Arrays of Binary and Ternary Particles and Their Replica Pores on Patterned Microchannels

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The fabrication of particle aggregates with a two- or three-dimensional ordered arrangement has attracted great interest because of their potential applications to photonic crystals,[1] optoelectronic devices,[2] biochip and sensors,[3] nanosphere lithography,[4] colloidal stamps,[5] and microlenses for projection photolithography.[6] For the practical application to optoelectronic devices, it is important to fabricate particle arrays onto a substrate with specific patterns.[2] Recently, many studies have been reported on the creation of patterned particle arrays with ordered structure onto well-defined confined geometry[7] or chemically modified surface.[8] Several research studies[9] have tried to fabricate patterned particle arrays with binary particles for photonic band gap materials[1] and electronic and optical devices.[2]

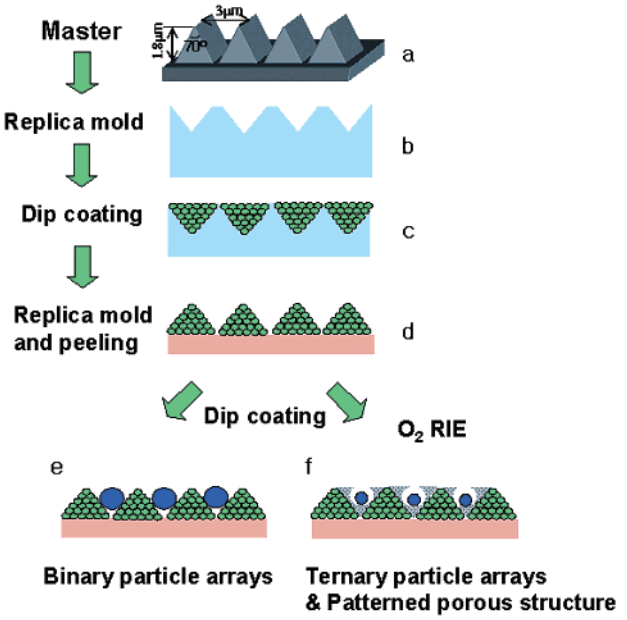

Figure 1. Schematic illustration for the fabrication of patterned particle arrays (a) V-shaped grooves. (b) PDMS replica mold. (c) Self-assembly of spherical colloids in V-shaped grooves. (d) V-shaped arrays of colloidal particles transferred onto a PU polymer film. (e) Binary particle arrays. (f) Ternary particle arrays and patterned pore structure by O_2 RIE.

Although several methods have been suggested for binary particle arrays, it is still challenging to fabricate ternary particle arrays, which is applicable, for instance, to the display devices composed of red, green, and blue phosphors.

In this communication, we report the novel method of fabrication of patterned binary and ternary particle arrays and their inverted pore structures. Specifically, we assembled ternary particle arrays onto V-shaped microchannels[10] that were fabricated by soft lithography[11] and patterned pore structures using the particle arrays as templates. The experimental scheme is illustrated in Figure 1. The first step was to fabricate a PDMS (poly(dimethylsiloxane)) mold by replica molding with a V-shaped diffraction groove (TGG01, Micro-Macsh) (Figure 1a). The angle between the edges of the V-shaped groove was 70°, and the pitch and height were 3.0 and 1.8 μm, respectively. A PDMS prepolymer (Sylgard 184 A:B = 10:1, Dow Corning) was mixed, degassed for 1−2 min, and subsequently cured for 2 h

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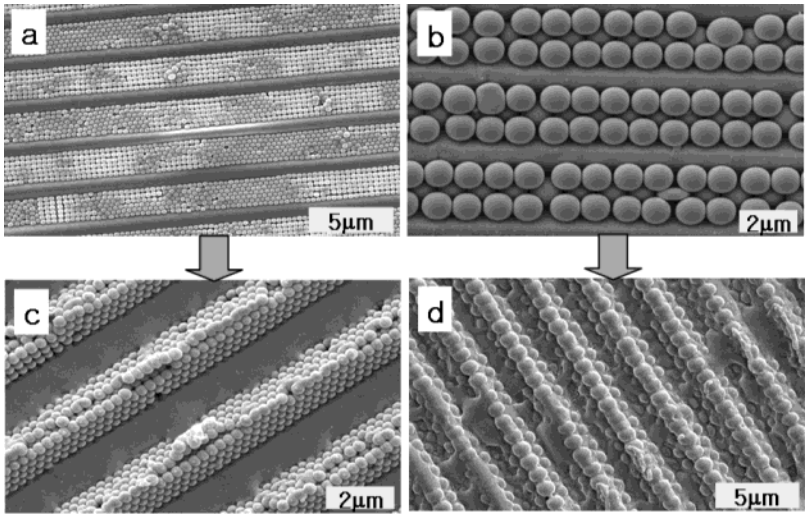

Figure 2. Particle arrays of (a) silica (320 nm) and (b) PS (1.01 μm) in V-shaped PDMS. (c, d) Their V-shaped arrays of colloidal particles transferred onto the PU films.

at 60 °C for the elastomeric stamp (Figure 1b). Monodisperse silica spheres were synthesized through sol−gel chemistry[12] and their size was either 320 or 600 nm in diameter. For organic particles, polystyrene (PS) beads of 1.01 μm in diameter were purchased from Magsphere. The particles were dispersed in water and the concentrations of silica and PS suspensions were 0.02 and 0.5 wt %, respectively. The silica and PS suspensions were dip-coated with a speed of 0.2 μm/s onto the V-shaped PDMS mold. When the monodisperse colloidal suspension was coated onto a patterned relief structure, the spherical beads were driven into the V-shaped grooves by capillary forces and close-packed inside the grooves (Figure 1c). Because of the confined geometry of the V-shaped grooves, the spheres self-organized within the grooves to assemble ordered colloidal crystal parallel lines. In parts (a) and (b) of Figure 2, SEM images of the colloidal silica and PS bead assemblies are reproduced, respectively. The colloidal crystal structure in the V-groove is determined by the groove geometry (angle, pitch, and height) and the diameter of the spherical colloids.[7a] As noted from Figure 2a for small silica spheres relative to the grooves, the defects are mainly grain boundaries due to stacking default and few point defects of vacancies. In this case, the grain boundaries are a few tens of micrometers and the point defects are less than 1%. Meanwhile, for larger PS spheres only vacancies are present with a fraction less than 1% as shown in Figure 2b. Also noted from Figure 2a,b is that colloidal crystals with the (100) plane oriented toward the facing surfaces were fabricated by using V-shape grooves.

Then, self-assembled V-shaped arrays of the microspheres were fabricated in the polyurethane (PU) matrix by replica molding for which NOA 61 (Norland) was used as a prepolymer of PU (Figure 1d). The resulting silica and PS bead arrays were shown in the SEM images of parts (c) and (d), respectively, of Figure 2. The slightly nonuniform PU surface in Figure 2d was due to the infiltration of PU prepolymer at the interstices between the large PS beads. Binary particle arrays were successfully fabricated by dip-coating colloidal beads of different sizes onto these V-shaped arrays of microspheres (Figure 1e) and the SEM images of the resulting binary arrays were shown in Figure 3a−c.

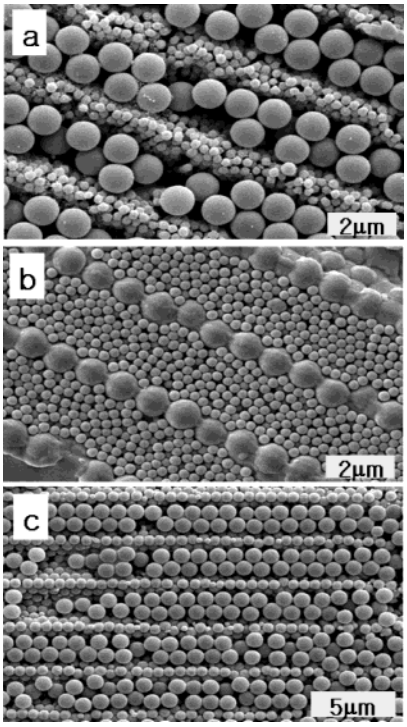

Figure 3. Binary particle arrays: (a) PS (1.01 μm) bead arrays between the V-shaped arrays of silica beads (320 nm). (b) Silica (320 nm) bead arrays between the V-shaped arrays of PS beads (1.01 μm). (c) PS (1.01 μm) bead arrays between the V-shaped arrays of silica beads (600 nm).

For ternary particle arrays, large (PS beads of 1.01 μm) and small particles (silica beads of 50 nm, Magsphere) were mixed and dip-coated onto the V-shaped arrays (Figure 1f). In the dip-coating of bimodal dispersion, the structure of the coated colloidal crystal depends on the size ratio of the binary spheres and their relative volume fraction in the dispersion.[13] From the ternary particle arrays, novel patterned pore structures were formed after removal of the PS beads by O_2 plasma

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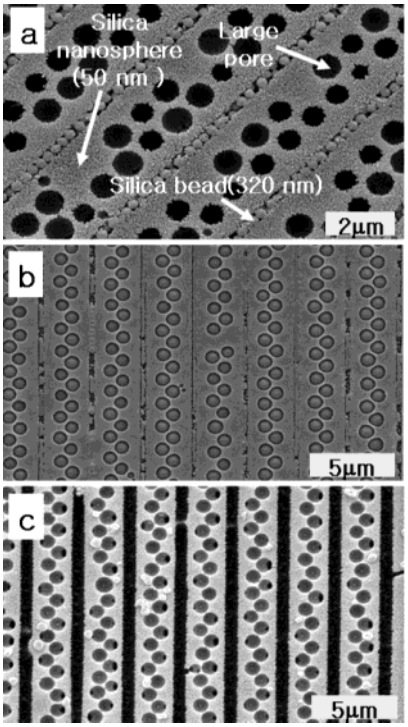

Figure 4. Ternary particle arrays and the replica pore structure after removal of PS beads by O_2 RIE: (a) Patterned pore structure in the V-shaped arrays of silica beads (320 nm) after O_2 RIE. Large pores were left behind in the matrix of silica nanospheres (50 nm) after PS beads (1.01 μm) were removed by RIE. (b) Intermediate structure after partial removal of the PS beads by O_2 RIE. (c) Patterned pore structure assembled onto V-shaped PU grooves instead of the V-shaped arrays of the silica beads.

etching (RIE). After a short exposure to O_2 plasma, the size of PS particles was reduced but still remained in the silica (50 nm) matrix as illustrated in Figure 1f. However, a sufficient O_2 RIE of the PS beads at 60 mTorr under a power density of 80 W for 10 min left behind large pores in the silica matrix that was formed with nanospheres of silica (50 nm) between the V-shaped arrays of silica beads (320 nm). The result is shown in Figure 4a. The pore density and size can be controlled by changing the size of PS beads. As noted from Figure 4b, the PS particles still remained in the silica (50 nm) matrix after an insufficient O_2 RIE of about 3 min. The SEM image of Figure 4c shows a patterned pore structure after removal of the micrometer-sized PS beads from the silica−PS composite fabricated within the V-shaped PU grooves instead of the V-shaped arrays of silica beads (320 nm). It can be expected that that these pore structures can be used as templates for assembling colloidal particle clusters. For instance, if small colloidal particles are filled into the pores by dip-coating, hemispherical colloidal aggregates are assembled in the pores.

In conclusion, we have fabricated various V-shaped arrays of spherical beads with different sizes by using a V-shaped PDMS mold as a template. Also, patterned binary, ternary particle arrays, and their replica pore structures could be fabricated onto these V-shaped arrays of colloidal particles by using replica molding and dip-coating. These structures are of potential significance in the display devices, 2D photonic crystals, and ordered open-pore structures can be used as templates for nonspherical aggregates of colloidal particles.

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Supporting Information Available: SEM images of (a) V-shaped PDMS grooves replicated from the silicon master and (b) V-shaped PU grooves replicated from the PDMS grooves of (a). This material is available free of charge via the Internet at http://pubs.acs.org.

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