Direct Preparation of Highly Ordered Multilayer-type Silica Nanocapsules Using Spontaneously Formed Vesicles as Templates

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Highly ordered multilayer silica nanocapsules were prepared using spontaneous vesicles formed by cationic surfactant mixtures as template. Transmission electron microscopy (TEM) and cryogenic transmission electron microscopy (Cryo-TEM) observation confirmed that the geometry of the silica particles was in good agreement with that of the vesicle template and that the particle wall had lamellar multilayer structure.

Metal oxide nanocapsules are known to show properties differing from those of common inorganic particles because they have a low specific gravity and high specific surface area. They possess a hollow structure that allows them to envelop various substances in the interior, and hence they are expected to be used as a carrier of drug delivery systems and a material of cosmetics.[1,2] In addition, they have also receive significant attentions with a view to application as low-refractive index materials.

In recent years, there have been many reports concerning the preparation methods of metal oxide particles with nanoscale periodic structure using molecular assemblies formed by surfactants as template.[3,4] Meanwhile, surfactants with two alkyl chains in a molecule form nanoscale closed cells composed of bimolecular membranes called vesicles.[5–8] Therefore, metal oxide nanocapsules are expected to be formed by hydrolysis and polycondensation reactions of a precursor in the presence of nanosize vesicles as a template. Although, German et al.[9] and Pinnavaia et al.[10,11] have reported the preparation of mesoporous silica particles using vesicles as template, the particles obtained neither directly reflect the shape of template nor keep the hollow structure after surfactant removal by calcination.

The present study aims to produce highly ordered multilayer silica nanocapsules using thermodynamically stable vesicles formed by double chain and single chain surfactant mixtures as template that can maintain hollow structure even after calcination.

Didodecyldimethylammonium bromide (DDAB, Tokyo Kasei, Co.) and dodecyltrimethylammonium bromide (DTAB, Tokyo Kasei, Co.) were used as double-tail and single-tail cationic surfactants, respectively. Spontaneously formable vesicles as template were prepared by adding 9:1 mixture of DDAB/DTAB to 25 mL of distilled water to give a total concentration of 60 mM solution, to which was added 25 mL of sodium hydroxide solution (pH 13) for pH adjustment. Silica nanocapsules were prepared by adding tetraethylorthosilicate (60 mM) to this basic vesicular solution to initiate hydrolysis and polycondensation and by leaving for 24 h, followed by hydrothermal treatment (120 °C, 48 h). The molar ratio of the final mixture was 1TEOS:0.9DDAB:0.1DTAB:1NaOH. The particles obtained were rinsed with water, dried (120 °C), and calcined (500 °C, 6 h, 1 °C/min) to remove the surfactant.

The size and shape of vesicles as template dispersed in aqueous solution were investigated with a dynamic light-scattering measuring apparatus (Nicomp 380ZLS particle sizer, Particle Sizing System Inc.) and cryogenic transmission electron microscopy (Cryo-TEM) (H-7650, cryo transfer CT3500, Hitachi Science Systems, Ltd.). The shape observation and pore structure evaluation of silica nanocapsules obtained were performed using a transmission electron microscope (TEM) (H-7650, Hitachi Science Systems, Ltd.).

First, formation of vesicles in an aqueous mixture of DDAB and DTAB (9:1) was checked by dynamic light scattering (Figure 1). A sharp particle size distribution was observed at around 200 nm. Direct observation was then performed using the Cryo-TEM to evaluate the structural characteristics of the vesicles obtained (Figure 2). The vesicles were found to have a diameter of about 200 nm and a multilayered and hollow structure. These findings verify the formation in aqueous solution of DDAB/DTAB mixture of vesicles to be used as the template suitable for silica capsule preparation.

Figure 3 shows a typical TEM image of silica particles prepared by the hydrolysis and condensation reactions of TEOS using these vesicles as template (after calcinations at 500 °C). Hollow particles with a diameter of about 200 nm were formed as seen in Figure 3a. Interestingly enough, the particle wall had a multilayered structure reflecting the structure of vesicles as template as shown in Figure 3b. In addition, ^{29}Si NMR measurements showed that the wall of capsule is composed of silica. Based on the findings that the particle size is in good agreement with that of the vesicles as template and that the particle wall is multilayered, the silica particles obtained no doubt are silica nanocapsules prepared using surfactant vesicles as template.

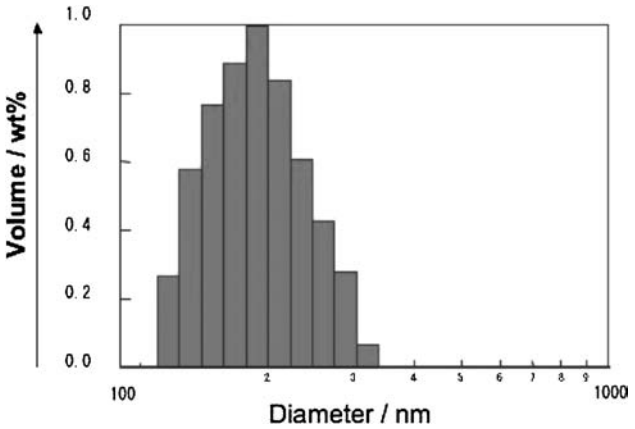

Figure 1. Size distribution of aqueous DDAB/DTAB solutions measured by the dynamic light-scattering method.

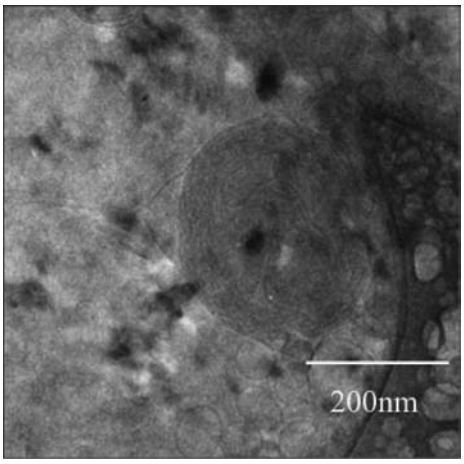

Figure 2. Cryo-TEM image of DDAB/DTAB (=9/1) vesicles.

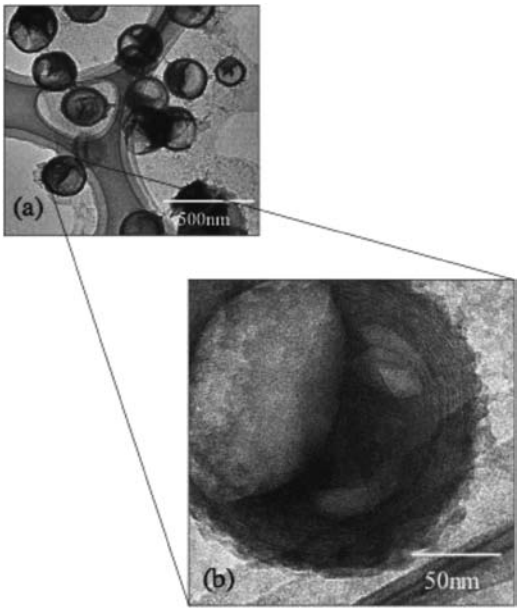

Figure 3. TEM-image of silica nanocapsules prepared using vesicles formed at DDAB/DTAB (=9/1) mixture as reaction template.

As mentioned earlier, German et al.[9] have reported the preparation of silica capsules using vesicles made of a double chain surfactant as template. Yet, the products they obtained are complex particles consisting of silica and surfactant, and hence the particles are not regarded as true capsules. In addition, according to our experiments, hollow structure cannot be maintained after removal the surfactant by calcination. This morphology change would be caused by the fragile structure of these vesicles and the destruction of hollow structure in the process of hydrolysis and polycondensation of silica precursor and/or calcination. That is, the addition of silica precursor to the vesicle containing solution in their system would destroy the structure of vesicles as template.

Vesicles formed by the double chain surfactant (DDAB) are thermodynamically metastable and gradually transformed to the flat elongated lamellar liquid crystals. Therefore, hollow structure of the vesicles is likely to collapse by the addition of other reagents like TEOS and calcination. On the other hand, when a small amount of a single chain surfactant (DTAB) is mixed with a double chain surfactant (DDAB), the average value of critical packing parameter (CPP) of surfactants becomes smaller than that of DDAB alone. The CPP value of DDAB alone is 1/2–1 which is favorable to form stable flat elongated lamellar liquid crystals. By adding single-tailed DTAB to DDAB, the CPP value decreases and curvature of the molecular assembly increases. In addition, Aratono et al. have reported that in the vesicles formed by the mixture of DTAB and DDAB, the mole fraction of DTAB is expected to be larger in outer than in inner monolayers.[12] Thus, DDAB/DTAB mixture more easily forms a closely packed membrane suitable for vesicle formation. It is suggested that the formation of stable vesicles allows them to maintain the structure even after silica precursor is added to the system and that this results in the formation of ca. 200 nm silica capsules templated by the vesicles. Recently, we have succeeded in preparing highly ordered mesoporous silica particles with a lamellar structure by utilizing hydrothermal treatment.[13] The lamellar molecular assembly was rearranged, and pillars between silica layers grew during aging by hydrothermal treatment. In the present study, hydrothermal treatment following hydrolysis and polycondensation is thought to enable the silica nanocapsules to maintain their structure even after calcination.

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