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Fabrication and optical properties of binary colloidal crystal monolayers consisting of micro- and nano-polystyrene spheres

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ABSTRACT

Self-assembling of binary colloidal crystals (bCCs) consisting of spherical particles with different diameters has been used for monolayer fabrication in glass cells. The procedure involves two crystallization steps. Upon crystallization of a colloidal suspension containing large spheres, a monolayer is formed on the bottom substrate of the cell. Then, a colloidal suspension containing small spheres, which assemble in the interstitial parts between the large spheres, is injected into the cell. The resulting bCC monolayers are characterized using scanning electron microscopy (SEM) and reflection spectroscopy. Reflection spectra reflect the bCC structure and forbidden bands corresponding to the grating constant of the second colloidal crystal. The structure and optical properties of the bCC monolayer can be specified depending on the ratio of the diameters of the spheres. The proposed process for bCC monolayer fabrication is extremely simple, and therefore ideal for practical uses.

1. Introduction

The self-assembly of colloidal micro- or nano-spherical particles is a useful technique for obtaining photonic crystals with face-centered cubic (fcc) crystal structures [1,2]. Light of certain wavelengths passing along the [1 1 1] direction of the fcc lattice is diffracted. Certain wavelengths of light that cannot pass through give rise to photonic band gaps, which produces brilliant structural colors in these opal structures. An inverted opal structure can be produced when the voids (i.e., the gaps between the spheres) are filled by substances and the spheres are then removed. These inverse opal structures also exhibit specific photonic bands [3,4]. In 1998, Busch and John revealed that a complete band gap arises in inverse opals made from materials possessing dielectric constants greater than 2.8 [5]. This was immediately confirmed by other groups [6,7], and since then, many research groups have developed processes for fabricating opals and inverse opals [8–10]. This intense research has led to the development of many highly functional photonic and optical devices.

In addition to the rapid advancement of nano and microfabrication processes, highly complex structures have been proposed, leading to versatile applications and/or fabrication processes. Hierarchical structures comprising different structural features also form well-known highly complex functional structures [11]. A lot of structures with specific functionalities have already been reported [12–15]. In colloidal crystals, binary colloidal crystals (bCCs) have been used to create complex structures [16–23]. Three-dimensional bCCs are usually fabricated using a mixture of two kinds of colloidal crystal suspensions via the self-assembly of their spherical particles, similar to normal colloidal crystals [17,20,21,23]. In bCCs, small spheres are located in the interspace of the array of large spheres. The different diameters of the small and large spheres give rise to different properties in bCCs [17]. Inverse opal structures of the bCCs have also been reported as hierarchical structures [21,23]. These highly regular structures formed on the nano and micrometer scale are expected to be used in future applications [24–27]. In particular, bCCs can be used as templates for patterning various materials in the fields of photonics, optics, electronics, materials science, biotechnology, and nanotechnology. However, the most fabrication processes of bCCs need specialized arrangements such as vertical deposition system [16,17,20], electrophoresis setups [19,24], and special spreading techniques [22,23].

In order to use bCCs as templates for two-dimensional patterning, a bCC monolayer configuration is preferred as this affords the removal of the spheres in subsequent epitaxial processes, and optical microscopy could be used to monitor and observe the processes. A simple bCC monolayer fabrication process has the potential to be used in many applications, including mass production technologies.

In this study, we report the simple fabrication using a glass cell and characterization of bCC monolayers. The fabricated samples were characterized using scanning electron microscopy (SEM) and optical spectroscopy. The optical properties related to the

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configurations of the bCC monolayers are discussed. The formation mechanism of bCCs is also discussed based on the capillary forces generated in the interstitial sites. To understand the behaviors of colloidal particles in the interspaces is very important for the application as a template.

2. Experimental

2.1. Fabrication of bCCs

We used colloidal suspensions of polystyrene (PS) spheres (Duke Scientific Corp.) with diameters of 200 nm, 240 nm, 269 nm, and 3 μm dispersed in aqueous solutions at concentrations of 1%.

The cell used in this experiment is shown in Fig. 1 and comprises two 1 mm-thick glass slides separated by glass spacers, which creates a cell gap of 1 mm. At least one opening is needed to inject and evaporate the aqueous solution. All parts are fixed together with an adhesive agent.

The large sphere (3 μm) colloidal suspension is injected into the cell, as shown in Fig. 1(a). The spheres are gravitationally sedimented for several minutes. Evaporation of the aqueous solution from the meniscus causes the colloidal suspension to flow, and induces crystallization of the monolayer [28,29], as shown in Fig. 1(b)–(d). The small sphere (diameter 200 nm, 240 nm, or 269 nm) colloidal suspension is then injected as shown in Fig. 1(e). The aqueous solution evaporates and the capillary force strongly rises in the narrow interspaces between the large spheres, leading to the formation of a bCC monolayer as shown in Fig. 1(f) and (g). All processes were performed at room temperature (around 10 °C) and 40–50% humidity. The resultant monolayer bCCs were characterized using SEM (S-4000, HITACHI). Among these, the wide gap of the cell plays a role of reservoir for the large sphere colloidal suspension. To obtain closely packed large sphere monolayers over the bottom substrates through the gravitational sedimentation, relatively large quantities of the suspension has to be injected because of the concentration of 1%. Consecutive injection of colloidal suspension into a cell needs special arrangements to the cell and the peripheral setup.

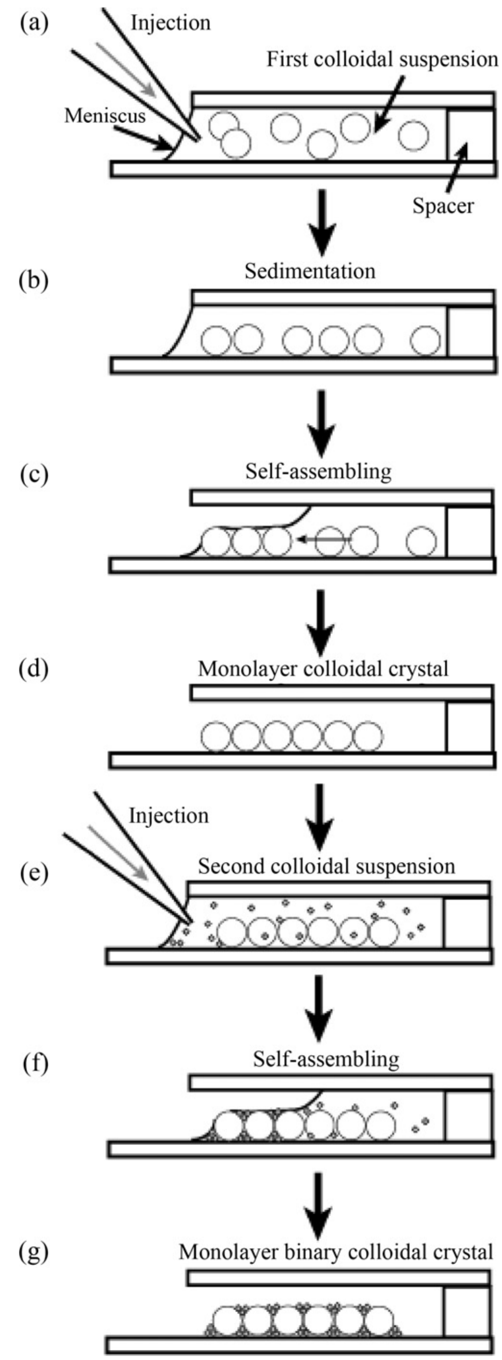

Fig. 1. Schematic illustration of the fabrication of a bCC monolayer using two kinds of colloidal suspensions in a sandwiched glass cell. (a) Injection of first colloidal suspension, (b) gravitational sedimentation, (c) self-assembly of spheres, (d) monolayer colloidal crystal, (e) injection of second colloidal suspension, (f) self-assembly of spheres, and (g) formation of a bCC monolayer.

2.2. Spectroscopy using a reflection microscope

The wavelength at the reflection maximum (λ_{max}) can be directly determined by Bragg's law [8], using the following equation:

$$\lambda_{max} = 2d\sqrt{n_{eff}^2 - \sin^2\theta}, \quad (1)$$

where d is the grating constant for the [1 1 1] in-plane, θ is the angle between the incident beam and the normal to the [1 1 1] plane, and n_{eff} is the effective refractive index. Assuming that the incident light is normal to the [1 1 1] plane of fcc colloidal crystals, Eq. (1) can be rewritten as follows:

$$\lambda_{max} = 1.633Dn_{eff}, \quad (2)$$

where D is the diameter of the colloidal sphere. The reflection spectra measurements evaluate the extent of crystallization in the self-assembly formation of the colloidal spheres.

Fig. 2 shows the optical setup used to obtain the reflection spectra. The setup has a reflection microscope (CK40M, OLYMPUS) to which both a CCD camera and a CCD arrayed spectrometer (USB4000, Ocean Optics) are connected, allowing us to obtain the reflection image and spectrum of a specific area simultaneously [9,30]. The microscopic field has a diameter of 860 μm. The CCD camera captures the center region of the microscopic field. The spectrometer measures the reflected light from all over the microscopic field. The reference spectrum for the reflection measurement is obtained by using an uncoated Al mirror that is placed in the sample plane. For the objective regions on samples, it is important that the optical image and the corresponding spectrum are obtained using a technique that can be carried out in situ as it is useful for the characterization and evaluation of the products. However, note that all optical paths are not consistent to the normal direction to the sample plane all over the microscopic field, as shown in the area enclosed by the dashed circle. The optical paths are deviated from the normal direction by the focusing the light waves using an objective lens and refracting them at the boundary between air and the sample. It is predicted that the tilted