Preparation of Siliceous Vesicles with Adjustable Sizes, Wall Thickness, and Shapes

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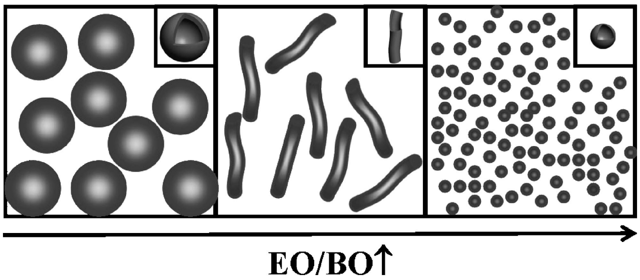
Siliceous vesicles with controllable sizes, wall thickness, and shapes have been successfully prepared by adjusting the hydrophilic/hydrophobic ratios of mixed block copolymer templates, which provides a feasible and designable approach to fabricate vesicular structures with controllable parameters that are important for their future applications.

Self-assembled organic vesicles[1–5] with controlled sizes and shapes have great applications in controlled trans-membrane transport, hemoglobin and DNA-encapsulation, and controlled release of plasmid for gene transfection.[6,7] In such applications, the stability of organic vesicles is crucial but intractable in cases where the aggregation of vesicles or the fusion of bilayers is unavoidable. Inorganic vesicles such as siliceous ones are more favorable compared to their organic counterparts because of their higher mechanical strength, enhanced thermal stability, and negligible swelling in organic solvents. Moreover, siliceous vesicles have more extensive applications in modern science including catalyst supports,[8] chromatography matrix,[9] and immunochemicals.[10] To explore the great potential of siliceous vesicles in these applications, controlling vesicular structural parameters is of great importance.

Siliceous vesicles have been successfully fabricated by direct vesicle-templating[11] or utilizing cooperative self-assembly of organic molecules and inorganic precursors.[12] Compared to the enthusiasm for the morphological study of organic vesicles,[13,14] much less attention has been paid in inorganic vesicular materials directed by organic templates. The general concept and mechanism of vesicle templating in a wide range should be further investigated. To the best of our knowledge, the preparation of inorganic vesicles with controlled size, wall thickness, and morphologies is a great challenge and has been rarely reported until now.

In the present work, we report the synthesis of various siliceous vesicular nanomaterials with controllable sizes (25–100 nm), shapes (such as spheres and tubes), and wall thickness (5–25 nm) via adjusting the hydrophilic/hydrophobic ratios of mixed block copolymers (Scheme 1). Commercial triblock copolymers $EO_{39}BO_{47}EO_{39}$ and $EO_{34}BO_{11}EO_{34}$ (Dow Company, EO is ethylene oxide and BO is butylene oxide) were used as co-templates and tetraethyl orthosilicate (TEOS) was chosen as the silica source. Keeping a total weight of mixed surfactants at 0.50 g, a series of silica samples were prepared at different weight percent (ω) of $EO_{34}BO_{11}EO_{34}$ ($\omega = 0\%$, 20%, 60%, 100%, synthesis details can be found in Electronic Supporting Information[22]).



Scheme 1. Schematic drawing of siliceous vesicular structures with various shapes and sizes via adjusting the EO/BO ratios of block copolymer mixtures.

The difference in morphology of silica materials is directly observed by transmission electron microscopy (TEM) studies. When $EO_{39}BO_{47}EO_{39}$ is utilized as the pure template ($\omega = 0$) and 0.01 mol TEOS as silica sources, unilamellar vesicles are obtained (Figure 1a). The diameters of vesicles are estimated to be 50–90 nm, and the mean wall thickness is 18 nm. When the amount of TEOS is increased to 0.016 mol while keeping the other synthesis parameters exactly the same, the resultant calcined siliceous materials show also vesicular structures with diameters of 60–100 nm, but the wall thickness is increased to ca. 25 nm (Figure 1b). When $\omega = 20\%$, TEM image shows that the calcined silica product has a tubular morphology with lengths up to ca. 200 nm (Figure 1c). At a high magnification, the TEM image reveals that the tubes have a diameter of ca. 25 nm and wall thickness of ca. 5 nm (Figure 1d). When ω is increased to 60%, ultrasmall siliceous vesicles are clearly observed (Figure 1e) with uniform sizes. From the higher-magnification TEM image shown in Figure 1f, the diameters and wall thicknesses of small unilamellar vesicles are ca. 20 and 4 nm, respectively. When ω is further increased to 100%, i.e., $EO_{34}BO_{11}EO_{34}$ is utilized as the single template, the obtained siliceous materials present a disordered mesostructure (Figure S1).[22]

Nitrogen sorption analysis was further employed to investigate the structures of various siliceous materials obtained at $\omega = 0$, 20, 60, 100%, while keeping 0.01 mol TEOS as silica sources. The N_2 adsorption–desorption isotherm of calcined sample obtained at $\omega = 0\%$ presents a capillary condensation step at a high relative pressure $P/P_0 > 0.9$ (left in Figure S2),[22] indicative of larger pore sizes. The isotherm of calcined sample fabricated at $\omega = 20\%$ shows two steps of capillary condensation, one at $P/P_0 = 0.8$, the other at $P/P_0 = 0.90$–0.98, indicating a bimodel pore structure. The siliceous material made at $\omega = 60\%$ has a N_2 adsorption–desorption isotherm similar to sample obtained at $\omega = 20\%$; however, the sample prepared at $\omega = 100\%$ shows only one steep capillary condensation step at $P/P_0 \approx 0.45$. Accordingly, the pore size distribution curves calculated from the BJH method for the above materials are displayed in the right of Figure S2.[22] The sample prepared at $\omega = 0\%$ has a broad pore size distribution curve (ca. 20 nm), which is in accordance with the structure as

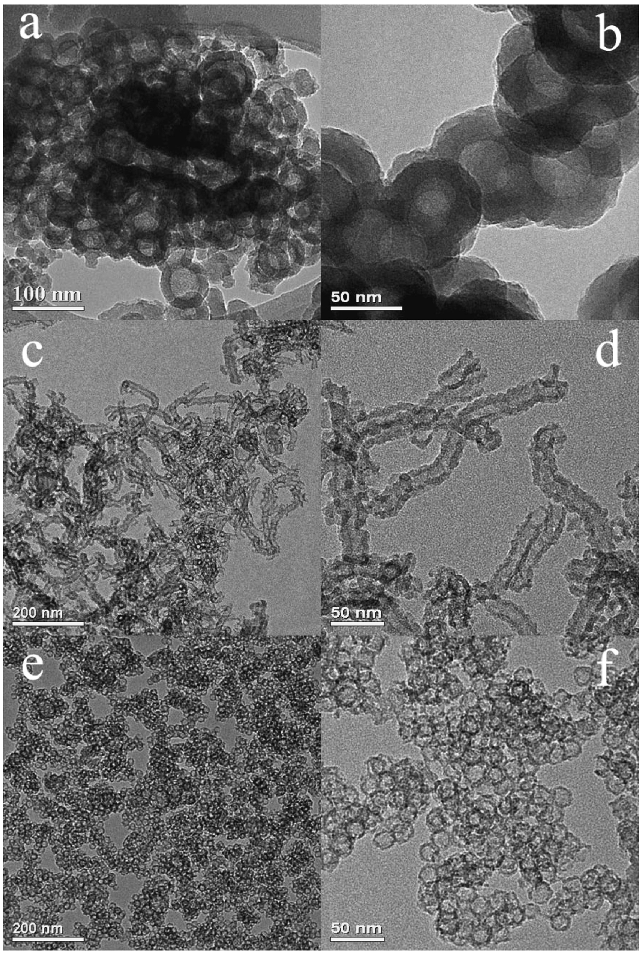


Figure 1. TEM images of siliceous materials prepared by using $EO_{39}BO_{47}EO_{39}/EO_{34}BO_{11}EO_{34}$ as cotemplates, certain amount of TEOS as silica sources at different weight percent (ω) of $EO_{34}BO_{11}EO_{34}$. (a) $\omega = 0\%$, 0.01 mol TEOS; (b) $\omega = 0\%$, 0.016 mol TEOS; (c), (d) $\omega = 20\%$, 0.01 mol TEOS; (e), (f) $\omega = 60\%$, 0.01 mol TEOS.

shown in Figure 1a. For the sample obtained at $\omega = 20\%$, the peak centered at 11.3 nm is associated with the pore diameters of the small tubes, in accordance with the TEM observation, while the broad pore size distribution in the range of 20–90 nm can be attributed to the voids caused by the aggregation of particles. The small vesicles made at $\omega = 60\%$ have a similar pore size distribution curve and pore diameters (10.9 nm for the small vesicles) compared to the sample obtained at $\omega = 20\%$. In contrast, the disordered mesostructured material utilizing pure $EO_{34}BO_{11}EO_{34}$ as the template ($\omega = 100\%$) has only one relatively narrow pore size of 4.2 nm.

The self-assembly of surfactant in solution is widely explained using the concept of g.[1,14–16] In block copolymer studies, increasing the hydrophobic/hydrophilic volume fraction may lead to a morphology change from tubules to vesicles.[1] In our experiments, when mixed surfactants $EO_{39}BO_{47}EO_{39}$ and $EO_{34}BO_{11}EO_{34}$ are used as cotemplates, increasing the weight percentage of $EO_{39}BO_{47}EO_{39}$ leads to the increase of hydrophobic/hydrophilic (BO/EO) volume fraction, thus g of the self-organized composite structure is increased. Consequently, a disordered mesostructure[17] → small vesicles[18] → small tubes → large vesicles structure transformation can be achieved (Scheme 1). Moreover, in a previous study, it was suggested that EO blocks bind with siliceous species and penetrate into the silica framework then form the organic–inorganic composite walls.[19] The disordered micropores in the framework of calcined SBA-15 are also suggested to come from the removal of EO blocks embedded in the silica walls.[20,21] We have also demonstrated that by increasing the silica/EO ratio, the wall thickness of siliceous vesicles can be enlarged (Figures 1a and 1b). In addition, in the preparation when $EO_{39}BO_{47}EO_{39}$ and $EO_{34}BO_{11}EO_{34}$ are used as cotemplates, the small vesicles obtained at $\omega = 60\%$ has a thin wall of ca. 5 nm (Figure 1f). The much smaller wall thickness compared with sample fabricated at $\omega = 0\%$ with a wall thickness of ca. 18 nm (Figure 1a) can also be explained by the decreased ratio of silica per EO unit.

In conclusion, various siliceous vesicular structures with controllable sizes, shapes, and wall thickness have been successfully fabricated. Such vesicular structures with controlled parameters are of great interest for diverse applications.

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22 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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