Synthesis of Monodisperse Spherical SiO\(_2\) and Self-Assembly for Photonic Crystals

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ABSTRACT

Monodisperse spherical SiO\(_2\) particles of various sizes (~350 nm and ~800 nm) and size distributions were synthesized from TEOS and MTMS. The particle size and size distribution were controlled by changing the volume ratio of water to ethanol and the reaction temperature. Narrow-sized SiO\(_2\) particles with ~3% size distribution were obtained. Self-assembly of the SiO\(_2\) particles for photonic crystals were performed by the solvent evaporation method. The number of ordered SiO\(_2\) layers can be controlled by changing the amount of the dispersed SiO\(_2\) volume fraction in the solvent.

Key words: Photonic crystal, Colloid, Silica, Monodisperse, Self assembly

1. Introduction

Some periodic dielectric structures-called photonic crystals-with a forbidden gap (photonic bandgap) can control the propagation of photons.\(^1\) It has been shown that such photonic crystals may exhibit a frequency band in which electromagnetic waves are forbidden to exist, irrespective of their directions of propagation in a three-dimensional (3D) space.\(^3\) This feature can be used to localize electromagnetic waves to specific areas, to inhibit spontaneous emission, and to waveguide the propagation of electromagnetic waves along specific directions as well as at restricted frequencies. If large-scale 3D photonic crystals working at the visible or near infrared (NIR) regions were achievable, new photonic devices would be possible.

There are two general methods to fabricate photonic crystals. The most extended fabrication method is the micro-machining of a bulk material by lithographic methods, but it is expensive and time consuming and only a few monolayers are achievable so far. The other method is the self-assembly method with colloidal particles. This method is simple, inexpensive, and suitable for producing large samples. Moreover, it can be possible to obtain 3D photonic crystals. These colloidal crystals are formed by packing uniform spheres into 3D arrays, and the interstitial space of lattice is filled with high refractive index materials. When the template spheres are removed, then an inverse opal is created.

The particle size and size distribution of the template is an important parameter to create a 3D photonic crystal with a complete photonic bandgap.\(^6\) Monodispersity is required to form ordered close-packed arrays, and diameters should not vary more than 5%.\(^5\) Spheres with ~350 nm are required to make photonic crystals with a bandgap at visible regions and spheres with ~800 nm are required with a bandgap at technologically important wave lengths such as 1.5 \(\mu\)m.\(^6\)

In this paper, ~350 nm and ~800 nm SiO\(_2\) spheres with narrow size distribution were synthesized from TEOS and MTMS. In the synthesis from TEOS, the effect of the volume ratio of H\(_2\)O to ethanol on the monodispersity of silica spheres was investigated. In the synthesis from MTMS, the effect of temperature on monodispersity was investigated. These synthesized spheres were self-assembled and the optical properties of self-assembled spheres were observed with different particle sizes and number of layers.

2. Experimental

2.1. Synthesis of monodisperse spherical SiO\(_2\)

Monodisperse spherical SiO\(_2\) particles were prepared from TEOS (Aldrich, 98%) by using the Stöber process.\(^7\) In the synthesis from TEOS, ethanol (Dongyang, 99.9%) and distilled water were used and NH\(_4\)OH (Junicell, 28% NH\(_3\) in water) was used as a catalyst. First, TEOS, ethanol, water, and ammonia solution were stirred using a magnetic mixer in a beaker with a polyethylene wrap at 22°C. Then the synthesized powder was washed out by distilled water or ethanol three times.

Unlike TEOS, MTMS is reactive, so ethanol used as a homogenizing agent in the synthesis from TEOS was not used in the synthesis from MTMS. NH\(_4\)OH was mixed with the distilled water heated up to reaction temperature. As
this solution was being stirred, the MTMS heated up to reaction temperature was added to the mixed solution. The reaction temperature varies from 40°C to 95°C. The following process was the same for the synthesis from TEOS.

2.2. Self-assembly

The assembly of silica powders was carried out on a micro slide glass substrate in a vial glass. The glass substrates and vial glasses were soaked in a sulfuric acid for 24h for cleaning and rinsed well with deionized water in an ultrasonic bath for 3h. The colloidal particles were dispersed in distilled water or ethanol to control the SiO$_2$ concentration. A clean slide glass was placed in the SiO$_2$ colloidal dispersion in a clean vial glass and the SiO$_2$ particles were self-assembled through the evaporation of colloidal dispersion in a vibration-free oven. Self-assembled SiO$_2$ layers were fabricated with thicknesses ranging from 61 layers to 50 layers.

3. Results and Discussion

3.1. Synthesis from TEOS

Fig. 1 shows the particle size of SiO$_2$ spheres as a function of the volume ratio of water to ethanol. The particle size is the maximum when the volume ratio of water to ethanol is 0.1 ([TEOS]=0.1 M) and 0.15 ([TEOS]=0.3 M). The size dispersity was changed as a function of the volume ratio of water to ethanol (Fig. 2). When the particle size is the maximum value, the size dispersity is the minimum value. If the concentration of TEOS is fixed, there is the most suitable volume ratio of water to ethanol to synthesize SiO$_2$ particles by hydrolysis and condensation. Arriagada synthesized nanosize monodisperse SiO$_2$ spheres from TEOS through a reaction of 21h. $^{8}$ Our results are in agreement with the results of Arriagada, which is the characterization of silica on concentration of TEOS and H$_2$O/surfactant molar ratio. As a result of our experiment, the most suitable volume ratio of water to ethanol is 0.1 at 0.1 M of TEOS and 0.15 at 0.3 M of TEOS. At the most suitable volume ratio of water to ethanol, monodisperse spherical SiO$_2$ with the minimum size dispersity can be synthesized as an increase of nucleation rates.

3.2. Synthesis from MTMS

Fig. 3 shows the particle size of SiO$_2$ spheres as a function of the reaction temperature. As the reaction temperature increased, particle size and size dispersity decreased in the synthesis from MTMS. It is known that particle size decreased as the reaction temperature increased in the syn-

![Fig. 1. (a) Particle size of SiO$_2$ spheres as a function of the concentration of TEOS: EtOH/H$_2$O=0.2. [NH$_3$]=0.7 M, respectively. Error bars represent standard deviation of particle size [nm]. (b) Particle size of SiO$_2$ spheres as a function of the volume ratio of water to EtOH. [NH$_3$]=0.7 M, respectively. Error bars represent standard deviation of particle size.

![Fig. 2. Size dispersity of SiO$_2$ spheres as a function of the volume ratio of water to EtOH. [NH$_3$]=0.7 M, respectively. Dispersity is defined as a percentage of the standard deviation to the average size.


This result can be explained by a Lamer graph that nuclei were formed and grown as super-saturation of a monomer. Hydrolysis and condensation rates are slower as the reaction temperature is lower; then the number of nuclei which are to grow has exhausted the necessity to remove the super-saturated monomer. Since the rest monomer is used for growth, the size of the formed SiO\(_2\) particles is bigger as the reaction temperature is lower. The time to form nuclei by a super-saturated monomer is longer as the reaction rates are faster; therefore, a SiO\(_2\) particle with a uniform size dispersity is synthesized as the reaction temperature increases. But above 90°C, near the boiling point of water, the size dispersity increased by the turbulence of water bubbles. In the experimental results, the most proper reaction temperature is 80°C to form SiO\(_2\) par-
ticles with the lowest size dispersity. Fig. 4 shows an arrhenius plot for the particle size as a function of the reaction temperature and Fig. 5 shows the size dispersity as a function of the reaction temperature.

### 3.3. Self-assembly of colloidal spheres and optical properties

The key idea in self-assembly is that the final structure is close to or at a thermodynamic equilibrium state. Thus, such a process tends to reject defects and often leads to structures having a greater order than could be reached in non-self-assembling systems. The inherently parallel nature of the self-assembly process should make photonic crystals well suited for a large-scale production process where low cost and high throughput are the key requirements.

The monodisperse spherical SiO\(_2\) particles are self-assembled on a glass substrate using an evaporation method by P. Jiang et al. Strong capillary forces at a meniscus between
a substrate and a colloidal sol can induce crystallization of spheres into a 3D array of controllable thickness. If this meniscus is slowly swept across a vertically placed substrate by solvent evaporation, thin planar opals can be deposited. Spheres with ~350 nm and ~800 nm are required to make photonic crystals with a bandgap at visible regions and frequency used telecommunication. Therefore, 360 nm SiO$_2$ spheres (S.D.=3.8%) in the synthesis from TEOS (Fig. 5(a)) and 822 nm SiO$_2$ spheres (S.D.=3%) in the synthesis from MTMS (Fig. 5(b)) were self-assembled using the evaporation method. As shown in the top view SEM micrographs in Fig. 6(a) and 6(b), the deposition of SiO$_2$ spheres is uniform and dense. SiO$_2$ spheres were deposited in {111} set of planes of an FCC structure parallel to the substrate.

The thickness of assembled SiO$_2$ spheres was controlled by changing the amount of dispersed SiO$_2$ volume fractions in the solvent and transmittance spectra were observed. Figs. 7(a), (b), and (c) are side view SEM micrographs of self-assembled SiO$_2$ with 0.5 vol%, 1 vol%, and 2.5 vol% dispersion. 10 layers, 18 layers, and 50 layers were deposited with 0.5 vol%, 1 vol%, and 2.5 vol% each. A linear graph of the number of layers versus the SiO$_2$ volume fraction was achieved (Fig. 8). That is, the number of deposited layers are linearly proportional to the SiO$_2$ volume fraction. Thus the thickness of self-assembled SiO$_2$ spheres that we want can be controlled by changing the SiO$_2$ volume fractions.

Normal incidence transmission spectra of the three samples with increasing layers by changing the volume fractions were observed (Fig. 9). The curves in Fig. 9 have been scaled to a constant height and the arrows indicate the expected positions of the peaks for each curve, calculated using Bragg's law at normal incidence. According to the result of Miguez et al., which measured the transmittance of self-assembled SiO$_2$ spherical particles with different particle sizes, the wavelength of the peak is about 790 nm on a self-assembled SiO$_2$ size of 350 nm. In Fig. 9, the wavelength of our study is in good accordance with the result of Miguez et al. As deposited SiO$_2$ layers are thicker, the peak is deeper.

The effect of thickness was observed through normalized reflection spectra by changing the volume fractions (Fig. 10). FWHM (Full Width Half Maximum) is 96.5 nm at 0.5 vol% and 74.5 nm at 1 vol%. That is, the intensity of the peak generally increased and FWHM decreased as the number of layers increased. The number of (111) planes increases as the number of assembled layers increases, therefore the intensity of the diffraction beam by Bragg diffraction increases.
4. Conclusion

Monodisperse spherical SiO₂ particles with various sizes and size distributions were synthesized from TEOS and MTMS by hydrolysis and condensation reactions. The particle size and size distribution were controlled by changing the volume ratio of water to ethanol and the reaction temperature. The most suitable size for the assembly of photonic crystal was found to be 350 nm with S.D.=3% from TEOS and 822 nm with S.D.=3% from MTMS. Colloidal photonic crystals, ordered in the area of about 1 cm², were self-assembled by using a vertical-substrate-solvent-evaporation method. The number of ordered SiO₂ layers could be controlled by changing the amount of dispersed SiO₂ volume fraction in the solvent. The optical properties of 3D photonic crystals were observed with different sizes and number of
layers. The positions ($\lambda_{\text{Bragg}}$) of the first-order Bragg diffraction peak increased as the self-assembled SiO$_2$ particle size increased. The intensity of Bragg diffraction peaks increased as the thickness of self-assembled SiO$_2$ increased.

REFERENCES