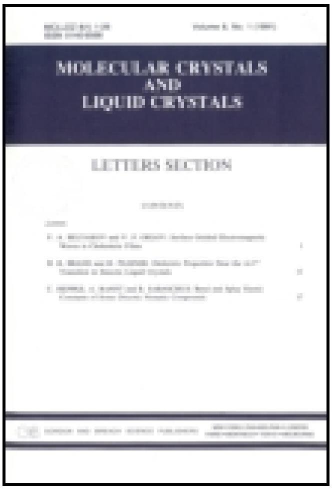

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Facile Fabrication of Various Submicron Functional Structures Using Colloidal Spheres

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Facile Fabrication of Various Submicron Functional Structures Using Colloidal Spheres

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Submicron-size of colloidal spheres itself and their self-assembled structures are useful basis for obtaining various functional structures. Up to now, we have succeeded to fabricate several unique structures that are expected to be applied to various components of a specific optical device, or the substrate for material- and/or bio-science research purpose. Facile fabrication procedures and obtained structures for an inverse opal structure, a binary colloidal structure, an alternating photonic crystal and glass structure, and an anisotropic hemispherical structure are introduced. Their optical functions are also described.

Keywords Submicron sturucture; colloidal sphere; facile fabrication procedure; binary colloidal crystal; photonic crystal and glass; dichroic reflection optics

Introduction

After a concept has been suggested by Yablonovich in 1980s, photonic crystals are energetically studied [1]. Especially, the structures with submicron-scale are useful for optical functional devices in visible light region. However, if a structure with submicron-scale is tried to fabricate by expensive top-down technology, it costs very much although quite precise fine structure could be obtained. Therefore, we have directed to develop a facile fabrication technique in order to establish a simple and low cost process (even though it might be lacking in precision at some extent) [2–6]. Then, it was noticed that submicron-size of colloidal spheres are one of the suitable item for obtaining various functional structures since its self-assembling nature would be ingeniously available. Further more, since self-assembly of the colloidal spheres is sensitively affected by the physical or chemical conditions during the self-organization process, tailored assembly of colloidal spheres could be obtained as far as the process conditions are carefully and adequately controlled. Self-assembled close-packed structure of multi- or mono-layered colloidal spheres, that initiated from a shallow meniscus of the dispersion, can be utilized itself or as a mold for replication. In this paper, four kinds of interesting functional structures among our research, that are an inverse opal structure, a binary colloidal structure, an alternating photonic crystal and glass structure and an anisotropic hemispherical structure, will be introduced about their outline

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of fabrication procedures and their characteristics. Several potential applications of those structures are also referred.

2. Experiment

Colloidal suspensions of polystyrene (PS) spheres (Duke Scientific Corp.) with diameters between 200 nm and 3 μm dispersed in aqueous solutions at the concentrations of 1% were employed in the experiment. A sandwich-type glass cell with an appropriate cell gap was used for assembling the PS spheres. In the cell, evaporation of the aqueous solution from the meniscus causes the colloidal suspension to flow, and induces crystallization of the closed-packed structure of the PS spheres [7]. As a result, hexagonally close-packed structures of multi- or mono-layered colloidal spheres have obtained according to the process conditions.

Obtaining an inverse opal structure, UV curable resin (NOA61, Norland Products Inc.) was impregnated into multi-layered hexagonally close-packed structures and cured by UV light irradiation. After that, the inverse opal structure can be fabricated by dissolving the PS particles in a toluene bath. The obtained structure was inspected by scanning electron microscope (SEM).

Binary colloidal structure was obtained via two-step fabrication procedures [8]. First, a monolayer of the 3 μm PS sphere was fabricated in the glass cell via a slow evaporation of the aqueous solution from the meniscus. Then, the small sphere colloidal suspensions, whose diameters were 200, 240 and 269 nm, respectively, were additionally injected and formed hexagonally closed-packed structures in the interspaces between the PS spheres of 3 μm diameter.

Concerning the alternating structure of photonic crystal and photonic glass, the surrounding humidity was controlled in order to change the growth rate of the self-assembling structures [9]. By just repeating open and close a lid of the Petri dish in which a glass cell was located, the humidity was adjusted. Temperature was kept at 20°C. At the high humidity (~60% RH), the growth rate was slow so that the multilayered hexagonally closed-packed structures (photonic crystal phase) could be formed. Contrary, at the low humidity (~20% RH), the growth rate was fast then the multilayered disordered structure (photonic glass phase) was formed.

For anisotropic hemispherical structure, first a monolayer of hexagonally close-packed PS spheres was formed by a dip-coating method on a glass substrate [10]. Then, a thermosetting silicone rubber resin (SIM-360, Shin-Etsu Chemical Co. Ltd.) was casted and thermally cured (30min at 60°C and 30min at 150°C, sequentially). After the thermal treatment, the silicone rubber resin was peeled away from the template and the rubber mold was obtained. Then, it was stretched to appropriate ratio (examined elongation range was between 1.0 and 1.3 times), and a UV curable resin (NOA61, Norland Products Inc.) was put on it and cured by UV light irradiation. Consequently, an anisotropic hemispherical replica was obtained, then a thin gold layer was deposited on the surface via sputtering.

Results and Discussion

Figure 1 shows a SEM image of an example of obtained inverse opal structure. The pore was 3 μm diameter in this case. It could be recognized that well-ordered three dimensional spherical voids have been fabricated. One example of the optical applications of the structure is for a field-responsible photonic crystal. If we filled the void with a field responsible material, such as liquid crystal, we can switch the value of the reflection by applying a field to modulate the molecular alignment such as electric-, magnetic-, optical-field and mechanical stress. Even more, it might be applicable for tunable lasing if the structure would be made by elastomers as analogy of cholesteric liquid crystalline elastomer's case [11].

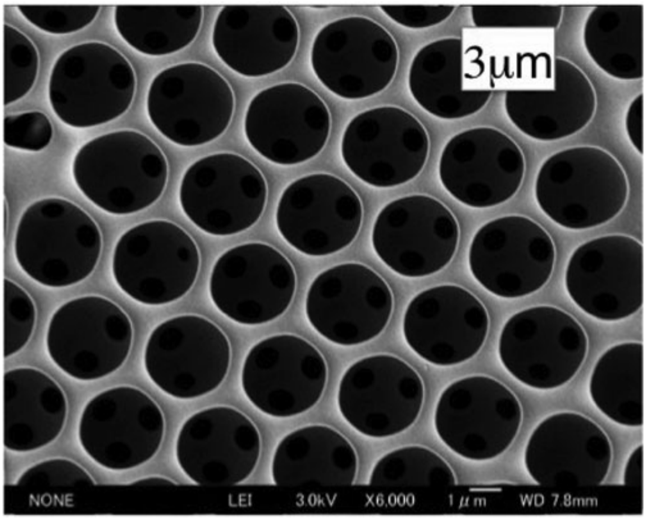

Figure 1. An example of obtained inverse opal structure.

Figure 2 shows a SEM image of obtained binary colloidal crystal consists of 3 μm- and 200 nm-diameter PS spheres, for example. Although the SEM images are not shown in the paper, we have also succeeded to fabricate the structure with 240 nm- and 269 nm-diameter PS spheres in the same manner. As is clearly indicated in the figure, the smaller spheres are filled in the vacant spaces of the closely packed large spheres and ordered very well to form hexagonally close-packed structure. Due to this assembling manner, a characteristic selective reflection could be observed, so-called structural color of blue, green and red corresponding to the diameter of the PS spheres with 200 nm, 240 nm and 269 nm,

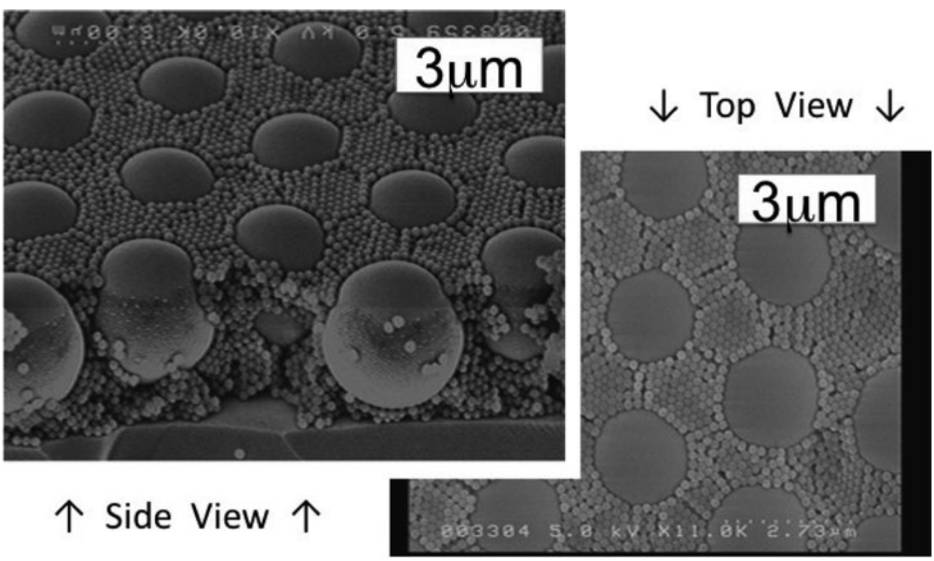

Figure 2. Side and top view of the SEM images of obtained binary colloidal crystal structure.

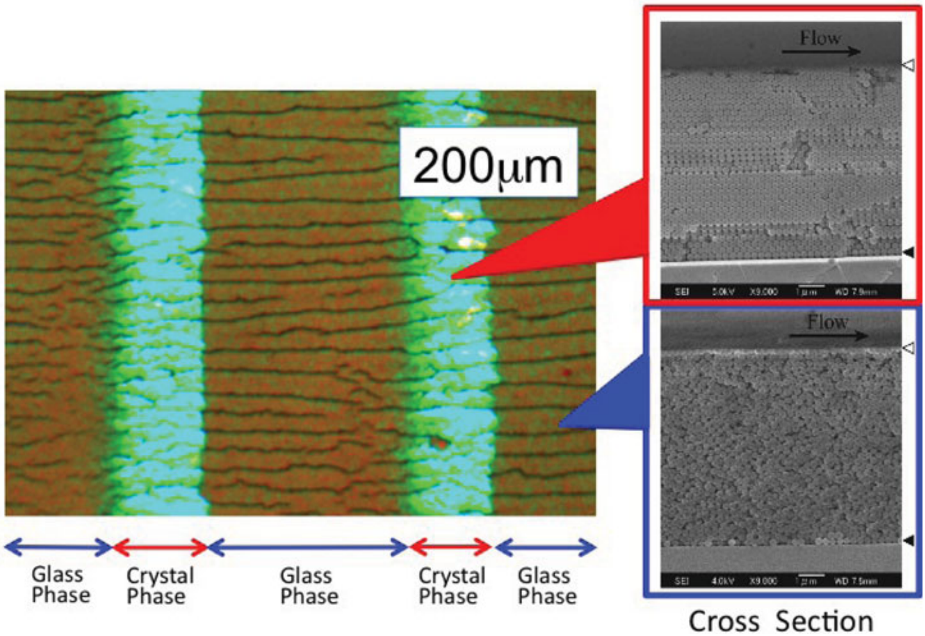

Figure 3. Typical optical microscopic image of the alternating structure of photonic crystal and glass (left) and the cross-sectional SEM image for photonic crystal and glass (right), respectively.

respectively. In addition to the optical application of the structure, it might be possible to apply it as a separation membrane with highly regulated pore size and path.

Figure 3 shows alternating domain structure of photonic crystal and photonic glass. The structure was composed from the PS spheres with 269 nm diameter in this example. Photonic crystal region exhibits vivid bright blue color due to a selective reflection of the light around 620 nm. The value is well coincide with the stop-band estimation based on Bragg's law. Photonic glass region exhibits obscure orange color due to rather broadened photonic absorption around 580 nm. By controlling the surrounding humidity during the PS sphere self-assembling process, such alternating structure can be easily obtained. Especially the phase transition instantly occurs from crystal to glass phase. Therefore, it might be possible to fabricate a unique optical filter or mirror with specifically designed characteristics. Also, it may be interesting to apply this kind of structure to a new kind of random laser, in which the one-dimensional periodic photonic structure is built-in into the lasing medium.

Figure 4 shows unidirectionally elongated structures of hexagonally closed-packed monolayer of 500 nm PS sphere. The stretching ratio was 1.3 in this case. For SEM observation, a thin gold layer of about 30 nm was deposited on the structure. And, for spectroscopic evaluation of the specular reflection, the surface was covered by a thick gold layer of about 100 nm. From the polarization dependent observation clear dichroism was observed. Namely, when we irradiate linearly polarized light with the direction parallel to the stretching direction, the absorption peak shifts to the longer wavelength along the elongation. On the contrary, opposite shift is observed for perpendicularly polarized light is irradiated. The maximum value of the difference in the wavelength of the absorption peaks experimentally confirmed was 70 nm for the sample with the stretching ratio of 1.3. Since such remarkable spectral shift between the two incident light polarizations and the each peak locates at 540 nm and 610 nm, the reflection color for each case recognized as

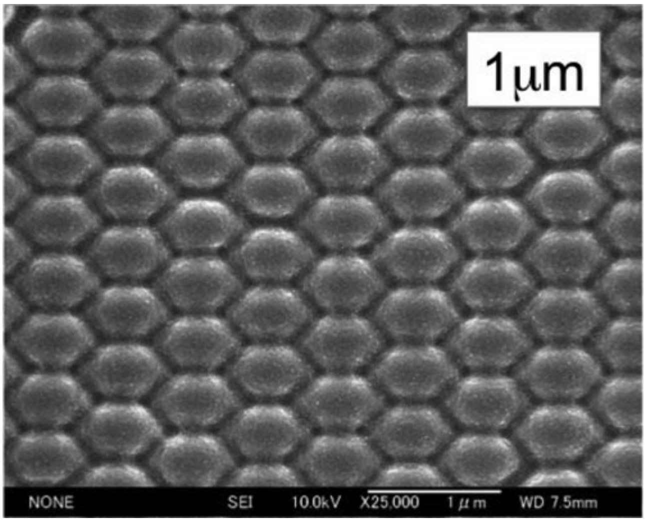

Figure 4. A SEM image of the anisotropic hemispherical structure that unidirectionally elongated to 1.3 times.

green and red in naked eye observation. Such anisotropic mirror with dichroic reflection characteristics is expected to be applicable for unique wavelength filters, dichroic mirrors, bifunctional biosensing chip, and so on.

4. Conclusion

Four examples of our fabrication method using colloidal spheres and the characteristics of the submicron structures have been introduced. It should be remarked that the various unique structures could be obtained via very facile and low-cost process. The point is that the process was based on tailored colloidal sphere self-assembly but not on an expensive top-down technology. These unique structures and characteristics introduced in the paper are applicable as an optical component for specialty purpose, or the substrate (or template) for fundamental research such as material science and/or biological science.

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