



Synthesis and characterization of highly reflective hollow silica particles



Jiwoong Kim^{a,b,*}, Chongmin Lee^b, Yong Jae Suh^{a,b}, Hankwon Chang^{a,b}, Ki-Min Roh^a, Hee Dong Jang^{a,b,**}

^a Rare Metals Research Center, Korea Institute of Geoscience and Mineral Resources, Gwahang-ro 92, Yuseong-gu, Daejeon 305-350, Republic of Korea

^b Korea University of Science and Technology, Gajeong-ro, Yuseong-gu, Daejeon, Republic of Korea

ARTICLE INFO

Article history:

Received 22 January 2015

Received in revised form 3 April 2015

Accepted 20 April 2015

Available online 22 April 2015

Keywords:

Microporous materials

Surfaces

Chemical synthesis

Sol-gel chemistry

Optical properties

ABSTRACT

Hollow reflective silica particles with various features were synthesized from sodium silicate. The hollow architecture was obtained using organic templates synthesized using various initiator concentrations and polymerization media. The concentration of sodium silicate was shown to affect the pore structure and shell thickness of the silica layers subsequently grown on the templates. Surface morphology was affected by the synthesis pH owing to its effects on the silica formation mechanism. The reflectivity of the hollow silica particles was measured in the UV–vis range. They were much better reflectors than a commercial reflection material and were more reflective than silica particles previously synthesized from tetraethyl-orthosilicate, suggesting that sodium silicate is a more ecologically compatible and less costly alternative material for the synthesis of reflective hollow silica particles.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The hollow architecture of nanometer and micrometer sized particles has several advantages, such as a high surface area due to the ordered internal pores and the highly porous shell [1–5]. It is potentially very useful in some specific applications, and the synthesis of hollow architectures for various purposes has been widely studied using diverse materials. For example, they have been employed in the development of heat insulators [6], semiconductors [7], catalysts [8], and nanobiotechnologies [9–13]. Various inorganic materials with hollow architectures have been prepared using ZnO, CdS, and TiO₂ [14–20], but silica is one of the most popular choices due to its useful properties and abundance [21].

There are two representative silica sources: tetraethyl-orthosilicate (TEOS) and sodium silicate (Na₂SiO₃). TEOS is an established silica precursor and is widely used, particularly to produce highly ordered materials. However, it is more expensive than sodium silicate, and its use leaves organic waste after processing. Sodium silicate is a cheaper and less polluting silica source; however, it contains salt ions that interfere with the

movements of other ions in the reaction medium. Furthermore, the rapid formation of silica induced by acid hydrolysis is difficult to control in a typical colloidal process. Accordingly, despite these advantages, sodium silicate is rarely used in applications or research. However, its cost and environmental advantages make it difficult to discount entirely as a silica precursor. Therefore, we investigated its use as a silica source for the controlled synthesis of hollow silica particles. Highly ordered hollow silica particles were consistently more difficult to prepare using sodium silicate than using TEOS. Therefore, we sought not only effective synthesis methods but also suitable uses for the resulting less well-defined hollow silica particles, such as light reflection. This work presents first a fundamental assessment of the synthesis from sodium silicate of hollow silica particles with various sizes, shell thicknesses, and morphologies, and secondly an exploration of the possibility of replacing TEOS in the production of hollow silica particles for light reflection applications.

2. Experimental

Styrene (99.5%, Junsei Chemical) with aqueous 2-(methacryloyloxy)ethyltrimethylammonium chloride (MTC; 72%, Alfa Aesar) was employed as a template. 2,2'-Azobis(isobutyronitrile) (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

* Corresponding author. Tel.: +82 42 868 3927; fax: +82 42 868 3415.

** Corresponding author. Tel.: +82 42 868 3612; fax: +82 42 868 3415.

E-mail addresses: jwk@kigam.re.kr (J. Kim), hdjang@kigam.re.kr (H.D. Jang).

(PS) particles with various sizes were prepared by dispersion polymerization [22]. To synthesize the PS organic templates, the proper amounts of PVP, AIBN, H₂O, ethanol, MTC, and styrene (monomer) were charged into a four-neck flask in an oil bath. The reaction solution was deoxygenated by bubbling argon gas at room temperature for 30 min. It was then heated at 70 °C with stirring at 100 rpm for 20 h to yield the mono-dispersed PS organic template particles. The stirring rate greatly influenced the final size of the template particles: stirring that was too slow or too fast resulted in poly-dispersed PS organic template particles with a broad size distribution. Therefore, once optimized, the effect of stirring speed was not further considered.

Controlling the size of the organic templates is crucial to the production of suitable hollow inorganic particles, because it is the dominant determinant of their final size [23]. The initiator concentration affected the size of the mono-dispersed styrene organic template particles. A pure distilled water reaction medium (120 ml) was compared against one comprising a water (5 ml)/ethanol (115 ml) mixture. An unvarying amount of styrene monomer (11 ml, ~10 g) was used in the tests to maintain consistency.

The prepared PS particles were washed twice in distilled water by centrifugation at 8000 rpm for 15 min. A 60 ml aliquot of the mono-dispersed PS organic template particles was injected into a three-neck flask at 50 °C. Aqueous Na₂SiO₃ solutions (60 ml, 0.08, 0.05, and 0.02 M) were blended with the PS organic template particles and then stirred at 100 rpm for 5 min. HCl and NH₃ were then added to the mixture to adjust it to the desired pH (2, 5, and 9); it was then stirred at 80 °C. The resultant was centrifuged and washed two or three times with distilled water to yield the silica-coated PS core-shell particles. The core-shell particles were

dispersed in tetrahydrofuran (THF, Samchun Chem., 99.5%) for 12 h and then washed.

The surface morphology and shell thickness of the prepared hollow silica particles and the shape of the organic template particles were observed by scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan) and transmission electron microscopy (TEM, JEM-3011, JEOL, Japan). The mean particle size was calculated by measuring the diameters of over the three hundred particles on the SEM micrographs. Fourier transform infrared spectrometry (FT-IR, Nicolet-380, Thermoelectron, Germany) revealed the structures of the core-shell and hollow silica particles. Surface and pore analyses were conducted by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) measurements (Tristar 3000, Micromeritics, USA). Reflection by the hollow silica particles was measured by diffuse reflection UV–vis spectrometry (S-4100, SCINCO). The relative reflectivity of the as-prepared particles was assessed using Spectralon (Labsphere, Model No. SRS-99) as a reflectivity standard [24]. The results were compared against those taken using a commercial reflective material Insuladd (~100 μm, Insuladd Asia) and hollow silica particles synthesized previously using TEOS as a silica source [23].

3. Results & discussion

3.1. Size control of organic template particles

The size of the organic template particles initially increased as the amount of initiator increased up to 0.1 g in pure water and up to 0.5 g in the water/ethanol mixture. Further addition of initiator led to smaller particles until eventually no organic particles formed in either reaction medium (Fig. 1). The thermal decomposition of the

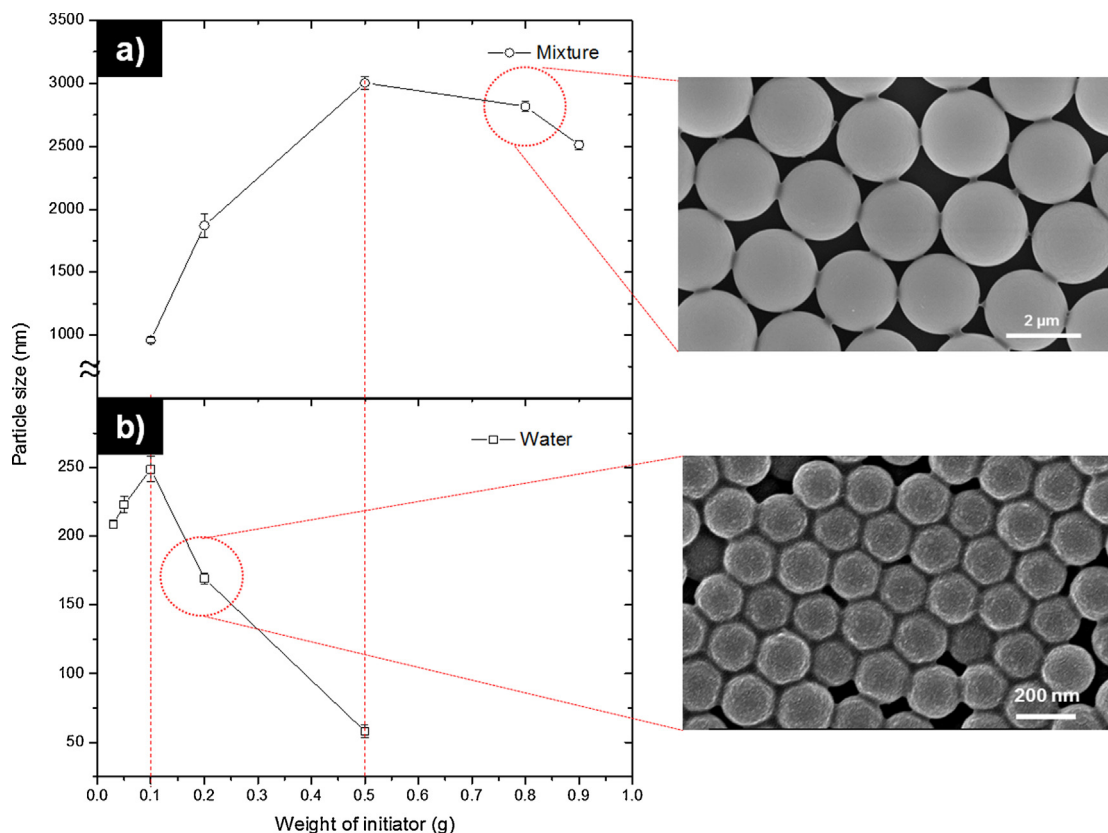


Fig. 1. Size of polystyrene organic template particles with respect to content of initiator in (a) water/ethanol mixed medium and (b) aqueous medium. (The included micrographs are SEM images of polystyrene organic template produced in the mixture (upper) and the aqueous (lower) medium, respectively.)

Download English Version:

<https://daneshyari.com/en/article/1487277>

Download Persian Version:

<https://daneshyari.com/article/1487277>

[Daneshyari.com](https://daneshyari.com)