

## Nanosized Polymer Particle-facilitated Preparation of Mesoporous Silica Particles Using a Spray Method

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Spherical silica particles with large mesopores and controlled particle size in the submicron range were prepared using a mixed solution of silica nanoparticles and nanosized polymer particle as a template via spray routes.

Porous materials are of interest to materials scientists because of their many possible applications, which range from gas storage to drug delivery.<sup>1</sup> Silica is widely used in porous materials because it is chemically and physically stable, harmless and inexpensive.<sup>2</sup>

Before certain applications can be realized, development of a simple process that results in controllable pore size and good pore arrangement is needed. A well-established process is the self-assembly template technique, which employs an organic material as the template (either surfactant or particle). Potential advantages of this process include pore formation that reflects the template shape<sup>3</sup> and complete removal of the template.<sup>4</sup> Organic surfactants (i.e., cetyltrimethylammonium bromide<sup>5</sup>) are well-known organic templates, which effectively produce MCM and SBA series.<sup>6</sup> However, limited pore size, difficulties with chemical diffusivity, and aspherical pores<sup>7</sup> are problems that remain to be overcome. To solve these limitations, organic particles have been used successfully as the template (i.e., polystyrene latex (PSL)<sup>4</sup>). However, the reported distribution was for macrosized pores because PSL greater than 80 nm was used.

Preparation of porous silica (with pore diameters between 2 and 50 nm) is attractive to researchers in material science.<sup>8</sup> In particular, materials with mesopores large enough to load molecules via adsorption are desirable. However, it is possible that the larger mesopores may result in carrying of molecules. With a pore size that is large enough, adsorbed molecules will not block pores upon adsorption; thus, additional adsorption inside both the pore and the particle is possible.<sup>9</sup> Hence, this method that produces material with controllable particle and mesopore sizes needs to be fine-tuned. In addition, while current methods have been used to create porous particles, to the best of our knowledge, reports of materials with controllable pore size in the range of 20–50 nm are virtually nonexistent. Further, the previously reported porous material showed the irregular pore shape and irregular pore arrangement. Different from previous result, the nanosized polymer particle as template was used to form porous structure in the present report. Interestingly, a spherical particle with ordered and spherical mesoporous structure could be produced well. The particle size could also be controlled by only changing the initial concentration.

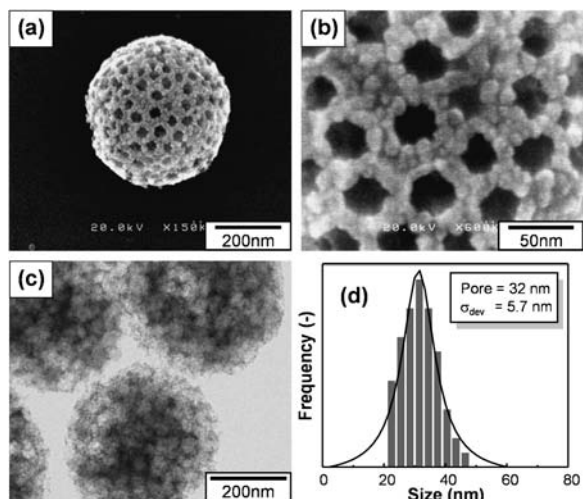
Previously, we successfully prepared an inorganic material with controllable particle and mesopore size (pore >80 nm) using a colloidal template.<sup>8,10,11</sup> Herein, submicron silica particles with pore sizes of less than 50 nm (e.g., mean diameter of

32 nm) were prepared using a mixture of silica nanoparticles (Nissan Chem. Ind., Ltd.; average size of 5 nm) and PSL (JSR Co., Ltd.; particle size of 39 nm) in aqueous solutions with different initial concentrations, ranging from 0.005 to 0.05%. The mass ratio of nanosized silica particle to nanosized PSL particle was fixed at 2 to 5. Prior to spraying, the mixed solution was sonicated in an ultrasonic bath for several minutes to obtain a homogenous solution. Then, the mixed solution was sprayed using similar to the previously described methods.<sup>11</sup> In briefly, the apparatus consists of ultrasonic nebulizer (Omron Corp., NE-U12, freq. 1.7 MHz) for generating droplets from the precursor, laminar flow tubular furnace (a ceramic tube;  $D = 13$  mm,  $L = 1$  m) and electrostatic precipitator or filter. The generated droplets were then heated with two heating zones in the tubular furnace. The first zone ( $T = 200$  °C) was used to evaporate the solvent (water) in the droplet, resulting in large particles of composite consisting of nanosized silica and nano-sized PSL. Then, the second zone ( $T = 500$  °C) was used to evaporate the nanosized PSL particles, which resulted in the releasing nanosized template from the composite silica/PSL particle, and formation of silica particles with mesoporous structure. With the second temperature zone, it is supposed that PSL is removed completely because thermal degradation of PSL occurs at 270 °C.<sup>12</sup> In addition, flow of N<sub>2</sub> gas, as the carrier gas, is approximately 1 L/min. Filter or electrostatic precipitator was used for collecting the particle.

The prepared particles were characterized using a scanning electron micrograph (SEM, Hitachi S-5000, 20 kV) and a transmittance electron micrograph (TEM; JEM-3000F, JEOL, Tokyo, 300 kV), which allowed for examination of particle size and morphology, as well as of pore structure.

Consistent with our previous report,<sup>11</sup> when porous materials are produced using template methods, several factors determine the pore structure. Simply stated, materials with good pore arrangements are obtained only under optimal conditions, especially with regard to the mass ratio of the primary precursor for the template particle.

Figure 1a shows a SEM image of the pore structure of a silica particle. Owing to buoyancy and surface forces, the PSL particles were arranged on the surface of the droplet, formed in the spray solution, and silica filled in the space. Next, PSL particles were removed completely leaving holes, the diameter of which corresponded to the original size of the PSL particles. To verify the pore arrangement, a high-magnification SEM image is shown in Figure 1b. The pore arrangement showed a good pattern that was close to hexagonal. It is possible that pore arrangement is determined by the void space between PSL spheres that are in contact with each other. In addition, for silica nanoparticles with diameters of 5 nm, the PSL spheres must be at least 32 nm for a single nanoparticle to fit within the void space.



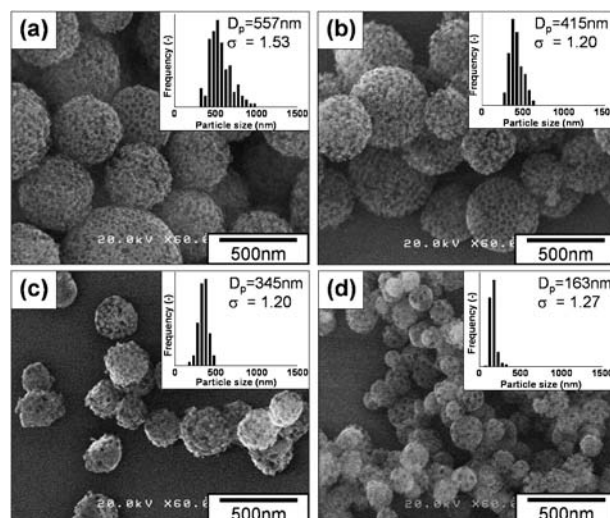
**Figure 1.** SEM images of mesoporous silica particle (under low (a) and high (b) magnification), a TEM image (c), and pore size distribution (d).

Thus, the PSL used in the present report resulted in a good pattern. Detailed calculations are reported elsewhere.<sup>11</sup>

TEM analysis was used to characterize the prepared particle porosity and pore structure (Figure 1c). Pores existed both on the particle surface and within the particles. Comparison of pore size (Figure 1d) with the initial size of the PSL used revealed slight shrinkage. This phenomenon occurred because the nanosized pores easily shrink when exposed to heat shock. Although shrinkage was observed, the standard deviation of the pore size was relatively similar to that of the initial PSL. Therefore, it was concluded that the process is stable with respect to the quality of the product. However, some regions of the particle were not arranged by PSL because PSL size was restricted to the size that allowed for it to be positioned between silica nanoparticles in a hexagonal pattern.

The effects of the precursor concentration were investigated using similar mass ratios of silica/PSL. Figure 2 shows SEM images of mesoporous silica particles of various sizes and size distributions. Spherical particles with mesoporous structure were obtained. Particle size was directly dependent on precursor concentration, consistent with a previous study.<sup>11</sup> Particle sizes were 688, 557, 415, 345, and 164 nm for concentrations of 2.02, 0.72, 0.05, 0.025, and 0.005 wt %, respectively. These results demonstrate that production of particles of any size is a significant advantage of this method.

Successful preparation of mesoporous silica particles with the desired pore-size range was achieved using an adsorption process.<sup>13</sup> It is worth mentioning that the pores were large enough to load various molecules, including large polymers and inorganic nanoparticles.<sup>9</sup> However, the mass transfer, diffusivity, and molecular penetration characteristics of the present pore system extend the range of possible applications, such as selective adsorption and catalytic activity. Because particle morphology is the primary focus of the current study, properties of the prepared material will not be reported at the present time. In addition, the detailed characterization for porous structure performance (i.e., surface area, mesopore volume) and its physical properties (i.e., mechanical strength), along with its application of mesoporous silica particle, will be investigated



**Figure 2.** SEM images and size distributions of prepared particles as a function of initial concentration ((a) 0.72, (b) 0.05, (c) 0.025, and (d) 0.005 wt %).

in our future work.

In summary, an efficient method for the preparation of silica particles with mesoporous structures was successfully developed. The method involves spraying of silica nanoparticles that are mixed with 39-nm PSL particles as the template in aqueous solution at two fixed temperature zones. The prepared particles, which were easily obtained using this method, were spherical, relatively monodisperse, and size-controllable. It is expected that the present method could be useful in several applications, such as with adsorbent and low dielectric constant materials. In addition, preliminary experiments suggest that mesoporous particles can be prepared from various inorganic materials, using either a metal solution or a nanoparticle suspension, if the void space of the template is large enough to contain multiple molecules of the primary inorganic compound at a mass ratio equal to the ratio of the primary inorganic template.

We acknowledge the Ministry of Education, Culture, Sports, Science and Technology (MEXT) for supporting this research (a Grant-in-Aid for Young Scientists (B), No. 20760516, 2008) and providing a scholarship to A.B.D.N.

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