

Fabrication of Uniform Hollow Silica Nanospheres using a Cationic Polystyrene Core

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Uniform, hollow nanosilica spheres were prepared by the chemical coating of cationic polystyrene (cPS) with tetraethylorthosilicate (TEOS), followed by calcination at 600 °C under air. cPS was synthesized by surfactant-free emulsion polymerization using 2,2'-azobis (2-methyl propionamide) dihydrochloride as the cationic initiator, and poly(vinyl pyrrolidone) as a stabilizer. The resulting cPS spheres were 280 nm in diameter, and showed monodispersity. After coating, the hollow silica product was spherically shaped, and 330 nm in diameter, with a narrow distribution of sizes. Dispersion was uniform. Wall thickness was 25 nm, and surface area was 96.4 m²/g, as determined by BET. The uniformity of the wall thickness was strongly dependent upon the cPS surface charge. The effects of TEOS and ammonia concentrations on shape, size, wall thickness, and surface roughness of hollow SiO₂ spheres were investigated. We observed that the wall thicknesses of hollow SiO₂ spheres increased and that silica size was simultaneously enhanced with increases in TEOS concentrations. When ammonia concentrations were increased, the irregularity of rough surfaces and aggregation of spherical particles were more severe because higher concentrations of ammonia result in faster hydrolysis and condensation of TEOS. These changes caused the silica to grow faster, resulting in hollow SiO₂ spheres with irregular, rough surfaces.

Key Words : Hollow silica sphere, Cationic polystyrene, TEOS, Sacrificial core method

Introduction

The hollow sphere is an important material form in many fields such as coating materials, toners, pigments and LCD board spacers, catalysis, the protection of biologically active agents and chromatography.¹⁻⁷ These applications require uniform, high-strength hollow spheres. Recently, a diversity of chemical and physicochemical methods have been developed for generating hollow spheres from polymeric or ceramic materials. These methods include the sacrificial core process, the nozzle-reactor system, emulsion/interfacial polymerization strategies and surface living polymerization processes.⁸⁻¹¹ The sacrificial core method is usually used to synthesize hollow spheres with a polymer core. Typically, core particles are coated in solution by either controlled precipitation of coating material precursors onto the surface, or by direct reaction to specific functional groups on the core surface, to create core-shell composites. Hollow silica spheres are synthesized by the sol-gel process by incorporation of silanol groups onto polystyrene (PS) by dispersion polymerization, and condensation reactions of tetraethylorthosilicate (TEOS) that take place exclusively at the particle surface in the presence of ammonia.^{12,13} Schmid *et al.* reported the preparation of hollow silica spheres by alcoholic dispersion polymerization of styrene, using 10-nm diameter commercial alcoholic silica sols as the sole stabilizing agent, followed by removal of the polymer by thermal treatment.¹⁴ Transmission electron microscopy (TEM) of images the polystyrene-silica nanocomposite particles and/or hollow

silica spheres above reported showed rough, agglomerating surfaces and the presence of secondary particles.

In this study, we synthesized uniform, monodispersed hollow silica particles by chemical reaction of the surface of cationic polystyrene (cPS) particles with TEOS, followed by calcination under air. Also, effects of TEOS and ammonia concentrations on shape, size, wall thickness, and surface roughness of the hollow SiO₂ spheres were investigated. The hollow silica spheres were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectrophotometry (FT-IR), thermogravimetric analyses (TGA), and BET.

Experimental

Synthesis of Cationic Polystyrene (cPS). cPS particles were synthesized by surfactant-free emulsion polymerization as described,¹⁵ with 25 g of styrene, 0.65 g of 2,2'-azobis (2-methyl propionamide) dihydrochloride (AIBA) as a cationic initiator, 3.75 g of poly (vinyl pyrrolidone) as a stabilizer, and 250 g of water charged in a 500 mL three-neck flask fitted with a mechanical stirrer and water-cooled reflux condenser. Flask temperature was controlled with an oil bath. The aqueous solution was heated to 70 °C for 24 h, with stirring with an impeller at 100 rpm. PS particles were washed with methanol and water, and dried at 50 °C for 24 h.

Synthesis of Hollow Silica Spheres. Hollow SiO₂ particles were generated with 400 mL of ethanol in a 500 mL round-bottomed three-neck flask, to which 3.4 g cPS particles were

added. The solution was sonicated for 10 min, and the cPS suspension was added to 10 g of 0.12 M TEOS and 30 mL of 2.1 M NH_4OH . The aqueous solution was heated to 50 °C for 1.5 h, with stirring at 300 rpm with a stir bar. The SiO_2 -coated cPS (cPS@ SiO_2) particles were filtered and washed with water and ethanol to remove residual TEOS and NH_4OH , before drying at 80 °C for 12 h. The cPS particles of cPS@ SiO_2 were removed by calcination in air at 600 °C for 6 h to obtain hollow SiO_2 particles.

Characterization. SEM (Topcon, SM-300) and TEM (Jeol JEM-2000EX) were used to determine the morphology, size, and wall thickness of the particles. The SiO_2 coating of cPS was investigated by FT-IR (Simazu Prestage 21) and TGA was carried out using a SDT Q600 TGA instrument. Samples were pretreated by heating in air to 1000 °C at a heating rate of 10 °C/min. The surface area and pore size were calculated from desorption isotherm curves using the BET method.

Results and Discussion

Figure 1 shows SEM and TEM images of cPS, cPS@ SiO_2 , and hollow silica spheres. The cPS particles synthesized using the cationic initiator AIBA were round, with a diameter of 280 nm, and showed no agglomeration, regardless of the charge valence of the cPS (Fig. 1(a)). Figure 1(b) shows TEM pictures of cPS@ SiO_2 , which clearly show the cPS core and the SiO_2 shell. The silica coated cPS particles were monodisperse spheres of 334 nm diameter, and a silica wall thickness of approximately 27 nm. No secondary SiO_2 particles are seen, indicating that hydrolysis and condensation occurred only at the cPS surface. This is attributed to the strong interaction between the negatively charged SiO_2 particles and the positively charged cPS particles. Good hollow SiO_2 spherical shapes were obtained in a narrow range of sizes following calcination at 600 °C under air. All sample sizes were approximately 330 nm with a uniform wall thickness of 25 nm. We attribute the uniform coating of SiO_2 on the cPS surface to the charge of the cPS. The cPS surface has NH_2^+ positive charges from the AIBA cationic initiator, so in a solution of cPS solution, silica particles with a negative charge easily nucleate on the surface of the cPS particles, and create a uniform, thin shell through hydrolysis and condensation. Lu *et al.* suggested that the coating of PS particles with silica shells is strongly affected by the charge on the core surface, since silica sols are negatively charged.¹⁶ When using PS particles that terminated in a negatively charged SO_3H group or a positively charged NH_2 group as the cores for SiO_2 coating, they found that when PS particles contained SO_3H groups, both PS and SiO_2 particles were found in the product. This result suggests that SiO_2 cannot form a uniform coating on the surface of negatively charged PS particles. PS particles with NH_2 groups showed a uniform coating of SiO_2 layers. Initiator charge is also reported to play a key role in the synthesis of polystyrene-silica nanocomposite particles.¹⁴ A comparison of neutral, anionic and cationic initiators showed that SiO_2 sol selectively coated PS particles when neutral and cationic initiators were used, but

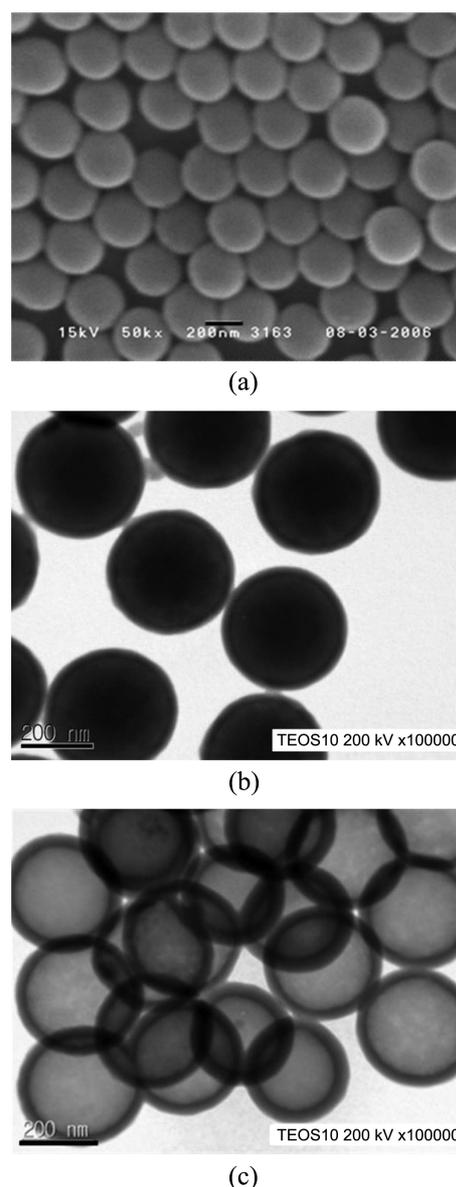


Figure 1. SEM and TEM images of (a) cPS, (b) cPS@ SiO_2 , and (c) hollow silica sphere.

no particles formed with anionic initiators.

Figure 2 shows FT-IR spectra of cPS, cPS@ SiO_2 , and hollow silica spheres. Characteristic bands for cPS were observed in the range of 3100-2900 (aliphatic/aromatic C-H stretching), 1600-1500 (stretching vibration of aromatic C=C), and 800-700 cm^{-1} (vibration of the aromatic C-H bands). In the cPS@ SiO_2 spectra, the main bands for cPS and SiO_2 appeared together. The cPS band intensities of the cPS@ SiO_2 were lower than those for pure cPS, however, and strong intensity bands characteristic of SiO_2 , showing Si-O-Si asymmetric stretching vibration at 1090 cm^{-1} , were observed.¹⁷ This suggested hydrolysis and condensation of TEOS on the cPS surface. After calcination of the cPS@ SiO_2 in air, bands characteristic of cPS at 3100-2900, 1600-1500 and 800-700 cm^{-1} disappeared. The observation of only bands characteristic of SiO_2 indicated successful formation of

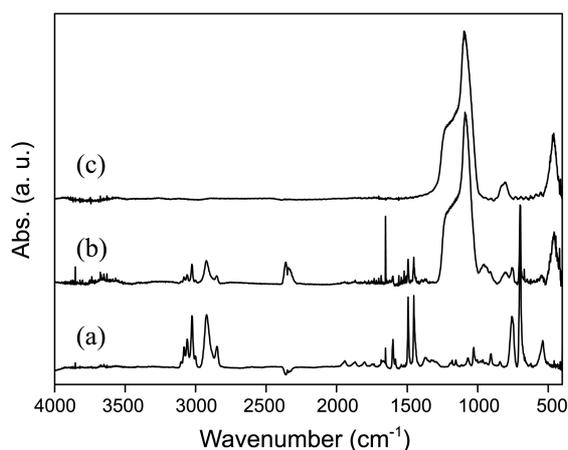


Figure 2. FT-IR spectra of (a) cPS, (b) cPS@SiO₂, and (c) hollow silica sphere.

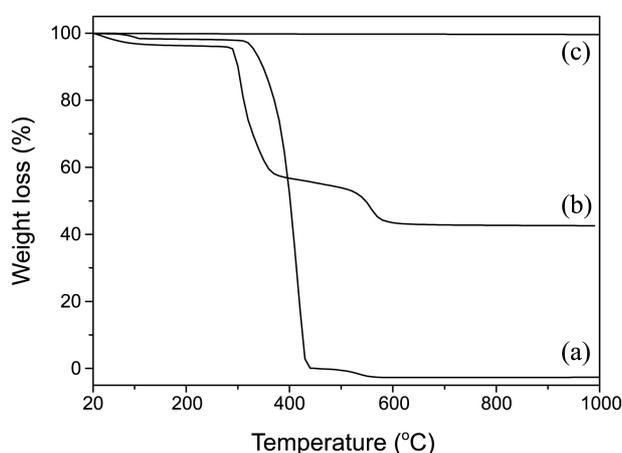


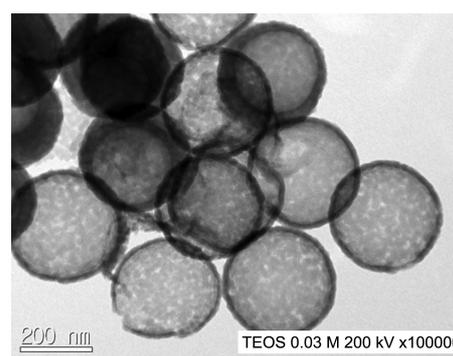
Figure 3. TGA curve of (a) cPS, (b) cPS@SiO₂, and (c) hollow silica sphere.

Table 1. Particle size, wall thickness, surface area, and pore volume of PS, cPS@SiO₂, and hollow silica sphere

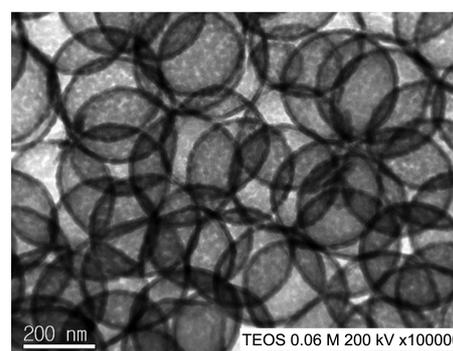
Sample Name	Particle Size (nm)	Wall thickness (nm)	Surface Area (m ² /g)	Pore Volume (cm ³ /g)
cPS	280	-	-	-
cPS@SiO ₂	334	27	12.3	0.03
Hollow SiO ₂ sphere	330	25	96.4	0.16

hollow silica spheres.

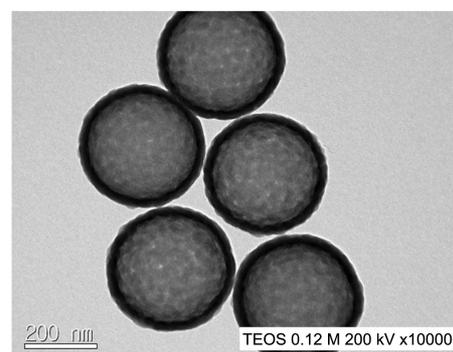
The thermal behavior of cPS, cPS@SiO₂, and hollow silica spheres was investigated with temperature increases up to 1000 °C under air flow (Fig. 3). Loss of weight of the cPS particles was observed at 90 °C due to loss of approximately 2% physisorbed water. Decomposition began at 320 °C and was complete by 550 °C (Fig. 3(a)). Loss of weight of cPS@SiO₂ occurred at 70 °C after removal of 5% physically adsorbed water (Fig. 3(b)). More than twice as much water was removed for the cPS@SiO₂ compared to the cPS, suggesting that the cPS@SiO₂ became hydrophilic after SiO₂ coating. The cPS of the cPS@SiO₂ began to decompose at 300 °C, which was a lower temperature than for cPS



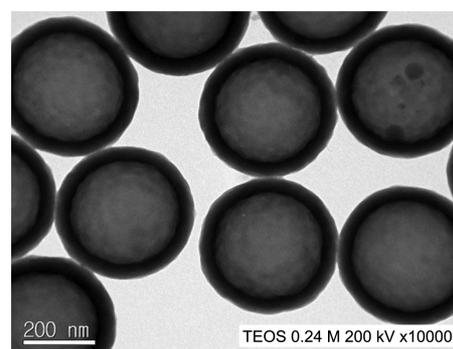
(a)



(b)



(c)



(d)

Figure 4. TEM images of hollow silica spheres obtained at various concentrations of TEOS: (a) 0.03 M, (b) 0.06 M, (c) 0.12 M, and (d) 0.24 M.

alone. This might be because the SiO₂ coating transferred heat to the cPS particles more efficiently than the cPS alone. PS particles at 600 °C lost about 52% of the total cPS@SiO₂

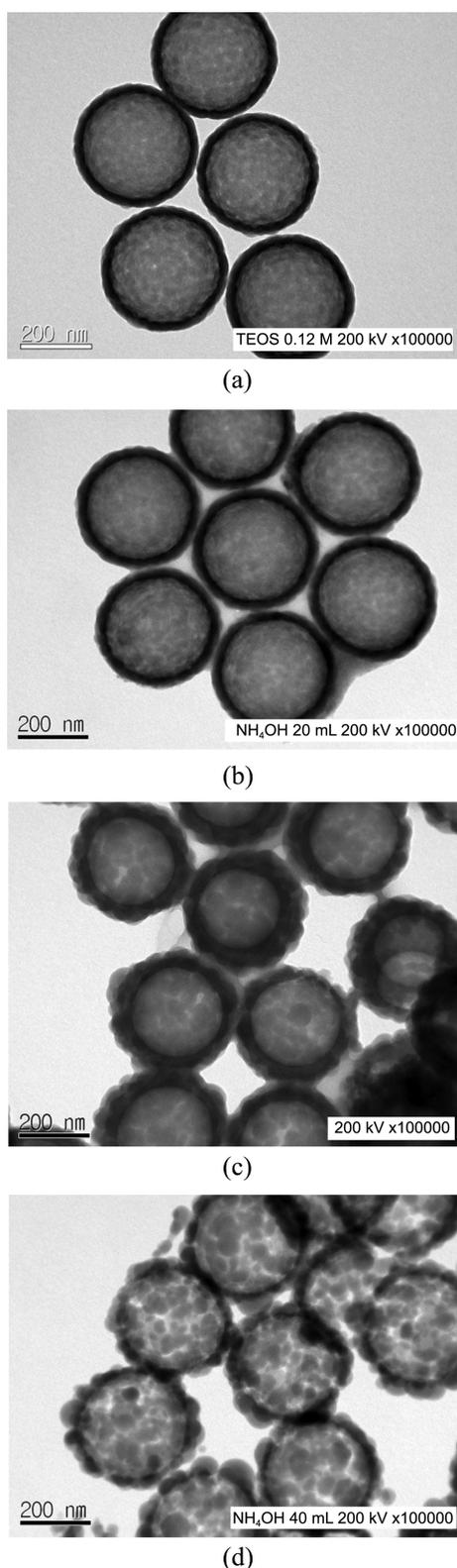


Figure 5. TEM images of hollow silica spheres obtained at various concentrations of NH_4OH : (a) 1.4 M, (b) 2.8 M, (c) 4.2 M, and (d) 5.6 M.

weight. The hollow silica spheres showed no change with temperature.

The surface area, pore volume, pore size, particle size, and

wall thickness for cPS, cPS@ SiO_2 and hollow silica spheres, are summarized in Table 1. The surface area was $12.3 \text{ m}^2/\text{g}$ for cPS@ SiO_2 and $96.4 \text{ m}^2/\text{g}$ for hollow silica spheres.

Figure 4 indicates the effects of TEOS concentration on shape, size, wall thickness, and surface roughness of hollow SiO_2 spheres. The particles were round, and surfaces remained smooth regardless of TEOS concentration. When the TEOS concentration was increased from 0.03 M to 0.24 M, the size and wall thickness of the hollow SiO_2 spheres increased from 280 to 353 nm and from 18 to 46 nm, respectively. In more detailed investigations, we found that the size and wall thickness of the hollow SiO_2 spheres are similar at 280 nm and 18 nm for 0.03 M TEOS, and 285 nm and 18 nm for 0.06 M TEOS, respectively. With increasing TEOS concentrations in the range of 0.12 M–0.24 M, the size and wall thickness (330 nm and 25 nm for 0.12 M TEOS and 353 nm and 46 nm for 0.24 M TEOS) was quickly enhanced. No secondary SiO_2 particles were observed on the surfaces of the hollow SiO_2 spheres.

TEM images of hollow silica spheres formed under various ammonia concentrations are shown in Figure 5. The hollow SiO_2 spheres that were synthesized using an ammonia concentration of 1.4 M were dense, 330 nm in size, and had smooth surfaces and uniform wall thickness of 25 nm. When the ammonia concentration was doubled, the silica began to aggregate. When the ammonia concentration was tripled, hollow SiO_2 spheres with irregular, rough surfaces were formed and some spheres became aggregated. The formation of irregular rough surfaces and aggregation are more severe with increasing ammonia concentrations because higher concentrations of ammonia result in faster hydrolysis and condensation of TEOS, which cause silica to grow rapidly.

Conclusions

Hollow silica particles were uniformly synthesized by chemical reaction of TEOS on the surface of cPS particles, followed by calcination at $600 \text{ }^\circ\text{C}$ under air. The resulting product was spherical and 330 nm in diameter with a narrow distribution of sizes, a wall thickness of 25 nm, and a surface area of $96.4 \text{ m}^2/\text{g}$. Size and wall thickness were uniform, which we attribute to the surface charge of the cPS. The cPS surface was positively charged with NH_2^+ groups from the AIBA cationic initiator. In the presence of cPS in solution, negatively charged silica particles easily nucleated on the cPS particle surfaces and generated a uniform thin shell by hydrolysis and condensation. The effects of TEOS and ammonia concentrations on shape, size, wall thickness, and surface roughness of hollow SiO_2 spheres were investigated. We observed that the wall thicknesses of hollow SiO_2 spheres increased and that silica size was simultaneously enhanced with increases in TEOS concentrations. When ammonia concentrations were increased, the irregularity of rough surfaces and aggregation of spherical particles were more severe because higher concentrations of ammonia result in faster hydrolysis and condensation of TEOS. These changes caused the silica to grow faster, resulting in hollow

SiO₂ spheres with irregular, rough surfaces.

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