Optimized Thermal Treatment for Preparation of Double Inverse Opals Incorporating Movable Cores

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A combination of the co-assembling process to fabricate binary colloidal crystals (BCCs) and the successive heat treatment to selectively remove the polymer component from the BCCs was conducted to create double inverse opals (DIOs) in which a movable sphere was embedded within each inorganic compartment of nanoparticles. Micron-sized silica cores coated with polystyrene shell and silica nanoparticles were used as the BCC components in the co-assembling process. According to the residue profile measured in thermogravimetric analysis, the heat treatment at low temperatures of 250, 300 and 350°C was conducted to find a cost-effective process, resulting in finding that 300°C heating for 7 h was suitable for obtaining the high movability of micron-sized cores in the compartment. Application of 1 kHz electric field at strength higher than 100 V/mm could suppress the random motion of cores in a wet-state DIO.

Introduction

Double inverse opals (DIOs) are a type of colloidal crystals composed of periodically arranged voids containing a sphere. Several methods for preparation of DIOs have been reported to be applied to optical waveguides and separation systems (Ruhl et al., 2006; Rhee et al., 2014). For the fabrication of DIOs containing silica spheres in the backbone of titania or tin disulfide, Ruhl et al. (2006) self-assembled silica-polymer core-shell spheres and deposited the backbone materials into the interstices of the core-shell spheres. Further, the polymer shell was selectively removed from the particle self-assembly in the calcination. They demonstrated in their theoretical calculations that DIOs had possibilities as controls over light emission and propagation by shifting the location of silica spheres within the voids.

Rhee et al. (2014) reported a similar structure of DIO fabricated using UV-curable resin as a backbone material. The DIO containing silica spheres in the polymeric backbone was fabricated for application to a nanoparticle separation system, because the DIO had interconnected nanochannels usable for mesoporous membranes.

Recently, we also fabricated a mono-layered type of DIOs via binary colloidal crystals (BCCs) composed of silica-polymer core-shell spheres and silica nanoparticles using the fabrication as shown in Figure S1 of the Supporting Information (Yamada et al., 2015). The binary colloidal crystals were heated at 550°C for 5 h, to completely remove the polymer component, resulting in mono-layered silica cores embedded in each hemispherical compartment of silica nanoparticles. In our study previously reported, it was demonstrated that the binary colloidal crystals could be used as an intermediate assembly of particles to fabricate DIOs containing submicron-sized spheres optically and physically accessible.

As mentioned above, although several methods have been proposed for the fabrication of DIOs, no one could intentionally move the inner cores in the backbone of DIOs. If the locations of inner cores in the compartment could be externally controlled, it would be applicable to various optical devices because the photonic band gap of DIOs is expected to change by shifting the locations of cores (Ruhl et al., 2006). In the present work, the fabrication process of DIOs, especially the calcination process to remove the polymer component, was examined to randomly move the inner cores after the heating process to remove the polymer component. The movement of micron-sized inner cores in the nanoparticle compartment was directly observed with an optical microscope to evaluate the movability of cores. To control the location of the micron-sized cores in the hemispherical compartment, an alternating electric field was applied to the movable-core-containing DIOs (Nagao et al., 2012; Vutukuri et al., 2012).

1. Experimental

1.1 Particle synthesis

The core-shell particles used for the fabrication of DIOs were prepared in soap-free emulsion polymerization in the presence of silica particles surface-modified with a silane coupling agent of 3-methacryloyloxypropyltrimethoxysilane (Okada et al., 2012; Yamada et al., 2015). The cores with an average size of 1.1 µm were employed in the polymerization, which were prepared in a seeded method where silica

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particles with an average size of 510 nm and a coefficient of variation \( (C_V) \) of 2.9% were grown by hydrolysis and condensation of tetraethylorthosilicate in a mixed solution of ethanol and water. The silica nanoparticles used as a backbone material in the DIO fabrication were prepared with a modified Stöber method (Sakurai et al., 2014). Figure 1 shows TEM images of the core-shell particles and the silica nanoparticles, respectively. Average sizes of the core-shell particles and the nanoparticles were 1.6 \( \mu \)m and 20 nm with coefficients of variation of 1.6% and 10%, respectively. According to the dimensions of core and core-shell particles, a 1.1 \( \mu \)m silica core moving in space with a diameter of 1.6 \( \mu \)m was designed.

1.2 Fabrication of double inverse opals

For fabrication of the BCCs composed of the core-shell particles and the silica nanoparticles, both suspensions of the particles were mixed with each other at the ratio of core-shell particles to nanoparticles = 5 : 1 with the total particle concentration of 5 vol%. The mixed suspension with a volume of 20 \( \mu \)L was dropped onto a hydrophilically treated Si substrate (1.5 \( \times \) 3 cm\(^2\)) that was then inclined at around 10° and dried at ambient temperature for 12 h or more. The dried samples on the substrate were heated to remove the polystyrene (PS) shell from the BCCs of core-shell spheres and silica nanoparticles. Typically, the particle assemblies were heated at 500°C for 7 h. The assemblies obtained in the five-sixth upper part of the Si substrate were observed with a scanning electron microscope (SEM) because of thick layers of suspension near the bottom of the substrate inclined at the beginning of suspension drying. The movability of cores in the compartment of silica nanoparticles was directly evaluated by observation with an optical microscope after a small amount of water was adsorbed by the particles assemblies. More than 800 particles in the optical microscope images were counted to evaluate the movability of cores randomly moving in the compartment of nanoparticles.

2. Results and Discussion

The particle assemblies after removal of PS at 500°C for 7 h were observed with an optical microscope to examine the movability of the silica cores in the compartment of silica nanoparticles. No moving cores were observed after the heat treatment because of being stuck onto the inner wall of the compartment. Then, according to our method previously reported (Okada et al., 2013), the assemblies were slightly etched with a basic solution of sodium hydroxide in the concentration range of 0.1–10 mM. Although some cracks were observed in the SEM images of Figure S2, each hemispherical compartment after the alkaline etching was found to hold a micron-sized sphere under SEM observation in the dry state. A typical structure of DIO that was etched at \([\text{NaOH}] = 1 \text{ mM}\) is presented in the SEM images of Figure 2. The movability of cores in a wet state, which is defined as a ratio of the number of moving cores to that of cores counted in optical images, was within several percent-ages and the rest of the cores were still stuck onto the inner wall of the compartment.

The movability of cores are summarized in the bottom of Figure S2 accompanied by the corresponding SEM images. The heating treatment at 500°C was shortened to suppress the sticking of cores. Figure S3 shows the particle assembly obtained by the heating of BCCs for different times of 4, 5, 6 and 7 h. The movability of cores directly counted in a wet state is shown in Table 1. The shortening of the heating time from 7 to 5 h could raise the core movability to 18%. An excess shortening of heating time, however, lowered the movability to 10% due to organic residues still being in the compartment, which indicates that there are heating conditions appropriate for the cores to randomly move in the compartment.

According to the residue profile measured in thermogravimetric analysis (see Figure S4 in Supporting Information), the temperature of heating for 7 h was then decreased to find a thermal process to cost-effectively remove the polymer component. The TEM images of DIOs obtained at the low temperatures of 250, 300 and 350°C are presented in Figure S5 where a decrease in heating temperature seems to suppress the formation cracks of DIOs. The movabilities of DIOs formed at the low temperatures are summarized in Table 2. For the same reason as that for the 4 h heating in Table 1, the heating at a low temperature of 250°C could not completely remove the polymer component for the random
moving of cores. On the other hand, the 7 h heating at 300 or 350°C successfully raised the movability to 34% or more.

In additional experiments, since the heating at 300°C for 5, 6 or 8 h did not exceed the core movability of 47%, the heating at 300°C for 7 h was employed in the following fabrication of DIOs to characterize core motion under application of alternating electric field.

Controls over location and/or motion of the cores in the compartment is a requirement for the application of DIOs to optical devices. Application of alternating electric field has been used as an effective approach to control the location and motion of particles in a wet state by changing field strength and frequency (Nagao et al., 2012; Vutukuri et al., 2012). Hence, in the present work, an alternating electric field was applied to the DIOs shown in Figure S5(b).

Video on core motion in a wet state under switching an electric field were recorded at different strengths of 50, 100 and 150 V/mm. A typical snapshot of the movie is presented in Figure 3 where one can identify a 2D assembly of cores in the compartment. Figures 4(a)–(c) show the motions of a movable core at the three different strengths of electric field. In Figures 4(a)–(c), the distances travelled by a core from its location at \( t = 0 \) are plotted in the application of electric field, where 1 kHz was chosen as a low frequency to suppress electroosmotic flow in the observation with an optical microscope. In general, assembled particles without any compartment cannot stay in the application of low-frequency field because of strong electroosmotic flow induced by the electric field with high strengths (García-Sánchez et al., 2015). On the other hand, the present work could for the first time observe the motion of assembled particles in water due to the compartment of silica nanoparticles even at the high strength of 150 V/mm.

Under no application of electric field in Figure 4, the distances for the core observed were within 0.4 µm, which was shorter than the maximum length of void space, indicating that the cores were randomly moving within the compartment. The fluctuation of cores was slightly suppressed by application of 50 V/mm electric field. Interestingly, the suppression was distinctly observed at high field strengths of 100 and 150 V/mm. The motion of cores under switching electric field at 150 V/mm can be observed in the video of the Supporting Information. The alternating electric field was applied to the horizontal direction (y-axis) in the movie corresponding to x-y plane. It should be noted in the video that the random motion of cores was almost stopped by application of electric field. Since the distinct suppression was not observed in a high frequency range of MHz, the suppression of fluctuation observed at a low frequency of 1 kHz was probably affected by interaction between electric double layers of the core and the compartment of nanoparticles.

### Conclusion

The thermal treatment to remove organic component from the organic-inorganic BCC was optimized to obtain DIO incorporating movable cores. A heat treatment at 300°C for 7 h attained 47% movability, indicating that almost half of the cores incorporated into DIOs could range...
domly move in the compartment of silica nanoparticles. There are some possible ways to increase the movability, including optimization on thickness of silica shell withstanding at a high concentration of NaOH and employments of core and shell materials etched at different rates in an alkaline solution. It is of great interest that the random motions of the cores was suppressed by application of electric field at 1 kHz to the DIOs. The transition between random and suppressed motions of cores could be controlled by switching on and off the application of electric field, suggesting that the application of electric field can be a promising approach to control the inner structure of colloidal crystals.

Supplementary Information

Supplementary Information is available at http://www.scej.org/publication/jcej/suppl/

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Literature Cited


