Self-Organization of Monolayer of Polystyrene Spheres Assisted with Silica Nanoparticles by Wet Coating

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INTRODUCTION

Self-organization is a pattern formation of built-up, and it is extremely useful technique for mass production using nanotechnology. In recent years, films of ordered colloidal particle monolayer have found a variety of applications, such as optical devices, magnetic devices and self-assembly nanosphere lithography. In our previous study, we indicated the highest limits of coverage by single particle monolayer films fabricated by an evaporation-induced self-assembly method [1].

In this research, we select two kinds of particles in order to achieve higher packing level than those obtained in the previous study of the single particle. Polystyrene latex (PSL) spheres are arranged highly ordered by fashion assisted by silica nanoparticles. The PSL spheres are fabricated by commercial available coaters, such as a spin coater and a capillary coater, in order to arrange in a wide area quickly. For the evaluation of self-organized arrangement, Voronoi diagram analysis, which has been able to analyze point patterns [2] is carried out. In this statistical analysis, the ratio of hexagons in all polygons and the average deviation of all hexagon angles are defined as the evaluation of hexagonal closed-packed structures. We also show the mechanism for the self-organization of PSL spheres with silica nanoparticles during drying by comparing experiments with modelings. Furthermore, we show some applications of synthesized films.

EXPERIMENTAL

The mixed suspensions of mono-dispersed PSL spheres (average diameter; 100-1700 nm) and silica nanoparticles were prepared with the range from 0.5 to 10 wt% for coating with a spin coater(ACT-300D, Active CO., Ltd.) and a capillary coater (CAP Coater III, HIRANO TECHSEED CO., Ltd.). The suspensions were coated on glass plates (15mm ϕx 0.3mm) at 3000 r.p.m. by using the spin coater. The suspensions were also coated on glass plates (100 x 100 x 1.8mm) at the velocity of 10-100cm/min by using the capillary coater. Figure 1 and Figure 2 show a photograph and a schematic feature of a capillary coater, respectively. The zeta potentials of the two kinds of suspensions were measured by

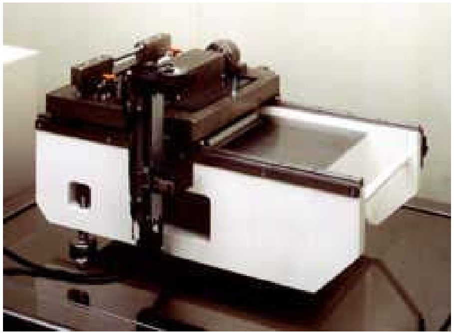

Figure 1. A Photograph of a capillary coater.

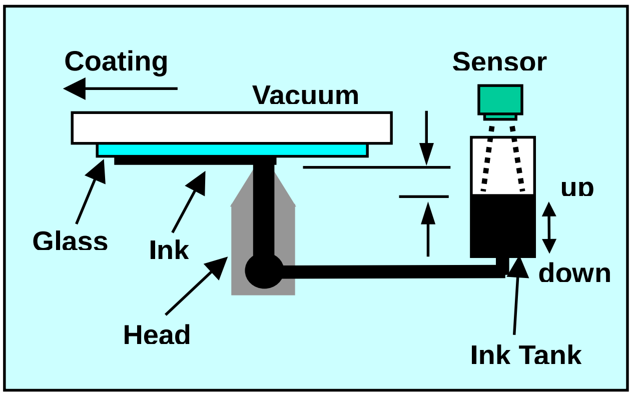

Figure 2. Schematic feature of a capillary coater.

using zeta potential analyzer (LEZA-600S, Otsuka Electronics Co., Ltd.).

The self-organized films of PSL spheres were evaluated by a scanning electron microscope (SEM: JSM-6340F, JEOL CO., Ltd.). The center positions of PSL spheres in each SEM image were determined by a computer image processing using a commercially available program (WinRoof; Mitani Corp.). The quantitative evaluation of organization could be carried out by characterizing the shape of the polygons that constitute the Voronoi diagram.

When the thin film of silica nanoparticles were used for an application, PSL spheres were calcinated at 450°C for 10 minutes in a muffle furnace (KDF S-70, DENKEN Co., Ltd.)

RESULTS AND DISCUSSION

Evaluation of surface morphology

The highly coved PSL monolayer could be obtained by spin coater and capillary coater. The Voronoi polygon analysis was carried out for evaluating the regularity of PSL spheres quantitatively. Each Voronoi polygon is generated from the intersection of perpendicular bisectors of the line segments connecting any center of gravity to all its nearest neighbors. The ratio of hexagons in all polygons, that is ordering factor; *OF_polygon* (1) as follows, is defined as the quantitative evaluation of hexagonal closed-packed structures.

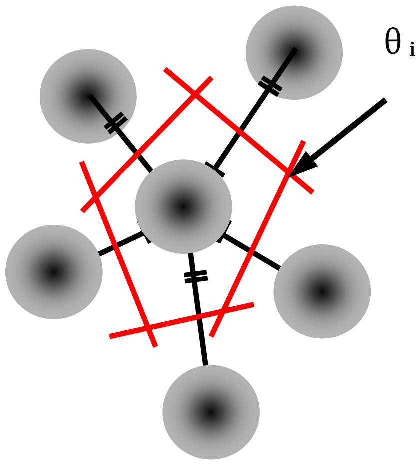

Figure 3. Schematic feature of Voronoi polygon

Ordering factor for polygon：*OF_polygon*

OF_polygon = (the number of all hexagons) / (the number of all polygons) (1)

Next the average deviation of all polygon angles from 120 degree, that is ordering factor; *OF_angle* (2) as follows, is also defined as the qualitative evaluation of hexagonal closed-packed structures.

Ordering factor for angle：*OF_angle*

$$OF\_angle = 1 - \frac{\sum_{i=1}^{n} \left|\theta_i - \theta_{hcp}\right|}{180 \cdot n} \qquad (2)$$

θ_i: Each angle of Voronoi polygons, θ_{hcp}: One angle of a regular polygon,
n: The number of all polygons constructed by the Voronoi polygon analysis

The arrangement of the PSL spheres with silica nanoparticles was evaluated by the Voronoi polygon analysis. In a wide area of the thin film, *OF_angle* analyzed by Voronoi diagram was 0.98. The result of the parameter indicates that almost all PSL spheres are arranged under hexagonal closed-packed structure. Furthermore, *OF_angle* analyzed by Voronoi diagram was 0.99. It is indicated that the average deviation of all hexagon angles from 120 degree is only 1.5 degree.

Mechanism of the self-organization

In order to investigate the effect of silica nanoparticles as the second particle, PSL spheres were arranged with and without silica nanoparticles. It was found that the boundaries of PSL spheres without silica nanoparticles were smaller than those of the hexagonal packed PSL spheres under the existence of silica. Zeta potentials of PSL and silica particles were –42mV and –30mV, respectively. The Zeta potentials are high enough to prevent the aggregation of both particles of silica and PSL. But the Zeta potential of PSL is not enough to arrange to hexagonal packing by electric repulsive force only.

The model was carried out to investigate the relationship between process condition and the structure of self-organized PSL spheres. Each nanoparticle is subject to multiscale surface force such as capillary force, contact force, electrostatic force, van der Waals force and substrate friction force. The result of modeling was as follows. Under drying process, PSL spheres were gathered by capillary attraction force. In the case of PSL without silica nanoparticles, the PSL spheres couldn't rearrange the hexagonal packing form after their collision, since the friction force of the PSL surface is strong. When the nano-sized silica particles as second particles existed in the PSL solution, a different phenomenon was occurred. First, PSL spheres were also governed by capillary attraction force and gathered each other. However, the existence of silica nanoparticles prevented the collision between PSL spheres by the elastic repulsive force of silica nanoparticles. It is indicated that, immediately before the collision, the elastic repulsive force of silica nanoparticles gives the chance for the self-organization to PSL spheres.

APPLICATIONS

A silica thin film with hemisphere macropores could be obtained after PSL spheres were calcinated at 450°C for 10 minutes in a muffle furnace. CNTs were grown in the hemisphere macropores selectively. The CNTs have applications in the cathode of field emission display (FED).

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