Facile synthesis of tailored nanostructured ORMOSIL particles by a selective dissolution process

Jong Woong Park, Jung Soo Kim, Tae Jae Park, Euk Hyun Kim, Sang Man Koo*

Department of Chemical Engineering, Hanyang University, Seoul 133-791, Republic of Korea

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Tailored nanostructured ORMOSIL particles, of raspberry shaped, hollow, and rattle type structures, were prepared by a selective dissolution of siloxane networks in composite ORMOSIL particles with a multi-layered structure. The synthesis of monodisperse ORMOSIL particles involved a one-pot process in an aqueous solution using a binary or ternary mixture from three organosilanes, (3-aminopropyl)trimethoxysilane (APTMS), vinyltrimethoxysilane (VTMS), and/or phenyltrimethoxysilane (PTMS). In the following step, ORMOSIL particles were treated with a mixture of water and alcohol with mild heating. This mild etching process was efficient to selectively dissolve some of organosilane functional groups within the ORMOSIL particles but not their main silica frameworks, leading to formation of mesoporous particles. The strategy developed in this study is not only very facile, economical, and less time-consuming, but also more environmentally friendly by avoiding the use of corrosive etching chemicals and harsh reaction conditions. Surface roughness, core diameter, and shell thickness of the resultant mesoporous ORMOSIL particles were controlled by manipulating synthetic parameters such as the relative ratios of the silane monomers as well as the dissolution parameters such as temperature and type of solvent.

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1. Introduction

Nanostructured materials with tailored morphology have attracted intense interest in diverse fields of nanotechnology due to their extraordinary properties, such as large surface area, controlled pores and channels, permeability, and low density [1–4]. For examples, 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 [5–8]. Hollow spheres of sub-micron size are widely used in industrial field as light weight substances and nano/micro reservoirs [9–11]. Rattle-type particles—kind of hollow 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 [12–20].

A variety of synthetic methods have been developed to produce these nanomaterials. For hollow and rattle type particles, the template-assisted selective etching approach has been considered to be the most effective strategy and thereby is commonly used [2,21–23]. Briefly, hard/soft templates are selected and then subjected to sequential coating of different materials to form multi-layered structures. By removing the core or the middle layer by etching agent or calcination, hollow or rattle type particles can be formed. 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 [24–27]. However, these methods are often associated with a couple of problems. First, the synthetic methods consist of multiple steps that are often quite tedious. They are also difficult to scale up. Second, the etching agents so far used in the synthesis process are strong acids or bases—such as NaOH, Na2CO3, HF, and so on—that are extremely corrosive and toxic, hence the handling is not convenient [22,23,28–30]. Calcination at high temperature is another way to generate hollow/rattle structures, but it often causes the porous shell or the entire morphology to collapse.

In this study, tailored nanostructured ORMOSIL particles, of raspberry shaped, hollow, and rattle type structures, were prepared by a simple two-step process: (1) one-pot synthesis of composite ORMOSIL particles with a multi-layered structure, without using any templates; (2) selective dissolution process with a non-corrosive mild etching agent. Compared to the previously developed synthetic methods, our strategy is very facile, economical, and less time-consuming by employing a one-pot synthetic method that does not require external templates for preparing the multi-layer particles.
It is also more environmentally friendly by avoiding the use of corrosive etching chemicals. The first step, synthesis of monodisperse ORMOSIL particles, involved a one-pot process in an aqueous solution using a binary or ternary mixture from three organosilanes, 3-aminopropyltrimethoxysilane (APTMS), vinyltrimethoxysilane (VTMS), and/or phenyltrimethoxysilane (PTMS). It is supposed that thus prepared ORMOSIL particles have heterogeneous multi-layered structures due to difference in the hydrolysis/condensation rates of the silane monomers in the initial reaction mixture solution. In the second step, the 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 organosilane functional groups within the ORMOSIL particles but not their main silica frameworks, leading to formation of mesoporous particles. Surface roughness, core diameter, and shell thickness of the resultant particles were controlled by manipulating synthetic parameters such as the relative ratios of the silane monomers as well as the dissolution parameters such as temperature and type of solvent. The proposed method offers a simple, economical way to produce complicated nanostructured particles that can provide several novel properties favorable for practical applications. For instance, raspberry shaped particles obtained from VTMS–APTMS based ORMOSIL particles exhibited super-hydrophobicity, a very useful property for producing non-adhesive and water-repellent surfaces.

2. Experimental section

2.1. Materials

Phenyltrimethoxysilane (PTMS, 97 wt%, Alfa Aesar), vinyltrimethoxysilane (VTMS, 98 wt%, Alfa Aesar), and 3-aminopropyltrimethoxysilane (APTMS, 97 wt%, Aldrich) were used without further purification. Ammonium hydroxide solution (30 wt% as NH₃) and nitric acid (60 wt%) were obtained from Sam-Chun Chemicals. Ethyl alcohol (EtOH, 99%, Sam-Chun Chemicals), isopropyl alcohol (iPr-OH, 99.5%, Sam-Chun Chemicals), acetonitrile (CH₃CN, 99.5%, Daejung Chemicals and Metals), tetrahydrofuran (C₅H₅O, 99%, Daejung Chemicals and Metals), and de-ionized (DI) water were used as solvents throughout entire synthesis.

2.2. Syntheses

2.2.1. Preparation of VTMS and APTMS based ORMOSIL particles

ORMOSIL particles with different compositions of vinylsilane and aminosilane were synthesized as described in previously reported method [31]. 156 ml of de-ionized water was placed in a 300 ml three-neck round bottom flask while maintaining a temperature of 60 °C, and 0.2 ml of nitric acid (2.75 mmol, 60 wt%) 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 APTMS with various stoichiometric ratios (0.5, 1, and 1.5 ml; 2.75, 5.50, and 8.25 mmol). After stirring for 90 s, 40 ml of ammonium hydroxide (635 mmol, 30 wt% as NH₃) was poured into the reaction mixture to induce condensation. The solution became turbid, indicating the formation of colloidal particles. After stirring for 4 h, the suspension was filtered through a membrane filter (Osmonics, pore size of 400 nm) and the filtered product was washed with 200 ml of de-ionized water three times. The product was dried under vacuum at 50 °C for 12 h and 2.24 g of vinyl-amine based ORMOSIL particles was obtained.

2.2.2. Preparation of PTMS and APTMS based ORMOSIL particles

The same experimental procedure and volume ratios of organosilanes as above were used except phenyltrimethoxysilane was used instead of vinyltrimethoxysilane.
2.2.3. Preparation of phenyl, vinyl, and amine based ORMOSIL particles
ORMOSIL particles with phenyl, vinyl, and amino silanes were also synthesized as described in previously reported method [31]. 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 (2.75 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 1.0 ml APTMS (5.50 mmol). The resulting solution was stirred for 90 s to allow hydrolysis followed by the addition of 40 ml of ammonium hydroxide (635 mmol, 30 wt% as NH₃) to induce condensation. The mixture became turbid and was stirred for an additional 4 h. 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 h 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 (PTMS:VTMS = 5 ml:0 ml, 3.5 ml:1.5 ml, 2.5 ml:2.5 ml, 1.5 ml:3.5 ml, 1 ml:4 ml, and 0 ml:5 ml), while the amount of APTMS was fixed as 0.5, 1, and 1.5 ml, respectively.

2.2.4. Formation of raspberry shaped ORMOSIL particles
0.2 g of vinyl-amine based ORMOSIL particles 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 h. 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 h in vacuum oven, raspberry shaped ORMOSIL particles were obtained.

2.2.5. Formation of hollow or rattle type ORMOSIL particles
0.2 g of phenyl-vinyl-amine based ORMOSIL particles 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 h. 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 h in vacuum oven, hollow or rattle type ORMOSIL particles were obtained depending on relative amount of phenyl and vinyl silanes.

2.3. Characterizations
Chemical compositions of ORMOSIL particles before and after selective dissolution were characterized using FT-IR (AAB FTLA2000) spectrometer. The morphologies of ORMOSIL particles before and after selective dissolution were investigated with transmission electron microscopy (TEM, JEOL JEM-2000EXII) and scanning electron microscopy (FE-SEM, JEOL JEM-6340F). Chemical compositions and morphologies of ORMOSIL particles after heat treatment have been investigated by the above mentioned methods. Water contact angle (WCA) was measured by contact angle meter (KRUSS DAS100). Flat ORMOSIL particle films on glass substrates were obtained by a screen printing using a paste mixture of 50 wt% ORMOSIL particle and decane and drying at 150 °C for 30 min. N₂ adsorption–desorption isotherm were investigated using BET measurement (Tristar II 3020 system, Micrometrics).

3. Results and discussion
First, ORMOSIL particles based on binary organosilane mixtures were investigated. For ORMOSIL particles obtained from a mixture of VTMS and APTMS, with a volume ratio of 10:1, 10:2 and 10:3, the dissolution of the particles—of a sphere shape with a smooth surface—in a mixture solution of 100 ml de-ionized water and 50 ml ethanol at 80 °C yielded raspberry shaped particles as demonstrated by representative images by TEM (Fig. 1a). However, ORMOSIL particles prepared using only VTMS maintained the same smooth-surfaced spherical morphology before and after the dissolving process (Fig. 1b). This suggests that APTMS may be a key component for the part of the ORMOSIL particles that is dissolved by the water–ethanol mixture, thereby leading to formation of raspberry particles from the VTMS–APTM based ORMOSIL particles. Note that these raspberry shaped ORMOSIL particles could be converted to raspberry shaped inorganic silica particles by the heat treatment at 600 °C in air, as will be discussed later.

The ORMOSIL particles were also prepared from a mixture of PTMS and APTMS, with the same volume ratio as that for PTMS–APMTMS based ORMOSIL particles, i.e., 10:1, 10:2 and 10:3, as well as from PTMS only. When these particles were treated with the 2:1 (v:v) water–ethanol mixture solution, there was no sign of dissolution of the particles and the particles were intact (Fig. 1c). However, when treated with the 1:2 (v:v) water–ethanol mixture—the relative amount of ethanol in the dissolution solution was doubled—hollow particles were produced (Fig. 1d).

Formation of raspberry-shaped particles from the VTMS–APTM based particles and hollow particles from the PTMS–APTM based particles indicates that APTMS monomers were condensed mostly on the shell for VTMS–APTM ORMOSIL particles while they were mostly in the core for PTMS–APTM ORMOSIL particles. This also suggests that the internal structure developed within ORMOSIL particles may be another key factor for formation of different types of mesoporous particles. It is known that different organosilanes exhibit different hydrolysis and condensation rates, which may result in heterogeneous distribution of organosilanes inside the condensed network of ORMOSIL particles. Considering steric, inductive, and solubility effects of organosilanes, their hydrolysis and condensation rates decrease as VTMS > APTMS > PTMS. During the synthesis of ORMOSIL particles from a mixture of VTMS and APTMS, following steps may occur: Upon addition of the VTMS–APTMS mixture in aqueous solution, first, condensation of some of VTMS molecules occurs to construct a homogeneous network that forms the core of the particles. Then, the slower reacting APTMS molecules and some of the unreacted VTMS molecules are co-condensed at surfaces of the core particles to form the shell of the particles. Treating the particles with the 2:1 (v:v) water–ethanol mixture dissolve selectively the structure made from mostly APTMS. It was found that the surfaces of raspberry shaped particles became rougher when the volume ratio of APTMS to VTMS used in the reaction mixture to form ORMOSIL particles was increased from 10% to 30% (v/v) (Fig. S1). However, when the volume of APTMS in the reaction mixture was exceeded more than 40% of the VTMS volume, the ORMOSIL particles were disintegrated after being treated with the water–ethanol mixture (Fig. S1). These two findings are in good accordance with our suggested mechanism.

Further supporting evidence about the dissolution of the APTMS-based network can be found from the calculated product yields for the raspberry particles. The calculated yields to produce the raspberry particles from the VTMS–APTMS based ORMOSIL particles were 31 wt% for the particles from 10:1 (v:v) VTMS–APTMS mixture but 18 wt% for the particles from 10:2 (v:v) VTMS–APTMS mixture. This demonstrates that higher the amount of APTMS is, more the amount of organosilanes were dissolved out from ORMOSIL particles. The low product yields for both cases indicate that not only the APTMS based network but also the neighboring VTMS-based network may be dissolved.

During the synthesis of ORMOSIL particles from a mixture of PTMS and APTMS, the hydrolysis/condensation reactions of APTMS
monomers may precede those of PTMS monomers so that the APTMS monomers mainly form a core network and the PTMS monomers form a shell. We note that the very hydrophobic PTMS based shell may prevent the 2:1 (v:v) water–ethanol mixture solution from entering into the core and thereby from dissolving the aminopropylsilane groups. However, the 1:2 water–ethanol mixture may be able to penetrate the PTMS-based shell to reach and dissolve it, forming hollow particles (Fig. 1d). We note that in our previous studies, PTMS based ORMOSIL particles were found to be intact after being treated with a water–ethanol mixture but yielded hollow particles when treated with pure ethanol [32,33]. Moreover, mesoporous particles were prepared by acetone treatment that dissolves selectively the phenylsiloxane network inside the ORMOSIL particles [34].

All these current and previous findings indicate that selection of right dissolving solvent—that have enough lyophilicity/hydrophilicity to wet and penetrate the hydrophobic/hydrophilic structure and that could dissolve the desired organosiloxane network selectively—is important to obtain the ORMOSIL particles of desired mesoporous structures using the proposed method here. We tested several different types of solvents for selective dissolution of aminopropylsiloxane network inside the ORMOSIL particles prepared from VTMS–APTMS mixture (Fig. S2). When the particles were treated only with an organic solvent such as iso-propanol, acetonitrile, acetone, or tetrahydrofuran, the particles were intact. However, when the particles were treated with a 2:1 (v:v) mixture solution of water and one of the above organic solvents, raspberry shaped particles were produced as in the case of the 2:1 (v:v) water–ethanol mixture. This indicates that water is an essential element in the formation of mesoporous particles by selective dissolution.

The hydrophobicity of raspberry shaped particles and VTMS based or VTMS–APTMS based ORMOSIL particles without dissolution process was examined by measuring the water contact angle (WCA) on a glass substrate coated with each type of particles as shown in Fig. 2. Note that WCA on a substrate is a good measure of the relative hydrophobicity or hydrophilicity of a substrate. A high WCA translates to a hydrophobic surface. It is known that hydrophobicity of particles can be controlled by surface compositions as well as surface roughness and porosity [8,35–37].

![Fig. 2. Surface wettability of (a) glass substrate without any coating and coated with (b) vinyl based ORMOSIL particles, (c) vinyl-amine based ORMOSIL particles without dissolution process, and (d) raspberry shaped particles.](image)

![Fig. 3. TEM images of PTMS–VTMS–APTMS based ORMOSIL particles after treatment at 80 °C for 6 h, with 2:1 (v:v) water–ethanol mixture (top). 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. (middle row) The volume of the APTMS was 1 ml and the volumes of the PTMS and the VTMS were the same as top row cases (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 [bar = 200 nm].](image)
found that the WCA of the uncoated glass surface was 58.8°, while the surface of coated film using VTMS based ORMOSIL particles exhibited WCA of 128.6°, indicating increased hydrophobicity. Also, the WCA of film surface coated with VTMS–APTMS (v:v = 10:1) based ORMOSIL particles was 123.5°, which reveals slightly decreased hydrophobicity due to hydrophilic amino-propyl functional groups in the ORMOSIL particles. In case of a glass substrate coated with the raspberry shaped particles obtained from the same ORMOSIL particles, WCA of 153.6° was observed, indicating the surface becomes very hydrophobic. This suggests that the water–ethanol mixture dissolved the hydrophilic part of the surface—made from mostly polar APTMS. Note that if the WCA has a value larger than 150°, a surface is super-hydrophobic—extremely difficult to wet—and exhibits self-cleaning and anti-fogging properties.

When 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, rattle type, hollow, raspberry-shaped or sphere particles were produced depending on the relative volume ratio of the three organosilanes. Fig. 3 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, 1 and 1.5 ml of APTMS for top, middle 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. We can notice several facts: (1) Particles in the top row have barely empty inner spaces. No hollow particles are found and rattle type particles have very large cores. (2) In the middle row, rattle type particles are dominant. Observing 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. (3) In the bottom row, hollow particles and rattle particles are observed. The core size and the outer shell thickness showed the same trend as those observed in the middle row. (4) The particles shown at the right end of the three rows—prepared using very low PTMS amount (0.5 ml)—were raspberry type particles just like the case for particles prepared from binary mixture of VTMS and APTMS. These facts about different structures of the particles after the water–ethanol treatment may also be explained as in the case of ORMOSIL particles from binary organosilane mixtures, using the two key factors: the selective dissolution of aminopropylsiloxane network within the particles by the water–ethanol mixture and internal structure of ORMOSIL particles depending on the relative ratio of organosilane monomers. Considering the relative hydrolysis and condensation rates of the three organosilane molecules, the formation of core parts with VTMS, and middle shells by the co-condensation of APTMS and VTMS would be the same as before. 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. The selective dissolution factor explains the noticed facts (1) and (2) as follows. 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 Fig. 3 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 Fig. 3 middle and bottom rows. The internal structure factor explains the noticed facts (3) and (4) above. 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,

Fig. 4. TEM images of ORMOSIL particles based on a mixture of PTMS (1.5 ml), VTMS (3.5 ml) and APTMS (0.5 ml) after the treatment with 2:1 (v:v) water–ethanol mixture for 6 h (top) and 24 h (bottom) at (a) RT, (b) 80 °C, and (c) 100 °C [bar = 200 nm].
the neighboring connected VTMS or PTMS based network may be removed together, resulting in larger voids. The analysis of IR spectra for ORMOSIL particles before and after the dissolution process confirmed such conjecture by showing that the vinylsiloxane network was mainly dissolved out (Fig. S3). These results 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.

In one previous method, hollow/rattle type silica particles were prepared by multi-step synthesis of core–shell type silica particles, consisting of silica core and mesoporous silica shell, followed by selective etching using Na$_2$CO$_3$ solution or by hydrothermal treatment in ammonia solution [23,30]. In another method, rattle type silica particles were prepared by multi-layer synthesis of organic–inorganic hybrid silica having a sandwich structure and subsequent etching of middle layer of organosiloxane networks using strong etchant such as HF [22].

The morphology of the mesoporous particles prepared by our approach can be manipulated by parameters involved in the synthesis and dissolution process. In the above, we investigated the effect of a synthetic parameter, ratios of organosilanes, and a dissolution parameter, type of solvents for dissolution process. In Fig. 4, the effect of another two dissolution parameters, dissolution temperature and time, on the structures of the ORMOSIL particles is displayed. The ORMOSIL particles obtained from a mixture containing PTMS 1.5 ml, VTMS 3.5 ml and APTMS 0.5 ml were treated with 2:1 (v:v) water–ethanol mixture at room temperature (RT), 80 °C and 100 °C. The particles treated at RT did not form rattle type particles even after 24 h dissolution process as can be seen Fig. 3a. When dissolution temperature was raised to 80 °C, particles with a rattle type structure were produced and the size of core parts in rattle type particles decreased—empty space within the particle increased—by increasing temperature to 100 °C (Fig. 4b and c). In a meanwhile, increasing the dissolution time from 6 h to 24 h did not make any recognizable effect on the structural evolution.

Thermal stabilities of mesoporous particles were investigated after heat treatment at 600 °C for 2 h in air. The morphologies of the particles were all maintained the same after heat treatment (Fig. S4). However, IR spectra analysis of the heat treated particles indicated that organic functional groups, such as phenyl, vinyl, and aminopropyl silanes, were disappeared, leaving only Si–O–Si frame works (Fig. S5). Upon heat treatment, organic functional groups in ORMOSIL particles were decomposed and water and alcohol molecules, produced by further condensation and vaporization, were evaporated along with decomposed organic functional groups resulting inorganic silica network in the heat treated particles. In order to investigate surface areas and pore distribution of meso-

![Fig. 5. Brunauer–Emmett–Teller (BET) N$_2$ adsorption–desorption curve (left) and pore distribution (right) of mesoporous particles; (a) hollow (PTMS:VTMS:APTMS = 2.5:2.5:1.5), (b) rattle type (PTMS:VTMS:APTMS = 1.5:3.5:1), and (c) raspberry shaped (VTMS:APTMS = 5:0.5) ORMOSIL particles.](image-url)
porous particles, Brunauer–Emmett–Teller (BET) N₂ adsorption–desorption analysis was carried out for hollow, rattle and raspberry particles prepared from the ternary or binary organosilane mixtures. As shown in Fig. 5, for rattle type particles, type IV hysteresis curve was observed indicating the presence of well-defined mesopores. The capillary condensation jump around 0.42 of P/P₀ in the isotherms might indicate the existence of a mesoporous structure with ink-bottle shaped pores, where the desorption situation is different from the absorption one [38,39]. These rattle type particles have relatively narrow pore size distributions in the range of 5–20 nm, with an average diameter of 12 nm. Specific surface area and pore volumes were 157.20 m² g⁻¹ and 0.36 cm³ g⁻¹ for rattle type particles. For ORMOSIL particles before selective dissolution, they were about 14.92 m² g⁻¹ and 0.0076 cm³ g⁻¹. In a meanwhile, hollow particles exhibited type II isotherm pattern without any pores. The pore size distribution curve also indicated that there are no apparent pores which might be too small to be calculated by Barrett–Joyner–Halenda (BJH) method. The specific surface area and pore volume were 56.96 m² g⁻¹ and 0.0636 cm³ g⁻¹. For ORMOSIL particles before selective dissolution, they were about 11.83 m² g⁻¹ and 0.0086 cm³ g⁻¹. In the case of raspberry shaped particles, N₂ adsorption–desorption curve seemed to be close to the type-IV isotherm pattern showing broad and low pore size distribution in a wide range. The specific surface area and pore volume were 17.44 m² g⁻¹ and 0.25 cm³ g⁻¹. For ORMOSIL particles before selective dissolution, they were about 13.23 m² g⁻¹ and 0.0206 cm³ g⁻¹.

4. Conclusion

In conclusions, we have developed a novel strategy to fabricate monodisperse, nanostructured ORMOSIL particles with tailored morphologies and pore sizes. It consists of one-pot synthesis of ORMOSIL particles using a mixture of two or three different organosilanes that have different hydrolysis/condensation rates and different solubility characteristics towards water-organic solvent mixtures; and a dissolution process that treats the ORMOSIL particles with a water–alcohol mixture. 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 ratios between the organosilane concentrations in the initial reaction mixtures. Raspberry shaped particles, obtained from VTMS–APTMS based ORMOSIL particles, exhibited super-hydrophobicity with WCA of 153.6°, which suggests their potential use for self-cleaning and anti-fogging applications. The core diameter and shell thickness in rattle type particles were adjusted by simply changing the relative ratios of PTMS, VTMS and APTMS in reaction mixture for ORMOSIL particles. These mesoporous ORMOSIL particles were converted to mesoporous silica particles, maintaining their morphologies, simply by the heat treatment at 600 °C in air. 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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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2014.10.002.

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