

Supporting Information

Synthesis of Monodisperse Mesoporous Silica Hollow Microcapsules and Their Release of Loaded Materials.

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1. Simple Static Light Scattering Method

To examine whether the PS360 particles were aggregated, we employed a simple static light scattering (SLS) method, utilizing the phenomenon that the scattered light intensity increases after the aggregation of particles. The optical setup for the SLS method is indicated in Figure S1. A He-Ne laser beam (633 nm) was irradiated into the dispersion in a glass cylinder perpendicular to the cylinder axis. The scattered light was projected on semi-transparent waxed paper as a screen placed perpendicular to the laser beam. A photograph of the waxed paper that projects the distribution of the scattered light intensity was taken by a digital camera from the rear side of the paper. To observe the intensity of the light scattered at an angle of ca. 14° within the plane of the beam axis and the cylinder axis, a gray-scaled digital image of the intensity distribution was analyzed by image processing software, ImageJ.¹ The value of the numerical gray level of a given point in the image was employed as the scattered light intensity in arbitrary units.

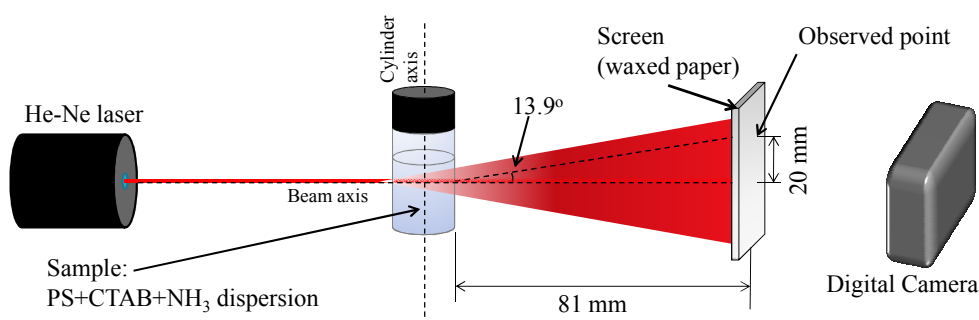


Figure S1. Optical setup for the simple light scattering method.

2. Synthesis of Sample at $C_{CTAB} = 0$ for Control Experiment

To confirm that the broad X-ray diffraction peaks shown in Figure 12(b) can be attributed to the periodic mesoporous structure formed by the templates of cylindrical CTAB micelles, we prepared a sample without CTAB, as a control. However, no capsules were formed at $C_{CTAB} = 0$ using the present procedure (Figure 1). This is because the surface of the PS particles and silica sol are negatively charged. To facilitate the adsorption of the silica sol on the surface of the PS template, we altered the surface charge of the PS particles to be positive by the Layer-by-Layer method.²

An aqueous solution of poly(diallyldimethyl ammonium chloride) (PDDA) at 1mg/mL with 0.5 M NaCl and of poly(sodium 4-styrenesulfonate) (PSS) at 1 mg/mL with 0.5 M NaCl were prepared. PDDA and PSS are positively and negatively charged, respectively. 250 μ L of PS360 dispersion at 10% w/v was diluted with pure water, centrifuged, and the supernatant was removed for washing. After a brief sonication of the sediment, 10 mL of the PDDA aqueous solution was added and PDDA

was allowed to adsorb on the PS360 for 15 min. After 15 min adsorption, the dispersion was centrifuged, the supernatant was removed, and the sediment was redispersed in pure water. This procedure was repeated three times to remove the excess PDDA, resulting in PDDA coated PS360 particles. On this PDDA layer, a second PSS layer and a third PDDA layer were sequentially adsorbed via electrostatic interaction using the same procedure as described for the first PDDA adsorption. Finally, 12 mL aqueous dispersion of the PS360 particles coated by the PDDA/PSS/PDDA layer was obtained and the outmost layer was the positively charged PDDA.

To carry out the sol-gel reaction, 12 mL of the coated PS360 dispersion and 4 mL of aqueous ammonia (25 wt%) were added to 180 mL of EtOH and stirred for 10 min at 30°C. The V/F_{EtOH} value of the mixture was ca. 0.92. Under continuous stirring, 2 mL of TEOS was then added to the mixture and stirred for 2 h for the sol-gel reaction. After 2 h reaction, the mixture was centrifuged, the supernatant was removed, and the sediment was redispersed in pure water to remove the excess TEOS and byproducts. This washing procedure using pure water was repeated twice, followed by two washes with EtOH to obtain a dispersion of the silica coated PS360 particles in EtOH.

The dispersion of the coated PS particles was centrifuged and the supernatant was removed. The sediment was replaced in a crucible and dried at room temperature. After evaporation of EtOH, the coated PS360 particles were calcined at 550°C for 6 h to remove the PS360 templates. A TEM image of the resultant sample is shown in Figure S2. Most of the capsules were broken and their shell thicknesses were not uniform. No X-ray diffraction peak was observed from this sample, as shown Figure 12(b), indicating that the diffraction peaks observed from the MSHCs could be attributed to the periodic mesoporous structure.

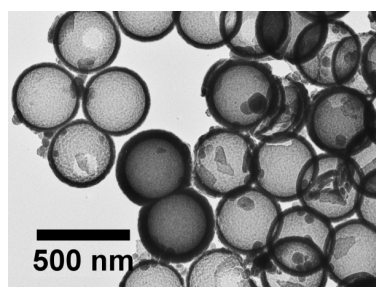


Figure S2. TEM image of the sample prepared without using CTAB.

References

- (1) Rasband, W. S., U. S. National Institutes of Health, Bethesda, Maryland, USA, <http://rsb.info.nih.gov/ij/>, 1997-2009.
- (2) Caruso, F. In *Colloids and Colloid Assemblies*; Caruso, F., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2004; Chapter 8.