

Colloidal Crystals Grown on Patterned Surfaces**

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The realization of photonic crystals based on colloidal crystal growth has emerged as a promising alternative, bottom-up approach to microfabrication.^[1] Colloidal crystallization occurs through self-assembly and assisted assembly of highly monodispersed, submicrometer-sized polymer or silica spheres into one-, two-, or three-dimensional periodic arrays.^[2-7] In these strategies, however, no mechanism exists by which a common lattice orientation can be imposed on the entire crystal. The resulting lack of long-range order can lead to a degradation of the optical properties of the crystal.^[8-10]

Recently, colloidal crystallization has been accomplished on substrates patterned with planar^[11-13] and topographic patterns.^[14-18] In the first case, isolated ionic and cationic regions were produced by chemical patterning of a substrate with self-assembled monolayers. Charged colloid particles were deposited from their aqueous dispersions onto those surface domains bearing an opposite charge. As the water evaporated, the lateral capillary forces brought the particles in contact and, under particular conditions, induced a reasonable extent of order in the colloid assemblies. In topographic patterning, the substrate relief was commensurate or incommensurate with a particular lattice structure. Particle deposition in the surface wells occurred via physical means (e.g., by sedimentation or during evaporation of a liquid from the colloid dispersion), thus no specific particle-surface interaction was involved. Capillary forces assisted colloid crystallization in the drying stage. Colloidal crystal growth accomplished by electrophoretic deposition of microspheres on patterned substrates combined features of the two methods described above: microbeads electrodeposited onto the oppositely charged electrode surface were physically confined by the rigid walls.^[19]

It should be noted that in topographic patterning the characteristic size of the pattern can be commensurate with several particle diameters^[20] or with the size of individual microbeads.^[14,15] In the first case, after particle deposition in the groove capillary, electrohydrodynamic forces led to colloid crystallization. In the latter case, the role of the pattern was to

provide well-defined sites for colloid deposition and thus to impose a specific arrangement of the beads in the layer adjacent to the substrate. This first layer was then assumed to provide, through colloid epitaxy, a defect-free template for the growth of forthcoming layers.^[14a] Using microscopic techniques, it was found that the surface pattern has a significant effect on the geometry and orientation of the three-dimensional lattice in colloid crystals.^[14a,15] To the best of our knowledge, the effect of colloid epitaxy on the long-range order and defects in the colloidal crystal and thus their optical properties has not been studied.

Here, our objective was to examine how colloid epitaxy enables better control of mono- and multilayers of colloidal crystals. In contrast to other studies reporting characterization of colloidal crystals on patterned substrates using microscopic techniques,^[12-16,19a,20a,c] which probed the local order, we used optical and laser diffraction to probe the long-range order in the crystals and to quantify the effect of the surface patterning on the crystal quality.

We demonstrate that the measurement of stop bands using optical diffraction is insensitive to the disorder associated with multiple domains present in polycrystalline samples, because it probes the periodicity in the vertical direction. Laser diffraction probed the periodicity along the surface of the sample and clearly revealed whether colloidal crystals were mono- or polycrystalline. In addition, the latter method provided quantitative information about the extent of the disorder in polycrystalline samples.

Figures 1a-c show a schematic of our approach to assembly of spherical colloidal particles with diameter D on a surface covered with a two-dimensional periodic pattern of grooves

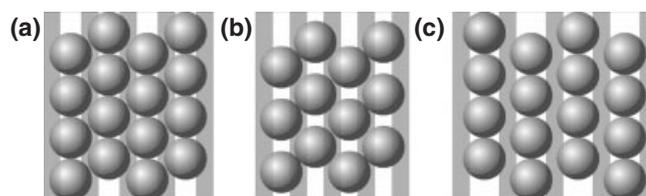


Figure 1. a) Close-packed 2D colloid crystal on a patterned surface with perfectly matched pitch $A = (\sqrt{3}/2)D$. Because the pitch of the pattern is smaller than microsphere diameter, the relative position of beads in adjacent rows is offset by half of a particle diameter. b) Colloid crystal grown onto a pattern surface with $A < (\sqrt{3}/2)D$. c) Colloid crystal grown onto a patterned surface with $A > (\sqrt{3}/2)D$.

with a pitch A . The depth of the grooves is sufficiently small ($\sim D/10$) that particles in adjacent grooves can contact each other. When $A = (\sqrt{3}/2)D$ (Fig. 1a), the surface is covered with a close-packed hexagonal monolayer of beads and the particles in adjacent grooves are offset by half of their diameter. This arrangement constitutes the (111) crystallographic plane of a face-centered cubic (fcc) lattice of close-packed microspheres. This monolayer can serve as a template for further growth of the crystal in an fcc lattice. When $A < (\sqrt{3}/2)D$ or $A > (\sqrt{3}/2)D$ (Figs. 1b,c, respectively) the particles can no longer assemble into close-packed monolayers and their

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arrangement is no longer conducive to the growth of fcc multilayer crystals.

We used a maskless holographic technique^[19a] to produce periodic arrays of straight ribs of insulating photoresist on conductive indium tin oxide glass (Fig. 1d). We used evaporative assembly^[2d] or electrophoretic deposition to deposit polymer microspheres ($D=685$ nm) into the conductive grooves. Figure 2a shows a scanning electron microscopy (SEM) image of the monolayer of colloid particles deposited on a patterned substrate with $\Lambda=595$ nm ($\Lambda/D=\sqrt{3}/2$). After the particles were deposited into the conductive grooves, electrohydrodynamic forces acting along the groove drove the beads into a close-packed array.^[19b,21] In a control experiment, we also carried out the deposition on a blank non-patterned substrate under similar conditions. There, the colloids adopted a disordered arrangement (Fig. 2c). Small gaps in the lattice were

local imperfections and had no effect on the overall lattice order; they do not impact laser diffraction.

In the laser diffraction experiments,^[22] for the crystal grown on a patterned substrate (Fig. 2b), most of the light was found in six bright diffracted beams forming a regular hexagon, reflecting the perfect hexagonal lattice (the seventh spot, caused by the undeflected beam, appears in the center). In contrast, the diffraction patterns obtained from patterned substrates alone featured only two spots plus the central one (Fig. 2e), since the pattern possessed only one-dimensional periodicity. The diffracted beams emerged from the sample at an angle, given by $\theta=\sin^{-1}(\lambda/d)$, where λ is the wavelength and $d=(\sqrt{3}/2)D$ is the distance between rows of particles in the lattice.^[23] The presence of a single and sharp diffraction pattern indicated that the lattice orientation was uniform throughout the area (ca. 1 mm²) probed by the beam. Furthermore, the sharpness of the diffraction pattern did not change when we examined the entire area of the two-dimensional crystal (>1 cm²) with the laser beam. In contrast, the colloid array deposited on the blank substrate did not produce a diffraction pattern with any discernable spots (Fig. 2d).

The effect of incommensurability between the pattern pitch and the colloid size (probed only by microscopic techniques^[11,14a,15] in earlier studies) is shown in Figure 3. In the colloid array electrodeposited onto the patterned substrate whose pitch was 10% smaller than the ideal value of $(\sqrt{3}/2)D$ (schematic of Fig. 1b), adjacent particles within the same groove were forced apart by particles in neighboring rows. The lattice was no longer close-packed hexagonal. Accord-

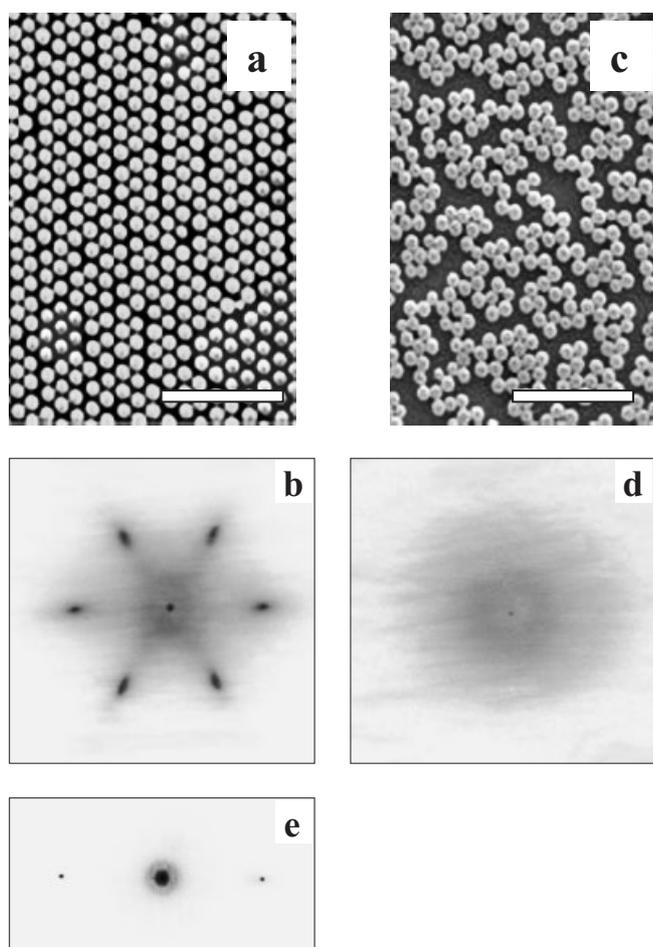


Figure 2. a) Scanning electron micrograph and b) laser diffraction photograph produced by the 2D colloid crystal grown by electrodeposition on a patterned substrate. A collimated laser beam ($\lambda=442$ nm) illuminated the crystal at normal incidence and a diffraction pattern was observed on a screen placed behind the sample. For clarity, the negative of the laser diffraction image is shown. c) Scanning electron micrograph and d) laser diffraction image obtained from a colloid crystal grown onto a nonpatterned ITO substrate. e) Laser diffraction pattern produced by the pattern alone. The scale bar is 5 μ m.

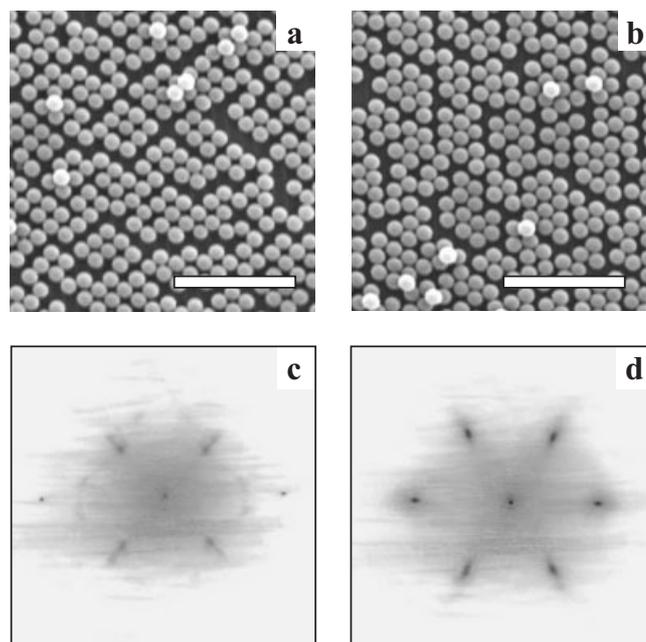


Figure 3. a) SEM image and b) laser diffraction photograph (negative) of a monolayer grown on a pattern with a pitch $\Lambda=(90\%)(\sqrt{3}/2)D$. The pattern ribs run from top to bottom. c) SEM and d) laser diffraction photograph of a two-dimensional colloid crystal grown on a pattern with $\Lambda=(110\%)(\sqrt{3}/2)D$. The scale bar is 5 μ m.

ingly, it produced a diffraction pattern with the shape of an irregular hexagon, since the particle row spacing was not the same in different directions. When the pitch was larger than the ideal value by 10 %, as in Figure 1c, gaps open between the rows of particles in adjacent grooves, since particles could no longer contact across many grooves. The laser diffraction pattern, however, still formed a regular hexagon because the size of the gaps parallel to the grooves and those perpendicular to the grooves were similar. SEM images also showed that some particles were not confined to the grooves in the first case, whereas all particles were in the grooves in the second case; accordingly, the diffraction pattern is sharper on the second sample.

The effect of surface patterning on three-dimensional (3D) colloidal crystals was examined on 7 ± 1 layer arrays grown by the meniscus method (details can be found in the Experimental section). Figure 4a shows an SEM image of a colloidal crystal grown onto a patterned substrate with $\Lambda = (\sqrt{3}/2)D$, and the ribs parallel to the direction of the colloidal crystal growth. Figure 4c shows the structure of the array grown on a blank substrate. On the basis of SEM imaging, both crystals feature good long-range order, with rows of particles oriented parallel to the growth direction. Careful examination of this sample, however, revealed several slightly misaligned domains (the inset of Figure 4c shows a boundary between two such

domains, with a misalignment angle of 17°). While this effect is not the focus of the present work, we point out that whereas the misaligned domains might have been missed by SEM analysis alone, laser diffraction unambiguously revealed the presence of such domains (Figs. 4b,d). The diffraction pattern for the crystal grown on the patterned substrate showed sharp and bright spots, similar to those obtained for monolayers of colloidal beads in Figure 2a. We note that an fcc lattice of spheres possesses only a threefold symmetry when viewed along the [111] direction (which is normal to the crystal surface), however a sixfold diffraction pattern can still be seen because the light is rapidly attenuated in the crystal (due to the relatively large index contrast, larger than that reported by Xia and co-workers^[16a]), preventing complete destructive interference between the light diffracted by different layers of particles. In contrast, the pattern produced by the crystal on the blank substrate consisted of large and blurred spots. In the second case, to a good approximation, the diffraction pattern could be considered as the average of the individual patterns produced by each domain in the crystal: misaligned domains diffract light in slightly different directions, causing an increase in the size of the diffraction spots.

These features were further put in evidence by plotting the variation in intensity in the diffraction pattern along a circle that intersects all six diffraction spots (Fig. 4f). For the sample

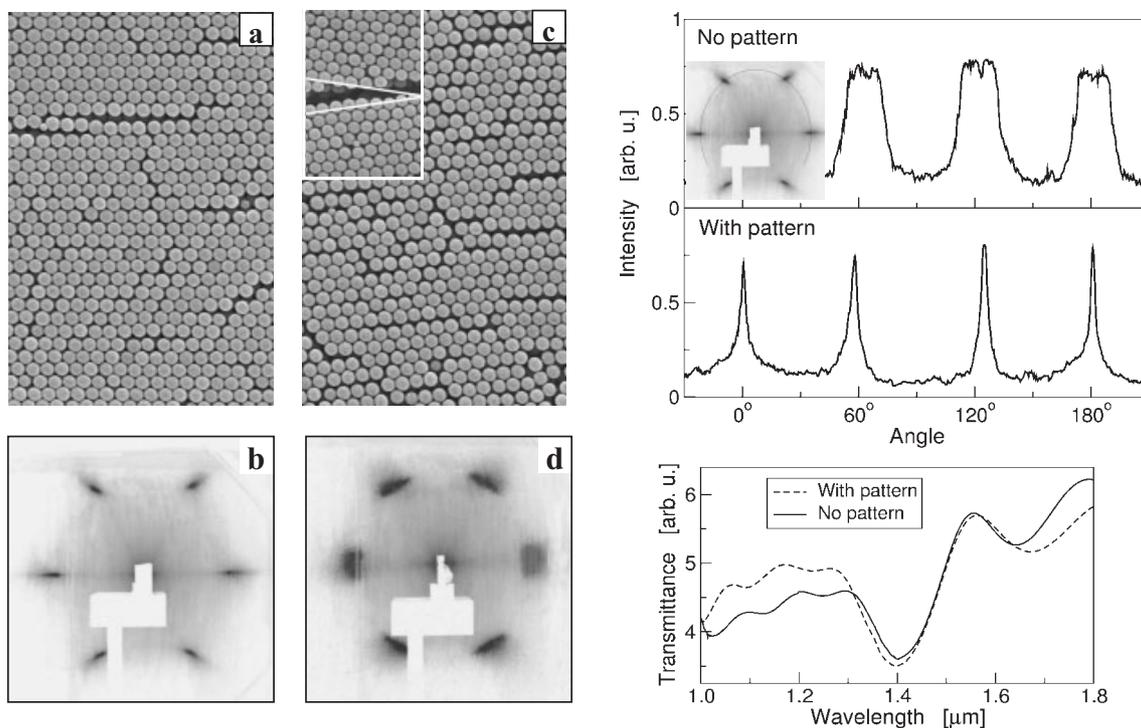


Figure 4. a) SEM and b) laser diffraction photograph (negative) of colloid crystals grown by the meniscus method [2c] on a silicon patterned substrate with ribs parallel to the direction of growth. The diffraction pattern was observed in reflection, since the silicon substrate did not permit transmission of light; the sample and its holder can be seen in front of the diffraction pattern. c) SEM image and d) laser diffraction photograph of a colloid crystal grown under identical conditions on a non-patterned substrate. The inset shows a grain boundary in the same sample: the orientation of the lattice in the two grains differ by an angle of 17° . The scale bar is $5 \mu\text{m}$. e) Intensity versus angle in the laser diffraction photos (b,d); the light intensity is measured along the circle arc shown in the inset. f) Transmittance of both samples (plotted on the same scale), measured at normal incidence with an infrared spectrophotometer.

grown on the patterned substrate, the angular extent of the diffraction spots (measured along the circle) is 3° , which comes from the finite size of the beam (about 1 mm in diameter) rather than from any imperfection of the lattice. Thus we infer that this sample is monocrystalline. On the sample grown onto the non-patterned substrate, the angular extent of the spots is 22° , which is the measure of the maximum misalignment of the domains in the crystal.

By contrast, a clear difference between the crystals grown on patterned and non-patterned substrates was not revealed in optical diffraction experiments.^[9,10] Figure 4e shows the transmission spectra for the same samples, measured at normal incidence. The spectra were almost identical, with a similar dip centered at $1.4 \mu\text{m}$ due to the first stop band in the [111] crystallographic direction. This similarity is explained by the fact that, in polycrystalline arrays, all domains have their (111) planes parallel to the surface; thus they share a common crystallographic axis. The (111) diffraction therefore takes place in the same direction and at the same wavelength for all domains, and is indistinguishable from the (111) diffraction of a monocrystal. Thus optical diffraction is sensitive to disorder only in a direction normal to the surface, while laser diffraction probes in-plane disorder caused by misaligned domains.

To summarize, we characterized colloidal crystals grown onto patterned substrates by microscopic imaging, optical diffraction, and laser diffraction. Our experiments revealed that laser diffraction studies can be efficiently used to probe long-range order in two- and three-dimensional crystals. This method is sensitive to small variations in the crystalline lattice induced by a mismatch between the pattern and the particle size, and to the presence of misaligned domains in polycrystalline colloid arrays. Laser diffraction was found to be the only suitable method to probe this kind of disorder. We have clearly shown that the surface pattern imposes a common, predetermined lattice orientation in colloidal crystals, which extends to the entire thickness of the crystal. The value of laser diffraction is increased by the fact that it is easy to implement, is non-destructive, takes only seconds to do, and is even amenable to the study of colloidal growth in situ.

Experimental

Colloid Particles: All experiments were performed with poly(methyl methacrylate) (PMMA) colloid particles ($D = 685 \text{ nm}$), with a polydispersity of 0.03, as measured by photon correlation spectroscopy (Zetasizer 3000, Malvern Instruments, UK). Latex particles were synthesized using surfactant-free starve-feed polymerization [24].

Preparation of Substrate Patterns: The substrates were either indium tin oxide (ITO) coated glass (for monolayers) or silicon (for multilayers). Shipley S1805 positive photoresist was diluted with Shipley Thinner P in a 3:2 ratio and spin-coated onto the substrate, to obtain a film about 80 nm thick. The film was exposed with a HeCd laser (35 mW, 442 nm); two beams, produced by a 50:50 beam splitter, were incident onto the sample at equal but opposite angles, θ , so that the film was exposed with a sinusoidal intensity profile with period $\Lambda = \lambda/(2 \sin \theta)$. The resist was developed in an alkaline solution.

Electrophoretic Deposition of Colloid Particles: The electrodeposition cell contained a brass electrode and an ITO-coated glass slide

separated by a 5 mm Teflon spacer. The cell was charged with a dispersion of PMMA particles ($D = 685 \text{ nm}$) in a mixture of water and ethanol (volume ratio 50:50). The concentration of colloid dispersions varied from 0.5 to 3 wt.-%. During electrodeposition a potential of 20 V was applied for 20 min. The negatively charged particles are depositing against gravity onto the positively charged anode. The resulting depositions were dried under an applied potential against gravity.

Deposition by the Meniscus Method [2c]: Silicon substrates were held vertically for 24 h in a vial containing a 0.5 wt.-% dispersion of colloid particles in water. The deposition took place at 80°C .

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