension, the results showed that the colloidal particles with various size are deposited and form the micropatterns of well-ordered colloidal assembly on the patterned hydrophilic domains over a large area. Since the materials used for patterning are cheap and commercially available, and the fabrication process is reliable, this approach carries potential for various applications toward photonic devices.

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References