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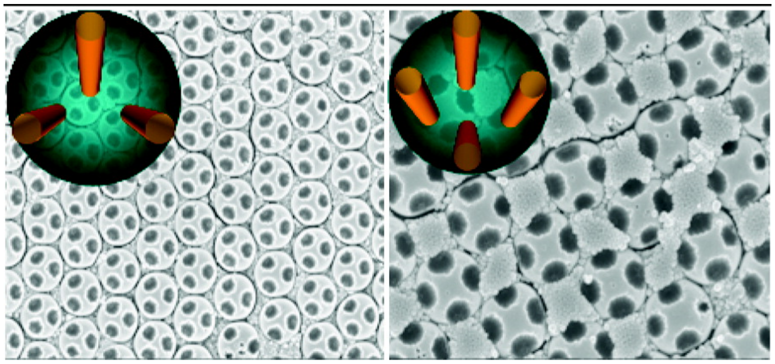

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Particle Arrays with Patterned Pores by Nanomachining with Colloidal Masks

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Monodisperse colloidal particles have attracted great attention because of their potential applications in biosensors,[1] photonic crystals,[2] colloidal lithography,[3] porous membranes,[4] nanostamp for soft lithography,[5] microlenses,[6] and seed particles for the core−shell and hollow spheres.[7] These monodisperse colloidal particles can be self-assembled, and the resulting self-assemblies have been used as nanostructured templates for the new functional materials.[8] Self-assembled nanofabrication processes with colloidal particles have advantages in that they are inexpensive, inherently parallel, and high-throughput processes.[3]

Meanwhile, reactive ion (plasma) etching (RIE) has been a useful technique for the control of surface morphology and surface chemistry.[9] RIE has been used to modify the shape and size of arrayed colloidal particles.[10] In particular, we have demonstrated that novel patterned arrays of nonspherical particles could be fabricated by anisotropic RIE.[10a] However, it is still challenging to fabricate particles with nanoscopic surface morphologies.

In this communication, we report a new nanomachining strategy for the fabrication of arrayed colloidal particles well-ordered nanometric holes of three or four fold symmetry by anisotropic RIE of self-organized layers of colloidal spheres. This is the first report on the fabrication of monodisperse particle arrays with regular pores by using a colloidal matrix with windows as lithographic mask.

A scheme of our nanomachining strategy by using a colloidal mask is shown in Figure 1. A colloidal double layer of polystyrene (PS) spheres with silica matrix is first prepared by dip-coating (Figure 1a). Then, the top layer of PS spheres is removed by O_2 RIE. By doing this, mesoporous silica matrix with windows open to the bottom layer of PS spheres can be formed (Figure 1c). This silica matrix with patterned windows will then be used as a colloidal mask for the subsequent RIE process (Figure 1d,e). As a result, the PS spheres of the bottom layer can be sculptured into arrays of particles with patterned pores as shown in Figure 1e.

Experimental details of the formation of a colloidal double layer can be found in our recent report.[10a] In this work, colloidal PS spheres of 1.01 μm and silica nanoparticles of 50 nm were mixed in aqueous medium and dip-coated on a silicon substrate at a controlled speed. The concentrations of PS and silica nanoparticles were 1 wt % and 0.13 wt %, respectively. Then, O_2 RIE (60 sccm at 80 W) was performed directly onto the preformed well-ordered colloidal arrays. A tilted SEM image in Figure 1b shows the PS beads embedded in the silica matrix after O_2 RIE for 4 min. The inset in Figure 1b is a planar SEM image. During a further anisotropic RIE, the upper layer of PS spheres was completely etched out and the silica mask with windows was formed (Figure ld). Finally, array of the colloidal PS particles with patterned pores could be formed by O_2 RIE for 8 min, as shown in Figure 1e and the SEM images in Figure 2.

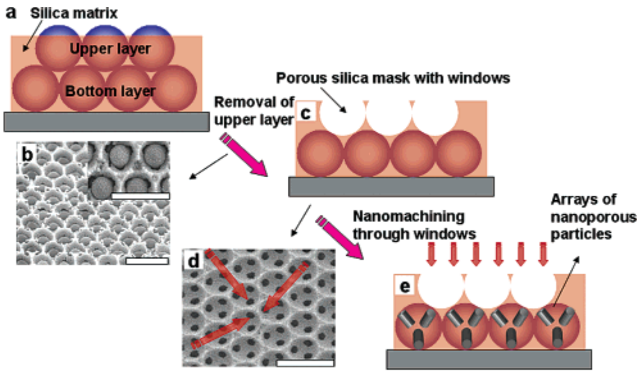

Figure 1. Schematic of nanomachining for the fabrication of an array of colloidal particles with patterned pores by using colloidal masks. Scale bar is 2 μm.

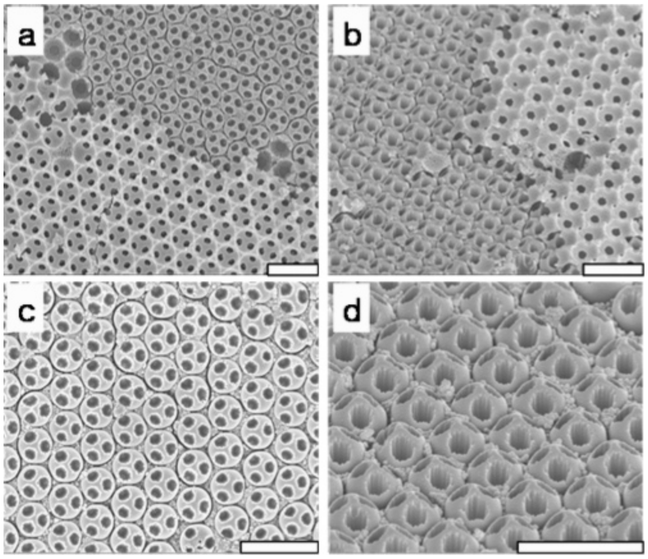

Figure 2. SEM images of PS particles with patterned pores of three fold symmetry, when the (111) plane was directed toward the etchant flow in RIE. (a) A planar SEM image of a silica colloidal mask and the bottom layer of arrayed PS spheres. (c) A planar SEM image of the bottom layer of arrayed PS spheres (1.01 μm in diameter) with three patterned pores. (b, d) Tilted SEM images of Figure 2, parts a and c, respectively, with a tilt angle at 52°. Scale bar is 2 μm.

The silica mask was removed by an adhesive tape to see more clearly the PS particles with regular pores of three fold symmetry because they were otherwise under the silica mask of the upper layer. The open-window structures of the upper layer shown in the lower part of the SEM image in Figure 2a and the right side of Figure 2b are the residual silica mask after detachment of the adhesive tape.

As noted from Figure 2, when the PS spheres were arranged into a face-centered cubic (fcc) packing with the (111) plane facing the substrate, three regular pores were produced on each sphere

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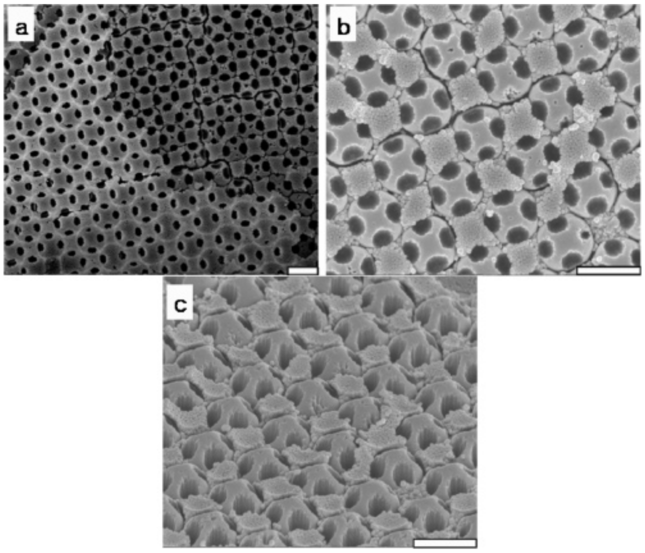

Figure 3. SEM images of PS particles with patterned pores of four fold symmetry when the (100) plane was parallel to the substrate and directed toward the etchant flow in RIE. (a, b) Planar SEM images with different magnifications for the bottom layer of arrayed PS spheres (1.01 μm in diameter) with four patterned bores. (c) A tilted SEM image of Figure 3b with a tilt angle at 52°. Scale bar is 1 μm.

after anisotropic RIE of the double layer of PS spheres embedded in the silica colloidal matrix. The depth of pores inside the PS particles can be controlled by RIE time. In principle, PS particles with anisotropic holes of different depths can be obtained by a tilted dry RIE process.[11] Also, the monodisperse PS particles with regular pores can be obtained when the silica matrix is etched by using HF solution.

Meanwhile, the square array on the (100) plane arrangement with large area ordering could be obtained by using a confined geometry such as microchannels, V-shaped grooves, and inverse pyramid patterns.[12] In this case, the (100) plane of fcc packing could be directed toward an etchant flow, and the array of the bottom layer of PS particles, each with nanopores of four fold symmetry, was fabricated by the same anisotropic O_2 RIE. The planar SEM images of Figure 3a,b show the square array of PS particles, each with regular four pores, and Figure 3c shows the tilted SEM image of Figure 3b.

It is noteworthy that the pore size can be tuned when a polymeric matrix such as polyurethane is used instead of silica nanospheres. In this case, the window size is decreased with the viscosity of the prepolymer solution that will infiltrate into the interstices between the microspheres and subsequently be photopolymerized. Experimentally, windows as small as about 50 nm have been fabricated by using 200−300-nm colloidal particles.[13]

Arrays of the PS particles with patterned regular pores produced from our nanomachining process can be applied for the fabrication of functional composite particles. A variety of organic and inorganic materials such as metals, DNA and proteins, semiconducting and ceramic materials, and other polymers and small chemicals for drug delivery can be incorporated via chemical and physical attachment, as depicted in Figure 4a. For an illustrative purpose, Pt-incorporated PS−Pt composite particles were fabricated by using ion sputtering at a speed of 100 nm/min, as shown in Figure 4b. To see the cross-sectional SEM image, Ga^+ focused ion beam milling (NOVA 200 in KAIST NanoFab Center) was performed.

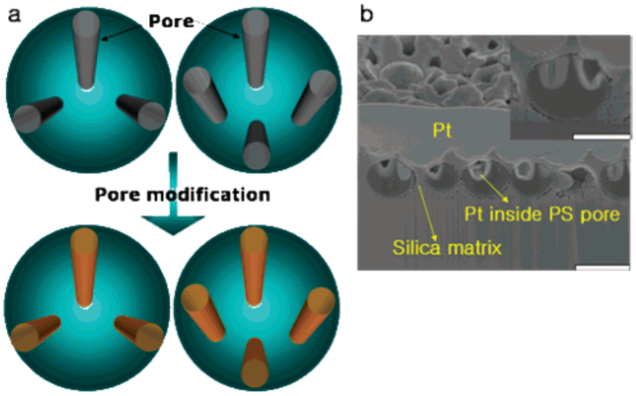

Figure 4. (a) Schematic of the fabrication of composite PS particles with regular pores. (b) A cross-sectional SEM image of Pt incorporated PS−Pt composite particles when the (111) plane of fcc packing of the colloidal layer was facing the sputtering flow. Scale bar is 1 μm.

In summary, we have developed a new strategy for the fabrication of arrayed colloidal particles with regular three or four pores by anisotropic RIE of self-organized layers of colloidal spheres. We demonstrated that a mesoporous silica matrix with regular open windows could be used as a lithographic mask and the resulting arrangement of pores on a particle was dependent on the orientation of the colloidal particle stacking. It is worth pointing out that our approach can be applied to other particle systems such as PMMA, silica or titania, and organic−inorganic core−shell particles.[7]

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