Pore-expansion of monodisperse mesoporous silica spheres by a novel surfactant exchange method†

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By adapting a novel surfactant exchange method, in which surfactants inside mesopores are completely exchanged by surfactants with longer alkyl chain lengths, pore-expansion of monodisperse mesoporous silica spheres (MMSS) with radially ordered hexagonal regularity was attained while retaining spherical morphology and high monodispersity.

Ordered mesoporous silicas synthesized by the surfactant-template method possess uniform mesopores and high specific surface areas.[1] These materials have been expected to become of increasing use as new types of catalysts,[2] adsorbents,[3] and host materials.[4] Controlling the morphologies of such materials is one of the major challenges that need to be solved to enable their use in industrial applications. Recent studies have focused on synthesizing particles with various shapes, such as sponge-like membranes,[5] rod-like powders,[6] fibers,[7] films,[8] polyhedral particles,[9] and spheres.[10] Non-porous monodisperse silica spheres in the micron-sized range were first synthesized in 1968 by Stöber and Fink, who employed a water–alcohol–ammonia–tetraalkoxysilane system.[11] Thereafter, this method was modified by the addition of cationic surfactants and/or other organic solvents, and mesoporous silica spheres have now been synthesized.[12]

In our laboratory we have developed a method for the synthesis of hexagonally-ordered and well-defined highly monodisperse mesoporous silica spheres (MMSS) from tetramethoxysilane and *n*-alkyltrimethylammonium bromide (C_nTMABr).[13] The pore sizes of the MMSS can be tuned by changing the lengths of the alkyl chains in the surfactant.[14] However, the maximum pore sizes of the MMSS was limited to 2.5 nm when using the BJH method. For mesoporous materials, the control of pore size is as important as controlling the particle size. Many methods have been reported that attempt to expand the pore sizes of mesoporous materials. The most commonly used technique is the introduction of a swelling agent into the structure-directing template, either in the preparation step,[15] or in the post-synthesis hydrothermal treatment.[16] In both of these techniques, the most commonly-used swelling agents are large organic molecules such as 1,3,5-trimethylbenzene, 1,3,5-triisopropylbenzene, dodecylamine and *N*,*N*-dimethyldecylamine. The diameters of the pores can easily be expanded by the use of these agents.

Recently, we have successfully fabricated colloidal crystals from MMSS and its composite.[17] Pore-expanded MMSS is a very promising route for the application of such colloidal films by the incorporation of large molecules, such as biomolecules and metal complexes.

We have tried to achieve the direct synthesis of pore-expanded MMSS by using C_{22}TMA as a surfactant. However, although we have changed many factors, such as the concentration of the surfactant and the silica source, the type and fraction of the solvent, the ratio of the surfactant and the silica source, monodisperse particles could still not be obtained. In this communication, we report on the pore-expansion of MMSS by a novel surfactant exchange method. There are a variety of possible applications for MMSS materials, and the method described here is an important step towards preparing them with high efficiency and in large quantities. Hydrothermal treatment of MMSS in a water–ethanol mixture using a surfactant with a longer alkyl-chain length leads to pore-expansion of the MMSS while retaining spherical morphology and high monodispersity. The mechanism for the pore-expansion process will also be described.

MMSS-*n* (where n = 10, 14, 18) silica/surfactant composites were prepared from C_{10}TMABr, C_{14}TMACl and C_{18}TMACl according to the literature.[13,14] In a typical treatment, an MMSS-*n* silica/surfactant composite was added to a 0.1 M C_{22}TMACl water–ethanol solution. The mixture was sealed and placed in an oven at 353 K for 7 days without stirring. The resulting white powder was filtered out and washed with distilled water and then dried. The powder was calcined in air at 823 K for 6 h to remove any remaining organic species. The incorporation of platinum was performed in two separate steps, as described elsewhere.[18] The surfactants in the composite were analyzed by electrospray ionization liquid chromatography mass spectrometry (ESI-LC/MS) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF/MS). The calcined products were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD) and nitrogen adsorption–desorption measurements. The specific surface areas were computed using the BET multi-molecular layer adsorption model, and the average pore sizes and cumulative pore volumes were calculated from the desorption branch by using the BJH model.

SEM images of MMSS-18 and hydrothermally treated MMSS-18 (PS22-MMSS-18) particles are shown in Fig. 1, and a summary of the results concerning the uniformities and pore properties of the particles are listed in Table 1. MMSS-*n* and PS22-MMSS-*n* particles both retained high monodispersity and spherical morphology before and after post-synthesis. Their average diameters

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† Electronic supplementary information (ESI) available: 1. Powder XRD patterns of MMSS-*n* and PS22-MMSS-*n* (Fig. S1). 2. MALDI-TOF/MS and ESI-LC/MS spectra of PS22-MMSS-10 and its extract (Fig. S2 and S3). See DOI: 10.1039/b613163h

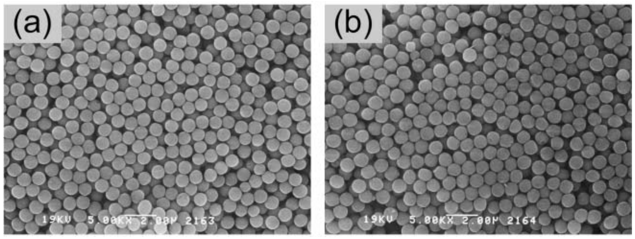

Fig. 1 SEM images of (a) MMSS-18 and (b) PS22-MMSS-18.

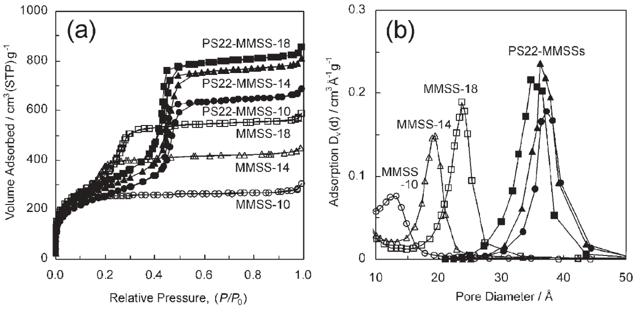

Fig. 2 Nitrogen adsorption–desorption isotherms (a) and pore size distributions (b) of MMSS-*n* and PS22-MMSS-*n*.

were 626–836 and 617–887 nm with standard deviations of 36–54 and 40–49 nm, respectively, with coefficients of variation of less than 10%.

The XRD patterns that were obtained for MMSS-*n* showed a reflection in the small-angle region (see Fig. S1, ESI†). The (100) diffraction peaks of MMSS-*n* were $2\theta = 2.6$–$3.4°$, which indicated the presence of a mesoporous structure. The d_{100} values calculated from 2θ were 25.9–34.1 Å, while the peaks for PS22-MMSS-*n* were $2\theta = 1.7$–$2.2°$ and the d_{100} values were 39.8–53.5 Å. Hydrothermal treatment led to the enlargement of the unit-cells.

The changes in the pore properties of PS22-MMSS-*n* were also explained by the results of nitrogen adsorption–desorption measurements. Fig. 2 shows the nitrogen adsorption–desorption isotherms and the corresponding pore size distributions for MMSS-*n* and PS22-MMSS-*n*. The isotherms are type IV curves. The MMSS-*n* exhibited a reversible adsorption–desorption isotherm with a characteristic nitrogen condensation–evaporation step at a relative pressure below *ca.* 0.3, while the volume adsorbed was between 270–560 cm^3(STP) g^{-1}. Meanwhile, PS22-MMSS-*n* exhibited the step at a relative pressure of *ca.* 0.45 and the volume adsorbed was between 660–820 cm^3(STP) g^{-1}. As shown in Fig. 2(b), the corresponding pore size distributions were very narrow. In Table 1, the specific surface area, the average pore size and the pore volumes of all of the samples are summarized: for the MMSS-*n*, these ranged from 878–1245 $\text{m}^2\ \text{g}^{-1}$, 13.3–23.8 Å and 0.42–0.86 $\text{cm}^3\ \text{g}^{-1}$, respectively; for the pore-expanded PS22-MMSS-*n*, they ranged from 934–1130 $\text{m}^2\ \text{g}^{-1}$, 34.9–37.3 Å and 1.01–1.27 $\text{cm}^3\ \text{g}^{-1}$. The pore sizes and the pore volumes increased substantially, becoming 1.5–2.8 and 1.5–2.4 times larger than the original values, respectively, while retaining high surface areas and narrow pore size distributions.

The d_{100} spacing and the average pore size of MMSS-*n* increased with increasing *n*, depending on the alkyl-chain length of the surfactant. However, although the d_{100} spacing and the average pore size of MMSS-*n* increased with increasing *n*, the equivalent values for PS22-MMSS-*n* slightly decreased. The regularity of the mesopores in MMSS-*n* was higher when a surfactant with a longer alkyl-chain length was used (see Fig. S1, ESI†). It is assumed that reorganization of the mesopores tends to take place more easily in mesoporous silicas with less regularity.

If we attempted to use a hydrothermal treatment using only water or ethanol, it was not possible to achieve pore-expansion of MMSS while retaining spherical morphology. In the former case, although the pores were expanded, the surface of the MMSS deteriorated considerably due to excessive dissolution of silica, while in the latter case, the pores had not been expanded at all.

In cases where swelling agents are used, the pores should be expanded by the introduction of those molecules into the surfactants inside the mesopores. If C_{22}TMA surfactants are introduced into mesopores of MMSS-*n*, both C_{22} and C_nTMA surfactants should be detected in PS22-MMSS-*n*. The surfactants inside the PS22-MMSS-*n* before it was calcined were analyzed by MALDI-TOF/MS and ESI-LC/MS (see Fig. S2 and S3, ESI†). The MALDI-TOF/MS spectra of PS22-MMSS-10 and the ESI-LC/MS spectra of the surfactant extracted from PS22-MMSS-10 show only dehalogenated C_{22}TMA peak ($m/z = 368.4$). On the contrary, the MALDI-TOF/MS spectra of PS10-MMSS-18, which was MMSS-18 that was treated with C_{10}TMABr with a shorter alkyl chain length, exhibited both dehalogenated C_{18} and C_{10}TMA peaks, and the pores had not been expanded. In addition, it was found that the organic content of the MMSS-*n* was increased greatly after pore-expansion. The organic contents of MMSS-*n* (n = 10, 14, 18) were 33.4, 43.4 and 51.0%, respectively, while the contents of the corresponding PS22-MMSS-*n* increased to 47.2, 52.8 and 55.2%, respectively. From the above results, it is obvious that the surfactants inside the mesopores had exchanged completely with the longer alkyl-chain length surfactants. It has been suggested that a strong hydrophobic interaction between surfactants with longer alkyl-chain lengths leads to this complete exchange. A silica source and quaternary ammonium surfactants are bound electrostatically in mesoporous silicas. When identical

Table 1 Properties of MMSS-*n* and PS22-MMSS-*n*

Sample	Average diameter/nm	Standard deviation[a]/nm	d_{100}/Å	Specific surface area/$\text{m}^2\ \text{g}^{-1}$	Average pore size/Å	Pore volume/$\text{cm}^3\ \text{g}^{-1}$
MMSS-10	786	47 (6.0)	25.9	878	13.3	0.42
MMSS-14	626	54 (8.6)	31.4	1179	19.6	0.66
MMSS-18	836	36 (4.3)	34.1	1245	23.8	0.86
PS22-MMSS-10	887	49 (5.5)	53.5	934	37.3	1.01
PS22-MMSS-14	617	45 (7.3)	47.2	1058	36.3	1.20
PS22-MMSS-18	793	40 (5.0)	39.8	1130	34.9	1.27

[a] Coefficients of variation (%) are in parentheses.

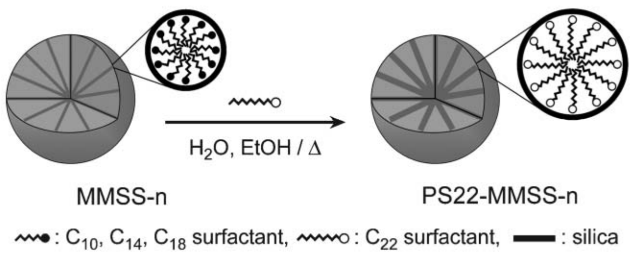

Fig. 3 Schematic representation of pore-expansion of MMSS-*n*.

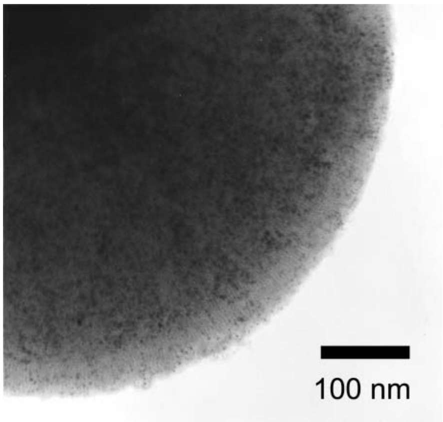

Fig. 4 TEM image of platinum-incorporated PS22-MMSS-10

numbers of surfactants with shorter alkyl-chain lengths are replaced by surfactants with longer alkyl-chain lengths, the pore sizes of the mesoporous silica should increase. The condensation of silanol groups in the as-prepared MMSS-*n* is incomplete, because the synthesis of the MMSS-*n* was conducted at 25 °C. Therefore, under post-synthesis conditions, small quantities of silica are dissolved in a water–ethanol mixture (as confirmed by the molybdenum-yellow method). This leads to a reorganization of the mesopores of MMSS-*n*, as illustrated in Fig. 3.

The internal structure of PS22-MMSS-10 was visualized by the partial incorporation of platinum.[18] A TEM image of platinum-incorporated PS22-MMSS-10 is shown in Fig. 4. The dark part of the micrograph represents the platinum incorporated into the mesopores. It can be seen that the mesopores were aligned radially from the center to the outside of the spherical particles.

In conclusion, we have successfully attained pore-expansion of monodisperse mesoporous silica spheres (MMSS) by a novel surfactant-exchange method. In this hydrothermal treatment, both the pore size and pore volume have increased while retaining good morphology, good monodispersity and a radially, highly-ordered hexagonal regularity. This was achieved by the hydrothermal treatment of MMSS using C$_{22}$TMACl with long alkyl-chain length in a water–ethanol mixed solvent system. MMSS materials with large pore sizes are very important for the introduction of large molecules such as metal complexes and proteins, for the size control of nanoparticles inside mesopores, and for the retention of pore space after the grafting of organic functional groups. MMSS materials have a particle diameter equivalent to the wavelength of visible light, and their optical use such as, for example, photonic crystals, is expected.

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