



Synthesis and Characterization of Hollow Silica Particles from Tetraethyl Orthosilicate and Sodium Silicate

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We herein introduce an effective method to synthesize hollow silica particles (HSPs) from tetraethyl orthosilicate (TEOS) and sodium silicate (Na_2SiO_3) as silica sources using a sacrificial template method with a simple modification. The advantage of the method is that it can be applied to synthesize HSPs from not only TEOS but also Na_2SiO_3 silica sources without changing the method adopted to obtain the sacrificial polymeric templates. Polystyrene particles are adopted as sacrificial templates to synthesize the HSPs, and a conventional dispersion polymerization method is used to synthesize polystyrene particles in an oil medium. Size control of HSPs is enabled by modulation of the polymerization initiator content (2,2'-Azobisobutyronitrile). The particle size, shell thickness, and morphology are analyzed. Light reflection spectra are measured to obtain the light reflection properties of the HSPs. The results indicate that the hollow architecture is the most important factor in determining the light reflection properties of the particles. Such particles are potential candidates for use in light reflectors and heat insulators, as they may reduce energy consumption in heating and cooling applications.

Keywords: Hollow Silica Particles, TEOS, Na_2SiO_3 , Dispersion Polymerization, Templates, Light Reflection.

1. INTRODUCTION

The fabrication of inorganic particles with a hollow architecture has been investigated due to their promising properties such as low density, large specific surface area, and high porosity.^{1–14} Accordingly, various methods have been developed in the past decade to synthesize hollow particles of inorganic materials, including sol-gel, spray-drying, and hydrothermal procedures,^{15–19} however, the most commonly used approach is the sacrificial template method, which makes use of sacrificial organic templates.^{20–22} After the formation of the templates, inorganic nuclei are deposited and nucleated on their surface. The templates are then dissolved by chemical or heat treatment, yielding inorganic particles with a hollow architecture. Consequently, the production of a suitable sacrificial organic template is the most important step in the formation of inorganic particles with a hollow architecture.

Two main methods are used to synthesize sacrificial organic templates: emulsifier-free emulsion polymerization and dispersion polymerization. The former method is generally used to obtain sacrificial templates with a narrow

size range,²³ although it is difficult to produce micro-sized organic templates compared with nano-sized templates when using this method.^{15, 24–26} The dispersion polymerization method enables good size control of the sacrificial organic templates, from hundreds of nanometers to micron scale. This method is generally employed in oil-based media, such as EtOH/ H_2O and BuOH/ H_2O (major and minor media, respectively). Therefore, oil-based inorganic particle sources (e.g., tetraethyl orthosilicate, TEOS) can be used with this method, but difficulties are encountered when using water-based inorganic particle sources such as Na_2SiO_3 .

Here, we present an effective method to synthesize hollow silica particles (HSPs) from not only TEOS but also Na_2SiO_3 silica sources using identical sacrificial templates. We adopt the dispersion polymerization method to produce micro-sized sacrificial organic templates, and a simple modification of the method is made to enable the use of a water-based inorganic source, Na_2SiO_3 . This modification enables the method to be used in both oil- and water-based systems. An advantage of this approach is that micro-sized HSPs are easily synthesized from Na_2SiO_3 , which is a more economical silica source than TEOS. The light reflection properties of the as-prepared HSPs

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are measured to estimate their reflectance for applying to energy saving materials.

2. EXPERIMENTAL DETAILS

2.1. Preparation Polystyrene Particles by the Oil-Based Dispersion Polymerization

Styrene (99.5%, Samchun Chemical) and 2-(methacryloyl) ethyltrimethylammonium chloride (MTC; 72%, Alfa Aesar) aqueous solution were used as a cationic monomer. 2,2'-Azobisisobutyronitrile (AIBN; 98%, Junsei) was used as the initiator for polymerization. Polyvinylpyrrolidone (PVP; mw = 30,000, Cica Reagent) was used as a stabilizer. Mono-dispersed, positively charged polystyrene (PS) particles were prepared by the oil-based dispersion polymerization.²⁶ First, the stabilizers, PVP, AIBN, H₂O, ethanol, MTC, and styrene (monomer) were charged into a four-neck flask with a mechanical stirrer, a thermometer with a temperature controller, an Ar inlet, a condenser, and an oil bath. The reaction solution was deoxygenated by bubbling argon gas at room temperature for 30 min. The solution was then heated to 70 °C with a stirring rate of 100 rpm for 20 h, yielding the mono-dispersed, positively charged PS particles.

2.2. Synthesis of Hollow Silica Particles from TEOS

The PS particles prepared by the oil-based dispersion polymerization were injected into a three-neck flask at 50 °C.

Ammonium hydroxide (25%, OCI Chemical Corporation) was blended into the mixture, which was then stirred at 100 rpm for 5 min. TEOS (98%, Samchun Chemical Company) was added to the mixture and the reaction allowed to progress for 3 h. The resultants were centrifuged and washed several times with ethanol. The PS particles were dissolved in tetrahydrofuran (THF; 99.5%, Samchun Chemical Company) for 6 h, and the final product was washed with ethanol three times.

2.3. Synthesis of Hollow Silica Particles from Na₂SiO₃

As-prepared PS particles were washed in distilled water several times and then dispersed in distilled water. The PS particles in the water-based medium were injected into a three-neck flask at 80 °C. A Na₂SiO₃ water solution was blended into the mixture, which was then stirred at 100 rpm for 5 min. Subsequently, HCl was added to the mixture at 80 °C. The resultants were centrifuged and washed two or three times with distilled water. After this step, the remaining experimental methods are the same as those for the TEOS system.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Hollow Silica Particles from TEOS

Figure 1 shows scanning electron microscope (SEM, Sirion, FEI) and transmission electron microscope

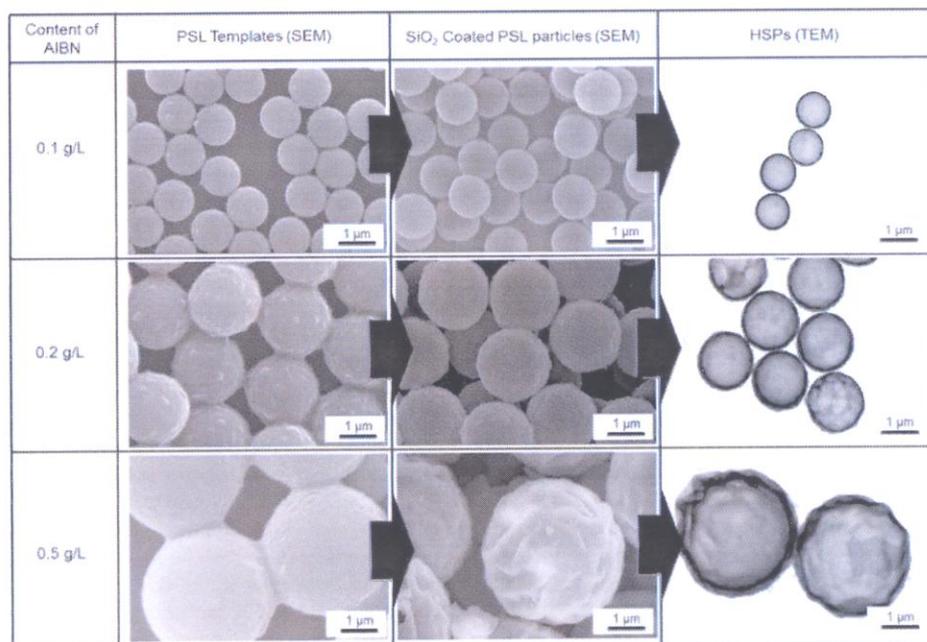


Fig. 1. SEM and TEM images of the PS templates, SiO₂-coated PS particles, and HSPs.

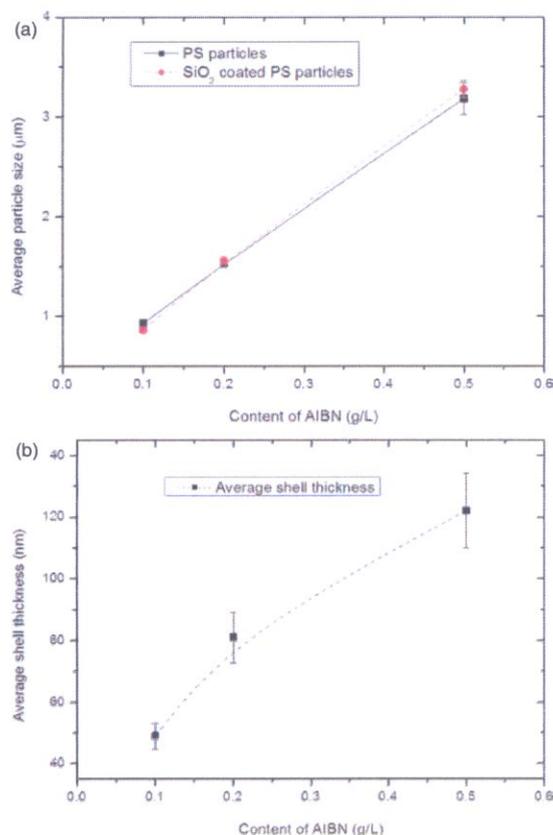


Fig. 2. Variation in the particle size and shell thickness of HSPs with AIBN content.

(TEM, JEM-3011, JEOL) images of the PS templates, SiO₂-coated PS particles, and HSPs prepared by the method as described in Sections 2.1 and 2.2, respectively. To obtain PS templates with different sizes, we modulated the polymerization initiator (AIBN) content, yielding templates with sizes ranging from 0.1 to 0.5 g/L.²⁷ The SEM images of the PS templates and SiO₂-coated PS particles show that the surface morphology varies with template size, especially in the case of the SiO₂-coated PS particles. The TEM images of HSPs (right-hand column in Fig. 1) show that each silica particle has a hollow architecture and that the shell thickness of the HSPs increases with increasing particle size (Fig. 2).

The surface morphology and shell thickness of the HSPs are strongly related to the experimental conditions. Here, we varied the AIBN content to control the size of the PS templates, keeping all other conditions unchanged. Therefore, the total surface area of the PS templates decreases with increasing particle size of the templates. In addition, we employed the same amount of TEOS as a silica source in all cases (i.e., the total amount of silica in the system was constant). Therefore, a decrease in the surface area

of the PS templates results in the formation of multiple coating layers of SiO₂ on the template surface, resulting in turn in an increase in shell thickness and a change in surface morphology.

3.2. Synthesis of Hollow Silica Particles from Na₂SiO₃

HSPs were successfully synthesized from Na₂SiO₃ using a simple modification to the dispersion polymerization method (see Section 2). The main aim of the modification was to enable a change in dispersion medium for sacrificial PS templates particles from an oil-based medium to a water-based medium. To assess the effects of the modification, we compare the experimental results obtained with and without modification (Fig. 3). Figures 3(a) and (b) show the as-prepared HSPs using the modified method. SiO₂ nanoparticles are well deposited on the surface of the PS templates and HSPs are successfully formed. In contrast, no HSPs are produced in the system without modification (Figs. 3(c) and (d)), in which the SiO₂ particles nucleated in the oil/water mixture medium rather than on the surface of the PS templates (Fig. 3(c)).

The driving force for the deposition of SiO₂ nanoparticles on the template surface is electrostatic attraction between the negative charge of the siliceous micelles and the positive charge of the surface.^{25,28} However, a repulsion force exists between the negatively charged ions and the positively charged surface when using the conventional dispersion polymerization method without modification. The anti-attraction force originates from the separation of the oil and water media in the PS templates and Na₂SiO₃, respectively. In the initial step of SiO₂ deposition, siliceous micelles must be uniformly attached to the surface of the PS templates by electrostatic attraction to form a nucleation site for SiO₂ particles; however, the anti-attraction force interferes with this attraction. Consequently, after dissolving of the PS templates, there are no HSPs in the system without modification. The proposed modification acts to reduce the medium separation because the oil-based medium for the PS templates is almost completely eliminated in the modified system. This simple modification is therefore a critical factor in the formation of HSPs from a water-based Na₂SiO₃ silica source.

3.3. Light Reflection Properties of Hollow Silica Particles

The hollow architecture of HSPs results in improved light reflection properties. Figure 4 shows the diffuse reflection spectra of the HSPs produced here. The light reflection properties are measured by a UV-Visible spectra spectrometer (S-4100, SCINCO). For comparison, also shown are the reflection spectra of micro-sized silica particles (~1 μm) and commercial Insuladd (~100 μm Insuladd Asia). The reflectance spectrum of the micro-sized silica

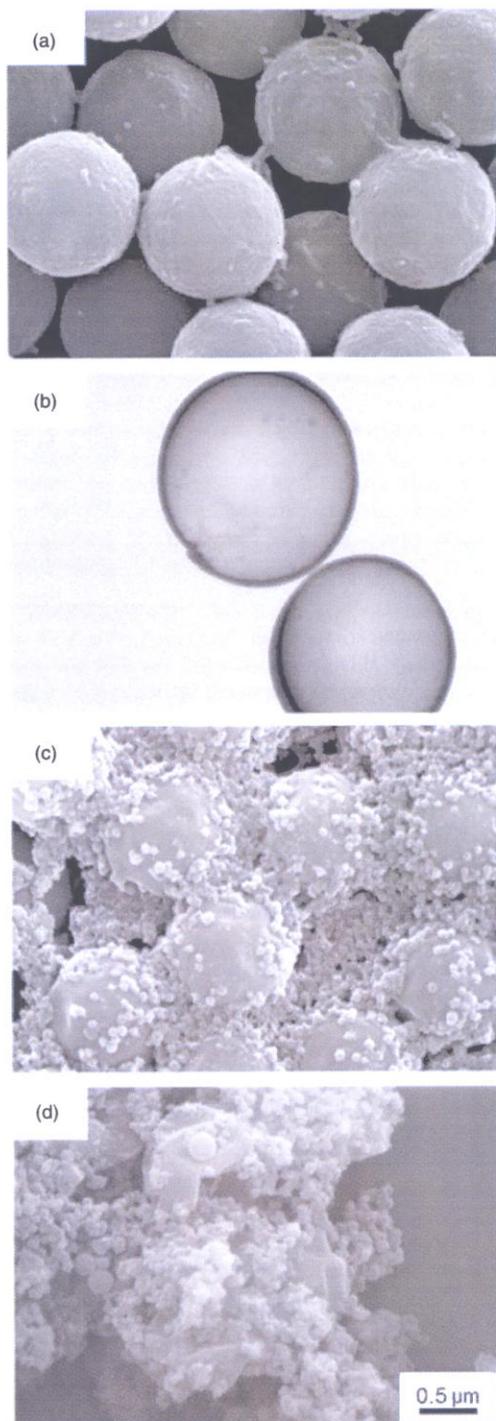


Fig. 3. SEM and TEM images of SiO_2 -coated PS particles and HSPs synthesized with and without modification of the dispersion polymerization method. (a) and (b): with modification, (c) and (d): without modification.

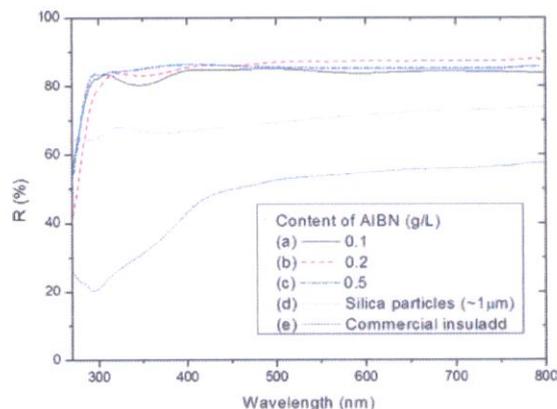


Fig. 4. Light reflection spectra of HSPs compared with micro-sized silica particles and commercial Insuladd.

particles shows a much lower reflectance than that of the HSPs. This result is attributed to the fact that when light passes from a material with a high refractive index to one with a low refractive index, strong reflection and refraction are generated at the interface.²⁹ This phenomenon is relevant here because the HSPs have a hollow space in their center, and the reflective indices of silica and air are 1.5 and 1.0, respectively.³⁰ Consequently, when light encounters the HSPs, strong reflection and refraction are generated at the shell of the HSPs.

In addition, the reflection properties of the HSPs are higher than those of the commercial Insuladd. The maximum difference in light reflectance between the HSPs and the Insuladd is $\sim 60\%$ at 300 nm (UV region), and the minimum difference is $\sim 25\%$ at 800 nm (infrared region). This result indicates that the HSPs are potential materials for heat insulating applications.

To understand the excellent light reflection properties of the HSPs, we measured the light reflectance of HSPs with different size, shell thickness, and surface morphology. As shown in Figure 4, there are no remarkable differences in light reflectance between the three types of HSPs, possibly indicating that the hollow size, shell thickness, and morphology of HSPs have relatively little effect on the light reflection properties of HSPs compared with the presence of a hollow architecture. Therefore, we conclude that the excellent light reflection properties of the HSPs originate mainly from their hollow architecture, and that these properties make HSPs potential candidates in light reflecting and heat insulating applications. HSPs may therefore be applied to reduce energy consumption in heating and cooling applications.

4. CONCLUSIONS

We successfully synthesized hollow silica particles from not only TEOS but also Na_2SiO_3 silica sources using a

sacrificial template method. To obtain polystyrene organic sacrificial templates, the oil-based dispersion polymerization method was employed with a simple modification. The major advantage of the present method is that it can be applied to synthesize HSPs from not only TEOS but also Na_2SiO_3 silica sources without changing the method employed to obtain the sacrificial templates. Size control of the HSPs was attained by modulating the polymerization initiator content (2,2'-Azobisisobutyronitrile). The shell thickness, and morphology of HSPs also varied with respect to the particle size. The modification enables the dispersion polymerization method to be used in both oil- and water-based systems, and enables the synthesis of micro-sized HSPs from Na_2SiO_3 , which is a more economic silica source than TEOS.

The results of light reflection measurements showed that the hollow silica particles have excellent light reflection properties, due to their hollow architecture. These properties make HSPs potential materials in light reflecting and heat insulating areas, thereby reducing energy consumption in heating and cooling applications.

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