

Fabrication of a Two-Dimensional Periodic Non-Close-Packed Array of Polystyrene Particles

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We report a simple technique for the fabrication of a two-dimensional periodic non-close-packed array of nonspherical particles. The technique exploits the self-assembly of uniformly sized colloidal microspheres on the surface of a Si substrate followed by reactive ion etching (RIE) that converts the spheres into nonspherical particles. Single and double layers of packed colloidal polystyrene microspheres of uniform size (diameter 1.2 μm) were spin-coated onto cleaned Si substrates. The samples were then exposed to reactive ions in an RIE unit operating under a mixture of CF_4 and O_2 gases. Due to preferential etching in the direction normal to the surface of the substrate, the microspheres were reduced to a nonspherical form resembling a biconvex microlens. Moreover, the periodic nature of the previously packed layer was preserved during the etching process. As a result, we obtained two-dimensional periodic non-close-packed arrays of nonspherical particles. In this work, we report the systematic dependence of the dimensions of the polystyrene particles on the duration of the exposure to RIE. In addition, the resultant patterned Si substrates were further utilized as templates for directed assembly of unique arrangements of microspheres with different diameters.

Two-dimensional (2D) and three-dimensional (3D) close-packed arrays of uniformly sized microspheres have often been utilized in a variety of experiments and applications.^{1–3} When packed into a thin layer on a flat substrate, these microspheres self-assemble into extended areas of ordered periodic arrays of packed spherical configuration. They can be used as a mask to fabricate a periodic array of nanosized particles with a technique known as nanosphere lithography.^{4,5} When the shape of the particles becomes nonspherical, it becomes more challenging to create ordered packed arrays of such particles. The task becomes even more challenging if the goal is to fabricate a periodic and yet non-close-packed array of nonspherical particles. Efforts aimed at achieving a non-closed-packed array of spherical particles include templating techniques,^{6,7} binary colloidal growth,⁸ and colloidal configurations in aqueous suspensions.⁹ To create an ordered arrangement of nonspherical particles, Jiang et al.¹⁰ developed the lost-wax approach to fabricate a 3D periodic assembly of elliptical particles. Lu et al.¹¹ proposed using the mutual electrostatic interaction of nonspherical particles and external field to achieve positional and orientational order. Another alternative is to make use of a combination of techniques to fabricate a non-closed-packed array of nonspherical particles. For example, one can exploit the properties of microspheres that naturally pack into an ordered arrangement and subsequently transform the microspheres into particles with a unique shape while maintaining the ordered arrangement of the particles.^{12–14} Haginoya et al.¹² and Fujimura et al.¹³ made use of reactive ion etching (RIE) with oxygen (O_2) plasma to modify a self-assembled 2D array of polystyrene microspheres on a Si substrate into periodic nanoscale-rugged

structures. In a similar approach, Choi et al.¹⁴ employed the RIE technique with a gas mixture of tetrafluoromethane (CF_4 ; 40 sccm) and O_2 (60 sccm) to create 2D and 3D arrays of nonspherical rugged particles of various shapes. Recently, Fenollosa and Meseguer¹⁵ reported a technique for the creation of non-close-packed three-dimensional opals comprising silica microspheres interconnected by narrow tubular necks. The method is based on a combination of colloidal self-assembly, thermal sintering, and acid etching techniques.

In this work, following a route similar to that of Choi et al.,¹⁴ we made use of microsphere natural assembly on a Si substrate followed by RIE with a gas mixture of primarily CF_4 (29.7 sccm) and O_2 (17.3 sccm) to fabricate non-close-packed periodic arrays of nonspherical polystyrene particles. It should be noted that our approach made use of a smaller amount of O_2 during the RIE process instead of the pure O_2 gas or gas mixture with a high O_2 content used by other researchers.^{12–14} As a result, the surface morphology of the polystyrene particles remained relatively smooth as compared with the rugged particles as reported earlier.^{12–14} Due to the preferential etching in the direction normal to the surface of the substrate, the microspheres were reduced to a nonspherical form resembling a biconvex microlens. Moreover, the periodic nature of the previously packed layer was preserved during the etching process. As a result, we obtained 2D periodic non-close-packed arrays of nonspherical particles. In this work, we report the systematic dependence of the dimensions of the nonspherical polystyrene particles on the duration of the exposure to RIE. The nonspherical particles can be resuspended into solution, and the patterned Si substrates that were created during RIE were further utilized as templates for directed assembly of microspheres of various diameters.

A drop of the solution from a commercially purchased suspension of polystyrene spheres (Polyscience, Inc.) with a

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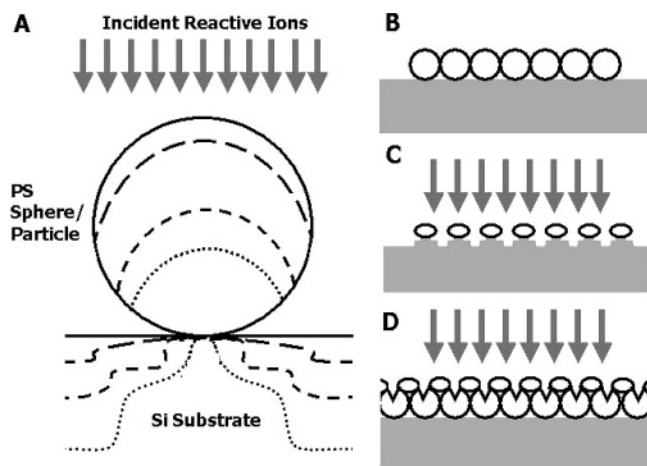


Figure 1. Schematic illustrating (A) the systematic etching of microspheres and Si substrate into nonspherical particles and Si microplatforms, respectively, (B) the side profile of Si substrate coated with a monolayer of packed uniformly sized microspheres before RIE, (C) the etched microspheres and substrate as a result of exposure to reactive ions, and (D) the profile of the first and second layers of the microspheres after etching.

diameter of $1.20 \pm 0.06 \mu\text{m}$ at a concentration of about 4% by volume was spin-coated onto the Si(100) wafer at a typical rotation rate of 950 rpm. The Si substrates with packed microspheres were then placed inside the chamber of a SAMCO RIE-10N reactive ion etching unit and pumped down to a base pressure of $\sim 7 \times 10^{-6}$ Torr. An rf glow discharge was used to generate the reactive ions. The samples were placed on an rf-driven capacitively coupled electrode. A gas mixture of CF_4 at 29.7 sccm and O_2 at 17.3 sccm was utilized during the etching. A small amount of O_2 in the reactive gases helped to encourage the formation of radicals and ions.¹⁶ On the other hand, such a small amount of O_2 was not found to be detrimental in maintaining the surface smoothness of the polystyrene particles. The forward rf power was 20 W, and the reflected power was 1–2 W. The duration of the etching was from 4 to 22 min.

The rf glow discharge created a gas-phase etching environment which consists of neutrals, electrons, photons, radicals, and positive and negative ions. The transport of these reactive species from the plasma to the sample occurred by diffusion. In addition, charged species from the glow region were accelerated toward the sample in the electric field created by the dc self-bias.¹⁶ A gas mixture of CF_4 and O_2 in plasma etching created the oxyfluoride ions, which are a highly reactive etching agent for a polymeric substance.¹⁷ The reactive species reacted with the polystyrene as well as the Si, forming volatile species that were readily pumped out of the vacuum system. In our work, we found that the reactive species that were directed normally to the substrate surface played a predominant role in the etching process. As a result, the microspheres and Si were preferentially etched perpendicular to the substrate. In this way, the isotropic microspheres were transformed into anisotropic particles. Figure 1 shows the schematics of preferential etching of the microspheres and Si substrate into biconvex microlenses and Si “microplatforms”, respectively, using directed reactive species.

After completion of the RIE, particle-coated Si substrates were imaged using a JEOL JSM-6400F field emission scanning electron microscope. To investigate the details of the etching process, each substrate was carefully cleaved into two pieces. In this way, the substrate can be mounted sideways to reveal its side profile under scanning electron microscopy (SEM) imaging. We observed that many particles in the periodic array

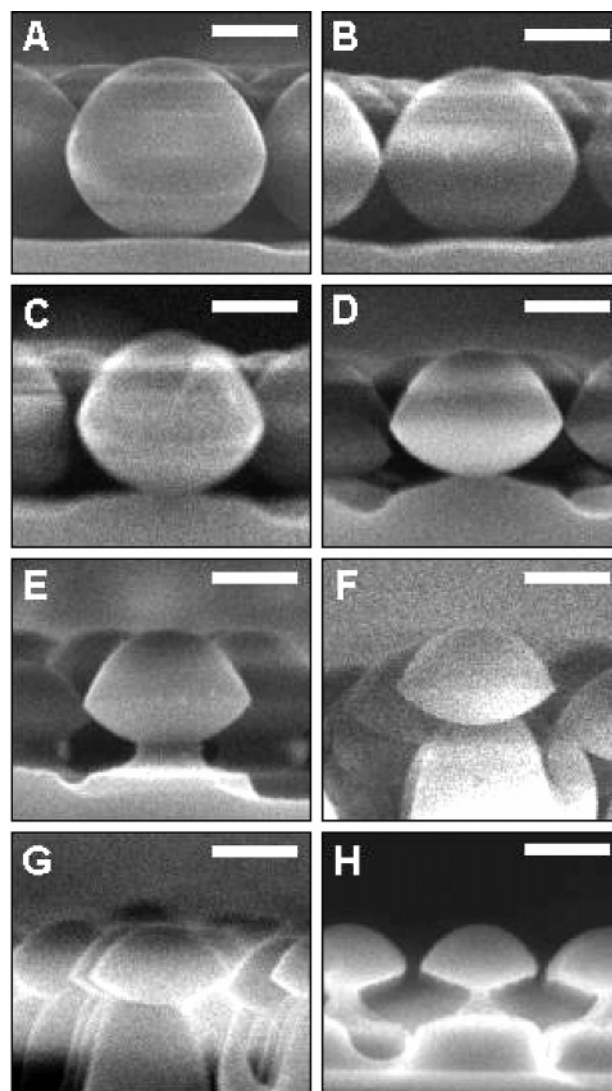


Figure 2. SEM images of the side view of the polystyrene particles created after (A) 4 min, (B) 6 min, (C) 8 min, (D) 12 min, (E) 14 min, (F) 16 min, (G) 18 min, and (H) 22 min of reactive ion etching. The diameter of the sphere prior to RIE is $1.2 \mu\text{m}$. Scale bars = 500 nm.

were not affected by the cleaving of the Si substrate and remained attached to the substrate. Figure 2 shows SEM images of the side views of the resultant polystyrene particles after different exposure durations to the reactive ions. The diameter of the polystyrene spheres prior to RIE is $1.20 \pm 0.06 \mu\text{m}$. The figures show the systematic anisotropic etching of an isotropic microsphere into a nonspherically shaped polystyrene particle resembling that of a biconvex microlens. We also observed that the bottom profiles of these polystyrene particles match each other independent of the RIE duration, indicating that the etching of the polystyrene spheres is predominantly from the top.

To quantify the etching due to the reactive ions, we denote the height of the particle along the direction perpendicular to the substrate surface as the axial diameter (D_A) and the width of the particle along the surface as the traverse diameter (D_T). We further defined two length scales, D_1 and D_2 , as indicated in Figure 3A to study the etch rate. D_1 and D_2 are the widths of the particle at distances of 156 and 313 nm, respectively, from the vertical center axis.

From the SEM images obtained, we determined the various dimensions of the polystyrene particles as depicted in Figure 3A. Figure 3B shows the measured axial diameter (circles) and traverse diameter (tilted squares) of the polystyrene particles

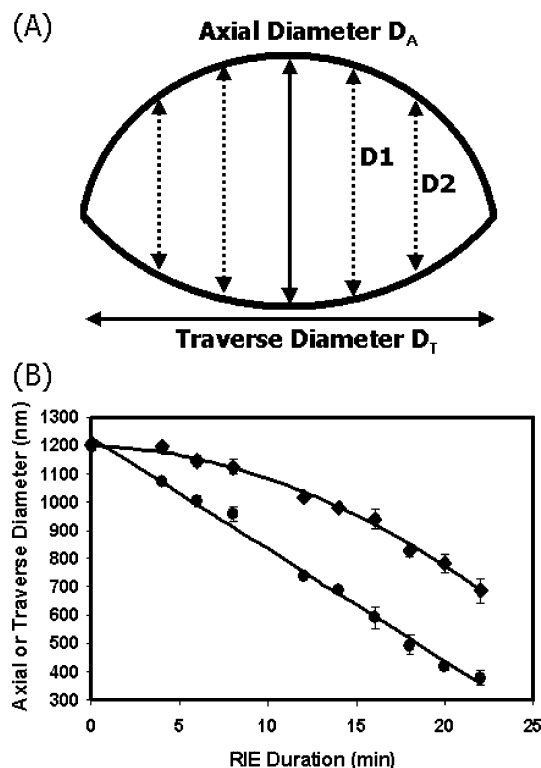


Figure 3. (A) Schematic of the nonspherical polystyrene particles labeled with the various dimensions. (B) Measured axial diameter D_A (circles) and traverse diameter D_T (tilted squares) of the polystyrene particles as a function of RIE time. The original diameter of the polystyrene sphere was $1.2\ \mu\text{m}$. The solid lines represent a linear fit to D_A and a quadratic fit to D_T . The gradient of the linear line is $-40 \pm 2\ \text{nm/min}$.

as a function of RIE time. The original diameter of the polystyrene sphere is $1.20 \pm 0.06\ \mu\text{m}$. In the case of the axial diameters D_A , D_1 , and D_2 , we found a linear variation of the etched dimensions with the RIE time. These dimensions were found to decrease at a rate of $40 \pm 2\ \text{nm/min}$, indicating that the etching of the polystyrene particle along the axial direction is uniform. With this, the traverse diameter D_T is expected to vary nonlinearly with the RIE time. A simple quadratic fit shows that $D_T = 1200 - 2.49t - 0.94t^2$, where t is the duration of RIE. In some of our samples, we can find regions covered with both a monolayer (see Figure 2A–E,H) and two (see Figure 2F,G) or more layers of packed spheres. For multiple layers, the transformation of the topmost layer of microspheres into nonspherical particles was found to be identical to that for the case of a monolayer of microspheres. This indicates again that the normally incident ions were primarily responsible for the etching of the polystyrene spheres. Since we used only a small amount of O_2 , the etching rate of the polystyrene was much slower as compared to those reported by Haginoya et al.¹²

The reactive ions transformed the polystyrene spheres into nonspherical particles without affecting the original periodic and ordered arrangement of the particles. Starting with an ordered close-packed monolayer of microspheres, we can thus make use of this behavior to generate a periodic non-close-packed array of nonspherical particles. Parts A–C of Figure 4 show SEM images of the periodic non-close-packed array of the nonspherical particles created after 6, 14, and 20 min of RIE, respectively. Figure 4B shows some of the polystyrene particles toppled from the supporting Si platform as a result of electrostatic repulsion during SEM imaging. As it is possible to generate a large extended area of close-packed spheres on the substrate, one can create a large extended area on the Si substrate that is covered

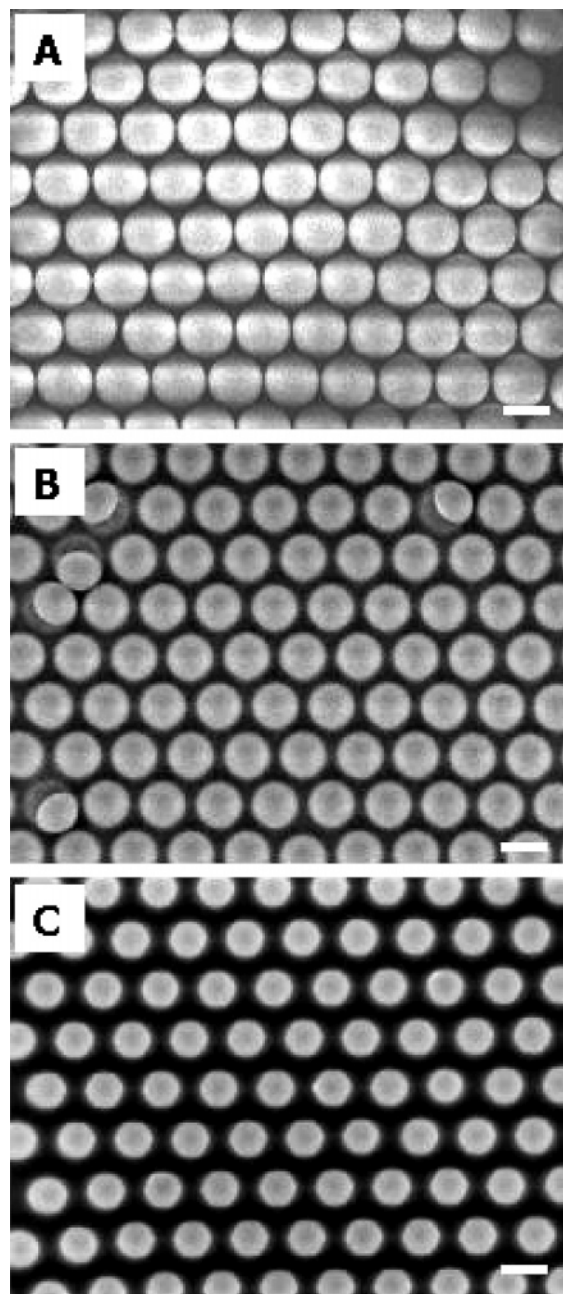


Figure 4. SEM images of the ordered array of non-close-packed polystyrene particles after different RIE durations: (A) 6 min (B) 14 min, and (C) 20 min. Scale bars = $1\ \mu\text{m}$. Note that SEM imaging caused some of the polystyrene particles to topple from the supporting Si platform.

with nonspherical particles. Parts A–C of Figure 5 show the side views of the ordered array of polystyrene particles on the Si substrate after 6, 14, and 20 min of RIE, respectively. Figure 5D shows the top view of the extended non-close-packed but periodic array of the polystyrene particles created after an ordered close-packed monolayer of microspheres on Si was subjected to 20 min of RIE.

In addition to the formation of the non-close-packed nonspherical particles, we found that the particles can be easily removed from the substrate by dissolving them in dichloromethane (CH_2Cl_2). However, it would be worthwhile to reuse the biconvex-shaped particles created instead of dissolving them chemically. For this purpose, each particle-coated Si substrate was first submerged into deionized water in a vial and sonicated for about 10 min. The polystyrene particles readily resuspended

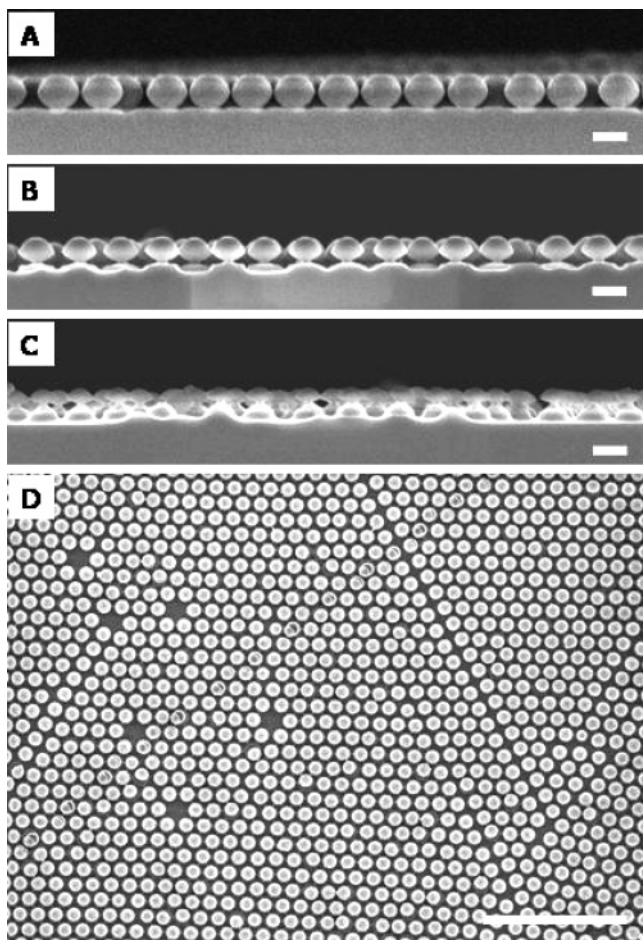


Figure 5. (A–C) SEM image of the side view of a periodic particle array. (D) SEM image of the top view of the non-close-packed particle array. The durations of the reactive ion etching are (A) 6 min, (B) 14 min (C) 20 min, and (D) 20 min. Scale bar: (A–C) 1 μm , (D) 10 μm .

into the aqueous medium. In this way, the particles can be further utilized for other purposes.

As shown in Figure 1, during the process of reactive ion etching, the Si substrate was etched away as well. The part of the Si substrate that was directly exposed to the incident reactive ions was etched away at a higher rate than the region shielded by the polystyrene particles. The polystyrene particles provided shielding to the Si underneath and resulted in the formation of Si microplatforms with a narrow neck (<50 nm) supporting the polystyrene particles. A typical example is illustrated in Figure 2H. The width of the microplatform corresponds to the traverse diameter of the polystyrene particle. The formation of the neck could be due to etching from scattered reactive ions and diffusive ions (low energy) that were in random motion. Such ions would be able to reach the region shadowed by the polystyrene particle.

Figure 6 shows an oblique SEM image of the resultant patterned Si substrate after 14 min of RIE and after the removal of the polystyrene particles. The image shows an ordered periodic array of Si microplatforms. The inset in Figure 6 shows the detailed features of a Si microplatform where the small neck can be clearly seen. This ease of removal of the polystyrene particles from the Si platform suggests that the RIE process did not result in the formation of chemical bonds between the polystyrene particles and the Si platform.

With an atomic force microscope, we measured the maximum depth of the Si etched in different samples. It was found that the depth varies linearly with the duration of the RIE. The

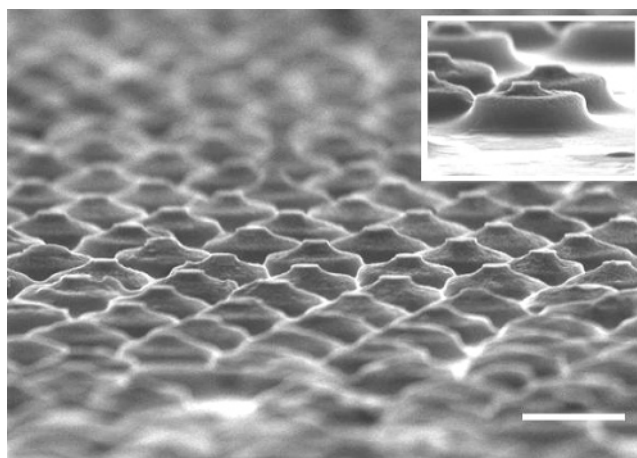


Figure 6. Oblique SEM image of the resultant patterned Si substrate after 14 min of RIE and removal of the polystyrene particles. The image shows an ordered periodic array of Si microplatforms. The inset shows the detailed feature of a Si microplatform. Scale bar = 1 μm .

observed rate of etching of the silicon in the region covered with a monolayer of the polystyrene particles was determined to be 19.8 ± 0.4 nm/min. On the other hand, the observed rate of etching of the silicon in the region covered with a double layer of polystyrene particles was found to be 8.3 ± 0.6 nm/min. For comparison, the rate of etching of bare silicon under the same RIE conditions was found to be 23 ± 1 nm/min. It is interesting that the etching rate of silicon depends on the number of layers of polystyrene particles. It is possible that, during the RIE, the polystyrene particles became charged, resulting in the generation of a localized electric field that affected the trajectory of the reactive ions. As a result, the effective number of reactive ions that reaches the Si substrate is reduced. For double layers, the ions have to travel a longer distance in these charged regions, and hence, the corresponding maximum depth of the etched Si becomes shallower. An additional contributing factor to the difference in the etching rate could be due to the difference in the amount of diffusive and scattered reactive ions that reach the Si substrate.

Template-induced directed assembly of colloidal microspheres is a promising technique for the creation of colloidal crystal patterns.^{6,7,9,18,19} The templates could be a patterned polymer layer on a glass substrate,^{6,18} a patterned Si substrate using a combination of e-beam lithography and RIE,⁷ or even a layer of close-packed microspheres on a glass substrate.⁹ The patterned etched Si substrate created in this work can be further utilized as a template for the directed assembly of other micro/nanoparticles. In these experiments, we put a drop of aqueous suspension of microspheres onto the etched Si template and then left it to dry in ambient conditions. As the water from the suspension evaporated away, the receding water level forced the spheres to occupy the etched crevices surrounding each microplatform, resulting in the formation of interesting configurations of microspheres. Parts A and B of Figure 7 show SEM images of two different configurations of self-assembled microspheres on the patterned Si substrate shown in Figure 6. The diameter of the microspheres is 0.6 μm . In Figure 7A, the microspheres filled all the hexagonally arranged crevices surrounding each Si microplatform. Each microsphere has three nearest neighbors. In Figure 7B, the spheres packed more closely together and, similar to those in Figure 7A, each Si microplatform was surrounded by six microspheres. However, the ring of microspheres was rotated by 30° compared to that in Figure 7A. Each crevice was filled with three microspheres arranged in a triangle. In this configuration, each microsphere has four

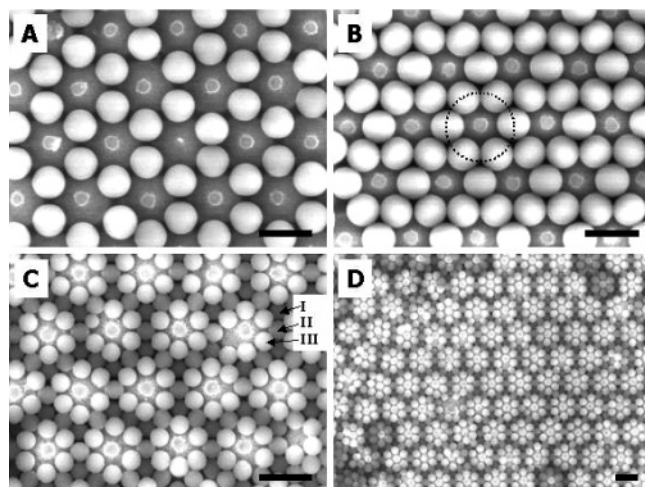


Figure 7. Directed assembly of microspheres using the patterned silicon substrate as template: (A, B) open packing with hexagonal symmetry where microspheres with a diameter of $0.6\ \mu\text{m}$ packed around the Si platform, (C) unique pattern formed when microspheres with a diameter of $0.365\ \mu\text{m}$ were deposited onto the template, (D) a larger field of view of (C). Scale bars = $1\ \mu\text{m}$.

nearest neighbors. It should be noted that Figure 7 shows configurations that are similar to those from the work reported by Velikov et al.⁹ in which a layer of close-packed spheres with larger diameter was used as the underlying template instead. One advantage of using the patterned Si template for template-directed assembly is that the template can be readily recycled. The $0.6\ \mu\text{m}$ polystyrene microspheres can be readily dissolved via sonication with CH_2Cl_2 . The cleaned template can be used for subsequent deposition of microspheres with different diameters.

Attempts in experiments with microspheres of diameters of 0.5 and $0.7\ \mu\text{m}$ did not yield any configuration with significant symmetry. This indicates that selection for symmetry in the system is highly specific with respect to the diameter of the microspheres used. In Figure 7A, microspheres sit in crevices which are of similar size. In Figure 7B, the circumference of the dotted circle traced out over the underlying templated surface is $3.77\ \mu\text{m}$. This is comparable to the sum of the diameters of the six microspheres ($3.6\ \mu\text{m}$) surrounding each platform.

Parts C and D of Figure 7 show SEM images of unique patterns formed when smaller microspheres of $0.365\ \mu\text{m}$ diameter were deposited on the same cleaned Si template. The configuration illustrated in Figure 7C,D comprises three sub-layers of microspheres. The first layer of microspheres deposited in "I" sites (as shown), corresponding to the crevices surrounding the microplatform. This was followed by a second layer of microspheres that went onto the "II" sites, the natural pockets formed by the first layer of microspheres and the Si microplatform. This second layer is slightly elevated compared with the first layer. The spaces between two adjacent microspheres in the second layer and the center of the microplatform form pockets where a third layer of microspheres can sit. As a result, a third layer of microspheres formed a hexagonal ring around each microplatform, sitting at the "III" sites as indicated. In this way, all three layers display 6-fold symmetry with the center of each microplatform as the axis of symmetry. It should be noted that the pattern results from a single-step deposition of microspheres and not from sequential deposition of the three layers. Typically, such a pattern can extend to an area of about

$60 \times 40\ \mu\text{m}^2$. The formation of a symmetrical pattern was not observed for smaller spheres (e.g., microspheres with diameters of 0.1 or $0.2\ \mu\text{m}$). In these cases, when the first layer of spheres sits in the crevices, the space between two adjacent microspheres is significantly larger than the diameter of the microspheres. Hence, there are too many possible sites for deposition available to each individual sphere such that periodic patterns are not possible. The complex self-organization of the microspheres on the template is the result of the interplay of geometrical packing, the size of the microspheres, the local concentration of the microspheres, the surface tension from the drying liquid film, and the forces due to the corrugated surface of the patterned Si template.

In conclusion, a simple technique to create two-dimensional periodic non-close-packed arrays of nonspherical polystyrene particles has been developed. The technique as described can be useful in the fabrication of uniquely shaped particles as well as the parallel generation of a 2-D periodic array of the particles in a non-close-packed configuration. Further investigations include the study of the optical properties of an ordered periodic array of particles with particle size reduction without changes in the lattice constant, extending the technique to microspheres made of other materials such as silica microspheres, investigating the parameters that dictate the microsphere configuration on the template, and improving the microsphere deposition technique to create larger extended areas with specific microsphere configuration. Moreover, the formation of the narrow necks in the Si substrate could potentially be useful as a template for the fabrication of quantum dots by way of deposition of appropriate thin films.

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