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# Electric Field-Reversible Three-Dimensional Colloidal Crystals

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We have developed a general method of ordering colloidal particles into three-dimensional crystals rapidly and reversibly using electric fields. The novel mechanisms involved appear to rely on a combination of induced dipole interactions and hydrodynamic flows to create close-packed, mechanically stable crystals. Because the effective interactions can be moderated using the applied field, colloids in a wide variety of size ranges can be crystallized. We show here the ordering of particles of diameter 200−450 nm and illustrate how the nucleation of these crystals can be directed through the selective application of the electric field. Since the time scale for crystallization is minutes, significantly faster than in previous methods, the crystallization method present here is expected to allow development of practical devices for photonics and other applications.

Depending on the nature of the interactions between individual particles, colloids will form a surprising variety of morphologies. For strongly attracting systems, for example, they will irreversibly aggregate into fractal structures.[1] In the opposite case of strongly repelling particles, similar systems will undergo an entropically driven disorder to order transition, forming colloidal crystals whose structure depends on the range of the repulsion, namely bcc for long-ranged[2−4] or fcc/Rhcp for short-ranged systems.[5−7] One of the technologically most compelling properties of these crystals is their ability to diffract visible light, a direct result of the length scales associated with these systems. Because of this and the ability of colloids to self-assemble, a number of researchers have attempted to take advantage of their optical properties for photonic applications, including photonic band gap materials[8−10] and diffraction-based sensors.[11,12] A number of significant limitations, however, have slowed the development of colloidal-crystal-based devices. The first is the difficulty in uncoupling particle−particle interactions, which are conventionally altered by modifying colloidal surface chemistry or solution properties, from the resulting crystal structure. Second, the structures that are created are not reversible over convenient time scales: colloidal crystals can take weeks to form.[2,13,14] In addition, once formed, these crystals can be exceedingly fragile; because they are typically created through long-ranged Coulombic interactions, they can have lattice spacings several times their diameter and any shear can destroy them. Attempts to create stable crystals whose spacings can be varied with time or condition have hitherto focused on locking in the structure using a matrix that can expand or contract in response to an environmental stimulus.[11,12]

For many desired applications, however, the ability to reversibly create crystals is desirable. Applications such as color displays where individual pixels must be switched is one example. To date, efforts to create reversible crystals have focused on two-dimensional systems[15−17] in the context of electrodeposition, where it has been shown than applied ac or dc electric fields will induce ordering in two dimensions. In this, the fields induce a strong attraction between particles causing a rapid aggregation into two-dimensional ordered domains. The effective interactions are due to electrokinetic flows induced by the applied electric fields and the presence of the colloids. In the dc field case, the effect is dominated by electroosmosis,[18] and in the ac field case, electrohydrodynamics dominates.[17,19] In previous work, we have shown that confinement can also play an important role in this process; if a second electrode is brought into close proximity, repulsions due

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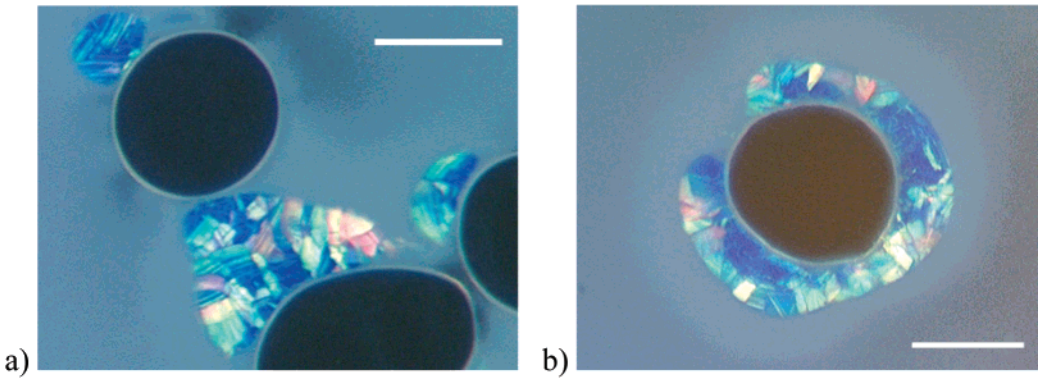


**Figure 1.** Colloidal polystyrene (300 nm) ordered through application of 12 V across the cell (the dark areas are air bubbles, the cell thickness is 8 $\mu$m, and the scale bars are 100 $\mu$m).

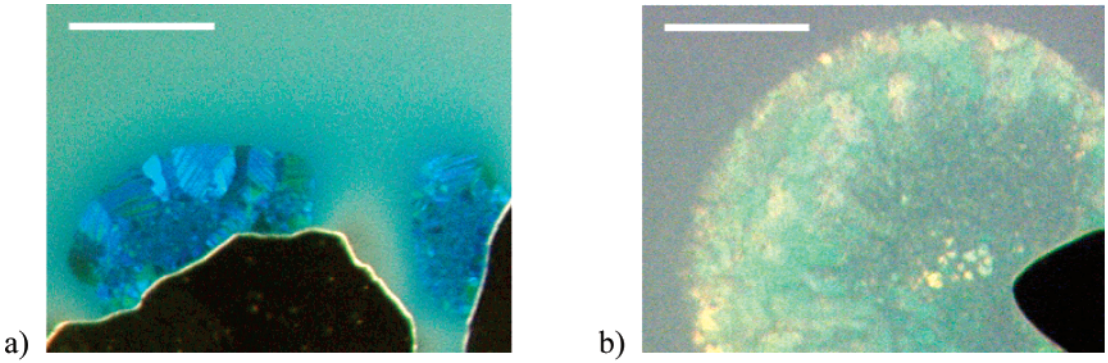


**Figure 2.** (a) Colloidal polystyrene (200 nm) ordered through conditions similar to those for Figure 1. (b) Ordered 450 nm colloids. The cell thicknesses are 7 $\mu$m, and the scale bars are 100 $\mu$m.

to dipole–dipole interactions can dominate.[20] By now varying the confinement and applied field strength, the range, strength, and sign of effective interactions can be independently tuned[21] and two-dimensional colloidal lattice morphology varied.[22]

By using relatively small colloidal systems in geometries of moderate confinement, we now show that electric fields can be used to not only create two-dimensional ordered systems but also quickly and reversibly create compact fully three-dimensional colloidal crystals. This is shown in Figure 1, where a colloidal crystal approximately 100 $\mu$m in width and 8 $\mu$m in thickness was created within 10 min after application of an ac field. In this system, crystal formation is fully reversible: upon removal of the field, these ordered structures melt into an isotropic colloidal suspension; upon reapplication of the field, crystals quickly re-form. These crystals also exhibit excellent optical properties, diffracting visible light with the differing crystal orientations visible. One reason for the well-developed diffraction is that these crystals are relatively thick, with approximately 40 lattice planes in the crystals of Figure 1. Also, colloidal particles of varying size can be crystallized using this approach. In Figure 2, colloids of both 200 and 450 nm diameter are crystallized through application of the electric field.

For our investigations, a wedge cell of very slight angle was used to study a variety of cell thicknesses within one experimental system. In this, two indium–tin oxide (ITO) coated glass slides, 3 in. by 1 in., were first coated with Triton X-100 and then placed, conductive sides facing, with a Kapton spacer of 12.5 $\mu$m between them at one end

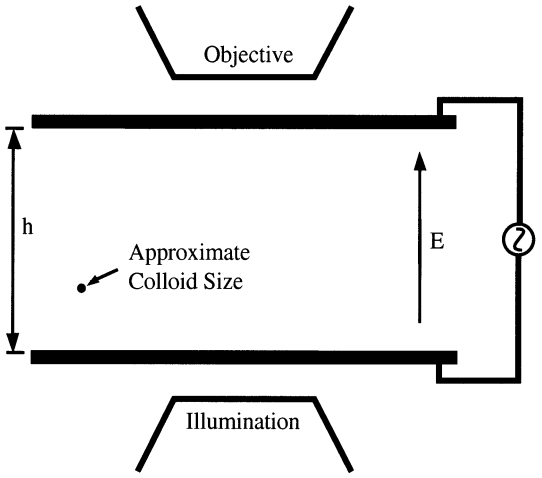


**Figure 3.** Sample cell illustration indicating colloid size relative to confinement dimension. The cell thickness, *h*, varies from 7 to 9 $\mu$m for the crystals shown in this paper.

and creating a cell whose thickness varies ~0.5 $\mu$m/mm. Poly(dimethylsiloxane) (PDMS) was cured around the slides to seal the edges together, leaving a chamber of air with an inlet and outlet for sample insertion. Sample solution was added to the cell via syringe, and more PDMS was used to seal the solution inside. The resulting cell is illustrated in Figure 3, where the sample is illuminated from below and viewed between crossed polarizers.

As purchased, carboxyl-coated polystyrene colloids of diameter ranging from 200 to 450 nm and surface charge 10–15 $\mu$C/cm$^2$ were centrifuged to high concentration and prepared in a $D_2O$/KCl solution of final ionic strength 0.001 M and volume fraction ~20%. Each solution consisted of ~0.5 wt % Triton X-100. Electric fields were applied to

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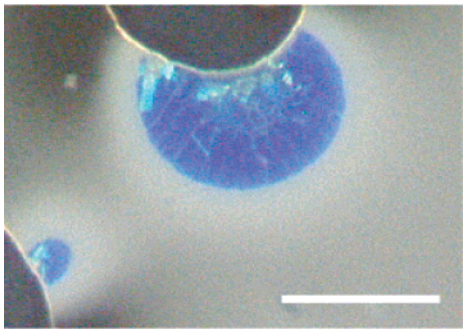

**Figure 4.** Colloidal crystal grown at 10 V using 300 nm colloidal polystyrene. Note the depletion layer of long range set up in the disordered colloidal fluid. The cell thickness is 8 $\mu$m, and the scale bar is 100 $\mu$m.

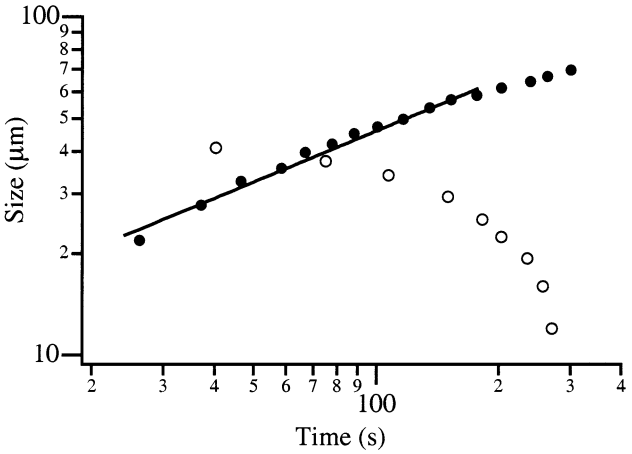


**Figure 5.** Example crystal growth ● and melting ○ kinetics (time = 0 corresponds to the application or removal of the external field). A line of slope $^1/_2$ fits the growth data well, indicating diffusion limitations for 300 nm colloids under an applied 10 V with a cell thickness of 8 $\mu$m.

the cell via wire connection to a function generator operating at 150 Hz with all voltages given as peak to peak.

The formation mechanism of these crystals appears to differ from those observed in other colloidal systems. In the present case, crystals nucleate and then grow by incorporation of colloids into crystal lattice positions on the growing surface. This is seen in Figure 4, where an 8 $\mu$m thick crystal has been formed from 300 nm colloids and a depletion layer of approximately 25 $\mu$m is readily apparent. As shown in Figure 5, the rate of growth of the crystal surface follows an approximate $t^{1/2}$ dependence, indicating diffusional rather than interfacial growth limitations.[23] The transport of particles is thus diffusive but driven by an electric field induced attraction. These attractions most likely include not only dipole−dipole but also significant electrohydrodynamic interactions, which have been clearly observed to dominate under moderate confinement between two electrodes, and grow as the electrode spacing increases.[21] These interactions likely play an important role here because the observed crystal growth does not display the pervasive perpendicular chain morphologies seen in electrorheological studies, in which dipole−dipole attractions dominate.[24] Once the crystal forms, however, the internal cohesion of the crystal may be predominantly stabilized by the dipole−dipole interaction, since flows are suppressed at the high volume fractions inside the crystals. This mechanism leads to tightly packed crystallites and has macroscopic consequences—these colloidal crystals are extremely robust. Strong tapping of the sample cell does not disrupt the crystal structure as seen in repulsively ordered colloidal crystals; the crystals presented here remain stable as long as the external field is applied. As also shown in Figure 5, once the field is removed, however, crystals do readily disappear, illustrating the reversible nature of these structures.

As seen in Figure 1, crystallites tend to form at available interfaces, including the air bubble surfaces present here. This may be due to dielectrophoretic concentration of the colloids set up by the strong lateral gradient in electric field arising from the interface between regions of high and low dielectric constant, creating nuclei and initiating growth. Once initiated, these crystals grow isotropically, independent of the air/water interface upon which they nucleated. Taking advantage of this, we have created other nucleation sites, both fixed sites that do not vary with time, as well as nucleation "sites" which are created through the manipulation of the spatial pattern of field strength. This is first seen in Figure 6a, where a thin polymer film is placed within the cell between the electrodes. Upon application of the electric field, the polymer acts to induce nucleation upon which subsequent growth proceeds. Figure 6b illustrates the use of applied

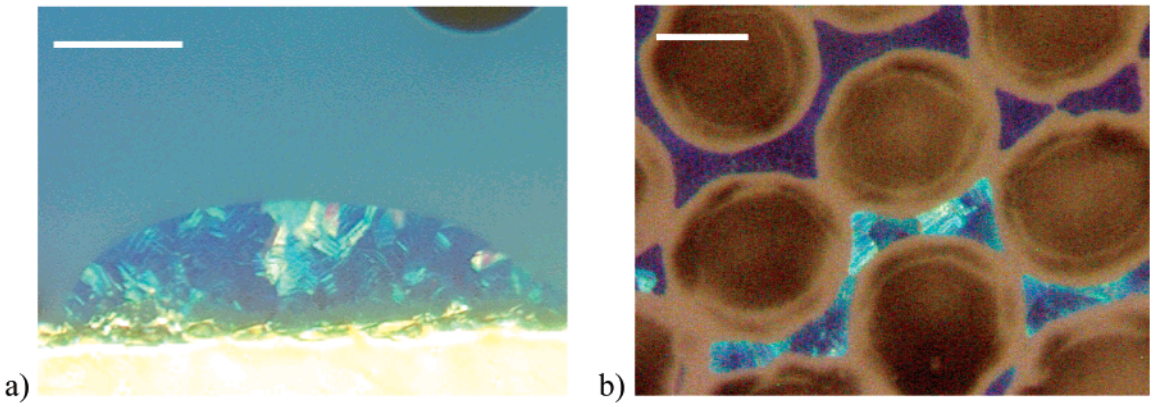


**Figure 6.** Crystal nucleation (a) using a static surface. A thin polymer region consisting of a 7.5 $\mu$m thick Kapton film (bottom surface of figure) was incorporated within the cell and used as a nucleating site. Shown here are 300 nm colloids under 12 V. (b) Using electric field concentration. In this image, circular regions of one ITO electrode were removed using photolithographic methods and acid etching. Once the resulting patterned ITO electrode was incorporated into the cell and upon application of 12 V, crystals rapidly formed in the regions between etched circles; upon removal of the field, the system returned to its original homogeneous state. The cell thicknesses are 9 $\mu$m, and the scale bars are 100 $\mu$m.

Ⓦ The rapid rate at which crystallization occurs is well shown in a short movie clip in Quicktime format (2× normal speed).

field variation to direct nucleation in specific regions. In this figure, circular regions of the electrode have been removed, creating interstitial regions of high field. It is in these regions that the colloidal crystals have homogeneously nucleated and subsequently grown together. This experiment illustrates that, by now using electrodes that allow the field distribution to be dynamically changed, one can "write" crystals in predetermined and variable patterns.

We have demonstrated that electric fields can be used to both nucleate and grow three-dimensional colloidal crystals in moderately confining geometries. The driving force for crystallization is very different in these systems from those traditionally used for the fabrication of colloidal crystals. Ordering is not left to occur as a result of the inherent colloidal interactions, but rather colloids are drawn together via field-controlled attractions which appear to be of both dipolar and electrohydrodynamic origin. The ability to fabricate colloidal crystals, not because of the classic interparticle interactions such as those described by DLVO, but despite them, is exciting because it may lead to the ordering of systems previously not amenable to crystallization. In addition, these crystals form reversibly and more rapidly than in previous approaches, making them outstanding candidates for photonic devices. Such applications, however, require the creation of relatively large single crystals, not the polycrystalline morphologies we have formed to date. In general, we have found that the nature of this novel three-dimensional crystallization process can be tuned via a number of factors including the applied voltage, frequency, and the spacing between electrodes. To investigate their specific roles and to determine how they can be used to influence the crystallization rate and morphologies that can be created, a more detailed study of the mechanisms involved is currently underway.

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