Self-assembly of multi-hierarchically structured spongy mesoporous silica particles and mechanism of their formation

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ABSTRACT: Here we report on self-assembly of novel multi-hierarchically structured meso(nano)porous colloidal silica particles which have cylindrical pores of 4-6 nm, overall size of ~10 micron and “cracks” of 50-200 nanometers. These cracks make particles look like micro-sponges. The particles were prepared through a modified templated sol-gel self-assembly process. The mechanism of assembly of these particles is investigated. Using encapsulated fluorescent dye, we demonstrate that the spongy particles are advantageous to facilitate dye diffusion out of particles. This multi-hierarchically geometry of particles can be used to improve the particle design for multiple applications to control drug release, rate of catalysis, filtration, utilization of particles as hosts for functional molecules (e.g., enzymes), etc.

INTRODUCTION

Mesoporous (also called nanoporous) silica materials obtained using templated so-gel chemistry is an interesting material with many unique properties, such as very high surface area and uniform pore-size distribution [1, 2]. The majority of these materials has cylindrical pores running in parallel packed in hexagonal order (nematic phase). By placing different functional moieties inside the pores, one can attain rather unusual properties of interaction between those moieties and the surrounding environment. As examples, fluorescent ultrabrightness [3-5], extended lifetime of biological active molecules [6], controlled drug release and gene transfection [7, 8], specific filtration [9, 10] can be attained in this way.

In many applications, it is advantageous to have nanoporous silica material hierarchically structured. For example, making nanoporous silica particles of microns in size is obviously useful in filtration. Such particles can be used in sensor applications [11], in catalysis [12, 13] and biocatalysis [14], molecular storage [6, 15], chromatography [16], photonic applications [4, 17], etc. A nontrivial micron shapes can also define specific photonic properties [18, 19]. It was previously found that cationic surfactants form and mineralize in the presence of metastable semi/metal oxides to a well-ordered nanostructure that can extend up to a few hundred microns [1, 20]. These shapes can extend up to a few hundred microns and form mesoporous thin films, [21-25] spheres, [26-28], curved shaped solids, [29, 30] tubes, [31, 32], rods and fibers, [33-35] membranes, [36] and monoliths [37] has been reported.

Multiple hierarchical structures of nanoporous are of particular interest because it can provide controllable kinetics of access to the encapsulated cargo/catalyst/functional moieties inside pores [15]. Well-known SBA-15 silica particles (typical pore size is 6-9nm), which were folded in ribbons with irregular holes of 50-100nm can example such structures [38]. A similar

size nanoporous silica foam was synthesized in [39]. Hollow micron nanoporous spheres were assembled using a sacrificial skeleton [40] or (polystyrene) cores [41]. Biological hierarchical structures like viruses can also be incorporated to manufacture hierarchical nanoporous materials [42]. Hierarchical structures were also synthesized using CO₂ water emulsion [43] and supercritical carbon dioxide [44]. It is also possible to synthesize hierarchical structure submicron particles by combining different templating molecules and swallowing agents [45, 46]. It is worth noting that the majority of hierarchical structures of nanoporous were obtained in the core-shell structures.

Here we describe a novel type of multi-hierarchical silica particles. We report the synthesis of multi-micron silica particles, which have nanoporous hexagonal structure of 4-6 nm. Furthermore, the surface of these silica particles features a spongy shape, cracks of 50-100nm. It is a one-bath synthesis which requires just a simple intervention by adding pure water. Further, we investigate the mechanism of self-assembly of these spongy shapes. Finally, using encapsulated fluorescent dye molecules, we demonstrate advantage of the reported spongy particles for controlled release of encapsulated cargo. In general, these particles can be used for the enhanced availability of cargo which may be encapsulated in nanopores, in controlled drug delivery, chromatography, filtration, etc.

EXPERIMENTAL SECTION

Materials. Tetraethyl orthosilicate (TEOS, 98%, Aldrich), cetyltrimethylammonium chloride (CTAC, 25 % aqueous, Aldrich), hydrochloric acid (HCl, 36% aqueous, J T Baker), Formamide (HCONH₂, 98%, Aldrich) and Rhodamine 6G (R6G, Exciton Inc.), ultrapure water (18 MΩ-cm, MilliQ Ultrapure) were used without further purification.

Synthesis. The synthesis procedure is a modified self-assembly previously reported in [20, 47]. The following molar ratio of the reactants $100\text{H}_2\text{O}:8\text{HCl}:0.11\text{CTACl}:0.13\text{TEOS}:9.5\text{HCONH}_2$ was used. At first, water, formamide and dye were mixed in a plastic bottle, and stirred using a magnetic stirrer (Hotplate stirrer, Lab Depot, Inc.) at 550 RPM for 5 min at room temperature. In the next step, hydrochloric acid was added to the reaction mixture. As a result the temperature of the reaction mixture raised to 40°C . The reaction mixture was then put in an ice bath and stirred until it reaches room temperature. Next, CTAC was added to the reaction mixture and stirred for 45 min. As a last step, TEOS was added and stirred for 2 hours. If needed, fluorescent dye was added together with TEOS. The reaction mixture was then kept in quiescent condition (without stirring) for up to 72 hours. Specific samples were prepared as follows:

Sample 1 (control): The synthesizing bath solution (with particles). The particles were extracted at a predefined time by centrifugation (Safeguard Centrifuge, 3000 rpm, 1min) and washing with water (by re-suspension in water, centrifugation, and discarding supernatant repeated 5 times).

Sample 2. Water was added to the synthesizing bath solution (with particles) at a 1:3 volume ratio at a predefined time. The obtained mixture was then kept in quiescent condition for 6 hours before being analyzed (with no centrifugation extraction).

Sample 3. It was obtained as sample 2 in which the particles were extracted and immediately washed with water by centrifugation as done for sample 1.

The predefined time for sample extraction starts from the time of TEOS mixing with rest of the reaction mixture. This time is taken to be 10 h, 13 h, 16 h, 18 h and 72 h.

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4 **Characterization.** Samples were characterized with confocal scanning laser microscopy
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6 (CSLM) (Eclipse C1, Nikon Inc.), with electron microscopy techniques, SEM (Phenom, FEI),
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8 FESEM (Zeiss Supra55VP Field Emission Scanning Electron Microscope), TEM (Tecnai G2 30
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10 UT), and porosity measurements using accelerated surface area and porosimetry system
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12 (Micromeritics ASAP 2020).
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17 To run CSLM imaging, a 25 μ L droplet of particles was sandwiched between a microscopy
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19 glass slide and cover slip. The change of the particle size after introducing water was calculated
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21 using ImageJ 1.41 software.
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25 For porosity measurements, samples were first dried (as described above for SEM
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27 imaging), further dried at 150° C for 2 hours in a vacuum chamber (Precision Scientific Model
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29 19), followed by calcination at 400° C for 4 hours in a furnace (Hot Spot 110, Zircar), ensuring no
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31 organic content leftover in the sample. This ensures degradation and elimination of all organic
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33 content such as dye molecules and surfactant inside the mesoporous structure. The same particles
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35 at 16th hours were also used for FESEM imaging.
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41 For scanning electron imaging, samples were first dried in an oven (Isotemp 500 series, 60°
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43 C) for 24 hours and then placed on a double sided carbon tape attached to the SEM stub, followed
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45 by a light gold coating (Hummer 6.2 sputtering system) for 1 minute.
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49 TEM study was done on crushed samples which were prepared by using an ultrasonic
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51 bath, dissolving in ethanol, and depositing on holey carbon grid. TEM was operated at 300 kV
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53 with 0.17 nm point resolution and equipped with an EDAX EDX detector. A low intensity
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55 electron beam and medium magnification were used in order to avoid the electron beam damage
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57 of the structure inside the microscope.
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The slow-release of the fluorescent dye from pores of particles was qualitatively tested on sample 3 extracted at 16 hours using CSLM as follows. The sample of particles in water was placed between a glass slide and cover slip. Approximately 15 μ L of glycerol was drop-casted at the edge of the cover slips. The diffusion of glycerin creates a gradient that forcefully pushes the dye out of the particles [48].

RESULTS AND DISCUSSION

Figure 1 demonstrates a comparative formation of spongy particles of samples 2 and 3. CSLM images are shown for the particles 9, 13, 16 and 18 hours of synthesis. Beyond 20th hour, however, the “spongy” shapes become less significant, and the particles gradually attain a smooth shape of control sample 1 (see, Figs.2d and 5a). This spongy geometry is particularly pronounceable when water was introduced to the synthesis bath between 13 to 18 hours after the synthesis start.

Figure 1: Confocal images of the particle morphology of Sample 2: (a), (b), (c) and (d) and Sample 3: (e), (f), (g) and (h). Pairs (a,e), (b,f), (c,g), and (d,h) are imaged at 9, 13, 16 and 18 hours, respectively. Scale bar is 20 microns.

One can see from Figure 1 that either gentle addition of water (sample 2) or vigorous washing with water (sample 3) give about the same result, the appearance of cracked “spongy” shapes. Thus, we assume that sample 3 can be a correct representation of sample 2 as well.

Because sample 3 was thoroughly washed with water, it can be dried and used for the electron microscopy study of both samples.

Figure 2 shows SEM images of sample 3. One can clearly see that a well-defined spongy morphology is developed around 16 hours since the synthesis start, Fig.2c. Before that time, the solid fraction of the synthesizing bath demonstrates rather irregular geometry, Figs.2a,b. Beyond 20 hours these particles are indistinguishable from the control, sample 1.

Figure 2: SEM images of Sample 3 at (a) 10h, (b) 13h, (c) 16h and (d) 20h samples with scale bars 20 μm, 10 μm, 10 μm and 25 μm, respectively.

Figure 3 shows a high resolution electron microscopy study of 16-hour particles of sample 3. Figures 3a,b show high resolution FESEM images of typical spongy morphology. One can clearly see the cracks and openings in the range of 40-100 nm. Figures 3c demonstrates TEM images of the particle edges. One can see the cracked structure. However, it is hard to observe any ordered mesoporous structure, though mesopores are clearly seen.

Figure 3: Sample 3 synthesized for 16 h. (a) and (b) high resolution FESEM images of spongy particles, (c) TEM images of the spongy edge at different magnifications.

Although it is unexpected to see any changes in nanoporous size (because it is mostly defined by the templating molecule), it is still worth of testing if the pore size remain the same

after developing the spongy morphology. To test a possible change of the pore size of spongy samples (samples 2 and 3) compared to the regular synthesis (sample 1), we measure the nitrogen adsorption/desorption isotherms of calcined particles.

Figure 4: Porosity measurements of (a) spongy particles (16h sample 1) and (b) regular smooth particles. N_2 adsorption/desorption isotherms at 77.3 K are shown. Insets are the size distributions.

Figure 4 shows the nitrogen adsorption/desorption isotherms of the spongy shapes (sample 3 at 16 h of the synthesis) and the regular smooth shapes (sample 1). In both cases one can see type IV isotherms with *H1* shape hysteresis [49] which is typical for mesoporous structures. The isotherms for both samples show a step rise at $\sim 0.2 P/P_o$ with a well noticeable hysteresis, indicating quite a broad distribution in mesoporosity [50]. The BJH pore adsorption areas for 16 h and 72 h samples are found to be 690 g/m^2 and 550 g/m^2 , respectively, with the average BJH pore radius of 3.9 nm (the most probable pore size is around 6.2 nm) for both samples. It implies that both samples demonstrate virtually the same pore size, while the spongy shapes have 26% higher BJH pore adsorption areas compared to the non-spongy (fully developed smooth) shapes. The

latter is presumably because a part of the nanoporous channels can be self-sealed inside the particles [5].

Let us analyze the mechanism of formation of the spongy shapes. The relative amount of water in the synthesizing bath defines the rate of hydrolysis of TEOS, and consequently, the rate of condensation of silicic acid [51], the building material of silica shapes. Dilution of the synthesizing bath with water also accelerates condensation of silicic acid by decreasing the relative concentration of ethanol. We see two possible mechanisms of appearance of spongy cracks. The first mechanism is as follows. As we noted, the addition of water changes the rate of silica condensation. During the condensation, $\text{Si-OH} - \text{HO-Si-}$ and $\text{Si-O} - \text{HO-Si-}$ bonds turn into shorter silica $-\text{Si=O=Si}-$ bonds. This leads to the development of differential mechanical stresses near the particle surface due to the different rates of condensation of silicic acid inside and near the particle surface [47, 52]. When this process is slow, the mechanical stresses may relax resulting in the overall complex morphologies of silica particles as was described in [20, 53]. However, if the process of condensation is fast, the developed internal stresses may result in fracture of silica material near the surface, i.e., lead to cracks seen on spongy shapes and chipping out the particle's material. As was shown [20, 53], the strain due to silica condensation can reach 70%. This alone can explain the observed spongy cracks. This mechanism is illustrated in Figure 5a.

The second mechanism can work in the opposite way, and “build” the spongy surface rather than crack it. This is because the addition of water also results in the growth of a large number of nanoparticles (the seed particles) in the synthesizing solution due to the increase of the speed of silica condensation. It can easily be detected visually; the solution becomes opaque, similar to the initial stages of the regular synthesis [54]. When these new seed nanoparticles

condense on the surface of already created micron size particles, it is plausible to expect that they may create irregular spongy structures. This mechanism is illustrated in Figure 5b.

Figure 5: Two suggested mechanisms explaining the development of the spongy structures. (a) Cracks developed due to excessive surface shrinkage, which occurs during condensation of silica and (b) Growth due to adsorption of seed-nanoparticles on the particle surface.

Thus, we will consider two mechanisms contributing to the creation of the spongy morphology: 1) Disrupting the surface of growing micron size particles due to excessive mechanical stresses developed near the particle surface due to the different degree of silica condensation, and 2) The growth of a sponge-looking layer due to the secondary precipitation of seed nanoparticles onto the micron size particles. Presumably both mechanisms are present. To check which of the above mechanisms might be dominant, we measure the particle's diameters right before adding water (the initial particles; when the particles are smooth) and after adding water (when the particles develop the spongy morphology). If we observe that the particles grow in size after adding water, the secondary precipitation of nanoparticles on the primary micron-size particles is the dominant mechanism. Otherwise, the rapture of the particle surface due to differential stresses in the silica matrix is the dominant. Figure 6 demonstrates how exactly the

change of the particle size was measured. The particles images with CSLM before (Fig.6a) and after adding water (Fig.6b) are shown. One can see that the majority of the particles seen in Fig.5a immediately develop the spongy shape. Comparing the sizes of particles before and after developing the spongy shapes, one can conclude about the possible mechanism of their information.

Figure 6: Representative confocal images of the particle morphology before and after adding of water to the reaction mixture. (a) Control sample 1. The particles were imaged after (16 hours) hours since the beginning of the synthesis. (b) Sample 2. It was obtained by adding water to sample 1 shown in panel (a), and imaged immediately.

Fig. 7 shows a statistical distribution of the relative change of the particle size after adding water. Negative numbers indicate the decrease in size. One can see from Fig.7 that there is a slight overall decrease of the particle size; the average decrease is -3.3%. This indicates the presence of both mechanisms with a minor domination of the disruption mechanism.

As we mentioned in the introduction, the spongy particles described above can find its use in a variety of applications. Because of thier structure, the synthesized particles (samples 2 and 3) should have higher accessibility of nanopores to the surrounding media compared to smooth particles (sample 1). This was already demonstrated by the observed 26% increase in the surface area of particles when they develop spongy geometry. Therefore, spongy particles may find its use in the control drug release. Next, mesoporous silica particles is advantageous for storage and use of biologically active molecules, in particular, enzymes [6]. Application to filtration is rather obvious. Larger open surface of microparticles will enhance the sorption of the moieties being filtered.

Figure 7: A relative change of the particle size one developing the spongy morphology (sample 2 with respect to sample 1). Water was added 16 hours since the beginning of the synthesis. The average percentage of difference is around -3.3%, indicating a slight decrease of the particle size, and consequently, a slight domination of the rapture mechanism in the formation of spongy morphology.

Let us now demonstrate a potential application of spongy particles for the enhanced release of encapsulated cargo. We can demonstrate it by using the release of encapsulated rhodamine 6G fluorescent dye (the gradient flow was created by glycerol as described in the Methods section). Fig. 8 shows an optical fluorescent image of the dye leakage from the particles of spongy simple 3 (16 hour synthesis) and sample 1 with no spongy structure. One can clearly see that the spongy particles release more dye molecules.

Figure 8: Dye leakage comparison shown for (a) particles of Sample 3 (16th hour synthesis) and (b) sample 1 (>20 hour synthesis). Both images have the same scale (200 μ m scale bar is shown).

CONCLUSIONS

We presented the synthesis of novel sponge-like mesoporous silica particles which feature multi-hierarchical geometry: being multi-micron size particles, they have irregular cracks of 50-200 nanometers (sponge-like structure), and 4-6 nanometers cylindrical pore. The formation of such structures was induced by the interruption of a templated sol-gel self-assembly by adding water to the reaction solution before particles were fully grown. While nanopores remain of the same size, the surface area of the spongy particles increases by 26% compared to the non-spongy “regular” synthesis. The analysis of the shape forming mechanisms showed that they are presumably formed as a balance between the rapture and regular precipitation mechanisms with a slight domination of the rapture mechanism. The reported multi-hierarchical porous particles can be effective in the controlled release, for storage of biologically active molecules, and in filtration applications. The enhanced release of encapsulated fluorescent dye from the spongy particles was demonstrated. Further benefits of the use of the developed particles will be studied in future works.

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Notes

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