Synthesis of Monodispersed Silica Microparticles in a Microreactor for Well-Organized Colloidal Photonic Crystals

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In this report, we describe the syntheses of monodispersed microparticles of silica, that is, polysilicate, in a microreactor based on Stöber method for fabrication of the well-organized colloidal photonic crystal (CPC) films with visible reflection properties. Although the bath synthesis of silica microparticles gave the relatively high coefficient of variation (CV) value of 14.1% in the particle diameter, we successfully improved the CV value from 14.1% to 5.5% by the microfluidic synthesis of silica microparticles in a flow reactor, arising from the separation of nucleation and growth processes. When we fabricated various CPC films of the silica microparticles by the vertical deposition technique, each CPC film showed a characteristic peak of Bragg reflection with a high reflectance over ~60% in the visible wavelength range. Moreover, we found that the experimental reflection spectra of CPC films have consistent with the theoretical spectra calculated by the scalar wave approximation (SWA) technique.

Keywords: Silica microparticle, Colloidal photonic crystal, Microreactor, Monodispersity, Vertical deposition technique

1. Introduction

Colloidal crystals are three-dimensional periodic arrays of monodispersed colloidal particles [1–5]. Colloidal crystals are one of the concrete forms of photonic crystals which show the photonic band-gaps in the visible wavelength range due to the spatial periodicity of the refractive indices of materials in the particles and surrounding background [6–8]. Therefore, they are also called colloidal photonic crystals (CPCs). So far, significant research developments of CPCs have established their applications to optical sensors, laser devices, and so forth [9–13].

Monodisperse microparticles of polystyrene (PS), poly(methyl methacrylate) (PMMA), and silica, that is, polysilicate, are frequently adopted for the fabrication of CPCs [2,14,15]. Among them, silica shows stability to high temperature and organic solvents rather than polymer materials. Consequently, the precise synthesis of monodisperse silica microparticles is very important for versatile applications of CPCs. In this context, Stöber method is most popular as the synthesis of silica microparticles through the sol-gel hydrolysis and polycondensation reactions of silicon alkoxides in alcohol–water media with ammonia catalysis. Moreover, the particle size depended on the parameters such as the precursor concentration and reaction temperature [16–20].

Including the Stöber method, most of the colloidal particles are synthesized by the batch process, where reagents are mixed and reacted at once in a flask. Although we require monodispersity and high sphericity of colloidal microparticles for the applications to CPCs, the batch process has problems in scale-up and high reproducibility due to ununiform heat transfer and solution mixing.
Therefore, our interest has been devoted on the demonstration of microfluidic synthesis for monodispersed and high spherical silica microparticles by using a microreactor. This synthetic procedure has several advantages of efficient solution mixing and uniform temperature control. Hitherto, many reports have been made on the syntheses of particles in microreactors [21–27]. In this report, we describe the microfluidic syntheses of silica microparticles in a flow reactor. Furthermore, the CPC films of monodisperse silica microparticles with diameters of several hundred nanometers were fabricated by the vertical deposition technique [28].

2. Experimental

2.1. Microfluidic syntheses of silica microparticles

All chemicals and solvents of tetraethoxysilane (TEOS), ~28% ammonia aqueous solution, and dehydrated ethanol were used as received without any further purification.

Figure 1 shows the experimental setup for microfluidic synthesis of silica microparticles in a flow reactor. First, we prepared three kinds of solutions. Solution A is a precursor solution of TEOS (1.21 g) in ethanol (4.99 g). Solution B is ethanol (5.79 g) and ultrapure water (0.28 g). Solution C is ethanol (15.64 g) and ammonia aqueous solution (2.58 g). These solutions were beforehand stirred for 30 min. Solution A and B were injected using polytetrafluoroethylene (PTFE) tubes with inner diameter of 1.0 mm. By using a syringe pump (Legato 200, KD Scientific), the solutions were flowed into a flow reactor of PTFE Y-type mixer (KC-M-Y-P, YMC), whose channel width and depth are 0.5 mm and 0.5 mm, respectively, at the constant flow rate for 20 min. Total volume in the mixer corresponds to 15.8 µL. After solutions A and B were mixed in the flow reactor, the mixture was flowed into a flask of solution C with stirring. At this time, the reaction temperatures of both flow reactor and flask were kept at 50 ºC. After the addition, the reaction was continued for 2 h.

After the reaction, the resultant suspension of silica microparticles was purified by several cycles of centrifugation at 1.0×10^4 rpm for 60 min, followed by the decantation and re-suspension in water or ethanol. Finally, the suspension was filtrated through PTFE membrane filters with pore sizes of 1.0 µm and 0.2 µm or less, and was gently dried in an oven at 60 ºC so as to be the constant weight.

As compared with the microfluidic syntheses, the silica microparticles were also synthesized by the batch synthesis by using a flask.

2.2. Fabrication of CPC films by the vertical deposition technique

As mentioned in the preceding section, we prepared three kinds of silica microparticles with the different diameters of 198 nm, 245 nm, and 280 nm by control of the reaction conditions. We prepared the CPC films by the vertical deposition technique as follows [28].

The silica microparticles were dispersed in ethanol to be 30 mg/mL. In this study, 30 vol% of water was added to ethanol. The clean glass substrate was vertically deposited into the suspension of silica microparticles, and successively stored in an oven heated at 60 ºC until the solvent was evaporated. As a result, we obtained a relatively uniform CPC film on a glass substrate.

3. Results and discussion

3.1. Syntheses of silica microparticles

Figures 2 (a) and 2 (b) show the distributions of diameters of silica microparticles synthesized by the batch synthesis and microfluidic synthesis, respectively. The average particle size was determined by measuring the diameters of 100 particles from the scanning electron microscopy (SEM) images, as shown in the insets of Figs. 2 (a) and (b). We estimated the coefficient of variation (CV) values, which mean the ratios of the standard deviation of particle diameters to the average particle diameters.

Although both batch and microfluidic syntheses provided the spherical silica microparticles with the diameters of ~220 nm, the CV values were quite different between them. In the batch synthesis, we found the small-sized silica microparticles with the diameters from 80 nm to 140 nm, as shown in Fig. 2 (a). Therefore, the CV value was calculated to
be 14.1%. On the other hand, the silica microparticles prepared by the microfluidic synthesis showed a relatively narrow distribution of particle diameters with the CV value of 5.5%. These experimental results suggest that the monodispersity of silica microparticles can be successfully improved by using a microreactor, and it can be explained by LaMer model.

According to LaMer model, in order to synthesize the monodisperse particles, it is necessary to arrange the reactions that all nucleation takes place in a beginning short period of time compared to nucleation growth, and new nucleation is suppressed during the nuclear growth period [29]. In the batch synthesis, both nucleation and growth occur concurrently throughout the particle formation. As a result, the resultant silica microparticles exhibit a broad diameter distribution. This is because H$_2$O, TEOS and NH$_3$ exist in the same reaction system. On the other hand, in the microfluidic synthesis, TEOS and H$_2$O are mixed and hydrolyzed in the flow microreactor, and most of them become nuclei in the tube and grow in the flask. In other words, it is anticipated that the monodispersity can be improved by using a microreactor because nucleation and growth processes are separated.

3.2. Control of diameters of silica microparticles

In order to fabricate the CPC films with visible reflection properties, we prepared the silica microparticles with various diameters. We attempted to control the particle diameters by changing the reaction temperature and TEOS concentration. When the TEOS concentration was changed, the injection time of solution A was increased with raising concentration so that the injection time of solution A and B would be the same. Figures 3 (a) and 3 (b) show the changes in average diameters of silica microparticles as functions of the reaction temperature and TEOS concentration in microfluidic syntheses, respectively.

As the reaction temperatures were changed from 45 ºC to 60 ºC, the particle diameters decreased from 300 nm to 190 nm, as shown in Fig. 3 (a). At this time, the CV values were constant between 4.0% and 5.6%. The reason is considered to be that the numbers of nuclei generated in the flow reactor increase, resulting in suppression of the particle growth. On the other hand, as given in Fig. 3 (b), the TEOS concentration was changed from 0.15 mol/L to 0.20 mol/L, the average diameters of particles concurrently increased from 231 nm to 356 nm. As evident from this profile, the particle diameters showed a nearly proportional relation with the TEOS concentration. Furthermore, we could prepare the monodisperse silica microparticles with relatively small CV values.

![Fig. 2. Distributions of diameters of the silica microparticles prepared by the batch synthesis (a) and microfluidic synthesis in the flow reactor (b). The insets show the SEM images of silica microparticles, and the scale bars represent 200 nm.](image1)

![Fig. 3. Changes in the diameters of silica microparticles as functions of reaction temperature (a) and TEOS concentration (b) in the microfluidic synthesis. The profile of (b) is fitted by the least squares method, as shown in the dashed line.](image2)
between 4.5% and 5.5% by the microfluidic syntheses with the limited TEOS concentration range from 0.15 mol/L to and 0.17 mol/L. In contrast, as synthesized at the TEOS concentration of 0.20 mol/L, the CV value slightly increased to 8.8%. It is anticipated that both nucleation and growth occur at in a flask the same time, because the hydrolysis reaction hardly proceeds in a tube. We consider that the silica microparticles monotonously grow as increasing the TEOS concentration, whereas the preservation of H₂O concentration makes the hydrolysis reaction difficult to occur.

3.3. Fabrication of CPC films and their optical properties

Finally, we fabricated three kinds of CPC films of silica microparticles with the diameters of 198, 245 and 280 nm by the vertical deposition technique. SEM observations of the CPC film allowed us to visualize the spatial arrangement state of silica particles at a microscopic level. Figure 4 (a) shows the SEM images of CPC film observed from the top surface and cross section. The top-viewed SEM image revealed that the silica microparticles adopt well-organized face-centered cubic (fcc) lattice structure in this CPC film. Furthermore, as observed from the cross section, this CPC film have a thickness of ~5.0 μm and a relatively flat surface. In addition, all kinds of CPC films showed similarly uniform arrangement of silica microparticles, as confirmed by SEM observations.

In order to unravel the relation of particle diameters and reflection wavelengths, the reflection spectra were measured for three kinds of CPC films. As shown in Fig. 4 (b), each CPC film showed a characteristic peak of Bragg reflection with a high reflectance over 60% in the visible wavelength range. By using the silica microparticles with the diameters of 198 nm, 245 nm, and 280 nm, the reflection peaks appeared at 415 nm, 515 nm, and 600 nm, respectively. Moreover, the theoretical reflection spectra of CPC films were calculated by the scalar wave approximation (SWA) technique [11,30,31]. This SWA technique closely resembles the analytic procedure of electron tunneling behavior in the quantum mechanics field. As compared between experimental and theoretical spectra, it turned out that the reflection spectra observed from our CPC films exhibit similar shapes to the corresponding theoretical spectra simulated by the SWA technique. In particular, the maximum peaks were good agreement between the experimental and theoretical spectra.

Based on the overall results, in the vertical deposition technique, we consider that the evaporation rate and interfacial tension of the dispersion medium were optimized by adding water to the ethanolic suspension. The treatment enabled the formation of homogeneous CPC films with high light-reflectance.

4. Conclusions

In this report, we have developed the microfluidic syntheses of spherical silica microparticles with monodispersity through the sol-gel hydrolysis and polycondensation reactions for the fabrication of CPC films with reflection peaks in the visible wavelength range. Because the nucleation and growth processes are separated in the reaction system. Moreover, the particle diameters were successfully controlled by adjusting the reaction temperature and silica precursor concentration. At this time, the monodispersity of silica microparticle was maintained.

Furthermore, we fabricated the CPC films of silica microparticles by the vertical deposition technique. As a result, the silica microparticles adopted well-organized fcc lattice structure, leading
to the formation of homogeneous CPC films with a high reflectance. These reflection spectra were agreed with the theoretical spectra derived from the SWA technique. Such CPC films are expected to be applied to versatile photonic devices with the photonic band-gaps. The present report provides promising guidelines to synthesize the monodisperse silica microparticles for the fabrication of CPC films with various reflection properties.

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