

## Template-directed convective assembly of three-dimensional face-centered-cubic colloidal crystals

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We demonstrate that square two-dimensional grating templates can drive the growth of three-dimensional, face-centered-cubic (fcc) colloidal crystals by convective assembly. The square symmetry [i.e., (100) planes parallel to the substrate] of the underlying template was transferred to the colloidal crystal and maintained throughout its growth of  $\sim 50$  layers. We characterized crystals grown on flat and on templated substrates using electron microscopy and small-angle x-ray scattering (SAXS). SAXS measurements of the templated samples clearly show fourfold diffraction patterns that arise from fcc domains without stacking faults. © 2002 American Institute of Physics. [DOI: 10.1063/1.1516614]

It is difficult, but desirable, to create patterned nano- and microscale materials ordered in three dimensions. Such materials can have novel optical properties,<sup>1,2</sup> potentially leading to new classes of optical filters, switches and photonic materials.<sup>3–5</sup> Alternatively, precision mesoporous materials have a wide range of potential chemical applications, for example, as catalytic supports<sup>6</sup> and separation media.<sup>7,8</sup> One important route for creation of three-dimensional patterned materials is through self-assembly. Under the right conditions, a variety of colloidal particle species can assemble spontaneously into ordered phases. Such crystals can form spontaneously in thermal equilibrium,<sup>9–11</sup> or via nonequilibrium schemes facilitated by gravity,<sup>12</sup> electrohydrodynamic forces,<sup>13,14</sup> chemical forces,<sup>15,16</sup> injection forces,<sup>17</sup> or convection.<sup>18–21</sup>

Convective assembly is arguably one of the simplest methods for the creation of ordered particle structures. It has been used with success to make two-dimensional<sup>20</sup> and three-dimensional monodisperse<sup>21</sup> and binary<sup>22</sup> colloidal structures, and even to make heterostructures.<sup>23</sup> In the convective assembly scheme, a colloidal crystal is formed through the evaporation of suspension solvent. The evaporation process causes suspended particles to flow through the liquid to the drying edge, where they assemble. Assembly is controlled by several factors that are not as yet fully understood: surface tension tends to pull the particles together to form close packed two-dimensional structures, and crystallization is facilitated via nucleation onto these two-dimensional structures. The resulting crystals are close packed with triangular (111) planes parallel to the substrate. Since energy barriers to the formation of stacking faults are very small, the resulting structures are generally not truly face centered cubic (fcc). Ultimately these stacking faults will have a negative impact on, for example, the photonic properties of the nanoscale material.

In this letter we use square two-dimensional grating templates to grow three-dimensional fcc colloidal crystals by

convective assembly. The square symmetry [i.e., (100) planes parallel to the substrate] of the template was transferred to the colloidal crystal and maintained throughout its growth. Crystals with thickness of  $\sim 50$  layers were grown. Using scanning electron microscopy (SEM) and small-angle x-ray scattering (SAXS) we characterize the square-symmetric structures and compare their yield on templates with different material compositions. SEM measurements are useful to observe isolated crystallites, and SAXS provides more complete information about bulk samples. We also describe *in situ* microscopic observations of the growth process. Our work shows that the natural tendency for convective assembly to form close-packed planes can be overcome in two and three dimensions.

Our convective assembly procedures largely follow previous work.<sup>20,21</sup> We immersed substrates (with and without templates) vertically in a glass vial containing an aqueous suspension of polystyrene spheres. The particle volume fraction of the suspension was  $\sim 0.01$ . The samples were placed in an oven (55 °C), and the solvent was slowly evaporated over a period of  $\sim 80$  h. On the flat substrates we used particles with diameters ranging from 250 to 750 nm. Most of the work on the templates, however, used  $\sim 500$  nm particles in order to match the template periodicity. After evaporation, we observed iridescent colloidal crystals on the substrate.

Our templates were fabricated by imprint techniques.<sup>24</sup> We used a commercial diffraction grating as our starting mold, and obtained a polyethylene replica of the original by pressing the diffraction grating into a polyethylene sheet held at 90 °C; in order to make two-dimensional square patterns the grating was imprinted twice with the grooves oriented in orthogonal directions. We made two types of template, one based on polydimethylsiloxane (PDMS) and one based on Norland Optical adhesive coated with a Au/Pd film. In the case of the Norland Optical glue, we placed the polyethylene grating replica face down on a glass coverslip, and applied a drop of Norland Optical Adhesive 63 (NOA63) to the glass coverslip. The optical glue droplet was pulled between the coverslip and the replica by capillary forces. The glue was

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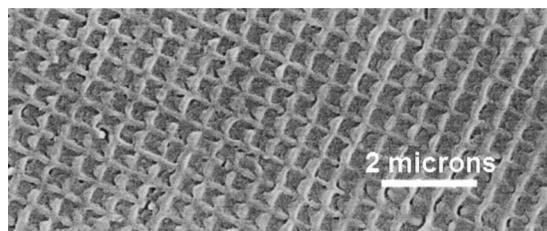


FIG. 1. SEM picture of a portion of our template. The groove spacing was 550 nm, groove depth was 100–200 nm, and lateral dimensions were 6 mm × 18 mm.

then cured by UV illumination for 1 min. The result was a NOA63 based template that could be peeled away from the polyethylene replica. We coated the surface of the NOA63 template with a thin layer (10–20 nm) of Au/Pd, because the adhesive was hydrophobic. For the PDMS films, we followed the same procedure, this time using a drop of PDMS precursor fluid (i.e., Sylgard 184 silicone elastomer/curing agent). We cured the PDMS by oven heating (55 °C) for ~36 h. The PDMS could be readily peeled from the replica template, and oxidized to make it more hydrophilic. Ultimately we found the Au/Pd coated NOA63 yielded far superior templated crystals, at least in part due to the improved wetting of the aqueous suspension onto its surface. An image of the final Au/Pd/(NOA63 adhesive) template is in Fig. 1.

In the two-dimensional convective assembly process a layer of particles is formed as the solvent evaporates. When the fluid thickness is comparable to the particle diameter, capillary forces pull the particles into contact with one another. On a flat surface, planar close-packed triangular crystals form (structures with the highest packing density). Thus far, templating has been used in convective assembly to produce ordered two-dimensional (single layer<sup>25</sup> or bilayer<sup>22,26</sup>) structures, which deviate from close packing. Square templates have also been used in equilibrium,<sup>27</sup> sedimentation,<sup>12</sup> and injection<sup>28</sup> assembly experiments to nucleate three-dimensional fcc colloidal structures. Our two-dimensional square template (see Fig. 1) introduces geometric barriers for convective assembly at the surface which favor the square lattice over the hexagonal one; our hypothesis was that this ordered two-dimensional structure would bias the system and induce a three-dimensional stacking-fault-free fcc crystal and form via convective assembly. This was observed.

In Fig. 2(a) we show a SEM picture of a (100)-oriented fcc colloidal crystal achieved with the Au/Pd template. This crystal is about 50 layers thick, and has a domain size of about 50  $\mu\text{m}^2$ . Square symmetry has been transferred from the two-dimensional template to the three-dimensional struc-

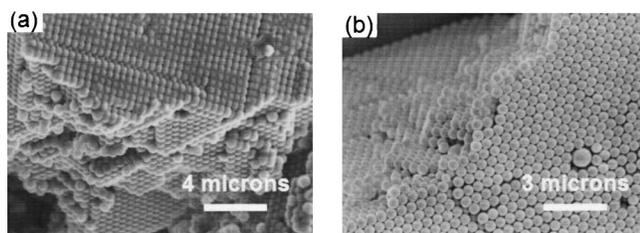


FIG. 2. SEM pictures of the crystal convective assembled (a) with a template and (b) without a template. The particle diameter was ~500 nm, and the template period was 550 nm.

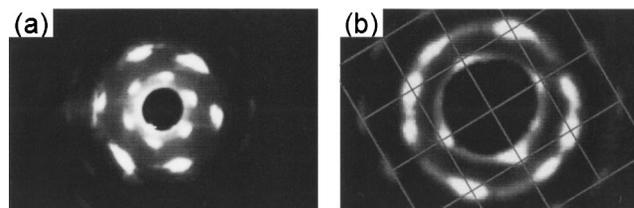


FIG. 3. Diffraction pattern from convective assembled crystals. (a) Hexagonal domains (without a template) and (b) square domains (with a template). In (b), the superimposed grid facilitates recognition of the square symmetry.

ture as can be readily observed on the top layer of the crystal. For comparison, in Fig. 2(b) we show a control sample grown under exactly the same conditions starting from a flat substrate. Hexagonal symmetry is clearly exhibited; the presence or absence of random stacking faults could not be deduced from these measurements.

The SAXS measurements used beamline 9-ID (CMC-CAT) at the Advanced Photon Source with a selected x-ray energy of 9.0 keV. The beam was collimated using vertical and horizontal mirrors and  $X$ - $Y$  slits, and the diffracted signals were measured using a Bruker charge coupled device (CCD) detector with a 5.2 m camera length. The beam size was approximately 200  $\mu\text{m}^2$ . Figure 3(a) shows a typical diffraction pattern from ~500 nm diameter colloidal spheres convectively deposited on a flat glass substrate. The sixfold symmetry is clearly seen, indicating the diffraction arises from three- or sixfold planes. This observation implies that triangular close-packed sheets of spheres must be parallel to the substrate; such sheets are found in fcc, hexagonal-close-packed, and random-close-packed lattices. Interestingly, the same orientation is observed over the entire sample; it is correlated with the growth front, suggesting that the growth process also induces a preferred orientation. Because the sample could be rotated tens of degrees relative to the incoming beam with only slight distortion of the pattern, the bright features in the pattern are actually cross sections of Bragg rods, which in turn indicate a high density of stacking faults. Similar features were seen over a wide range of particle sizes, although in general a higher degree of orientation was observed for smaller particles (250–400 nm) than for larger particles (450–750 nm).

In Fig. 3(b) we exhibit the diffraction pattern from 550 nm colloidal spheres convectively assembled on the templated (Au/Pd) glass substrate. Several types of patterns were seen: Bragg rings corresponding to a powder of unoriented domains, sixfold patterns such as those in Fig. 3(a) (but with poorer orientational order), and fourfold patterns. The fourfold patterns always had some admixture of hexagonal symmetry. The fourfold patterns are indicative of the underlying square structures. By scanning the x-ray beam over the surface we found the diffraction pattern changed when the beam was displaced a distance comparable to its size, indicating that typical domain sizes were less than 200  $\mu\text{m}^2$ . We also estimate that 10%–40% of the sample has square symmetry. The rest is disordered or hexagonal. This observation is in agreement with rough estimates from SEM, where we found 30%–50% square-symmetric crystals.

In order to improve on the present scheme it is desirable to understand the underlying growth mechanisms. While we

cannot offer a full explanation, we have made several observations about this system that provide pieces of information that may be useful for future work.

Growth on Au/Pd-NOA63 templates was superior to growth on NOA63-only and PDMS templates. We believe the most important reason for this effect is that water wets the Au/Pd-NOA63 template extremely well. The PDMS templates showed only 5%–10% square-symmetric regions, but was still superior to the NOA63 template (which had the worst wetting properties of the three templates). It is also very likely that the yield could be improved by increased groove depth and quality; the groove depth was not controlled well, varying from 100 to 200 nm, and growth was better in the deeper regions. Finally, it is important to match particle size to groove spacing. The same experiment with 400 nm particles did not exhibit square symmetry, and showed no difference for samples with and without the template.

In a second set of observations we used optical microscopy to investigate the real-time crystallization of a drop of colloidal suspension on a glass coverslip. This slightly different system shares some of the same mechanisms as the three-dimensional convective assembly processes of our primary experiments. By direct visualization, we noticed that (except in the area right on the drying edge) the crystallization process appeared to be similar to the equilibrium hard-sphere (Kirkwood–Alder) phase transition; the high local particle concentration required for the transition was driven by convective flow. The particle concentration was higher near the substrate, and crystallization started from the substrate. Thus many of the standard considerations about crystallization kinetics should apply to these systems.

In summary, we have demonstrated that square two-dimensional grating templates can be used to grow three-dimensional fcc colloidal crystals by convective assembly. The square symmetry of the template was transferred to the colloidal crystal and maintained throughout its growth. This method provides an important advance towards the fabrication of large defect-free colloidal crystals.

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