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Multiple-Layered Colloidal Assemblies via Dipping Method with an External Electric Field

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Abstract: When using the dipping method for crystal formation, mono-layered colloidal crystal structures depend upon the lift-up rate of a glass substrate. The mono-layered colloidal crystals showed the highest quality when the glass substrate was raised at a rate of 3 mm/min at 25 °C in a 1 wt% polystyrene colloidal suspension (ethanol medium). In addition, in order to obtain multiple-layered colloidal crystals, an external electric field was introduced. Multiple-layered colloidal crystals were successfully obtained via this method. The colloidal particles were well ordered over large areas and assembled into a homogeneous structure.

Keywords: colloidal crystals, mono-layer, multiple-layer, colloidal suspension.

Introduction

Two-dimensionally arrayed photonic bandgap crystals can be used as masks for two-dimensional arrays,[1] Bragg reflectors,[2] and band wave guides.[3] Accordingly, intensive studies have been performed over the last few decades in this field. At the same time, three-dimensionally ordered photonic bandgap crystals have also been studied because of their potential applications such as use in tunable lasers,[4] optical filters,[5] and switches.[6]

Two-dimensional assemblies of colloidal crystals have been investigated mainly by Nagayama groups.[7-11] They have established an effective mechanism of two-dimensional assembly of colloidal particles. However assembling methods for three-dimensional colloidal crystals have not yet been clearly established. Recently methods to assemble colloidal particles three-dimensionally over a large area have been reported. The typical methods are gravitational sedimentation of colloidal particles,[12] vertical deposition,[13] vertical deposition with temperature gradient,[14] electrophoresis,[15] colloidal assembly at an air-water interface,[16] and colloidal assembly on a liquid metal surface.[17] In addition to the aforementioned, we propose a new method to assemble colloidal particles three-dimensionally. We have found optimal conditions for a dipping method for mono-layered colloidal crystals and fabricated multiple-layered colloidal crystals by introducing an external electric field on the dipping method.

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Experimental

PS Colloidal Particle Preparation. Polystyrene (PS) submicron-sized particles as building blocks of photonic crystals were synthesized by emulsifier-free emulsion polymerization, the details of which are reported elsewhere.[18-21] Deionized water (450 g) was poured into a reactor and the water was kept at a temperature of 80 °C and stirred at 350 rpm. Sodium styrene sulfonate (0.1 g) as an emulsifier and sodium hydrogen carbonate (0.25 g) as a buffer were inserted into the water. After 10 min, styrene monomer (50 g) was inserted into the solution. After 1 h, potassium persulfate (0.25 g) was introduced as an initiator into the solution. Finally, polymerization was performed under a nitrogen atmosphere for 18 h.

The effective diameter of the prepared PS colloidal particles estimated by a Zeta Plus (Brookhaven Instrument Corp.) was 450 nm, and their polydispersity was 0.005 (these values are average values of five measurements). However the diameter of the corresponding PS colloids obtained by scanning elec-

tron microscopy (SEM) was 440 nm.

PS Colloidal Suspension (Ethanol Medium) Preparation. In order to separate PS colloidal particles from water medium, the equivalent amount (240 g) of PS colloidal suspension was poured into 250 mL two polypropylene (PP) bottles (Nalgene®), respectively, and the suspension was centrifuged (Supra 22 K) under 5000 rpm at 10 °C for 30 min. The PS colloidal particles sediment on the bottom of PP bottles were then redispersed in ethanol.

Results and Discussion

Mono-Layered Colloidal Crystal. In order to obtain mono-layered colloidal crystals, a dipping method was adopted. First, a clean glass substrate was dipped vertically into a 1 wt% PS suspension (ethanol medium) at 25 °C at a rate of 10 mm/min to a depth of 20 mm. These conditions were then held for 5 min in order to eliminate interface fluctuation. The dipped glass substrate was subsequently extracted vertically from the suspension at a rate of 1, 3, 5, and 10 mm/min, respectively, in order to examine the effect of crystalline quality on the lift-up rate. The procedure is illustrated schematically in Figure 1(a).

When a glass substrate is dipped into a PS suspension, the surface of the suspension is distorted toward the glass substrate as depicted in Figure 1(b). Once the surface is distorted, colloidal particles move toward the edge of the interface between the glass substrate and the suspension medium (meniscus) because of influx toward the edge. These phenomena are a result of colloidal particles being pinned at the edge of the meniscus (contact line) because an evaporation of suspension medium is highest at the edge. Accordingly, the pinned colloidal particles fix the contact line at the edge and consequently cause an inflow of the suspension.[22-24]

The colloidal particles existing along the contact line assemble (one-dimensional assembly) due to lateral capillary force, as illustrated in Figure 1(b). In addition, colloidal particles assemble into an ordered structure (two- or three-dimensional assembly) by movement of colloidal particles toward the contact line edge. Accordingly, the characteristics of colloidal crystals such as colloidal crystal thickness and number of defects are related to the evaporation rate of the suspension medium, the evaporation temperature endowing colloidal particles with kinetic energy, and the thinning rate of the meniscus relating to the lift-up rate of a glass substrate. Numerous other factors such as the density difference between colloidal particles and the suspension medium and interfacial tension also influence the characteristics of the colloidal crystals. In the present study, however, we focus on the effects of the thinning rate of the meniscus on the colloidal characteristics. We have performed experiments controlling the lift-up rates of the glass substrate (1, 3, 5, and 10 mm/min, respectively) as illustrated in Figure 1(a). The resulting

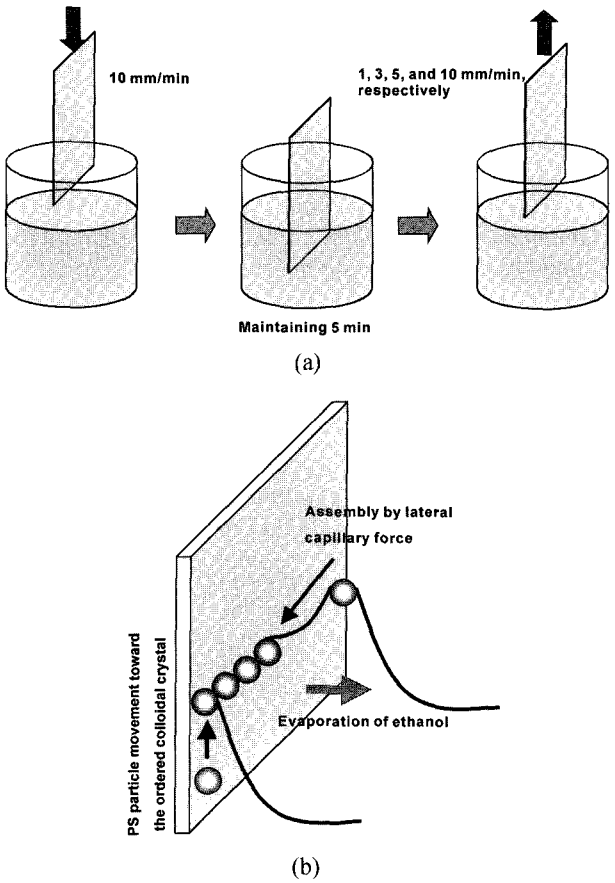

Figure 1. (a) Procedure of a dipping method and (b) schematic illustration of the meniscus.

scanning electron microscopy (SEM) surface images of mono-layered colloidal crystals with varied lift-up rates are shown in Figure 2. Figure 2(a) shows that colloidal particles do not assemble into a monolayer. The inset reveals clearly that there exists another layer below the top layer. The reasons are systematically illustrated in Figure 3(a). When the lift-up rate is 1 mm/min, the meniscus is relatively smooth and consequently the colloidal particles have sufficient time to move toward the ordered region of the contact line edge. This smooth meniscus also enables colloidal particles to assemble into multiple layers. Figure 2(b) and (c) show colloidal particles ordered into a monolayer. Figure 2(b) reveals only a triangular lattice structure but Figure 2(c) shows a dominant triangular lattice structure and a scattered square lattice structure. When the lift-up rate is 3 and 5 mm/min, respectively, the meniscus becomes sufficiently sharp so as not to form multiple colloidal layers (see Figure 3(b)). However, as the lift-up rate becomes faster, colloidal particles are fixed onto the glass substrate more easily. Accordingly, when employing a slower lift-up rate, colloidal particles have adequate time to form a thermodynamically stable lattice structure (the triangular lattice structure). When the lift-up rate is 10 mm/min, colloidal particles reveal a sparse structure

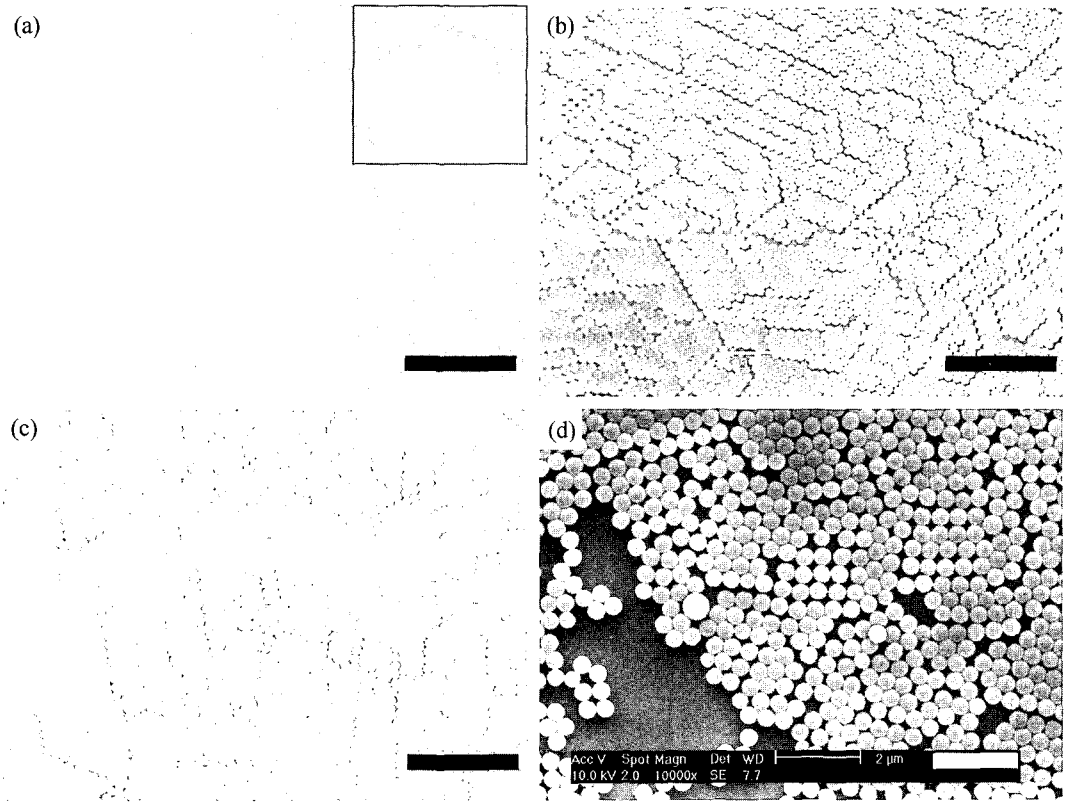

Figure 2. SEM surface images of mono-layered colloidal crystals with lift-up rate. (a) 1 mm/min, inset shows that colloidal particles assemble into multiple-layers, (b) 3 mm/min, (c) 5 mm/min, and (d) 10 mm/min. Scale bars: (a), (b), and (c) = 5 μm, (d) = 2 μm.

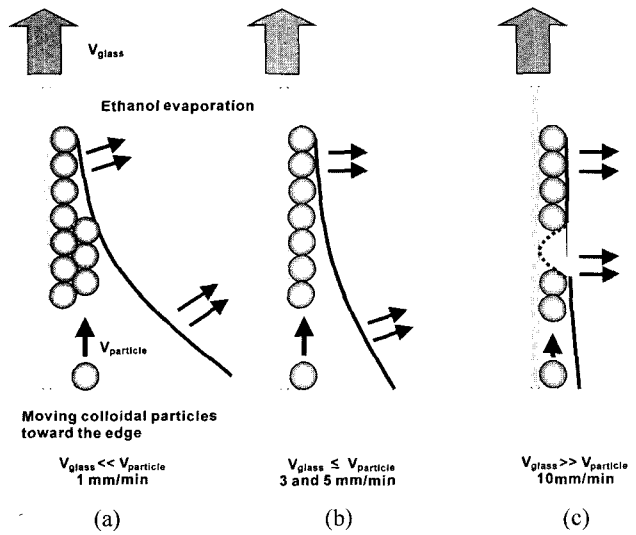

Figure 3. The meniscus shapes with lift-up rate (a) 1 mm/min, (b) 3 and 5 mm/min, and (c) 10 mm/min.

because they are fixed onto the glass substrate before reaching the ordered region of the contact line edge due to the very steep meniscus (see Figure 3(c)). Therefore the lift-up rate of 3 mm/min is optimal to obtain two-dimensionally ordered colloidal crystals (mono-layered crystals) under the current experimental conditions.

The crystal structure reveals some defects in optimal condition. The parameters controlling the order of colloidal crystals are the medium evaporation rate, the processing temperature (which is related to the kinetic energy of colloidal particles), the lift-up rate of the glass substrate, applied voltages, etc. In the current experiments, we only examined the order of colloidal crystals with the lift-up rate. Therefore, we believe that the order of crystals structure will be enhanced by controlling the other parameters.

Multiple-Layered Colloidal Crystal. Multiple-layered colloidal crystals have been studied intensively because they can be used as a template of photonic bandgap crystals. In order to fabricate multiple-layered colloidal crystal, we introduced an external electric field to the above-referred dipping method because negatively charged PS colloidal particles respond to the electric field. The experimental scheme is illustrated in Figure 4.

An ITO (Indium Tin Oxide) coated glass substrate was connected to an anode and a polished aluminum substrate was connected to a cathode, as depicted in Figure 4. Then 3 DC volts of electricity were applied. The ITO substrate on which the colloidal particles are deposited was dipped vertically into a 1 wt% PS suspension (ethanol medium) at 25 °C

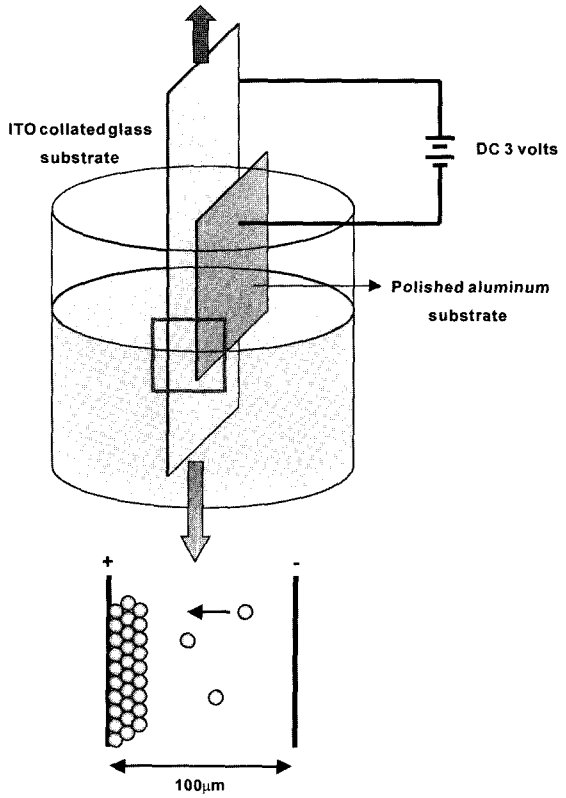

Figure 4. Scheme of experiments for assembly of a multiple-layered colloidal crystal.

to a depth of 20 mm. The aluminum substrate was separated from the ITO substrate with a gap of 100 μm and was placed into the PS colloidal suspension to a depth of 1 mm.

When the aluminum substrate was dipped into the colloidal suspension to a depth of 20 mm, PS colloidal particles were deposited immediately onto the ITO substrate by the electric field. Colloidal crystals assembled within a colloidal suspension have multiple domains. To eliminate unfavorable crystal structures, the aluminum substrate was dipped into the colloidal suspension as depicted in Figure 4. When colloidal particles assemble within a suspension, they are randomly deposited onto an ITO substrate as the first layer. Subsequent layers are then deposited onto the first deposited layer. Accordingly, the resulting colloidal crystal has multiple domains. The first deposited layer assembles randomly because an assembling force between colloidal particles does not exist within a colloidal suspension. On the other hand, at the meniscus, colloidal particles deposit onto the ITO substrate with ordered structure because there is a capillary force assembling colloidal particles. Therefore the ordered structure of the meniscus can be extended successively through this method. In addition, the applied shear rate resulting from the movement of the ITO substrate enhances the ordering of the deposited colloidal crystal.[25]

In this experiment, the ITO substrate was raised at a rate

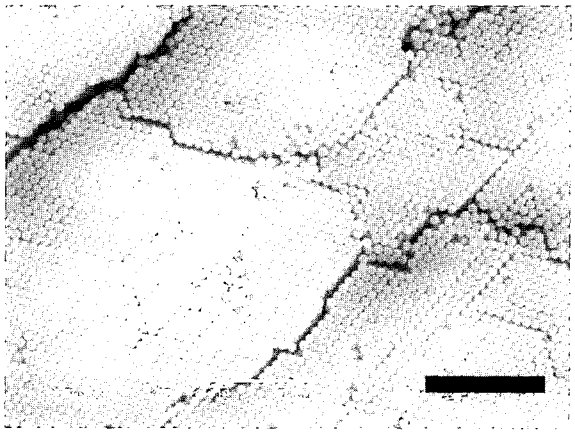

Figure 5. SEM surface images of multiple-layered colloidal crystals. Scale bar: 5 μm.

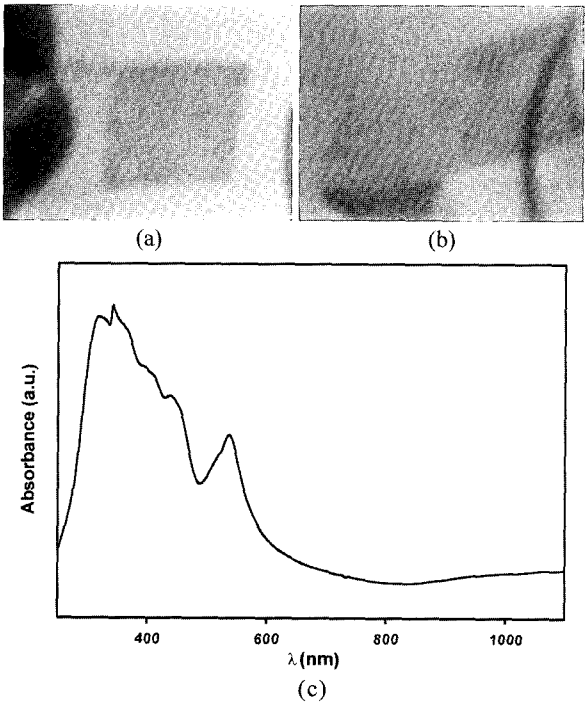

Figure 6. Photographs of (a) a mono-layered colloidal crystal, (b) a multiple-layered colloidal crystal, and (c) UV-Vis absorbance spectrum of the mono-layered colloidal crystal.

of 3 mm/min because mono-layered colloidal crystals show the best quality under this condition. The resulting SEM surface images are shown in Figure 5. These figures show that colloidal particles are highly ordered over large areas with homogeneous structure and the (111) plane of face centered cubic (*fcc*) structures orients parallel to the ITO substrate. Cracks observed in the colloidal crystals are created in the drying process. Figure 6(a) and (b) show photographs of mono-layered and multiple-layered colloidal

crystals. Both figures show iridescent color typically appearing in ordered colloidal crystals. These photographs also show that the colloidal particles are ordered highly over large area. Figure 6(c) shows UV-Vis (ultraviolet-visible) absorbance spectrum of the mono-layered colloidal crystal. Absorption of PS colloidal particles in visible region is negligible and thus this absorbance spectrum represents a transmittance spectrum. This spectrum shows that colloidal crystals reflect light around 530 nm wavelength (green color).

Conclusions

We have found that there is an optimal lift-up rate of a glass substrate for mono-layered colloidal crystals formed via the dipping method. The mono-layered colloidal crystals reveal the best quality when the glass substrate was extracted at a rate of 3 mm/min at 25 °C in a 1 wt% PS colloidal suspension (ethanol medium). Multiple-layered colloidal crystals have been successfully obtained by introducing an external electric field on the dipping method. The resulting multiple-layered colloidal crystals are well ordered over large areas with a homogeneous structure.

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