

Monitoring Defect Formation in Colloidal Self Assembly using Photonic Bandgap Variations

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Abstract —Defect control in colloidal crystals is essential for these nanostructures to be effective as photonic bandgap (PBG) materials. We have used in-situ monitoring of the PBG of a colloidal crystal to study the structural changes during colloidal self assembly, with a focus on the formation of macroscopic defects such as cracks. These findings allow us to model the final stages of colloidal self assembly and explain the formation of growth defects in colloidal crystal. Our model suggests that cracks are intrinsic to self assembly growth methods. . However, by tuning the interaction potential between the colloids, it is possible to minimize the cracks in colloidal crystals.

Index Terms —Colloid, Defects, Photonic bandgap, Self assembly.

I. INTRODUCTION

COLLOIDAL self assembly (CSA) is a bottom-up method of fabricating highly ordered nanostructures. This method has the advantage over conventional top-down methods as it is highly parallel. These nanostructures, known as colloidal crystals, have enormous potential for photonic [1]-[3], and biological [4] applications. For example, it has been shown that a complete 3D photonic bandgap (PBG) can exist in colloidal crystals [5] The PBG is a band of wavelength of light that is forbidden to propagate in structures with a periodic variation of the dielectric constant. These PBG materials have been used in various optical applications such as enhanced LEDs [6], waveguides [7] and suppression of emission from quantum dots [8]. However, several hurdles still remain to be overcome before colloidal crystal can be used as PBG material. The defect density in colloidal crystal must be sufficiently low as these defects can introduce energy states within the bandgap and degrade the quality of the PBG. At the same time, controlled defects have to be

introduced into the structures because optical applications of PBG typically require intentional doping of defects. Despite these challenges, colloidal self assembly remains extremely attractive as it is more efficient than conventional lithographic methods. In order to overcome the hurdles, defect formation in colloidal crystal has to be explained and controlled. In this report, the in-situ monitoring of the PBG variation is used to explain the formation of cracks in colloidal crystal. The in-situ PBG change is associated with changes in the structure of the colloidal crystal which helps to explain the formation of cracks.

Certain defects are consistently observed in colloidal crystal. For example, stacking faults are found to be intrinsic to colloidal crystals [9], [10]. This is because the energy difference between the HCP and FCC structure is small, typically 10^{-3} kT per particle in a hard sphere model [11]. Stacking faults has been shown to widen the PBG in FCC structures [10]. Another growth defects that are consistently observed are macroscopic cracks in the colloidal crystals. The growth of the crack in colloidal suspension has been observed in various other studies [12], [13]. However, the microscopic origin of cracking of colloidal crystal is still not well understood. Various models have been proposed to describe the crack morphology qualitatively but there is sparse quantitative analysis of the theory to correlate to the numerous controlled experiments. It is imperative to understand the microscopic origin of stresses in colloidal crystals and extract quantitative data about the stresses. The possibility of extracting the stresses in drying colloidal crystal is the focus of this paper. We demonstrate here that it is possible to monitor the structural changes in-situ and obtain a model of crack formation in colloidal crystal. The model will provide means to derive quantitative understanding of the stresses in drying colloidal crystals. It also opens up the possibility of controlling the cracks by tuning the colloid interaction.

II. EXPERIMENTAL SECTION

The colloids used are polystyrene suspended in water.

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The colloids are synthesized by emulsion polymerization. The diameter of the colloids measured by light scattering method is 180nm. The initial volume fraction of the colloids is 0.023. The initial appearance is white in colour as the colloids of this size scatter visible light randomly. The glass substrate on which colloid is deposited is a colourless borosilicate glass cover slide. This substrate has no absorption in the visible range and has a constant light transmittance of 90% for wavelength of light between 350 and 750 nm. The flat glass substrate ensure that the (111) plane of the colloidal crystal is parallel to the substrate.

A sessile drop configuration is used to investigate the CSA process. For a sessile drop of colloidal suspension, a ring shaped deposit is formed after drying. Under the scanning electron microscope (SEM), the deposit is found to be an ordered close-packed structure. Throughout the drying process, the contact line is found to be pinned with an initial contact angle of 30° . As the volume of the drop decreases with drying, the contact angle is found to be decreasing. With this static characteristic at the edge of the sessile drop, it is possible to monitor the reflectance spectrum with a static optical setup.

For the measurement of the reflectance spectra, the incident light is from an optical fiber (200 μ m diameter) that is coupled to a UV-Vis light source (Deuterium-Tungsten halogen type). The light is deflected onto the sample by a series of mirrors which can be rotated to measure the reflectance spectra at various angles. The reflected light is collected with another similar optical fiber to a spectrometer. A series of runs are done at different angle of incidence with each run done at a constant angle of incidence. Throughout each run, the reflectance spectra are collected at one minute intervals until the sessile drop is totally dried after 3 hours.

III. RESULTS AND DISCUSSION

The photonic bandgap (PBG) is used to monitor the changes in the structure of the colloidal crystal. The main method used is the in-situ reflectance spectroscopy. However, since the colloids used in our experiment are of sizes in the optical range, direct observation of the PBG change with optical microscope is done initially. The PBG changes manifest as colour changes under the optical microscope in reflection mode. Surprisingly, cracks are observed to form at the same time that the colour change is occurring.

The edge of a drying sessile drop of colloid suspension is observed under the optical microscope as it is where the colloidal crystal forms in a sessile drop. Initially, this region appears white but after a while, an orange region starts to form from the edge of the drop towards the center. Near the end of drying, changes in the PBG occur and an optical snapshot of the crack formation is shown in Fig. 1. Three regions of different colours can be seen in this

picture. Initially, the whole region is orange in colour and free of any cracks. After a while, parallel cracks starts to form perpendicularly to the drying front. The cracks grow inwardly towards the center of the drop in an intermittent manner. After a while, a green band starts to form at the edge and propagate behind the first crack front. At the same time, secondary cracks which are perpendicular to the initial cracks form in this green band. The change from red to green shows that the PBG has shifted towards the blue edge. After the green band pass through the colloidal crystal, a stable blue region is left behind. This confirms that the PBG has shifted even further into shorter wavelengths. As the PBG is directly related to the structure of the colloidal crystal, this observation suggests that there are changes in the structure as the cracks are formed.

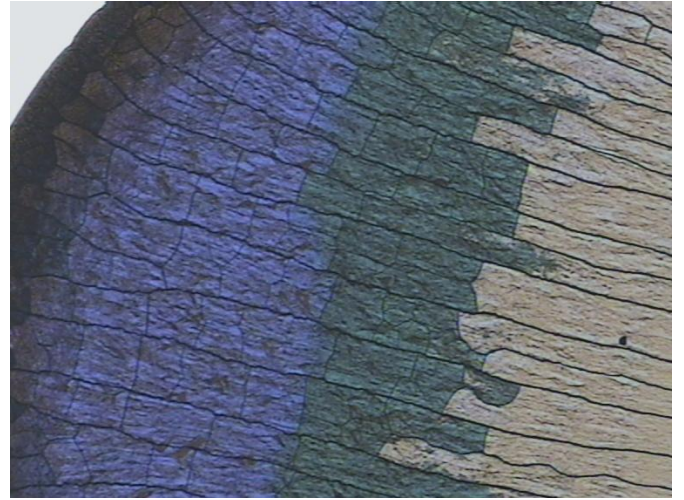


Fig. 1. Optical microscope image showing the colour changes during the cracking process. Notice the colour change from orange to green to blue. This occurs within 30 seconds.

In order to quantify the change in the PBG, the reflectance spectrum from the edge of the sessile drop is monitored in-situ. The typical evolution of the reflection spectrum is shown in Fig. 2. This is measured from the beginning when the drop edge has stabilized to the end when the drop is totally dried.

A few characteristics can be identified and help to reveal the dynamics of CSA. After the drop is deposited on the substrate and reaches equilibrium, the reflectance spectrum shows no distinct peak. This is expected as the colloid suspension is homogenous. The uniform scattering of light in a homogenous colloid suspension prevents a dominant peak from appearing. As the drop dries up, a small peak starts to appear in the spectrum gradually. This peak is due to the initial appearance of a PBG structure in the colloid suspension. Using a constant evaporation rate as reported by Popov [14] for a sessile drop, the volume fraction after this induction period is approximately 0.142. After further drying, the peak position shifts toward the shorter wavelength and increases in intensity. Finally, when the drop is totally dried up, the reflectance peak stabilizes at a

fixed position and achieves the final ordered structure. It has been shown in various theoretical and experimental studies that when the volume fraction of a colloid suspension reaches a threshold value, the FCC structure becomes the stable structure and the colloids start to agglomerate. Thus, the ordered structure that forms in the initial stage of ordering is a FCC colloidal crystal.

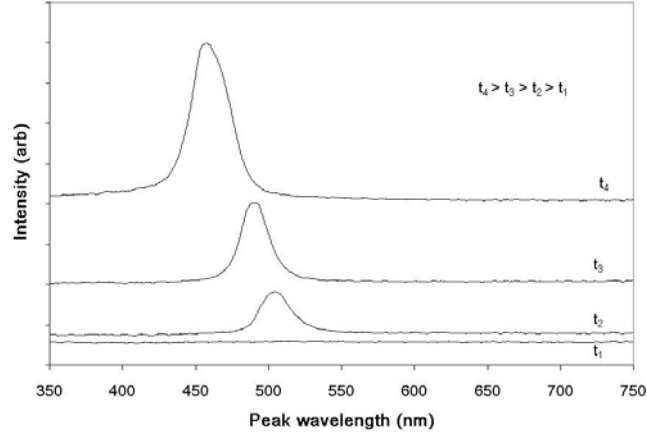


Fig. 2 Time evolution of the reflectance spectrum of a drying colloidal crystal. Peak shifts to the blue region of the spectrum and increase in intensity. The spectra are offset for clarity and share the same baseline.

For a FCC colloidal crystal, the shift of the reflectance peak is related to the change in the lattice parameter of this ordered structure. When the light is incident on the FCC colloidal crystal the relation between the reflection peak position and the lattice parameter can be modeled by a modified Bragg's law [15],

$$\lambda_{\max} = 2d\sqrt{n^2(\lambda) - \sin^2 \theta} \quad (1)$$

where θ is the angle of incidence and $n(\lambda)$ is a effective refractive index. The spacing between each (111) plane is $d = 0.577a$ where a is the lattice parameter. The effective refractive index, $n(\lambda)$, is taken as,

$$n(\lambda) = n_{\text{medium}}(1 - f) + n_{\text{colloid}}(\lambda)f \quad (2)$$

where f is the packing fraction of the structure. ($f=0.74$ for close packed structures) In the same medium, the peak wavelength is proportional to the lattice constant of the FCC colloidal crystals.

In order to understand the dynamics of CSA, the peak position is converted to lattice parameter plotted against the time and shown in Fig. 3. Two distinct regions of evolution can be seen in the plot. After the first appearance of an ordered structure, the lattice parameter shrinks at a gradual rate of 1.14nm/min.

The gradual decrease in the lattice parameter indicates that the lattice of the FCC structure is shrinking with time.

This can be explained by the increasing influence of the liquid-vapor interface on the colloidal crystal. At the edge of the drop, the contact angle is decreasing with time as the drop dries up. This confines the colloids and reduces the Brownian motion of the colloids. As a result, the lattice spacing becomes smaller and the intensity of the reflected light also increases with less disorder in the structure. This transition state of the colloidal crystallization offers an opportunity to remove point defects like vacancies. The final FCC colloidal crystal is mechanically confined and the colloids have no mobility to anneal out any growth defects. However in the transition state, the colloids are mobile enough to anneal out the defects. This can be achieved by controlling the environment to increase the period at which the transition state is stable.

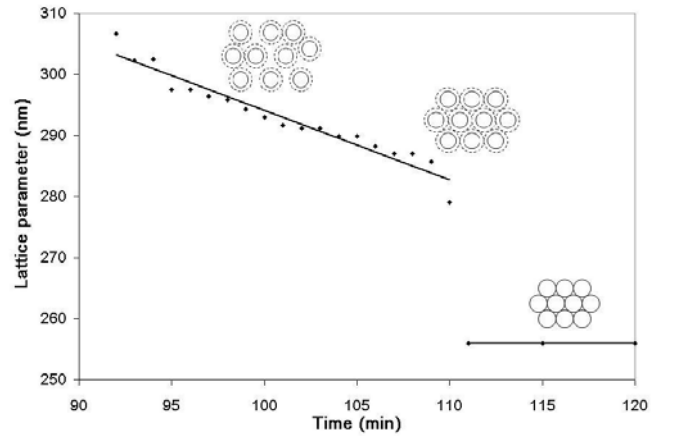


Fig. 3 Lattice parameter change with time at 30° angle of incidence. During the first 92 minutes, no discernible peak is observed. The insets are schematics of the structural changes within the colloidal crystal.

In Fig. 3, the most interesting feature is the sharp drop in the peak position just before the colloidal crystal is totally dried. This sharp drop indicates that there is a sudden decrease in the lattice parameter at the end of ordering in CSA. In order to quantify the change in the lattice parameter, the in-situ reflectance spectrum is taken at different angles of incidence. This allows for the delineation of the effect of the change of the medium from water to air and the effect of the lattice parameter change. This can be seen by rearranging the modified Bragg's law.

$$\lambda^2 = 4d^2[n^2(\lambda) - \sin^2 \theta] \quad (3)$$

Thus, if the plot of λ^2 against $\sin^2 \theta$ is a straight line, the slope of the line can be used to obtain the lattice parameter. Fig 4 shows the plot of the results. It can be seen that throughout the assembly process, the modified Bragg's law is obeyed and it shows that the FCC structure is maintained throughout. From the slope of the two straight lines, the lattice parameter at before and after the transition is obtained. The change in lattice parameter is 23.17 nm and this corresponds to shrinkage of 16.46 nm for each pair of

colloidal particle. This is equivalent to a rate of 23.17 nm/min and indicates an abrupt decrease in lattice parameter relative to the initial rate of decrease.

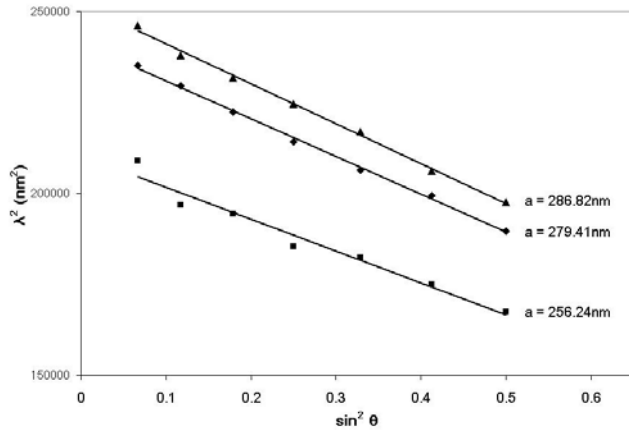


Fig. 4 The plot of λ^2 against $\sin^2 \theta$. \blacktriangle : 10 minutes before abrupt transition \blacklozenge : Immediately before transition \blacksquare : After transition. Notice that the points fit onto a straight line, indicating that the structure stays FCC throughout the transition. All lines have different slopes.

In polar solvent like water, charged colloids acquire on their surface an electric double layer. From Gouy-Chapman theory, this double layer is formed from the charged surface and a neutralizing diffuse layer of counterions. The thickness of the diffuse layer is of the order $1/\kappa$, the Debye screening length. The Debye screening length emerges naturally in the theory and is given by [16],

$$\frac{1}{\kappa} = \left(\frac{\epsilon_o \epsilon_r kT}{\sum_i (z_i e)^2 c_{io}^*} \right)^{1/2} \quad (3)$$

where ϵ_r is the solvent dielectric constant, T in the temperature, z_i is the valency of the counterion and c_{io}^* is the bulk concentration. For most application of aqueous medium at 25°C with a 1:1 electrolyte at molar concentration C_o , the Debye length is given by $0.304/C_o^{1/2}$ nm. The layer of counterions acts like a diffuse shell around the colloid preventing the colloids from coming into mechanical contact. This helps to explain the sudden decrease of the lattice spacing during the final stages of CSA. As the colloids become more confined by the liquid-vapor interface, it will reach a state when the colloids with their diffuse shell of counterions in the FCC structure are in contact with each other. The colloidal crystal will stay in this metastable state as long as there is solvent around it. However, the solvent will eventually be removed by further evaporation and the diffuse layer of counterions cannot be sustained. This is an abrupt process and the sharp drop in the lattice spacing is the result of this. During this transformation, no diffusion of the colloids occurs and it is extremely fast relative to the time scale of the colloid

motion. It is commonly associated with lattice-distortive transitions [17], and has been reported for martensitic phase transitions in geometrically confined colloidal crystallization [18]. This transformation results in a dilatational lattice distortion of the transition state. Using the shrinkage as an estimate for the Debye length, it is found to correspond well to the calculated Debye length of 7.9nm for the colloid suspension used. Thus the final disappearance of the screening layer corresponding to the change in surface medium gives rise to a martensitic-like phase transition that could exert shock stresses on the crystal, given its short time-scale.

These stresses are likely to be the main cause for cracking in self-assembled colloidal crystals. This is the reason for concurrent formation of cracks and changes in colours that is observed under the optical microscope. SEM images of the cracks show that on both sides of the cracks, the colloidal crystals retain the same orientation across the crack. This supports the observation that the colloidal crystal is already in the FCC structure before cracking and it undergoes a uniform shrinkage to form the final cracked morphology.

This model of crack formation has a few implications on

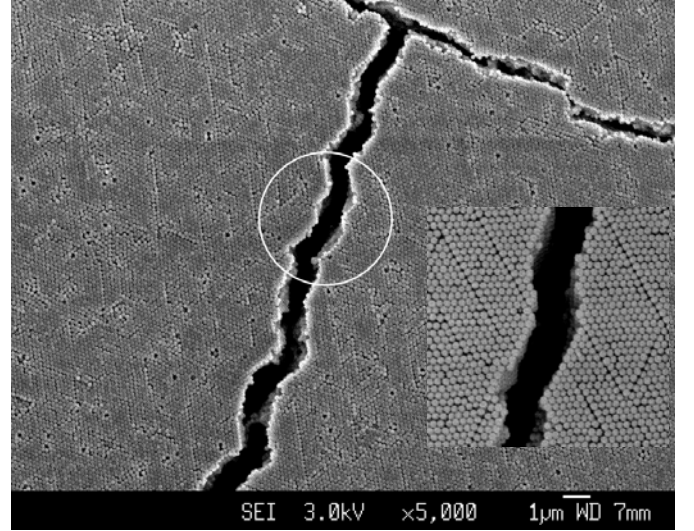


Fig. 5 SEM picture of the vicinity of the cracks. The inset shows the magnified circled section. It shows that there is orientation relationship between the colloidal crystals on both side of the crack.

the control of cracks in colloidal self assembly. Firstly, it is evident that the amount of tensile stress buildup in the colloidal crystal film is a function of the shrinkage that is associated with drying. By measuring this shrinkage, it is possible to obtain quantitative understanding of the tensile stress buildup during drying. At the same time, this shrinkage is affected by the thickness of the electrical double layer around the colloids. It is possible to adjust this thickness in the colloid suspension by tuning the interaction potential between the colloids and this is well understood by the DLVO theory. With this insight, it becomes possible to optimize the conditions of the colloids

to obtain colloidal crystals with low crack density. However, it must be noted that if the thickness of double layer is too thin, the colloids will be kinetically trapped and form glassy structures instead of well ordered FCC structures. This supports the hypothesis that cracks are intrinsic defects in self-assembled colloidal crystals and explains the consistent observation of cracks in these nanostructures.

IV. CONCLUSION

In conclusion, we have shown that in-situ reflectance spectroscopy can be used to monitor structural changes in CSA by treating ordering colloidal system as a photonic crystal. Using this method, we have shown that an FCC structure first appears after an initial induction period, followed by a gradual reduction of the lattice parameter. When the inter-colloid separation is on the order of a Debye screening length, an abrupt lattice-distortive martensitic-like transformation takes place, coincident with the final disappearance of the solvent medium. This transformation is the cause for the formation of cracks in the colloidal crystal. The model suggests that cracks are intrinsic to colloidal crystal and can be controlled by tuning the interaction between colloid particles.

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