One-Step Synthesis of Monodisperse and Hierarchically Mesostructured Silicon Particles with a Thin Shell

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Monodisperse, uniform, and hierarchically mesostructured silicon particles with a thin shell have been fabricated via one-step synthesis using dodecanethiol (C_{12}-SH) and CTAB as dual templates. A series of hierarchically mesostructured silicon particles with a morphology similar to that of pomegranate can be obtained by simply adjusting the mass ratio of C_{12}-SH to CTAB. When the mass ratio is increased, a mesophasic transformation occurs from a mesoporous material to a mesostructured cellular foam in the core of the hierarchically mesoporous silicon particles. These unique silicon particles are characterized by small-angle X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FT-IR), and nitrogen adsorption−desorption measurements. The formation mechanism of the hierarchically mesostructured silicon particle with a thin shell is proposed according to the experimental results. Synergistic self-assembly of C_{12}-SH and CTAB in the solution is believed to play a key role in mediating the formation of these hierarchical silicon mesostructures, and the hydrophobic dodecanethiol can act as both the swelling agent for CTAB micelles and coagent for the formation of a microemulsion with CTAB micelles. This synthesis method is simple, straightforward, and suitable for the preparation of the other biomimetic nanostructures that are unique scaffolds in biological, medical, and catalytic applications.

1. Introduction

Recently, synthesis of hierarchically silicon mesostructures has attracted much attention due to promising applications1 and the possibility to elucidate the fundamental mechanisms about biomineralization.2 The important goal and big challenge concerning the design and fabrication of silica mesostructures are to

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approaches for the synthesis of silica materials with the designed composition, pore structure, function, and morphology.\(^\text{19}\) Despite success in the synthesis of mesoporous silica nanostructures (including spheres, rods, fibers, tubes, films, and foams, etc.) with single-pore by surfactant-assisted assembly, it is not easy to fabricate hierarchical silica mesostructures using only one template. It is known from the chemistry of surfactants that surfactant assemblies with varied morphologies and supermolecular structures, including micelles, vesicles, liquid crystals, and other assemblies, can be obtained in mixed surfactant solutions by the interactions with cотemplate such as hydrogen bonding, van der Waals forces, and electrostatic interaction.\(^\text{19}\) Hence, a cотemplate approach has been proposed to produce hierarchical silica structures. By simple regulation of the ratio of the cosolvents or cosurfactants, silica nanostructures with varied morphologies and pore structures have been successfully synthesized.\(^\text{21–29}\)

One of the general synthetic routes is by electrostatically matching various anionic organalkoxysilanes with the cationic surfactant micelles in a base-catalyzed condensation reaction of tetraethoxysilane (TEOS) based on the structure-directing effect.\(^\text{21–24}\) Moreover, siliceous nanopods, helical structures, and ordered mesoporous silicas have also been prepared using dual template\(^\text{27}\) and silica cosurfactants, silica nanostructures with varied morphologies and structures.\(^\text{29}\) to the best of our knowledge, hydrophobic anionic surfactants on) have been successfully used as cosurfactants to prepare silica hydrophilic surfactants (carboxylate, sulfate, sulfonate, and so forth) have been used throughout the experiments.

Obtained from a Millipore Milli-Q purification system was used in all experiments.\(^\text{24}\)

| Table 1. Summary of the Different Amounts of C12-SH and CTAB Added with R Values Change in Reaction Solution |
|---|---|---|---|
| sample | R | C12-SH (mL) | CTAB (g) | corresponding figure |
| S1 | 0.04 | 0.01 | 0.2 | Figures 1a and 2 |
| S2 | 0.08 | 0.02 | 0.2 | Figures 1b and 3 |
| S3 | 0.20 | 0.05 | 0.2 | Figures 1c and 4 |
| S4 | 0.40 | 0.10 | 0.2 | Figures 1d and 5 |
| S5 | 0.80 | 0.20 | 0.2 | Figure 6a |
| S6 | 2.0 | 0.50 | 0.2 | Figure 6b |
| S7 | 4.0 | 1.00 | 0.2 | Figure 6c |
| S8 | 0 | 0 | 0.2 | Figure 7 |

| Table 2. Physicochemical Properties of Fabricated Mesoporous Silica Nanospheres |
|---|---|---|---|
| sample | d (nm)\(^a\) | BET surface area (m\(^2\)/g) | pore volume (cm\(^3\)/g) | pore size distribution (nm) |
| S1 | 4.211 | 763 | 0.299 | <2 |
| S2 | 4.203 | 707 | 0.612 | 2.6 |
| S3 | 1036 | 0.711 | 2.7 |
| S4 | 1078 | 0.751 | 3.1 |

\(^a\) Estimated from SA-XRD patterns of samples. \(^b\) Estimated from the amounts of N\(_2\) adsorbed at a relative pressure (P/P\(_0\)) of 0.99. \(^c\) Central value of the pore size distribution as calculated from the N\(_2\) adsorption branch using the BJH method.

containing the mercapto functional group (−SH) have not been adopted in the synthesis of hierarchically silica structures. In this paper, we report a simple and easy synthetic technique to produce monodisperse and hierarchical mesostructured silica particles with a uniform size by using C\(_{12}\)-SH and CTAB as cosurfactants. The dual-surfactant-template technique conducted under optimal conditions and selecting the proper ratio of the two surfactants enable independent control of structural parameters such as the particle diameter (less than 200 nm), shell thickness, pore structures, and morphologies. The formation mechanism of the hierarchically mesostructured silica particles is proposed and discussed. This technique can be readily extended to synthesize other mesostructures with specific morphologies and architectures by fine-tuning the value of the carbon chain of thiol.

2. Experimental Section

2.1. Materials. Cetyltrimethylammonium bromide (CTAB), sodium hydroxide (NaOH), 1-dodecanethiol (named as C\(_{12}\)-SH), and tetraethoxysilane (TEOS) were purchased from Sigma-Aldrich. All the chemicals were analytical grade and used without further purification. Ultrapure water with a resistivity 18.2 M\(_2\)O\(_2\) cm obtained from a Millipore Milli-Q purification system was used throughout the experiments.

2.2. Preparation of Mesoporous Silica Nanospheres. Mesoporous silica nanospheres were prepared in a basic solution using C\(_{12}\)-SH and water as cosolvents and CTAB as the surfactant. In a typical procedure, 0.2 g of CTAB was dissolved in an emulsion composed of 96 mL of H\(_2\)O, 0.7 mL of 2 M NaOH, and the appropriate amounts of C\(_{12}\)-SH. After the mixture was vigorously stirred for 0.5 h at 80 °C, 1.5 mL of TEOS was quickly added. The resulting mixture was again vigorously stirred for 0.5 h at 80 °C. A white precipitate was obtained, filtered, washed with pure water, and dried in air at 60 °C for 24 h. The organic and other components in the products were eventually removed by calcination in air at 550 °C for 5 h. The amounts of C\(_{12}\)-SH and CTAB added to the reaction solution during the synthesis of the silica samples with different mass ratios (R) of C\(_{12}\)-SH/CTAB are shown in Table 1, and the other experimental parameters were the same as those aforementioned.

2.3. Characterization. Scanning electron microscopy (SEM) was carried out on a JEOL JSM-7001F field emission scanning electron microscope.
electron microscope operated at 5 kV. The powder products were dispersed in ethanol by sonication for 10 min, put on a silicon wafer, and dried at 60 °C overnight. The white powders were coated with a layer of gold before SEM observations. Before transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) observations, the powder products were dispersed in ethanol by sonication for 10 min and put on carbon-coated copper grids. After drying at 60 °C overnight, they were observed in a JEOL JEM-2100F transmission electron microscope at an acceleration voltage of 200 kV. Small-angle X-ray diffraction (SA-XRD) patterns of the prepared products were acquired on a Philips X’Pert-MPD (PW 3040) X-ray diffractometer using Cu Kα radiation operated at 40 kV and 40 mA. Fourier transform infrared spectroscopy (FT-IR) was carried on a Perkin-Elmer spectrum 100 FT-IR spectrometer using KBr pellets. Nitrogen adsorption–desorption measurements were carried out on a Quantachrome NOVA 1200e surface area and pore size analyzer at −196 °C using the volumetric method. The products were dried at 200 °C before the analysis. The Brunauer--Emmett--Teller (BET) specific surface areas were calculated by using adsorption data according to \( P/P_0 = 0.04–0.20 \) (six points collected). The pore size distributions were estimated from the adsorption branches of the isotherms using the Barrett, Joyner, and Halenda (BJH) method. The pore volumes were determined from the amounts of adsorbed N₂.

3. Results and Discussion

3.1. Effects of the Mass Ratio (R) of C12-SH/CTAB on the Morphology and Structure of Silica Products. By varying the mass ratios of C₁₂-SH/CTAB, hierarchical silica particles with varied pore structures can be readily fabricated. For convenience, the samples synthesized at varied R values are referred as S₁, S₂, S₃, S₄, S₅, S₆, and S₇ here. Their morphology and structure are determined by SEM and TEM, and the physicochemical properties of S₁–S₄ are summarized in Table 2.

The SEM images in Figure 1 show monodisperse spherical particles with a uniform size and smooth surface. The diameter of the silica spheres ranges from 100 to 200 nm. These silica samples have porous structures as shown by the TEM images. Figures 2–7 display the typical TEM images of the samples. S₁ (R = 0.04) consists of spherical particles of ~200 nm in size (Figure 2a,b). These spherical particles are hollow (capsules) as revealed by the contrast between the dark edge and pale center in the spheres (Figure 2). The shells of these hollow nanospheres have a thickness of about 12 nm (Figure 2a and magnified TEM image in Figure 2b). Few connecting necks are observed between the hollow spheres from Figure 2, showing that the hollow spheres are well monodisperse. The higher magnification image in Figure 2b reveal ordered porous structures composed of the 2D hexagonal phase in the core, and the pore size is about 3.9 nm.

Figure 1. Typical SEM images of mesoporous silica nanospheres of S₁ (a), S₂ (b), S₃ (c), and S₄ (d). Scale bar: 1 um.

Figure 2. Typical TEM images of mesoporous silica nanospheres of S₁.
More accurate pore size information is obtained by SA-XRD and nitrogen sorption analysis, and it will be discussed later. There are two different pore images from the same viewing angle according to Figure 2b, one corresponding to the ordered hexagonal mesoscopic structures indicated by squares mainly distributed in the center of the spheres and the other associated with the fringe mesoscopic structures as marked by ovals. The porous structures marked by squares and ovals are likely to be 2D hexagonal phase but viewed from different directions. In other words, there is just one pore structure showing two types of images depending on the orientation.

Increasing the $R$ value does not alter the morphology, but the pore structures are changed from being orderly to less orderly.

As shown in Figures 1b and 3, S2 ($R = 0.08$) has a better spherical morphology than S1. The high contrast between the dark edge and pale center in the spheres observed from Figure 3 indicates its hollow nature. The magnified TEM image in Figure 3b corroborates the hollow core together with a thin shell 10 nm thick. Most of the pores show the weakly ordered 2D hexagonal mesophase.

S3 ($R = 0.20$) also consists of spherical nanoparticles ~180 nm in size (Figure 4). All of them have perfect spherical-like structures which are uniform in size and monodisperse. The TEM image in Figure 4b discloses a well-defined shell-like structure with the shell being about 9 nm thick. Although a few fringes can be observed from the inside of the spherical particles (indicated by ovals in Figure 4b), the pore structures are disordered.

By further increasing the $R$ value to 0.40, the porous core–shell structures (S4) are retained, but the shell thickness is changed to about 5 nm. The contrast between the core and shell is not well-defined as shown in the TEM images in Figure 5. The pore size which is larger than that in S1–S3 is about 6 nm. The whole silica structure is similar to that of the natural product of pomegranate, as shown in Figure 5c.

With the $R$ values equal to or larger than 0.8, special pore structures and connecting necks between the hierarchical porous spheres emerge (Figure 6). As shown in Figure 6a, S5 consists of spherical particles, and bigger hollow cores can be found inside the structures. The cavity of the hollow cores is about 50 nm as estimated from the TEM images. Some larger hollow regions are homogeneously covered by many smaller ones. In the structure of S6, some bigger hollow cores exist in a particle at the same time, and many smaller hollow regions are distributed around these larger hollow cores (Figure 6b). By further increasing $R$ to 4.0, the particles have bigger hollow cores (Figure 6c) and thinner shells than S5 and S6. The TEM results show that all the products consist of mesostructured cellular foams.

In contrast, without the addition of C$_{12}$-SH, monodisperse mesoporous silica spheres (30–60 nm) can be obtained. MCM-41 mesochannels are observed from the TEM results of the calcined sample (Figure 7). Notably, compared to the silica samples obtained in the presence of C$_{12}$-SH, no thin shell is found on the
Also, without the addition of CTAB, the sol–gel process of TEOS did not happen even if the solution was kept overnight under vigorous stirring as TEOS disperse into hydrophobic C12-SH emulsion. The results suggest that C12-SH plays a key role in mediating the formation of the monodisperse hierarchically mesostructured silica particles with a thin shell with assistance from CTAB.

Figure 8 shows the typical SA-XRD patterns of calcined S1–S4. The calcined silica samples obtained at different R values show an obvious diffraction peak at about 2.1° (2θ) which can be indexed to the different planes of the p6mm mesostructure. Only one strong characteristic diffraction peak is observed for S1, and that can be identified at (10) diffraction based on the two-dimensional p6mm unit cell. S2 has a weak peak at 2.3° (2θ), and that is more likely (11) or (20) peaks, and the (10) peak is outside the range according the MCM-41 XRD. The diffraction peaks observed from S1 and S2 corresponding to the other planes of p6mm become ambiguous and broader, or disappear, and S3 and S4 show no identifiable diffraction peaks in their XRD results, indicating that these samples have weak ordered or disordered mesoscopic structures. The broad diffraction peak was in agreement with the aforementioned TEM observations. The d spacings calculated from the SA-XRD peak of the (10) diffraction are summarized in Table 2.

The nitrogen adsorption/desorption isotherms obtained from S1–S4 (Figure 9a) show typical type IV features indicative of the presence of mesopores.32 A sharp capillary condensation step in the relative pressure range 0.85–0.95 is observed from every mesoporous silica sample, suggesting the presence of textural (disordered) porosity.35 Nitrogen isotherms for calcined samples S1 and S2–S4 are different, and S2–S4 have similar nitrogen sorption isotherms, indicating that S2–S4 have similar pore structures. The H2 hysteresis of S2–S4 suggests the formation of large mesopores with narrow windows in contact with adjacent pores.34 The shape of the isotherm and hysteresis loop suggests that these materials consist of large cells that are connected to each other as well as the matrix of the particle by much smaller windows.35

Figure 6. Typical TEM images of mesoporous silica nanospheres: S5 (a), S6 (b), and S7 (c).

Figure 7. Typical TEM images of mesoporous silica nanospheres obtained without adding C12-SH: (a) low magnification; (b) along different vision: the channel direction (c-axis; b) and perpendicular to it (c).

Figure 8. SA-XRD patterns of fabricated mesoporous silica nanospheres of S1–S4.

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In addition, the pore size distribution curves (Figure 9b) of S1–S4 are determined from the adsorption branch of the isotherms. Except that the pore size distribution of S1 is smaller than 2 nm, all the pore size distributions of S2–S4 exhibit a sharp peak centered at the value of around 2–4 nm, implying a uniform mesopore size. According to previous reports, the classical BJH method underestimates the pore width for MCM-41, when it is smaller than 4 nm. In the current results, the pore width might have also been underestimated. It may be estimated more accurately on the basis of condensation pressure. However, large mesopores are not predicted by calculation using the BJH method, and this may result from that small mesopores are usually dominant in hierarchically porous systems. In addition, according to the nitrogen adsorption–desorption results (Table 2), addition of C_{12}-SH affects the mesoporosity of the silica particles, including pore size, pore volume, and BET surface area. The BET surface area and pore volume are around 700–1100 m^2/g and 0.3–0.75 cm^3/g, respectively.

### 3.2. Formation Mechanism of the Hierarchical Mesostructured Silica Particles with a Thin Shell

Based on the experimental results, a mechanism describing the formation of the hierarchical mesostructured silica particles by regulating the mass ratios of dual templates is postulated. It is believed that the evolution of the morphology of the silica particles should be closely related to the interactions among C_{12}-SH, CTAB, and silica oligomers during the aqueous sol–gel process. Hydrophobic C_{12}-SH molecules can act both as a swelling agent for CTAB surfactants micelles and as a coagent for the formation of microemulsion with CTAB surfactant micelles in addition to the swelling effect. The majority of the formed supermolecular aggregates via electrostatic interaction of C_{12}^- and CTA'^+ structures are involved in the formation of the silica structures. Various complex architectures are quickly realized due to
self-assembly between silica oligomers and CTAB around the formed C12-SH/CTAB supermolecular aggregates.

As the C12-SH molecules are hydrophobic and function as a pore expander or microemulsion with the assistance of CTAB, under strong basic conditions during the synthesis, the formed anionic C12-S\(^{-}\) molecules have strong electrostatic interactions with the cationic surfactant CTA\(^{+}\) and silica oligomers.\(^{(39)}\) C12-SH molecules have weak characteristic peaks of S-H in 2750–2550 cm\(^{-1}\) and weak characteristic peaks of C-S in 720–570 cm\(^{-1}\).\(^{(38)}\) It is not found the characteristic peaks of S-H in the structure of S4 before calcination (Figure 10a), but the weak characteristic peaks of C-S in 720–570 cm\(^{-1}\) could be found. The EDX result in Figure 10b indicates S element exists in its structure. On the basis of the FT-IR and EDS results, it is believed that C12-S\(^{-}\) could form in the basic solution (ca. pH = 11).\(^{(39)}\) Scheme 1 shows the possible binding model of the interaction among C12-S\(^{-}\), CTA\(^{+}\), and partially hydrolyzed products of TEOS precursor in the interface of the micelles or microemulsion or vesicles.\(^{(39)}\)

C12-SH can bind to the CTAB micelle via electrostatic interaction to generate several C12-SH/CTAB aggregates resulting in the formation of the structures in the cores. At the same times, many more CTAB molecules are involved in the formation of the C12-SH/CTAB micelle aggregates giving rise to the structures of the shells. Finally, cross-linking polymerization of TEOS around the CTAB template simultaneously occurs among several different C12-SH/CTAB aggregate interfaces, leading to the formation of the hierarchical structures of the particles.

When a relatively small amount of C12-SH (R < 0.04) is added, the C12-SH molecules can insert into the formed CTAB micelles. In fact, hydrophobic C12-SH molecules function as the pore expander to produce 2D hexagonal phases with larger periodicities under the experimental conditions.\(^{(41)}\) Moreover, anionic C12-S\(^{-}\) molecules exist in the mixture and have electrostatic interactions with the CTA\(^{+}\) supermolecular aggregates.\(^{(39)}\) However, small amounts of anionic molecules cannot successfully break up the stability of aggregates. Unilamellar vesicles of CTAB which surround the above C12-S\(^{-}\) and CTA\(^{+}\) supermolecular aggregates (2D hexagonal phases) are formed in order to preserve the less stability of the whole supermolecular systems. Finally, a hierarchical silica structure with a thin shell and a hexagonal weak ordered mesoporous core is obtained. With further increasing of the R values (0.08 < R < 0.2), more amounts of C12-S\(^{-}\) are formed to destroy the stability of the interfacial layer of the C12-SH/CTAB aggregates, and then these hydrolyzed TEOS molecules can further cross-link around the destroyed surface of the large C12-SH/CTAB aggregates. This cross-linking condensation proceeds further with these C12-SH/CTAB micelles as the template, finally leading to the formation of the hierarchical mesostructured silica particles with disordered pores. The increased electrostatic interactions between C12-S\(^{-}\) and CTA\(^{+}\) have the ability to break up the stability of CTA\(^{+}\) hexagonal phases, making them shorten or converting them to unilamellar vesicles.\(^{(39)}\) Silica foams with a uniform cavity are produced when R is increased to 0.4, and the morphology is similar to that of pomegranate (Figure 5c) with a lot of small and uniform hollow spheres in a big hollow sphere. Owing to the fusion of soft vesicles at higher mass ratios, siliceous foams with a multidispersed cavity are synthesized.\(^{(13a,23a)}\) Vesicles fuse to become a big emulsion and

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(38) Sigma-Aldrich, FT-IR spectra of 1-dodecanethiol: http://www.sigmaaldrich.com/catalog/ProductDetail.do?D7=0&N5=Product%20No.|BRAND_KEY&N4=


function as a soft template to form silica capsules. Because of the electrostatic interactions between CTA$^+$ and C$_{12}$S$^-$, some compound folds are observed inside the hollow structures.

According to the results, the formation mechanism is illustrated in Scheme 2. It is concluded that with increasing $R$ values the self-assembled materials produced using the dual C$_{12}$SH and CTAB templates undergo transformations from the hexagonal mesostructures to the vesicular structures and finally to foams during the formation of the core structures. Generally, increasing the hydrophobic/hydrophilic volume fraction may lead to a morphology change from hexagonal mesostructures to vesicles. According to the geometric packing model in which the organization of surfactant molecules is described by the packing parameter ($g$): $g = V/a$, where $V$ is the effective volume of the surfactant tail region, $a$ refers to the effective headgroup area at the micelle surface, and $l$ is the surfactant tail length proposed by Israelachvili and co-workers, the value of $g$ may determine the structure of the self-assembled surfactant aggregates as well as surfactant-templated composite materials. The interactions between C$_{12}$S$^-$ and CTA$^+$ may counteract part of the cationic charges in the CTA$^+$ molecules, and thus $a$ is reduced. In addition, the C$_{12}$S$^-$ molecules may insert into the hydrophobic part of the mixed micelles (increasing $V$). However, when $R = 0.04$, the small amount of C$_{12}$S$^-$ may be insignificant to change the hexagonal packing in the cylindrical micelles. The R-S$^-$ structures mainly play a role in reducing the surface free energy and promoting the formation of the pomegranate-like morphology. When the $R$ value is adjusted to 0.08–0.4, the $g$ value is increased and the vesicular structure is favored. The above discussion provides an explanation for the structure transformation from the hexagonal to the vesicular structures. A simple interpretation is that during the synthesis using various mass ratios the multilamellar vesicular structures coexist with the hexagonal mesostructures and foam structures.

4. Conclusion

We demonstrate that hydrophobic dodecanethiol can be employed to fine-tune hierarchical silica mesostructures by simple regulation of the mass ratio of surfactants in the starting solution. Weak ordered 2D hexagonal mesophases and foam structures can be prepared in one-step synthesis, and both of the mesostructure structures are enshrouded by thin shells with a morphology similar to that of pomegranate. Dodecanethiol can act as both a swelling agent for the CTAB micelles and a coagent for the formation of the microemulsion with the CTAB micelles. At a low mass ratio of C$_{12}$SH/CTAB, dodecanethiol acts mainly as a swelling agent by penetrating into the core of the surfactant micelles. At high mass ratios, dodecanethiol can form a microemulsion with CTAB in addition to rendering the swelling effect. Our results indicate that the mesostructure (hexagonal or disordered) and shape of the inner cavity (hexagonal or spherical shape) of the silica structures can be facilely tuned. These hierarchical mesostructures provide an unique scaffold structure suitable for biological, medical, and catalytic applications. The approach described here can be extended to the synthesis of hierarchical structures having other compositions. In addition, the results may shed light on the fundamental mechanisms of biomineralization.

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