Dynamic control of lattice spacing within colloidal crystals

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Abstract. In this study, we demonstrate reversible changes in lattice spacing within colloidal crystals controlled by an electric field. Crystals are assembled from negatively charged, monodisperse latex particles (945 nm) in an aqueous dispersion, by the application of an alternating electric field (1 kHz, ~35 kV m\(^{-1}\)). The lattice spacing within the colloidal crystals is determined by optical microscopy, laser and white light diffraction. Temporary dipoles induced by the electric field cause particles to aggregate into crystal structures; however, electrostatic repulsion prevents adjacent particles touching. One-dimensional (1D) and 2D crystals can be assembled, which act as diffraction gratings with electrically controllable diffraction properties. Two methods of tuning the lattice spacing are presented. In the first method, 1D crystal ‘strings’ are formed, where the effective lattice spacing is controlled by changing the orientation of the electric field and consequently the orientation of the strings. In the second method, a rotating electric field generates 2D crystals where lattice spacing is controlled by varying the field intensity.
1. Introduction

Structures with periodic changes in refractive index can form photonic crystals, which have a broad range of applications including lasers [1], optical circuits [2], optical fibres [3, 4], lenses [5, 6] and display devices [7]. Fabrication of photonic crystals is frequently achieved by the self-assembly of colloidal particles into crystals [8]. A key parameter of these colloidal photonic crystals is the lattice spacing, which influences the optical properties. Typically lattice spacing is determined by the diameter of close-packed, monodispersed spheres, which remains fixed once the crystal structure has formed [8].

The lattice spacing of colloidal particles polymerized within a hydrogel has previously been tuned by swelling and deswelling the hydrogel [9]. More recently, techniques involving polyelectrolyte multilayers have been used to create tunable defects in silica colloidal photonic crystals, where spacing changes between spheres in the crystal are controlled by solvent vapour pressure, light, temperature and redox cycling, thereby inducing changes in the photonic stop-band [10]. In another study by the same research group, tuning the lattice spacing of photonic crystals has been achieved by mechanical deformation of an elastic inverse-opal structure, templated from silica colloids [11]. This latter method achieves significant changes in lattice spacing, which produces changes in the position of the photonic crystal stop-band. In each case, the effect of changing the lattice spacing on the optical properties of the photonic crystal is clearly demonstrated and motivates further research in this area.

In an effort to find an alternative method of tuning lattice spacing, suitable for tuning reflected colour in an electronic display device, we have extended the work of Lumsdon et al [12], which demonstrated that alternating electric fields could rapidly assemble sub-micron spheres into crystal structures. The spheres in this study are dispersed in a low viscosity aqueous phase [12], and on application of an electric field are aggregated into crystals by induced dipoles associated with each particle. Nevertheless, because the latex particles in this study [12] are negatively charged, electrostatic forces prevent the particle surfaces from touching [13]. Although Lumsdon et al [12] showed that lattice spacing could be controlled by changing electrolyte concentration and therefore the range of electrostatic repulsion (characterized by the Debye length), control of lattice spacing by a change in field intensity was not demonstrated [12].

In this study, we investigate a similar experimental system to Lumsdon et al [12] but importantly we demonstrate significant changes in lattice spacing induced by changes in the electric field. We also employ a four-electrode rotating electric field to fully control
two dimensional (2D) crystals. Particles with a diameter of 945 nm are used, so that direct measurements of lattice spacing can be determined optically, which confirm the changes in lattice spacing calculated from laser and white light diffraction. Although the colloidal crystals we generate in this study will possess the characteristic stop-bands associated with photonic crystals, the measurement is problematic because of the limited thickness of the crystals (we would expect to see stop-bands in the infra-red for propagation in the plane of the crystals). Therefore, we have focused on demonstrating the range of lattice tunability, as determined by diffraction effects, with a view to applying the principles to generate a larger 3D photonic crystal with a tunable stop-band in future study.

2. Experimental materials and methods

Colloidal crystals have been assembled with polystyrene latex particles synthesized using a standard technique [14]. A particle electrophoretic mobility of \(-5.38 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}\) in 0.01 m M KCl was determined using a Brookhaven Zetaplus lightscattering instrument. Analysis of scanning electron microscope images (Jeol JSM-6330F) revealed an average diameter of 0.945 \(\mu\text{m}\) (standard deviation 22 nm). Experiments were performed with dilute aqueous suspensions (0.5–1.5 wt\%) with a conductivity of less than 0.5 \(\mu\text{S cm}^{-1}\).

A schematic of the experimental equipment is given in figure 1. Observations were made in the central region between four lithographically patterned, indium tin oxide electrodes. The four
coplanar electrodes were connected to two signal amplifiers outputting sinusoidal alternating voltages with a frequency of 1000 Hz (figure 1(a)). Typically this arrangement produced field strengths between 15 and 80 kV_{rms} m^{-1}, causing the particles to arrange into 1D crystal ‘chains’ or hexagonal close packed (HCP) 2D crystals, depending on the relative magnitude and phase of the applied voltages. Measurements were performed with 10 µl of latex particle suspension placed between the electrodes and covered with a standard microscope coverslip. The sheet resistance of the ITO electrodes was of order 15 Ω/square and resistance between any two electrodes was greater than 10 MΩ with the suspension present. Positive phase shifts, referred to later in the text, indicate that signal amplifier 1 is leading signal amplifier 2.

Diffraction patterns were produced by the crystals when illuminated by laser light of 531 nm wavelength (Swutech DPGL-3005) normal to the electrode surface. The patterns were imaged using a screen 20 mm from the electrode surface (figure 1(b)). Diffracted colours from white light were imaged via a colour video CCD camera and optical microscope fitted with a low numerical aperture objective lens (NA 0.055). The sample was illuminated with collimated white light incident at 33° (figure 1(c)).

High resolution optical images, used for directly measuring particle separations, were achieved using the same microscope fitted with a high power objective lens (Mitutoyo M Plan Apo 100x/0.7), with the sample backlit by white light. Measurements were calibrated using a stage micrometer (Agar L4202L).

3. General observations

Video 1 demonstrates crystal structures formed by a sequence of electric field configurations that are summarized in the ‘Guide to Videos’. The following paragraphs detail the observations at each stage of the video and will be easier to understand if video 1 is viewed first.

Without any electric field applied, the random Brownian motion of the particles could be clearly observed, and the particles did not aggregate (video 1, 0–1 s). When only one signal amplifier was operating, the particles spontaneously formed 1D crystals that resembled a flexible ‘chain of pearls’. As more chains formed with time, adjacent chains periodically drifted together to form HCP 2D crystal structures (video 1, 1–11 s). We observed that the chains formed in a non-rotating alternating field were aligned with the predicted field lines. With only signal amplifier 2 (see figure 1(a)) operating vertical chains of particles formed (video 1, 1–11 s). Switching to only signal amplifier 1 operating, caused a rapid reordering of particles into horizontal chains (video 1, 11–21 s). The field direction in the central region between the electrodes could be predicted by a simple vector addition of the theoretical fields produced by each amplifier. With both signal amplifiers operating with a relative phase shift of 0°, diagonal chains of particles formed (video 1, 21–31 s).

By adjusting the relative phase difference between the signals applied to amplifiers 1 and 2, a rotating electric field of constant magnitude could be generated. At field strengths above 15 kV_{rms} m^{-1} this caused 2D crystals to rapidly assemble, and with a phase difference of 90° between the amplifiers, produced a clockwise rotation of the crystals (video 1, 31–41 s). With a phase difference of 180°, diagonal strings formed again (video 1, 41–51 s), which were perpendicular to those formed with a phase difference of 0°. Counter-clockwise rotation of crystals was observed with a phase difference of 270° (video 1, 51–61 s). Furthermore, spinning of the crystals could be prevented within a rotating field by alternating the relative phase difference.
between 90° and 270° every cycle (video 1 61–71 s), a method used while measuring the particle spacing.

When the electric field was removed, particles within the crystal structures immediately redispersed under Brownian motion (video 1, 51–61 s). However, even with the electric field applied, some random motion of particles within the crystals was observed. Random motion of particles within the crystals was higher for 1D chains than within 2D crystals. Particles on the perimeter of 2D crystals exhibited more random motion than those inside the crystal, and in the case of rotating electric fields resulted in particles moving around the perimeter of the 2D crystals. These observations reflect the strength of dipole attractions and confinement of the particles, which can diminish towards the exterior of crystal structures ([15], p. 163).

The observations that have been reported relate to video 1. However, corresponding videos of white light diffraction and laser diffraction patterns are also provided in video 2 and video 3 respectively. Videos 2 and 3 were generated with the same sequence of electric fields, and complement the observations of video 1.

As identified by Lumsdon et al [12], charged particles within an alternating electric field are attracted towards each other by the action of temporary dipoles, induced by the electric field. Similar to their report [12], we also observed that at alternating frequencies above approximately 100 Hz, inertia of the particles prevents significant movement due to electrophoresis. However, as frequencies increase beyond 10 kHz the strength of interacting dipoles decreases and crystal structures no longer form. This suggests that dipole formation occurs due to counter-ion movement in the diffuse electrical double layer surrounding the particles [16], a mechanism not widely studied in the literature. The precise origin and mechanism of the dipole formation in the present case is beyond the scope of this paper. However, we are currently addressing this complex problem.

4. Lattice spacing in 1D crystal chains

Figure 2 demonstrates the formation of vertical and diagonal strings, and the corresponding transmitted diffraction pattern from a laser light source and a white light source. With the collimated white light source at a 33° incident angle (in-plane with electrodes C and D see figure 1(a)), the vertical strings with a string angle of 0° (θs, figure 1) transmit red/orange light and the diagonal strings (θs = 45°) transmit blue light, when viewed from an incident angle of 90° with a low numerical aperture objective lens (0.055). Videos 1–3 demonstrate that the changes in string angle are rapid, occurring within a tenth of a second. Laser diffraction patterns in figure 1 reveal that three lines are generated, orientated at 90° to the strings at every string angle.

We can explain these observations by simple diffraction theory. For a grating period L and normal illumination by light of wavelength λ, the mth order diffracted angle θ, measured from the normal is given by the grating equation:

\[ m \lambda = L \sin \theta. \]  \hspace{1cm} (1)

In figures 2(b) and (c), the particles experience a non-rotating, alternating electric field of 36 kVrms m⁻¹. Analysis of the corresponding laser diffraction pattern reveals a first order diffraction angle of 27°. Using equation (1), this results in a particle centre separation of 1170 nm within the string, which is in agreement with direct optical measurements of the particle spacing.

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**Figure 2.** Video frames and diffraction patterns of crystals formed in the central region between quadrupole electrodes. Upper row: laser diffraction patterns, scale bar 1 cm. Middle row: white light diffraction, scale bar 200 µm, electrodes positions are labelled A, B, C and D. Lower row: optical micrographs, scale bar 10 µm. Column (a) shows images taken when no electric field is applied. Column (b) shows images taken when an electric field of strength 36 kVrms m$^{-1}$ is generated by applying an alternating voltage to electrodes C–D only. Column (c) shows images taken when an electric field of strength 36 kVrms m$^{-1}$ is generated by applying in-phase alternating voltages of 25.5 kVrms m$^{-1}$ to both electrodes C–D and A–B.

In figure 2(b), the observation of colour is made when the incident angle of transmitted white light is 33°. Using equation (1), this corresponds to a first order diffraction of light with a wavelength of 637 nm, which accounts for the red/orange colour observed. When the string angle is 45°, the effective grating period is reduced by a factor of $\cos(\theta_s)$ so the calculated wavelength is 450 nm, accounting for the blue colour observed in figure 2(c).

Various colours are also produced around the electrode tips. Since the electric field lines radiate perpendicularly from the semi-circular electrode tips, a range of string angles are produced giving rise to a range of observed colours. These images include black regions, which may correspond to first order diffraction in the ultra-violet wavelengths that are not visible; this is particularly evident around electrodes A and B in video 2 (11–21 s). The white colour observed in the central region of this particular video segment represents diffraction from the randomized spacing between adjacent strings with respect to the observation point.

5. **Lattice spacing in 2D crystals**

Particle spacing within HCP 2D crystals was measured at various field strengths in a rotating field by both direct measurement of calibrated, high resolution optical images, and by analysis...
Figure 3. Centre-to-centre spacing of adjacent particles within HCP crystals versus field strength. ‘○’ denote lattice spacings calculated from laser diffraction patterns using equation (1). ‘●’ denote measurements from optical microscopy images. Error bars indicate 95% confidence intervals.

Both measurements revealed that the centre to centre separation of adjacent particles in the crystal could be varied from 1300 to 1150 nm (figure 3) by increasing the field strength. This corresponds to surface separations between adjacent particles of 355 and 205 nm. Below field intensities of 15 kV\textsubscript{rms} m\textsuperscript{−1}, no regular crystal structures were observed, although localized clustering of particles was observed between 12.75 and 15 kV\textsubscript{rms} m\textsuperscript{−1}. Above 80 kV\textsubscript{rms} m\textsuperscript{−1} electrolysis and electrohydrodynamic flows [17] disrupted the formation of crystals. Figures 4(b) and (c) show the effects of changing the field intensity between 20 kV\textsubscript{rms} m\textsuperscript{−1} and 80 kV\textsubscript{rms} m\textsuperscript{−1}. A corresponding video shows the effect of changing field strength on optically observed lattice spacing (video 4).

When calculating the spacing for figure 3 from optical images of the crystals, it must first be appreciated that HCP crystals can generate first order diffraction effects between adjacent rows of particles, as well as between adjacent particles (as is the case for 1D strings). The centre-to-centre spacing of particles in a HCP crystal must be multiplied by a factor of sine (60°) to obtain the row spacing. By analysing the first order laser diffraction patterns of HCP crystals, where diffraction from adjacent rows predominated, a diffraction angle could be determined, and using equation (1) the associated row spacing was obtained. Dividing the row spacing by the sine (60°) factor results in the centre-to-centre spacing of adjacent particles (lattice spacing), which is plotted against field strength in figure 3. The agreement with calibrated optical measurements is within experimental error and verifies that the lattice spacing can be varied by 150 nm.

Figure 4 demonstrates the effects of changing the lattice spacing from 1270 nm (figure 4(b)), to 1140 nm (figure 4(c)). The predominant first order laser diffraction patterns from HCP crystal monolayers consist of six dots arranged in a hexagon, surrounding a central dot associated with zero order diffraction. Because the diameter of the laser beam is approximately 100 µm, diffraction from multiple crystals with different orientations are superimposed, giving the
In stages 5 and 7 of video 2 (31–41 and 51–61 s), the 2D crystals are rotating, and because the diffraction from each crystal is constantly varying between diffraction from adjacent rows or particles, the crystals appear to flash. Note that in the transition from stage 7 and 8 of video 2 (61 s), when rotation of crystals is prevented, the flashing stops immediately.
Decreases in lattice spacing generally occur within two video frames which cover a 66 ms time period, although increases in lattice spacing seem significantly slower, particularly at low-field strengths (video 4). This observation is related to the strength of the driving force which moves particles to their equilibrium positions, and its origin is related to the phenomena of secondary potential energy minima associated with reversible aggregation ([18], p. 193). Preliminary calculations of potential energy minima between two particles suggest that deep, steep-sided potential energy ‘wells’ dictate the equilibrium position of particles at high field strength, whereas relatively shallow potential energy wells occur at low field strength. A consequence of this is that changes from small to large lattice spacings are driven by weaker forces due to the smaller gradient of the potential energy well.

6. Discussion and conclusion

In this study, we have shown that the lattice spacing within colloidal crystals can be dynamically and reversibly tuned over a significant range. This study builds on the findings of Lumsdon et al [12] who only controlled lattice spacing by changes in electrolyte concentration for a similar experimental system. Our first method of tuning the effective lattice spacing involves a simple geometric rotation of 1D crystal strings, and is capable of filtering white light over the entire visible spectrum for a given observation and illumination angle. The second method of tuning the lattice spacing within 2D colloidal crystals is achieved by changes in electric field strength of a rotating electric field.

The rotation of particles in a rotating electric field (electrorotation) has been observed for over a hundred years, and is commonly used for cell characterization [15]. Although there have been recent studies involving electrorotation of single particles [19, 20], pairs of particles [21] and aggregates [22], the formation of colloidal crystals in a rotating field does not appear to have been reported. A rotating electric field is frequently generated by the use of a quadrupole electrode [15]. Interestingly, the use of coplanar quadrupole electrodes has been used to assemble 2D and 3D crystal structures previously, although this has been performed using negative dielectrophoretic forces at high frequency (3 MHz) to cluster the particles into a confined region [23].

In our study, we report that changes in electric field intensity induce changes in lattice spacing. Changes in field intensity have previously been reported to change the lattice spacing within 1D crystal strings, and the phase of 3D crystals [24]. The key difference in our study is the use of a 2D rotating field, which allows the 2D HCP crystal phase to remain constant, while lattice spacing is changed. By comparison, the application of a 1D alternating field to a 3D crystal causes crystal phase changes [24]. Electrically induced changes in lattice spacing are highly desirable for achieving tunability of stop-bands within photonic crystals. The findings presented here may help to achieve this goal.

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