Template-directed colloidal crystallization

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Colloidal crystals are three-dimensional periodic structures formed from small particles suspended in solution. They have important technological uses as optical filters, switches, and materials with photonic band gaps, and they also provide convenient model systems for fundamental studies of crystallization and melting.

Unfortunately, applications of colloidal crystals are greatly restricted by practical difficulties encountered in synthesizing large single crystals with adjustable crystal orientation. Here we show that the slow sedimentation of colloidal particles onto a patterned substrate (or template) can direct the crystallization of bulk colloidal crystals, and so permit tailoring of the lattice structure, orientation and size of the resulting crystals: we refer to this process as 'colloidal epitaxy'. We also show that, by using silica spheres synthesized with a fluorescent core, the structural disorder in the colloidal crystals that result from an intentional lattice mismatch of the template can be studied by confocal microscopy, we suggest that colloidal epitaxy will open new ways to design and fabricate materials based on colloidal crystals and also allow quantitative studies of heterogeneous crystallization in real space.

Epitaxial growth of a thin crystalline layer onto a template that the growth of pure hexagonal close-packed (h.c.p.) crystals on a face-centred cubic (f.c.c.) crystal (Fig. 1A inset), a pure f.c.c. crystal was formed (Fig. 1B, C). By use of light scattering, we found that the f.c.c. crystal extended as far as the sedimented layer is thick (several millimetres). Also, the single crystals grew as large as the size of the pattern.

The reason for the formation of the f.c.c. crystal is that the (100) face can induce a three-dimensional structure with only one possible way the second layer can be placed on the holes created by the first layer. In other words, there is no twinning possibility along the growth direction (twinned crystals share a common set of atoms, but have a different orientation of their atomic lattices). A sphere dropping into a hole 300 nm deep loses 0.66 kT gravitational energy, where k is Boltzmann's constant and T the absolute temperature. Apparently, the small increased likelihood of a square symmetry as induced by the pattern shown in Fig. 1 is enough to start the crystal growth with the (100) plane instead of the (111) plane which is the denser crystal plane. For the growth of the crystal, the balance between diffusion and sedimentation is important. This balance is described by the Peclet number $Pe = \frac{m g R^2}{kT}$, where $m_g$ is the buoyant mass of a particle with radius $R$ and $g$ is the gravitational acceleration. $Pe$ is defined as the ratio of the time it takes a particle to diffuse over a distance $R$ and the time it takes to settle over the same distance; in this work $Pe = 1$. For the crystal layers close to the template, the situation is very different at the end of the growth. Here the weight of several thousand layers exerts such a pressure that osmotic pressure can only balance this at a crystal volume fraction experimentally indistinguishable from close packing, 0.74.

The growth of macroscopic f.c.c. single crystals on the (110) plane, which is even less dense than the (100) plane and also has no twinning directions, was also possible. These results make it likely that the growth of pure hexagonal close-packed (h.c.p.) crystals on a non-dense h.c.p. plane that has no associated twinning direction will be feasible as well.
In Fig. 2 and Table 1 we show the defect structures that result from a mismatch of the (100) f.c.c. lattice parameter \(a\) (expressed in particle diameters). At small mismatches (\(1.1 < a < 1.2\)), the first few layers start out with a perfect square symmetry, but in subsequent layers the symmetry changes into hexagonally packed and randomly stacked layers through the gradual introduction of defects similar to Fig. 2A and B. At larger mismatch (\(a \approx 1.2\)) the template imposes a square symmetry in the first layer only in certain bands (Fig. 2C). Again, several layers higher, random stacked (111) planes are found everywhere. A similar structure is found for heteroepitaxial growth of CdTe on GaAs(100). Because of a large mismatch (in one direction 14.6%) CdTe grows with (111) planes on the (100) template\(^9\). Of course, the interaction potential in this system is not hard-sphere-like, but the structural resemblances are striking. With still larger mismatch even the first layers is (defect-rich) hexagonal and the layers above stack again randomly, similar to Fig. 2D. For \(a = 1.2\) the square lattice is, after rotation of 45°, commensurate similar to Fig. 2A and B. At larger mismatch (\(a = 1.3\)) the template with the original (100) plane with \(d = 1\). The missing holes (Fig. 2E) impose a square symmetry in the first layer only in certain bands in the first layer do not prevent the growth of a full f.c.c. crystal on the template. Around this lattice mismatch, the defect structures are similar to those found close to \(a = 1\) (Table 1). It is interesting to note that at no lattice spacing was a body-centred (b.c.c.) crystal, 

**Table 1 Crystal structure formed on f.c.c. (100) plane as function of lattice spacing \(a\)**

<table>
<thead>
<tr>
<th>Symmetry of first layer</th>
<th>(a)</th>
<th>(1.0)</th>
<th>(1.1-1.2)</th>
<th>(1.2-1.3)</th>
<th>(1.3-1.4)</th>
<th>(1.4-1.5)</th>
<th>(1.5-2.0)</th>
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<tr>
<td>(Fig. 1B, C)</td>
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<table>
<thead>
<tr>
<th>Symmetry of tenth layer</th>
<th>(a)</th>
<th>(1.0)</th>
<th>(1.1-1.2)</th>
<th>(1.2-1.3)</th>
<th>(1.3-1.4)</th>
<th>(1.4-1.5)</th>
<th>(1.5-2.0)</th>
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<td>(Fig. 1B, C)</td>
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Here the lattice spacing \(a\) is given in multiples of the particle diameter. The symbols represent the symmetry of the crystalline layer: square (O), hexagonal (D), \(45^\circ\) rotated square (\(45^\circ\)), \(90^\circ\) rotated square (\(90^\circ\)).
Figure 2. Local crystal plane symmetry of crystals grown on f.c.c. (100) planes with different lattice spacing \(a\) (given in multiples of the particle diameter). A, Part of optical section showing (100) symmetry of the first and the (first visible) second layer of spheres on a template with \(a = 1.35\). B, As A, but ten layers above the template showing defect-rich hexagonal (111) symmetry. C, First layer above the template with \(a = 1.3\) showing bands of (111) symmetry (left) and (100) symmetry (right). D, First layer of spheres with \(a = 1.6\) showing a defect-rich hexagonal symmetry. E, First and second layers on a template with a close to \(2\) showing (100) symmetry, but rotated 45° compared to the crystal shown in Fig. 1. Scale bar, 5 \(\mu m\). The "rainbow" false-colour table allows for easy visualization of which particle belongs in which layer and also makes it possible to recognize the template.

which has a (100) crystal plane with the same symmetry, formed. Probably, the difference in free energy of the less-dense b.c.c. crystal is too far off to be induced by the template.

Figure 3 gives another example of the manipulative possibilities of colloidal epitaxy. A simple change in the spacing between two adjacent (100) f.c.c. planes determines whether the (100) plane continues over the unpatterned region or whether a stack of (111) planes will form between the two f.c.c. crystals. Structures like these are important for the creation of optical waveguides.

Here we have shown that with colloidal epitaxy it is possible to create large hard-sphere-like single crystals oriented along crystal directions without twinning. It has also been shown that tailored crystals with different crystal orientations can be grown next to each other. Hard-sphere-like crystals are important for applications, because after slow drying these crystals can be turned into connected dielectric structures. In the case of particles with a silica coating this can be achieved through a mild sintering around 100 °C which forms chemical siloxane bonds between the particles. Subsequently, the solvent can be changed without changing the dielectric structure.

Moreover, particles that interact with a hard-sphere-like potential provide the simplest model system with which to study quantitatively the defects that form after mismatching of the template lattice. Such mismatches can almost never be avoided in atomic heteroepitaxy. There is no reason, however, why our technique could not be extended to charged spheres as well. In this case ionizable groups would have to be present on the template. Larger templates could be more easily created with other methods like photolithography or, as recently has been demonstrated with feature sizes of 25 nm thickness, with imprint lithography. Further work is necessary to determine the influence of the sedimentation rate and volume-fraction on the epitaxial structures; preliminary experiments have already given indications of an interesting growth mechanism. For photonic bandgap materials it would be advantageous if the method could be extended to binary crystals as well. The use of a template could help systematic study of heterogeneous crystallization by observing the effects of the template under conditions at, or close to, homogeneous crystallization.

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