

Ordering Control of Self-Assembled Colloidal Crystals

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Abstract — Colloidal crystals are 3D nanostructures formed by self assembly of nanoparticles in suspension. The interaction forces between the colloid particles are expected to affect the ordering and the defect density in the resultant crystal. Based on this insight, the effect of ionic strength on the quality of the colloidal crystal is examined. It is found that at intermediate ionic strength, it is possible to get the best ordering of the colloidal crystal. The reason for this is explained based on previous work on the structural changes in an assembling colloidal crystal. A method for reducing the defect density in colloidal crystal will also be proposed.

Index Terms — Colloid, Self assembly.

I. INTRODUCTION

COLLOIDAL suspension of nanoparticles can self-assemble into highly ordered 3D nanostructures called colloidal crystals [1-3]. For a monodisperse suspension, the equilibrium crystal structure for the colloidal crystal is known to be the FCC structure [4, 5]. Due to the periodic variation of the refractive index in colloidal crystals, they possess a photonic bandgap [6, 7] - the photonic analogue of the electronic bandgap in semiconductors. It is a band of photon frequencies which is not allowed to propagate within the ordered nanostructure. The presence of the photonic bandgap in these materials makes them attractive for future integrated photonic circuits [8, 9].

Presently, the ordering mechanism in colloidal self assembly is not well understood and thus, the quality of the colloidal crystals cannot be easily controlled. A reasonable premise is that the quality of the colloidal crystals obtained by self assembly is strongly dependent on the interaction forces between the colloidal particles. For colloidal interactions, one important parameter is the ionic strength

of the suspension [10]. The ionic strength affects the electrostatic forces between the colloidal particles and in extreme cases, destabilizes the colloidal suspension. This highlights the possibility that the ionic strength can affect the quality of the colloidal crystals significantly.

A transitional structure has been identified during the colloidal self assembly process previously [11]. This structure is similar to the final FCC colloidal crystal structure, albeit with a larger lattice constant. In this structure, the colloidal particles are not in mechanical contact with one another. However, the particles are surrounded by a layer of solvent and prevented from coming into mechanical contact. These particles are arranged in a FCC structure and they stay in that arrangement for a period of time determined by the balance between capillary-driven solvent flow into the transition structure and the evaporation flux of the solvent phase. In the final stage of self assembly, there is not enough solvent in the suspension to support this structure. An abrupt collapse of the solvent layer will occur and this leads to macroscopic cracking consistently observed in colloidal crystals. The layer of solvent is expected to vary with the ionic strength of the solvent due to the screening by the counter-ions.

In this report, we vary the ionic strength of the starting colloid suspension and check on the final order of the colloidal crystal. The ionic strength is found to affect the order quality of the colloidal crystal profoundly. An explanation with the transition structure is presented.

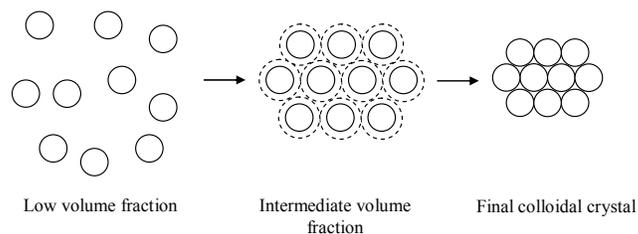


Fig. 1. The proposed mechanism for colloidal self assembly. A transition structure with a larger lattice constant has been observed [11].

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Utilizing the same ideas about the transition structure, a mechanism by which defects can be removed in the colloidal crystals is also proposed.

II. EXPERIMENTAL SECTION

A. Synthesis of polystyrene colloids

Firstly, the colloids were synthesized by surfactant-free emulsion polymerization method. In emulsion polymerization, the monomer is dispersed in water by creating an emulsion of the mixture. Surfactants are added into the reaction vessel and they are adsorbed onto the interface between the organic monomer and water. Above a certain concentration of surfactant known as the Critical Micelle Concentration (CMC), the surfactant starts to form micelles around the monomer molecules. The monomer is stabilized and stay dispersed in water by the encapsulation in these micelles. In order to initiate the polymerization process, free radical initiators are added at elevated temperature. Highly monodisperse polymer colloid particles can be synthesized in this way. However for our study, the added surfactants contribute to the concentration of counterions in the suspension and limit the range of ionic strength that can be reached. Excess amount of the surfactant is also added to ensure the stability of the monomer-water suspension. This is extremely difficult to remove in the final colloid suspension and typically reappear in the final colloidal crystal.

It is also possible to synthesize polymer colloid particles without added surfactant. In this case, the monomer is dispersed in the water by mechanical agitation. A propeller is used to stir the suspension of monomer and water. At high revolution, the monomer will be broken into small droplet in water. Polymerization of the monomer can take place in the same way as emulsion polymerization. The obvious advantage of this method is the cleanliness of the colloid synthesized. However, size uniformity is more difficult to control in this method.

The monomer used for polymerization was styrene. Initial washing of the styrene was carried out with 1M sodium hydroxide solution. The two liquids were immiscible and mixed in a separating funnel. The mixture was shaken vigorously to disperse the monomer and remove the inhibitor present in the monomer. The mixture was then left to stand for a while to separate the two liquids. The NaOH solution was removed from the separating funnel and the monomer was washed with deionized (DI) water for another two times. The DI water was filtered with a Barnstead ion exchange system and had a resistivity of 18 M Ω .cm. This indicated that the water was ultra-pure.

After the monomer was cleaned, it was mixed with water in a reaction vessel and agitated with a Teflon propeller driven by an overhead stirrer. The reaction vessel was kept in a water bath and maintained at a temperature of 60 °C. At the same time, pure nitrogen was injected into the

system. This was to provide a stable environment to stabilize the free radical produced during polymerization. A condenser was also connected to the system to make sure that the evaporated reagents did not escape. After the system was left to stand for 15 minutes to completely purge the vessel of oxygen, the initiator was added to start the polymerization process.

The free radical initiator used in the synthesis was Potassium Persulfate (KPS). The choice of the initiator for the synthesis was very important as it determined the final surface properties of the colloids. Using KPS, the surface functional group will be sulfate type and this gave negatively charged particles. It was possible to use other kind of initiators to get particles of positive surface charge. In our experiments, we found that the negatively charged particles gave better quality colloidal crystals.

After the initiator was added, the system was continuously stirred and kept in nitrogen atmosphere for another 24 hours. The long standing time was to ensure that all the monomer had reacted. The resulting colloidal suspension was milky in color. The colloidal suspension was cleaned by centrifugation. The colloid particles sediment at the bottom after centrifugation and the top layer of clear solvent was poured away. DI water was added into the container and the colloid was redispersed in an ultrasonic bath. This was repeated for a few times to ensure that the colloids suspension was clear of any leftover reagents. For the comparison of the effect of ionic strength, the colloid used was 280 nm polystyrene particles suspended in DI water.

B. Vertical Deposition of Colloidal Crystal

A good method to deposit uniform colloidal crystal is by vertical deposition. In this technique, the substrate is dipped into the colloidal suspension and the solvent is allowed to evaporate off. As the meniscus recedes, a layer of colloidal crystal is deposited on the substrate. We found that the hydrophilicity of the substrate is important to the

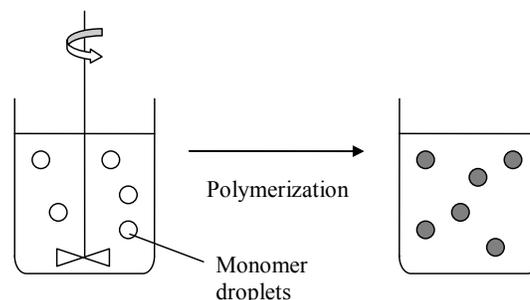


Fig. 2. Surfactant-free emulsion polymerization.

formation of good quality colloidal crystals. Hydrophilic substrates like glass generally produce better quality colloidal crystals.

In order to ensure that the glass substrate is hydrophilic it is cleaned in a mixture of hydrogen peroxide and sulfuric acid (2:1 ratio). The glass substrate was submerged in the cleaning solution and stirred periodically to ensure efficient cleaning. After 20 minutes, the substrate was transferred into a beaker of DI water to clean off the solution. The substrate was then rinsed with more DI water and kept in a container of DI water before it was used for deposition.

For the vertical deposition process, the colloidal suspension of desired starting chemical composition was mixed in a clean glass container. After that, the glass substrate was dipped into the suspension and the container was placed in an oven at 60 °C. This was left overnight in the oven for the solvent to be evaporated off totally. The final colloidal crystals showed iridescence indicative of the photonic bandgap structure. In order to compare the ordering quality of the colloidal crystals, SEM images of the colloidal crystal was also taken.

III. RESULTS AND DISCUSSION

Colloidal suspensions of different starting ionic strength are deposited on glass substrates. SEM images of the resulting colloidal crystals are shown in the Fig. 3.

It can be seen that without any salt added, the structure is less ordered. The structure looks like there are still a lot of empty spaces between the colloid particles. This is related to the transition structure previously observed. The lattice constant of this transition structure is related to the ionic strength of the system. At high ionic strength, stronger screening by the counterions decreases the Debye length. For the low ionic strength, the final colloidal structure has significant amount of void between the particles because the initial transition structure has a larger lattice constant. The large shrinkage stresses prevent the capillary forces from packing the colloids into a truly close packed structure.

In the case of intermediate ionic strength, it can be seen that better ordering of the colloidal crystal is achieved. This can be attributed to the decreasing lattice constant of the transition structure in suspension of intermediate ionic strength. This suggests that the optimum condition for colloidal self assembly is with high ionic strength of the solvent. The strong screening by the counterions reduces the electrostatic repulsion and minimal shrinkage stress will be experienced by the colloidal crystals. In this way, highly ordered colloidal crystal can be formed. However, this is not what we observe experimentally. This is due to the requirement for the stability of the colloids in suspension.

At high ionic strength, colloid particles agglomerate into small aggregates. These aggregates are disordered and very strongly held together by the Van der Waals forces between the particles. During colloidal self assembly, capillary forces are not strong enough to break up these aggregates for rearrangement into the final FCC colloidal

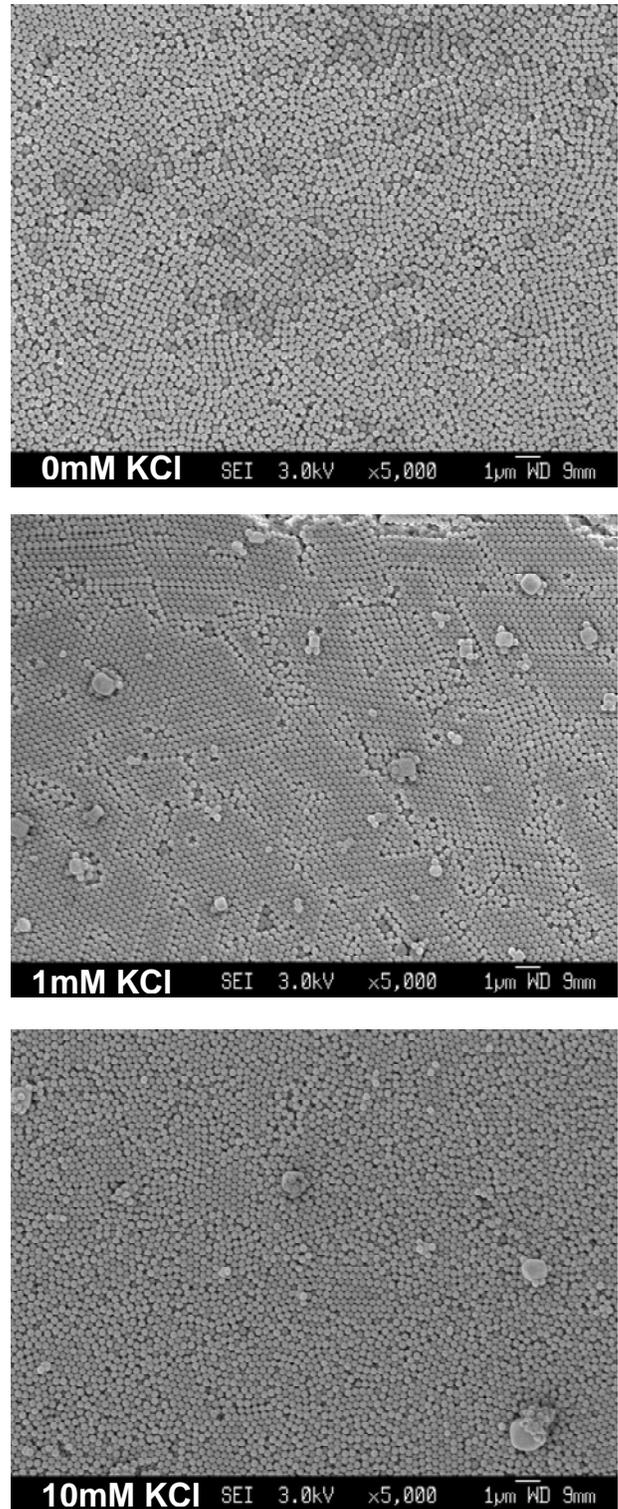


Fig. 3. SEM images of colloidal crystals grown from different starting ionic strength of suspension.

crystal. This can be thought as a colloidal glassy phase.

The presence of the transition structure presents an opportunity to anneal out the defects associated with colloidal crystals. Various kinds of defects like vacancies and dislocations are observed in the colloidal crystals

grown in our experiments. This can affect the photonic bandgap properties of colloidal crystals. These defects act as scattering centers in the photonic bandgap and in extreme cases, eliminate the bandgap altogether. In the transition structure, the particles have higher mobility to

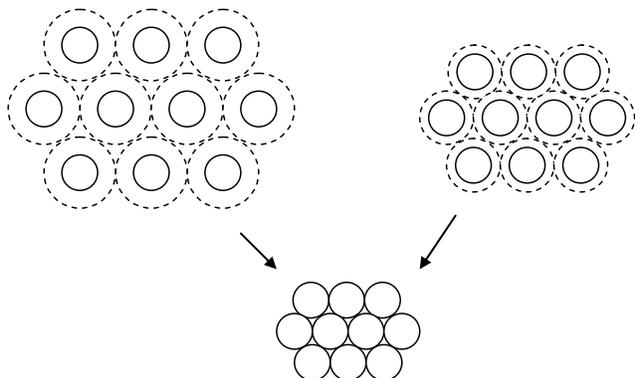


Fig. 4. Smaller shrinkage from the transition structure causes more stress to develop in the final colloidal crystal. This decreases the quality of the colloidal crystals grown from low ionic strength suspensions.

rearrange themselves. This is not possible in the final dried colloidal crystals as the particles become mechanically fixed in their respective lattice position. By extending the lifetime of the transition structure during self assembly, it becomes possible for the defects to be annealed out by rearrangement of the colloidal particles.

IV. CONCLUSION

The effect of the starting solvent ionic strength is investigated in this report. Other chemical additives like surfactants can be added to the colloidal suspension to investigate their effect on colloidal self assembly. The possibility of making use of the transition structure to anneal out defects in colloidal crystal is proposed. We believe that this will present a path to achieving low defect density colloidal crystals which can be used as photonic

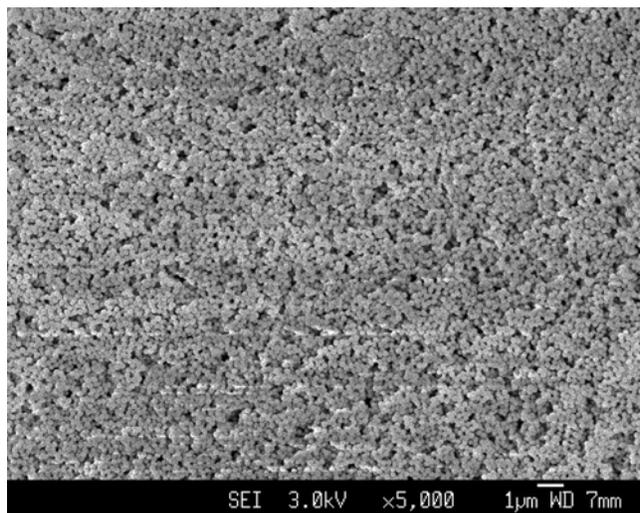


Fig. 5. Colloidal glassy phase grown from a starting ionic strength of 100mM KCl.

bandgap materials.

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