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HIGHLY ORDERED ASSEMBLY OF MONODISPERSED PARTICLES PREPARED BY CONTINUOUS CAST COATING PROCESS

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The method using a colloidal liquid film coated on the solid substrate, which results the convective self-assembly, is one of the most promising approaches to prepare the particle array having a large area with high regularity for novel functions. The objective of this paper is to understand the fabrication phenomena of colloidal particle array by the continuous cast coating process.
The micrometer-sized particles were deposited by feeding the colloid suspension into the feeder and dragging the substrate. The deposited particles in the thin wetting film are crystallized to the monolayer particle array by convective self-assembly. At the steady state of the continuous cast coating process, a simple equation balancing the volumetric fluxes of particles was proposed, which agreed well with the experimental results. The evaporating region of a thin wetting film increased with the humidity, but the coating speed of particle assembly did not changed. The defects of the particle array were observed. The number of defects decreased at the continuous cast coating process comparing with the batch operation. The effect of the contact angle of the substrate on the fabrication of particle array was also carried out. Finally, the multilayer of particle assembly could be prepared by controlling the feed rate and the coating speed according to the proposed mass balance equation.

1. INTRODUCTION

Three-dimensional highly ordered assembly of particles are expected as the structure having novel functions such as light-emitting diodes (Coe et al., 2002), solar batteries (Huynh et al., 2003), photo-switch (Ohtsu et al., 2002), and photonic crystals (Fudouzi and Xia, 2003). The colloid-based antireflective coating (Prevo et al., 2007) is one of the two-dimensional particle array applications. The method using a colloidal liquid film coated on the solid substrate, which is used convective self-assembly phenomena, is one of the most promising approaches to prepare the regular packing structure of particles, such as the applications mentioned above. Dimitrov and Nagayama (1996) reported that this method could be made highly ordered particle array when the substrate was pulled up from colloidal suspension. Prevo and Velev (2004) proposed the horizontal coating method using high concentrated colloidal suspension for the rapid deposition of particles to make a large area. But their proposed method was the batch type operation, so that the fabrication method of the particle array having a large area with high regularity for industry level may be still under development. Nonaka et al. (2007) developed the continuous cast coating process for large area fabrication of the particle array, which was a similar operation of that proposed by Prevo and Velev (2004). They found that the formation rate of particle array increased with flow rate of feed suspension and its regularity became higher than that using the batch type.
The objective of this report is to understand the fabrication phenomena of colloid particle array prepared by a continuous coating process, that is, the effects of the relative humidity and the contact angle of the substrate on the fabrication speed of particle array were investigated. This paper also showed the fablication of multilayer particle assembly prepared by the continuous cast coating operation at once.

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2. EXPERIMENTAL

2.1 Continuous coating method

Figure 1 shows the schematic diagram of the apparatus of the continuous coating method. The colloidal suspension was fed to the fixed feeder by a micro syringe pump (KDS100, KD Scientific, Hollistor, MA, USA), and flowed out from the slit with 250 μm height and 12 mm width of the fixed feeder. The substrate was drawn at the constant speed by a stepping motor (Orientalmotor, Tokyo, Japan), to make a particle array. Polystyrene particles (PSL) whose diameter was 1.0μm (PS2538B, Magsphere, Pasadena, CA, USA), 5.0 μm (PS2829B, Magsphere) or 10 μm (PS/DVB2633B, Magsphere) was used as model particles. The experiment was carried out at the room temperature (about 293 – 298 K) with controlled relative humidity of 30, 50, or 70%.

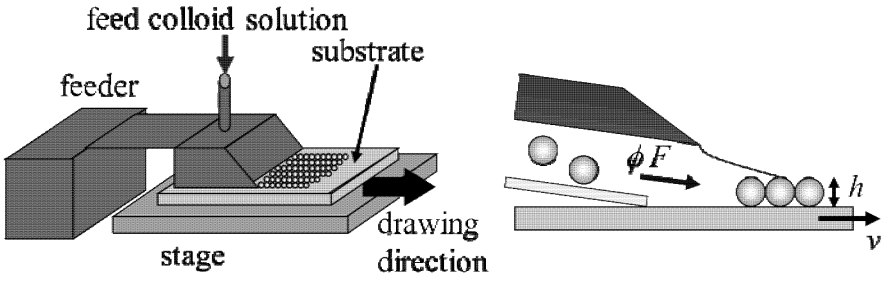

Figure 1: schematic diagram of the continuous coating method and definition of operation parameters.

2.2 Hydrophilic treatment of substrate

The substrate used was a cover glass (No. 5, Matsunami Glass, Kishiwada, Japan), whose width was 26 mm and length is 100 mm or 300 mm, with different cleaning procedures to examine the effect of hydrophobicity or a contact angle of the substrate on particle array structure. Table 1 shows four kinds of cleaning procedures at 353 K and the resulted contact angle of colloidal suspension on the substrate.RCA cleaning solution was prepared with the fresh mixturesolution of distilled water, 30% hydrogen peroxide aqueous solution, and 28% ammonia aqueous solution, whose volume ratio is 5 : 1 : 1. Most experiments were done using the substrate with ethanol treatment (cleaning No. 2).

Table 1: Cleaning procedure and contact angle of substrate after cleaning

No.	solution	cleaning period [minutes]	contact angle [degree]
1	water	10	30
2	ethanol	10	15
3	RCA cleaning solution	1	10
4	RCA cleaning solution	10	less than 5

2.3 Evaluation of particle array

Evaluation methods for the regularity of particle array were proposed such as Laue pattern measurement or UV-visible absorbance spectra. We proposed the very simple method (Nonaka et al., 2007), which was counted the number of defects along the straight line on the image of particle array as shown in Figure 2. We drew straight lines at the interval of 5 times width of particle size, counted the number of the defects per 100 particle in which the straight line was crossed, and classified into the point defect and the line defect as shown in the right hand of Figure 2. The point defect was defined as the hole of one particle, corresponding with lattice defect, while the line defect indicated the multi domain of colloid crystal array.

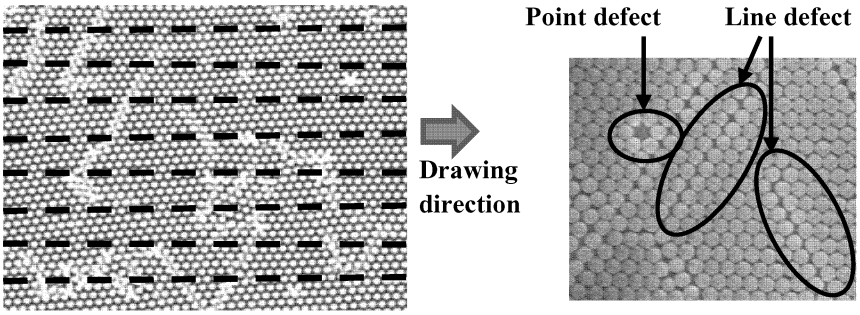

Figure 2: Evaluation and classification of defects in particle array

3. RESULTS AND DISCUSSION

3.1 Flow rate of feed suspension

At the steady-state of a continuous coating process, a simple equation balancing the volumetric fluxes of particles can be expressed as follows;

$$\phi F = h v W \left(1-\varepsilon\right) \tag{1}$$

ϕ is volume fraction of particles in the feed suspension, which is fed to the feeder with constant flow rate, F. v is the drawing speed of the substrate, i.e. coating speed of particle assembly. W is the width of the slit at the outlet of the fixed feeder, that is, the width of the particle assembly layer. h and ε are the height and the porosity of the particle assembly layer, respectively. Figure 3 shows the effect of the flow rate of the feed suspension, F, on the coating speed, v, using 5.0 μm PSL of ϕ = 10% at 30% relative humidity. The structure of particle array was changed from multilayer, monolayer, and submonolayer, as v increased at constant F. The broken line in Figure 3 was the calculation line by using Equation (1) with the monolayer condition, that is h is equal to particle diameter, d, and ε = 0.395, which corresponded with the hexagonal close packing condition. The calculation line agreed well with the experimental data observed monolayer particle assembly. When the coating speed increased from the value calculated by Equation (1) with monolayer condition, some parts of the particle assembly were observed as the bilayer, which indicated as multilayer with diamond key in Figure 3. Decreasing the coating speed, the submonolayer was appeared, which indicated as triangle keys in Figure 3. Figure 4 shows the photographs of the typical experimental results obtained as the multilayer or submonolayer particle assembly.

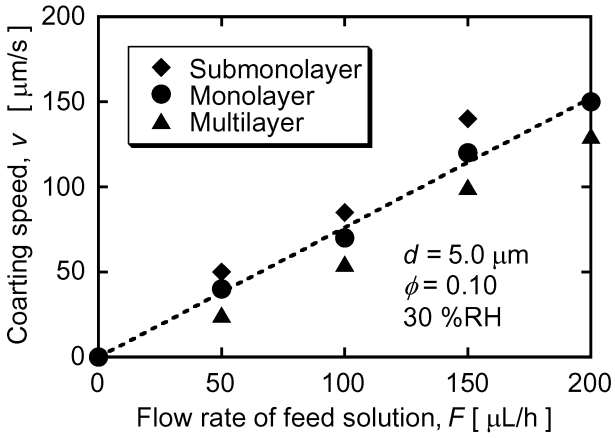

Figure 3: Effect of flow rate of feed suspension on coating speed using 5.0 μm diameter of PSL.

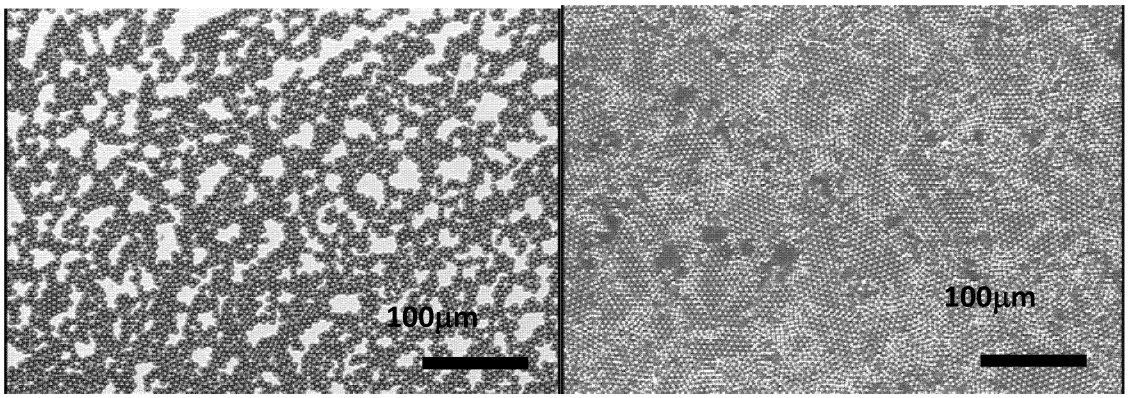

Figure 4: Photographs of submonolayer particleassembly(left) and multilayer particle assembly (right) using 5.0 μm diameter of PSL.

Figure 5 shows the effect of F on the number of defects when monolayer particle array was produced at 30% relative humidity. The number of the point defect of the particle assembly prepared at various flow rates of feed suspension drastically decreased to 1/2 – 1/3 from that at F = 0 condition. The operation of F = 0 was corresponding to the batch coating type experiment by using a similar equipment reported in Prevo and Velev (2004). This means that the continuous coating process is suitable to make less defect assembly than the batch coating system. On the other hand, the number of the line defect of the particle array decreased slightly as F increased.

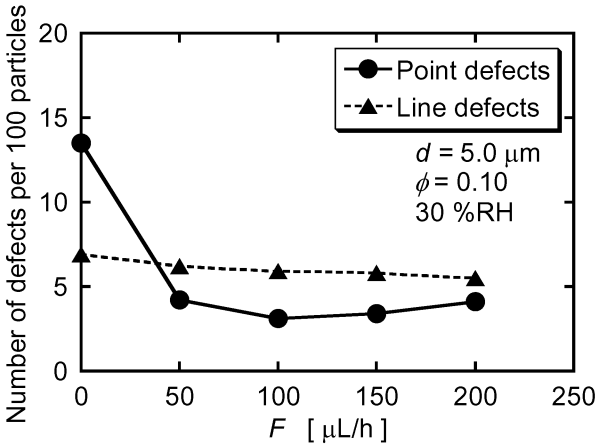

Figure 5: Effect of flow rate of feed suspension on defects of monolayer particle array.

3.2 Particle size and volume fraction of particles in feed suspension

Figure 6 shows the relationship between the flow rate of the feed suspension, F, and the coating speed, v, at the monolayer condition using 5.0 or 10.0 μm PSL. The experimental results using both particles agreed with the calculation line of monolayer condition ($h = d$), where d is particle diameter. When small particles were used, v should increase to prepare monolayer particle array.

Figure 7 indicates the effect of volume fraction of particles in feed suspension, ϕ. When ϕ was changed from 2.5% to 10%, the monolayer particle array could be fabricated by adjusting operated parameters such as v and F, as expected from Equation (1).

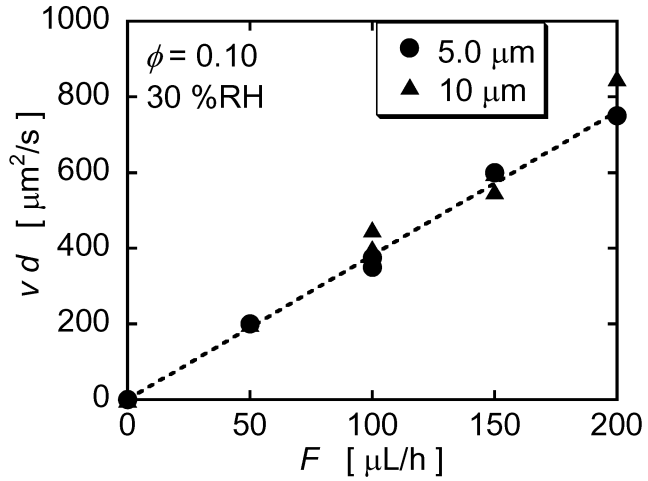

Figure 6: Effect of particle diameter of feed suspension on coating speed using 5.0 or 10 μm diameter of PSL.

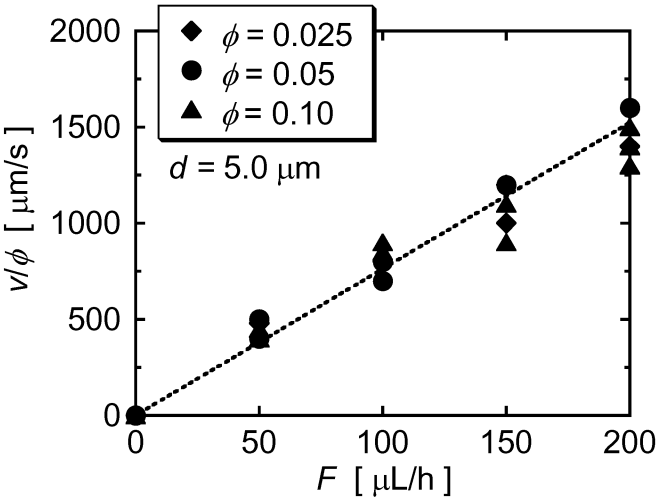

Figure 7: Effect of particle volume fraction of feed suspension on coating speed using 5.0 μm diameter of PSL.

3.3 Relative humidity of surroundings during particle array formation

The effect of the relative humidity of surrounding on the particle assembly behavior was studied. Figure 8 shows the effect of the relative humidity on the coating speed of particle assembly. The coating speed of particle assembly did not change as expected from Equation (1). The area of evaporating region, which defined as the width of the particle array multiplied by the length, l_e, from the outlet of feeder to the growth front of the particle assembly, should be increased with relative humidity, because the evaporation flux, which defined as the amount of evaporated water per unit area per unit time, decreased with increasing relative humidity. The length of the evaporating region, l_e,was observed by using microscope during the coating experiment, and shown as Figure 9. The evaporating region of a thin wetting film increased with the humidity at the certain flow rate of feed solution, because the amount of water to evaporate was same, even if the humidity was changed. The evaporation flux, j_e, on the thin wetting film could be assumed to depend on the difference between the saturated vapor pressure, P_s, and the presentvapor pressure, P, at operated temperature, as written by Equation (2).

$$j_e \propto P_s - P \propto (P_s - P)/P_s = (1 - RH) \tag{2}$$

Equation (2) means that the solvent evaporation flux depends on the relative humidity, *RH*. The evaporation rate, *q*, during the fabrication of particle assembly can be expressed as Equation (3).

$$q = F(1-\phi) = l_e W\, j_e \propto l_e W (1 - RH) \tag{3}$$

Equation (3) can be rewritten as Equation (4).

$$l_e (1 - RH) \propto F(1-\phi) \tag{4}$$

As thelength of the evaporating regionshould depend on the flow rate of the feed solution, *F*, the volume fraction of particles in the feed suspension, ϕ, andthe relative humidity, *RH*, Figure 10 was obtained from the data of various humidity experiments. As most data could be followed to one straight line, the evaporation flux could be expressed as Equation (2).

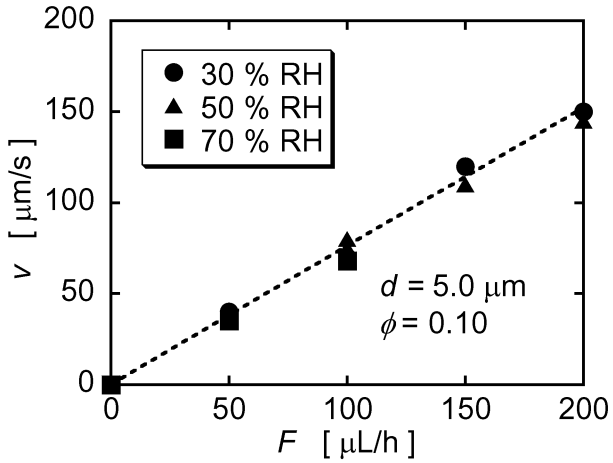

Figure 8: Effect of relativehumidity on coating speed using 5.0 μm diameter of PSL.

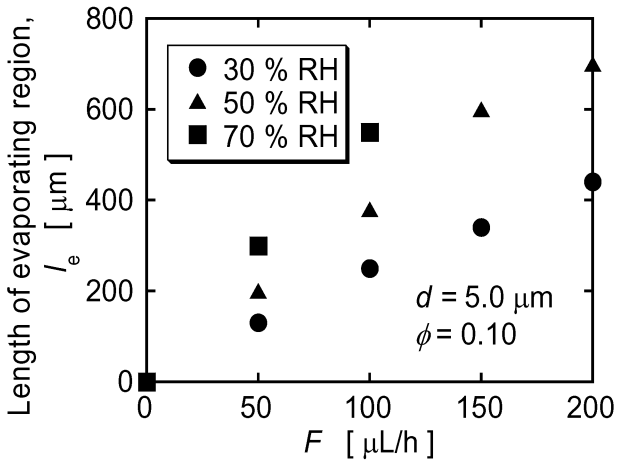

Figure 9: Length of evaporationregion at various relative humidity and flow rate of feed suspension using 5.0 μm diameter of PSL.

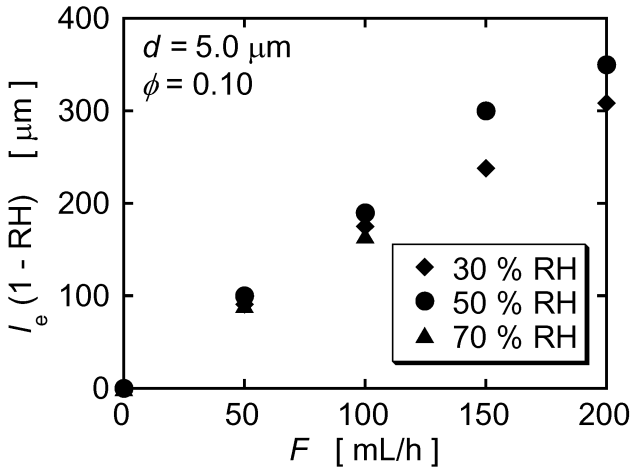

Figure 10: Effect of length of evaporation region on flow rate of feed suspension using 5.0 μm diameter of PSL.

For the effect of the relative humidity on the defects of the particle assembly, the number of the line defects decreased as the relative humidity increased, especially from 30 to 50%. However, the number of the point defects did not depend on the relative humidity so much.

3.4 Contact angle of substrate

Tables 2 and 3 indicated the effect of the contact angle of the substrate mentioned in the section 2.2 on the coating speed of particle assembly using 1.0 μm and 5.0 μm diameter PSL, respectively. The coating speed calculated by Equation (1) was also indicated in the Tables. When PSL with 1.0 μm diameter was used, the particle assembly was prepared on the substrate with less than 30 degree of the contact angle of the substrate. If the higher contact angle and/or the higher flow rate of the feed suspension were used, the coating speed to prepare the monolayer particle assembly should be controlled to the more exact value calculated by Equation (1). For the fabrication of the particle assembly of 5.0 μm diameter PSL, there was similar tendency in the case of 1.0 μm diameter PSL. On the other hands, the particle assembly using 5.0 μm diameter PSL was not observed at the condition of less than 5 degree contact angle, while those PSL could be arranged on the substrate with 10 – 30 degree contact angle. This result indicated that the thickness of the front edge of a thin wetting film was too small for 5.0 μm diameter PSL to deposit on the substrate at the condition of less than 5 degree contact angle.

Table 2: Effect of contact angle on coating speed of particle assembly using 1.0 μm diameter of PSL.

Flow rate [μL/h]	Calculation by Eq. (1)[μm/s]	Contact angle< 5° [μm/s]	Contact angle 10° [μm/s]	Contact angle 15° [μm/s]	Contact angle 30° [μm/s]
50	19.1	10 ~ 30	10 ~ 20	20 ~ 25	20
100	38.3	30 ~ 50	40 ~ 45	35 ~ 40	40
150	57.4	50 ~ 70	50 ~ 70	60	60
200	76.5	70 ~ 80	75	75	75

Table 3: Effect of contact angle on coating speed of particle assembly using 5.0 μm diameter of PSL.

Flow rate [μL/h]	Calculation by Eq. (1)[μm/s]	Contact angle< 5° [μm/s]	Contact angle 10° [μm/s]	Contact angle 15° [μm/s]	Contact angle 30° [μm/s]
50	38.1	—	20 ~ 50	30 ~ 45	40
100	76.2	—	60 ~ 90	70 ~ 80	75
150	114.3	—	95 ~ 130	105~120	115
200	152.4	—	140~160	150	150

3.5 Multilayer of particle array

When the coating speed and the flow rate of the feed suspension were controlled according to Equation (1), the multilayer particle assembly could be obtained. Figure 11 shows the operated results to fabricate the multilayer particle assembly. The keys indicated the experimental results, and the doted lines were calculated by using Equation (1), where the height and the porosity of the particle assembly were taken as the values in Figure 11, that is, the hexagonal closed packing condition. The calculated lines agreed with the experimental data, which means the number of particle layers could be controlled and predicted by Equation (1) and the hexagonal closed packing condition.

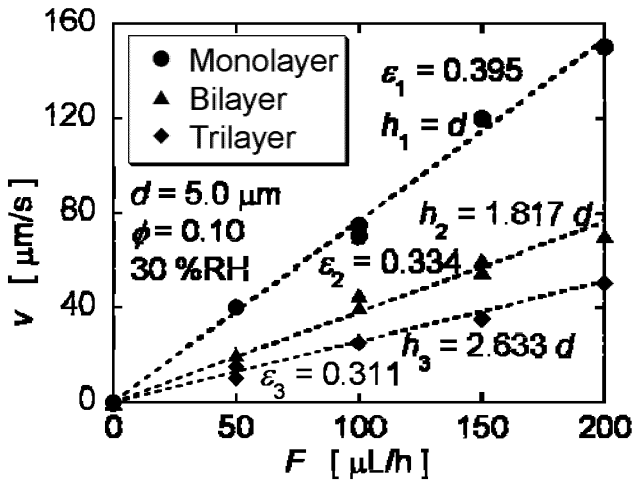

Figure 11: Fabrication of multilayer particle assembly using 5.0 μm of diameter PSL.

4. CONCLUSIONS

We proposed the continuous process to fabricate the particle array thin film by cast coating at a high speed, and then found the following conclusions.

The coating speed to prepare the particle array increased with the flow rate of feed suspension and was much higher than that of the batch type coating process. This coating speed can be predicted by using the proposed mass balance equation of particles. The defects were categorized the point defect and the line defect, and the number of point defects using the continuous coating process decreased comparing those of the batch type coating process. The number of defects also decreased when coating was conducted under high relative humidity. The relative humidity did not affect the coating speed, but the area of the evaporating region on the wetting thin film of particles increased with the relative humidity. The contact angle of the substrate should decrease when the particle diameter became small.

5. ACKNOWLEDGMENT

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