

# Formation of Spatially Patterned Colloidal Photonic Crystals through the Control of Capillary Forces and Template Recognition

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We report the formation of microscopic patterns of substrate-supported, 3D planar colloidal crystals using physical confinement in conjunction with surfaces displaying predetermined binary patterns of hydrophobicity. The formation process involves a primary self-assembly wherein nano- and microscale colloids order into a photonic fcc lattice via capillary interactions followed by a secondary template-induced crystal cleavage step. Following this method, arbitrary arrays of pattern elements, which preserve structural and orientational properties of the parent crystal, can be easily obtained.

The ability of monodisperse colloids to organize spontaneously into a face-centered cubic (fcc) lattice<sup>1</sup> over macroscopic areas has important practical ramifications. It provides a simple self-assembly route for the design of three-dimensionally ordered structures that exhibit periodic spatial variation in refractive index with lattice constants on the order of the wavelength of light.<sup>2,3</sup> Such structures, also called synthetic opals, can be used directly or as a template for photonic band-gap (PBG) crystals to confine, manipulate, and guide the propagation of light.<sup>4–6</sup> Moreover, these colloidal crystals provide useful templates for the design of nanoporous materials<sup>7,8</sup> and are potential candidates as optical transducers for chemical and biological sensors.<sup>9,10</sup> Several methods including sedimentation,<sup>11</sup> electrophoretic deposition,<sup>12,13</sup> substrate drawing,<sup>14</sup> physical confinement,<sup>15,16</sup> shearing,<sup>17</sup> and spinning<sup>18,19</sup> have proven successful in producing planar colloidal crystals. These methods rely on controlled gravitational settling or solvent evaporation from starting

colloidal sols. Recently, significant attention has been focused on patterning<sup>20–27</sup> colloidal crystals into complex geometries useful for photonic device integrations and the design of sensor microarrays. In this regard, the use of patterns of electric field and those of substrate topographies have become popular.<sup>22,23</sup> The field-assisted methods require conducting substrates (e.g., ITO) and cannot be easily generalized. The physical templating method circumvents this issue. More recently, a chemical templating method based on wettability contrast has also been reported.<sup>25–27</sup> The latter method relies on the selective wetting of chemically structured surfaces during withdrawals from the colloidal sol to guide the crystal formation in well-defined regions of the substrate surface. However, the crystal morphologies were found to depend critically on the meniscus stability, colloidal sol concentration, withdrawal directions and speeds, and feature dimensions and orientations. As a result, a uniform crystal thickness on features of different dimensions on single substrates cannot be easily obtained using these methods.<sup>26</sup> Furthermore, in all of the patterning methods mentioned above, the nucleation and growth occurs independently when used for designing discrete crystal islands. Thus, the elements of the resulting crystal arrays lack uniformity in crystal structural properties (e.g., orientation and/or thickness).

Here, we report a simple alternative wherein physical confinement, employed in conjunction with a substrate surface displaying prepatterned variations of interfacial energies, results in the formation of well-defined arrays of 3D, planar colloidal crystals. The colloids order into an fcc lattice, and the arrays “epitaxially” reflect the underlying pattern of the substrate hydrophobicity. The self-assembly was achieved simply by a slow evaporation of solvent from a concentrated aqueous colloidal sol sandwiched between a clean, hydrophilic glass and a patterned

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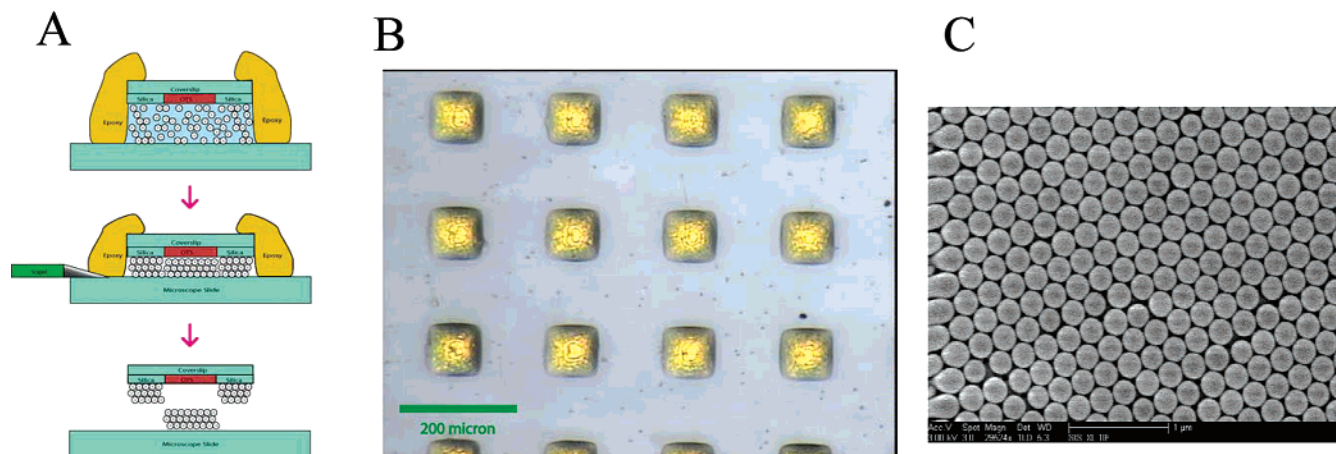
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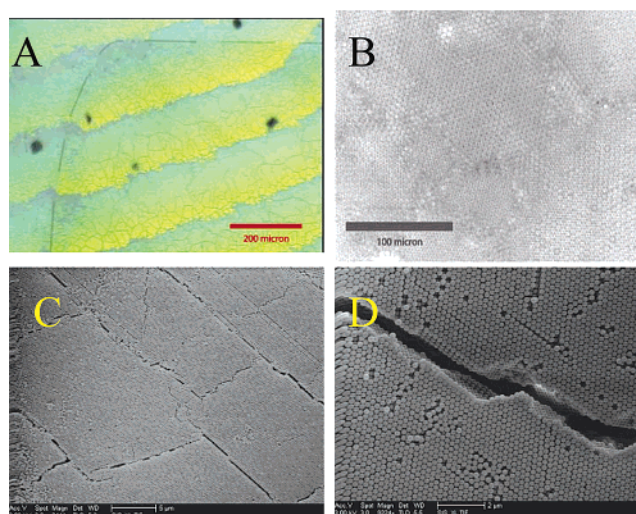
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**Figure 1.** A. Process of creating and patterning a colloidal crystal. A high concentration sol is sealed between a slide and a patterned OTS coverslip, and allowed to dry. Once dry, the sample is opened with a scalpel. B. An optical image of a sample array of polystyrene colloidal crystals produced by physical confinement and chemical templating. C. SEM micrograph of a PS (260 nm) colloidal crystal element obtained by our method (see text for details).

wettability glass surface. The disassembly of the sandwich resulted in two complementary micrometer-scale spatial patterns of colloidal crystals that reflect the pattern of substrate hydrophilicity. The capillary forces order the colloids into a large crystal within the sandwich (primary self-assembly), which subsequently cleaves with remarkable regularity at the hydrophilic/hydrophobic boundary of the patterned substrates (secondary patterning). Because the arrays were generated from a single parent crystal, each element is structurally (e.g., orientationally) similar to every other element in the array. Furthermore, the technique was found to be applicable to larger micrometer-scale colloids as well as variously functionalized colloids. We demonstrated the approach using monodisperse colloids of silica (330 nm and  $5.66\ \mu\text{m}$ ) and polystyrene (PS, 240 nm, 260 nm, and  $5.43\ \mu\text{m}$ ) and carboxylated PS (250 nm). High-density arrays of colloidal crystals with features as small as  $100\ \mu\text{m}^2$  separated by distances as small as  $100\ \mu\text{m}$  could be routinely obtained, and the crystal thickness could be conveniently controlled by inserting a spacer between the substrates or varying the amount and/or concentration of the colloidal sol.

The general strategy that was used to form patterned colloidal crystals is schematically shown in Figure 1a. The process begins with the creation of a hydrophilic/hydrophobic patterned surface. We used lithographically patterned *n*-octadecyltrichlorosilane (OTS) monolayers on oxidized silica substrates. Preassembled OTS monolayers, prepared by following a standard solution self-assembly procedure,<sup>28</sup> are patterned using an ozone-generating, short-wavelength-ultraviolet-emitting mercury lamp (184–257 nm) in conjunction with a photomask.<sup>29</sup> The treatment results in a surface energy pattern comprising intact OTS in UV-protected regions and oxidized silica in the UV-exposed regions. Simple condensation patterns, such as those derived by selective vapor depositions,<sup>30</sup> and ellipsometric imaging measurements confirm the patterned hydrophilicity of the resulting surfaces. Typically, a 4–20  $\mu\text{L}$  aliquot of a colloidal sol near the critical concentration (44–56% v/v)<sup>31</sup> is sandwiched between the chemically



**Figure 2.** An optical image of a colloidal crystal formed using (A) 240 nm polystyrene colloids and (B)  $5.66\ \mu\text{m}$  silica beads sandwiched between a patterned OTS coverslip and a clean coverslip. The dotted line in (A) is a guide to eye. (C–D) SEM images of cracks in 260 nm colloids after opening the sandwich.

patterned surface and a clean, hydrophilic glass surface. The physical confinement of the sol was achieved by gluing the two surfaces together (with and without a Mylar spacer) using epoxy into a sandwich cell following Xia et al.<sup>16</sup> The cell was stored for  $\sim 3$  days with the patterned OTS side up and then opened simply by separating the two glass surfaces using a scalpel. Following this approach, micropatterns of silica and PS colloidal crystals, such as those shown in Figure 1b and c, were routinely obtained. The highest quality silica crystal arrays were achieved at  $\sim 40\ ^\circ\text{C}$  whereas room-temperature conditions were found to be optimal for the PS beads.

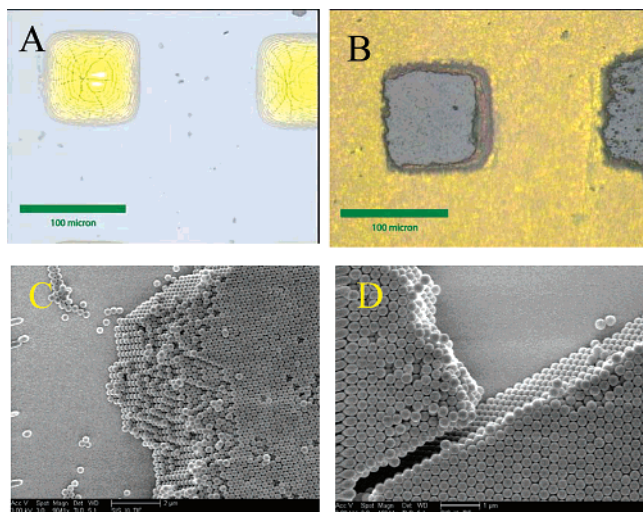
The optical image shown in Figure 2a represents the typical crystal morphology obtained before the sample sandwich was disassembled for nanoscopic beads. Many salient features of the assembly process are revealed in Figure 2a. First, the image reveals the presence of a faint but reproducible contrast in color reflecting the underlying OTS pattern. This color contrast is probably due to the differences in the amount of entrapped water, giving rise to different effective indices of refraction, in crystal regions supported on the hydrophilic and the hydrophobic parts of the substrate. Second, the images show a series of

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**Figure 3.** Pictures taken after opening the sandwich. All optical images are taken in reflection mode taken with a color camera. A and B. Optical images of complementary patterns of 260 nm polystyrene colloidal crystals obtained on patterned OTS and unpatterned coverglass. C and D. SEM images of similar complementary patterns for 260 nm polystyrene patterned colloidal crystals.

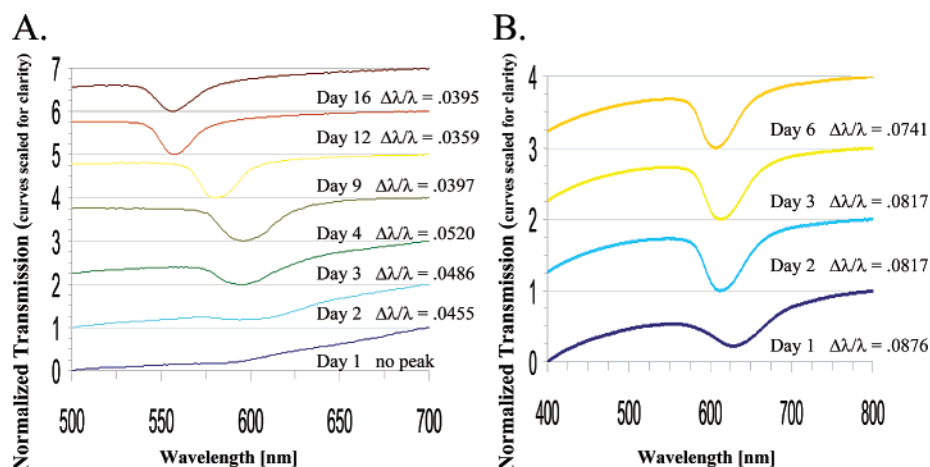
parallel stripes  $\sim 300 \mu\text{m}$  in width. Such stripes, reminiscent of stick-slip motion, have been observed<sup>32–34</sup> previously in capillary-force-driven assemblies of colloidal particles. They are generally attributed to the competition between the surface tension of the wetting film and the frictional force experienced by the contact line due to the convective transport of the colloidal particles to the evaporation boundary. Each stripe further reveals a random assortment of hexagonal and parallel boundaries between  $\sim 100 \mu\text{m}^2$  single-crystal domains, also consistent with previous observations. Ordered crystal structures were also obtained using microscopic beads such as those shown in Figure 2b. Field-emission scanning electron microscopy (FE-SEM) images of nanoscopic colloidal crystals in Figure 2c and d reveal the general preservation of the crystal order across the crack boundaries. This indicates that the individual crystal domains are not the result of uncorrelated nucleation processes but form via cracking after crystal nucleation and growth.

When the sandwich cell was disassembled, the colloidal crystal cleaved with a remarkable reproducibility along the hydrophilic/hydrophobic boundary. The colloidal phase

was retained on the hydrophilic regions of the patterned OTS surface, and the complementary crystal phase was observed for the uniformly hydrophilic silica substrate. These results are shown in Figure 3a–d. These show that the entire crystal is preserved on one of the two bounding surfaces. The cleavage occurs preferentially at the substrate planes rather than at other arbitrary planes within the crystal. Occasionally, a partial cleavage leaving behind residual crystal on each of the two bounding surfaces was also observed. Parts c and d of Figure 3, the FE-SEM images, further show that the layers retain their essential fcc crystallographic ordering on each of the two surfaces and across the crystal cracks. Because the cleaved crystals were generated from an original single parent crystal (albeit cracked), the elements of the array preserve the ordering of the parent crystal, thereby forming an array of microscopic colloidal crystals in a single, uniform orientation.

These findings are further confirmed by the optical properties of the colloidal crystals. Normal incidence transmission spectra shown in Figure 4 reveal a characteristic dip in the transmission traces that correspond well to the expected stop band for the colloidal dimensions. Observations of the changes in the spectral properties during the drying period (Figure 4) yield useful insights into the ordering process. In all cases, the colloids ordered rapidly as indicated by the early appearance of the stop-band peak. Slow drying resulted in a gradual blue shift that reflects the approach to close packing. Final peak positions observed for 240 and 260 nm polystyrene and 330 nm silica colloids were  $530 \pm 7$ ,  $584 \pm 3$ , and  $603 \pm 6$  nm, respectively. These values are slightly lower than theoretically predicted values but are consistent with previous experimental results obtained for comparable aqueous-phase crystallization<sup>35</sup> and presumably reflect small colloidal shrinking due to dehydration. In our samples that were dried at room temperature, the peak location occasionally shifted by as much as  $\sim 20$  nm when the final traces of water were allowed to evaporate by opening the confinement cell. The peak location after opening the cell was the same as for the samples dried at elevated temperature ( $40^\circ\text{C}$ ).

In summary, our results suggest a general methodology for the construction of two-dimensional patterns of three-dimensionally ordered photonic colloidal crystals applicable to a wide range of colloid types, dimensions, and surface functionalities. The method depends on a slow crystallization from aqueous sols in sandwich cells to form



**Figure 4.** Time-lapse UV-vis transmission spectra for (a) a colloidal crystal of 240 nm polystyrene colloids in a sandwich at room temperature and (b) a colloidal crystal of 330 nm silica colloids in a sandwich at  $40^\circ\text{C}$ . The spectra reveal predicted shifts in optical stop-band during drying.

large colloidal crystals. The use of a patterned OTS surface in the sandwich cells provides a simple means of cleaving the crystal into regular complementary patterns on the two surfaces upon disassembly. The capillary forces during physical confinement give rise to the primary self-assembly of colloids whereas the subsequent crystal cleavage results in predetermined geometric patterns. A useful feature of our approach is that larger, micrometer-sized beads can also be organized and patterned. Other methods that depend on evaporation by withdrawal are difficult because beads larger than  $1\ \mu\text{m}$  in size do not remain suspended in the solution long enough to be deposited onto the

substrate. Methods based on gravitational settling are also limited as to the size of the beads they employ, presumably because larger beads experience much larger gravitational forces relative to thermal forces. Another notable feature of our method is that the pattern elements preserve the parent structural order of the starting crystal. In this regard, by improving the structural uniformity of the starting crystal it should be possible to produce crystal microarrays of uniform thickness and orientational and optical properties. A systematic study toward this end is currently being carried out in our laboratory.

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