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Synthesis of Silica Particles with Precisely Tailored Diameter

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A modified seeded growth process of silica particles with a continuous addition of tetraethyl orthosilicate (TEOS) was presented to control the diameter of silica particles. The diameter of particles was monitored by dynamic light scattering to control the addition of TEOS. The increase in the diameter of the silica particles with time and the addition of TEOS was investigated. The diameter of silica seeds increased from 193 nm to 446 nm in 4 h. The final diameter of silica particles was tailored within the range of ±5 nm to the target diameter. Silica particles with diameter of 446 nm were synthesized and assembled into photonic crystals with a pseudo band gap centered at just 1000 nm. The feasibility and practicability of this modified seeded growth process was verified.

Key words: Silica particle, Dynamic light scattering, Seeded growth process, Photonic crystal

I. INTRODUCTION

Colloidal silica particles (CSP) have attracted attention from scientists of not only materials science, chemistry but also biology since Stöber synthesized monodisperse spherical silica through hydrolysis of alkoxysilanes and subsequent condensation in alcoholic solutions [1]. The overall reaction can be written as:

$$\mathrm{Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH} \quad (1)$$

$$n\mathrm{Si(OH)_4 \rightarrow } n\mathrm{SiO_2} + 2n\mathrm{H_2O} \quad (2)$$

The rate of hydrolysis of tetraethyl orthosilicate (TEOS) and condensation of $\mathrm{Si(OH)_4}$ into small resolvable oligomers are relatively high, leading to the supersaturation of the latter in Stöber process. When the supersaturation of oligomers reaches a critical value, nucleation occurs spontaneously with high randomicity, which leads to a fluctuation in final particles diameters (D_f). D_f is as important as distribution of CSP in some applications, such as the calibration of particle-size measuring instruments [2], self assembling into photonic crystals, of which the pseudo band gap depends on the diameter of nanospheres [3].

Some work has been done on the prediction or control of D_f. Bogush *et al.* gave the correlation relating D_f to initial reagent concentrations through enormous experiments [4]. Nagao *et al.* investigated the effects of electrolytes [5], solvents [6], and amine catalysts [7] on the diameter of silica particles in Stöber process. Yu *et al.* controlled the size of silica particles by varying the reaction temperature in a sodium acetate solution [8]. Rao *et al.* reported the effect of TEOS, ammonia, ethanol, water, and temperature on particle diameter in a sequential method with ultrasonication [9]. Xu *et al.* adjusted silica particle sizes as well as pore sizes by varying the concentration of reactants [10]. Nozawa *et al.* implemented a continuous addition of TEOS in a Stöber-like process, in which a power law was used to predict the D_f [11]. However, due to the randomicity of nucleation, the experimental results may deviate from the calculated results by 20% or more [4].

To receive bigger particles and higher solid contents, Bogush described a seeded growth technique and developed a following equation from theoretic analysis,

$$D_\mathrm{f} = D_\mathrm{s}\left(\frac{W_\mathrm{f}}{W_\mathrm{s}}\right)^{1/3} \quad (3)$$

where D_s is the average diameter of the seed particles, W_s is the weight of TEOS used to produce the seed particles, and W_f is the total weight of TEOS added to the solution (including W_s) [4]. The polydispersion of seeded growth particles decreases as their size increases. Therefore, for a certain target D_f, smaller seeds will benefit the monodispersion of final CSP. For the formation of smaller silica seeds, instead of ammonia, arginine was demonstrated to be a catalyst by Watanabe *et al.* and larger CSP were obtained using similar seeded growth process and assembled into colloidal

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crystals [12]. Dong *et al.* employed Bogush's equation to predict D_f in a seeded growth process with a continuous addition of TEOS and a commercial silica sol particle as seeds [13], and the average deviation between actual result and predicted value was given as 10% [14]. Although composition of reactants and corresponding particle sizes about seeded growth process has been reported in Refs.[2, 4, 12, 15, 16], more and sufficient data about the accuracy of diameter controlling were little reported. Moreover, to control D_f precisely into a target value, multiple separation of CSP from the latex is needed for determining the diameter by using transmission electron microscope (TEM) [4, 13, 15, 16] or scanning electron microscope (SEM) [2, 12, 15], then dispersing in new solution for a regrowth. These multiple separation and dispersion will be time consuming and less cost effective. Furthermore, second nucleation happens when the addition of TEOS exceeds a critical value, which depends on initial particle size, number density, and reaction temperature [4, 13].

To achieve an effective control on D_f, dynamic light scattering (DLS) was employed in this work to monitor the growth of silica particles. With the DLS technique the diameter of CSP and their distribution can be investigated in less than 5 min [2, 8, 17, 18], which makes it possible to quasi real-time monitor and control the growth of CSP. The multiple separation and re-dispersion of CSP can be avoided because of this quasi real-time monitor in stead of SEM or TEM. Furthermore, to avoid the second nucleation, a continuous introduction of TEOS, instead of batch addition, was used in seeded growth, which could decrease the temporal concentration of TEOS. By using this method, CSP with a target diameter of 446 nm were precisely synthesized and assembled into photonic crystals with a pseudo band gap of exact 1000 nm.

II. EXPERIMENTS

A. Chemicals

All reagents except water used were purchased from Sigma-Aldrich. TEOS, as silica source, was vacuum distilled with CaO before use. Ammonia solution (25%) and absolute ethanol were used without further purification. Pure water was prepared by a pure water system (CSR-1-30T).

B. Preparation of silica particles and photonic crystals

For seeds preparation, 150 mL ethanol, 22 mL water, and 9 mL ammonium solution (25%) were mixed in a 1000 mL reactor equipped with paddle stirrer in a constant temperature bath at 40 °C, followed by stirring for 30 min. A mixture of 5 g TEOS and 20 mL ethanol is added into the reactor quickly. To monitor the growth process of silica particle size, after every desired interval, two drops of latex were withdrawn from the reactor. One drop of sample was added into a cuvette containing 2 mL water, immediately followed by DLS test. Another drop was applied to a clean slide for SEM later.

After seeds preparation, the latex was kept in the same reactor without separation. The temperature of water bath was set to 25 °C for the seeded growth experiments. After 30 min balance, 40 g TEOS was mixed with 160 mL ethanol and added into the reactor with a peristaltic pump. The flow rate was adjusted carefully to a desired value. To keep the concentration of ammonium unchanged, necessary amount of ammonium hydroxide solution and water were added into the reactor with another peristaltic pump. Two drops of latex were withdrawn from the reactor and tested every 15 min and were tested as above. The pumps were shut down when the result of the DLS test reached the target value. The stirring was stopped 8 h later. The silica particles were separated by centrifugation and resuspended in ethanol for further self-assembly.

The photonic crystals were synthesized according to the method described in Ref.[19]. Concentration of silica particle in dispersion was 5wt%.

C. Characterization

SEM images were obtained on a Hitachi SU 8010 microscope operated at 15 kV. The average diameter (D_{SEM}) and polydispersity index (PDI_{SEM}) of silica particles were calculated from more than 100 particles. $PDI_{SEM}=(D_m/D_n)-1$, where D_m and D_n were the weight-average and number-average diameters, respectively. The DLS measurement was performed on Malven Zetasizer Nano ZS90. A minimum of three measurements were carried out for one sample. The result of the diameter (D_{DLS}) with the least polydispersity index (PDI_{DLS}) in the measurements was adopted. If PDI_{DLS} of all measurements were higher than 0.05, the DLS result of this sample would be rejected. The normal-incident reflection spectra of photonic crystals were obtained from Ocean Optics NIRQuest with a reflection probe.

III. RESULTS AND DISCUSSION

A. Monitoring on the seeds preparation process

To achieve better monodispersity of final particles, small seeds were synthesized by choosing low concentration of NH_3 (0.58 mol/L). The concentration of NH_3 lower than 0.58 mol/L can lead to a long nucleation time. Elevated temperature was favored in seed preparation for it can reduce total reaction time, diameter of seeds and polydispersity [4]. However, too high tem-

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TABLE I Diameters of silica particles at different time in seed preparation.

Time/min	D_{SEM}/nm	PDI_{SEM}	D_{DLS}/nm	PDI_{DLS}
15	135	0.019	131	0.004
30	159	0.019	162	0.040
60	169	0.003	170	0.021
90	162	0.008	165	0.011
120	161	0.017	162	0.005

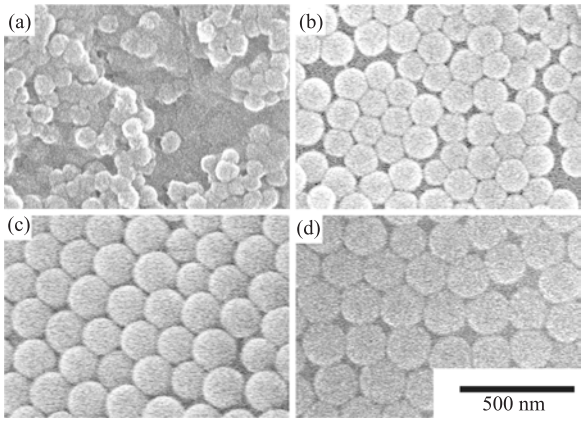

FIG. 1 SEM images of silica particles after the reaction time of (a) 10 min, (b) 15 min, (c) 30 min, and (d) 60 min.

perature (60 °C) would lead to polydispersion, and the reason may be possibly due to the low NH_3 concentration. So the silica seeds were synthesized at 40 °C in this work.

The diameters determined by DLS and SEM at different reaction time in seed preparation are shown in Table I. The SEM images of samples taken at 10, 15, 30, and 60 min are shown in Fig.1. It can be found in Fig.1(a) that particles were pasted together by amorphous silica and the diameters of particles are hard to determine. The DLS results of the same sample were unstable too. So samples taken within 15 min after first addition of TEOS were rejected. The particles for the sample taken at 15, 30, 60 min are well spherical and monodisperse. As shown in Table I, the average diameter reached the peak point at 60 min and shrank several nanometers in the next hour. The experiments were repeated carefully several times with this shrinkage occurring every time, which may be on account of internal Ostwald ripening. The growth of particles finished after 1 h from the first addition. Therefore the regrowth process was initiated at this time.

B. Controllable regrowth process of silica seeds

To demonstrate the control on the CSP diameter in this modified seeded growth process, a synthesis with a target diameter of 446 nm was carried out. Although

TABLE II Diameters of silica particles at different time in seeded growth process.

Time/min D_{calc}	D_{DLS}/nm	PDI_{DLS}	D_{SEM}/nm	PDI_{SEM}
0	195	0.019	193	0.0112
15	241	0.021	247	0.0064
243				
45	320	0.005	316	0.0043
306				
90	371	0.036	369	0.0025
369				
120	428	0.022	424	0.0015
401				
135	437	0.031	433	0.0009
415				
195	448	0.023	446	0.0011
429				

higher temperature is in favor of monodispersity of silica particles, ammonia and water tend to vaporize from heated latex and condense at outlet of TEOS, leading to a pre-hydrolysis of TEOS, which can result in secondary nucleation and the jam of the outlet. To solve this problem, Giesche rinsed his outlet of TEOS with dry air [15]. However, the ammonia, ethanol and water will be carried out by air flow. So herein seeded growth of silica particles was performed at room temperature and highly diluted TEOS (40 g TEOS/160 mL ethanol) was used to increase the total flow rate since high total flow rate can restrain pre-hydrolysis. A series of flow rate of 0.083, 0.167, 0.250, 0.333, 0.417 g TEOS/min, was tried in seeded growth process. All flow rates except the last one worked well without secondary nucleation. So the initial flow rate of TEOS was set at 0.333 g TEOS/min, corresponding to 4 times of W_s in 1 h. In contrast, a high concentration of TEOS solution (40 g TOES/80 mL ethanol) was tried in seeded growth process with a flow rate of 0.16 g TEOS/min, in which second nucleation soon occurred.

The SEM and DSL results at different time in the demonstration are shown in Table II and the SEM images are shown in Fig.2. At the beginning, diluted TEOS was added into reactor with a flow rate of 0.333 g TEOS/min. As Table II shows, the diameter of silica particles increases gradually with the addition of monomer. Crowns are found around silica particles in some area of Fig.2 (c) and (e), which suggest the existence of uncondensed oligomers in the uncompleted system. However, in some area of same SEM image, good spherical particles without crown can be found, suggesting the concentration of uncondensed oligomers is very low. This is consistent with the result that after the addition of TEOS was shut off the oligomers left in latex did not lead to a noticeable increase of D_{SEM}.

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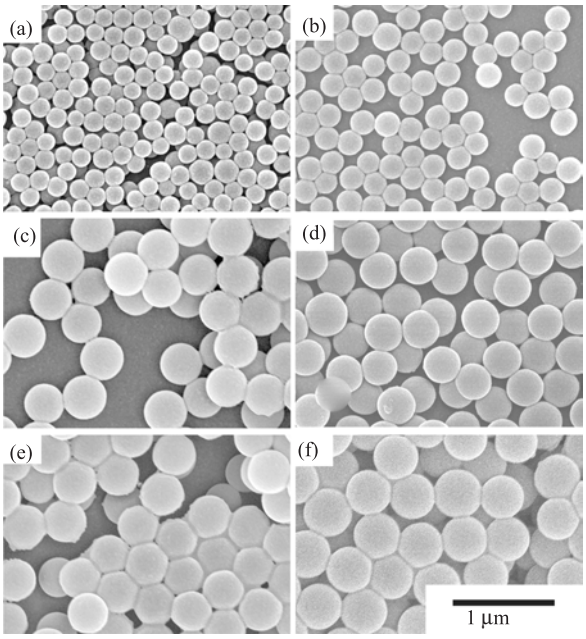

FIG. 2 SEM images of silica particles in seeded growth process at different time (a) 0 min, (b) 15 min, (c) 45 min, (d) 90 min, (e) 120 min, and (f) 195 min.

When the D_{DLS} reached above 436 nm, which happened at 135 min in this demonstration, the addition rate was adjusted to 0.083 g TEOS/min, corresponding to the same amount of W_{s}, or about 3 nm increase of diameters in 15 min. The addition of TOES stopped at 195 min, when D_{DLS} went to 448 nm. The final diameter was determined as 446 nm by SEM. Diameters calculated from Bogush's equation, D_{calc}, are also listed in Table II. The results show that D_{calc} are not always consistent with D_{SEM}. The highest deviation of D_{calc} from D_{SEM} is up to 23 nm. The experiments were repeated several times. This unusual deviation occurred at different time during growth process randomly. The reason behind unexpected increase in the diameter of the CSP still lays unknown. In all experiments, diameters of CSP reached above 446 nm in 4 h without second nucleation, much faster than the situation where it will take 50−100 h usually in seeded growth process. The polydispersity decreased with the increase of CSP diameter. The average deviation of D_{f} from target value was 5 nm.

C. Self-assembly of silica particles

CSP can be assembled into highly ordered colloidal crystals [20] with some fascinating properties [21, 22]. UV, visible, and near-IR light can be strongly Bragg diffracted by colloidal crystals made of monodisperse silica spheres for their highly ordered structure. As a result, a reflection peak rises with a position, λ, which

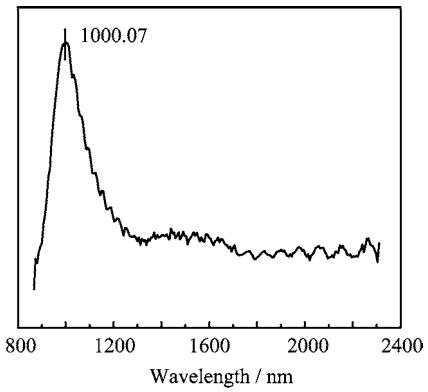

FIG. 3 Reflection spectrum of photonic crystals assembled from CSP with diameter of 446 nm.

can be predicted by Bragg-Snell laws [23]:

$$\lambda = \sqrt{\frac{8}{3}} D_{\mathrm{f}} \sqrt{{n_{\mathrm{eff}}}^2 - \sin^2\theta} \tag{4}$$

where θ is the incidence angle, n_{eff} represent for effective refractive index. n_{eff} can be expressed as:

$$n_{\mathrm{eff}} = \sqrt{{n_{\mathrm{s}}}^2 f + {n_{\mathrm{air}}}^2 (1-f)} \tag{5}$$

where n_{s} is the refractive index of silica particles, which is 1.45 at wavelength of 1000 nm [24], n_{air} is the refractive index of air, which is 1.00, f is the volume filling fraction, which should be 0.74 in a close-packed array of hard spheres. However, it is impossible for any material to be ideally rigid. The silica spheres will be "sintered" to each other a little bit. Herein f is set to 0.80.

Colloidal crystals with a pseudo band gap centered at 1000 nm should be prepared by CSP with diameter of 446 nm, according to Eq.(4) described above. The desired CSP was prepared and assembled into photonic crystals. Its reflection spectrum is shown in Fig.3. A peak centered at 1000 nm is found as expected. The result suggests that both the diameter and the monodispersion of CSP were successfully controlled by the method described above.

IV. CONCLUSION

For precise controlling the diameter of silica particles, a modified seeded growth process was demonstrated in which dynamic light scattering and continuous addition of TEOS was employed. For better monodispersion, low concentration of NH_3 and elevated temperature were used to form smaller seeds. The results show that the growth of silica seeds finished in 1 h and shrank several nanometers in the following hour. The diameter of silica particles increased gradually with the addition of diluted TEOS in seeded growth process, in which TEOS can be introduced as fast as 4 times of W_{s} in 1 h without second nucleation. Diameter of silica particles was

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tailored to the target value, which was 446 nm in the demonstration, with a minor deviation. The residual TEOS and its oligomers in reactor did not lead to a noticeable increase of D_f after the addition of TEOS was shut off. Photonic crystals with a reflection peak centered at 1000 nm were fabricated with tailored CSP to validate the feasibility and practicability of this modified seeded growth process.

V. ACKNOWLEDGMENTS

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