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A Self-Assembly Approach to the Formation of Asymmetric Dimers from Monodispersed Spherical Colloids

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This paper describes a procedure for generating asymmetric dimers from two types of monodispersed, spherical colloids that could be different in size, chemical composition, surface functionality, density or sign of surface charges, bulk properties, or a combination of characteristics.

The availability of colloidal particles that are uniform in size, shape, composition, and surface or bulk properties has played an important role in elucidating and understanding the optical, rheological, and electrokinetic behaviors of these materials.[1] Spherical colloids have been the predominant subject of research for many years due to their ease of production as monodispersed samples.[2,3] They may also represent the simplest form of building blocks that could be readily self-assembled into three-dimensionally ordered structures: colloidal crystals or opaline arrays.[4] The capability to crystallize spherical colloids into highly ordered, 3D structures has allowed one to obtain interesting and useful functionality not only from the constituent materials but also from the long-range, 3D order (or periodicity) that characterizes these crystalline lattices.[4,5]

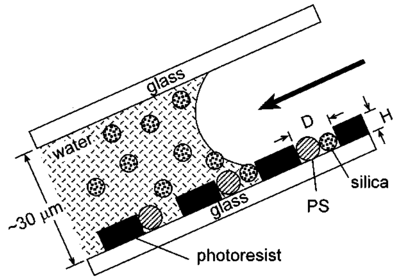

Figure 1. Schematic illustration of the experimental procedure. The liquid was allowed to dewet from the surface along the direction indicated by the arrow.

Despite of their predominant roles in colloid science, spherical colloids are not necessarily the best option for all fundamental studies or real-world applications that are associated with colloidal particles. They cannot, for example, model the behaviors of highly irregular colloids that are more commonly found in industrial products.[1] Theoretical studies have also indicated that they are not well-suited as building blocks in generating 3D photonic crystals with complete band gaps because of a degeneracy in the photonic band structure as caused by the spherical symmetry of the lattice points.[6] Nonspherical particles offer some immediate advantages over their *spherical* counterparts in applications that require lattices with lower symmetries and higher complexities. Although a variety of chemical methods have been developed for synthesizing spherical colloids (e.g., polymer latexes or silica beads) as monodispersed systems, only a few methods are available for generating nonspherical colloids as truly monodispersed samples, in which the shape, size, and charge chemically fixed on the surface are all identical to within 2%.[7−11] Here we describe a general approach that uses geometrical confinement and attractive capillary forces to self-assemble two different types of monodispersed spherical colloids into a specific class of nonspherical colloids: asymmetric dimers.

The key strategy of this assembly approach (Figure 1) is the dewetting of an aqueous dispersion of spherical colloids that has been confined within a parallel cell composed of two glass substrates.[12] The surface of the bottom substrate has been patterned with a 2D array of cylindrical holes. When this dispersion was allowed to dewet slowly across the cell, the capillary force exerted on the rear edge of this liquid slug would drag the spherical colloids across the surface of the bottom substrate until they were physically trapped in the arrays of cylindrical holes. The maximum number of particles that could be retained in each hole was determined by the ratios between the dimensions (*diameter D and height H*) of the holes and the diameter (d) of the spherical colloids. When $0.50d \le H \le 1.37d$ and $d \le D \le 2d$, only one single polystyrene bead could be retained in each cylindrical hole. The yield of such a self-assembly process could be as high as 95%.[13]

Figure 2A shows the SEM image of an array of 2.8-μm polystyrene beads that were trapped in a 2D array of cylindrical holes ($D = 5.0$ μm, $H = 2.5$ μm) patterned in the photoresist film spin-coated on a glass substrate. The polystyrene bead in each hole tended to be in physical contact with the wall of the hole due to the attractive capillary forces between these two surfaces during the evaporation of solvent.[14] As a result, we could permanently fix the position of the polystyrene bead in each cylindrical hole by heating the sample to a temperature slightly higher than the glass transition temperature of polystyrene (~93 °C) for 5−10 s. Afterward, such a surface that contained a 2D array of polymer beads could be used in another step of self-assembly to add a different spherical colloid into the remaining void space of each cylindrical hole. Figure 2B gives an SEM image of the sample shown in Figure 2A, after 1.6-μm silica colloids had been added through a second step of dewetting. The key to this process is to control the ratio between the dimensions of the holes and the diameters of the colloidal particles to ensure that only one colloidal particle could be added into the hole in

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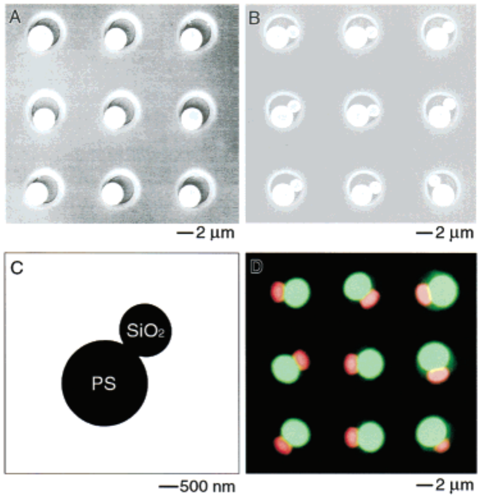

Figure 2. (A, B) Scanning electron microscopy (SEM) images that illustrate the procedure used to assemble two different types of spherical colloids (2.8-*μ*m polystyrene beads, 1.6-*μ*m silica balls) into dimeric units under the physical confinement exerted by the cylindrical holes (5 and 2.5 *μ*m in diameter and height, respectively) patterned in a thin film of photoresist. (C) The transmission electron microscopy (TEM) image of one of the dimers after they had been released from their original support by dissolving the photoresist pattern in ethanol, followed by redeposition onto a TEM grid. (D) The fluorescence microscopy image of a 2D array of dimers that were self-assembled from polystyrene beads that were different in both size and color: 3.0-*μ*m beads doped with a green dye (FITC) and 1.7-*μ*m beads doped with a red dye (Rhodamin). The green and red dye molecules were selectively excited and recombined into an overlapped image.

each step. Again, the two spherical colloids in each hole were in physical contact because of the attractive capillary forces between the surfaces of these two objects as caused by solvent evaporation. Once formed, the two particles in each hole could be permanently welded into a single piece by heating the sample to a temperature slightly higher than the glass transition temperature of polystyrene.[15] Such fixed dimers could be released into an aqueous dispersion by dissolving the photoresist pattern in ethanol under sonication. Figure 2C shows the TEM image of a dimer that was generated by releasing the sample from the original glass substrate and subsequently redepositing it onto a TEM copper grid. This TEM image clearly suggests the formation of a seamless bonding between the polystyrene bead and the inorganic ball made of silica. Figure 2D shows the fluorescence microscopy image of a 2D array of asymmetric dimers formed from polystyrene beads that were not only different in size (3.0 and 1.7 *μ*m in diameter) but also doped with different fluorescent dyes. These images were obtained using a Leica inverted optical microscope (DMIRBE, Germany) fitted with blue (BP 480 ± 40 nm) and green (515−560 nm) excitation cubes. After the glass substrate had been patterned with a 2D array of cylindrical holes (in a photoresist film), its surface was sputtered with a thin layer of gold. This gold-coated substrate was subsequently used to generate asymmetric dimers from 3.0-*μ*m polystyrene beads (labeled with FITC) and 1.7-*μ*m polystyrene beads (labeled with Rhodamin 6G). Separate fluorescence images could be obtained when the green or red dye was selectively excited. Figure 1D shows a combination of these two images, indicating a seamless welding between the two beads confined in each hole.

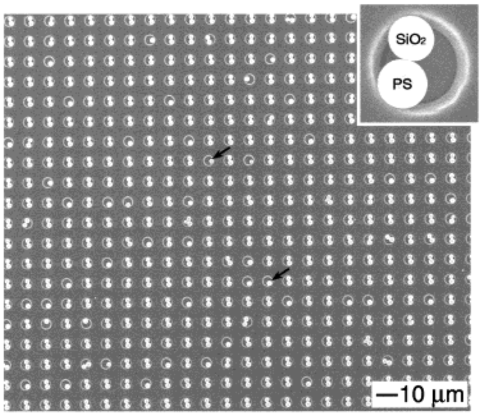

Figure 3. The SEM image of a large-area array of dimers that was formed by 2.5-*μ*m polystyrene beads and 2.3-*μ*m silica balls in an array of cylindrical holes (5 and 2.5 *μ*m in diameter and height). Some of the holes were only filled by one colloidal particle (the large one), and the percentage of this kind of defect was approximately 9% in this 2D array that contained ∼500 elements.

The major concern that one might have in considering this procedure for large-scale production is the yield of the entire process. We found that the total yield of the final product—dimers as expected from the geometric argument—depended on the difference between the diameters of colloidal particles involved in each dimer. When the sizes of these two colloidal particles were relatively close to each other (they had to be different to avoid the formation of homogeneous dimers), a yield of as high as 90% could be routinely achieved. Figure 3 shows the SEM image of an array of asymmetric dimers that were formed from 2.5-*μ*m polystyrene beads and 2.3-*μ*m silica balls. The cylindrical holes were ∼4.9 *μ*m in diameter and ∼2.5 *μ*m in height. This array contained ∼500 elements, and there were about 47 defects (single particle, as indicated by the arrow). The yield of the expected dimers was ∼91%. In another demonstration, we have also been able to obtain defect-free, 2D arrays of dimers over areas as large as ∼2 × 2 mm^2 (or as many as ∼10^5 members in the array). Once released from the surface, the monomers mixed in the dimers could be removed by filtrating through polymeric membranes.

In summary, we have demonstrated that geometric confinement, dewetting on contoured surfaces, and attractive capillary forces could be combined to provide an effective approach for assembling two different types of spherical colloids into asymmetric dimers. The experimental procedures described here had always led to the quantitative formation of dimers with pre-designed shapes, dimensions, compositions, and structures. We believe that the geometric shape of the liquid traps, the ratios between the dimensions (both lateral and vertical) of the holes, and the size of the polymer beads can all be further changed to obtain 3D, self-assembled structures with even higher complexities than those illustrated in this paper. We also believe that the present approach should be extendable to a much smaller scale than those suggested by the present examples; the only requirement seems to be the availability of holes with smaller dimensions, which can now be easily accomplished using advanced nanolithographic techniques.[16] The ultimate limit to the feature size should be determined by a number of parameters such as the density of the colloidal spheres, the temperature, and the rate at which the rear edge of the liquid slug moves. These parameters determine the balance of forces exerted on the colloidal spheres—that is, gravitational force, Brownian motion, and hydrodynamic force—that plays an important role in controling the yield of this process.

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