

Formation mechanism of supraparticles obtained by drying of colloidal suspension droplet on a superhydrophobic substrate

Y. Hirano, S. Inasawa, M. Fujita and Y. Yamaguchi

(*) Department of Chemical System Engineering, Graduate School of Engineering

The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656 Japan

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1. Introduction

Drying of colloidal suspension droplet on substrate is a simple process to control the structure of colloidal particles, which is used for ink-jet printing, coating, etc. The mechanism of the structure formation in this system is so perplex, because the field forming the structure and the structure formed by the field influence with each other: drying rate of suspension determines the evolution of particle structure, and the evolution of particle structure determines drying rate.

In the previous research, the structure formation of colloidal particles during drying is understood as follows.[1][2] (1) If recession of air-water interface due to evaporation of solvent is faster than the diffusion of particles, particles are caught at the interface and a particle layer forms. Otherwise, particle layer does not form and dense particles would be obtained. (2) The particle layer behaves as viscous fluid before it transforms into elastic shell. This transition occurs when capillary force between particles exceeds the electrostatic repulsive forces between particles. (3) The elastic shell starts to get buckled by the capillary force. However, some important understandings to draw a clear picture of structure formation of particles during drying, such as where the buckling starts and what the driving force of buckling is, have not been clear. As a simple model case for those phenomena during the suspension droplet drying, we observed the structure formation of drying silica colloidal suspension droplet on a superhydrophobic substrate.

2. Experimental Methods

Silica particle suspension of initial volume fraction 0.72%, 7.2%, 15% were prepared. To prepare the solution of 0.72%, silica suspension KE-W10 (particle volume fraction 7.2%, Nihon Shokubai, no surfactants) was diluted with Milli-Q water. As for 15%, KE-W10 was concentrated by skimming supernatant after centrifugation and redispersed by shaking. Superhydrophobic substrate was prepared by drying 100 μ l ethanol dispersion of hydrophobic silica particles (average diameter 120nm, kindly given by Tokuyama corp.) coated on a 20mm \times 20mm Teflon substrate. The surface of the substrate is covered with particles, and its contact angle with the suspension is more than 160 $^{\circ}$.

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We dropped a suspension droplet of $3\mu\text{l}$ on the substrate, and immediately introduce the substrate into the drying chamber. The drying process of the droplet is observed by CCD camera (CS6910CL, Toshiba Teli). The structure of the supraparticle was observed by SEM (TM-1000, Hitachi and S-900, Hitachi).

We controlled the evaporation rate of the suspension in two ways. (1) Reduce the pressure in the chamber (atmospheric pressure $\sim 1.5\text{kPa}$) at room temperature (20°C). (2) Increase the temperature in the chamber (room temperature $\sim 200^\circ\text{C}$) The chamber for pressure reduction is an acryl box connected to vacuum pump and digital pressure gauge (Fig. 1(a)). We open the valve to evacuate the chamber (this

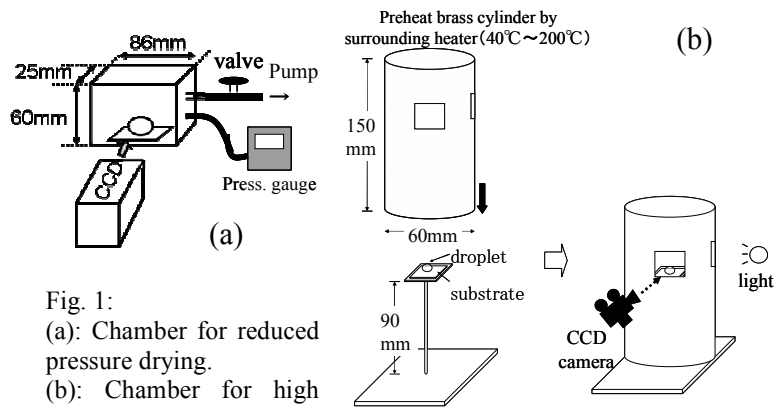


Fig. 1:
(a): Chamber for reduced pressure drying.
(b): Chamber for high temperature drying.

point is defined as the time $t = 0$ (s)), and close the valve when the pressure reaches a certain value. The chamber for heating is a brass cylinder, wrapped with heater and thermal insulant (Fig. 1(b)). We pre-heat the cylinder, put it on the substrate just after the droplet is dropped on, and droplet starts to dry (this point is $t = 0$ (s)).

We evaluated the evaporation rate of the droplet by analyzing the sequential images taken by the CCD camera. We approximate the droplet volume at time t as the rotated body of the droplet image. From the change of this volume, we evaluated the evaporation rate.

3. Results

Morphology of supraparticles

Three types of morphologies were observed after drying the droplet: (1) Buckling from bottom of the droplet. (2) Buckling from top of the droplet. (3) Buckling from both top and bottom. We show the SEM images of whole supraparticles in Figs. 2 (a)-(f).

In reduced pressure drying experiment, the obtained morphologies were strongly dependent on the pressure in the chamber. On the other hand, in high temperature drying experiment, the morphology depended more on the initial volume fraction of particles. The summary of obtained morphologies is shown in Fig.2(a)(b).

Time evolution of drying rate

The time evolution of drying rate of the droplet is shown in Fig. 3(a) (pressure in chamber 20kPa , room temperature). After the drying starts, (1)drying rate decreases accordingly. (2)After

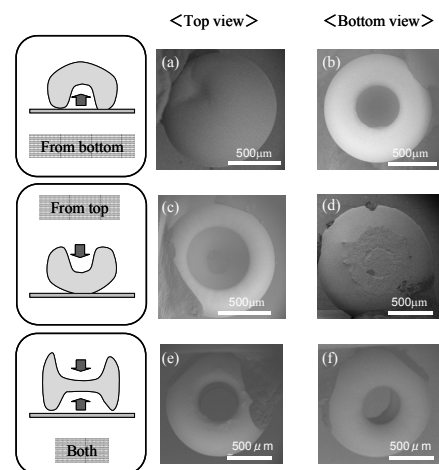


Fig. 2: SEM images of supraparticles. (a)(b) Buckled from bottom. (c)(d) Buckled from top. (e)(f) Buckled from bottom. (a)(c)(e) are the view from top, and (b)(d)(f) are the view from bottom.

reaching the inflection point, drying rate starts increase gradually. (3)The droplet starts to buckle, and drying rate starts to increase. (4)The drying rate starts to fall, and apparent drying rate become zero because the surface invaginate into the shell. In high temperature drying, stage (1) was not observed (Fig. 3(b)). The drying rate at stage (2) was within $7.0 \times 10^{-3} \sim 2.0 \times 10^{-2}$ (mol/m²/s) for all conditions of reduced pressure drying. On the other hand, the drying rate at stage (2) in high temperature drying is within $7.0 \times 10^{-3} \sim 1.5 \times 10^{-1}$ (mol/m²/s).

Mechanical reaction of particle shell

In all experiments, particle shell starts to buckle at the later stage of drying. If the pressure inside the chamber is suddenly reduced down to 0.5 kPa while the shell is buckling, buckling stops. This critical pressure, 0.5 kPa, is constant for all initial volume fractions and the pressure in the chamber before reduced.

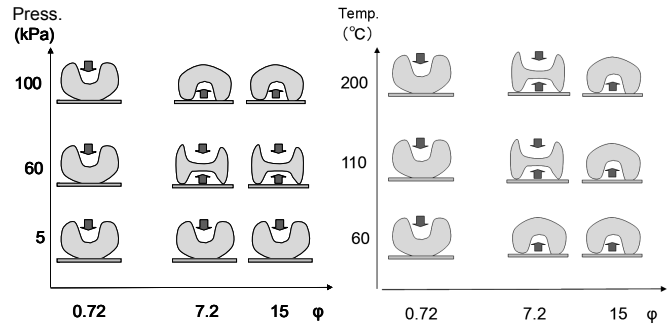


Fig. 2 : (a)Morphologies in reduced pressure experiment. (b)Morphologies in high temperature experiment.

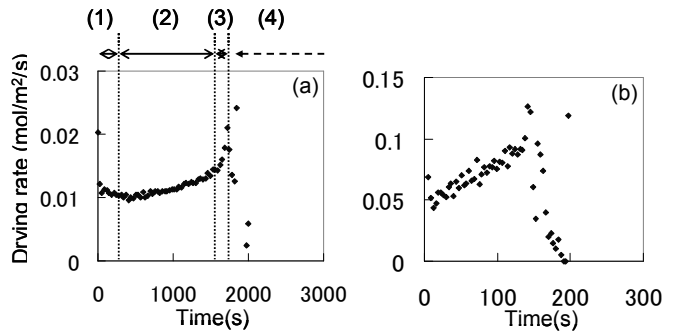


Fig. 3: (a) Drying rate of droplet in reduced pressure experiment (40 kPa, $\phi = 7.2$ vol.%), (b) Drying rate of droplet in high temperature experiment (200 °C, $\phi = 7.2$ vol.%)

4. Discussion

Modeling of drying rate of suspension

We simulated the time evolution of drying rate by solving mass conservation of water and energy conservation in the droplet. The assumptions are as follows: (1) The droplet is a sphere with radius r and there is no temperature gradient inside. (2) The vapor pressure near the surface of the droplet is the saturated vapor pressure at the droplet temperature. (3) There is no flow in the gas phase, and the boundary layer around the droplet is equivalent to the droplet radius r . (4) The humidity in the chamber does not change due to evaporation.

The simulation results showed good match with the observed drying rate near the room temperature or near the atmospheric pressure,. However, the model overestimates the drying rate when the temperature is high or the pressure is low. This is because temperature gradient caused by the latent heat is not negligible when drying is fast.

According to the simulation for reduced pressure experiment, the evaporation rate is limited by diffusion of vapor in the gas phase when the pressure is higher than 10 kPa. If the pressure is lower than 10 kPa, droplet temperature becomes 0 °C and the model cannot simulate the drying rate. In this pressure region, drying rate is limited by the heat transfer from substrate and the gas phase. However, in the temperature range of this experiment, there was no heat-transfer-limited temperature region.

Comparison of morphology obtained under reduced pressure drying and high temperature drying

Although the observed range of drying rate in high temperature drying was wider than reduced pressure experiment, morphology in high temperature drying is less dependent on temperature than that in reduced pressure experiment. This suggests that where buckling starts depends on the anisotropy of drying rate. The possible structure formation mechanism is as follows.

- (1) In heat-transfer limited drying condition, evaporation near the contact line is faster than that at top because the time constant of heat transfer from substrate is shorter than that from gas phase (Fig 4). On the other hand, in diffusion limited drying condition, the drying rate on top is supposed to be faster than that near the contact line.
- (2) The particle layer before the onset of buckling becomes thicker at the surface where the evaporation rate is high.
- (3) The thinnest point of the layer gets buckled by the atmospheric pressure, after it becomes an elastic shell.

In reduced pressure experiment, the heat transfer limited pressure range corresponded to the pressure range where the shell buckled from the top.

Driving force that deforms particle shell

In all experiments, particle shell starts to buckle at the late stage of drying. When the pressure inside the chamber is suddenly reduced down to 0.5 kPa while the shell is buckling, buckling stops. This pressure corresponds to the vapor pressure of water at 0 °C. This implies that the vapor prevent the shell from buckling caused by the pressure in the chamber.

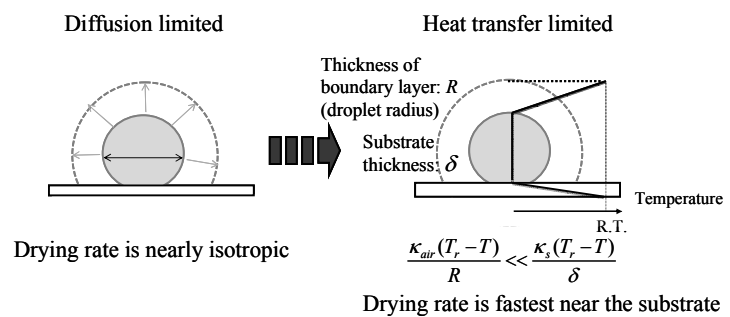


Fig. 4: Transition of rate limiting process

5. Conclusion

We observed drying process of colloidal silica suspension droplet on superhydrophobic substrate. We obtained supraparticles with three types of morphologies: buckled from the top, buckle from the bottom, buckled both from top and bottom. The obtained morphologies were dependent on pressure and temperature in the chamber, and initial volume fraction of particles. We discussed the anisotropy of the drying rate from the viewpoint of rate limiting process of drying. The point where the buckling takes place depended on the anisotropy of the drying rate. The pressure difference between inside and outside of the particle shell formed at the surface of the droplet is supposed to be the force that drives buckling of the shell.

References

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