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Synthesis of Hollow Silica Nanospheres Templated by Micelles of Poly{styrene-*b*-[3-(methacryloylamino)propyl]trimethylammonium chloride-*b*-ethylene oxide}

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A micelle of poly{styrene-*b*-[3-(methacryloylamino)propyl]trimethylammonium chloride-*b*-ethylene oxide} with *core–shell–corona* architecture in aqueous solutions has been successfully applied to the synthesis of hollow silica nanospheres as a new template. Tetramethoxysilane, phenyltrimethoxysilane, and their mixtures were used as silica precursors and the ratio of the precursor to the template influences the shell thickness of the obtained hollow silica.

Silica hollow spheres have been prepared by templating routes that make use of polystyrene latex spheres,[1,2] colloidal arrays,[3] vesicles,[4,5] and lyotropic liquid crystals.[6–8] Templates are often indispensable as not only do they stabilize these nanoparticles but also arrange them into desired superstructures.[9–11] However, most of these approaches produce non-uniform spheres, have shells of undesirable thickness, lack structural stability, or require high-temperature routes.

Recently, polymeric micelles have been explored for the synthesis of nanoparticles because the size and morphology of the micelles can be tuned by adjusting block size and polymer combination.[7,8,11] The commonly used polymeric micelles exclusively contain a *core–corona* architecture formed by AB diblock or ABA triblock copolymers.[12–14] However, the use of these polymers has inherent drawbacks because the template micelles become very unstable when the inorganic precursor is sorbed into the corona which often gives second order or higher-order aggregates. In order to overcome these difficulties, ABC triblock-copolymeric micelles of poly(styrene-*b*-2-vinylpyridine-*b*-ethylene oxide) (PS-*b*-PVP-*b*-PEO) with *core–shell–corona* structure have been explored and successfully used for the fabrication of uniform hollow silica nanospheres in our laboratory.[15,16] For *core–shell–corona* micelles, the shell of the micelles acts as a reservoir of the precursor of desired inorganic material, and the core acts as a template of the hollow void. The corona stabilizes the precursor-loaded micelles by steric repulsion to prevent the formation of the secondary aggregates.

In order to generalize the strategy of *core–shell–corona* micelles, we have prepared a new ABC triblock-copolymer micelle of poly{styrene-*b*-[3-(methacryloylamino)propyl]-trimethylammonium chloride-*b*-ethylene oxide} (PS-*b*-PMAPTAC-*b*-PEO) and explored the synthesis of hollow silica nanospheres. A typical ABC triblock polymer with each block length employed in the present study is shown in the Supporting Information (Scheme S1).[17] The micelle formed from PS-*b*-PMAPTAC-*b*-PEO gave a *core–shell–corona* architecture in aqueous solution, i.e., the PS block forms the core, positively charged PMAPTAC acts as the shell, and PEO as the corona. Silica sources such as tetramethoxysilane, phenyltrimethoxysilane, and their mixtures were used to synthesize the hollow silicas. (Scheme S1 depicts the schematic representation of formation of hollow silica nanospheres.)

The PS-*b*-PMAPTAC-*b*-PEO triblock copolymer was synthesized via a reversible addition–fragmentation chain-transfer-controlled radical polymerization and the number-average degree of polymerization for each block was estimated to be 47, 106, and 80 by ^{1}H NMR.[18] The polymer was then dissolved in H_2O to prepare polymeric micelle (template) solution at an initial concentration of $1\,g\,L^{-1}$. The hydrodynamic diameter of thus prepared PS-*b*-PMAPTAC-*b*-PEO micelle was measured by dynamic light scattering (Otsuka ELS-800 spectrophotometer) and the value was found to be 75 nm. Transmission electron microscopy (TEM, using a JEOL JEM-1210, 80 kV) of the same micelle sample stained with phosphotungstic acid revealed spherical morphology and gave white spheres of a 22-nm average diameter which correspond to the hard PS core as shown in Figure 1. The TEM observation gave lower micelle size than the dynamic light scattering experiments mainly because TEM accounts for only the core–shell and excludes the corona and furthermore the shell also shrinked due to staining with phosphotungstic acid. In the present study, similar to PS-*b*-PVP-*b*-PEO, the PMAPTAC block (shell) acts as a reaction field for the sol–gel reaction. Another important feature of this micelle is that it can be ionized over a wide range of pH from acidic to basic conditions unlike PS-*b*-PVP-*b*-PEO which is ionized below pH 5. Therefore, this polymer is advantageous for the synthesis of various kinds of inorganic hollow nanoparticles.

An appropriate amount of TMOS or mixture of TMOS and PTMOS was mixed with 5 mL of polymeric micelle solution ($1\,g\,L^{-1}$) and the solution was gently stirred for 3 days using a magnetic stirrer and stored for 2 more days to allow the complete condensation of silica by sol–gel reaction. The silica/polymer composite particles were separated by centrifugation and dried in an oven at 50 °C. Template polymer was removed by calcinations at 500 °C for 4 h in air (ramping rate: $8\,°C\,min^{-1}$). FT IR spectra of calcined silica (Figure S1) shows the absence

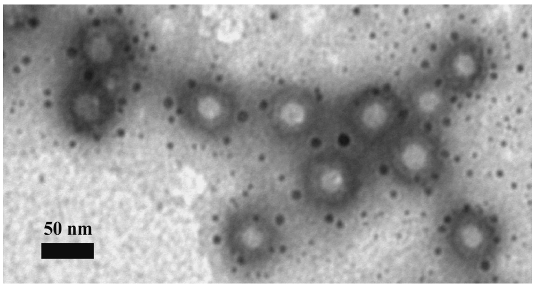

Figure 1. TEM image of the PS-*b*-PMAPTAC-*b*-PEO micelle ($1\,g\,L^{-1}$). The micelle was stained with phosphotungstic acid.

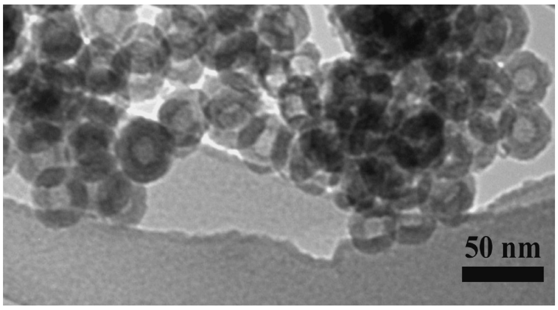

Figure 2. TEM image of hollow silica nanospheres prepared by templating the PS-*b*-PMAPTAC-*b*-PEO micelle. TMOS/PTMOS = 1 and template:precursor = 1:20.

of –C=C– bond vibration of the phenyl group at 1600–1430 $\mathrm{cm^{-1}}$ and the CH_2 vibration of the polymer backbone at 3000–2800 $\mathrm{cm^{-1}}$ indicating the complete removal of the polymer.[17] Different samples with varying wall thickness and void space prepared under the present study are listed in Table S1.[17]

Figure 2 exhibits a typical TEM image of hollow silica synthesized using TMOS/PTMOS ratio of 1. TEM images of samples with different precursor ratios are given in the Supporting Information (See Figure S2).[17] It is seen from TEM observation that all particles show a nearly uniform spherical shape with a narrow size-distribution. The cavity size and silica wall thickness were calculated from the TEM pictures. Samples with different template/precursor molar ratio of 1:10, 1:20, and 1:30 (at TMOS/PTMOS = 1) show wall thickness of 11.1, 14.0, and 14.6 nm, respectively. The void space diameters of these samples are in the range of 18.1–19.1 nm. The detailed description of other samples under the present investigation is provided in the Supporting Information (see Table S1).[17]

It should be noted here that high-temperature template removal sometimes leads to aggregation and breakage of silica hollow particles. It is also worth mentioning that the wall thickness of the silica wall prepared by PS-*b*-PMAPTAC-*b*-PEO template in the present study is slightly larger than that in the previous study using PS-*b*-PVP-*b*-PEO template. This may be due to the reason that PVP is not completely ionized at pH 5 in the latter case.

The notable feature of micelles with *core–shell–corona* structure is that wall thickness can be tuned simply by changing the precursor concentrations. In the case of TMOS as precursor, the wall thickness increases from 12.8 to 14.3 nm when template:precursor ratios changed from 1:10 to 1:30. A similar trend was also noticed for mixed silica precursors of TMOS and PTMOS. The increased wall thickness may be attributed to extensive hydrolysis and cross-linking of silica species. Furthermore, one should expect the size of void space of hollow silica be 22 nm as that of PS core estimated from TEM image of stained micelles. However, shrinking needed to be accounted for because hollow inorganic oxides might shrink during calcinations to a different degree, and which would result in minor differences between cavity sizes.[10,15,16,18,19] We noted that the obtained cavity diameter of silica was between 17.3 and 20.7 nm, which corresponds to a shrinkage between 21% and 6% compared to the original value of the PS core. In addition, the use of PTMOS not only leads to pronounced shrinkage as observed in the present study but also expected to lower the density of silica.

The introduction of organic moieties within the silicate network may further tailor the functionality of the hollow nanospheres. Integration of organic moieties into the framework will modify the surface properties of the materials and also endow the hollow silica with different physical and mechanical properties. Our preliminary investigation shows that hollow silica could be readily synthesized by replacing 50% of TMOS by phenyltrimethoxysilane. However the yield of silica decreased mainly due to difference in the rate of hydrolysis and overall cocondensation of mixed silica precursors. Furthermore, to induce porosity in the shell, the polymer/hybrid silica composite was calcined but nitrogen adsorption data reveals no porosity in the shell. Further investigations are underway to synthesize hollow spheres with porosity within the shell.

In summary, we have generalized the suitability of *core–shell–corona* micelles toward synthesis of hollow silica nanospheres by employing a polymeric micelle of PS-*b*-PMAPTAC-*b*-PEO as a new template. Polymer/precursor ratios influenced the wall thickness of obtained hollow silica nanospheres. Mixed silica precursors smoothly produced nanoparticles under similar experimental conditions.

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