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Preparation of Chiral Mesoporous Materials with Helicity Perfectly Controlled

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S *Supporting Information*

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Recently, a series of anionic surfactant templated mesoporous silicas (AMS) has been developed.[1−3] The AMS-*n* series ($n = 1-10$) of novel structures has been synthesized based on the self-assembly of anionic surfactants and silica precursors by using aminosilane or quaternized aminosilane as costructure-directing agent (CSDA). We employed 3-aminopropyltrimethoxysilane (APS) or 3-trimethylammoniopropyltrimethoxysilane (TMAPS) chloride as CSDA. The methoxysilane moiety of CSDA is co-condensed with the silica precursor, $Si(OC_2H_5)_4$ (TEOS), to form the silica framework. Note that anionic surfactants derived from diverse amino acids can be used for the synthesis of AMS.

In particular, the use of chiral anionic surfactants, *N*-myristoyl derivatives of L- and D-alanines (C14-L-AlaA and C14-D-AlaA), provides chiral mesoporous silica (CMS) with helical mesopores about 2.2 nm in diameter.[4−7] CMS has a twisted hexagonal rod-like morphology with hexagonally well-ordered mesopores. The left-/right-handed ratios of the helical particles synthesized with the L- and D-isomers have proved to be 75/25 and 25/75, respectively, indicating that the predominant handedness of helices is directed by the handedness of the surfactants.

Periodic mesoporous organosilicas (PMOs) occupy a special position in the class of hybrid materials,[8−12] and the chirality assumes particular importance for PMOs both with regard to the fundamental aspects of chirality and in relation to possible applications. We reported the preparation of chiral mesoporous organosilicas (CMOS) by using achiral fluorinated surfactants and either 1,2-bis(triethoxysilyl)ethylene (BTEE) or 1,4-bis(triethoxysilyl)benzene (BTEB).[13] However, the left-/right-handed ratios of the helical particles synthesized was 50/50 because of the use of achiral surfactants.

Although the CMS and CMOS materials are structurally unique, there have still been problems in its production by the original method as follows.[7] When the synthesis conditions such as temperature, the stirring rate and purity of chemicals were slightly changed, spherical and irregular particles were obtained in addition to the desired helical rods. Therefore, advanced methods for controlling the morphology as well as improving the uniformity in the morphology had been required for applications of CMS and CMOS with a high quality.

It has been found that the use of basic amino acids with the chiral anionic surfactant is advantageous for the formation of CMS in terms of uniformity in the twisted morphology.[14] Note that a vital difference in the method for preparing CMS between the conventional and novel methods is the use of basic amino acids such as arginine and lysine in place of a combination of NaOH and HCl. The handedness of chiral helices in CMS was essentially governed by the stereoisomerism of the surfactant, not that of arginine. Weakly basic conditions given by the basic amino acids are advantageous for the formation of CMS with a high quality. Thus obtained CMS can be applied to the enantioselective separation of racemic solutions; the helical rod-shaped CMS is found to be effective for asymmetric separation of racemic *N*-trifluoroacetylalanine ethyl ester (CF_3CO-Ala-OEt).[14] The left handedness-rich CMS shows asymmetric preferential adsorption of the L-isomer and vice versa. Although extensive studies on the synthesis of chiral mesoporous materials have been done, the handedness of chiral helices in CMS and CMOS has not been controlled perfectly; the barrier of the imperfect left-/right-handed ratio of 75/25 or 25/75 has never been overcome to date.

Here we report on the first preparation of CMOS and CMS with helicity perfectly controlled by using a chiral anionic surfactant, C_{14}-L-AlaA, and an organosilane compound, BTEE, in the presence of L-arginine; the left-/right-handed ratio for the helical particles has proved to be 0/100. The 100% right-handed CMS was formed by calcination of thus formed CMOS. CMOS and CMS with the left-/right-handed ratio of 100/0 have also been prepared by using C_{14}-D-AlaA and BTEE in the presence of D-arginine.

In a typical synthesis procedure for the 100% right-handed CMOS, C_{14}-L-AlaA was added to a solution of L-arginine and deionized water with stirring at 30 °C. After stirring for 30 min (white-colored dispersion of the surfactant was formed), a mixture of BTEE and TMAPS was added to the dispersion with stirring at 30 °C. The gel composition was 0.47 BTEE: 0.06 TMAPS: 0.13 C_{14}-L-AlaA: 0.12 L-arginine: 220 H_2O (pH 7.4). The mixture was allowed to react under stirring conditions for 4 min and static conditions for 2 h at 30 °C. Then, the product was cured at 80 °C for 2 h. The products were collected by centrifugal separation and dried at 100 °C for 12 h. The as-synthesized product (1.0 g) was stirred in HCl/EtOH solution (100 mL of EtOH containing 10.42

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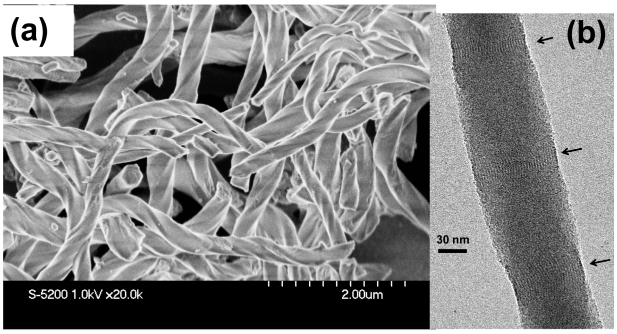

Figure 1. Typical (a) SEM and (b) TEM images of the surfactnat-extracted 100% right-handed chiral mesoporous organosilica.

g of HCl aq. concentrated ∼35 wt %) at 80 °C for 24 h to remove the surfactant and the basic amino acid with the 3-trimethylammoniopropyl moieties and bridging ethynylene groups intact. The product was designated as L-C_{14}/L-Arg-CMOS. The ^{13}C CP-MAS NMR, CHNS elemental analysis and TG-DTA analysis of the extracted products revealed that the surfactant and the basic amino acid were mostly removed by the extraction.

Figure 1a shows the typical scanning electron microscope (SEM) image of the product after extraction, indicating that the discrete twisted hexagonal rod-like particles are formed and that neither spherical- nor irregular-shaped particles are observed. The product has a twisted hexagonal rod-like morphology with a diameter of 0.2−0.3 μm, a length of 3−5 μm, and a helical pitch of 0.7−1.5 μm. By counting all the helical rods through FE-SEM observations, the left-/right-handed ratios for the helical particles have proved to be 0/100. Other SEM images of the product are shown in the Supporting Information, Figure S1. The existence of a chiral channel in the materials was confirmed by a transmission electron microscope (TEM) image (Figure 1b); the fringes appeared to be moving along the axis or curved when the sample was rotated or tilted along a different axis (see Figure S2 in the Supporting Information).

The XRD pattern of the 100% right-handed CMOS exhibited an almost exclusive peak at $2\theta = 2°$ (see Figure S3 in the Supporting Information), indicating that uniform-sized mesopores were formed and their arrangement was not a perfect 2d-hexagonal. Nitrogen adsorption - desorption isotherms revealed the existence of uniform mesopores with a BJH (Barrett−Joyner−Halenda) pore diameter of 2.1 nm (see Figure S4 in the Supporting Information). The BET (Brunauer−Emmett−Teller) surface area and mesopore volume were 853 and 0.66 $cm^3\ g^{-1}$, respectively.

The solid-state ^{29}Si MAS and ^{13}C CP/MAS NMR spectra are shown in Figure 2, indicating that the framework of the prepared CMOS consists of a covalently bonded organic−inorganic network composed of the $O_{1.5}SiCH{=}CH{-}SiO_{1.5}$ unit and trimethylammoniopropyl moieties derived from BTEE and TMAPS, respectively, and that there were a few carbon−silicon bond cleavages of BTEE in the framework as revealed by the appearance of Q^n peaks ($Q^n = Si(OSi)_n(OH)_{4-n}$).[8−10] The signals for T^2 (that is, $CH{=}CH{-}Si(OH)(OSi)_2$) were stronger than those for T^3 (namely, $CH{=}CH{-}Si(OSi)_3$), indicating that the condensation of the framework was not complete, which could be attributed to the relatively short synthesis time. It should be noted that a longer synthesis time resulted in the evolution of spherical and irregular morphologies at the expense of the helical morphology.

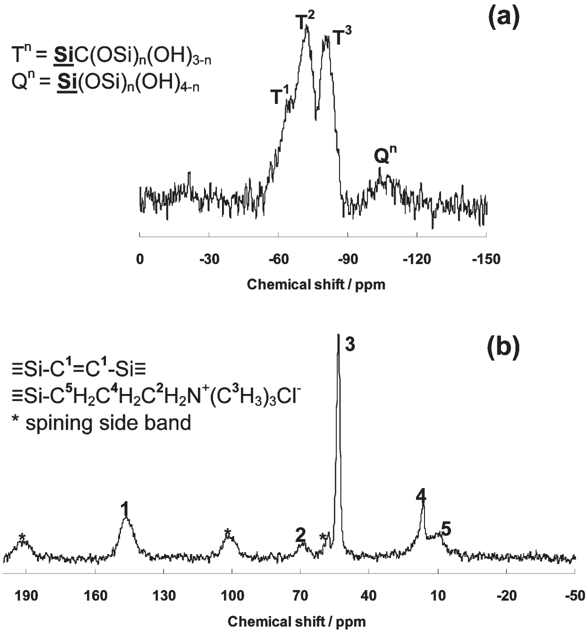

Figure 2. Solid-state (a) ^{29}Si MAS and (b) ^{13}C CP/MAS NMR spectra of the surfactant-extracted 100% right-handed chiral mesoporous organosilica.

In the synthesis of the 100% right-handed CMOS, the morphology was highly sensitive to the amount of L-arginine in the synthesis gel; at the amount of L-arginine below 0.11 and over 0.14, the resultant organosilicas mainly assumed irregular morphologies. The temperature in the aging process on the mesostructure and the handedness affected the mesostructure and morphology. At the temperatures below 80 °C, less-ordered mesoporous organosilica was formed and the resultant particles were a mixture of helical and irregular morphologies. Note that the left-/right-handed ratio in twisted hexagonal rodlike particles of all of the particles formed was found to be 0/100, implying that the handedness was not affected by the temperature in the aging process (see Figure S5 in the Supporting Information).

The CMOS with the left-/right-handed ratio of 100/0 has also been prepared by using C_{14}-D-AlaA and BTEE in the presence of D-arginine. The typical SEM images of the product after extraction are shown in Figures 3 and S6. The 100% left-handed CMOS has the same structural properties as those of the 100% right-handed CMOS.

The CMSs with the left-/right-handed ratio of 0/100 or 100/0 were successfully prepared by calcination of the corresponding CMOS samples at 600 °C. The solid-state ^{29}Si MAS NMR spectrum of the calcined product showed the only peaks corresponding to the Q^3 and Q^4 silicons, indicating the presence of purely siliceous materials (see Figure S7a in the Supporting Information). The typical SEM image of the 100% right-handed CMS is shown in Figure 4. The particles have a twisted hexagonal rod-like morphology and the left-/right-handed ratio of the helical particles has proved to be 0/100. The XRD pattern of the calcined product exhibited one pronounced peak at $2\theta = 2.4°$ (see Figure S7b in the Supporting Information), being suggestive of mesostructured silicas. The BET surface area, BJH pore diameter and mesopore volume of the 100% right-handed CMS were 568 $m^2 \cdot g^{-1}$, 1.8 nm and 0.44 $cm^3 \cdot g^{-1}$, respectively. The calcination process promotes the change from the ethynylene unit ($\equiv Si{-}CH{=}CH{-}Si\equiv$) to the siloxane one ($\equiv Si{-}O{-}Si\equiv$) and the

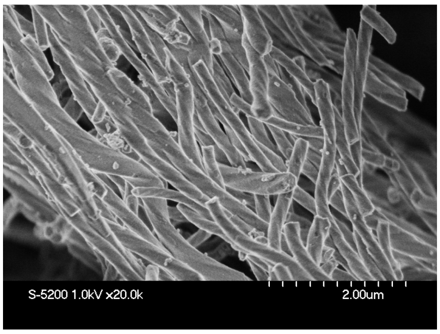

Figure 3. Typical TEM image of the surfactant-extracted 100% left-handed chiral mesoporous organosilica.

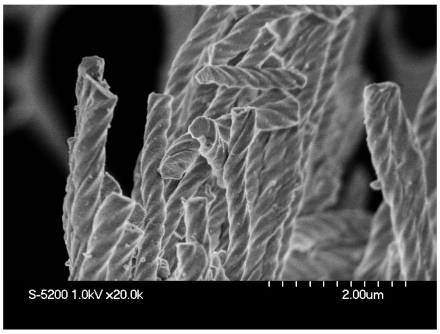

Figure 4. Typical SEM image of the calcined 100% right-handed chiral mesoporous silica.

siloxane cross-linking, leading to the shrinkage of the pore size. The water adsorption−desorption measurements were conducted to evaluate hydrophobicity/hydrophilicity. Although only a small amount of water was adsorbed on the CMOS, the silica-based CMS adsorbed plenty of water molecules (see Figure S8 in the Supporting Information); the hydrophobicity/hydrophilicity of the chiral mesoporous materials can be controlled by changing the calcination temperature. This property would be an important factor when the chiral mesoporous materials are applied in the asymmetric separation of racemic compounds.

To reveal the importance of the relationship between stereoisomerism of the surfactant and basic amino acid added, we synthesized the CMOS samples with the enantiomerism of the surfactant and/or arginine varied. Surprisingly, no helical rods were formed when either combination of C_{14}-L-AlaA and D-arginine or that of C_{14}-D-AlaA and L-arginine was employed (see Figure S9 in the Supporting Information). Although the formation mechanism in terms of the roles of BTEE as well as the basic amino acid are still unclear, it can be concluded that the same enantiomerism of the surfactant and the basic amino acid is indispensable for the formation of CMOS and CMS with helicity perfectly controlled.

The effect of the ratio of BTEE and TEOS was investigated; in the formation system of the 100% right-handed CMOS, BTEE was gradually replaced with TEOS. The proportion of the spherical and irregular shaped particles to helical rods was drastically increased with an increase in the proportion of TEOS. Interestingly, the handedness of the helical particles was inverted along with the proportion of TEOS; in the helical rods, the right-handed rods were decreased along with the proportion of TEOS, and finally the CMS with the left-/right-handed ratio of 75/25 was formed when only TEOS was used. The helicity as well as the morphology of CMOS can be controlled by changing the ratio of BTEE and TEOS as Si sources. Attempt to use either 1,2-bis(trimethoxysilyl)ethane or 1,2-bis(trimethoxysilyl)methane in place of BTEE for synthesizing 100% right- or left- handed chiral CMOS have failed even though periodic mesoporous organosilicas were formed. Considering these facts, we speculate that a structural rigidity of BTEE would be a key to the success in the perfect control of helicity.

In conclusion, we first demonstrated the preparation of 100% right- or left- handed chiral mesoporous materials by using BTEE and TMAPS in the presence of the chiral anionic surfactant and the basic amino acid. Furthermore, the properties of these materials would be manipulated through the functionalization of the organic fragment. These achievements could lead to new uses of mesoporous materials for catalysis and separation media, where enantiomeric space could be applied to the manufacturing of enantiomerically pure chemicals and pharmaceuticals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. SEM and TEM images, XRD patterns, etc., of the products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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