Cracks formation in the vertical co-depositing colloidal crystal

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Abstract: It is a cost-efficient approach to take the colloidal crystals (CCs) as template to fabricate three-dimensional photonic crystals. However, cracks occurring in the colloidal crystal synthesis process typically divided a colloidal crystal film into single crystalline domains of several tens of micrometers size, setting a major obstacle to the application of CCs template method. As a modified method, the co-deposition of microsphere and nanoparticles in CCs formation was put forward to reduce the formation of cracks. However, the physical mechanism of crack inhibition in co-deposition process was not well studied.

In this paper, we reported an in-situ observation study on the crack formation in the co-deposition process. It was found that the crack morphology has a large difference compared with that in the normal CCs template method. The cracks in normal CCs growth are usually formed and developed as parallel straight lines along the substrate surface in the growth direction. In contrary, the cracks present a pattern of regular triangular lattices in co-deposition. The crack morphology changes from CCs process to co-deposition process was considered to have a strong relationship to the gel formation in co-deposition procedure which can be ignored in the normal CCs growth. The corresponding physical model was developed and compared with the experimental results. The present study was helpful to give a deep insight into the crack formation mechanism in the colloidal spheres (CSs) assembling process.

Keywords: **Crack, co-deposition, colloidal crystal**

1. Introduction

Vertical self-depositing (VSD) method has proven to be highly-efficient for the synthesis of the colloidal crystals (CCs) which cannot be got by conventional top-down methods. The CCs are three-dimensional periodic structures formed from colloidal sub-microspheres. [1] The most remarkable property of the CCs is the photonic band gap (PGB)[2], which makes the CCs have great potential application in photonic crystals. At the same, the CCs can be as a template to get well-ordered, porous “inverse opal” structures for optical, electronic, and (bio) chemical application.[3] Such ordered, high surface area nanoporous solids are important for potential applications in fields from catalysis to tissue engineering, drug delivery, gas sensing, and filtration and PGB devices. Compared to conventional top-down process, this kind of bottom-up self-depositing method shows its low-cost and high-efficiency. However, during the deposition of the CCs, a number of defects such as cracks, domain boundaries and vacancies will be produced. Among them, the large length scale defects, cracks, will split the CCs into countless small domains, which make the practical applications of the CCs impossible.

In order to reduce or even eliminate cracks, researchers developed many growth methods of the CCs. van Blaaderen A. et al. [4] invented “colloidal epitaxy” to fabricate CCs. They made the slow sedimentation of CSs onto a patterned substrate (or template), which could direct the crystallization of bulk CCs, and permit tailoring of the lattice structure, orientation and size of the CCs.

Rudolf Zentel et al. [5] spread the colloidal suspension on the surface of the liquid substrate (gallium or mercury) and the crystallization and drying of the CCs were finished at room temperature for about one day. In this way, they got crack-free CCs of a size of nearly a centimeter square. Norris et al. [6] found that the cracks could be avoided in fabricating adverse opals by sintering the silica spheres prior to assembly of the CCs. However, the methods mentioned above were too complicated, high cost and not reliable to produce crack-free CCs with large domains.

The co-depositing method was first used by Meng et al. [7] to fabricate ordered porous materials. Due to the co-assembly of the CSs and the ultrafine particles, such as TiO_2 or SiO_2, the researcher can get the CCs by a one-step process. With the water evaporation at the meniscus, the ultrafine particles were infiltrated into the voids of the CSs during the co-deposition. The following investigators went beyond the co-deposition of the binary particles and got crack-free colloidal films of centimeter square through co-assembly of the CSs and polymer precursors [8] or salt precursors [9]. The infiltrated materials could be as a sacrifice to be got rid of, and the large area CCs would be left.

In fact, cracking during drying of colloidal dispersion has been investigated for many years and made the model system for crack study [10-15]. In order to understand the mechanism of cracking, it is base to study the dying process and the crack morphology. Drying accompanies the whole process of the thin film formation and has very important effects on the quality and shape of the colloidal film. [16-19]Although through the co-depositing method researchers could improve the CCs' quality and get crack-free CCs of large domain, it is not clear whether there are differences between deposition of the CSs of single size and co-deposition of the binary particles. In this paper, we show the cracking process during the deposition of the CSs of 360nm and the binary deposition of the CSs (360nm) with the SiO_2 nanoparticles (7nm) by real time observation method. It is noteworthy that in spite of the same drying condition absolutely, the morphology of cracks is different from each other.

2. Experiment

The experimental set-up for the in-situ observation was shown in Fig. 1. A magnified schematic of the observed region is shown, as well as the image observed at the initial growth stage. To have a comprehensive understanding of the assembly process, large colloid spheres with the diameter of 3 micrometers were used for the observation of the initial assembly process. Cracks formation process by VSD was observed in a transparent glass cell and the inner temperature could be controlled. Polystyrene latex spheres (from Duke Scientific Corporation, California, USA) with 360nm diameter were used in this work. Polystyrene spheres were mono-dispersed in Milli-Q water with 0.1% volume fraction. The Silica nanoparticles with mean diameter of 7nm were used for co-deposition. A 4x1.5 mm rectangular, 1 mm thick glass substrate was inserted vertically into a semi-cylindrical glass growth cell. To guarantee good water wetting, the glass substrate and the growth cell walls were cleaned with detergent, followed by immersion in chromic acid for about 24 hours. Cleaned glass plates were kept in Milli-Q water for about 8 hours, and dried naturally in the clean room environment before experiments. The growth temperature was kept at 55 °C during the experiment. Mean water evaporation rate was about 0.19 grams/hour. A long working distance optical microscope (Questar QM100, USA) was used to carry out experimental observations. The crack growth process was recorded with a digital video recorder connected to the microscope camera.

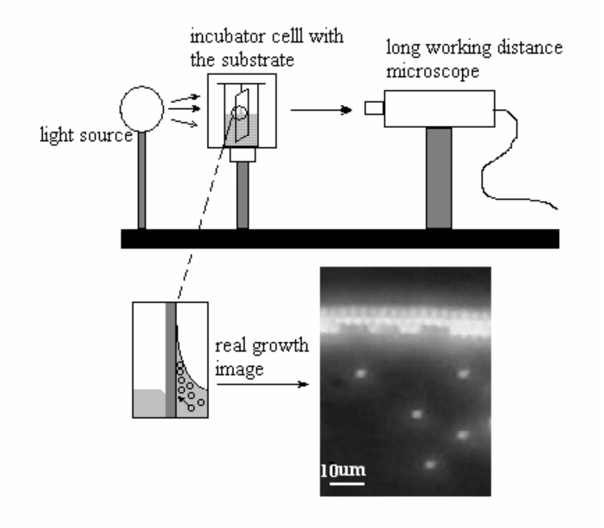

Figure 1. A schematic diagram of the experimental setup. A magnified schematic of the observed region is shown at the vicinity of the meniscus, as well as the image observed at the initial growing stage. Large colloid spheres with the diameter of 3 micrometers were used in the observation of the initial assembly process.

3. Results

The VSD experimental system of CSs is different from conventional colloidal suspension drying system [16-19]: a) it is capable of growing large-scale crystals from low particle concentration suspensions (0.1% volume fraction); b) without gel formation, the colloidal particles self-assemble to be a film by capillary forces and micro flow at the vicinity of the solvent menisci; c) a film with uniform thickness is formed of close-packed spheres. For the co-deposition, the CSs are close-packed orderly, and the nanoparticles infiltrate into the void among the CSs. [7]

Figure 2 shows the cracks of the colloidal films drying from the suspensions with different ratio of the CSs and silica nanoparticles. In all suspensions, the volume fraction of the CSs was 0.1%, and mixed the CSs with the silica nanoparticles in volume ratio of 5:0, 5:1, and 5:2. The line in fig.2 denotes the crack's tip and the arrows was the growth direction of the colloidal films. In fig.2a, the growth directions of the cracks and the colloidal film are same, the cracks are longitudinal. When the nanoparticles are added, the crack patterns change significantly (Fig. 2b, c). From fig. 2b, c, it is clear that the crack density has a relationship with the amount of the silica nanoparticles. There is higher crack density in fig. 2b. From the insets of the fig. 2, the directions of the crack also change with the addition of the nanoparticles.

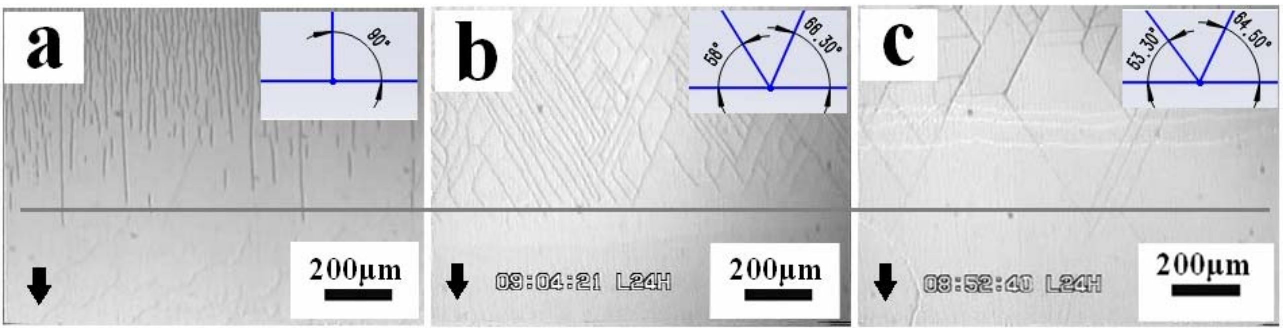

Figure 2 Different crack morphology drying from mixed suspension. The CSs with the silica nanoparticles in volume

ratio of a5:0 (a), 5:1(b), and 5:2 (c). The direction of the arrows is x axis. The insets show the angles between the cracks and x axis.

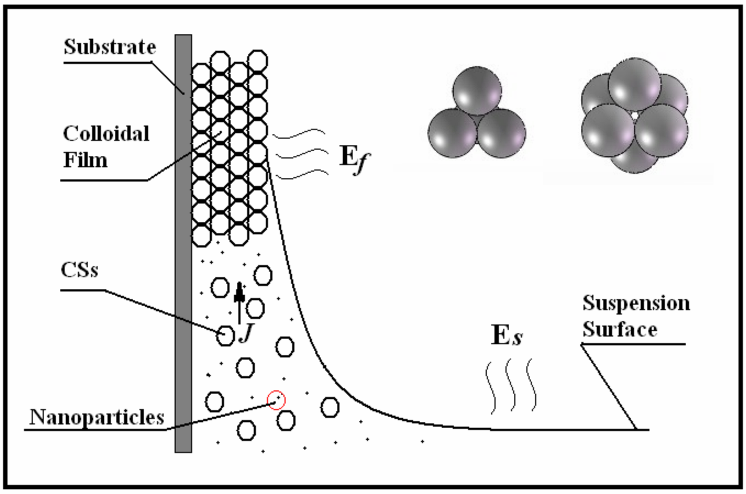

Figure 3 The VSD process of the CSs (or co deposition with nanoparticles) in meniscus region of the suspension. E_f and E_s are the evaporation of the colloidal film and the suspension respectively. J is the diffusive flux of the CSs (nanoparticles). Left inset is tetrahedral site. Right inset is octahedral site.

The VSD method (showed by Fig. 3) gets the colloidal film at the air-water-substrate interface from low-viscosity suspensions. The evaporation-driven flow makes the spheres or particles deposited in the meniscus. When the water reservoir is sufficiently large, the evaporation process does not significantly enrich the colloidal density. As the water evaporates, more substrate is exposed and coated colloidal film. The CSs or nanoparticles in suspension, within the solid-liquid-gas interface, are deposited on the substrate subject to interfacial forces. In this process, the thickness of the film can be adjusted by the concentration of the suspensions or by the descent speed of the suspension surface.

At the very beginning, the CSs and the silica nanoparticles are entrained toward the growth front at the same velocity, and the large spheres nucleate first in a close-packed network because of their higher volume fraction and larger size. With the evaporation and convective flow of the liquid medium through the pore space of the network, the nanoparticles can easily move and fill the voids of the fcc structure (formed by the CSs). From a simple geometric analysis indicated that, in the close-packed colloidal sphere arrays, two types of interstitial sites exist: the tetrahedral site and the octahedral site. One cubic unit cell contains four large spheres, eight tetrahedral voids, and four octahedral voids.

During the evaporation of the film, the strong particle wetting prevents the invasion of air into the colloidal film. With the sustained water loss, the nanomenisci will occur in the film interface, which create capillary the capillary tension to pull water through the network deposited by CSs (nanoparticles) to replace the lost by evaporation. For the wet film (no crack), the rate of fluid flow through (J) must balance the evaporation rate (E_f). The fig. 2a shows the directional cracks which indicate there is nearly uniaxial stress and the stress $\sigma_{xx} >> \sigma_{yy}$. When the nanoparticles were added into the suspension, the film stress state was changed into biaxial stress which leaded to a crack pattern of triangular lattices.

4. Conclusions

In summary, the comparison study of the crack formation during the VSD process with and without nanoparticles. It was found that co-deposition lead to different crack morphology and decreased the crack density. In contrary, the cracks present a pattern of regular triangular lattices in co-deposition. The crack morphology changes from CCs process to co-deposition process was considered to have a strong relationship to the gel formation in co-deposition procedure which can be ignored in the normal CCs growth. This study indicates the co-VSD method is a cost-efficient approach to get single colloidal crystal of large domain.

5. Acknowledgements

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6. References

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