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

J. Kim*, J. LEE* , H. Chang*, J. Choi**, and H. Jang*

*Korea Institute of Geoscience and Mineral Resources,
92 Gwahang-no, Yuseong-gu, Daejeon, 305-350, Republic of Korea
**Department of Chemical Engineering, Sogang University, Seoul, 121-742, Korea

ABSTRACT

We present simple methods to control the particle size, shell thickness, and the morphology of hollow silica particles (HSPs). To synthesize the HSPs, we employed polystyrene (PS) particles as a template. The size of the PS particles was controlled by the monomer content. A various amount of TEOS and ammonium hydroxide was added into the system to modify the shell thickness and morphology of the HSPs. The result indicated that effects of the TEOS and the ammonium hydroxide addition on the shell thickness illustrated a similar trend each other, on the other hand, the effects on the morphology were significantly different from each other.

Keywords: Hollow silica particles, Template, TEOS

1 INTRODUCTION

The synthesis of micro- and nano-particles with hollow architecture has been issued because of their extra ordinary properties such as high surface area and promising applications in capsulation, etc. [1, 2]. Therefore, various inorganic hollow particles, such as TiO_2, WO_3, Fe_2O_3, $CoCO_4$, MgO, SiO_2 and noble-metal nanoparticles were investigated and successfully synthesized. Several methods, sol-gel, spray-drying method, and hydrothermal methods, have been used to fabricate the hollow inorganic particles [3-9]. Particularly, layer by layer (LbL) method using sacrificial organic template is the favorite method to synthesize the hollow inorganic particles.

The LbL method is becoming an interesting issue for producing the hollow inorganic particles since the pioneering work by Caruso et. al.[10]. The basis of the LbL method is electrostatic attraction force between the charged sacrificial template and target inorganic materials. Charged nanoparticles can be used as the target materials for hollow architecture regardless their composition and crystal structure. Therefore, this method has been easily applied to diverse charged materials not only single but also multi composite layered particles [11-13]. Unfortunately, although the LbL method is very simple and able to apply to diverse materials, the size and the shell thickness control of the hollow particles is still challenging.

In this study, we present simple methods to control the particle size, shell thickness, and the morphology of hollow silica particles (HSPs). Tetraethoxysilane (TEOS) and polystyrene (PS) particles used as a silica source and a sacrificial template, respectively. We synthesized the various PS particles with different size to control the size of the HSPs. The addition of different amount of the TEOS and the ammonium hydroxide was conducted to understand effects on the shell thickness and morphology change of the HSPs

2 EXPERIMENTAL

Styrene (99.5 %, Samchun chemical) and 2-(methacryloyl)ethyltrimethylammonium chloride (MTC, 72 %, Alfa aesar) aqueous solution were used as a cationic monomer. 2,2′- Azoisobutyronitrile (AIBN, 98%, JUNSEI) was used by initiator for polymerization. Poly vinyl pyrrolidone (PVP, mw = 30000, Cica Reagent) was used as a stabilizer. Monodispersed positive charged PS particles were prepared by dispersion polymerization [14]. First, the stabilizers, PVP, AIBN, H_2O, ethanol, MTC and various amount of the styrene (monomer) were charged into a four-neck flask with a mechanical stirrer, thermometer with a temperature controller, an Ar inlet, a condenser, and oil bath. The reaction solution was deoxygenated by bubbling argon gas at room temperature for 30 min. Then, the solution was heated to 70℃ with a stirring rate of 100 rpm for 20 h. As a result, the monodispersed positive charged PS particles were obtained.

As prepared PS particles were charged into three-neck flask and heated to 50 ^{o}C and then, ammonium hydroxide (OCI company, 25%) were added into the mixture. The mixture was stirred 100 rpm for 5 min. After that, TEOS (Samchun chem., 98%) was added into the mixture and the mixture reacted at 50 ^{o}C for 3 h. The resultants, HSPs, were centrifuged at 8000 rpm and washed several times with ethanol. The PS particles were dissolved by Tetrahydrofuran (THF, Samchun chem., 99.5%) for 6 h, thereafter the resultants were washed with ethanol several times.

3 RESULTS & DISCUSSION

Particle size control of the PS is strongly related to thermodynamic and kinetic factors such as, stability and solubility of monomer, reactant composition, concentration of initiator and stabilizer, and temperature. There are several methods to control the factors among them, the amount of monomer is important to define the thermodynamic and the kinetic condition of the present system. It determines solubility and stability of the monomer, and overall composition of reactants. Here, we therefore, adopted an addition of different amount of monomer to control the factors.

The size of the PS particles was controlled by addition of different amount of the monomer. Figure 1 shows the effect of different amount of the monomer on the particle size of the PSL. We added polystyrene from 3 – 10 g/L to synthesize the PS particles with different particle size. When the addition is 3 g/L, size of the PS particles represents 0.9 μm. As increasing the addition, the PS particles size also increases steadily to about 1.5 μm. The overall results of the Fig. 1 demonstrate that the amount of the monomer is the factor affecting to the PS particles size at the given conditions. It is noted that the size of the PS particles determines the size of the HSPs because the present fabrication uses the PS particles as a sacrificial template. Therefore, the size control of the PS particles is important technique to fabricate the HSPs with tunable properties.

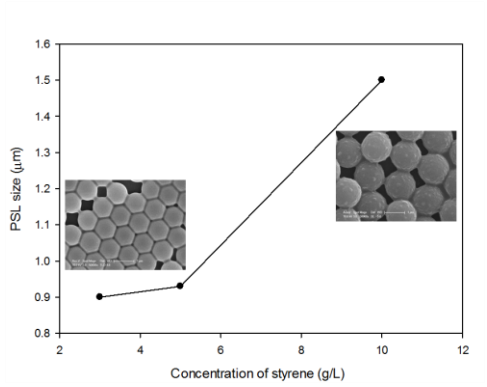

Figure 1. Variation of PS particle size with increasing monomer content.

The amount of TEOS and ammonium hydroxide strongly affect to the morphology and the shell thickness of the HSPs. We synthesized HSPs using addition of different amount of TEOS and ammonium hydroxide to understand the effects of silica source and catalyst. Figure 2 shows morphology evolution of HSPs with increasing the amount of TEOS at constant ammonium hydroxide. When the amount of the TEOS is 0.073 mol/L, broken silica particles are observed in Fig. 2 (a). With increasing the amount of the TEOS, the number of the broken HSPs are decreased (Fig. 2 (b)). When the system contains 0.213 mol/L of the TEOS, the broken HSPs are disappeared completely and the HSPs have a spherical shape (Fig. 2 (c)). Further increase in the TEOS content induces no remarkable changes in shape, however, surface roughness is reduced (Fig. 2 (d)).

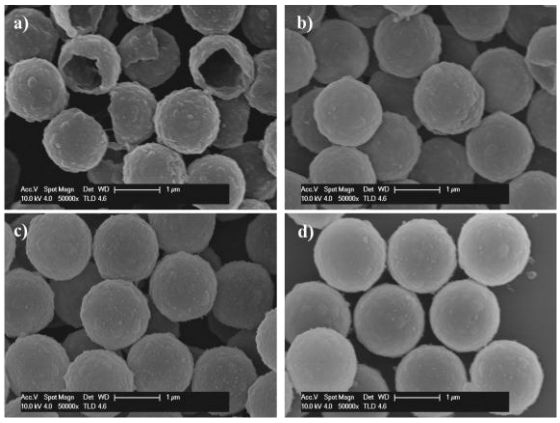

Figure 2. Morphology evolution of HSPs with increasing TEOS content at constant ammonium hydroxide content of 0.47 mol/L. (a) 0.073, (b) 0.144, (c) 0.213, and (d) 0.279 mol/L.

Content of the TEOS (g)	Shell thick of the HSPs (nm)
1	51
2	58
3	109
4	111

Table I: Shell thickness of HSPs depending on the content of the TEOS.

As increases in the TEOS content, the shell thickness also increases. Table 1 demonstrates the shell thickness variation with increasing the TEOS content. Below the content is 2g, the shell thickness maintains near the constant value. That means the system is deficient in silica precursors to cover the whole of the sacrificial templates. Above this content, shell thickness increases with increasing the TEOS concentration because there are enough silica precursors to thicken the shell thickness in the system.

The concentration of ammonium hydroxide is another factor affecting to not only the morphology but also shell thickness of the HSPs. Fig. 3 shows the morphology variation of HSPs with different the content of ammonium hydroxide. When the content of the ammonium hydroxide is 1ml, broken and dented particles are observed in Fig. 3

(a). On the one hand, the broken and dented particles disappear with increasing the content of ammonium hydroxide (Fig. 3 (b) and (c)). Similar to the case of the TEOS addition, shell thickness of HSPs increases with increasing the ammonium hydroxide addition (Table I and II). Compared to the effects of TEOS, there is significant difference in the effects of ammonium hydroxide. The difference is surface roughness of the HSPs (Fig 2 and 3).

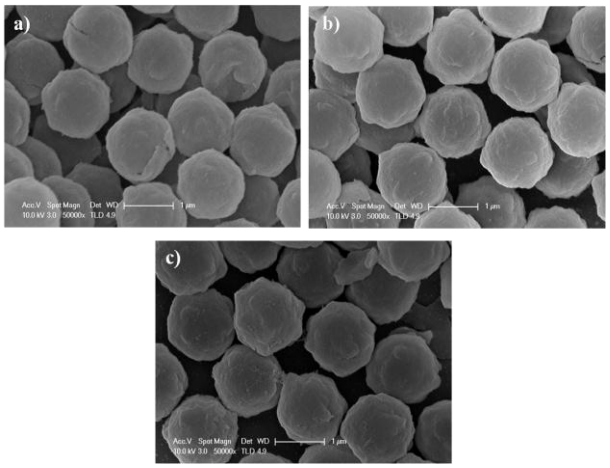

Figure 3. Morphology evolution of the HSPs with increasing ammonium the hydroxide content at constant TEOS content of 0.213 mol/L. (a) 0.1, (b) 0.47, and (c) 0.65 mol/L.

Content of the ammonium hydroxide (ml)	Shell thick of the HSPs (nm)
1	79
5	83
7	86

Table II: Shell thickness of HSPs depending on the content of the ammonium hydroxide.

4 SUMMARY

We synthesized the hollow silica particles (HSPs) using polystyrene (PS) particles as a sacrificial template. To control the particle size of HSP, we produced the different size of the PS particles by addition of the different amount of the monomer. The addition induced to change the thermodynamic and kinetic conditions of total system. As a result, the PSL particle size was varied with proportional to the amount of the monomer.

TGA analyses showed that we could fabricate HSPs without PS through the method. Shell thick and morphology change was observed as a function of TEOS and ammonium hydroxide content, respectively. The effects of TEOS and ammonium hydroxide content on the shell thickness of HSPs were similar to each other. However, the resultant morphology by the addition was significant different due to their roles in the present system.

The simple methods to control the size, shell thickness, and the morphology of HSPs, here in, may provide the best way to modify the overall properties of the HSPs for numerous applications.

REFERENCES

[1] M. Kellermeier, F. Glaab, A. M. Carnerup, M. Drechsler and B. Gossler, Crystal structures of bacterial peptidoglycan amidase ampd and an unprecedented activation mechanism, J. Cryst. Growth 311 (2009) 2530-41.

[2] J. Gu, S. Li, M. Ju and E. Wang, In situ carbon template-based strategy to fabricate ferrite hollow spheres and their magnetic property, J. Cryst. Growth 320 (2011) 46-51.

[3] W. Shen, Y. Zhu, X. Dong, J. Gu, and J. Shi, A New Strategy to Synthesize TiO2-hollow Spheres Using Carbon Spheres as Template, Chem. Lett. 34 (2005) 840-41.

[4] X. Li, T. Lou, X. Sun and Y. Li, Research of nitrogen oxide sensing by sol-gel method to synthesis nano-crystalline tin oxide doping with tungsten thin film, Inorg. Chem. 43 (2004) 5442-49.

[5] M. M. Titirici, M. Antonietti, and A. Thomas, A generalized synthesis of metal oxide hollow spheres using a hydrothermal approach, Chem. Mater. 18 (2006) 3808-12

[6] H. Wang, R. Wang, X. Sun, R. Yan, and Y. Li, Synthesis of red-luminescent Eu3+-doped lanthanides compounds hollow spheres, Mater. Res. Bull. 40 (2005) 911-19.

[7] L. Y. Song, X. W. Ge, M.Z. Wan, Z. C. Zhang, Direct preparation of silica hollow spheres in a water in oil emulsion system: The effect of pH and viscosity, J. Non-Cryst. Solids, 352 (2006) 2230-35.

[8] R. K. Singh, A. Garg, R. Bandyopadhyaya, B. K. Mishra, Density fractionated hollow silica microspheres with high-yield by non- polymeric sol-gel/emulsion route, Colloids Surf. A: Physicochem. Eng. Aspects 320 (2007) 39-45.

[9] M. Lida, T. Sasaki, M. Watanabe, Titanium dioxide hollow microspheres with an extremely thin shell, Chem. Mater. 10 (1998) 3780-82.

[10] F. Caruso, R. A. Caruso, H. Mohwald, Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating, Science 282 (1998) 1111.

[11] G. Decher and J. D. Hong, Buildup of Ultrathin Multilayer Films by a Self-Assembly Process: II. Consecutive Adsorption of Anionic and Cationic Bipolar Amphiphiles and Polyelectrolytes on

Charged Surfaces, Makromol. Chem. Macromol. Symp. 46 (1991) 321.
[12] G. Decher, Fuzzy nanoassemblies: toward layered polymeric multicomposites, Science 277 (1997) 1232.
[13] F. Caruso, L. Niikura, D. N. Furlong, Y. Okahata, Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating, Langmuir 13 (1997) 3427.
[14] Kar. P. Lok, Christopher K. Ober, Particle size control in dispersion polymerization of polystyrene, Can. J. Chem. 63 (1985) 209.

The present results will be published in
Journal of Crystal Growth (In press article)
http://dx.doi.org/10.1016/j.jcrysgro.2012.09.047