Fabrication of Rod-Shaped Photonic Structures Using Self-Assembled Colloidal Particles

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In this paper, we propose a simple self-assembly technique to fabricate rectangular rod-shaped photonic structures with micrometer-scale thickness and width using silica nanoparticles. Colloidal nanoparticles were crystallized from the colloidal suspensions injecting the micro-channels with hydrophilic substrates, and then a lot of rectangular rods were rapidly fabricated with relatively low defects by a rotational drying process. The fabricated micro-rods have a specific structural color and a rectangular cross-section where the width is about 1∼2 times larger than the thickness, which is identical to the gap of the micro-channel. As the gap is decreased, the ratio of the width to the thickness of the rectangular rods and the structural irregularity become increasing.

Keywords: Self-Assembly, Micro Rods, Nanoparticle, Photonic Crystal, Micro Channel.

1. INTRODUCTION

In photonic crystal structures for visible light, the reflective index is repeated in the lattice structure with a periodicity of half the wavelength of the light. Most wavelengths propagate through the periodic structure, but the wavelength of the specific range called the photonic-band-gap is reflected by the constructive interference. The production of visible color by the photonic structure is called the structural color.\textsuperscript{1,2} Since the photonic band gap can be controlled by adjusting the geometric shape of the photonic structure, various visual effects occur which are not expressed by the chemical dye. The photonic structure is used in various fields such as structural colors in electronics and fabrics or the color-change sensors.\textsuperscript{3-8}

Various methods for fabricating the photonic structures are being studied in a wide range of areas and they are largely divided into top-down and bottom-up methods. The bottom-up method is to make the desired photonic structure by accumulating a specific size of unit particle in a regular lattice structure from the bottom. The simple drying by precipitation, dip coating, and capillary method are mainly used for the self-assembly. The self-organized process is simple and economical since it can reduce the unit size of the photonic structure into the nano-size level and the consumption quantity of the energy and material is relatively low. However, the limitation of the self-assembly technique is the existence of structural defects such as cracks, vacancies and faults. The defects result from the non-uniformity of the unit particle size, drying process and the complex interaction between the substrate and the particles.\textsuperscript{9-18}

The self-assembly techniques cause not only unwanted structural disorders in the local areas compared to top-down lithography methods, but they also cause difficulty in fabricating colloidal structures with specific shapes. Strip or rectangular rod is one of important shapes for its potential applications as optical devices.\textsuperscript{19} Moreover, photonic crystals with the micro-rod pattern offer unusual visual effects for the biomimetic applications to mimic unique structural colors of organisms in nature.\textsuperscript{3,21} There exists a few studies to overcome the inherent problem in fabricating patterned self-assembly structures.\textsuperscript{20,22} Lu et al. fabricated the belt-shaped structures by a novel vertical deposition method of poly acrylic acid (PAA) nanoparticles in negative pressure based on curvature of glass vial.\textsuperscript{20} Lee et al. also have reported the rapidly self-assembled fabrication of patterned photonic structures in centrifugal microfluidic chips with the pre-patterned micro-channel.\textsuperscript{22}

In this paper, we propose a simple self-assembly technique to fabricate rectangular rod-shaped photonic structures with micrometer-scale thickness and width using colloidal nanoparticles. The rod-shaped photonic
structures are fabricated in the rotational micro-channel with hydrophilic substrates. Colloidal suspensions are used to disperse specific nanoparticles into the micro-channel having an inner spacer, and then long rectangular rods were rapidly fabricated with relatively low defects using the rotational effect. For the micro-channels with different gaps, the colloidal photonic structures were fabricated to compare the dimensions and uniformity of the rectangular rods.

2. EXPERIMENTAL DETAILS
2.1. Materials and Apparatus
A schematic of the experimental apparatus and the fabrication process for rod-shaped photonic structures with micro-scale thickness and width is shown in Figure 1. A micro-channel consists of two tempered class substrates, and each substrate is made of tempered glass with the size of 25 mm × 75 mm × 2 mm (width × length × thickness), having a hydrophilic surface. The colloid storage container is connected for colloidal particles to be dispersed with a specific concentration at the end of the hose. A spacer, located between two substrates, sets the thickness of rod-shaped photonic structures. Parafilm (M, Bemis) is used as spacer to provide the stable adhesion and removal between two substrates. The width and length of Parafilm are 5 mm and 75 mm, respectively. The thickness is prepared to be about 45, 130 and 220 μm to investigate the characteristics of the rod-shaped photonic structure depending on the gap of the channel. Parafilm as spacer was located on both sides of the bottom substrate and then the top substrate was covered on it. Finally, both substrates were bonded by heating at 80 °C for 15 min in the vacuum oven.

The hose was used for the colloidal transfer from the container to the micro-channel, and the coupling parts between components were sealed and combined without the leakage, having the sequential layers in each substrate: Parafilm-hose-Parafilm-glue-epoxy. The loss of the inner pressure was prevented by the rubber stopper or the one-way check valve in the container, and the colloidal suspension of silica with diameter of 240 nm was filled in the container. The colloidal suspension was prepared using the silica particles with the diameter of 240 nm to be dispersed with the concentration of about 20 vl% in the deionized (DI) water solvent.

2.2. Fabrication Process
Figure 2(a) shows a novel fabrication set-up to build colloidal photonic structures sequentially inside the micro-channel. The first step is that the surface of the channel contacting atmosphere is set to be vertical to the direction of gravity for natural dispersion of colloidal suspensions without rotation of the fabrication system. It was naturally dried for about 1 hour at the relative humidity of 25%, temperature of about 20 °C, and pressure of 1 atm. During natural dispersion, the colloidal particles move to the outside end and begin to crystallize a local area and form...
the uniform lattice structure. The barrier-seed area is about 3~5 mm in the longitudinal direction from the outside air-contacting end. Moreover, it plays a role in blocking the leakage of the suspension to the atmosphere from the inside.

Secondly, the centrifugal force was applied to the self-assembly apparatus by rotating the fabrication system at the rotational speed of 180 rpm. As shown in Figure 2(b), the direction of centrifugal force was parallel to the longitudinal direction of the channel, and vertical to the direction of width. Thus, the rotating self-assembly method is different from the generally used spin-coating one. It takes about 150 min on average to fabricate the photonic structure with the size of 15 mm × 75 mm by using both the natural dispersion and rotating processes. The fabrication speed of the photonic structures depends mainly on the thickness of the micro-channel, increasing with decreasing thickness. The time required for the colloidal crystallization is dramatically reduced, compared to conventional evaporation processes.

2.3. Fabrication of Rod-Shape Photonic Structure

The photonic structure formed inside the micro-channel includes the water solvent in air gaps. Since the remaining colloidal suspension could be transferred to the channel, all the colloidal suspension remained in hose were removed for the ineffective vaporization of the solvent. After removing the remaining colloidal suspension, the self-assembly system was rotated at the speed of 180 rpm and the micro-channel was dried from the outside end contacting atmosphere. As the inner solvent of the photonic structures begins to be eliminated, the long rod patterns are being produced from the end of the atmosphere-contacting surface onto the uniform photonic structure inside the micro-channel.

Since Parafilm, glue and epoxy around the hose-combined part are vulnerable to heat, they can be easily removed by heating after the rod-shaped photonic structures are formed. The top-substrate is removed by increasing the temperature over about 40 °C to Parafilm used as spacer.

In order to compare the structural features of the fabricated rod-shaped structure with a rectangular cross section, the dimensions of the rectangular rods and surface defects were observed by a commercial SEM (Scanning Electron Microscope, genesis-1000, EmCrafts). Moreover, the photonic band gap of the fabricated photonic structures was measured using a spectrometer analyzer (CCS100, Thorlabs). The theoretical reflection wavelength of photonic structures composed by the spherical particles was predicted using the modified Bragg’s equation.23

\[ \lambda = \left(\frac{8}{3}\right)^{1/2} D (\eta^2 f + \eta_{air}^2 f_{air})^{1/2} \]

Here, \( \lambda \) is the peak wavelength of photonic band gap, \( \eta \) and \( \eta_{air} \) are the reflective indices of the colloidal particle and the air gap, respectively. Also \( D \) is the mean diameter of colloidal particles, \( f \) and \( f_{air} \) are the volume fraction of the colloidal particles and the air gap when forming the photonic structures. The photonic structures fabricated by the self-assembly of colloidal particles have the face centered cubic (FCC) structure. Therefore, by the calculation of (1), the photonic structure produced using colloidal particles of 240 nm diameter has the theoretical reflection wavelength of 578 nm corresponding to green color in visible spectrum.

3. RESULTS AND DISCUSSION

Figure 3 shows the optical images of the fabricated rod-shaped photonic structures measured by SEM. Figure 3(a) displays a top view from above of the photonic structures. The amplified top view in Figure 3(b) shows the width of each rectangular rod. The width of the rod patterns had a range from minimum 220 µm to maximum 430 µm. Figure 3(c) shows a side view shot from the open end of the channel. A lot of rod-shaped patterns were created on the self-assembled structure. The amplified side view in Figure 3(d) clearly displays the rectangular cross-section of the rods. Figure 3(e) is a side view shot from the longitudinal direction (length × thickness). The rod-shaped photonic structures have the thickness of 220 µm. The thickness is the same size as one of the inner spacer (Parafilm) which is also the thickness of the channel.

![Figure 3](image-url)
micro-channel. It is noted that silica particles of 240 nm diameter were self-assembled in the uniform FCC opal structure in Figure 3(f). Some dot or line defects were intermittently distributed on the colloidal crystallization structure. The unintended structural defects in the local areas could occur mainly due to the adhesion of some nanoparticles to the substrate when the top substrate is removed.

When the surface of the substrate falls short of the hydrophilic property, the ratio of width and thickness in each rod-shaped structure is not consistent. The hydrophilic property of the substrate plays a main role in dividing the colloidal structures into the rod shapes in the fabrication process.

The further self-assembly experiments were implemented for the cases with different thickness of the micro-channel. The experimental results of the cases with the spacer thickness of 130 µm and 45 µm are shown in Figures 4(a–d). For the case of 130 µm thickness, the fabricated rods have a rectangular cross-section with the thickness of 130 µm and the width of 130–230 µm, as shown in Figures 4(a and b), respectively. When the spacer thickness of 45 µm is used, the fabricated rectangular rods have the thickness of about 45 µm (Fig. 4(c)) and the width with a range from 45 µm to 95 µm (Fig. 4(d)).

Based on the experimental results of the three cases, it is noted that the fabricated micro-rods have a rectangular cross-section where the width is about 1–2 times larger than the thickness.

In the case of the spacer thickness of 45 µm, the ratio of the width to the thickness of the rectangular rods becomes intermittently over 2 and the uniformity of the rectangular shape would be degraded, when compared to other cases of 220 and 130 µm.

Figure 5(a) shows the photo image of the rod-shaped photonic structure with the size of 15 mm × 60 mm, which is manufactured by the micro-channel having the thickness of 130 µm. The green colored photonic structure was fabricated with relatively low defects. The amplified images of the left and center regions clearly show a lot of long rectangular rods with green color detached from the self-assembled photonic structure. Figure 5(b) indicates the reflected wavelength of the rod-shaped photonic structure after the white light source is projected onto the surface. The experimental photonic band-gap of 572.8 nm agrees well with the theoretical band-gap of 578 nm, calculated by the Eq. (1) for the photonic structure of FCC lattice structure with the silica particles of the diameter 240 nm.

4. CONCLUSION
A simple and rapid self-assembly method is proposed to fabricate rectangular rod-shaped photonic structures with micrometer-scale thickness and width using colloidal nanoparticles. Colloidal suspensions are used to disperse specific nanoparticles into the micro-channel having an inner spacer, and then long rectangular rods were rapidly fabricated with relatively low defects using the rotational effect. The fabricated micro-rods have a specific structural color and a rectangular cross-section where the width is about 1–2 times larger than the thickness. The ratio of the width to the thickness of the rectangular rods and
the structural irregularity increases with decreasing the channel gap.

The proposed self-assembled fabrication process to manufacture photonic micro-rods with rectangular shapes can be applied to many applications as optical devices, biomimetic structural colors and micro-cantilever sensors.

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References and Notes


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