Poster Presentation : Material Session

2021년도 한국현미경학회

춘계학술대회

X-ray imaging for crack and shear banding of colloidal droplets

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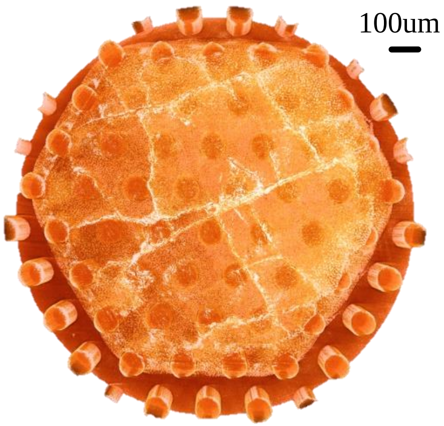
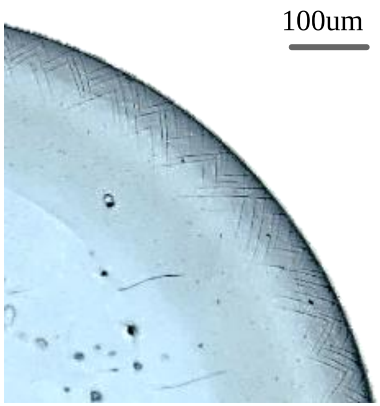
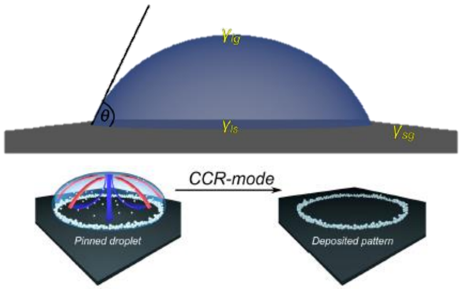
Different crack formation in colloidal droplets





Contact angle θ of the liquid droplet on a normal solid substrate and CCR mode



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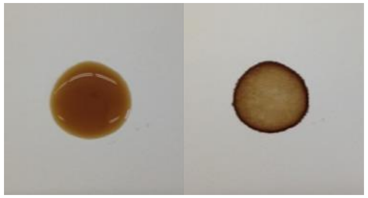
Coffee ring effect (before & after)



- Abstract

Nanotechnology represents a rising industry in the most diverse fields, including biopharmaceutical, electronic devices development, and material science. The main advantage of nanotechnology comes from the outstanding properties of nanoparticles. Their good performance for both chemical reactivity and electrical conductivity makes them unique and preferable when compared to macroscale particles. One important application of nanoparticles is in the formation of thin films for electronic or display devices with **inkjet printing techniques**. Particularly for colloidal droplets, where colloidal nanoparticles are uniformally distributed in a solution, evaporative deposition through inkjet printing is a promising technology.

However, due to the coffee-ring effect or the edgeward solute segregation that occurs during droplet evaporation, crack-free uniform deposition of colloidal nanoparticles is not fully achieved. Here, we explore the crack formation process of colloidal droplets in real time with a three-dimensional microscopic approach by using **X-ray microtomography**. Particularly, we study the **shear banding phenonenon** which is formed periodically near the edge of the evaporating droplet. We analyze the X-ray microtomographic images for crack and shear banding of colloidal droplets and consider their physical origins. Finally, we suggest a feasible solution to minimize cracking and shear banding of the deposits of colloidal nanoparticles by optimizing colloidal nanoparticle mixture.

- Background

When we put the colloidal droplet on normal solid surface, the droplet makes hemisphere. Usually, all the particles moves toward edge part of the droplet during evaporation and this phenomenon is well known as coffee ring effect. Colloid particles inside droplets will be subjected to interfacial tension and that induce a transverse tensile stress. This stress even cause various form of cracks and that is treated like defects in a colloidal film and device, and we should eliminate them.

Defect formation is inevitable during the evaporation of colloidal solutions because too much larger particles are included, empty space between them are also big and they are all remains as defects. But what if we add more smaller particles to fill between empty space of large particles, and eventually make particle packing with larger density? Particle size and mixing ratio should chosen carefully because too much large particle or small particle included can even cause negative effects.

Changing the surface wettability to more hydrophobic helps fixing droplet spherical shape and make uniform evaporation in every direction with constant contact angle. For example, using hydrophobic surface like PDMS. or we can even add micropillar array on that PDMS substrate to satisfying wettability change and particle diagonal pinning.

X-ray 3D tomography image of 10+2um, 5wt%, 2uL colloidal mixture on hexagonal pillar substrate with different mixing ratio

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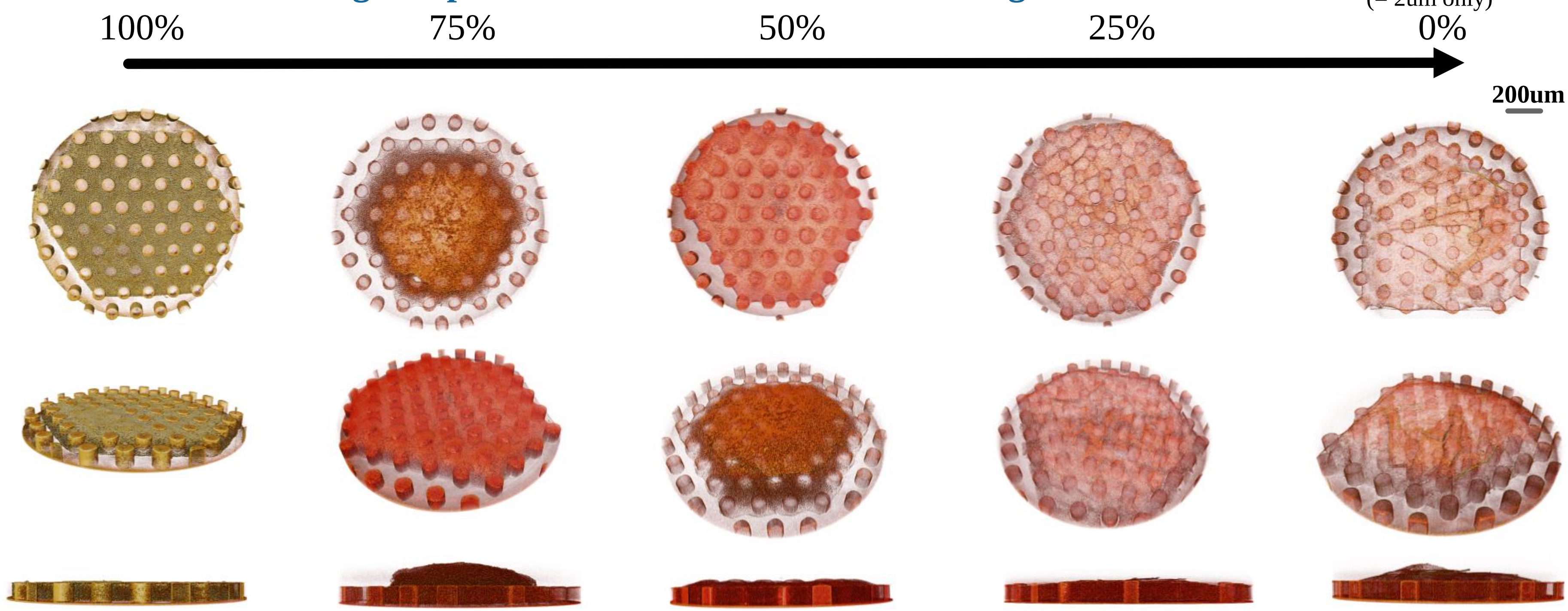


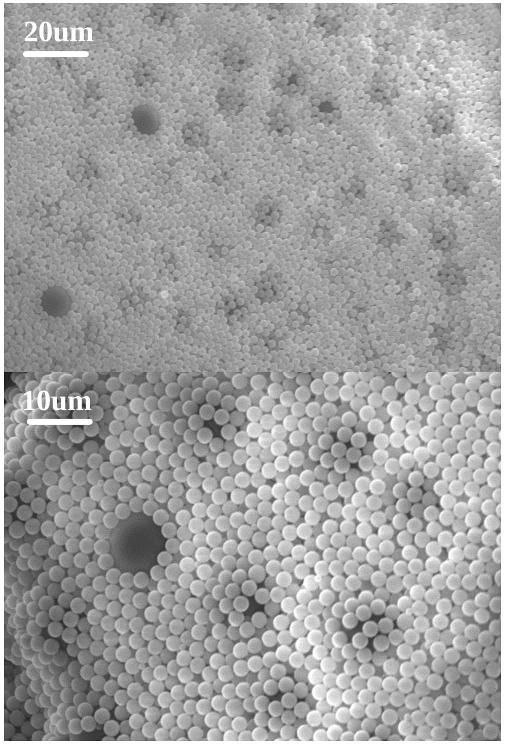
- X-ray 3D tomography

X-ray imaging experiments were conducted in the 6C Bio Medical Imaging beamline from Pohang Light Source (PLS-II) that provided monochromatic synchrotron x-rays with **24-keV energy and a 1.4 × 1.7 mm^2 beam size.** After penetrating samples, x-rays were converted into visible lights by the scintillator (LuAG:Ce 50 μm) and corrected by the Scientic Complementary Metal-Oxide-Semiconductor (sCMOS) camera (Andor Zyla) **with magnification of 10×**. The **minimum pixel size was approximately 0.66 μm, and the field of view was 1.70 × 1.40 mm^2.**

Our hypothesis is that when only a single particle exists, it becomes random packing, but it is relatively regular and pillar-dominated to form a polygonal deposition.

However, mixing two particles of different sizes changes the shape of the post-evaporation deposition pattern depending on which particle contains more. If more large particles are contained, the capillary force acts more heavily only for the smaller particles, resulting in particle separation. As a result, small particles are concentrated on the edge of the deposition pattern, and large particles are concentrated in the center, creating an uneven shape.

If more small particles are contained, the friction between the particles and the substrate becomes weaker, resulting in a relatively stronger capillary force acting throughout the droplet, resulting in the destruction of the deposition pattern.



Particle mixture and scale down to nano-sized particle

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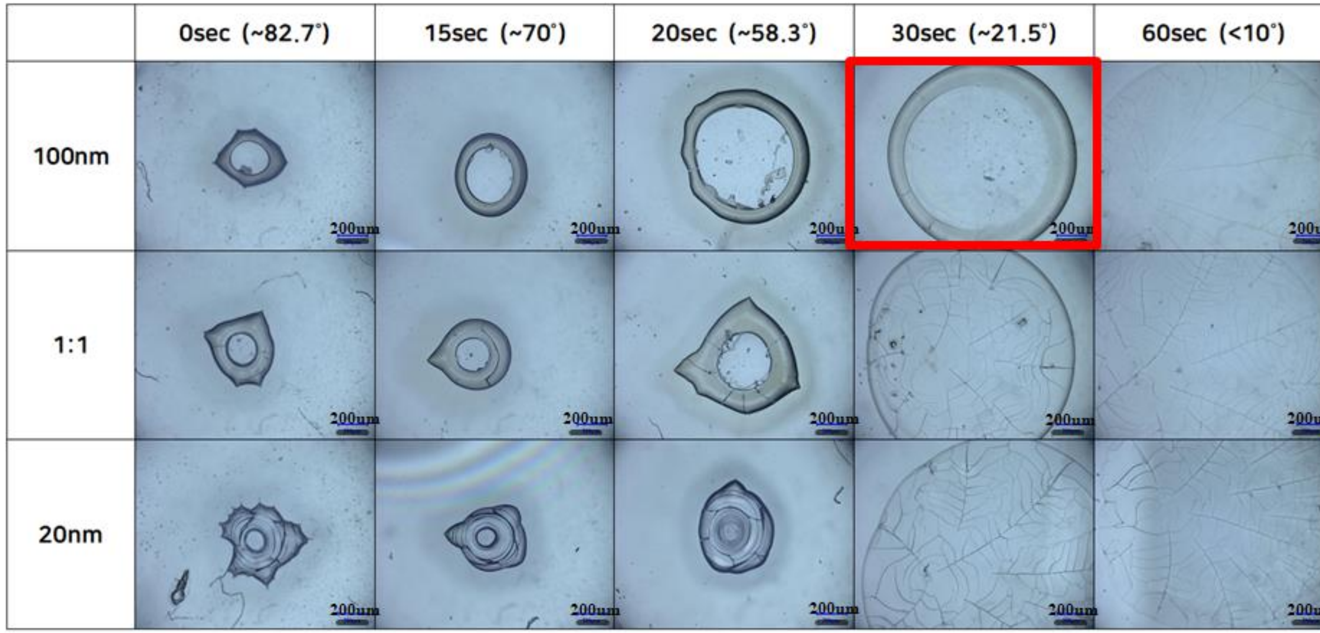


- Particle arrangement

Particle assembles are not perfectly single-layered, but relatively uniform arrangements can be identified. Contrary to the expectation that small particles would penetrate between large particles, small particles surround them, and volume fractions would be larger than 10 um particles alone.

- Scale down to nano-size

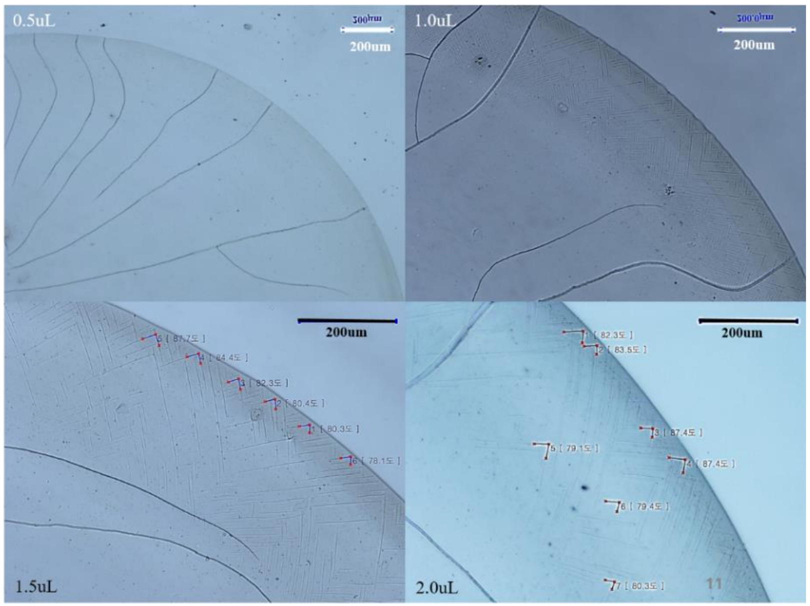
Usually, the nozzle hole which need for inkjet printing is much smaller than um size. If our ink has too large particles, they are going to block all nozzle and we cannot use it. Also, empty space between them are also big and they are all remains as defects.

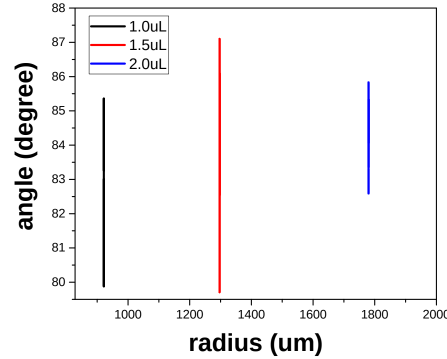
Here, if too much smaller particles are included, particle dynamics toward droplet edge moves faster and induces more destroyed pattern. Flat PDMS substrate for hydrophobicity was used, but also did plasma treatment to control the wettability. After air plasma treatment, the surface has more oxide ions and hydrophilic property. As a proof, the longer the plasma exposure time, contact angle between the substrate and the droplets become smaller.

If only large particles are used on the nanoscale, the empty space in the middle of the pattern is too wide, and if only small particles are used, the pattern is severely destroyed. However, as used in the case of micro-particle, mixing in a 1:1 volume ratio reduces the destruction and the emptiness of the core. Further adjustments to additional conditions are thought to create a fully filled pattern. And one more outcome to note was observed among the single particle deposition.

IV. Conclusion & Discussion 4. 결론 & 토의

Shear-banding structure analyzing





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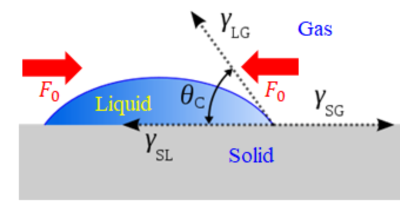
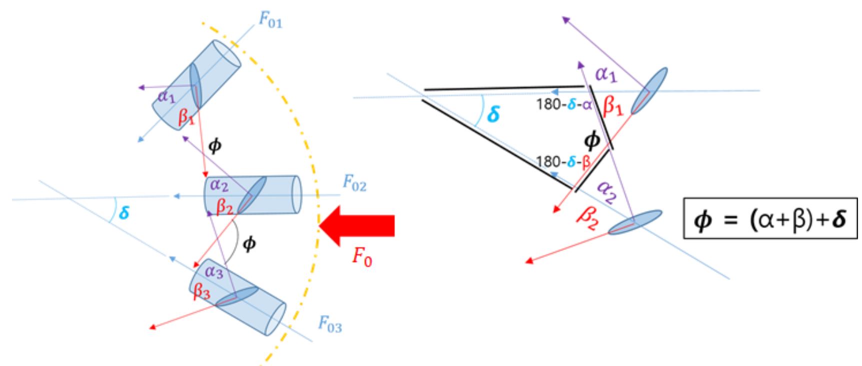


▲ Side view



▲ Top view

- Structure analyzing with formula and observation

This pattern is a kind of crack called shear banding and have angle range of approximately 80~90 degree. If droplet volume is over critical value(> 0.5 uL), it doesn't have that much angle difference until now and almost have same state. Additionally, if our droplet volume is too small, it's directly spread and almost attach totally with a substrate.

We all know that if colloidal particles are included in suspension, they moves toward edge. It's also happens here too and that assemble make particle packing or crystal structure. When we apply force to polycrystalline structure, crystal will split and slip through grain boundary and crack will be created. Of course, the amount of force exerted here will vary depending on the applied direction, and face area which received force. we can express it with cosine a and b angle.

This is called **Schmid's law** and we should analyze what is the origin of F_0 in our case. The source of F_0 is the destruction of balance. Our droplet contact line was pinned and due to **Young's equation**, when the droplet contact line was pinned, the three interfacial force which exist between solid, air, and liquid make balance. But as time goes by, our droplet will be going to evaporate, and the contact angle will be decreased. Eventually the initial equilibrium will be disappearing, and the interfacial energy difference makes force to separate crystal through slip plain. That's why our herringbone crack is made. Our droplet is round, so applied force will have tangential direction difference. Here, we should vary the force definition with contact line and force applied angle difference and modifying with arbitrary angle delta through out whole circle. This droplet sample has different local curvature especially at the edge part. The slight difference in size between each pattern is also considered a consequence of this. This fact should also be applied to modification of the expression, but still requires further research.

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