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Growth of Highly Ordered Colloidal Crystals Using Self-Assembly at Liquid−Liquid Interfaces

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A photonic crystal (PhC) is a new type of optical material in which the refractive index changes periodically with periodicities on the order of the wavelength of the light. PhCs can have interesting optical properties, including the possibility of exhibiting a photonic band gap (PBG) for a certain range of photon energies.[1] For the past decade, PhCs have attracted enormous interest from both fundamental and practical points of view because they offer unprecedented opportunities for the miniaturization and integration of optical devices.[2,3] To date, numerous applications have been proposed and demonstrated using PhCs fabricated by various techniques such as photolithography, electron-beam lithography, self-assembly, multiphoton polymerization, and interference lithography.[4−9]

Self-assembly of colloidal crystals offers a simple and inexpensive route to three-dimensional (3D) PhCs.[10−16] However, they typically contain a high density of defects such as stacking faults, vacancies, and dislocations. Crystalline quality is among the most important parameters in determining the performance of colloidal crystals in optical applications. Until now, therefore, much effort has been made to improve the quality of the crystals using convenient methods. Convective assembly, which uses the capillary forces at the meniscus of a colloidal solution and a substrate to draw colloids into close-packed arrays, is useful.[14,18] In this approach, a substrate is immersed vertically into a suspension containing monodisperse spheres. As the solvent evaporates, the surface of the liquid slowly travels down the substrate, coating it with spheres that can assemble into a highly crystalline arrangement. Similar colloidal crystals can be obtained by lifting the substrate out of the suspension at a constant speed instead of relying on the evaporation of the solvent, so-called "dip-coating".[19] However, to obtain high-quality films, the lifting speed must be slow, which leads to long crystallization times. In addition, precise control of both temperature and humidity is required in the convective assembly. In this communication, we report a novel approach to achieving a highly ordered colloidal crystal.

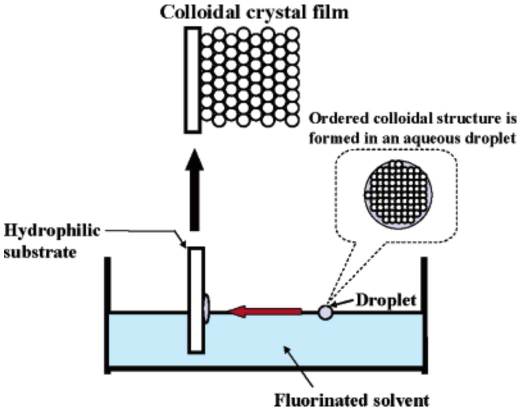

Figure 1. Schematic illustration for fabricating highly ordered three-dimensional colloidal crystal films on a flat hydrophilic substrate utilizing floating droplets containing self-assembled colloids formed at liquid−liquid interfaces.

Our approach is shown schematically in Figure 1. First, droplets of an aqueous suspension containing monodisperse negatively charged polystyrene (PS) microspheres are deposited on the surface of a fluorinated solvent (hydrochlorofluorocarbon) whose surface tension is significantly lower (16.2 mN/m) than that of water (72.8 mN/m). In addition, the solvent is immiscible with water and the density (∼1.5 g/cm^3 at 25 °C) is higher than that of water. Thus, if droplets of aqueous suspension containing PS microspheres are deposited onto the solvent, they will not mix with the solvent and will instead float on top of it, forming an interface. Interfaces between immiscible fluids have been shown to be ideal for the assembly of colloidal particles[20−22] and nanoparticles[23,24] and for the fabrication of high-quality and large protein crystals.[25] At the interface, the particles are highly

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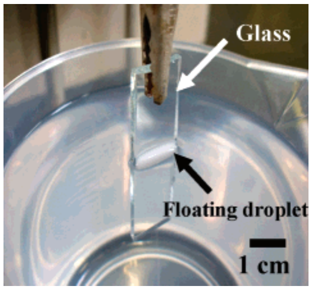

Figure 2. Photograph of our dip-coating method utilizing floating droplets containing polystyrene microspheres (466 nm in diameter) on fluorinated solvent. The droplets move readily to the surface of an immersed hydrophilic glass substrate and coalesce at the surface.

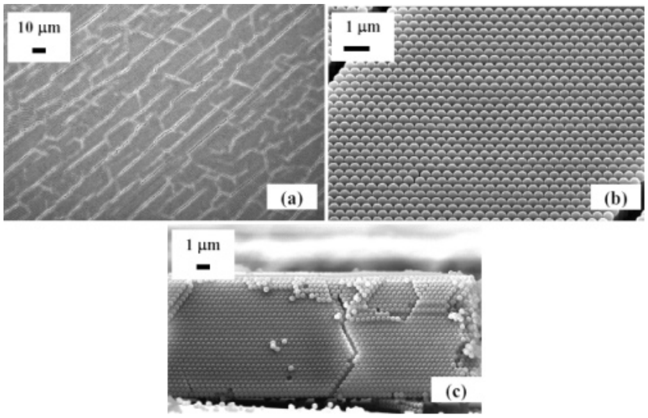

Figure 3. SEM images of colloidal crystal films on flat glass utilizing floating droplets containing polystyrene microspheres (466 nm in diameter) on fluorinated solvent: (a) low-magnification surface image, (b) high-magnification surface image, and (c) cross-sectional image. The thickness of the layers is ~10 μm.

mobile and rapidly achieve an equilibrium assembly. That is, liquid−liquid interfaces are considered to be a very useful field for the self-assembly of colloidal particles. Subsequently, the floating droplet within which the colloidal particles may be well-ordered is transferred from the solvent surface onto a hydrophilic flat substrate using a dip-coating technique.[19] The floating droplet will move readily to the surface of an immersed hydrophilic substrate. During the deposition, the particles can be rearranged by the capillary forces at the meniscus of the colloidal solution and the substrate, leading to a more well-ordered structure.

In the present work, glass was used as a hydrophilic substrate. Figure 2 shows a photograph of our dip-coating method utilizing floating droplets containing polystyrene microspheres (466 nm in diameter). The floating droplets move immediately to the glass substrate and coalesce at the surface, as shown in Figure 2. The water of the droplets did not completely evaporate during the deposition. Figure 3 shows SEM images of the colloidal crystal film on flat glass substrates fabricated by the method described above. Highly ordered three-dimensional colloidal crystal arrays with a thickness of ~10 μm are clearly observed over a large area. The crystalline quality is apparently better than that of the colloidal crystal film prepared by a conventional dip-coating method at a lifting speed of 0.2 μm/s, as shown in Figure 4. By optimizing the droplet densities, we may obtain more

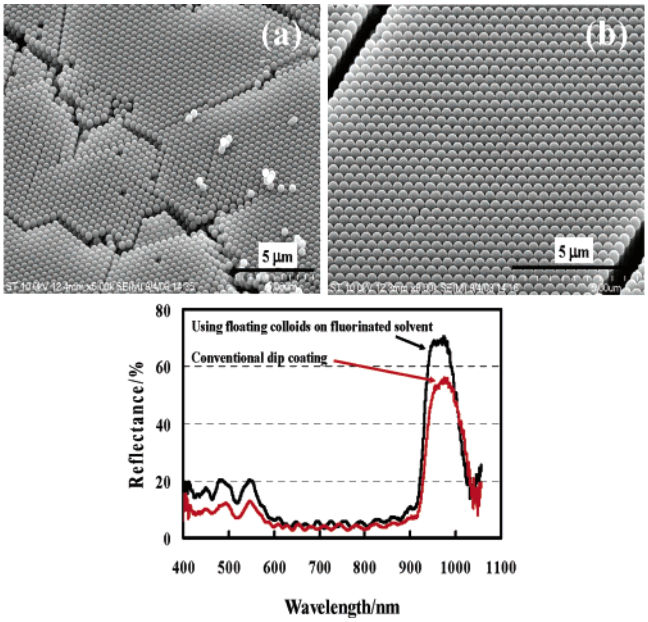

Figure 4. SEM images and optical reflection spectra of colloidal crystal films on flat glass grown by (a) a conventional dip-coating method and (b) our novel method at a lifting speed of 0.2 μm/s, with assembly from polystyrene microspheres with a diameter of 466 nm.

ordered structures. The thickness of the film can be controlled by simply changing the concentration of suspension. However, this method does not work for silica particles because the density of silica is larger than that of water, so the silica particles sediment during the deposition. If a fluorinated solvent with high vapor pressure (volatile solvent) is used, the preparation time of the samples could be shorter than that of the conventional dip-coating method because the surface of the liquid travels down the substrate faster because of the rapid evaporation of the solvent (The colloidal crystal shown in Figure 3 was fabricated using a volatile fluorinated solvent, AK-225[26] from Asahi Glass Co., Ltd.). Figure 4 shows SEM images and the optical reflection spectra of a colloidal crystal film prepared by the conventional dip-coating method and our novel method. A well-ordered structure is clearly observed for our sample. In addition, a strong reflection peak is clearly observed for both samples, but the peak height is greater for our sample than for the film fabricated by conventional dip coating, although the film thickness is almost the same, indicating that our colloidal crystal film more ordered. The reason why the reflectance of the samples is much less than 100% may be attributed to defects and drying cracks of the colloidal crystals.[27,28] Here, it is also found that the stop band is slightly blue-shifted from a peak position estimated from the Bragg equation.[16] Further investigation is necessary to clarify this.

Furthermore, this method can be applied for coating both sides of a substrate with different colloids with a single step, which cannot be achieved by the conventional dip-coating method. Placing droplets of PS spheres with a different refractive index or size on each side of the substrate leads to both sides being simultaneously coated by different

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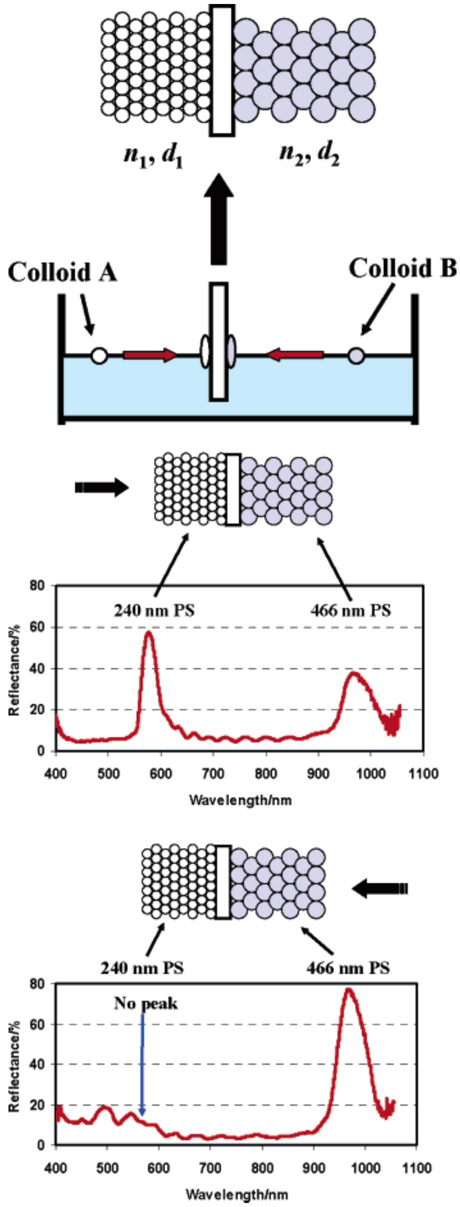

Figure 5. Schematic illustration of both sides coating a hydrophilic flat substrate with different colloids (*n*, refractive index; *d*,, diameter of microsphere). The optical reflection spectra of a glass coated with different sizes of polystyrene microspheres (diameters of 240 and 466 nm).

colloidal crystal films. The fluorinated solvents are suitable for this purpose because it is easier to separate floating droplets onto both sides than other solvents because of its lower surface tension. Figure 5 shows a schematic illustration of this process and the optical reflection spectra of the sample with 240 and 466 nm PS colloidal crystal films on either side of the glass substrate. When the light comes from the 240 nm PS side, two reflection peaks are clearly observed. In contrast, when the light comes from the 466 nm PS side, one peak is observed. This is because the shorter wavelength light is scattered more strongly by 466 nm PS colloidal crystals than by the smaller-sized ones. This observation suggests that the 240 nm reflection peak can be switched by simply rotating the substrate.

In summary, we have reported a novel approach for fabricating highly ordered three-dimensional colloidal crystals by transferring the floating droplets within which the colloidal particles are ordered onto a hydrophilic flat substrate without the need of special experimental conditions such as a temperature gradient.[18] The ordered colloids are formed by self-assembly at the liquid−liquid interface. This method is a very effective and convenient approach for fabricating highly ordered colloidal crystals quickly using a very small amount of colloidal suspension. This approach will open new ways for fabricating materials based on colloidal crystals as well as applying the colloidal photonic crystals to optical devices.

The glass substrates were cleaned with a 5% HF(aq) solution. They were then rinsed with deionized water and dried under a flow of nitrogen gas. After the treatment, the contact angles of water on the substrates were below 5°. The hydrophilic glass substrate was immersed vertically into a fluorinated solvent. Afterward, droplets of a 2 vol % aqueous suspension containing monodisperse polystyrene (PS) microspheres whose surface is terminated by sulfate and carboxylate groups were deposited on the surface of the solvent. All the experiments were carried out with about 100 μL of droplets for a 1.5 cm × 2.0 cm size glass substrate (The size of each droplet was about 2 mm). PS microspheres with a diameter of approximately 240 and 466 nm (Interfacial Dynamics Co., Portland, OR) were used. After a few minutes, the immersed glass substrate was withdrawn at a lifting speed of 0.2 μm/s to lift the floating droplets out of the solvent, yielding colloidal crystal films. The same procedure was performed using various solvents. The fluorinated solvents we used in the present study were AK-225, which is a blend of $CF_3CF_2CHCl_2$ and CF_2ClCF_2CFHCl (Asahi Glass Co., Ltd.; density, 1.6 g/cm^3 at 25 °C; surface tension, 16.2 mN/m; vapor pressure, 37.7 × 10^3 Pa at 25 °C),[26]and Fluorinert FC-77, which is a perfluorocarbon (3M; density,1.78 g/cm^3 at 25 °C; surface tension, ~13 mN/m; vapor pressure, 5.62 × 10^3 Pa at 25 °C).[29]

The surface morphology of the films was examined using SEM (Hitachi S-4700 field-emission scanning microscope). Vis−near-IR spectroscopy was carried out using a microspectrometer consisting of a reflecting-light microscope (Zeiss Axiovert 135) with light output coupled to a linear photodiode array spectrometer (Control Development, Inc., South Bend, IN) via an optical fiber. A 10×/0.25NA objective was used in combination with a 100 μm pinhole placed directly in front of the optical fiber, resulting in a nominal spot size of 10 μm. All spectra were referenced to a silvered mirror.

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