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Communication

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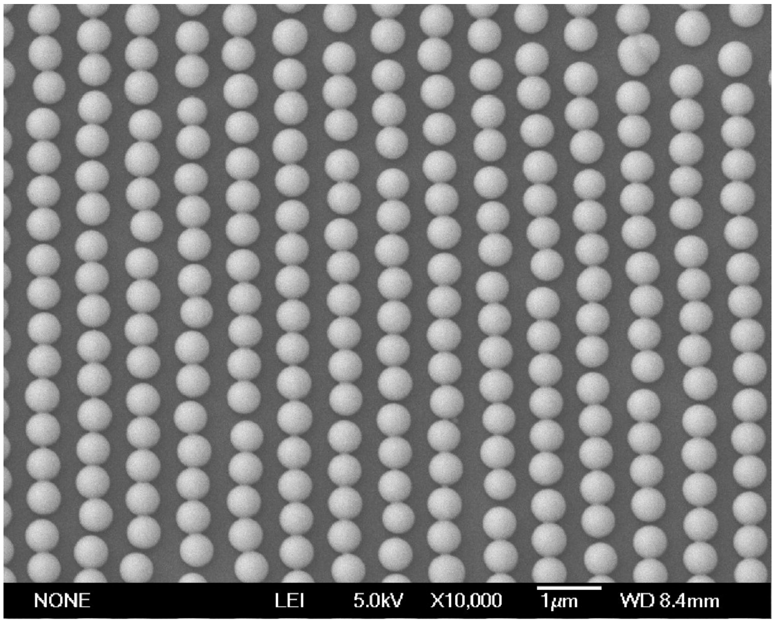

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Fabrication of Non-Close-Packed Arrays of Colloidal Spheres by Soft Lithography

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The ordered non-close-packed (ncp) arrays of nano- and micro-scaled colloidal spheres on solid substrates have attracted extensive interest due to their potential applications in fields, such as optics, photonics, sensing, and surface patterning.[1] Various manipulation techniques based on optical tweezers,[2] microrobot,[3] laser beams,[4] or AFM[5] have been developed to precisely place the spheres one by one at the desired position on a substrate, but the serial processing speed is a limitation to achieve acceptable throughputs. Although templating methods using structure-[6] or property-patterned surfaces[7] are effective in the simultaneous fabrication of a large area of 2D arrays with designable structures, the involved patterning techniques (such as advanced photolithography, focused ion beam lithography, and dip-pen nanolithography) for templating single submicrometer-scaled spheres are usually not accessible to common labs.

It is well-known that conventional self-assembly methods could be applied to produce 2D or 3D ordered hexagonal close-packed (hcp) arrays of colloidal spheres. By combining with etching techniques[8] or using charged spheres,[9] ncp arrays with controllable spacing between spheres could be created, but it is difficult to obtain new lattice structures other than hexagonal arrays. Recently, a 3D colloidal crystal has been encapsulated in the polymer matrix by infiltration and then postpolymerization of monomers. By using the solvent-swelling and mechanical deformation behaviors of the polymer matrixes, it is possible to adjust the lattice spacing and structures of colloidal crystal, which has rendered the colloidal crystals as materials for novel optical devices and sensors.[10] However, the ncp structures of sphere assembly cannot be reserved out of the polymer matrix. Recently, we have demonstrated a lift-up soft lithography to form a layer of an ordered array of hcp spheres on the protruding surface of the PDMS stamp.[11] In this communication, we report the utilization of the solvent-swelling[12] and mechanical deformation behaviors of PDMS to adjust the lattice structures of 2D arrays of spheres. More importantly, the as-prepared 2D ncp sphere array could be kept and transferred onto the surface of solid substrate by using a modified μCP transfer technique.[13]

Figure 1 outlines the procedure for the fabrication of 2D ncp arrays of spheres with tunable lattice structures. Silica spheres were assembled into hcp arrays on a silicon wafer by the evaporation of suspension.[14] By using the lift-up soft lithography, a single layer of hcp spheres was transferred to the surface of PDMS film, which was subsequently stretched or swollen with the solution of toluene in acetone (in this solution, only toluene, one of nonpolar solvents, was capable of swelling the PDMS film), to transform the hcp array into the ncp one. The obtained 2D ncp array on the deformed PDMS film was transferred to the surface of substrate that was spin-coated with a thin film (~200 nm) of poly(vinyl alcohol) (PVA) by using the modified μcp technique.

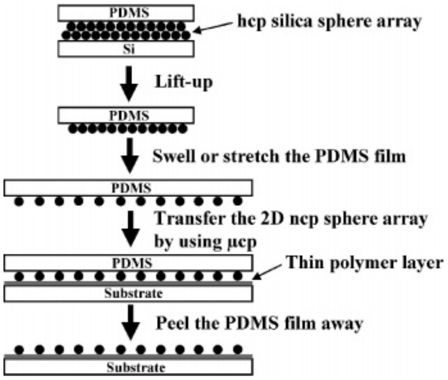

Figure 1. A schematic illustration of the procedure for the fabrication of 2D ncp array of spheres with tunable lattice structure.

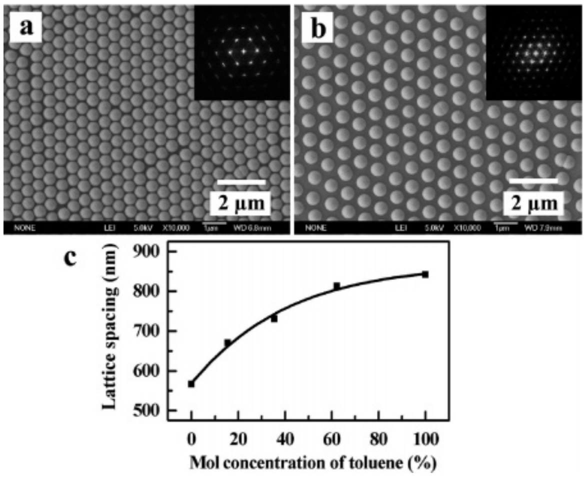

Figure 2. (a) SEM image of the 2D hcp array of 566 nm silica spheres assembled on a silicon wafer by the evaporation of suspension; (b) SEM image of the hexagonal ncp array on a PVA-coated substrate fabricated by swelling the PDMS film with pure toluene; (c) a plot showing the dependence of lattice spacing on the concentration of toluene in solution. Insets display the Fourier transforms of the corresponding images.

During the evaporation of solvent, the capillary force drove silica spheres to assemble into a close-packed array on substrate. Figure 2a shows a typical scanning electron microscopy (SEM) image of the ordered array of silica spheres. Every silica sphere with an average diameter (D) of 566 nm contacted with six other spheres and arrayed in the classic hexagonal lattice structure. Usually, intrinsic point and line defects appeared in the resulting structure, and typical defect-free domain sizes are in the 10−100 μm^2 range. Figure 2b displays an ordered 2D hexagonal ncp array of spheres

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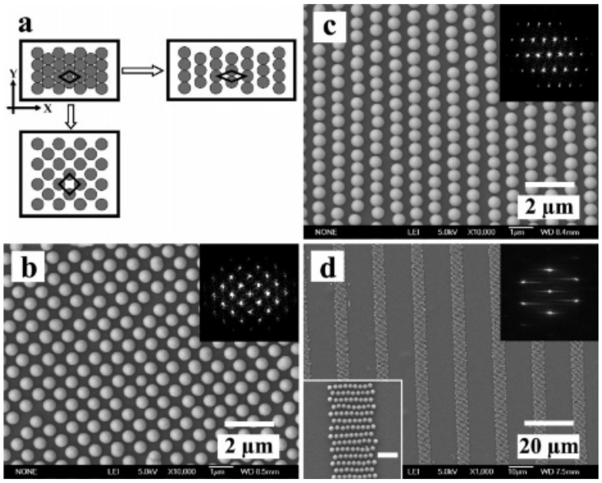

Figure 3. (a) A schematic illustration of the 2D ncp sphere arrays with new crystal lattices formed by stretching the PDMS film along one direction while maintaining the length in the orthogonal direction; SEM images of 2D ncp arrays on PVA-coated substrates with (b) square lattice, (c) parallel single sphere−wires; and (d) ordered array of parallel lines of the 2D ncp array. Insets in the right display the corresponding FFT images. A high magnified view of Figure 3d is shown in the left inset (the scale bar is 2 μm).

transferred to a polymer-coated substrate by using a PDMS film swelled with pure toluene. The lattice spacing of the obtained crystal structure was extended to about 1.49 D, while the highly ordered hexagonal arrangement was preserved (see inset in Figure 2b). Using the two-step transfer process, >95% spheres could be transferred onto the polymer-coated substrate in an ncp array from the original hcp one, and the ncp structure of the sphere array was mechanically stable because the spheres sank into the polymer film during the μcp process (see Figure S3).[13] Because the swelling magnitude of PDMS film strongly depends on the polarity of solution, we could flexibly control the lattice spacing of the resulting system by tuning the concentration of toluene. Figure 2c shows the toluene concentration dependence of the lattice spacing of the obtained hexagonal ncp structure. For the typical sample, the lattice spacing could be tuned from 1.00 to 1.49 D while maintaining the ordered hexagonal arrangement of spheres.

We also tried to design and create ncp arrays with new crystal lattices by stretching the sphere-coated PDMS elastomers. Figure 3a schematically illustrates two typical crystal lattices of the resulting ncp array of spheres. The square ncp structure with lattice spacing of about 1.16 D was formed by stretching the PDMS film along the *y*-axis by about 166% while maintaining the length of the *x*-axis (Figure 3b). As a result of the controllable homogeneous macroscopic elongation of PDMS film, the original hcp array was transformed into a square ncp lattice. Although the crystal lattice is greatly changed, the long-range ordering was essentially preserved in the resulting ncp array (see inset in Figure 3b). Figure 3c shows an SEM image of the quasi-one-dimensional parallel wires of silica spheres that were fabricated by stretching the PDMS film along *x*-axis by about 163% while maintaining the length of *y*-axis. These wires were assembled by spheres touching each other along *y*-axis and separated along *x*-axis by about 1.41 D. The change of lattice structure could also be evidenced by the FFT image (see inset in Figure 3c). Besides the plane PDMS film, the PDMS stamp with a micrometer-sized feature could be used to generate the patterned ncp array. Figure 3d shows an SEM image of parallel lines consisting of 2D ncp arrays on a polymer-coated substrate by using a PDMS stamp. These lines were approximately 5.0 μm wide and were separated by 11.0 μm. A high-magnification SEM image reveals the dual scale-ordered microstructures in the array of spheres (see the left inset in Figure 3d); the structural ordering on the micrometer scale was patterned by a PDMS stamp, whereas 2D-ordered ncp arrays at the submicrometer scale resulted from the transformation of a self-assembled hcp array with retention of the long-range ordering.

In conclusion, using the solvent-swelling and mechanical deformation behaviors of the PDMS elastomer, we have developed a simple soft lithography technique to fabricate ncp sphere arrays with designable lattice structures on solid substrates. This technique provides a simple and flexible route for creating microlens arrays[9,15] and adjustable templates for the systematic study of the epitaxial growth of 3D colloidal crystals[16] and for the fabrication of novel nanostructures, such as ordered arrays of nanoholes[17] or nanodots on various substrates.

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Supporting Information Available: Experimental procedures, SEM images of large-area sphere arrays, and typically optical diffraction pattern of hexagonal ncp structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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