Synthesis of Carboxylic Group Functionalized Monodispersed Mesoporous Silica Spheres (MMSSs) via Costructure Directing Method

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MMSSs with radially oriented porous structure were successfully synthesized by using cationic gemini surfactant as template and carboxyethylsilanetriol sodium salt (CES) as costructure-directing agent (CSDA). Particle size can be controlled by adding different cosolvent such as isopropanol, methanol, ethanol, or dimethyl sulfoxide.

Monodispersed mesoporous silica spheres (MMSSs) with high surface area and large pore volume have attracted great attention due to their potential applications in chemical, material, and biological areas.[1–6] The combination of the properties of organic groups and inorganic building blocks within a single material is particularly attractive from the viewpoint of materials scientists because of the possibility to combine the enormous functional variation of organic chemistry with the advantages of a thermally stable and robust inorganic substrate.

Yano et al. have synthesized various organofunctionalized MMSSs by cocondensation of organosilane and silica source through cationic surfactant templating.[7–12] Amino group functionalized MMSSs have been obtained by cocondensation of tetramethoxysilane and 3-aminopropyltrimethoxysilane;[7,8] carboxyl-functionalized MMSSs have been formed by introducing 3-cyanopropyltrimethoxysilane synthesis system and subsequent hydrolysis with sulfuric acid;[9] and the sulfonic acid group functionalized MMSSs has been synthesized by a similar two-step process involving cocondensation and subsequent oxidation of 3-mercaptopropyltrimethoxysilane.[10] Among them, it is known that the carboxylic group in the pore structure may serve as anchor sites for biomolecules and for polypeptide syntheses due to their capability of removing cationic species from aqueous solution.[13]

Herein we report a synthesis route of carboxylic group functionalized MMSSs based on the self-assembly of gemini cationic surfactant, a costructure-directing agent (CSDA) containing carboxylate groups and an inorganic source. The costructure directing method for synthesizing functionalized mesoporous silica was proposed by Che et al.,[14–18] for the first time, which provides an efficient route in producing a uniform distribution of the organic groups by the strong interaction between the surfactant (anionic or cationic surfactant) and the CSDAs (positively or negatively charged organosilane). Thus, a regular array of CSDA will be formed following the arrangement of the surfactant, which enables the functional groups to be condensed onto the pore surface in the expected ratios based on the stoichiometry of the molecules and the geometric arrangement of the surfactant.[17] For example, we have found that helical arrangement of the quaternary ammonium groups can be induced by the helical propeller-like packing of chiral amphiphiles owing to the paired electrostatic interaction between the anionic chiral surfactant and cationic quaternary ammonium groups of CSDA.[18]

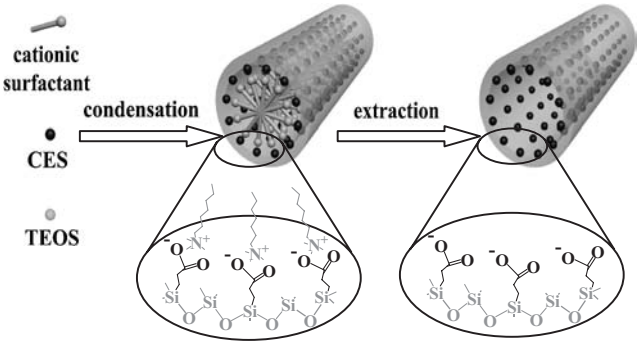

Figure 1. Schematic illustration of the formation of regularly arranged carboxylate groups on pore surfaces via interaction between the head groups of the surfactant and the carboxylic groups of CES.

In this paper, carboxylic group functionalized MMSSs were successfully synthesized by using cationic surfactant as structure-directing agent and carboxyethylsilanetriol sodium salt (CES) as a CSDA in the presence of cosolvent (isopropanol, methanol, ethanol, and dimethyl sulfoxide).[17] The positively charged head group of the surfactant interacts electrostatically with the negatively charged carboxylate site of CES, through double decomposition of the cationic surfactant salt and the CES carboxylate salt (Figure 1). The triol site of CES is cocondensed with the silica source TEOS, to be assembled subsequently to form the silica network. The triol groups of CES covalently tether the silicon atoms incorporated into the framework to the anionic carboxylate groups. Since CES is a strong base because of the sodium alcoholate group, it is favorable for the condensation of alkoxysilane without any additional base. After removal of the cationic surfactant by exhaustive solid–liquid extraction, the carboxylic groups will remain on the surface of the mesopore (Figure 1).

The synthesis was performed as follows: the cationic gemini surfactant $[C_{18}H_{33}N^+(CH_3)_2(CH_2)_3N^+(CH_3)_3]Br_2$ ($C_{18\text{-}3\text{-}1}$), distilled water, and cosolvent were mixed to obtain a homogeneous solution. Descrete amounts of CES and TEOS were added at 80 °C, stirred for 1 h, and then allowed to stand for 2 days. The resultant white precipitates were filtered and dried at 100 °C overnight. Surfactant molecules were extracted by a tetrahydrofuran solution of HCl for 12 h at reflux.

The TEM images of MMSSs are shown in Figure 2. It was found that the spherical particles were highly uniform in size of ca. 400, ca. 520, ca. 540, and ca. 670 nm (standard deviation <5%) (Figures 2a_1, 2b_1, 2c_1 and 2d_1). The unique result attained herein can be attributed to the very slow condensation reaction due to the cosolvents, which results from the relatively high cosolvent concentration in our study. Provided that the hydrolysis

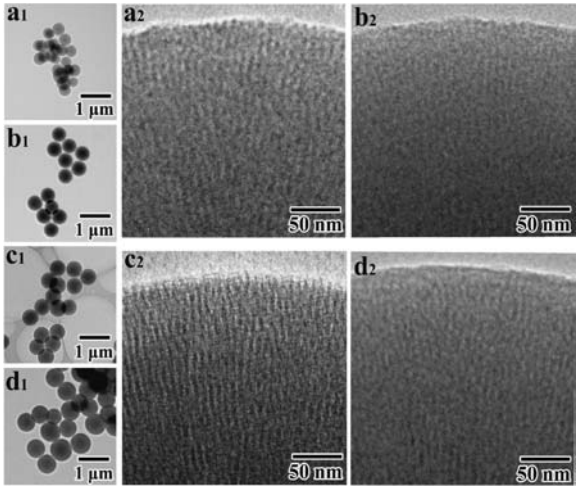

Figure 2. TEM images of extracted monodispersed mesoporous silica nanospheres. The molar composition is: $1C_{18\text{-}3\text{-}1}$: 20TEOS:1CES:14000$H_2O$:*x*(cosolvent), where *x* is 670 for isopropanol (a), 5000 for methanol (b), 2000 for ethanol (c), and 1550 for dimethyl sulfoxide (d).

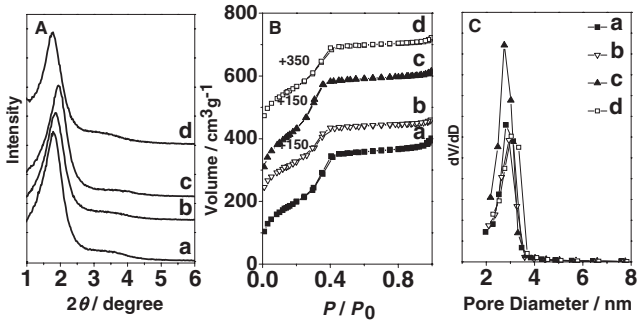

Figure 3. XRD pattern (A), N_2 adsorption–desorption isotherm (B), and pore size distribution (C) of the sample shown in Figure 2.

and condensation reaction proceeds slowly in the solution, the growing particle generally minimizes its surface free energy by forming a spherical shape. From the enlarged images (Figures $2a_2$, $2b_2$, $2c_2$ and $2d_2$), it can be seen clearly that the MMSSs have radially oriented pores within spherical particles and that the close-packed cylindrical pores make up the radial structures in these particles.

Figure 3A shows the powder X-ray diffraction (XRD) patterns of four types of extracted MMSSs. The reflections at around 1.9° and broad diffraction peaks in the region between 3 and 4.5° could be associated with a less-ordered pore system of the MMSSs.

Nitrogen adsorption–desorption isotherms (Figure 3B) of MMSSs show typical type IV isotherms with an evident hysteresis loop in the range of $P/P_0 = 0.35$–0.6. The samples exhibited high Brunauer–Emmett–Teller (BET) specific surface areas of 727.5 (a), 654.1 (b), 1051.6 (c), and 728.6 $m^2\,g^{-1}$ (d); total pore volumes of 0.62 (a), 0.48 (b), 0.72 (c), and 0.58 $cm^3\,g^{-1}$ (d); Barett–Joyner–Halenda (BJH) pore diameters of 3.06 (a), 2.92 (b), 2.86 (c), and 3.12 nm (d) (Figure 3C). Assuming the mesostructure to be 2D hexagonal, we calculated the wall thickness of these samples from the *d* spacing values given by XRD patters and pore sizes, which were 3.96 (a), 3.80 (b), 3.58 (c), and 3.90 (d), respectively. The largest specific surface area of MMSSs synthesized with ethanol would be caused by the thinnest wall thickness it had.

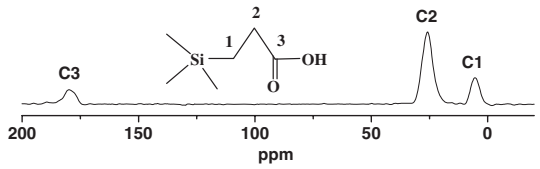

Figure 4. ^{13}C MAS NMR spectra of the extracted sample shown in Figure 2c.

The removal of surfactants while keeping the functional groups was confirmed by solid-state ^{13}C MAS NMR spectra of the MMSS after extraction (Figure 4). The NMR spectrum of the extracted mesoporous silica shows three resonance signals at 5.3, 25.7, and 180.0 ppm that could be assigned to C1, C2, and C3 of the CES, respectively. This demonstrates that the surfactant molecules were removed and that carboxylic groups were present on the surface of the mesopores. It can be calculated that the carboxyl loading is ca. 1 molecule·nm^{-2} from elemental analysis of an extracted sample made with ethanol. Almost all of the CES introduced to the synthesis system was cocondensed and present on the pore surfaces of the mesoporous silica.

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