Template-directed Convective Assembly of Colloidal Crystals

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Introduction

There is currently considerable interest in periodic dielectric materials for applications as photonic band gap materials. Colloidal crystals form a natural route to periodic dielectric structure on the submicrometer scale. It was recently shown that single crystal colloidal multilayers could be grown by a "convective assembly" technique using capillary forces [1]. A clean slide is placed in a vial containing a colloidal suspension, and the solvent is allowed to gradually evaporate. The resulting crystals are close-packed with triangular (111) planes parallel to the substrate. However, there is almost no energetic barrier to the formation of stacking faults, and the crystals are more accurately described as random-close-packed than either hexagonal close-packed (hcp) or face-centered cubic (fcc). These stacking faults will ultimately have a negative impact on the optical qualities of the photonic crystals.

We have developed a templating technique that uses a polyethylene square imprint on the substrate to nucleate planes with square symmetry parallel to the substrate [2]. The goal is to induce the formation of pure fcc lattices with few or no stacking faults. Electron microscopy confirms the existence of square domains in these films. We have now used small-angle x-ray scattering (SAXS) at the APS to study colloidal multilayer films formed with and without the templating process.

We used the CMC-CAT small-angle diffractometer at end station 9-ID-B. The beam was collimated by vertical and horizontal mirrors and X-Y slits, and the diffracted signal was measured with a Bruker charged-coupled device (CCD) detector. The beam size was on the order of 200 μm^2.

Results

Figure 1 shows a typical diffraction pattern from 550-nm colloidal spheres convectively deposited on a nontemplated glass substrate. The sixfold symmetry can clearly be seen, indicating that the diffraction arises from three- or sixfold planes. In the context of close-packing of spheres, this means that the 111 planes of a fcc crystal, the basal planes of a hcp crystal, or the triangular nets of a random close-packed structure must be parallel to the substrate. The same orientation is observed over the entire slide and is correlated with the direction of movement of the growth front, indicating that the growth process also induces a preferred orientation. The sample could be rotated tens of degrees relative to the incoming beam with only a slight distortion of the pattern, indicating that the bright features 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 larger particles (450-750 nm).

Figure 2 shows a diffraction pattern from 550-nm colloidal spheres convectively deposited on a templated glass substrate. In this case, several types of patterns are seen: (1) Bragg rings corresponding to a powder of unoriented domains, (2) sixfold patterns such as that in Fig. 1 but with somewhat poorer orientational, indicating

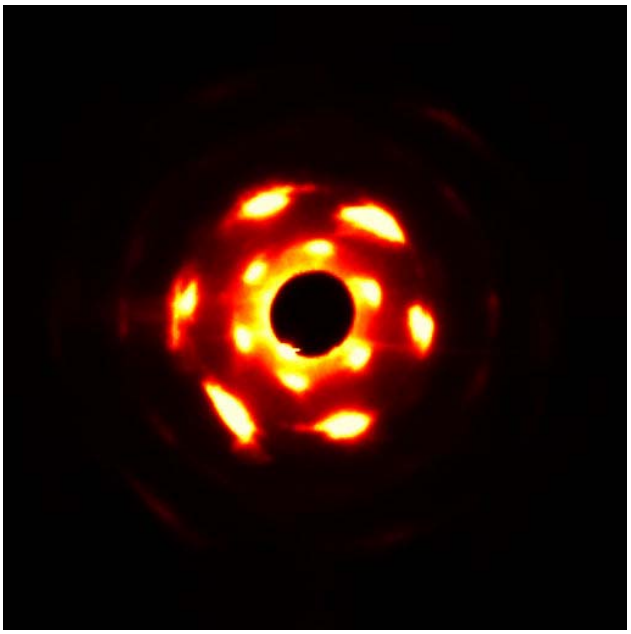

FIG. 1. Diffraction pattern from a typical hexagonal domain of 550-nm silica particles convectively assembled on a glass substrate (no template). Full scale is ± 0.01 $Å^{-1}$.

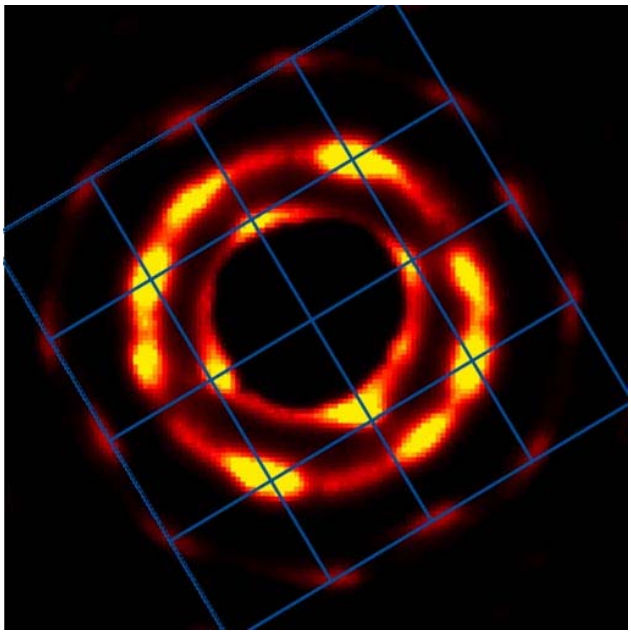

FIG. 2. Diffraction pattern from a square domain of 550-nm silica particles convectively assembled on a square template. The superimposed grid helps with recognition of the square symmetry. Bright spots that do not lie on the grid arise from hexagonal domains that were also in the illuminated region. Full scale is ± 0.01 Å^{-1}.

111 planes parallel to the surface, and (3) fourfold patterns such as that in Fig. 2. (The fourfold patterns, however, always have some admixture of hexagonal symmetry.) By scanning the x-ray beam over the surface, we established that typical domain sizes were less than the 200-mm beam size. We estimate that 10-30% of the sample shows the square symmetry [i.e., (100) planes parallel to the substrate].

We have thus demonstrated for the first time the use of a templating grid in nucleating the growth of fcc colloidal crystals with the (100) plane parallel to the substrate surface, and we have shown that SAXS can be a valuable tool in quantifying the resultant structures.

Acknowledgments

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