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In Situ Production of Spherical Silica Particles Containing Self-Organized Mesopores

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ABSTRACT

A spray drying method was used to produce a silica powder that contained ordered mesopores. A colloidal mixture of silica nanoparticles and polystyrene latex nanoparticles was mixed and sprayed as droplets into a vertical reactor that contained two temperature zones. The solvent in the droplets was evaporated at the front part of the reactor to produce a powder composite consisting of silica and PS nanoparticles. The PS nanoparticles in the powder were evaporated in the back portion of the reactor to produce a silica powder consisting of mesopores. The mesopores was observed to be arranged into a hexagonal packing, indicating the self-organization process occurred spontaneously during the solvent evaporation. The entire process was completed in only several seconds, which is contrary to currently available methods that require several hours or up to several days to complete this self-organization process.

Introduction. The synthesis of mesostructure's porous silica represents a fascinating and intellectually challenging problem due to its potential for applications in catalysts, chromatography, the controlled release of drugs, low dielectric constant fillers, pigments, microelectronics, and electro-optics.[1−3] When supramolecular surfactant micelles are used in the synthesis, the pore sizes are in the range of 10 nm or less.[4−8] Synthesis via colloid crystallization allows the pore sizes to be controlled in the range of nanometers to micrometers.[1] In this study, we report on the production of spherical-shaped porous silica particles with nanoscale ordering porosity by means of a spray drying method using a colloidal mixture of silica and polystyrene (PS) latex as the precursor. Production via the use of aerosols has also been reported by Lu et al.[9] using a different precursor, i.e., a silica solution and a surfactant. These workers, however, did not report on the controllability of pore sizes or on the space between the pores. The approach described herein allows for their easy tunability as well as avoiding the necessity of a complex chemistry process.

Experimental Section. Figure 1 schematically depicts the equipmental set up used in this work, which consists of a nebulizer (Omron Corp., operated at 1.7 MHz), a vertical tube reactor, and an air filter. Colloidal silica particles (Nissan Chemical Ind. Ltd., particle size around 5 nm) were used as a precursor, which was mixed with polystyrene latex (Japan Synthetic Rubber Corp., various particle sizes) in a certain fraction in water to form a dilute solution, which was then atomized to generate droplets. The reactor consisted of two heating zones, the first having a fixed temperature of 200 °C and the second, a fixed temperature of 450 °C. The first zone is used to evaporate the solvent in the droplet, resulting in large particles of composite consisting of primary silica particles and PS latex particles. The second zone was used to evaporate the PS latex particles, which resulted in the formation of porous silica particles. The filter was maintained at a temperature of 150 °C to avoid water condensation. The flow rate of the nitrogen carrier gas was maintained at 1 L/min.

Compared to the available methods that are typically time-consuming, the method described here operates very fast and is relatively simple. A large amount of porous particles can be produced in just several seconds. The production rate can be easily controlled by appropriate control of the rate of flow of the nitrogen carrier gas. Several steps that are normally used in previously described methods can be ignored in our method. Indeed, our method is an in situ process. No posttreatment is required in order to produce porous particles. The ability to control particle size by altering the droplet size as well as the concentration of primary particles in a precursor represent additional advantages of the present method.

Results and Discussion. Scanning electron micrographs (SEM, Hitachi S-5000, operated at 20 kV) in Figure 2 reveal the ordered arrangement of pores on the surface of spherical particles. The pore sizes are similar to the PS latex particle sizes. This suggests that the pore size can be easily controlled

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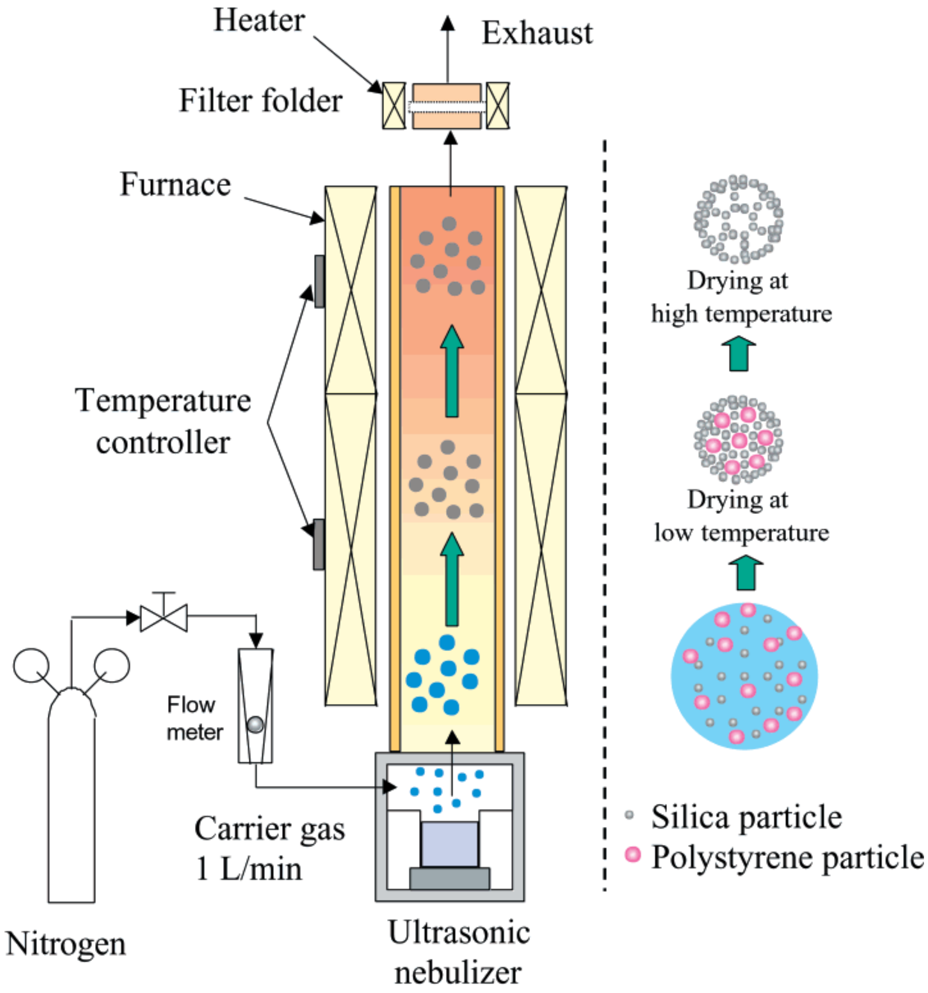

Figure 1. Schematic diagram of experimental apparatus. A detailed explanation can be found in the text.

by changing the size of the PS latex particles. This observation revealed that, during the evaporation of solvent, a spontaneous self-organization of the PS latex particles took place in the droplet. To our knowledge, this result is the first observation of such a self-organization process of particles in the environment formed by other colloidal particles. The observed self-organization, to date, has only been observed in a solvent environment.[1,8,13,14] Observations of broken particles reveal that the pore arrangement persists throughout the entire volume of the particles (not only on the particle surface). The observed hexagonal packing of the porous particles on the surface of the spherical particles is exactly similar to that observed for flat surfaces.[8] The spacing between the pores is very homogeneous, approximately two primary silica particles in thickness. This result indicates that the spacing between the pores can be easily controlled by changing the size of the primary silica particles.

We measured diameters of several hundreds of the produced particles on the SEM picture. We found that the average particle size is 300 nm with a geometrical standard deviation of about 1.4. Indeed, the average size and standard deviation of the produced particles depend on the initial concentration of the precursor and the size distribution of the droplets. The average size of particles increases with the initial concentration of precursor. Using the laser scattering method (Malvern), we found that the geometrical standard deviation of the droplets produced by our nebulizer is almost fixed at 1.5.

The mechanism of porous particles formation can be simply explained as follows. During the evaporation of the droplets, there is a rearrangement of the PS latex particles inside the silica nanoparticles environment to occupy a hexagonal packing. This process completed only in a few seconds, after which the droplets transformed into solid particles. When leaving the first zone, silica nanoparticles and well-ordered PS latex particles occupied fixed positions in the solid particles. In the second zone, with the temperature higher than the evaporation temperature of the PS latex, the PS latex particles evaporate to leave pores on their position. Finally, we then obtained silica particles containing ordered mesopores (left by PS latex particles).

We also observed that the range of pore ordering on the surface of a particle decreases with decreasing droplet size. It is likely the increase in the curvature of particle surface reduces the net interaction force (that responsible for the occurrence of the well-arrangement) on the PS latex particles occupying the surface of a droplet by the remaining PS ones. Since those particles are also affected by random force (Brownian motion) that tends to force the particles into irregular positions, it is clear that the decrease in inter PS

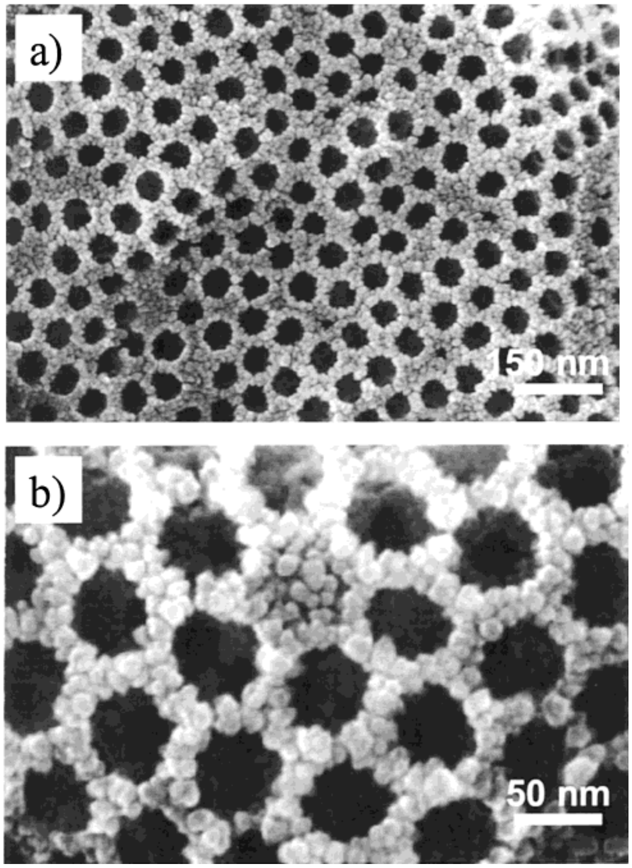

Figure 2. SEM images of the surface morphology of silica powders using 79 nm PS latex particle size: (a) low magnification and (b) high magnification. The hexagonal packing of porous in produced powders can be clearly observed, indicating that a self-organization of PS latex particles had taken place during the drying process in reactor tube.

latex particles interaction due to the increase in the curvature of the droplets (the decrease in the droplet diameter) reduces the pores ordering. Another possible explanation is the decrease in the droplet size reduces the space allocated for the rearrangement of the PS latex nanoparticles (to increase the restriction of packing configuration).

We also did experiment using different sizes of PS latex particles. We still observed the hexagonal packing of the pores inside the produced particles. In addition, the ordering of the pores increases with the increase in the PS latex particles size. Indeed, this result is in agreement with the commonly observed ones that ordering of larger particles in general is easier than ordering of the smaller particles.

Figure 3 shows data on the variation of pore spacing for distinct fractions of PS latex and primary silica particles. As expected, the spacing between the pores increases when the fraction of PS latex is decreased. However, the long-range ordering of pores on the particle surface is reduced. A further increase in the PS latex fraction results in the formation of brittle particles, many of which are broken. There is an optimum fraction of PS latex and primary silica particles to result in the formation of spherical particles with an organized pore arrangement. In our experiment we found the optimum values are 10 mL of silica colloids (0.05%) mixed with 1 mL of PS latex colloid (3.6×10^{13} particles/mL).

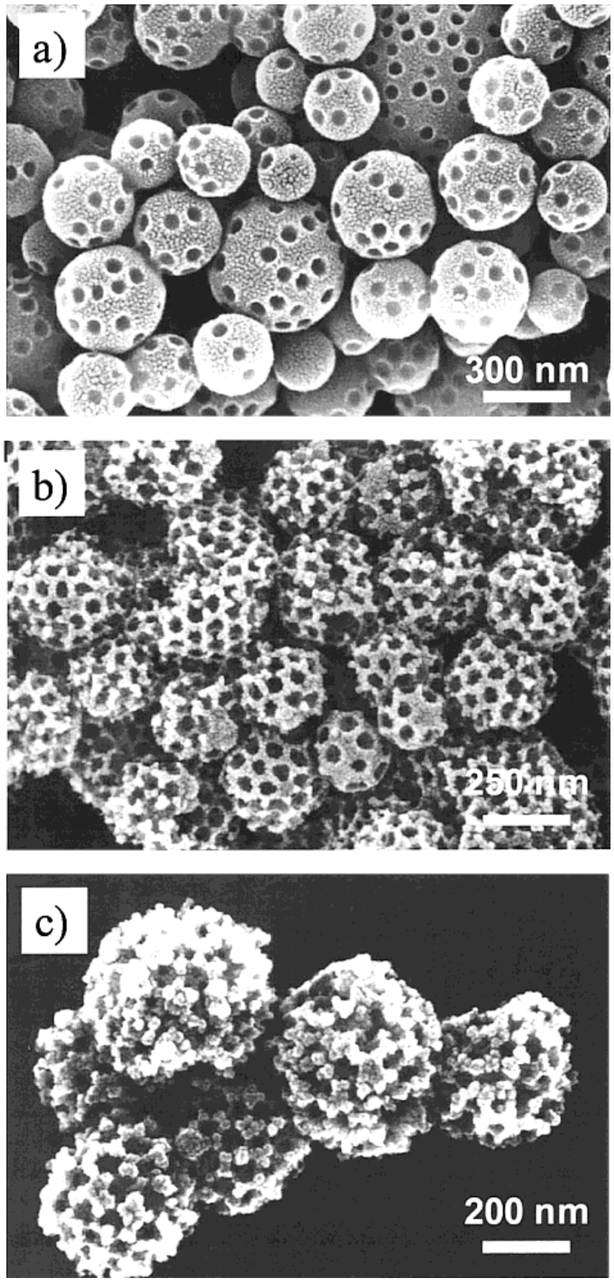

Figure 3. SEM images of a spherical silica powder produced by varying the content ratio of PS latex & silica: 10 mL of silica colloids (0.05%) mixed with (a) 0.5 mL, (b) 1 mL, and (c) 2 mL of PS latex colloid (3.6×10^{13} particles/mL). The size of PS latex particles were maintained at 79 nm.

Generally, the collected porous particles are not monodisperse due to the dispersion in the size of droplets produced by the nebulizer. However, monodisperse particles can be easily obtained by placing a differential mobility analyzer (DMA) prior to the particle collector position. The use of a DMA to select particle size has been previously reported by several research groups.[10,11]

Despite the observation of spherical-shaped particles, we also observed the presence of a small amount of doughnut-shaped porous silica particles, as shown in Figure 4. This

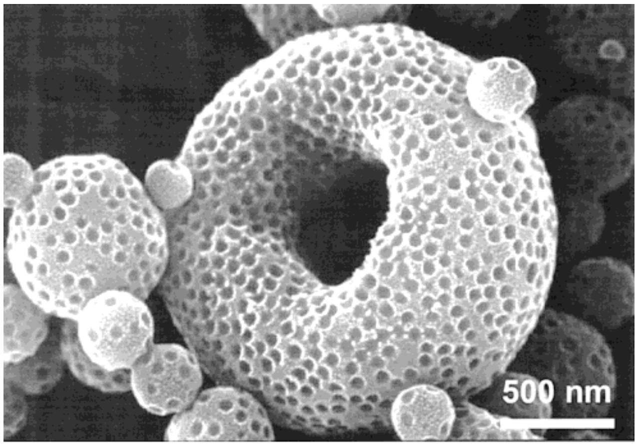

Figure 4. SEM image of a doughnut-shaped particle. This was frequently observed in the case of large droplets, which evolved to a doughnut shape, rather than a spherical shape.

shape appeared when the droplet size was relatively large. We assume that the presence of this shape was initiated by the oscillation of the droplet shape to deviate from the spherical one. The oscillation frequency has been derived by Rayleigh[15] and some experiments have been conducted by Nelson et al.[16] and Takaki et al.[17] During the oscillation and evaporation, there is possibility for the presence of oval particles to result a very high evaporation on the curvature surface, leading to the quick formation of solid ring along the curvature surface. A solid ring pins the contact line of the remaining liquid in the droplet to induce a mass flow (solvent and particles) from the droplet center toward the ring. Particles will then concentrate around the ring, leaving the inner part of the liquid droplet to become thinner and finally creating a hole. This mechanism leads to the formation of doughnut-shaped particles, similar to the formation of a ring when a droplet of colloid is evaporated on a flat surface.[12]

Particles produced by our method appear as powders. This powder can be used as a basic material for use in a variety of technological formulations such as low dielectric constant materials and filter material that can be easily handled and assembled into various forms, such as pellets, ribbons, paste, etc. Such flexible porous materials cannot be achieved by using the existing method of synthesis.

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