

Morphology and size control of mesoporous ORMOSIL particles prepared from organosilane mixtures

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Mesoporous organically modified silica (ORMOSIL) particles, having various morphologies such as raspberry-shaped, hollow, rattle-type, as well as solid sphere structures, were synthesized through selective etching of organosiloxane groups in ORMOSIL particles prepared using a simple two-step process. The first step, synthesis of monodisperse ORMOSIL particles, utilized a one-pot process in an aqueous solution of a mixture comprised of various combinations of organosilane monomers: 3-aminopropyltrimethoxysilane (APTMS), vinyltrimethoxysilane (VTMS), 3-mercaptopropyltrimethoxysilane (MPTMS), methyltrimethoxysilane (MTMS), and phenyltrimethoxysilane (PTMS). In the second step, the ORMOSIL particles were treated with a mixture of water and alcohol with mild heating. This process was employed to selectively etch some of the organosiloxane groups 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 type and relative concentration of 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.

Key words: Size control, Morphology, Mesoporous ORMOSIL, Selective etching, Organosilane mixtures.

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 remarkable properties, such as large surface area, controlled pore size, and low density [1-3]. For examples, hollow spheres are widely used in industrial and biological fields as nano/micro reactors and drug-delivery systems [4-7]. Rattle-type particles with a core-void-shell structure have also recently emerged as attractive nanostructured materials that have great potential for use in catalysts, bio-medicine, and lithium-ion batteries [8-10]. In addition, raspberry-shaped materials with high surface roughness have been used for self-cleaning and anti-fogging applications due to their super-hydrophobicity [11-13].

Various preparation techniques have been employed to produce the mesoporous particles with controlled morphology and size. For hollow and rattle-type particles, the template based selective etching method has been used as the most effective strategy [14-16]. Hard and/or soft templates are used and then successive coating of different materials is employed in order to obtain multi-layered structures. Then, the removal of the core or middle layer by etchants or calcination produces hollow or rattle-type particles. Raspberry-shaped particles are commonly obtained by

self-assembling of particles with different sizes or by selective etching of the surface of multi-layered particles [17, 18]. However, these methods are often faced with several problems: 1) the multiple steps in synthesis are required, which is often quite tedious, 2) the etching agents used in the synthesis are usually strong acids or bases that are extremely hazardous and so are difficult to handle [19, 20], and 3) calcination at high temperature often causes collapse of the porous shell or the entire morphology [21, 22]. For wider economical applications, the development of a simple and efficient preparation method for mesoporous particles of various sizes and structures is of great importance.

This study reports the preparation of mesoporous organically modified silica (ORMOSIL) particles with controlled morphology and size using a simple two-step process. The first step, synthesis of monodisperse ORMOSIL particles of uniform size and morphology, involved a one-pot process in an aqueous solution using the mixture of various combination of organosilane monomers. In the second step, the ORMOSIL particles were treated with a mixture of water and alcohol with mild heating. This process was employed to selectively etch some of the organosiloxane groups 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 type and relative concentration of silane monomers. Compared to the previously developed synthetic methods, our method offers a simple, economical,

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and environmentally friendly way to produce complicated mesoporous ORMOSIL particles that can provide several novel properties favorable for practical applications. The described method is also more environmentally friendly as it avoids the use of corrosive etching chemicals and external templates.

Experimental

Materials

Phenyltrimethoxysilane (PTMS, 97%, Alfa Aesar), vinyltrimethoxysilane (VTMS, 98%, Alfa Aesar), 3-mercaptopropyltrimethoxysilane (MPTMS, 97%, Fluka), 3-aminopropyltrimethoxysilane (APTMS, 97%, Aldrich), and methyltrimethoxysilane (MTMS, 95%, Aldrich), were used without further purification. Ammonium hydroxide solution (30% as NH_3) and nitric acid (60%) were obtained from Sam-Chun Chemicals. Ethyl alcohol (EtOH, 99%, Sam-Chun Chemicals), isopropyl alcohol (iPr-OH, 99.5%, Sam-Chun Chemicals), acetonitrile (CH_3CN , 99.5%, Daejung Chemicals and Metals), tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$, 99%, Daejung Chemicals and Metals), and de-ionized (DI) water were used as solvents throughout entire synthesis.

Synthesis

Preparation of PTMS, VTMS, and APTMS based ternary ORMOSIL particles

ORMOSIL particles with phenyl, vinyl, and amino silanes were synthesized as described in the previously reported method [23]. A 250 mL Erlenmeyer flask maintained at 60 °C was charged with 156 mL of de-ionized water, and then 0.2 mL of nitric acid (2.67 mmol, 60%) was added while stirring at 300 rpm. Next, 3.5 mL of PTMS (17.42 mmol) and 1.5 mL of VTMS (9.62 mmol) were 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%) to induce condensation. The mixture became turbid and was stirred for an additional four hours. The resulting ORMOSIL particles were filtered through a membrane and washed several times with 10 mL of de-ionized water. 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 ratios of silane functionalities, different stoichiometry values of silane monomers were used ($\text{P} : \text{V} = 3.5 \text{ mL} : 1.5 \text{ mL}$, $2.5 \text{ mL} : 2.5 \text{ mL}$, $1.5 \text{ mL} : 3.5 \text{ mL}$, $1 \text{ mL} : 4 \text{ mL}$, and $0.5 \text{ mL} : 4.5 \text{ mL}$), while the amount of APTMS was fixed at 0.5 and 1.5 mL ($[\text{P} + \text{V}] : \text{A} = 10 : 1$ and $10 : 3$ in $\text{v} : \text{v}$), respectively.

Preparation of binary ORMOSIL particles with various combination of organosilane monomers

Binary composite ORMOSIL particles with vinylsilane

and aminosilane functional groups were synthesized as described in previously reported method [23]. 156 mL of de-ionized water was placed in a 250 mL three-neck round bottom flask, while maintaining at temperature of 60 °C, and 0.2 mL of nitric acid (60%, 2.67 mmol) was added with stirring at 300 rpm. 5 mL of VTMS (32.06 mmol) was added to an acidic aqueous solution, followed by the addition of 0.5 mL of APTMS. After stirring for one minute, 40 mL of ammonium hydroxide (30%, 305 mmol) was poured into the reaction mixture to induce condensation. The solution became turbid, indicating the formation of colloidal particles. After stirring for 4 hours, the suspension was filtered through a membrane filter (Osmonics, pore size of 400 nm) and the filtered product was washed with 10 mL of de-ionized water three times. The product was dried under vacuum at 50 °C for 12 hours and 2.2 g of vinyl-amine based ORMOSIL particles was obtained.

For other binary composite ORMOSIL particles, various combination of organosilane monomers were used (PTMS/VTMS, PTMS/APTMS, MPTMS/APTMS, and MTMS/APTMS).

Selective etching of ternary ORMOSIL particles to produce raspberry-shaped, rattle-type, and hollow ORMOSIL particles

The first step of this process was suspension of 0.2 g of phenyl-vinyl-amine based ternary ORMOSIL particles with different relative ratios of $[\text{PTMS}]/[\text{VTMS}]/[\text{APTMS}]$ in a mixed solution containing 100 mL of de-ionized water and 50 mL of ethanol. The resulting mixture was sonicated for dispersion and then heated at 80 °C for six hours. Finally, the reaction mixture was cooled to room temperature and washed four times with de-ionized water. After drying at 50 °C for 12 hours in a vacuum oven, raspberry-shaped, rattle-type, and hollow ORMOSIL particles were obtained depending on the relative ratio of $[\text{VTMS}]/[\text{PTMS}]/[\text{APTMS}]$.

Characterizations

Chemical compositions of ORMOSIL particles were characterized using FT-IR (AAB FTLA2000) and solid state ^{13}C NMR (Bruker Advance II) spectrometer. The morphologies of ORMOSIL particles before and after selective etching were investigated with transmission electron microscopy (TEM, JEOL JEM-2000EXII) and scanning electron microscopy (FE-SEM, JEOL JEM-6340F).

Results and Discussion

For ternary ORMOSIL particles

An overall schematic diagram of the preparation and selective etching processes of mesoporous ORMOSIL particles using a two-step sol-gel process is shown in Fig. 1. In the first step, monodispersed ORMOSIL

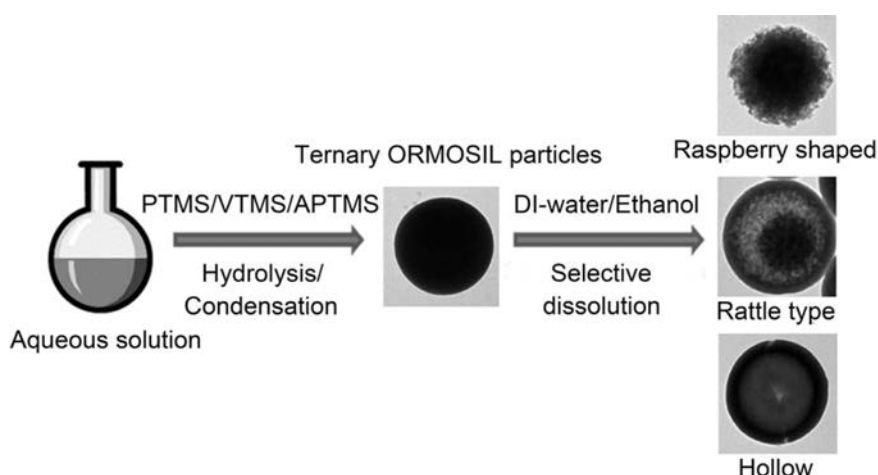


Fig. 1. Schematic diagram of the preparation of mesoporous ORMOSIL particles using a two-step sol-gel process.

particles with ternary organosilane functional groups were prepared through a two-step acid-base sol gel process. In acidic conditions, the hydrolysis of a mixture of three organosilane monomers simultaneously occurred, and emulsion droplets with homogeneous silane mixtures were formed. In basic conditions, homo- and hetero-condensation occurred between the hydrolyzed organosilane mixtures in the emulsion droplets. The mixture of organosilane monomers for ternary ORMOSIL particles included phenyltrimethoxysilane (PTMS) and vinyltrimethoxysilane (VTMS) as major functional components and 3-aminopropyltrimethoxysilane (APTMS) as a minor functional component.

The existence of multiple functional groups in ORMOSIL particles was confirmed by FT-IR and solid state ^{13}C NMR spectra as shown in Fig. 2. The FT-IR spectrum exhibits characteristic stretching vibrational absorption bands for the corresponding organosilane functionalities such as unsaturated C-H stretching vibrations from vinyl and phenyl groups between 3050 and 3100 cm^{-1} and C-H stretching vibrations from aliphatic aminopropyl groups at 2900 cm^{-1} . In addition, CH_2 stretching deformation from vinyl groups and C-C ring stretching vibration from phenyl groups were observed at 1411 and 1430 cm^{-1} , respectively. However, N-H stretching vibrations from aliphatic amino-propyl groups could not be found due to relatively small amount compared to other two functional groups in ternary ORMOSIL particles. Vibrational absorption peaks around 1000–1200 cm^{-1} corresponding to Si-O and Si-C functional groups were also observed. Solid-state ^{13}C NMR analysis reveals typical carbon resonance peaks for the three functional groups. For instance, strong peaks between 125 and 140 ppm are from unsaturated carbons, demonstrating the presence of vinyl and phenyl functionality, while the peaks between 0 and 50 ppm correspond to aliphatic carbons from aminopropyl functional groups.

In the second step, ternary ORMOSIL particles, based on PTMS, VTMS, and APTMS, were added to

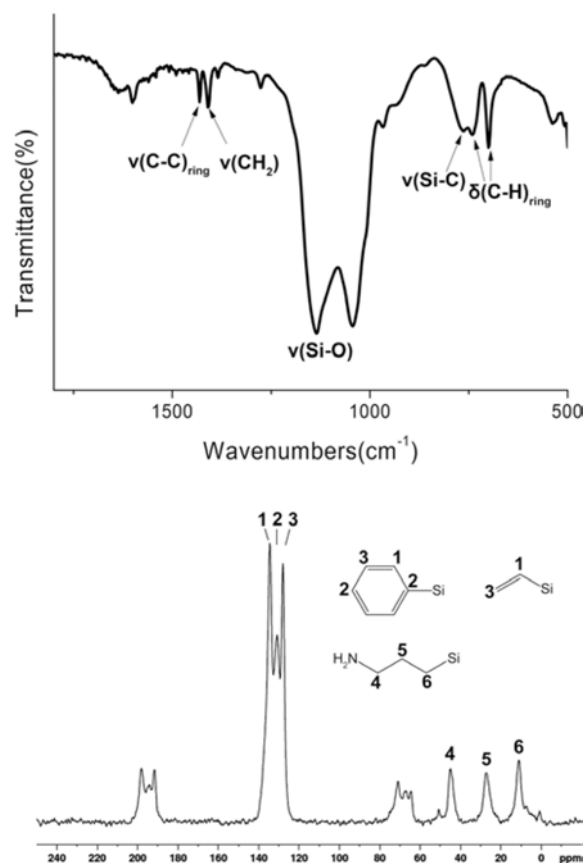


Fig. 2. Structural drawing, FT-IR (ν = stretch, δ = bend), and solid state ^{13}C NMR spectra of PTMS, VTMS, and APTMS based ternary ORMOSIL particles.

2 : 1 (ν : ν) water-ethanol solution at 80 $^{\circ}\text{C}$ for selective etching of the organosiloxane groups formed by the condensation. Raspberry-shaped, rattle-type, or hollow particles were obtained depending on the relative ratio of the three organosilanes. Fig. 3 shows TEM images of the selectively etched ORMOSIL particles prepared from various ratios of PTMS-VTMS-APTMS. Particles shown in top and bottom row were prepared from mixtures containing a fixed volume of APTMS-0.5 and

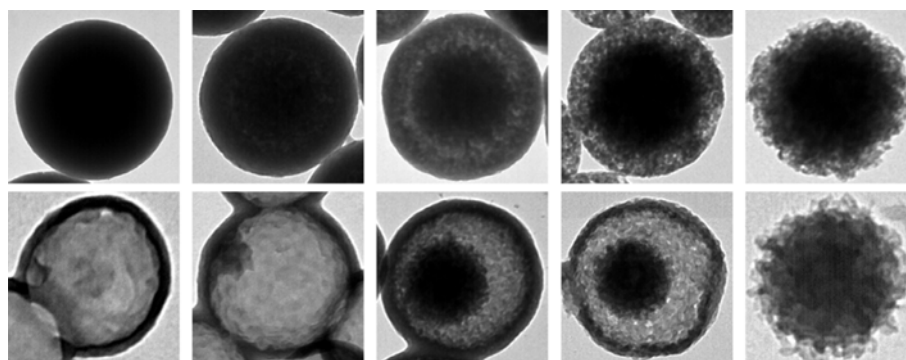


Fig. 3. TEM images of PTMS, VTMS, and APTMS based ORMOSIL particles after selective etching. (top row) The volume of APTMS in the reaction mixture for the particle was fixed at 0.5 ml, while the PTMS and VTMS volumes were varied as follows: from left to right, 3.5 and 1.5 ml, 2.5 and 2.5 ml, 1.5 and 3.5 ml, 1 and 4 ml, and 0.5 and 4.5 ml, respectively. (bottom row) The volume of the APTMS was 1.5 ml, and the volumes of the PTMS and the VTMS were the same as noted for the top row.

1.5 mL of APTMS, 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, respectively. As can be seen from the TEM images in the top row of Fig. 3, the particles had very small, empty inner spaces, where no hollow particles are found, while the rattle-type particles also had very large cores. For ternary ORMOSIL particles having the volume ratio of VTMS/PTMS larger than 4/1, raspberry-shaped particles were formed after the selective etching. In the bottom row, hollow particles and rattle particles are visualized. The formation of different structures in ORMOSIL particles after water-ethanol treatment can be explained by following factors: 1) the selective etching of the aminopropylsiloxane group in ORMOSIL particles by the water-ethanol mixture and 2) the formation of different internal structure in ORMOSIL particles depending on the change in the ratio of organosilane monomers. Taking into account the different hydrolysis/condensation rates of the organosilane monomers, the core part is formed by mainly with VTMS, while the middle shells are made by the co-condensation of APTMS and VTMS. Finally, PTMS monomers are condensed on the surfaces of the core-middle shell intermediate particles, thereby producing a triple-layered structure. As the amount of APTMS in the reaction mixture increases, a proportion of amino-siloxane

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/V 3.5/1.5	P/V 2.5/2.5	P/V 1.5/3.5	P/V 1/4	P/V 0.5/4.5
A (0.5)	Sphere	Sphere	Rattle	Raspberry	Raspberry
A (1.5)	Hollow	Rattle	Rattle	Rattle	Raspberry

network formed inside the particles also increases, producing hollow or rattle-like particles, as shown in the bottom rows of Fig. 3. The variation in the morphology of mesoporous particles depending on the relative ratio of organosilanes in ternary ORMOSIL particles is summarized in Table 1.

SEM images of PTMS, VTMS, and APTMS based ternary ORMOSIL particles after the selective etching were shown in Fig. 4. It could be found that for hollow and rattle type ORMOSIL particle, SEM image shows spherical particles having smooth surfaces with monodispersity in size and shape, while the rougher surfaces were formed for raspberry shaped particles.

The sizes of mesoporous particles, obtained after the selective etching, are also varied with the relative ratio of organosilanes (PTMS : VTMS) in ternary ORMOSIL particles. As shown in Fig. 5 (a), the size of mesoporous particles decreases from $373(\pm 9)$ nm to $291(\pm 8)$ nm as

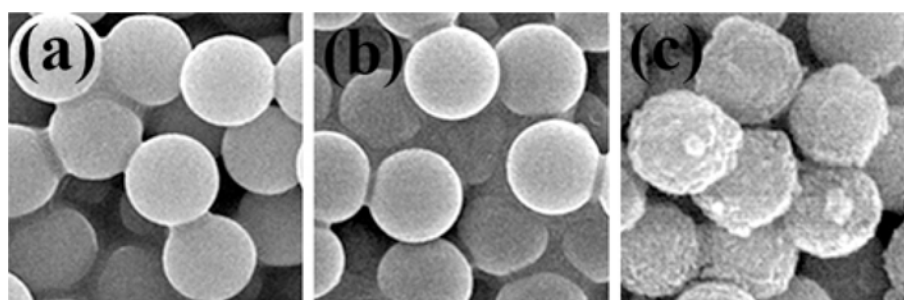


Fig. 4. SEM images of PTMS, VTMS, and APTMS based ternary ORMOSIL particles after the selective etching: (a) hollow (b) rattle-type, and (c) raspberry-shaped particles.

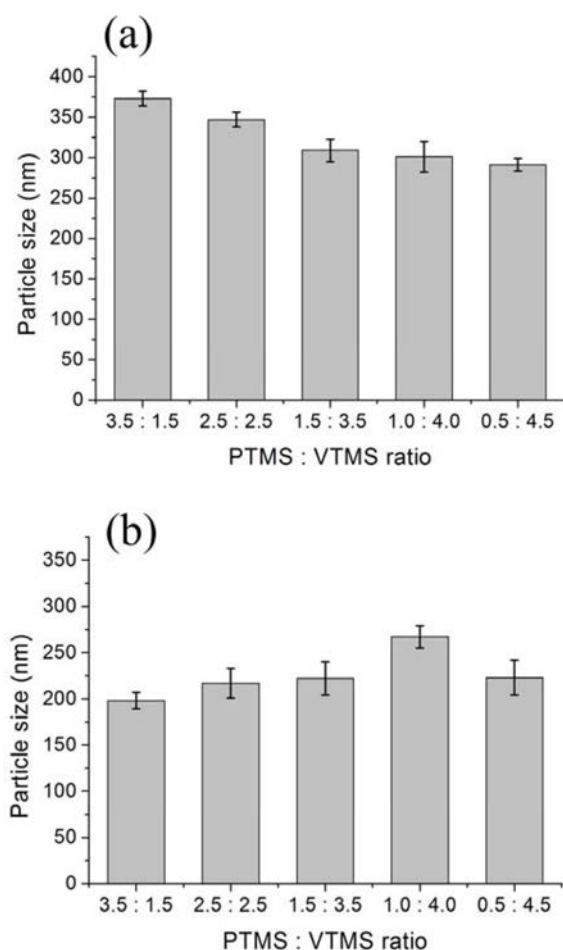


Fig. 5. Variation in the size of mesoporous particles depending on the relative ratio of organosilanes (PTMS : VTMS) in ternary ORMOSIL particles. (a) 0.5 mL of APTMS and (b) 1.5 mL of APTMS.

the volume ratio of VTMS/PTMS (v/v in mL) increases from 1.5/3.5 to 4.5/0.5, when the amount of APTMS in ternary ORMOSIL particles was 0.5 mL. Previous studies have found that the sizes of mono-functional ORMOSIL particles prepared from VTMS are usually

smaller than those prepared with PTMS. Therefore, it can be expected that the sizes of ORMOSIL particles would be reduced with an increase in the relative amount of VTMS in organosilane mixtures. It was also confirmed that, as the amount of APTMS in ORMOSIL particles increases to 1.5 mL, the size of mesoporous particles obtained after the selective etching is reduced further to $198(\pm 9)$ nm for VTMS/PTMS = 1.5/3.5 and $223(\pm 19)$ nm for VTMS/PTMS = 4.5/0.5, compared to the case of 0.5 mL of APTMS used, as can be seen in Fig. 5 (b). However, no evident relationship between the size and the relative ratio of organosilanes (PTMS : VTMS) in ternary ORMOSIL particles could be found. It might be explained that the amount of selectively etched organosiloxane in ternary ORMOSIL particles is the major factor to determine the size of mesoporous particles after the selective etching.

For binary ORMOSIL particles

Binary ORMOSIL particles with various combination of organosilane monomers were also synthesized using a similar method as described earlier. Four different binary ORMOSIL particles based on RTMS (R = mercaptopropyl, phenyl, methyl, or vinyl) and APTMS were prepared using the relative volume ratio of RTMS:APTMS = 10 : 1 and etched selectively with 2 : 1 (v : v) water-ethanol solution at 80 °C. Fig. 6 exhibits SEM and TEM images of binary ORMOSIL particles before and after selective etching. It could be found that there was no sign of the formation of mesoporous particles, irrespective of the type of the organosilane monomers used. All binary ORMOSIL particles, except the ones from the combination of VTMS and APTMS, maintained hard spheres even after selective etching, suggesting that the co-presence of VTMS and APTMS is required for the development of mesoporous structures. SEM images also shows that the sizes of particles are varied with the different combination of organosilane monomers in binary ORMOSIL particles. As shown in Fig. 7, the

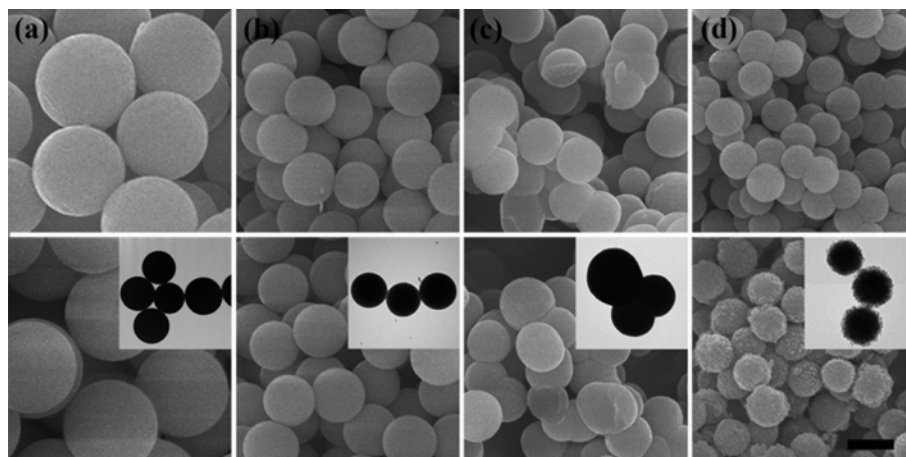


Fig. 6. SEM and TEM (inset) images of binary ORMOSIL particles before (top) and after (bottom) selective etching: a) MPTMS-APTMS, b) PTMS-APTMS, c) MTMS-APTMS, and d) VTMS-APTMS. The volume ratio of RTMS:APTMS = 10 : 1. Bar = 500 nm.

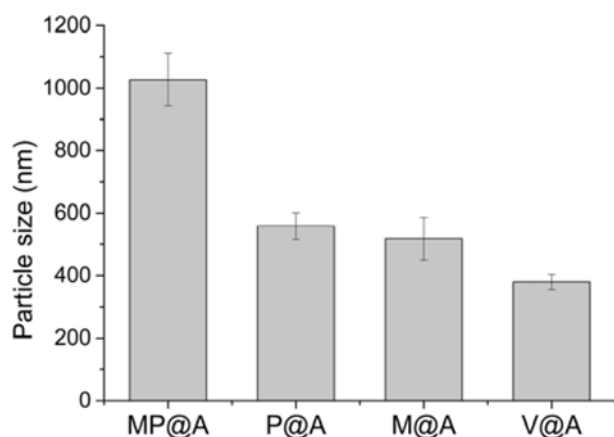


Fig. 7. Variation in the size of binary ORMOSIL particles before selective etching: a) MPTMS-APTMS, b) PTMS-APTMS, c) MTMS-APTMS, and d) VTMS-APTMS based ORMOSIL particles.

size of binary ORMOSIL particles decreases from 1027(± 84) nm to 558(± 43), 518(± 68), and 379(± 25) nm as the type of organosilane monomers changes from MPTMS to PTMS, MTMS, and VTMS, while the volume ratio of RTMS : APTMS is fixed at 10 : 1. It has been known that the sizes of mono-functional ORMOSIL particles were decreased from MPTMS to PTMS, MTMS, and VTMS. Therefore, it could be postulated that APTMS, a second organosilane monomer, in binary ORMOSIL particles has no effect on the size of binary ORMOSIL particles.

Conclusions

In summary, we prepared mesoporous ORMOSIL particles with controlled morphologies and sizes. The process consists of 1) one-pot synthesis of binary or ternary ORMOSIL particles using a mixture of organosilane monomers that have different hydrolysis/condensation rates and 2) subsequent selective etching process by means of different solubility characteristics of organosilane groups in water-alcohol mixtures. The method described herein is universal in a point that the same experimental conditions for different mesoporous structures are employed and the size and morphology of mesoporous ORMOSIL particles could be easily adjusted by simply changing the combination and relative ratios of organosilanes, such as MPTMS, PTMS, MTMS, VTMS, and APTMS, in the reaction mixture. The strategy developed in this study is not only a simpler, less time-consuming, and more environmentally friendly way than previous methods, but also could be applied to other types of mesoporous particles with novel properties that can satisfy the needs of various applications in nano- and bio-technologies.

Acknowledgments

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