

## Synthesis of Silica Nanoparticles Having a Well-Ordered Mesostructure Using a Double Surfactant System

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Silica nanoparticles having mesopores with a uniform aperture of ca. 2 nm were prepared using a cationic surfactant as a templating agent and a nonionic surfactant as a suppressant of grain growth, respectively. A well-ordered hexagonal arrangement of the mesopores was produced in nanoparticles by previous hydrolysis of tetraethoxysilane with hydrochloric acid and subsequent assembly of cationic surfactant micelles and anionic silicate species at a basic condition. The growth of the silica particles was suppressed by the coexistence of a block copolymer as a nonionic surfactant. The diameter of ca. 20 nm was achieved as the minimum grain size without deformation of the hexagonal mesostructure.

Since the synthesis of the M41S family by templating techniques using surfactant micelles,<sup>1</sup> mesoporous silica has received much attention in diverse areas, such as catalysis, adsorption, separation, and chromatography. Controlling the ordered arrangement and apertures of mesopores has been investigated by changing the templates and preparation conditions.<sup>1–6</sup> Recently, studies on macroscopic forms of mesoporous silica have been noticeable for a variety of applications. Because fine particles in a nanometer scale exhibit a remarkable potential as an easy-to-handle form having highly accessible mesopores, synthesis methods for the nanoparticles have been reported by many researchers in the field of mesoporous silica.<sup>7–13</sup> However, there are few reports concerning small particles (<50 nm),<sup>10–13</sup> and the hexagonal arrangement of the mesopores was generally disordered in the small grains. A well-ordered mesostructure was obtained only in relatively large particles (ca. 100 nm).<sup>7–9</sup> Here, we propose a novel method for the synthesis of small nanoparticles having hexagonally ordered mesopores. Complete hydrolysis of precursor alkoxides at an acidic condition and subsequent steady assembly of negative silicate species and positive surfactants at a basic condition were effective for improvement of the order of the mesostructure. Moreover, the preparation of nanoscale particles with a diameter of 20–50 nm was successfully achieved by suppression of the grain growth with the presence of a nonionic surfactant. This new type of mesoporous nanoparticle that has accessible ordered pores would be applicable to a wide variety of practical fields as a useful component in nanotechnologies, such as those for nanoscopic reactors and containers.

As a typical synthesis procedure, tetraethoxysilane (TEOS, 3.5 g, 0.0168 mol) was added to a hydrochloric acid solution (30 g, pH 0.5) at room temperature, previously dissolving cetyl trimethylammonium chloride (CTAC; 2.6 g, 0.00814 mol) and a triblock copolymer (Pluronic F127; EO<sub>106</sub>PO<sub>60</sub>EO<sub>106</sub>, 2.0 g, 0.000159 mol) as cationic and nonionic surfactants, respectively. The mixture became a clear solution with vigorous stirring. After being stirred for 3–24 h, the solution was changed into a white gel by adding 3.0 g of 14.7 M ammonia water. An increase in the stirring time showed a tendency to decrease the grain size finally obtained. The gel was aged at room temperature for 24 h and then dried at 333 K in air for 24 h. The surfactants were removed from the dried

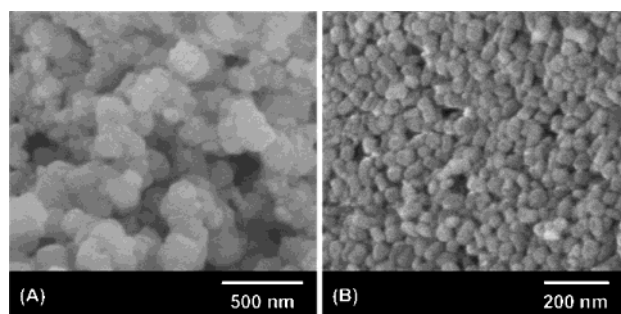


Figure 1. SEM images of silica particles produced without (A) and with F127 (B) obtained using a Hitachi S-4700.

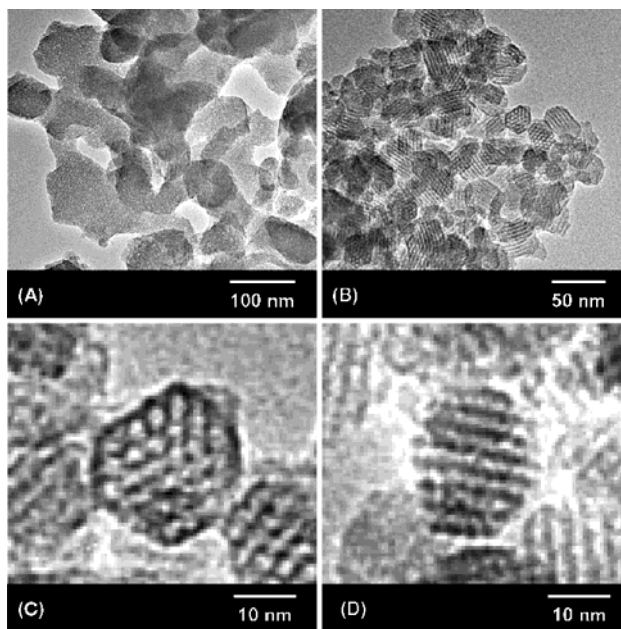
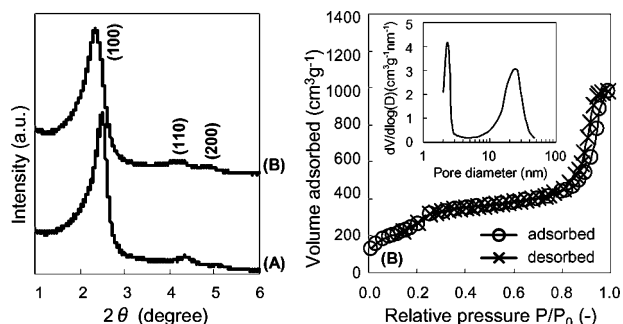


Figure 2. TEM images of silica particles produced without (A) and with F127 (B) obtained using a Philips TECNAI F20. High magnification of top view (C) and side view (D) of the hexagonal arrangement of mesopores.

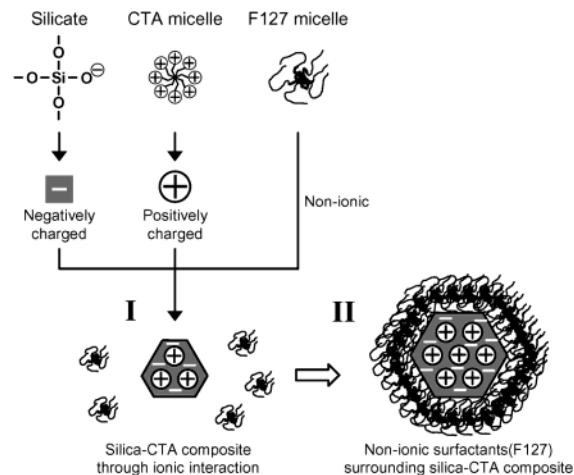
products by calcination at 873 K in air for 3 h. We prepared samples without addition of the block copolymer F127 as a control experiment.

Figure 1 shows SEM images of silica particles produced without and with F127. Although the control sample without F127 was composed of relatively large particles above 100–200 nm, the coexistence of F127 clearly reduced the size of the particles below 50 nm. The grain sizes had a relatively sharp distribution which ranged through 20–50 nm. The TEM images (Figure 2) and XRD patterns (Figure 3 left) reveal that the particles contained hexagonally ordered mesopores regardless of the presence of F127. The  $d_{100}$  value of ca. 3.7 nm estimated by the XRD patterns agreed



**Figure 3.** (Left) XRD patterns of silica particles produced without (A) and with F127 (B) monitored using a Rigaku RAD-C system with Cu K $\alpha$  radiation. (Right) Pore size distribution and nitrogen adsorption–desorption isotherm of silica particles produced with F127 collected using a Micromeritics TriStar 3000.

with the distance between the arranged mesopores observed in the TEM images. The similarity between both samples without and with F127 indicates that the mesopores of ca. 2 nm in diameter are ascribed to the templating effect of cetyltrimethylammonium (CTA) micelles. Because the coexistence of F127 obviously decreased the particle size, it is assumed that the nonionic surfactants suppressed the growth of the mesostructured silica-CTA composites. The minimum diameter prepared without deformation of the mesostructure was ca. 20 nm (Figure 2C,D). The side length of the minimum hexagon was ca. 10 nm, which corresponded to the arrangement of only three micelles. This is close to the minimum architecture for the hexagonal arrangement. The pore size distribution obtained from nitrogen adsorption–desorption isotherms (Figure 3, right) indicates that the apertures of the mesopores show a sharp distribution around 2.3 nm due to the well-ordered arrangement. The large pores of around 20 nm were attributed to the interparticle spaces among the nanoparticles. Previous addition of hydrochloric acid and the presence of nonionic surfactants were essential for the formation of hexagonal structures in the nanoscale grains of less than 50 nm. Although hexagonally ordered mesoporous silica was obtained without addition of hydrochloric acid,<sup>14</sup> the mesopore arrangement was destroyed with the miniaturization of the particles. Lin et al. prepared mesoporous silica under acidic conditions and then improved the order of their hexagonal mesostructures by treatment at a basic condition.<sup>15</sup> The acidic condition promotes hydration of TEOS and decreases the residual ethoxy groups affecting the ordered assembly. Moreover, subsequent addition of ammonia water is effective in the construction of well-ordered mesostructures through steady self-assembly of negatively charged silicates and positively charged CTA micelles. Thus, the hexagonal structure was predominantly constructed with negatively charged silicates and positively charged CTA micelles regardless of the presence of nonionic F127 (Figure 4, I). Because the polarity decreased with the assembly of the anionic and cationic species, the nonionic surfactant could surround the hexagonally ordered silica-CTA composites with a certain size due to a weak interaction between ionic and nonionic hydrophilic groups (Figure 4, II). Thus, the presence of F127 micelles covering the nanoparticles suppressed the grain growth and stabilized the ordered mesostructures. The grain size of the mesostructured composites would be determined by the balance between the assembly of the ionic species and the



**Figure 4.** Schematic representation of the functions of two surfactants.

suppression of the nonionic species. Finally, we successfully obtained a highly ordered hexagonal array in isolated nanograins with a diameter below 50 nm with a simple double surfactant system. In this method, binary surfactants perform different functions, such as a template agent and suppressant of grain growth, independently, while both of the surfactants were used as a template for the formation of mesostructures in previous studies.<sup>16–18</sup> The present synthesis strategy could be applied for other mesoporous materials.

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