

## Size Selective Assembly of Colloidal Particles on a Template by Directed Self-Assembly Technique

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We report a simple and effective approach to organize micron- and submicron-sized particles in a size selective manner. This approach utilizes the template assisted directed self-assembly technique. A topographically patterned photoresist surface is fabricated and used to create an ordered array of colloidal particles from their aqueous suspensions. Assembly of particles on this template is then achieved by using a conventional spin coating technique. Feasibility of this technique to form a large area of patterned particle assemblies has been investigated. To arrange the particles on the template, the physical confinement offered by the surface topography must overcome a joint effect of centrifugal force and the hydrophobic nature of the photoresist surface. This concept has been extended to the size selective sorting of colloidal particles. The capability of this technique for sorting and organizing colloidal particles of a particular diameter from a mixture of microspheres is demonstrated.

### Introduction

Ordered arrays of micron or submicron sized particles have attracted much scientific attention because of their potential application as new advanced materials for emerging fields of nanotechnology, photonic crystals, and miniaturized sensors.<sup>1–4</sup> Physical properties of particles in this size range are strongly dependent on their relative dimensions, and hence, particle sorting and positioning according to their size is a major requirement in many of the applications. Size selective positioning of small particles is always challenging, and special techniques are often needed to achieve this goal. Template assisted self-assembly of colloidal particles has proven to be a versatile approach for organizing small particles in an effective way with reasonable control.<sup>5–11</sup> In template assisted self-assembly process, a topographically patterned or chemically patterned surface is normally

used as a template to form particle structures that are either commensurate or incommensurate with the template geometry. However, templates of patterned topography offer more accurate positioning of particles compared with a chemically patterned surface. The availability of a template with feature size comparable with the particle size is a major requirement in this field. Templates of micrometer or nanometer feature size can be achieved using techniques of photolithography, electron beam lithography, soft lithography, chemical etching, and ion beam etching. Depending on the nature of the interaction between the particles themselves and the template surface, adequate driving forces such as gravitational sedimentation by solvent evaporation,<sup>12–14</sup> fluid flow,<sup>15–17</sup> electric field,<sup>18–21</sup> or centrifugal force due to spinning<sup>4,22,23</sup> are employed to facilitate the assembly process.

Template assisted colloidal assembly has two major advantages over the nontemplated assembly. First, colloidal crystals grown

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on templates are less defective and possess a long range order in their structure. Second, by using templates, new crystal structures can be engineered, which will otherwise be hard to achieve. More recently, Fan et al. have extended the application of templated assembly technique to the size selective positioning of particles.<sup>24</sup> This approach utilized a surface of patterned wettability for the size selective sorting and deposition of lyophilic colloidal particles.

In this work, we report an effective method for the size selective positioning of colloidal particles on a topographically pre-patterned photoresist surface. The template was fabricated using a direct laser writing technique. This approach utilizes centrifugal force due to spinning as the driving force to form a large area of patterned colloidal particle assemblies. Competition between the physical confinement effect of the surface topography and the centrifugal force, together with the hydrophobic nature of the photoresist surface, favor the assembly of particles of certain size range exclusively on the patterned channels. We demonstrate the capability of this technique in size selective assembly of colloidal spheres from an aqueous solution of a mixture of particles of different sizes.

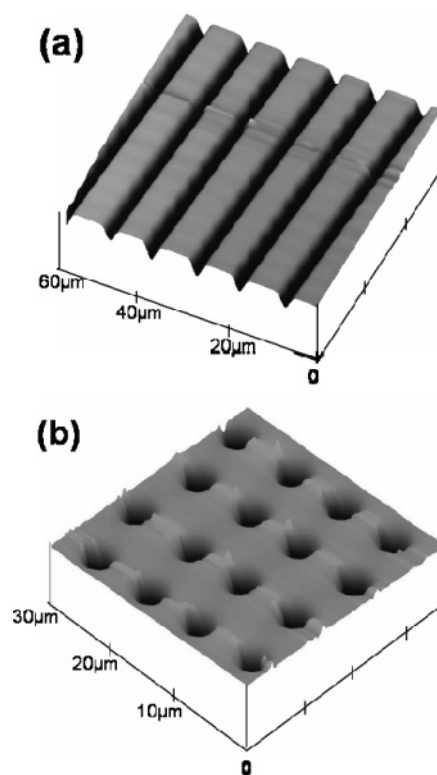
### Experimental Section

Monodispersed colloidal solutions of polystyrene spheres used in this study were purchased from Polysciences, Inc. and used without any further dilution. A thin film of SU8 photoresist on the glass substrate was formed by spin coating a pre-polymer solution at a speed of 1500 rpm. The film was subjected to prebaking at 80 °C for 10 min and then exposed to UV light for cross-linking. Further cross-linking was achieved by postbaking at a temperature of 250 °C for 30 min.

Micron sized features on the SU8 thin film were created by a direct laser writing system. The direct laser writing system primarily consists of a tightly focused laser beam. Light from a diode laser (wavelength: 532 nm) was guided into a Leica DMLM optical microscope using mirrors. The dichroic mirror inside the microscope reflects this laser light into a 100 $\times$  objective lens. The laser beam was then focused down to a spot size  $< 1 \mu\text{m}$ . A computer controlled movable stage replaced the original stage of the microscope, and the sample was put on it. The high temperature at the focus due to light absorption evaporates the SU8 photoresist readily. This results in the formation of cylindrical holes on the film. By moving the sample with respect to the fixed laser beam, micron sized parallel channels were created on the film. Particularly, the width and depth of the channels created can be controlled by varying the power of the laser beam. A CCD camera along with a TV was used for the visualization of the whole process (see the Supporting Information). Besides the channels, a wide variety of patterns can be created by this method. Details of this technique are described elsewhere.<sup>25</sup> In an earlier report, we demonstrated that this setup is useful in creating microstructures on aligned carbon nanotubes (CNT) grown by plasma enhanced chemical vapor deposition technique.<sup>26</sup> Characterizations of the patterned SU8 surfaces as well as microsphere arrangement on these patterns were carried out using a JEOL JSM-6400F field emission scanning electron microscope (FESEM) and a DI-NanoMan atomic force microscope (AFM). The substrate was coated with a very thin layer of platinum prior to the SEM analysis.

### Results and Discussion

Micron sized channels were first created on SU8 photoresist film by moving the sample stage of the laser writing system with a constant speed of 50  $\mu\text{m/s}$  with respect to the fixed laser beam.



**Figure 1.** AFM images of (a) channels and (b) cylindrical holes on SU8 photoresist created by the direct laser writing technique.

Figure 1a shows an AFM image of the channel formed on SU8 thin film using a laser power of 3.6 mW measured at the entrance to the sideport of the optical microscope. The Gaussian profile of the laser beam intensity at the focus favored the formation of V-shaped channels. Due to heat transfer, the channels were wider than the spot size at the focus. The average width and depth of these channels measured using AFM were around 1.5 and 0.36  $\mu\text{m}$ , respectively. Figure 1b shows an AFM image of an array of cylindrical holes on SU8, drilled by exposing the film to the focused laser beam for 5 s. The average diameter and depth of these cylindrical holes were 1.7 and 1.8  $\mu\text{m}$ , respectively.

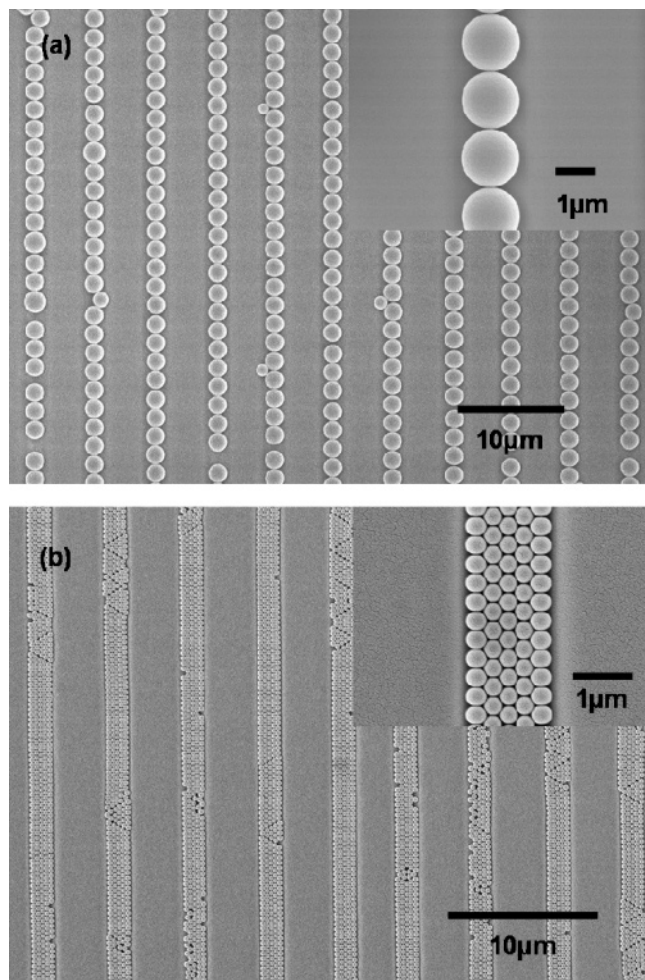
The substrate with patterned photoresist film was then put on the chuck of the spin coater and a drop of the monodispersed colloidal suspension of polystyrene beads in water was added onto it. The spinning parameters were set such that it takes about 1 min to reach the maximum speed, and the total spinning time was 3 min. After spin coating, the samples were dried at room temperature and then characterized. Figure 2a,b shows the SEM images of polystyrene spheres filled SU8 channels. It is clear that there are no spheres on the SU8 surfaces other than those in the channel. The hydrophobic nature of the SU8 and centrifugal force prevented the particles from resting on the SU8 surfaces. On the other hand, physical confinement provided by the channel effectively trapped the spheres and the lateral capillary force between the colloidal particles drove the spheres to form closely packed configurations in the channels during the drying process.

The assembly process depends on the spinning speed. A speed in the range of 700–900 rpm was found to be suitable for the selective arrangement of  $1.5 \pm 0.04 \mu\text{m}$  spheres on the channels (Figure 2a). A spinning speed less than 700 rpm could not completely remove colloidal particles from the photoresist surface, resulting in colloidal crystallization on the entire surface. On the other hand, a spinning speed greater than 900 rpm causes centripetal force to overcome the physical confinement of the template and that led to the escape of the microspheres from the

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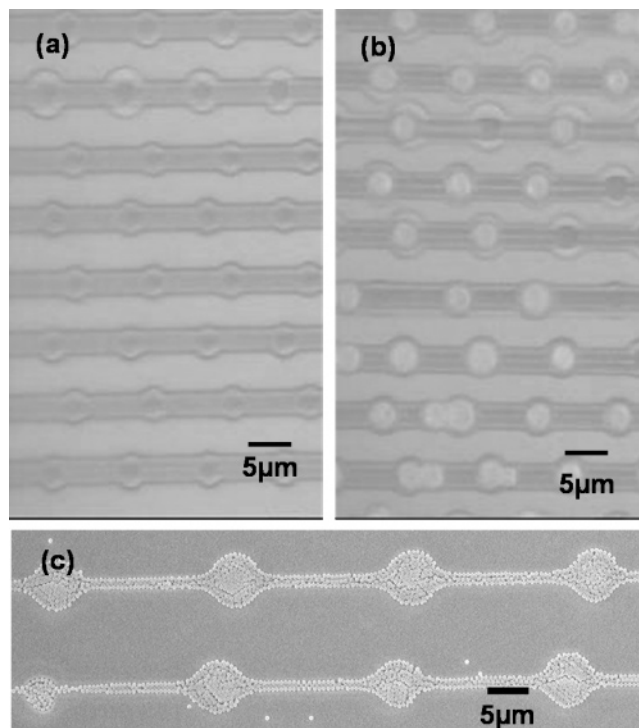
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**Figure 2.** SEM images showing large area of patterned polystyrene spheres on SU8 template. The channel was created by the direct laser writing technique with a laser power of 3.6 mW and the channel width was approximately 1.5  $\mu\text{m}$ . Diameters of the polystyrene spheres used for the assembly are 1.5  $\mu\text{m}$  (a) and 310 nm (b), respectively. Inset in each image shows magnified image of the channel.

channel. A spinning speed of 1000–1200 rpm allowed the polystyrene spheres of diameter  $0.310 \pm 0.014 \mu\text{m}$  (Figure 2b) to arrange into a hexagonal close packed structure on channels of the same dimensions. The structure of the microsphere assemblies depends on the channel width ( $w$ ) to sphere diameter ( $D$ ) ratio.<sup>16,17,27</sup> For example, a  $w/D$  value in the range 0.9–1.1 led the microspheres to assemble in the form of a linear chain of single spheres as shown in Figure 2a. Using direct laser writing technique, channels of different widths can be created by simply varying the laser power. With a wider channel, other interesting assemblies of microspheres were obtained. Examples of such microspheres assemblies are available in the the Supporting Information (see Figure 2 in the Supporting Information).

Different types of patterns can be readily created using the laser writing technique. With a different pattern, formation of colloidal assemblies with different configurations can be achieved. For example, cylindrical holes of different sizes can be created by using the laser writing technique by varying the laser power. A colloidal solution of polystyrene spheres was then spin coated in the same way as described earlier, to form colloidal aggregates of different sizes and configurations (see Figure 3a–d in the Supporting Information). The formation of aggregates of colloidal particles with various configurations is potentially useful as a



**Figure 3.** (a) Optical micrograph of the template with channels with periodic pockets. (b) Optical micrograph taken after spin coating colloidal solution from aqueous suspension of polystyrene microspheres (diameter 4.6  $\mu\text{m}$ ) on this template. The microspheres were found to arrange into the pockets along the channels. (c) SEM image showing the arrangement of smaller microspheres (diameter 0.45  $\mu\text{m}$ ) on the same type of template.

building block of three-dimensional colloidal crystal as well as other advanced materials. Likewise, by controlling the movements of the stage of the direct laser writing system various periodic structures can be created on the photoresist thin film. One of the important attributes of this technique is the feasibility of making extended structures of a wide variety of patterns formed by the microspheres (Figure 3e–h in the Supporting Information).

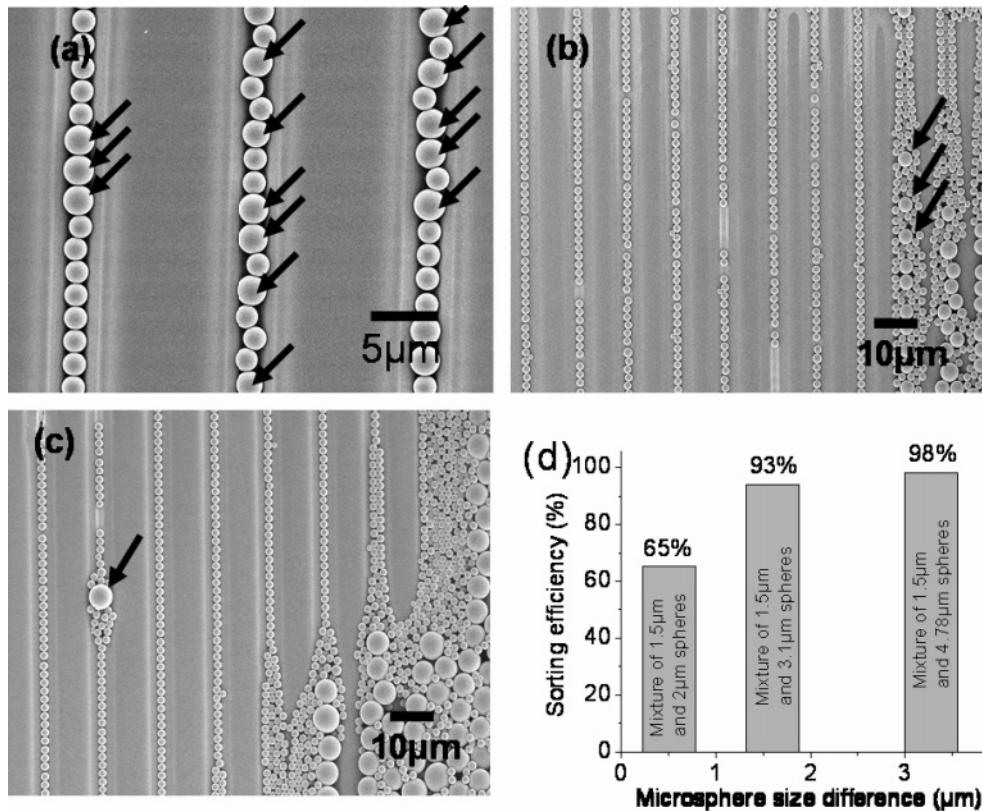
An assembly of microspheres can be used as a template for the further colloidal assembly of different sized particles to form binary colloidal structures. Previously reported methods used a self-assembled monolayer of colloidal arrangement as a template for the further assembly of different sized particles.<sup>28,29</sup> However, the structures formed by the self-assembly method are limited. By using a patterned substrate, more complicated and useful structures can be created. Colloidal particles of bigger size (diameter 4.6  $\mu\text{m}$  for example) were first assembled in parallel lines on laser created channels on SU8 photoresist thin film. After drying, a second colloidal solution containing particles of smaller diameter (say, 0.45  $\mu\text{m}$ ) was then spin coated on this microsphere template. By increasing the separation between the channels, a different binary colloidal arrangement can be obtained (see Figure 4 in the Supporting Information).

The feature size of the template is related to the maximum size of the microsphere that can be arranged on it for a particular spinning speed. For example, we created a template consisting of channels with periodic pockets using the direct laser writing technique (Figure 3a) and used it for the assembly of microspheres with better control. The average width of the channels is 3.6  $\mu\text{m}$ , and the average size of the pockets is 5  $\mu\text{m}$ . A monodispersed colloidal solution of polystyrene spheres of

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**Figure 4.** SEM images of polystyrene sphere patterned on identical SU8 template by spin coating a mixture of colloidal solution of diameters (a) 1.5 and 2  $\mu\text{m}$ . (b) 1.5 and 3.1  $\mu\text{m}$ , and (c) 1.5 and 4.78  $\mu\text{m}$ , respectively. Arrows show the positions of bigger spheres. The coating solution was prepared by mixing 1:1 volume ratio of monodispersed colloidal solutions of different diameters. The coating speed was set at 800 rpm in all three cases. (d) Sorting efficiency versus difference in size of the microspheres comprising the coating solution.

diameter 4.6  $\mu\text{m}$  was then spin coated on this patterned surface at a spinning speed of 600 rpm. The spheres were found to be deposited primarily in the pockets as shown in Figure 3b. Exclusively, there are no spheres in the channels. This is attributed to the fact that the physical confinement of the small channel was not high enough to trap the spheres of diameter 4.6  $\mu\text{m}$  at a spinning speed of 600 rpm, whereas the bigger pockets are well suited to trap and confine the bigger spheres. On the other hand, by using spheres of smaller size (0.45  $\mu\text{m}$ ), this template could be used to create periodically varying colloidal structures as shown in Figure 3c.

The dependence of particle arrangement on channel geometry as well as on the spinning speed offers a simple and yet efficient route for sorting and assembling microspheres of smaller diameter from a mixture of colloidal particles. To demonstrate this feasibility, we used colloidal solutions comprised of microspheres with different diameters as the starting solution and select a template geometry as well as a spinning speed favorable for the arrangement of one of the microspheres. In these studies, microspheres of diameter 1.5  $\mu\text{m}$  were chosen as the spheres to be separated from a mixture of microspheres. The ratio of the microchannel width to the microsphere diameter to be separated ( $w/D$ ) was selected in the range of 0.9–1.1, and a spinning speed of 800 rpm was used. As shown earlier, these conditions permit the microspheres to arrange in the form of a linear chain of single particles.

Three distinct coating solutions were utilized in order to investigate the sorting capability. The solutions were prepared by mixing monodispersed colloidal suspensions of polystyrene spheres of diameters (1) 1.5 and 2  $\mu\text{m}$ , (2) 1.5 and 3.1  $\mu\text{m}$ , and (3) 1.5 and 4.78  $\mu\text{m}$ , in a 1:1 volume ratio followed by sonication. Figure 4a shows a SEM image of the microsphere arrangement

on a laser patterned photoresist surface from colloidal solution with spheres of diameters 1.5 and 2  $\mu\text{m}$ . The channels were mostly occupied by the smaller microsphere (1.5  $\mu\text{m}$  in diameter) with only a few bigger ones (2  $\mu\text{m}$  in diameter, indicated by arrows in Figure 4a). Figure 4b shows the SEM image of microsphere arrangement after a coating solution containing spheres of diameters 1.5 and 3.1  $\mu\text{m}$  was used. This image was taken from the vicinity of a cluster region, to illustrate that the coating solution was a mixture of two different sized spheres. These results clearly demonstrate that the sorting capacity has improved for a mixture of spheres with large differences in size. A much better improvement in the sorting ability was observed when spheres of an even bigger size difference were used in the coating solution. Figure 4c shows the SEM image of the microsphere arrangement using the third solution which contains microspheres of diameters 1.5 and 4.78  $\mu\text{m}$ . The sorting efficiency was calculated by counting the number of bigger and smaller spheres in a given area of the patterned surface. As the size difference between the two spheres in the mixture is increased, the sorting efficiency improved as well (see Figure 4d).

The size selective arrangement of microspheres on the microchannels is due to the fact that the physical confinement offered by the channels to the bigger spheres was not sufficient to surmount the combined effect of centrifugal force due to spinning and the hydrophobic nature of the photoresist surface. On the other hand, the smaller spheres become trapped on channels as a result of the leading confinement effect compared with the other competing forces. Accordingly, by properly engineering the channel geometry as well as the spinning speed, it is possible to separate and arrange colloidal spheres of required diameter with a narrow size distribution. Following a similar approach, it will be worthwhile to extend this technique down to the

nanometer regime, provided the feature size of the template can be made comparable with the particle size.

### Conclusions

We have introduced a simple method to construct an array of colloidal particles using the template-assisted self-assembly technique. We demonstrated that centrifugal force is a viable driving force for the formation of large areas of colloidal sphere assemblies as well as particle sorting. The particle sorting method described here is applicable to a wide range of particles, and the only requirement is the availability of a template with a feature size comparable with the size of the particles to be separated. Additionally, the processing time is extremely short, in the range of a few minutes. We believe that this technique could be useful

in the fields of photonic crystals, micro addressable sensors, nano or microelectronics, and high-density data storage applications.

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**Supporting Information Available:** Schematics of the direct laser writing setup, dependence of the structure of the microsphere arrangements on channel width, colloidal assemblies in various extended patterns, and binary colloidal structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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