

Dielectrophoretic assembly of oriented and switchable two-dimensional photonic crystals

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We show that one- and two-dimensional crystals can be assembled from suspensions of latex or silica microspheres subjected to an alternating electric field in a gap between planar electrodes on a surface. These crystals, with areas above 25 mm^2 , are specifically oriented without the need for micropatterned templates. The order-disorder transitions take place within seconds and can be repeated tens of times by switching the field on and off. The particles accumulate on the surface between the electrodes due to the field gradient, align into rows along the field direction, and then crystallize into hexagonal arrays. The lattice spacings can be controlled via the electrostatic repulsion. © 2003 American Institute of Physics. [DOI: 10.1063/1.1541114]

Three-dimensional (3D) and two-dimensional (2D) photonic crystals, with periodicity comparable to the wavelength of light, promise to revolutionize the way light is manipulated on the microscale.¹ Such crystals can be fabricated by simple and inexpensive assembly of colloidal microspheres followed by replication of the structure into continuous matrices.²⁻⁴ The practical use of these self-assembled “opals,” however, has been inhibited for two major reasons: the assembly process is slow, often requiring as long as days to complete, and the resulting samples are typically conglomerates of many crystalline domains with random orientations. The orientation, and to some extent the symmetry, of the crystals can be controlled by the use of micropatterned templates, which guide the position of the first adjacent layer of particles and thus the growth of the crystal above it.⁵⁻⁸ The use of micropatterned templates is likely to increase, as inexpensive substrates are easily made via soft lithography.⁸ However, the templated assembly at present typically relies on sedimentation and diffusion,⁶ polymer addition,⁷ and capillary forces⁸ to put the particles in place, which can be slow or complex to control, so it is desirable to complement this technique with simpler and more rapid processes.

The crystal assembly can be accelerated by the use of electric fields. Two-dimensional colloidal crystals have been assembled in thin cells, where the particles are attracted towards the oppositely charged electrode in a constant field⁹⁻¹¹ or brought together in an alternating field.^{12,13} These methods, however, produce samples that have random orientation of some crystallographic axes and are usually polycrystalline. Structure formation in electrorheological fluids often involves the formation of 3D bct crystals.^{14,15} This effect can be used to anneal or to induce long-range alignment of 3D crystals formed by sedimentation,¹⁶ but the reliance on gravity restricts the speed and versatility of such methods.

We report here an assembly technique based on a cell in which both electrodes are deposited on the same side of the suspension and the particles assemble in the planar gap between them (Fig. 1). This geometry allows rapid electrically driven assembly of 2D crystals with long-range ordering and specific orientation. The concentration of the particles is enough to form a densely packed monolayer when attracted by the field towards the substrate ($\sim 0.5 \text{ vol } \%$ for radius $r = 0.5 \text{ } \mu\text{m}$). After a period ranging from less than a second to a few seconds, a bright diffraction color appears between the electrodes (see EPAPS Ref. 17). The excellent uniformity of the diffraction color demonstrates that the particles have assembled in a single crystal in which particle rows have the same orientation throughout the area between the electrodes (even though there may be some defects, misalignments, and empty or bilayer areas). When the electric field is switched off, the system relaxes to the original state of an opaque white dispersion. The crystal is recovered within seconds of

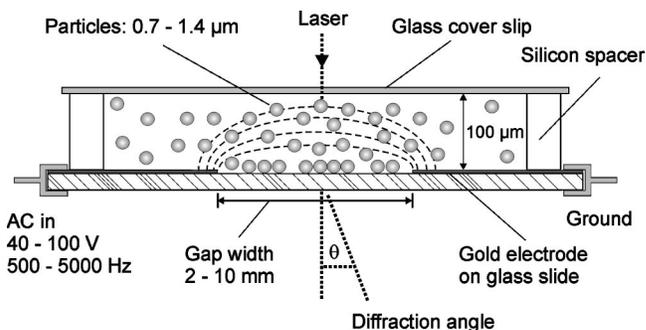


FIG. 1. Schematics of the experimental setup. The 2D particle array is assembled between the two gold planar electrodes in the thin chamber. The aqueous suspensions of latex microspheres stabilized by surface sulfate groups or silica particles with silanol surface groups is contained inside a silicon spacer covered with a glass cover slip. Alternating square-wave electric field is applied. The diffraction pattern from a 4 mW He-Ne laser is collected on a screen below.

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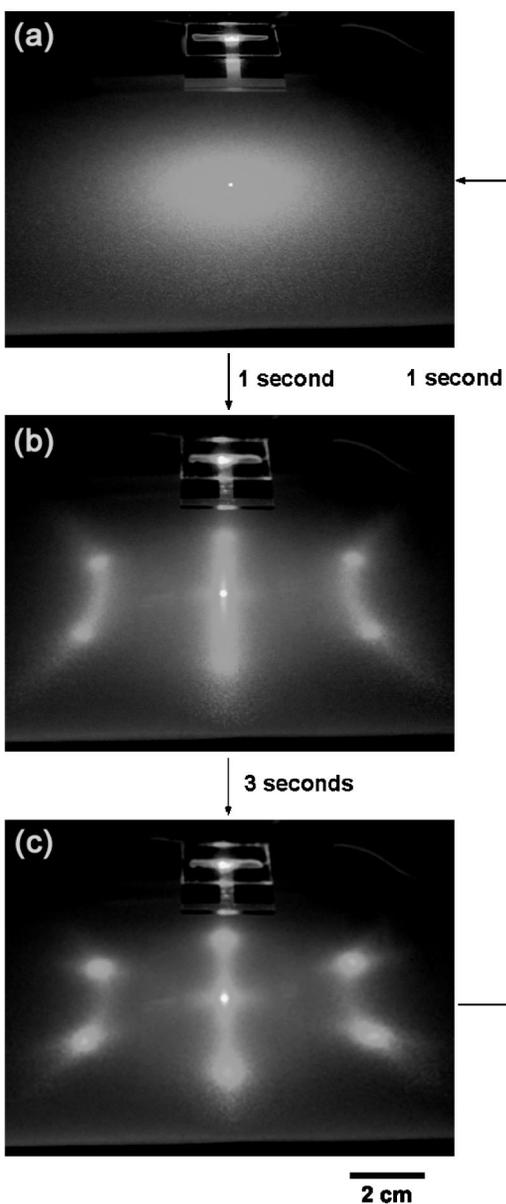


FIG. 2. Diffraction patterns obtained from a crystallized monolayer of $0.7\text{-}\mu\text{m}$ latex particles: (a) before the electric field is applied, disordered particles; (b) 1 s after voltage is applied, the particles align along the field; and (c) 3 s after voltage is applied, the particles have crystallized into a hexagonal, close-packed array.

the field being reapplied. This switching process can be repeated tens of times.

The structure of the crystal is characterized by diffraction of a transmitted laser beam (Fig. 2). The transition from diffuse scattering to vertical lines to hexagonal pattern is repeated with each application of the electric field. Thus, both the structure and orientation of each crystal remain uniform and invariable throughout the area between the electrodes, and are reproducibly recovered when the field is reapplied. The size of the ordered area ranges from $5\times 5\text{ mm}$ to more than $10\times 10\text{ mm}$, depending on the dimensions of the experimental cell. This size is orders of magnitude larger than the typical domain size of tens of micrometers encountered in multicrystal arrays obtained by conventional methods such as convective assembly or sedimentation.³

Additional information is obtained from high-

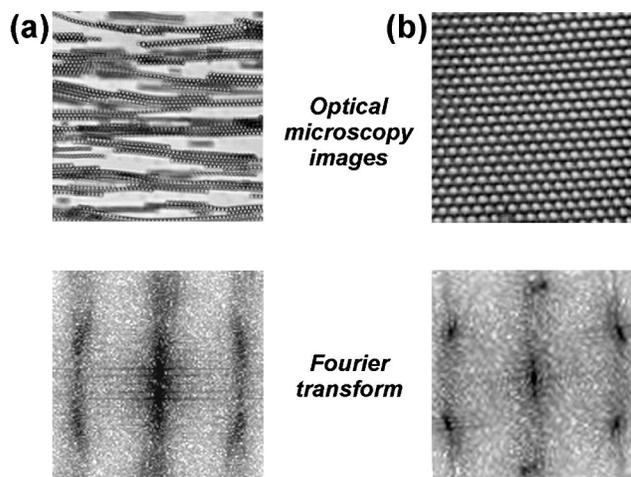


FIG. 3. High-magnification optical micrographs and schematic illustration of the stages of crystallization. (a) Immediately after the field is applied, the particles are attracted to the surface and form chains via the attraction of the field-induced dipoles. (b) A few seconds later, the chains attract each other and the microspheres crystallize into a single hexagonal array. In the presence of glycerol the process stops at the first stage. The fast Fourier transforms of the optical images simulate the diffraction patterns [compare with Figs. 2(b) and 2(c)]. A suspension of $1.4\text{-}\mu\text{m}$ latex particles was used.

magnification microscopy by observation of the dynamics of individual microspheres inside the cell during the assembly process (Fig. 3). The scattering patterns from 2D particle arrays can be simulated by the Fourier transform of their optical images. The pattern of three vertical lines from the photographs of the chains [Fig. 3(a)] is similar to the scattering pattern in Fig. 2(b), and confirms that the diffraction observed at the intermediate state arises from particle chains. The Fourier transform of the hexagonal crystal is a hexagonal array of spots [Fig. 3(b)] that echoes the macroscopically observed diffraction pattern at the end of the process [Fig. 2(c)]. Even though such defects as vacancies, bilayer spots, and minor misalignments can eventually be observed by microscopy, the overall quality and precise orientation predominate and lead to sharp and reproducible scattering patterns.

The center-to-center spacing h of a 2D crystal of point scatterers can be obtained via the von Laue equation from the angle of diffraction θ , for the first six diffraction spots $h = n\lambda_c / \sin \theta$, where n is an integer (equal to 1) and λ_c is the wavelength of the laser light. In order to take into account the refractive properties of the media, λ_c is corrected for the refractive index of the composite media in the scattering environment,¹⁸ and the measured values of θ are corrected for refraction of the scattered beams exiting the cell (using Snell's law). We measured the center-to-center spacings for three different-sized latex particles at three different concentrations of electrolyte in the aqueous phase (Table I).

TABLE I. Particle diameter and the center-to-center spacing (h) in the 2D crystals, calculated from the measured scattering angle θ .

Particle diameter [μm]	Lattice spacing in 10^{-3} M NaCl [μm]	Lattice spacing in 10^{-4} M NaCl [μm]	Lattice spacing in pure water [μm]
0.70	0.71	0.78	0.85
1.0	1.01	1.04	1.10
1.4	1.41	1.45	1.51

As expected for close-packed arrays, θ increases as the particle size decreases. When the particles are suspended in pure water, the calculated distance between particle centers (h) is about 10%–15% larger than that in an ideal, close-packed monolayer (d). The polystyrene microspheres are stabilized by negatively charged sulfate groups on their surface, so the separation may be attributed to repulsive electrostatic interactions between the particles in deionized water. Indeed, the difference between the particle diameter and the center-to-center distance decreases by about half when 10^{-4} M NaCl is added to the water phase, and almost disappears in 10^{-3} M NaCl. This is consistent with the Debye length of the counterionic atmosphere.¹⁹ Addition of electrolyte suppresses the electrostatic repulsion, and the particles come into almost complete contact. The controlled modulation of the electrostatic repulsion via the electrolyte concentration can be used as a means of tuning the lattice spacing in the crystals to any value between the particle diameter and the spacing in pure water with a precision of ≈ 10 nm.

The crystal assembly could be stopped at the intermediate stage of formation of chains by adding 40–60 vol % glycerol to the water phase. Notably, these chains, which are dielectrophoretically confined to the plane of the glass surface, act as a one-dimensional photonic crystal (diffraction grating), showing bright diffraction colors for inclined light beams falling in the direction of the chains, and no diffraction for beams perpendicular to the direction of the chains.

The origin of the observed phenomena can be explained on the basis of the combination of alternating field induced dipole–field and dipole–dipole particle interactions. This alternating field driven particle mobility is commonly called dielectrophoresis (DEP),^{20,21} and has been used previously in the manipulation of colloidal particles²² and their assembly into structures such as electrically conductive microwires,²³ or microscopic sensors.²⁴ The cell geometry used here creates a gradient of the field that attracts the particles to the gap via DEP. The particles are driven towards the substrate and assemble because of the interaction of their induced dipoles with the gradient of the field, instead of gravity or electrostatic attraction as in previous studies.^{8–11} The role of DEP was verified in an experiment in which the cell was rotated so that the electrodes were on top, and yet the crystal assembled as rapidly as usual. The particle chaining and crystallization processes subsequent to the DEP confinement bear some resemblance to the structure formation in 3D electrorheological fluids.^{14,15} However, the process here is not a 2D version of electrorheological crystallization. Because the solvent is water instead of organic oils, the source of the dipole moments is the mobile counterionic atmosphere, so the operating voltages, frequencies, and assembly times in the observed system are orders of magnitude smaller than the ones in 3D electrorheological suspensions.¹⁵ An unexpected aspect of the particle dynamics is the lateral attraction of the chains and their compression into 2D crystals. The fact that this effect is suppressed when the viscosity of the medium is increased (with glycerol) suggests that a possible explanation could involve electrohydrodynamic currents, broadly analogous to reports of particle assembly by electrophoretic fluxes created by low-frequency fields.¹³

In conclusion, dielectrophoresis between planar electrodes creates, within seconds, homogeneously aligned crystals over areas that are orders of magnitude larger than crystalline domains previously formed without templating. The method is not viewed as a substitute for the more elaborate and precise assembly techniques based on micropatterned templates or micromolds,^{5,6} but rather is as a complementary technique that allows simple and rapid formation of long-ranged colloidal crystals. The electrically switchable arrays act as rudimentary photonic devices and point the way to assembling a variety of photonic structures and materials. To make solid-state materials, the obtained arrays can be embedded in solid media by photopolymerization or sol-gel processes.

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¹⁷See EPAPS Document No. E-APPLAB-82-025305 for a color figure and movie. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from <ftp.aip.org> in the directory /epaps/. See the EPAPS homepage for more information.

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