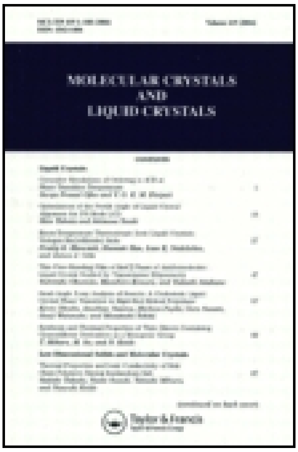

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Ring Structures Prepared by Self-Assembled Particle Layers

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In this paper, thermal fusion of polymer spherical particles was examined to prepare ring structures on a solid substrate. Polystyrene particles (200 nm diameter) were two-dimensionally arrayed by an evaporation-driven method. The self-assembled structures, i.e., two-dimensional colloidal crystals, were kept under 50° C for 20 minutes. Three peeling methods were tried after the thermal fusion treatment: manual peeling, peeling by polydimethylsiloxane adhesion and mechanical peeling. We show that using these peeling methods we were able to obtain the ring structures as well as other interesting structures.

Keywords Artificial opal; particle array; polystyrene; self-assembly; self-organize

Introduction

Self-assembly is a bottom-up fabrication technique employed to construct a material from a molecular level. It is completely different from top-down processing technologies such as lithography. Considerably important papers, reviews, and books have been published regarding self-assembly [1]. Two-dimensional (2D) colloidal crystals (also called fine particle films or fine particle arrays), in which fine particles are two-dimensionally arrayed in a desired number of layers, are used in various fields such as electronic devices and tissue engineering [2–3].

Methods to prepare the 2D colloidal crystals include dynamic thin laminar flow [4], spin coating [5], electrophoresis deposition [6] and evaporation-driven assembly [7]. To arrange submicro- and nano-particles, the electrophoresis deposition or evaporation-driven methods are regarded as the most effective. In electrophoresis deposition, fine particles are arranged on an electrode by applying an electric current to the electrode dipped in a particle suspension. When a direct current is applied, fine particles accumulate on the electrode; however, when an alternating current is applied, the particles are periodically arranged. Because the fine particles are

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assembled in solution, a process to solidify the self-assembled structure in solution is needed. In the evaporation-driven method, particles in the suspension are assembled into a film by surface tension and capillary forces at the meniscus. The fine particles are arrayed in a close packing structure as Nagayama et al. reported in 1993 [8]. In that work, the particles were observed to self-assemble by capillary forces, resulting in a fast water evaporation speed. Therefore, water from the bulk suspension flowed to the edge of the meniscus, and the other particles in the suspension were driven to this nucleus by the resulting convective transport. This method caused direct arraying of the fine particles on the solid substrate, such that a further solidification process was not needed.

The fine particles constituting the 2D colloidal crystals can be deformed by an etching processes. For example, the polystyrene or SiO_2 spherical particles can be deformed and show various interesting patterns by oxygen plasma etching [9–10]. However the plasma etching equipment is expensive and considerable experience is needed to manipulate the equipment. Thermal fusion presents an attractive alternative to plasma etching, as it can be used to process fine particles easily at a low cost [11]. Solid particles, when in contact with each other at elevated temperatures, tend to minimize the total surface area by coalescence. This process is called sintering. It is usually accompanied by a decrease in the total volume of the particle structures. In this paper, a new processing method of fine particles utilizing this characteristic of thermal fusion is researched.

Experimental

Preparation of 2D Colloidal Crystals by Self-Assembly

An evaporation-driven method was used to prepare 2D colloidal crystals. The substrates were non-fluorescent glass slides (“Micro-slide” glass, Matsunami, Co., Japan) cut to 38 × 13 mm. The substrate was rinsed with distilled water and methanol and soaked in 1 wt% NaOH aqueous solution for approximately 30 minutes. A 1.0 wt% water suspension of monodisperse polystyrene (PS) particles (particle size 200 ± 6 nm, Duke Scientific Co.) was used to prepare 2D colloidal crystals. The inclined glass substrate was dipped using an angle controllable clip attached to a dip coater (D-0407, Asumigiken) into the suspension at constant speed (a range of 730–835 μm/sec) and pulled out at constant speed (Fig. 1). The angle of the substrate

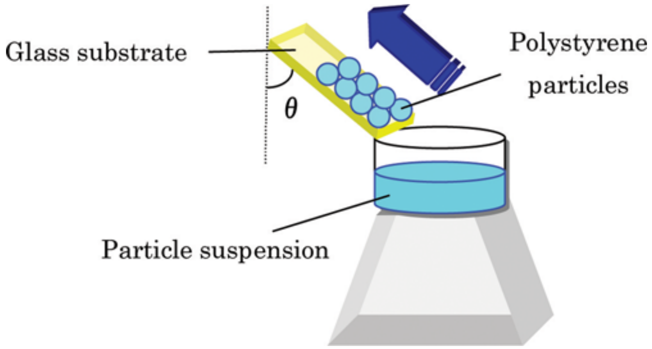

Figure 1. Schematic image of the preparation of 2D colloidal crystals.

Table 1. The preparation parameters for 2D colloidal crystals

Parameter	Temperature (°C)	Moisture (%)	Suspension concentration (wt%)	Coat speed (μm/sec)
Range	22.0–30.0	25.1–53.5	0.5–2.5	730–835

was 60° from the vertical. Temperature, moisture, suspension concentration, and coat speed were examined (Table 1).

The Peeling of Fine Particles in 2D Colloidal Crystals

The formed colloidal crystals were kept under 50°C for 30 min, and three peeling methods were examined: 1) manual peeling, 2) peeling by polydimethylsiloxane (PDMS) adhesion and 3) mechanical peeling. All samples were examined with atomic force microscopy (AFM, SPM-9500 Shimadzu). The peeling procedures are described below.

1. Manual peeling. Non-fluorescent glass slides (76 × 26 mm, "Micro-slide" glass, Matsunami, Co., Japan) were held at a constant angle (about 30° from the substrate) by hand and pressed and dragged on the sample after thermal fusion. After dragging, an ultrasonic cleaning was carried out on the sample. The sample was vacuum-dried in an aspirator for 20 min.
2. Peeling by PDMS adhesion. Polydimethylsiloxane, a thermosetting resin, (PDMS, Sylgard® 184 Silicone Elastomer Kit, Dynamic Viscosity = 3900 Centipoise and Sylgard® 170 Silicone Elastomer Kit, Dynamic Viscosity = 2900 Centipoise, Dow Corning) was dripped on the prepared 2D colloidal crystals and dried in a fume hood for one day. The corner of the dried PDMS film was lifted by the edge with a micro-spatula and the PDMS film was peeled off gently from the glass substrate using tweezers. After peeling, an ultrasonic cleaning was carried out on the sample and the sample was vacuum-dried in an aspirator for 20 min.
3. Mechanical peeling. A 2D colloidal crystal was placed on the X-axis of the stage. A glass slide and an aluminum board (size: 50 × 18 mm) was alternately set on the Z-axis stage with angles at 25° or 90° (measured from the Z-axis). These boards were lightly impressed on the 2D colloidal crystal after thermal fusion. The impressed 2D colloidal crystal was moved with a speed of 1000 μm/sec in the direction of the X-axis. No ultrasonic cleaning after the mechanical peeling was carried out on the sample.

Results and Discussion

Self-Assembled Particle Structures

Typically, small polystyrene particles do not self-assemble into arrays on substrates at large contact angles. The substrate surface was covered with hydrophilic termination groups (OH) by a hydroxylation treatment, resulting in a decrease in contact angle to 16.9°. This small contact angle prompted the preparation of a 2D colloidal crystal with a greater surface area. The digital camera image of the produced 2D colloidal crystal (Fig. 2) demonstrates that it is possible to produce a monolayer (brighter area) of significant surface area. It was observed that the 60° coat angle was most suitable to prepare a large surface area of 2D colloidal crystal using 202 nm polystyrene particles. A meniscus was formed on a substrate by dipping the substrate into a suspension. The shape of the meniscus depended on the angle of inclination of the substrate. The advection flow of the particles onto the substrate surface was related to the meniscus shape. As a result, monolayers of large surface area could be obtained by control of the inclination angle (unpublished work).

The experimental parameters in regards to 2D colloidal crystal monolayer preparation were examined to maximize surface area. A theoretical formula has been reported to prepare monolayers by the method of withdrawing a plate from a suspension [12]:

$$v_c = \frac{\beta l j_e \phi}{h(1-\varepsilon)(1-\phi)} \cdots \tag{1}$$

Where,

v_c = velocity
β = coefficient that accounts for the fact that the velocity of the particles convected by the flow could be somewhat different from the hydrodynamic velocity of water
l = the width of the meniscus
j_e = the evaporation flux of water molecules per unit area of the evaporating surface
ϕ = particle volume fraction
h = the thickness of the meniscus normally the diameter of the particles for the monolayer
ε = porosity of the colloidal crystals (for the hexagonally packed spheres, $1 - \varepsilon = 0.605$)

A detailed description of each parameter is discussed by Prevo *et al.* [13]. Although Prevo et al. used 1.1 μm diameter particles, the fact that fast-drying films

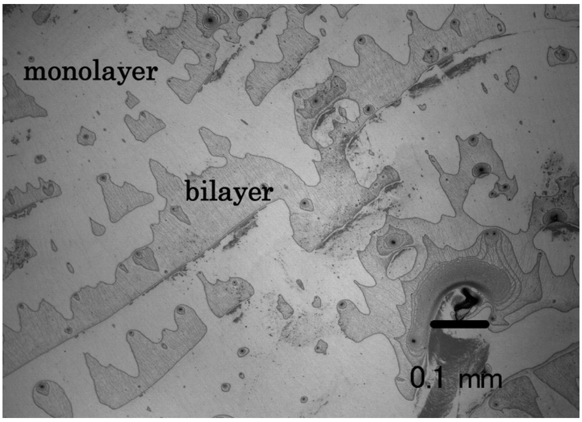

Figure 2. An optical microscope image of a 2D colloidal crystal. Coat speed was 745 μm/sec and the suspension concentration was 1 wt%.

should have a correspondingly shorter drying length j_e^{-1} at low humidity should also be true in the current experiments.

In our results, monolayers of 2D colloidal crystals were optimally formed under higher temperatures, fast coat speeds, and low suspension concentrations. Concentration was seen to have the greatest impact of all the parameters. These results were similar to the results of the dip coat method.

The current experiment parameters were substituted into equation (1). In this system, the greatest monolayer area of the 2D colloidal crystal is obtained with parameters 1.0 wt%, 60° and 745 μm/sec as the suspension concentration, coating angle and coating speed, respectively. Here, h was 2.24×10^{-6} m by substituting 745 μm/sec as v_c, and was 4.48×10^{-6} m by substituting the cosine component of v_c, 372.5 μm/sec. According to equation (1), h should be close to the particle diameter of 202 nm. Our experimental results were an order of magnitude larger than the calculated results. This result implies two points: Primarily, the transfer rate of the meniscus edge on the substrate has a larger influence on self-assembly than that of the gravitational force. Secondally, in the self-assembled preparation with an inclined substrate, factors that were negligible in the case of a perpendicular substrate (convection flow, for example) had considerable influence.

Manual Peeling

The two-dimensional colloidal crystals after thermal fusion were peeled by three methods with the expectation to form a new self-assembled pattern.

1) Manual peeling was examined to simplify experimental parameters such as force, strength and peel angle. The peeling process was carried out deeply and slowly to peel off the particles. As a result, fine particles could be readily peeled off.

AFM observation revealed that the ring structures were periodically colloidal-crystallized (Fig. 3). The reason of the ring structure formation should be as follows: first, the polymer particles became gel-like under heating. Then the polymer close to the bottom of particles forms a gel meniscus on the substrate, which is stretched in two-dimensions toward the edge of the meniscus by the capillary force. As a result, the polymer forms ring-like structures (Fig. 4). This result shows that thermal fusion was effective for the preparation of new ring-like structures. However, it can be said that this manual peeling method has low reproducibility and was not adequate for actual preparation.

Peeling by PDMS Adhesion

The AFM image of the sample after peeling by PDMS adhesion is shown in Figure 5. The fine particles after thermal fusion were not peeled off from the glass substrate. It has been reported that the multi layers may be peeled off by PDMS adhesion [14]. In the current experiments, it was also confirmed that multi layers were peeled off by PDMS. However, the bottom layer fused on the substrate could not be peeled off, even with the lower-viscosity PDMS (Sylgard® 170 Silicone Elastomer Kit: viscosity = 2900 Centipoise) than the previously-used PDMS (Sylgard® 184 Silicone Elastomer Kit: viscosity = 3900 Centipoise). There is a possibility that repeated peeling would lead us to peel off the bottom layer, however, there was also a possibility that the repeated peeling would cause the particle shape to deform. Thus, we did not repeat the mechanical peeling on any samples.

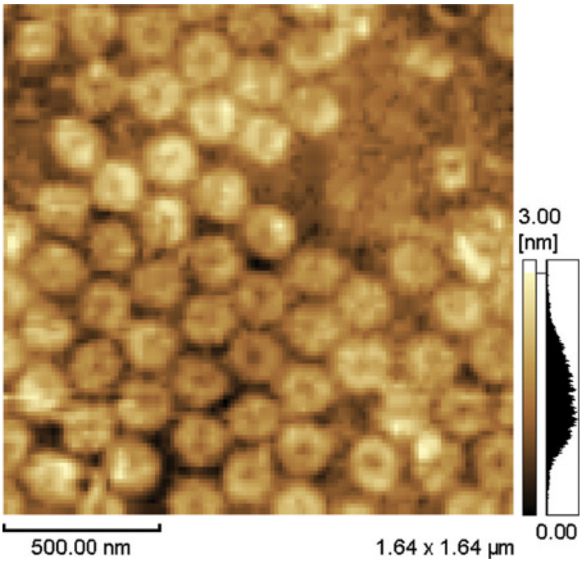

Figure 3. AFM image of the structure prepared by manual peeling with a glass board.

Mechanical Peeling

As a similar method to manual peeling, the mechanical peeling using a x-y electric stage was examined. The material and the angle of the peeling board was changed. As a result, in either case, the ring structures were formed, however, the prepared ring-shapes were not arrayed.

Rings with smaller inside diameters were prepared by peeling at smaller angles, and rings with larger inside diameters were prepared by peeling at larger angles. Similar angle dependence was observed by manual peeling with a glass board.

When an aluminum board was used, the rings with larger inside diameters were prepared at smaller peeling angles (25°, Fig. 6a), and the rings that had smaller inside diameters were prepared at larger peeling angles (90°, Fig. 6b). The thickness of the aluminum board was 0.30 mm and was easily transformed by mechanical pressure (the board was not broken even whilst bending at 180°). The rigidity difference

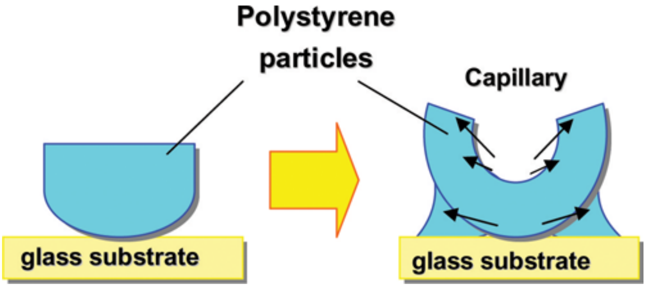

Figure 4. Schematic image of the ring-like shapes by thermal fusion.

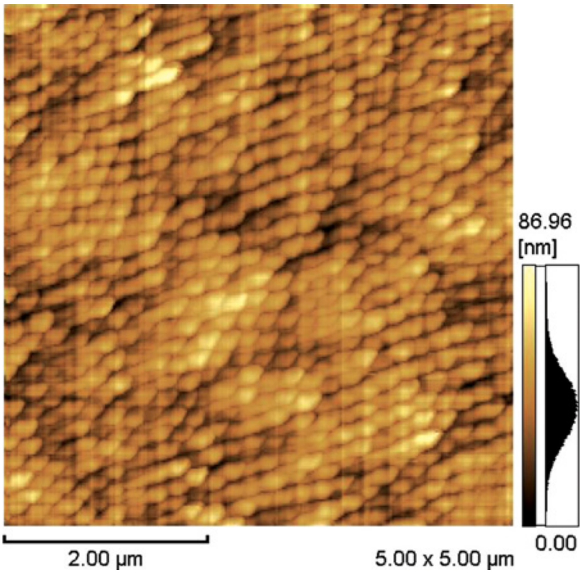

Figure 5. AFM image of the structure prepared by peeling by PDMS adhesion.

between the glass board and the aluminum sheet caused the difference of the angular dependence of prepared shapes. It should be noted that the Young's modulus of glass and aluminum are approximately equal ($\sim 7.03 \times 10^{10}$).

When highly rigid material such as a glass board was used, the particles were easily peeled off at larger peeling angles. Meanwhile, in the case of a less rigid material, such as the aluminum board, the particles were easily peeled off at smaller peeling angles because the board was bent at larger peeling angles. Actually, the particles were deeply peeled at a low angle of peeling (25°), and all the fine particles were peeled off. However, in the case of an angle of 90°, only the top of the 2D colloidal

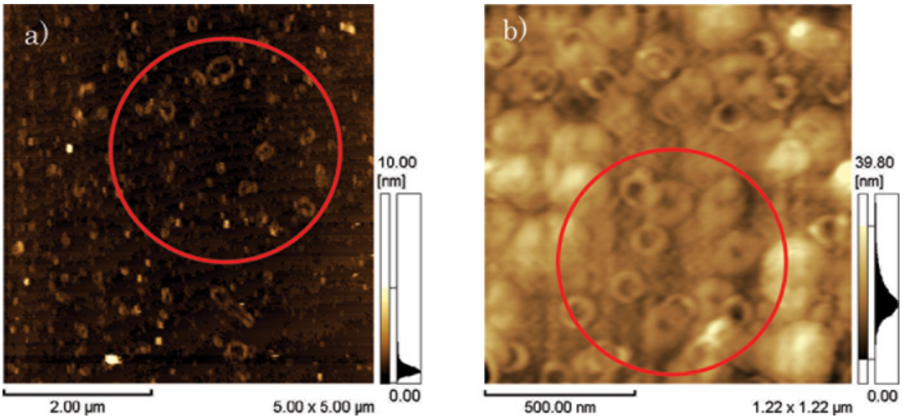

Figure 6. AFM image of the structures prepared by mechanical peeling with an Aluminum sheet. Peeling angle is 25° (a) and 90° (b).

Table 2. Difference of ring structures by 3 peeling methods (units of nm)

	Manual peeling with a glass board	Peeling by PDMS adhesion	Mechanical peeling with a glass board	Mechanical peeling by an aluminum sheet
Diameter of fine particles (d_{out})	186.01	185.55	182.00	127.7
Height (h)	0.79	11.5	9.62	7.89
Inner diameter (d_{in})	35.04	–	46.28	50.04
Depth of the hole (a)	0.12	–	1.41	2.05

crystal was peeled off, resulting in the preparation of ring-like structures. In summary, the ring-like structure that had a larger inside diameter was formed under the conditions in which the particles were easily peeled off.

To examine the above consideration, the distance between an aluminum board and 2D colloidal crystal was changed with a constant peeling angle. A shorter distance resulted in a ring with a larger inside diameter (Table 2). This result supports the above consideration.

Conclusions

In this study, as a new method for processing fine particles, we focused on thermal fusion of polymer particles. The polymer which constitutes the fine particles becomes gel-like by heating. The polymer close to the bottom of the particles forms a gel meniscus on the substrate, and stretches in two dimensions outward to the edge of the meniscus by capillary force. We were able to obtain ring structures by manual peeling and mechanical peeling methods. The more reproducible was provided by the mechanical peeling method.

The major difference between these two methods is the outer diameter of the ring structures. In the manual glass peeling method, only the top parts of the particles were peeled. The outer diameter was ~180 nm and was approximately the same as the original outer diameter (200 nm). In contrast, the outer diameter became smaller in the mechanical aluminum board peeling method, ~120 nm. The ring-like structure with the larger inside diameter was formed under the conditions in which the particles were easily peeled off. This consideration was also supported by the lower height of the ring structure prepared by manual peeling, in which the particles were easily peeled off.

From these results, it can be said that rings of various shapes can be prepared by varying the modulus of rigidity of the peeling material, the peeling angle and the distance between the peeling material and the 2D colloidal crystals. These structures were easily prepared without any expensive apparatus. These structures are expected to have applications in metamaterials in the future.

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