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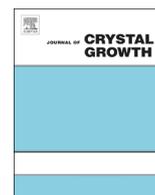
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# Synthesis of hollow silica particles with tunable size, shell thickness, and morphology

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## ABSTRACT

We herein present a simple and effective method to control the particle size, shell thickness, and morphology of hollow silica particles (HSPs). To synthesize the HSPs, polystyrene (PS) particles were employed as a sacrificial template. Size tuning of the HSPs could therefore be achieved by using PS particles of varying sizes. The size of the PS particles was easily controlled by modulation of the monomer content used in the particle synthesis. Varying amounts of TEOS and ammonium hydroxide were systematically added to the system in order to modify the shell thickness and morphology of the desired HSPs. The results indicated that the effects of TEOS and ammonium hydroxide concentrations on the HSP shell thicknesses were similar whereas the effects on morphologies differed significantly.

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## 1. Introduction

The synthesis of micro- and nanoparticles with hollow architectures has been to date actively pursued owing to their extraordinary properties such as high surface area as well as promise in applications requiring encapsulation, etc. [1, 2]. Hollow particles of inorganic materials such as TiO<sub>2</sub>, WO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CoCO<sub>4</sub>, MgO, SiO<sub>2</sub>, and noble-metals have been successfully synthesized and their properties thoroughly investigated. Several methods, including sol-gel, spray-drying, and hydrothermal procedures have been used to prepare hollow inorganic particles [3–9].

The layer-by-layer (LbL) method, originally pioneered by Caruso et al. [10], makes use of a sacrificial organic template to synthesize hollow inorganic particles. The basis of the LbL method is electrostatic attraction between the charged sacrificial template and the target inorganic materials. Charged nanoparticles can be used as the template materials for hollow architectures regardless of their composition and crystal structure. This method has therefore been applied for the preparation of a diverse range of both pure and composite hollow materials [11–13]. Although the LbL method is very simple and versatile, good size and shell thickness control of the desired hollow particles unfortunately remains challenging.

In this study, we present a simple method to control the particle size, shell thickness, and the morphology of hollow silica particles (HSPs). Tetraethoxysilane (TEOS) and polystyrene (PS)

particles were used as the silica source and the sacrificial template, respectively. To produce HSPs of varying diameter, we synthesized different sized PS template particles. Manipulation of TEOS and ammonium hydroxide concentrations were conducted to determine their effect on the resulting HSP shell thickness and morphology.

## 2. Experimental

Styrene (99.5%, Samchun chemical) and 2-(methacryloyl)ethyltrimethylammonium chloride (MTC, 72%, Alfa aesar) aqueous solution were used as the cationic monomer. 2,2'-Azobisisobutyronitrile (AIBN, 98%, JUNSEI) was used as the initiator for the polymerization. Poly(vinyl pyrrolidone) (PVP, M<sub>w</sub> = 30,000, Cica Reagent) was used as a stabilizer. Monodisperse positively charged PS particles were prepared by dispersion polymerization [14]. For the polymerization, the stabilizers, PVP, AIBN, H<sub>2</sub>O, ethanol, MTC, and various amounts of styrene (monomer) were charged into a four-neck flask fitted with a mechanical stirrer, thermometer with a temperature controller, an Ar inlet, and a condenser. Prior to heating, argon gas was bubbled through the reaction solution at room temperature for 30 min. The solution was then heated to 70 °C with an oil bath and stirred at a rate of 100 rpm for 20 h affording the desired monodisperse PS particles.

As prepared PS particles were charged into a three-neck flask and heated to 50 °C at which point ammonium hydroxide (OCI company, 25%) was added and the prepared mixture stirred at 100 rpm for 5 min. TEOS (Samchun chem., 98%) was then added to the mixture and allowed to react at 50 °C for 3 h. The resulting

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silica-coated PS particles were subsequently collected by centrifugation at 8000 rpm and washed repeatedly with ethanol. The desired HSPs were obtained upon removal of the PS cores of the SiO<sub>2</sub>-coated PS particles. The PS cores were dissolved away via treatment of the coated particles with tetrahydrofuran (THF, Samchun chem., 99.5%) for 6 h followed by repeated ethanol washing.

The morphologies of the as prepared HSPs were observed by TEM (CM12, Philips) and FE-SEM (Sirion, FEI). The shell thicknesses of the hollow spheres were also measured by TEM. About 10 mg of the PS particles and the SiO<sub>2</sub>-coated PS hybrid particles were dried at 40 °C overnight and subsequently examined by Thermogravimetric Analysis (TGA, SETSYS Evolution, Staram instrument).

### 3. Results and discussion

#### 3.1. Synthesis and size control of PS particles

PS particle size control is strongly related to thermodynamic and kinetic factors such as stability and solubility of the monomer, reactant composition, concentration of initiator and stabilizer, and temperature. Therefore, multiple variables can be manipulated in order to control particle size. The amount of monomer is particularly relevant as such defines the thermodynamic and the kinetic conditions of the present system.

In the present study, the size of the PS particles was controlled by the reaction concentration of the styrene monomer. Fig. 1 shows the resulting PS particle and HSPs sizes as a function of varying monomer content over a monomer concentration range of 3–10 g/L. At 3 g/L, the average size of the PS particles obtained was 0.9 μm. The PS particle sizes increase with increasing monomer concentration to a maximum value of approximately 1.5 μm corresponding to the monomer concentration of 10 g/L. Under the given reaction conditions, the amount of monomer introduced evidently determines the size of the resulting PS particles as well as that of the desired HSPs. The size of the PS particles determines the size of the HSPs because the PS particles serve as the sacrificial template in the employed synthetic methodology (Fig. 1(b)). Therefore, good size control of the template PS particles is key to fabricating HSPs with tunable properties.

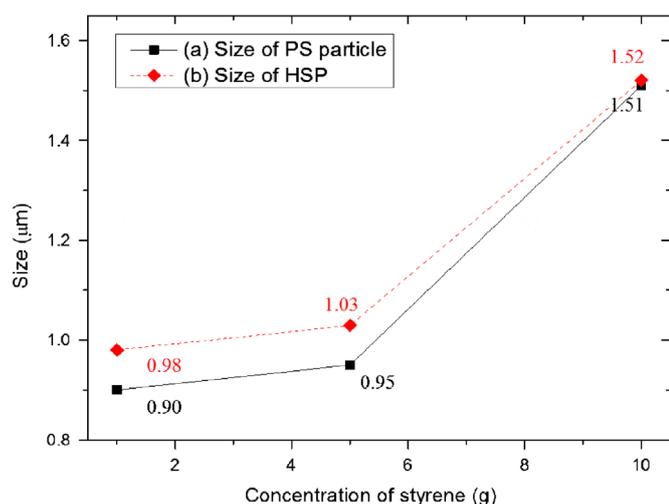


Fig. 1. Variation of PS particles (a) and HSPs size (b) with increasing monomer content.

#### 3.2. Synthesis of HSP

Fig. 2 illustrates the thermogravimetric analysis (TGA) curves of the HSPs with and without the template. Tetrahydrofuran (THF) was employed to dissolve the sacrificial PS template from the SiO<sub>2</sub>-coated PS particles. The weight loss (~2 wt%) below 300 °C results from the evaporation of residual moisture in the sample. The TGA curves show intense weight loss over two temperature ranges, i.e. 300–350 °C and 350–430 °C. Over the first range, the TGA curve of the SiO<sub>2</sub>-coated PS particles (i.e. the particles with the template) labeled (b) in Fig. 2 shows intense weight loss (~38 wt%). On the other hand, curve (a), which corresponds to the TGA of the HSPs (i.e. the particles without the template), displays no noticeable change over this range. This weight loss therefore originated mainly from the decomposition of the sacrificial PS template. Over the second range of interest, both curves show intense weight loss of greater than 40 wt%. This weight loss is attributed to the decomposition of residual groups on the silica surface such as -OH and unhydrolyzed -OR which are of course present on both types of particles considered.

#### 3.3. Effects of concentration of TEOS and ammonium hydroxide

The amount of TEOS and ammonium hydroxide strongly affect the shell morphology and thickness of the desired HSPs. To elucidate the effects of the silica source and catalyst on the formed structures, we synthesized HSPs from varying amounts of TEOS and ammonium hydroxide. Fig. 3 includes the morphology and the shell thickness evolution of HSPs with increasing TEOS content and a fixed ammonium hydroxide concentration. At a TEOS concentration of 0.073 mol/L, rough and discontinuous silica particles were obtained as illustrated in Fig. 3(a). By increasing the amount of TEOS in the reaction solution, the quality of the formed HSPs could be improved (Fig. 3(b)). In particular, at a TEOS concentration of 0.213 mol/L, the HSPs adopted a continuous spherical shape (Fig. 3(c)). Further increase in the TEOS content induced no remarkable changes in shape however a reduction in surface roughness and an increase in shell thickness were concomitantly observed (Fig. 3(d)). The shell thickness as a function of increasing TEOS content is tabulated in Table 1 after it was determined by counting more than 100 particles from TEM images. The standard deviation of HSPs particles was less than 5% in all cases. Below a TEOS concentration of 0.114 mol/L, the shell thickness assumes a nearly constant value, which most likely indicates that the system at this

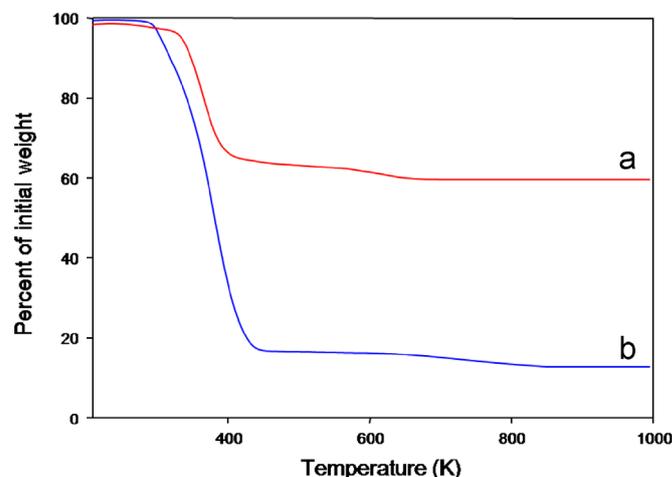
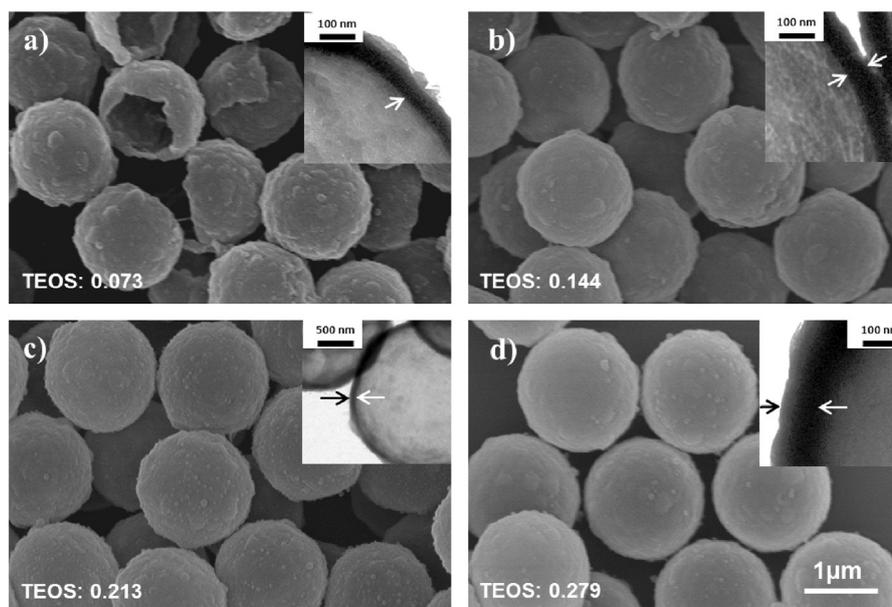


Fig. 2. TGA diagrams of HSPs (a) and HSPs with sacrificial PS templates (b).



**Fig. 3.** Morphology evolution of HSPs with increasing TEOS content at a constant ammonium hydroxide concentration of 0.28 mol/L. (a) 0.073, (b) 0.144, (c) 0.213, and (d) 0.279 mol/L.

**Table 1**  
Dependence of HSP shell thickness on TEOS content (ammonium hydroxide content = 0.28 mol/L).

TEOS concentration (mol/L)	HSP Shell thickness (nm)
0.073	51
0.144	58
0.213	81
0.279	111

**Table 2**  
Dependence of HSP shell thickness on ammonium hydroxide content (TEOS content = 0.213 mol/L).

Content of the ammonium hydroxide (mol/L)	Shell thick of the HSPs (nm)
0.1	79
0.28	81
0.47	83
0.65	86

particular TEOS content lacks sufficient silica precursors to cover the entire surface of the sacrificial template. Above this concentration, the HSP shell thickness increases with increasing TEOS concentration because there is now sufficient silica precursor present to thicken the shell of the system (Table 2).

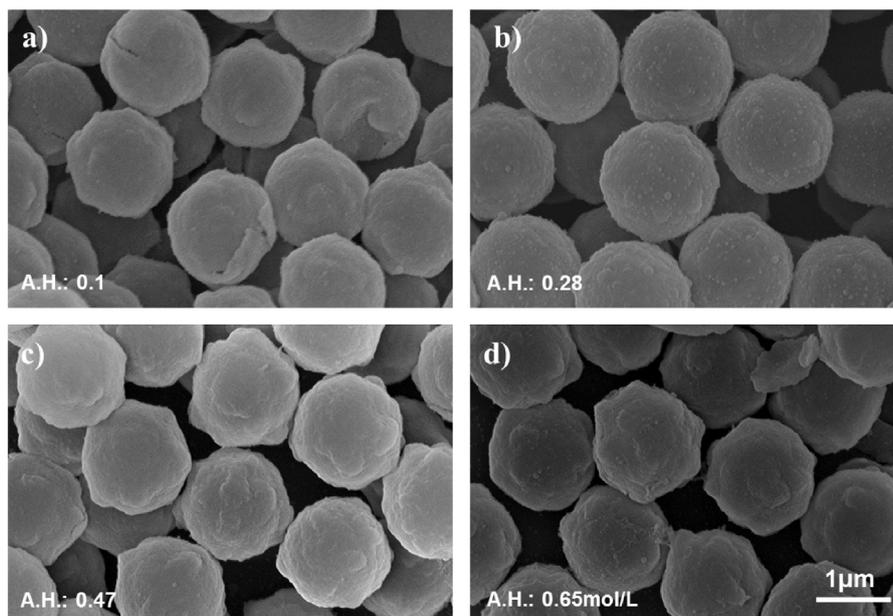
The concentration of ammonium hydroxide is another factor affecting not only HSP morphology but also shell thickness. Fig. 4 illustrates how the morphology of HSPs prepared at a fixed TEOS concentration varied with increasing ammonium hydroxide content. When the concentration of ammonium hydroxide was 0.1 mol/L, only rough and discontinuous particles were obtained. The quality of the HSPs could be remedied by increasing the content of ammonium hydroxide (Fig. 4(b) and (c)). However, the surface roughness of the HSPs was observed again at the higher content of ammonium hydroxide (Figs. 3(d) and 4(d)).

The effects of varying TEOS and ammonium hydroxide concentrations differ in the present system. As mentioned briefly above, with increasing TEOS content, the surface roughness of the formed HSPs remains nearly constant to that imaged in Fig. 3. On the other hand, the surface roughness increased with increasing ammonium hydroxide concentration as highlighted in Fig. 4. It is well known that ammonium hydroxide serves as a source of ammonia in the present system, which acts as a catalyst for the hydrolysis and condensation reactions of the silica source, TEOS [15]. The catalyst decreases the energy barrier for collisions and therefore, increases the rate of collisions between silica micelles. The greater the concentration of ammonium hydroxide, the faster is the rate of reaction. Therefore, increased ammonium hydroxide content stimulates rapid silica particle growth and most likely changes the mechanism of silica deposition onto the surface of the sacrificial template from a slow and controlled layer-by-layer process to a fast and abrupt reaction. The latter favours asymmetric particle formation with high surface roughness. In contrast, a TEOS rich system can sustain the silica deposition onto the surface of the PS particles without noticeable reaction rate change. Consequently, in a TEOS rich system, the HSPs develop a thick and smooth surface.

#### 4. Conclusions

We synthesized hollow silica particles (HSPs) using polystyrene particles as sacrificial templates. To control the particle size of the desired HSPs, we employed different size PS templates, which could be easily achieved during PS particle synthesis by the addition of different amounts of monomer.

TGAs showed that we could fabricate HSPs without PS through the method. Shell thickness and morphology change were observed as a function of TEOS and ammonium hydroxide content, respectively. The effects of TEOS and ammonium hydroxide content on the HSP shell thicknesses were similar whereas that on the resultant morphologies were significantly different. The simple and effective method to control the size, shell thickness, and the morphology of HSPs, described herein provides an



**Fig. 4.** Morphology evolution of the HSPs with increasing ammonium hydroxide content at a constant TEOS concentration of 0.213 mol/L. (a) 0.1, (b) 0.28 (c) 0.47, and (d) 0.65 mol/L.

efficient way to modify the properties of the HSPs for numerous applications.

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