

Morphology and Size Control of Mesoporous ORMOSIL Particles Prepared from Ternary Organosilane Mixture

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ABSTRACT

Tailored mesoporous ORMOSIL particles, having various morphologies such as raspberry shaped, hollow, and rattle type structures, were synthesized by a selective dissolution of organosiloxane networks in ternary ORMOSIL particles prepared using a simple two-step process. The first step, synthesis of monodisperse ORMOSIL particles with multi-layered structure, comprised a one-pot process in an aqueous solution using ternary mixture from three organosilane monomers, 3-aminopropyl-trimethoxysilane (APTMS), vinyl-trimethoxysilane (VTMS), and phenyltrimethoxysilane (PTMS). In the second step, the ORMOSIL particles were treated with a mixture of water and alcohol with mild heating. This mild etching process was employed to dissolve selectively some of organosiloxane networks within the ORMOSIL particles but not their main silica frameworks, leading to formation of mesoporous particles. Surface roughness, shell thickness, and size of the resultant particles were controlled by manipulating synthetic parameters such as the relative concentration of the silane monomers. Compared to the previously developed synthetic methods, our method offers a simple, economical, and environmentally friendly way to produce complicated mesoporous ORMOSIL particles that can provide several novel properties favorable for practical applications.

Keywords: size control, morphology, mesoporous, ormosil, selective dissolution

1 INTRODUCTION

Mesoporous colloidal particles with tailored morphology and/or controlled size have recently emerged with great promise in diverse fields of nanotechnology due to their extraordinary properties, such as large surface area, controlled pores and channels, permeability, and low density [1,2]. For examples, hollow spheres are widely used in industrial field as light weight substances and nano/micro reservoirs [3,4]. Rattle-type particles with a distinctive core@void@shell configuration have also recently emerged as enticing nanostructured materials that have great potentials for use in various applications such as drug delivery system, catalysts, bio-medicine, and lithium-ion batteries [5,6]. In addition, raspberry shaped materials, which exhibit high surface roughness or porosity, have been

used for self-cleaning and anti-fogging applications due to their super-hydrophobicity [7,8].

A variety of preparation techniques have been developed to produce these mesoporous particles. For hollow and rattle type particles, the template-assisted selective etching approach has been known as the most effective strategy and thereby is commonly used [9,10]. Hard and/or soft templates are employed and then subjected to sequential coating of different materials to obtain multi-layered structures. Then, the removal of the core or the middle layer by etching agent or calcination produced hollow or rattle type particles. Raspberry shaped particles have been usually prepared by self-assembling of particles with different sizes or by surface-etching of multi-layered core-shell type particles [11,12]. However, these methods are often associated with several problems: 1) the synthetic methods consist of multiple steps that are often quite tedious. 2) the etching agents so far used in the synthesis process are strong acids or bases that are extremely corrosive and toxic, hence the handling is not convenient [13,14]. 3) calcination at high temperature often causes the porous shell or the entire morphology to collapse. For wider economical applications, the development of a simple and efficient preparation method for mesoporous particles having various sizes and structures is of great importance.

In this study, the preparation of mesoporous ORMOSIL particles with tailored morphology and/or controlled size by a simple two-step process was reported. The first step, synthesis of monodisperse ORMOSIL particles of uniform size and morphology with multi-layered structure, involved a one-pot process in an aqueous solution using the mixture of three organosilane monomers. In the second step, ternary ORMOSIL particles were treated with a mixture of water and alcohol with mild heating. This mild etching process was efficient to dissolve selectively some of organosiloxane networks within the ORMOSIL particles but not their main silica frameworks, leading to formation of mesoporous particles. Surface roughness, shell thickness, and size of the resultant mesoporous particles were controlled by manipulating synthetic parameters such as the relative concentration of the organosilane monomers. Compared to the previously developed synthetic methods, our strategy offers a simple, economical synthetic way to produce complicated nanostructured particles that can provide several novel properties favorable for practical applications. It is also more environmentally friendly by avoiding the use of corrosive etching chemicals and external templates.

2 EXPERIMENTAL

2.1 Materials

In this study, the preparation of mesoporous ORMOSIL particles with tailored morphology and/or controlled size by a simple two-step process was reported. The first step, synthesis of monodisperse ORMOSIL particles of uniform size and morphology with multi-layered structure, involved a one-pot process in an aqueous

2.2 Synthesis

2.2.1. Preparation of phenyl, vinyl, and amine based ternary ORMOSIL particles

ORMOSIL particles with phenyl, vinyl, and amino silanes were synthesized as described in previously reported method [15]. A 250 mL Erlenmeyer flask maintained at 60 °C was charged with 156 mL of de-ionized water and 0.2 mL of nitric acid (2.67 mmol, 60 wt. %) was added while stirring at 300 rpm. 3.5 mL of PTMS (17.42 mmol) and 1.5 mL of VTMS (9.62 mmol) were first injected to an acidic aqueous solution, followed by the addition of 0.5 mL APTMS (2.75 mmol). The resulting solution was stirred for 90 seconds to allow hydrolysis followed by the addition of 40 mL of ammonium hydroxide (305 mmol, 30 wt. %) to induce condensation. The mixture became turbid and was stirred for an additional 4 hours. The resulting ORMOSIL particles were filtered through a membrane filter and washed with 10 mL of de-ionized water several times. The filtered products were dried under vacuum at 50 °C for 12 hours and 3.42 g of phenyl-vinyl-amine based ORMOSIL particles was obtained. For ORMOSIL particles having various ratio of silane functionalities, different stoichiometries of silane monomers were used (P:V = 3.5 ml:1.5 ml, 2.5 ml:2.5 ml, 1.5 ml:3.5 ml, 1 ml:4 ml, and 0.5 ml:4.5 ml), while the amount of APTMS was fixed as 0.5 and 1.5 mL, respectively.

2.2.2. Selective dissolution of ternary ORMOSIL particles to produce raspberry shaped, rattle-type, and hollow ORMOSIL particles

0.2 g of phenyl-vinyl-amine based ternary ORMOSIL particles, having the different relative ratio of [PTMS]/[VTMS]/[APTMS], were suspended in a mixed solution containing 100 mL of de-ionized water and 50 mL of ethanol and the resulting mixture was sonicated for dispersion. Then, the suspension was heated at 80 °C for 6 hours. Finally, the reaction mixture was cooled down to room temperature and washed with de-ionized water 4 times. After drying at 50 °C for 12 hours in vacuum oven, raspberry shaped, rattle-type, and hollow ORMOSIL particles were obtained depending on the relative ratio of [VTMS]/[PTMS]/[APTMS].

2.3 Characterizations

The morphologies of mesoporous ORMOSIL particles were investigated with transmission electron microscopy (TEM, JEOL JEM-2000EXII).

3 RESULTS AND DISCUSSION

Overall schematic diagram for the preparation and selective dissolution processes of mesoporous ORMOSIL particles using two step sol-gel process is shown in Figure 1. In the first step, monodispersed ORMOSIL particles with ternary organosilane functional groups were prepared by two step acid-base sol gel process. In acidic conditions, the hydrolysis of a mixture of three organosilane monomers occurred simultaneously and emulsion droplets with homogeneous silane mixtures were formed. In basic conditions, homo and hetero-condensation between the hydrolyzed organosilane mixtures in the emulsion droplets occurred. The mixture of organosilane monomers for ternary ORMOSIL particles included phenyltrimethoxysilane (PTMS) and vinyltrimethoxysilane (VTMS) as a major functional component and 3-aminopropyltrimethoxysilane (APTMS) as minor functional components.

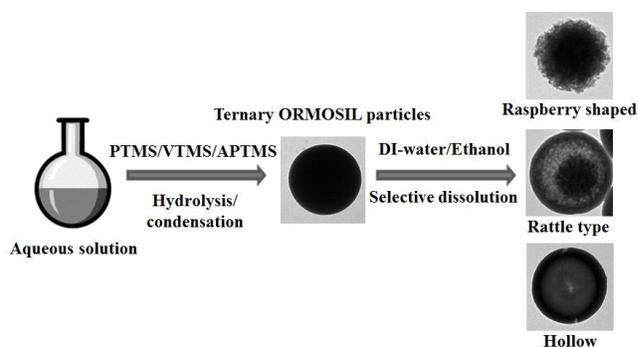


Figure 1: Schematic diagram of the preparation of mesoporous ORMOSIL particles using two step sol-gel process.

In the second step, ORMOSIL particles obtained from a mixture of three organosilanes, PTMS, VTMS, and APTMS, were treated at 80 °C with the 2:1 (v:v) water-ethanol mixture solution for the selective dissolution of the parts of organosiloxane networks formed by the condensation. Raspberry-shaped type, rattle type, or hollow particles were produced depending on the relative volume ratio of the three organosilanes. Figure 2 shows TEM images of the 2:1 (v:v) water-ethanol mixture treated ORMOSIL particles from various mixtures of PTMS-VTMS-APTMS. Particles shown in each row were prepared from mixtures containing a fixed volume of APTMS—0.5 and 1.5 mL of APTMS for top and bottom rows, respectively. In each row, the volumes of PTMS and VTMS were varied as follows: from left to right, 3.5 and 1.5 mL, 2.5 and 2.5 mL, 1.5 and 3.5 mL, 1 and 4 mL, and 0.5 and 4.5 mL. As can be seen from TEM images at the top row in Figure 2, the particles have barely empty inner spaces, where no hollow particles is found, and rattle type particles also have very large cores.

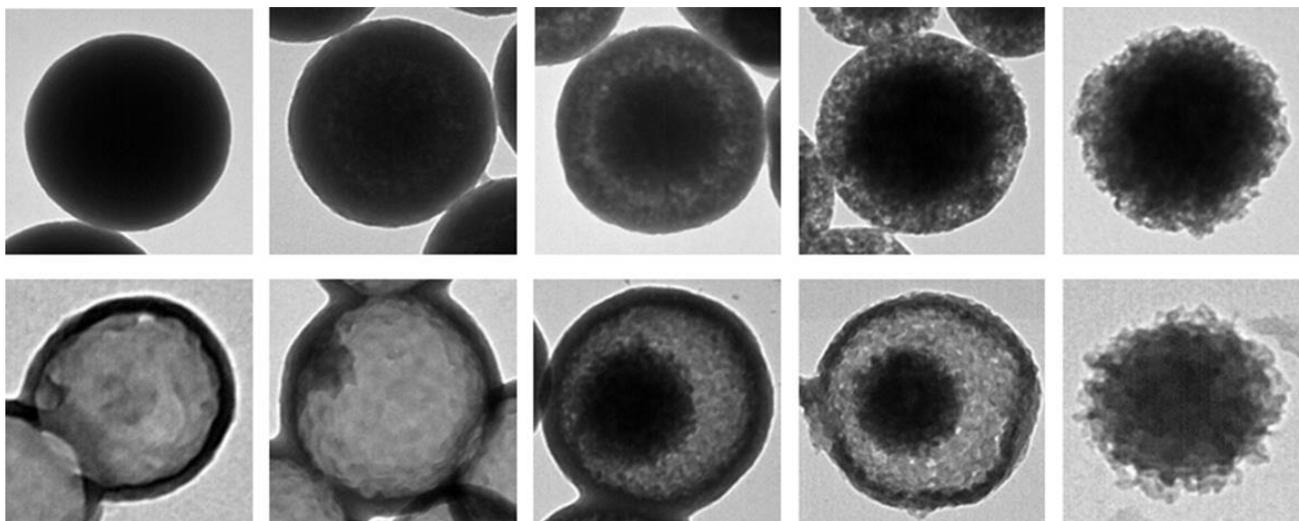


Figure 2: TEM images of PTMS, VTMS, APTMS based ORMOSIL particles after the selective dissolution. (top row) The volume of APTMS in the reaction mixture for the particle was fixed to be 0.5 ml while the volumes of the PTMS and the VTMS were varied as follows: From left to right, 3.5 and 1.5 ml, 2.5 and 2.5 ml, 1.5 and 3.5 ml, 1 and 4 ml, and 0.5 and 4.5 ml. (bottom row) The volume of the APTMS was 1.5 ml and the volumes of the PTMS and the VTMS were the same as top row cases.

In the bottom row, hollow particles and rattle particles are observed. Looking at the images from left to right—the VTMS volume increases while the PTMS volume decreases—the size of core particles inside rattle shaped particles increases but the outer shell thickness decreases. Finally, the particles shown at the right end of the each row—prepared using very low PTMS amount (0.5 mL)—were raspberry type particles. The formation of different structures in ORMOSIL particles after the water-ethanol treatment may be explained by the two main factors: 1) the selective dissolution of aminopropylsiloxane network within the particles by the water-ethanol mixture and 2) internal structure of ORMOSIL particles depending on the relative ratio of organosilane monomers. Taking into account of the relative hydrolysis and condensation rates of the three organosilane molecules, the formation of core parts occurs mainly with VTMS, while middle shells are made by the co-condensation of APTMS and VTMS. Then, hydrophobic PTMS molecules are finally condensed alone or along with other two unreacted organosilanes on the surface of the core-shell intermediate particles, producing a triply layered structure of organosiloxane network. It might also be inferred that the difference in the re-hydrolysis rates of three organosilanes play an important role on the formation of triply layered structures through an Ostwald ripening process. With a low amount of APTMS in the reaction mixture, a low portion of the dissolvable aminosiloxane network would be formed inside the particles. Therefore, it is less likely to form hollow or rattle particles than filled sphere particles as shown in Figure 2 top row. On the other hand, with a fair amount of APTMS

in the reaction mixture, hollow or rattle particles may be formed as in Figure 2 bottom rows. It is interesting to note that the empty space in the particles is much larger than the volume fraction (or mole fraction) of the APTMS in the initial reaction mixture. Although the main components for the core, intermediate shell, and final shell of the ORMOSIL particles are considered to be VTMS, APTMS and PTMS, respectively, each layer may consist of their mixture. When the aminosiloxane network is removed during dissolution process, the neighboring connected VTMS or PTMS based network may be removed together, resulting in larger voids. The variation in the morphology of mesoporous particles depending on the relative ratio of organosilanes in ternary ORMOSIL particles is listed in Table 1. The sizes of mesoporous particles, obtained after the selective dissolution, are also varied with the relative ratio of organosilanes in ORMOSIL particles. As shown in Table 2, the size of mesoporous particles is decreased as the VTMS volume increases regardless of the relative ratio of APTMS in ternary ORMOSIL particles. In previous studies, it has been found that the size of monofunctional ORMOSIL particles prepared from VTMS is usually smaller than that prepared with PTMS. Therefore, it can be expected that the size of ORMOSIL particles would be reduced with the increase in the relative amount of VTMS in organosilane mixtures. It is also confirmed that as the amount of APTMS in ORMOSIL particles increases, the size of mesoporous particles obtained with the treatment of water-alcohol mixture is reduced due to the selective dissolution of organosiloxane networks.

Ratio of Silanes (in ml)	P(3.5)/V(1.5)	P(2.5)/V(2.5)	P(1.5)/V(3.5)	P(1)/V(4)	P(0.5)/V(4.5)
A (0.5)	Sphere	Sphere	Rattle	Raspberry	Raspberry
A (1.5)	Hollow	Rattle	Rattle	Rattle	Raspberry

Table 1: Variation in the morphology of mesoporous particles depending on the relative ratio of organosilanes in ternary ORMOSIL particles. (P: PTMS, V: VTMS, A: APTMS)

Ratio of silanes (in ml)	P(3.5)/V(1.5)	P(2.5)/V(2.5)	P(1.5)/V(3.5)	P(1)/V(4)	P(0.5)/V(4.5)
A (0.5)	373(±9) nm	347(±9) nm	309(±14) nm	301(±19) nm	291(±8) nm
A (1.5)	198(±9) nm	328(±18) nm	222(±18) nm	267(±12) nm	223(±19) nm

Table 2: Variation in the size of mesoporous particles depending on the relative ratio of organosilanes in ternary ORMOSIL particles. (P: PTMS, V: VTMS, A: APTMS)

The results obtained in this study demonstrate that our approach, one-pot synthesis of ORMOSIL particles followed by mild, selective dissolution of organosiloxane network, is capable of producing hollow, rattle and raspberry type particles in a simpler, less time consuming and more environmentally friendly way when compared to the previously reported methods.

4 CONCLUSIONS

In conclusions, we have developed a novel strategy to fabricate monodisperse, nanostructured ternary ORMOSIL particles with tailored morphologies and sizes. It consists of one-pot synthesis of multifunctional ORMOSIL particles using a mixture of three organosilane monomers that have different hydrolysis/condensation rates and different solubility characteristics towards water-alcohol mixtures and a dissolution process that treats ternary ORMOSIL particles with this mixed solvent. It is a universal method in that all the experimental details to prepare the different type of mesoporous particles, raspberry shaped, hollow, and rattle type are the same except for the combination of organosilane monomers in the reaction mixtures. The size and morphology of mesoporous ORMOSIL particles could be easily adjusted by simply changing the relative ratios of PTMS, VTMS and APTMS in reaction mixture for ORMOSIL particles. The strategy developed in this study could be extended to synthesize other raspberry shaped, hollow, and rattle type structures with various chemical compositions and hence to develop nanostructured materials with novel properties that can satisfy the needs of various applications such as drug delivery, nano-reactors, and catalysts.

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