

Fine-tuning Cavity Size and Wall Thickness of Silica Hollow Nanoparticles by Templating Polymeric Micelles with Core–Shell–Corona Structure

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Hollow silica nanospheres have been successfully prepared by templating the polymeric micelles of poly(styrene-*b*-2-vinylpyridine-*b*-ethylene oxide) (PS–PVP–PEO), which shows a core–shell–corona structure in aqueous solutions. In this template, each block has its own function; the PS block (core) works as a template of the void space of hollow silica, the PVP block (shell) acts as a reaction field for the sol–gel reaction of silica precursor, and the PEO block (corona) stabilizes the polymer/silica composite particles. It was found that the diameter of the void space of the hollow silica spheres can be fine-tuned on a several nanometer scale by changing the chain length of the PS block. The wall thickness of the hollow silica is also fine-tuned by varying the concentration of the silica precursor.

Inorganic hollow nanoparticles are now becoming popular in the chemical and material communities because of their low density, large specific area, and surface permeability.^{1–3} Various strategies have been developed to prepare hollow nanoparticles, such as templated,¹ sonochemical,⁴ and hydrothermal methods.⁵ Among these techniques, template synthesis is attracting much attention because it enables us to easily control the structures as well as to have access to a wide range of different materials.^{2,3} Therefore, many templates have already been reported, and polymer nanoparticles (e.g., latex particles and polymeric micelles) are some of the most promising templates owing to their well-tuned size and morphology.^{6,7} Generally, latex particles have been employed for fabricating relatively large hollow particles with diameters ranging from submicrometers to micrometers,^{1,8} while polymeric micelles are used for smaller hollow particles with diameters of less than one hundred nanometers.⁹ Although there have been many studies of latex templates, only a few reported the use of polymeric micelle templates.^{10,11}

We have recently succeeded in preparing hollow silica nanoparticles by templating a polymeric micelle with a core–shell–corona structure in aqueous solutions.¹² We used the micelle of poly(styrene-*b*-2-vinylpyridine-*b*-ethylene oxide) (PS–PVP–PEO) as a template and tetramethoxysilane (TMOS) as a silica precursor. The feature of our method is that each block of the copolymer has its own function during the silica synthesis; (i) the PS block forms the core of the micelle to be a template of the void space in the hollow silica, (ii) the PVP block forms the shell to be a reaction field of the sol–gel reaction of TMOS, and (iii) PEO forms the corona to stabilize the polymer/silica intermediate composites. After removing the template polymer from the polymer–silica composite particles by calcinations, we obtained hollow silica nanoparticles. The obtained hollow silica nanoparticles were found to have a spherical structure with narrow distributions of void volume and shell thickness.

In the present study, we tried to control the structural param-

eters of the hollow silica, i.e., the void volume by changing the PS chain length and the wall thickness by changing the amount of the silica precursor. As expected, the void volume of the obtained hollow silica regularly increased with the increase in the PS chain length, and the wall thickness increased with the increase in the concentration of the precursor. To the best of our knowledge, this is the first study in which the cavity size and wall thickness of the hollow silica were successfully fine-tuned on a scale of several nanometers.

We employed three kinds of PS–PVP–PEO block copolymers with different chain lengths of PS, PVP, and PEO, i.e., PS(14.1k)–PVP(12.3k)–PEO(35k), PS(20.1k)–PVP(14.2k)–PEO(26k) and PS(45k)–PVP(16k)–PEO(8.5k). The numbers in the parentheses are the molecular weights of the block chains (14.1k, for example, denotes 14100). All of them were obtained from Polymer Source, Inc and used without further purification. The micelles of PS(14.1k)–PVP(12.3k)–PEO(35k) and PS(20.1k)–PVP(14.2k)–PEO(26k) were prepared according to the method of Gohy et al.¹³ and described in detail in our previous paper.¹² The micelle of PS(45k)–PVP(16k)–PEO(8.5k) was prepared according the method of Zhang and Eisenberg for the “crew-cut” micelles,¹⁴ because the PS chain is much longer than the water-soluble PEO chain. PS(45k)–PVP(16k)–PEO(8.5k) was dissolved in DMF at the initial concentration of 1 wt %. After the polymer was completely dissolved, water was added dropwise to the solution with vigorous stirring until the water content reached 5 wt %. The rate of the water addition was 1 wt % per min. More water was added to the solution to make the final polymer concentration 0.5 wt %. The solution was then dialyzed against water to obtain the micelles.

The pH of the solution was then adjusted to 4 using a diluted HCl solution. The PS–PVP–PEO micelle solution was slowly stirred for 2 days after the desired amount of TMOS was added. For control of the silica wall thickness, different amounts of TMOS were used (PVP:TMOS = 1:10, 1:15, 1:20, and 1:25 in a base molar unit). The solution of the template micelle and the precursor was then stored for 4 more days without stirring to allow the silica network to be formed by the sol–gel reaction. After the sol–gel reaction was completed, the obtained silica/PS–PVP–PEO composite particles were separated from the solvent by centrifugation (at 6000 rpm) and dried at 50 °C for several hours. The template polymer was removed from the composites by calcination; the temperature of the furnace was raised to 500 °C at the rate of 10 °C min^{−1} and kept at 500 °C for 4 h in air.¹⁵

Figure 1 illustrates examples of the transmission electron microscope (TEM) images of the hollow silica nanospheres. The hollow structure can be clearly observed. The TEM images for other typical samples are given in the supporting materials section.¹⁶ Almost all the hollow silica particles show a uniform

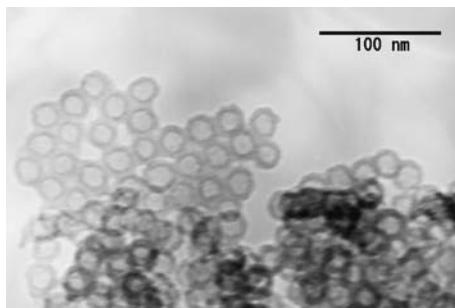


Figure 1. TEM pictures of hollow silica nanospheres prepared by templating the micelles of PS(20.1k)-PVP(14.2k)-PEO(26k). The concentration of PS-PVP-PEO is 0.9 g/L and the molar ratio of PVP/TMOS is 1:15.

Table 1. Void space diameters and shell thicknesses of the hollow silica nanospheres

Template polymer (M _{PS} -M _{PVP} -M _{PEO})	PVP:TMOS	Void space diameter/nm	Wall thickness /nm
14.1k-12.3k-35k	1:10	10.1 ± 0.8	5.9 ± 1.0
	1:15	9.7 ± 0.6	5.7 ± 0.5
	1:20	10.3 ± 1.0	6.4 ± 0.7
	1:25	10.8 ± 1.0	7.8 ± 0.8
20.1k-14.2k-26k	1:10	14.5 ± 1.4	5.3 ± 0.5
	1:15	13.9 ± 1.7	5.8 ± 0.4
	1:20	13.8 ± 1.2	7.5 ± 0.7
	1:25	14.0 ± 1.5	7.7 ± 0.8
45k-16k-8.5k	1:10	18.0 ± 1.7	6.0 ± 0.7
	1:15	18.3 ± 1.6	6.4 ± 1.0
	1:20	20.4 ± 2.1	7.4 ± 0.9
	1:25	19.6 ± 2.2	8.1 ± 0.8

spherical shape with a smooth shell wall. Only when PVP:TMOS = 1:10 does the hollow silica show a nonhomogeneous structure in all of the three types of PS-PVP-PEO templates. This may be due to the low concentration of TMOS. The size of the void space and wall thickness of the obtained hollow silica spheres are listed in Table 1.

It is clear from Table 1 that the void space diameter of the hollow silica can be correlated with the chain length of the PS block of the template copolymer. As the molecular weight of the PS block increased from 14k to 20k and then to 45k, the void space diameter of the hollow silica increased from 10 to 14 and then to 20 nm. It should be noted that the void space diameter can be fine-tuned on a scale of several nanometers by changing the PS block length. This fact strongly demonstrates the usefulness of the present method.

It is interesting to compare the size of the template micelle with the size of the hollow silica. According to Gohy et al.,¹³ the size of PS core of the PS(20.1k)-PVP(14.2k)-PEO(26k) micelle is 20 nm, while the void space diameter of the corresponding hollow silica obtained by us is 14 nm. This indicates that the hollow silica particles shrunk during the calcinations. The extent of the shrinkage is around 30%. This kind of shrinkage during the calcination has also been reported for hollow titania particles.^{8,17} In a similar way, the size of the micelle of PS(14.1k)-PVP(12.3k)-PEO(35k) (PS core diameter: 14 nm¹³) was compared to the void space diameter (11 nm) of the resulting hollow

silica. The rate of shrinkage is about 20% in this case. It seems that the rate of shrinkage increased with the increasing particle size.

We realize from Table 1 that the wall thickness of the hollow silica increased with the increasing TMOS concentration. This fact proves that the wall thickness of the hollow silica particles is tunable by changing the TMOS concentration. It is also expected that the wall thickness of the hollow silica can be controlled by the chain length of the PVP block, because the sol-gel reaction of the silica precursor mainly occurs in the PVP domain of the template micelle.¹² However, the three template copolymers employed in this study have similar PVP sizes, so that we cannot discuss the effect of the chain length of the PVP block on the wall thickness. This will be examined in a future study.

In summary, we have successfully prepared hollow silica nanospheres using three kinds of PS-PVP-PEO triblock copolymer micelles with a core-shell-corona architecture. The obtained hollow silica nanospheres have a uniform shape. We have found that the void space diameter can be fine-tuned on a several nanometer scale by changing the length of the PS block. We have also confirmed that the wall thickness of the hollow silica nanoparticles can be easily controlled by varying the concentration of the silica precursor. The most interesting feature of this approach is the possibility that it might be applied to the preparation of other inorganic hollow particles with a controlled cavity size and wall thickness.

The present study was supported by a Grant-in-Aid for Scientific Research (No. 20310054) from Japan Society for the Promotion of Science (JSPS).

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