Microspheres pattern forming using self-assembly template prepared by convective deposition

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Abstract. Stacks pattern of microspheres and nanoparticles can be deposited by layer-by-layer coating with several techniques. In this work, we fabricated two pattern monolayers of polystyrene microparticle by convective horizontal deposition. For initial layer, glass substrate was dragged with velocity of 25 μm/s and also applied horizontal vibration with frequency of 50 Hz in order to supply higher kinetic energy for better assembly. Sizes of polystyrene microparticles were 3.2 micrometer for this initial template coating. For the second layer, the microparticle size was varied with 0.93, 1.00, and 1.50 micrometer. The packing of the second layer was investigated by scanning electron microscope. The filling quality of second coating layer strongly depend on particle size and dragging velocity. For the same dragging speed, the microparticle of 0.93 micrometer trended to be well arrangement on the initial template with honeycomb pattern.

1. Introduction

By self-assembly processes such as vertical deposition [1], inward growing [2], or drop coating [3], common obtained structure was face centered cubic (fcc) especially (100) fcc can occur in case of convective deposition with vibrating assistance [4]. For monolayer particle packing, it appeared to be hexagonal packing when the film was deposited by conventional coating. However, an additional arrangement of particle can be appeared by coating particle on self-assembly template [5,6]. The various self-assembly methods have been reported, nevertheless, the convective deposition is very interesting for horizontal coating.

The convective deposition is an assembling mechanism of nanoparticle or microparticle studied by Nagayama and Dimitrov [7]. The particles were pulled into the forming region by evaporation flux and mass gradient. Then, when water film had thickness around particle height, particles were closed to each other by capillary force which was higher influence than Van der Waals and electrostatic force. The advantages of convective deposition are using a little of suspension and rapid fabrication around 15 minutes. The convective deposition was applied in many applications, example of extending luminescence angle of solar cell [8]. The potential of convective deposition was not only the effective of using colloidal and time coating, but also packing quality can be improved by vibrating substrate that was difficult for other methods [9]. Vibrating substrate during coating provided larger size of grain and

higher cover area, because the kinetic energy of particles was increased and thus they can delocalize to optimize energy.

In this work, we studied microparticle pattern on self-assembly template by using convective deposition. For preparing monolayer template, polystyrene microparticles of 3.2 µm (10% w/w) were assembled on hydrophilic glass-substrate which was vibrated with frequency of 50 Hz. In second layer, the patterns of polystyrene microspheres at 10% w/w were investigated for various microparticle sizes of 1.5, 1.0 and 0.93 µm. The smaller particles were deposited with conventional method which was no vibration. The experiment was carried on humidity around 60% at room temperature. The packing patterns were then observed by scanning electron microscope (SEM).

2. Experiments

Polystyrene microspheres (Thermo scientific) for coating the first and second layers had the concentration of 10% w/w and were dispersed in water. Size distribution of microparticle were less than 5%. Before the first layer coating, the glass substrate was sonicated in acronox and isopropyl alcohol to clean and create hydrophilic surface. The polystyrene microsphere of 3.2 µm was assembled as template by moving and vibrating substrate with velocity of 38 µm/s and frequency of 50 Hz. The deposition suspension was dropped within tiny gap between substrate and glass blade which aligned at 45 degree with respect to substrate surface. After that, each polystyrene microparticles of 1.5, 1.0, 0.93 µm was coated on template as the second layer. In second layer coating, there was no vibration because it will increase film thickness. The optimization velocity for dragging substrate reached 4000 µm/s for 1.5, 1.0, and 0.93 µm. Due to water absorption from template, the concentration of suspension was rapidly changed and thus it was important to coat second layer with high speed to reduce this effect. The packing patterns were observed by SEM.

3. Results and discussion

In the first self-assembly layer, the polystyrene microspheres of 3.2 µm were coated on hydrophilic glass-substrate and exhibited monolayer structure of hexagonal closed-packing under the condition at vibrating frequency and dragging velocity of 50 Hz and 38 µm/s, respectively. By using vibrating-assistance, the gain crystals of microparticle was larger than that in conventional deposition, due to higher energy for large area forming. The dragging velocity for moving substrate must agree with vibrating frequency. Vibrating substrate increased evaporation rate of suspension, hence the dragging velocity must be fast enough to still forming monolayer. This template was prepared for the second coating with smaller microparticles.
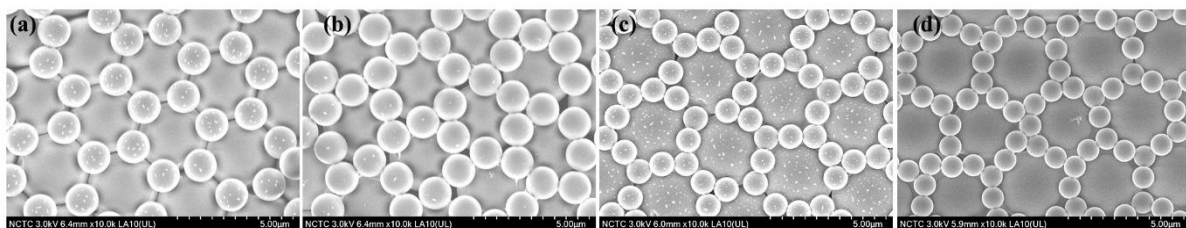

Figure 1. SEM images showing filling pattern of polystyrene microparticle in second layer, (a) and (b) for 1.5 µm, (c) for 1.0 µm, and (d) for 0.93 µm.

The polystyrene microparticle of 1.5 µm had ratio between diameters of small and large particles (γ) about 0.47. The microparticle was coated on template with dragging velocity of 4000 µm/s and this velocity was 105 times faster than speed for template coating. The main reason that the velocity for coating in second layer must be greater than that of first layer was the rapid changing of suspension concentration due to water absorption into the first layer. By instability of colloidal concentration, small particle can form non-uniform cluster. The SEM images of 1.5 µm polystyrene particles indicated the six small particles filled on template defined as type A as shown in figure 1 (a). The microparticle packing was honeycomb pattern with the first nearest neighbour distance of 1.767±0.105 µm. This

structure had symmetrical identity after rotated 30 degree with respect to hexagonal pattern in template. It was noticed that the gap between small particles in second layer was around 200 nm. The maximum ratio γ for closed packed honeycomb structure was calculated to be 0.577. Thus, if the size of second layer microparticle was larger than 1.85 µm, the second layer will not form the closed hexagonal packing.

However, the 1.5 µm polystyrene particles did not exhibit an unique packing as shown in figure 1 (a) only, they can fill in different form. In figure 1 (b), it was seen that in some area the 1.5 µm particles filled in template with closer to each other than the previous pattern. The void position of three first layer particles packing in template in some position can be filled by three small particles as triangle in the second layer which defined by type B as shown in figure 1 (b). For this forming type, the pattern was also honeycomb which had six particles, but they closely packed and aligned with nearly the same directions as those in template.

In case of polystyrene microparticle of 1.0 µm coated as the second layer, the pattern was observed and showed in figure 1 (c). The microparticles were deposited with dragging velocity of 4000 µm/s. The polystyrene particle had size ratio about 0.31 and formed the pattern with 9-11 particle ring. The number of filling particle depended on the type of forming. In case of 9 particle forming, the structure had a half filling of type A and B. The type A provided 3 particles and the 6 microparticles from type B. For the pattern with 10 filling particles, there were 4 particles from type B, 4 particles from type A and 2 particles filled at space between filling of type A. An another pattern that formed with 11 particles was composed of 5 particles from type A, 2 particles from type B and 4 particles filling the free spaces. By sampling images, the pattern which was consisted of type A and type B with 4 and 2 points from 6 points around middle large microparticle was the highest percentage of 56%. Moreover, for this pattern, the type B cannot form at the next position due to the size of polystyrene microparticle. The calculated ratio γ for filling with fully type B in adjacent point was 0.268.

The 0.93 µm polystyrene microparticle had ratio γ of 0.29 and can be well packed on large microparticle template as shown in figure 1 (d). The patterns indicated the packing of 11-12 small particles. For filling with 11 particles, there was a single forming of type A, in other words, the type A was formed by 5 particles and there were 4 particles inserting between type A. In case of type B forming with 3 particles, the type A filled in other positions. When the small polystyrene microparticles formed type A with 6 particles, there were 6 particles filled the gaps between former particles. Thus, this pattern had 12 particles forming. The probability to filling with 11 and 12 particles was comparable.

From deposition of small particles with diameter of 1.5, 1.0, and 0.93 µm, the smaller size of microparticle trended to have higher covering area when compared with same dragging velocity. Coating the second layer was faced the crucial problem of highly change in concentration for all size of polystyrene microparticle. This problem may be solved by infiltration with some sol-gel or polymer to prevent absorption of water into the first layer.
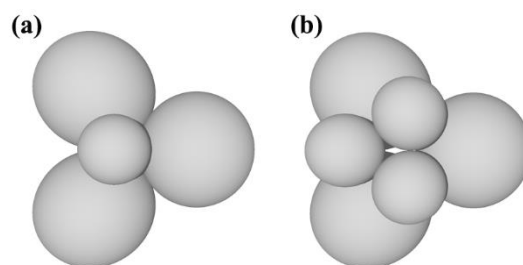

Figure 2. Possible filling types i.e. (a) type A and (b) type B at the void template position forming three large adjacent particles.

Table 1. Number of particles in second layer for microparticle forming with different types at various particle diameter.

Particle size (µm)	Ratio (γ)	No. of filling particles	No. of filling particles in each type		
			Type A	Type B	free area
1.5	0.47	6	6	-	-
		6	-	6	-
1.0	0.31	9	3	6	-
		10	4	4	2
		11	5	2	4
0.93	0.29	11	5	2	4
		11	3	6	2
		11	4	6	1
		12	6	6	-

Conclusion

The self-assembly of microparticle was prepared by convective deposition with vibrating-assistance for template deposition and non-vibration for second coating. The polystyrene microparticle of 3.2 µm was used as template coating, and polystyrene microparticles of 1.5, 1.0, and 0.93 µm were deposited in second layer with very high speed due to optimize the rapid change of concentration. The 1.5 µm polystyrene microparticles formed the honeycomb structure with 6 particles surround. For 1.0 µm microsphere, the patterns were composed of 9-11 particles. The polystyrene microparticles filled with 11-12 particles for the diameter of 0.93 µm. For each size of small particles, they can form with type A, type B, or mixing between type A and B. In this study, the convective deposition technique can provide uniform packing for some small area due to concentration disturbing. This problem may be helped by infiltration of sol-gel or polymer to replace the gap between microparticle in template.

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