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# A Novel Method for the Fabrication of Monodisperse Hollow Silica Spheres

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In this paper, we report a novel method for the fabrication of small monodisperse hollow silica spheres. In this approach, when silica shells were coated on polystyrene particles by the sol–gel method, the polystyrene cores were dissolved subsequently, even synchronously, in the same medium to form monodisperse hollow spheres. Neither additional dissolution nor a calcination process was needed to remove the polystyrene cores. Transmission electron microscopy, scanning electron microscopy, and porosity measurements were used to characterize the monodisperse hollow silica spheres.

## Introduction

Hollow nano- and microspheres with well-defined structures have been attracting interest because of their potential applications in catalysis, chromatography, the protection of biologically active agents, fillers (or pigments, coatings), waste removal, and large bimolecular-release systems.<sup>1–7</sup> Since the pioneering works on the fabrication of hollow spheres were performed by Kowalski and colleagues at Rohm and Haas,<sup>8,9</sup> the question of how to fabricate monodisperse hollow spheres in the micrometer to even the nanometer-scale range and with tailored structural shape and surface properties has remained a great challenge in the area of materials research.

Recently, a variety of chemical and physicochemical methods have been developed, including heterophase polymerization combined with a sol–gel process,<sup>10–12</sup> emulsion/interfacial polymerization strategies,<sup>13,14</sup> nozzle reactor approaches (spray-drying or pyrolysis),<sup>15–17</sup> self-assembly techniques,<sup>18,19</sup> and surface living polymerization processes,<sup>20,21</sup> for the preparation of hollow spheres comprised of polymeric or ceramic materials.

Two of these methods are particularly interesting and are usually used to fabricate hollow spheres with homogeneous, dense layers. One is templating against colloid particles (including CdS,<sup>22</sup> Pb,<sup>5</sup> and mesoscale ZnS<sup>23</sup> or polymer beads<sup>24,25</sup>). In a typical procedure, template particles are coated in solution either by controlled surface precipitation of inorganic molecule precursors (silica, titania, etc.) or by direct surface reactions utilizing specific functional groups on the cores to create core–shell composites. The template particles are subsequently removed by selective dissolution in an appropriate solvent or by calcination at elevated temperatures in air to generate ceramic hollow spheres. For instance, Xia et al.<sup>26</sup> prepared mesoscale titania hollow spheres by templating the sol–gel precursor solution against crystalline polystyrene (PS) beads. By infiltrating dried, physically contacted PS beads between two glass substrates with a titania precursor solution and exposing them to moisture in air, the precursor hydrolyzed into titania sol, which subsequently aggregated into a network of gel. The gel precipitated out, and a coating formed around each PS bead while the solvent evaporated. The titania-coated PS beads were immersed in toluene to dissolve the PS template to obtain titania hollow spheres. Bourgeat-Lami et al.<sup>11</sup> synthesized PS latex particles bearing silanol groups on the surface via emulsion polymerization using 3-(trimethoxysilyl)propyl methacrylate as the functional comonomer. These PS colloids were then transferred into aqueous ethanol solution by the exchange of solvent, wherein the co-condensation of the silanol groups with tetraethoxysilane (TEOS) was carried out via an ammonia-catalyzed sol–gel process, producing composite particles with PS as the core and silica as the shell. Hollow silica spheres were obtained in a subsequent step by thermal degradation of the PS cores at 600 °C. Another method, termed the layer-by-layer (LbL) self-assembly technique, has become a very attractive topic of investigation since the pioneering work done by Caruso.<sup>1,27</sup> The basis of this process is the electrostatic association between alternately deposited, oppositely charged species. Multilayered shells are assembled onto submicrometer-

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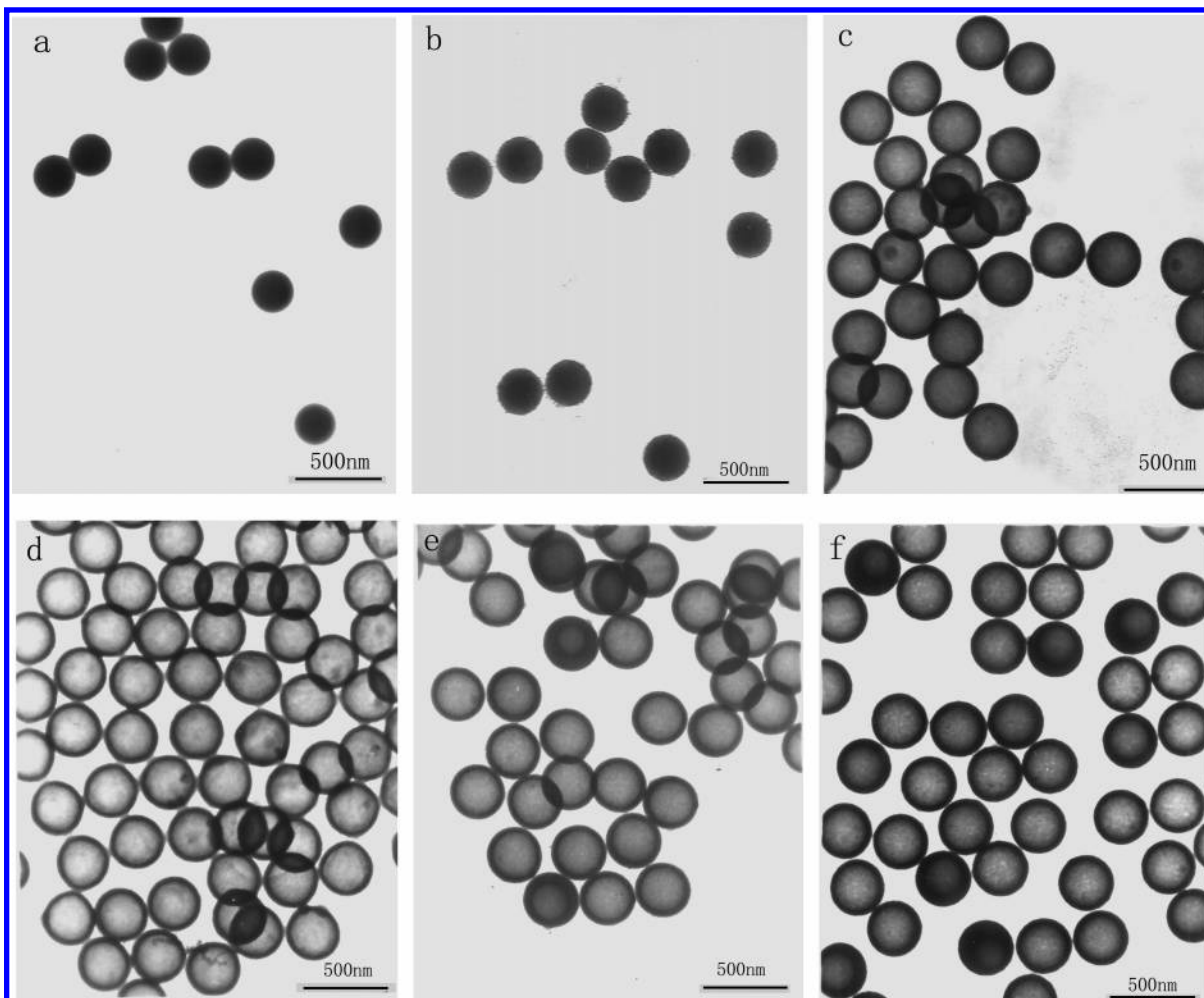
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**Figure 1.** TEM images of the original PS particles (a) and all the coated spheres obtained at various amounts of ammonia: (b) 0.5 mL, (c) 2.0 mL, (d) 3.0 mL, (e) 4.0 mL, (f) 5.0 mL. TEOS: 1 g; PS emulsion (6.67 wt % solid content): 5.0 g;  $T = 50\text{ }^{\circ}\text{C}$ .

sized colloidal particles by the sequential adsorption of polyelectrolytes and oppositely charged nanoparticles. Upon calcination of the obtained core-shell particles, the uniform-sized hollow spheres of various diameters and wall thicknesses are generated for a variety of inorganic materials, including silica, iron oxide, titania, zeolite, clay, and inorganic heterocomposites.

Unfortunately, although the above pioneering works are very interesting, the preparation processes seem to be time-consuming; for example, multistep processes are needed for the synthesis of core-shell composite particles, such as, the surface-functionalization of templating particles/exchange of solvent/coating reaction for the templating particles approach, or the repeated adsorption/centrifugation/water wash/redispersion cycles for the LbL method. Moreover, to obtain hollow spheres from the core-shell composite particles, removing the core particles by selective dissolution in an appropriate solvent or by calcination at elevated temperatures in air is required. Therefore, developing facile and feasible methods to prepare hollow spheres continues to be a great challenge to materials scientists.

In our previous works, we reported that micro-sized, monodisperse, hollow silica<sup>28</sup> and titania<sup>29</sup> spheres were fabricated via a one-step process, which means that the formation of the inorganic shells and the dissolution of core particles occur in the same medium. In that method, micro-sized, monodisperse, positively charged PS particles were prepared by dispersion

polymerization using the cationic monomer 2-(methacryloyl)-ethyltrimethylammonium chloride (MTC) as the comonomer,<sup>30</sup> which ensured that the generation of silica or titania sol from the hydrolysis and condensation of TEOS or tetra-*n*-butyl titanate (TBT) could be rapidly captured by PS particles via electrostatic interaction in an aqueous ammoniacal alcohol medium at  $50\text{ }^{\circ}\text{C}$ , in which PS particles were “dissolved” subsequently, even synchronously, to directly form microscale hollow silica or titania spheres. Neither additional dissolution nor a calcination process was used to remove the PS cores to form hollow spheres. In this work, we further prepared small hollow silica spheres via a one-step method using  $\sim 260\text{ nm}$  PS particles as the template particles, which were synthesized via emulsifier-free emulsion polymerization using  $\alpha,\alpha'$ -azodiisobutyramidine dihydrochloride (AIBA) as the initiator and poly(vinylpyrrolidone) (PVP) as the stabilizer. These small PS template particles without a positively charged comonomer could also be dissolved in the same medium subsequently, even simultaneously, during the coating of silica shells to directly form hollow spheres. Neither additional dissolution nor a calcination process was needed to remove the PS cores.

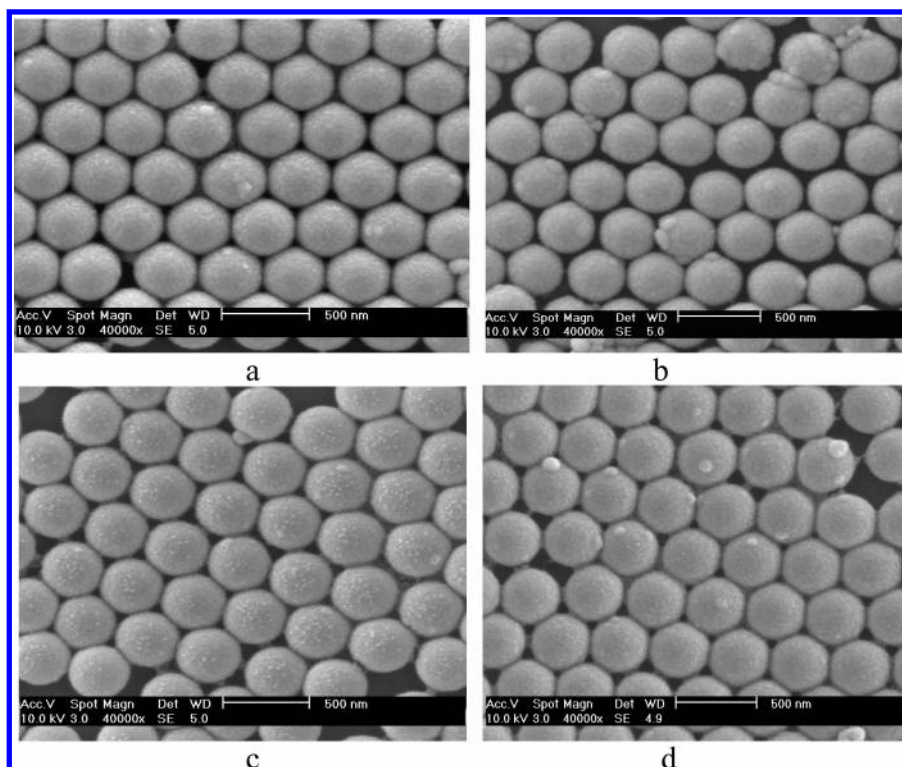
### Experimental Section

**Materials.** Styrene (St) was purchased from Shanghai Chemical Reagent Co. (China) and distilled to remove the inhibitor in a vacuum and stored at  $4\text{ }^{\circ}\text{C}$  until use. Both PVP ( $M_r = 40\text{ }000$ ) and AIBA

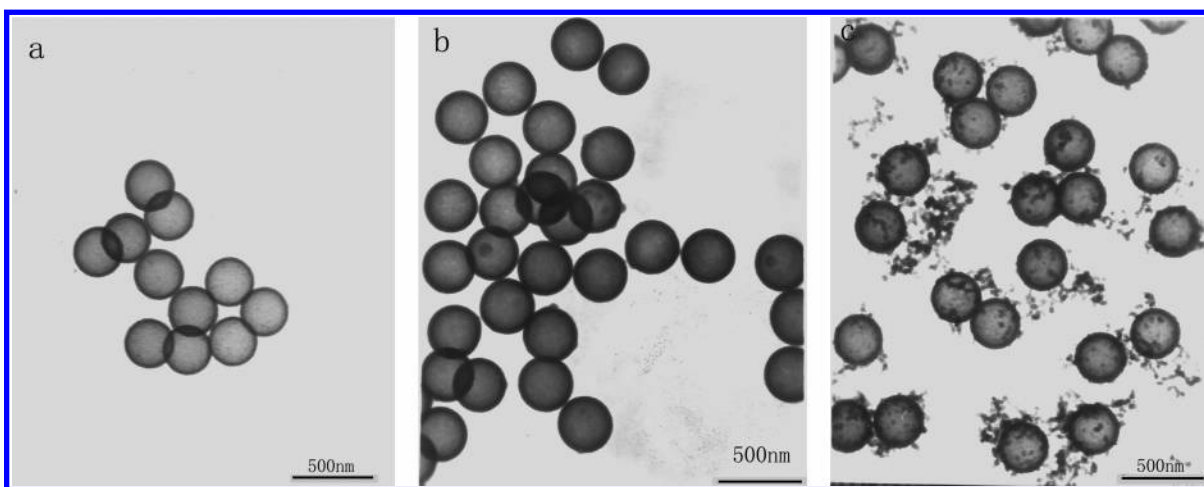
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**Figure 2.** SEM images of the hollow silica spheres obtained at various amounts of ammonia: (a) 2.0 mL, (b) 3.0 mL, (c) 4.0 mL, (d) 5.0 mL. TEOS: 1 g; PS emulsion (6.67 wt % solid content): 5.0 g;  $T = 50\text{ }^{\circ}\text{C}$ .



**Figure 3.** TEM images of the hollow silica spheres generated at various amounts of TEOS: (a) 0.5 g; (b) 1.0 g; (c) 2.0 g. Ammonia: 2 mL; PS emulsion (6.67 wt % solid content): 5.0 g;  $T = 50\text{ }^{\circ}\text{C}$ .

were supplied by Fluka (USA) and used as received. TEOS, absolute ethanol, and aqueous ammonia solution (28 wt %) were purchased from Shanghai Chemical Reagent Co. (China) and used as received. Ultrapure water ( $> 17\text{ M}\Omega\text{ cm}^{-1}$ ) from a Milli-Q water system was used throughout the experiment.

**Synthesis of PS Template Particles.** The monodisperse PS particles were prepared by emulsifier-free emulsion polymerization as follows: 10.0 g of St, 1.5 g of PVP, 0.26 g of AIBA, and 100.0 g of  $\text{H}_2\text{O}$  were charged into a 250-mL three-neck flask equipped with a mechanical stirrer, a thermometer with a temperature controller, a  $\text{N}_2$  inlet, a Graham condenser, and a heating mantle. The reaction solution was deoxygenated by bubbling nitrogen gas at room temperature for  $\sim 60$  min. Then, under a stirring rate of 100 rpm, the reaction was carried out at  $70\text{ }^{\circ}\text{C}$  for 24 h.

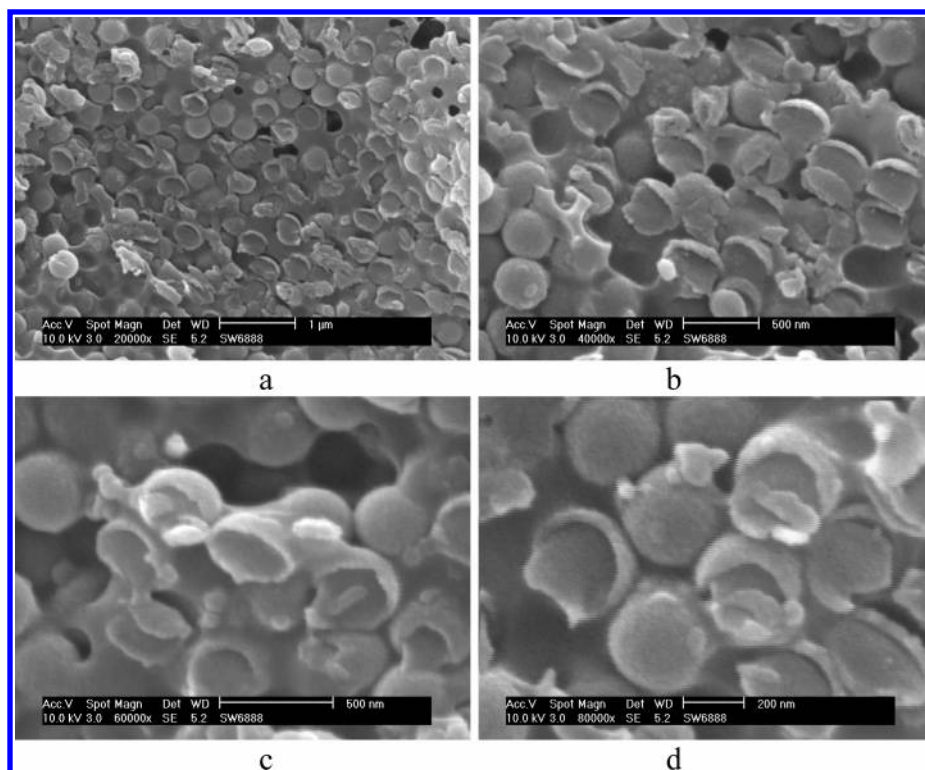
**Synthesis of Hollow Silica Spheres.** The obtained PS suspension was dialyzed in ethanol using a cellulose membrane, and the solid content of the PS suspension could be tailored through the addition of ethanol. Then various amounts of ammonia and TEOS and 40

mL of ethanol were added into 5.0 g of the PS suspension, in which the sol-gel reaction was carried out at  $50\text{ }^{\circ}\text{C}$  for 1.5 h, and the hollow silica spheres could be directly obtained.

**Characterization. TEM Observation.** A transmission electron microscope (TEM; Hitachi H-800, Hitachi Corp.) was used to observe the morphologies of the obtained spheres. The dispersions were diluted with ethanol and ultrasonicated at  $25\text{ }^{\circ}\text{C}$  for 15 min and then dried onto carbon-coated copper grids before examination.

**SEM Observation.** (1) The morphologies of the hollow silica spheres were further characterized by using a scanning electron microscope (SEM; Philips XL30 apparatus). The dispersions of the obtained hollow silica spheres were diluted and dried on a cover glass and sputter-coated with gold prior to examination. (2) The typical hollow silica spheres were dehydrated and subsequently embedded in epoxy for microtoming, the obtained ultrathin sections were sputter-coated with gold, and then the morphologies of the broken hollow silica spheres were observed by SEM.





**Figure 4.** SEM images of the broken hollow silica spheres observed at different magnifications: (a)  $\times 20\,000$ ; (b)  $\times 40\,000$ ; (c)  $\times 60\,000$ ; (d)  $\times 80\,000$ .

**Porosity Measurements.** Nitrogen sorption measurements were performed on the cleaned powder, which was degassed at  $80\text{ }^{\circ}\text{C}$  under vacuum, at  $77\text{ K}$  using an ASAP 2010 analyzer. The pore size was calculated from the desorption isotherm curves using the Brunauer–Joyner–Halenda (BJH) method.

## Results and Discussion

**Effect of the Amount of Ammonia.** The monodisperse small PS template particles were prepared by emulsifier-free emulsion polymerization using AIBA as the cationic initiator and PVP as the stabilizer. The TEM image in Figure 1a demonstrates that uniform spherical PS particles with an average diameter of  $\sim 260\text{ nm}$  were obtained.

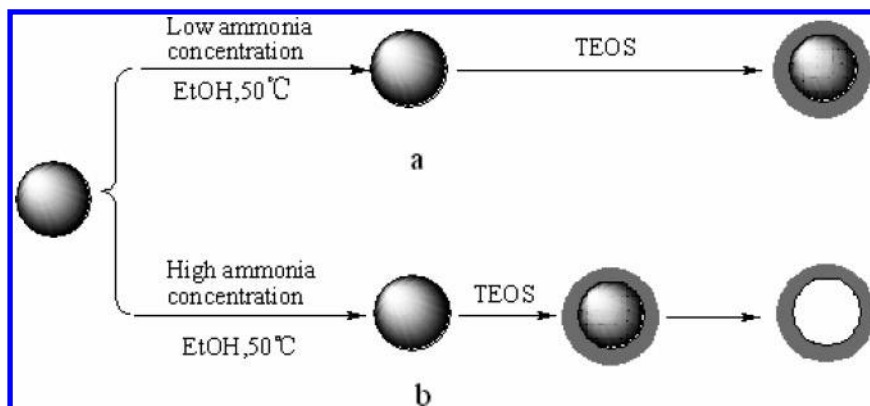
In the subsequent coating process, ammonia and TEOS were added to the PS suspension for the sol–gel reaction. Figure 1b–f displays the TEM images of the five samples obtained from different amounts of ammonia. At the ammonia concentration of  $0.5\text{ mL}$ , the PS particles could not be dissolved in the medium, and the composite particles with PS as the core and silica as the shell formed, as shown in Figure 1b. The surface roughness of the spheres compared to that of the original PS particles confirmed the formation of silica shells surrounding the PS core particles. However, when the concentration of ammonia was increased to  $2.0\text{ mL}$ , the PS cores began to “dissolve” in the medium, but the cores were incompletely dissolved in the medium, as can be seen comparing the image in panel c with those in panels b and d. When the concentration of ammonia continued to increase to  $3.0\text{ mL}$ , the high contrast of the shells and the cores denoted that the PS particles inside the spheres were completely dissolved, and homogeneous, dense silica layers formed, producing monodisperse hollow silica spheres, as demonstrated in Figure 1d. As the ammonia content was further increased to  $4.0\text{ mL}$  and even  $5.0\text{ mL}$ , monodisperse hollow silica particles were obtained, and no free silica particles were observed, as demonstrated in Figure 1e,f. Thus, the monodisperse

hollow silica spheres could be easily obtained by adjusting the amount of ammonia. To further understand the formation process of the hollow silica spheres, a control experiment omitting TEOS in the formulation was carried out as follows: The same amount of PS suspension was heated to  $50\text{ }^{\circ}\text{C}$  in the presence of  $3.0\text{ mL}$  of ammonia for  $1\text{ h}$  and then examined by TEM. As a result, all of the particles disappeared, indicating that the PS particles were completely dissolved in the medium.

Figure 2 illustrates the SEM images of the hollow silica spheres prepared at ammonia concentrations ranging from  $2.0$  to  $5.0\text{ mL}$ . It was found that all the hollow silica spheres maintained their uniform spherical morphology and narrow size distribution.

**Effect of the Amount of TEOS.** Hollow spheres with different wall thicknesses were prepared by simply tailoring the concentration of the TEOS precursor ( $0.5\text{ g}$ ,  $1.0\text{ g}$ , or  $2.0\text{ g}$ ), as shown in Figure 3. When the concentration of TEOS was  $0.5\text{ g}$  in the formulation, the hollow spheres were as monodisperse as the original PS particles, with a wall thickness of  $20\text{ nm}$  (see Figure 3a). When the amount of TEOS was increased to  $1.0\text{ g}$ , as indicated in Figure 3b, the wall thickness of the silica increased accordingly to  $30\text{ nm}$ . However, when a much thicker shell was tried in our experiment ( $2.0\text{ g}$  of TEOS in the formulation), the wall thickness of the hollow silica was increased to  $45\text{ nm}$ , but there were some secondary silica particles surrounding the hollow silica spheres, as shown in Figure 3c, suggesting that the PS core particles are unable to capture the rapidly forming silica particles absolutely and equably at high TEOS concentrations. Thus, the uniform wall thickness of the monodisperse hollow silica spheres could easily be tailored by simply altering the concentration of TEOS in the present study.

To further confirm the hollow structures of the silica spheres obtained by this facile method, the typical hollow spheres were dehydrated and subsequently embedded in epoxy for microtome,



**Figure 5.** Schematic diagram of the formation mechanism of the hollow silica spheres at various amounts of ammonia.

**Table 1. Typical Pore Diameters of the Hollow Silica Spheres**

sample	ammonia (mL)	pore diameter <sup>a</sup> (nm)
a	2	24.3
b	3	31.1
c	4	37.4

<sup>a</sup> Calculated by the BJH method from the desorption curves.

and the obtained ultrathin sections were observed by SEM. As shown in Figure 4, a hollow structure was clearly observed.

**Porosity and Pore Size.** The silica shells prepared by the Stöber method are usually porous,<sup>11,12</sup> and the typical pore diameters of the obtained hollow silica spheres were measured by the nitrogen sorption method and calculated by the BJH method from the desorption curves, as shown in Table 1. As the ammonia concentration increased, the pore size tended to increase.

**Formation Mechanism.** On the basis of all the experimental results and discussions, a possible formation mechanism of the composite particles and hollow spheres is described in Figure 5. When the concentration of ammonia was relatively low (e.g., 0.5 mL in the formulation), the PS particles were not able to dissolve in the medium, and PS/SiO<sub>2</sub> hybrid particles with PS as the core and silica as the shell formed, as displayed in Figure 5a. If the amount of ammonia was increased to 3.0 mL, PS/SiO<sub>2</sub> core-shell particles were obtained, as shown in Figure 5b. However, since the silica shells prepared by the Stöber method are usually porous, the sizes of the pores are sufficiently large

for the dissolving PS macromolecule chains and their congregates to diffuse out gradually through the porous silica shells; thus, hollow silica spheres formed, as shown in Figure 5b.

## Conclusion

In this study, a facile and novel method for the fabrication of monodisperse hollow silica spheres based on PS template particles and the sol-gel process has been proposed, in which monodisperse, small PS particles were first prepared by emulsifier-free emulsion polymerization using PVP as the stabilizer, then the silica shells were coated on the PS particles via ammonia-catalyzed hydrolysis and condensation of TEOS. The PS particles were dissolved subsequently, even synchronously, during the coating process. This technique presented a new paradigm in the preparations of inorganic hollow spheres. On the basis of this technique, other inorganic hollow spheres with various shell compositions (e.g., TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, etc.) or different cavity sizes (e.g., ~100 nm to ~micrometers) could also be prepared.

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