Mesoporous Materials

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Synthesis and Characterization of Chiral Periodic Mesoporous Organosilicas**

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Chirality is an important topic both in fundamental research and for practical applications in fields as diverse as biology, functional materials, fine chemistry, and pharmacy. Some pioneering work on inorganic materials with chiral nanochannels has recently been reported.[1–5] The first example is chiral spiral silica obtained by sol–gel polycondensation of tetraethoxysilane (TEOS) in cholesterol and diaminocyclohexane-based organogel systems.[1,2] Another successful example is well-ordered chiral mesoporous silica prepared by using chiral anionic surfactants as templates.[3] Moreover, the synthesis of chiral mesostructured silica in the absence of such chiral additives has also been reported, thus opening a door for the preparation of chiral mesoporous materials using achiral templates.[4,5] Periodic mesoporous organosilicas (PMOs) are a special class of hybrid materials, in which chirality assumes a particular importance both with regard to fundamental aspects and in relation to possible applications.[6–10] However, there are no reports on chiral channels in PMO materials up to now. Herein, we report on achiral-fluorinated surfactant-templated PMOs that contain chiral channels. Such chiral PMOs include twisted hexagonal rods synthesized using 1,2-bis(triethoxysilyl)ethene (BTEE), as hybrid silica precursors, and spiral hexagonal rods prepared using 1,4-bis(triethoxysilyl)benzene (BTEB). The spiral samples synthesized with BTEB exhibit structural periodicity, with a spacing of 0.85 nm in the crystal-like mesoporous wall. Thus, we expect our chiral PMOs to lead to new applications, for example, in the development of enantioselective catalysts, adsorbents, sensors, although—currently—the enantiopurity of the helical channels is not high.

To produce the chiral PMO materials, the achiral cationic fluorinated surfactant [$CF_3(CF_2)_3SO_2NH(CH_2)_3N^+(CH_3)_3I^-$] (FC-4911) and the cationic hydrocarbon surfactant cetyltrimethylammonium bromide (CTAB) were employed as structure-directing agents, while BTEE or BTEB were used as hybrid silica precursors. The ratio of FC-4911 to CTAB was the key factor for the formation of chiral products. Low reactant concentrations and relatively short reaction times were also important factors. The final products—after removal of the templates by means of solvent extraction—showed a rodlike morphology (see Figure 1). The sample prepared using BTEE (designated as sample A) exhibited a twisted rodlike morphology with distinguished bent crystal facets that had an outer diameter of 120–150 nm and a length of 1–2 μm (see Figure 1a and the Supporting Information). Periodic fringes were observed along the axes of the rods (with a length $L = 300$–450 nm) and the helical pitches (that is, $6L$) were estimated to be 1.8–3 μm (Figure 1b).[3,11] On the other hand, the sample prepared using BTEB (designated as sample B) exhibited a spiral rodlike morphology with distinguished twisted crystal facets that had an outer diameter of 100–120 nm and a length of 1–3 μm (see Figure 1c). Periodic fringes were also observed along the axes of these rods (with a length $L = 100$–200 nm) and the helical pitches were estimated to be about 0.5–1.2 μm (Figure 1d). The fringes of both samples appeared to be moving along the axis or curved when

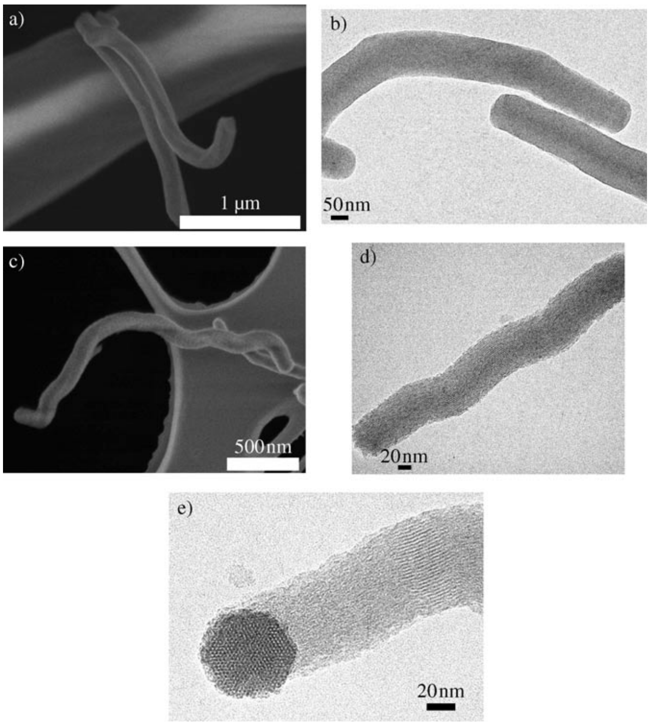

Figure 1. a) SEM image of sample A; b) TEM image of sample A; c) SEM image of sample B; d) TEM image of sample B; e) TEM image of sample B taken with a [100] incidence.

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the samples were rotated or tilted along a different axis (see the Supporting Information). These observations confirmed that both PMO samples were composed of helical channels.[3–5,11]

The X-ray diffraction (XRD) patterns of the two samples exhibited three typical peaks in the small-angle region (namely, 1–6°)—indexed to the *p6mm* hexagonal symmetry (Figure 2). The lattice constant of sample A was 5.05 nm and that of sample B was 4.57 nm. Furthermore, the N_2 adsorption isotherms showed a type-IV curve with a well-defined capillary-condensation step at a relative pressure (p/p_0) of 0.2–0.4 (Figure 3), thus confirming the existence of uniform mesopores.[12] The structural parameters are summarized in the Supporting Information. The ^{29}Si and ^{13}C MAS NMR spectra showed that the framework of the PMOs consisted of a covalently bonded organic–inorganic network composed of $O_{1.5}Si{-}CH{=}CH{-}Si{-}O_{1.5}$ or $O_{1.5}Si{-}C_6H_4{-}Si{-}O_{1.5}$ units, and that there were almost no carbon–silicon bond cleavages of BTEE or BTEB in the framework.[8–10] However, the signals for T^2 (that is, $CH{=}CH{-}Si(OH)(OSi)_2$ or $C_6H_4{-}Si(OH)(OSi)_2$) were stronger than those for T^3 (namely, $CH{=}CH{-}Si(OSi)_3$ or $C_6H_4{-}Si(OSi)_3$), thus indicating that the condensation of the framework was not complete, which could be attributed to the relatively short synthesis time (2 h). It should be noted that a longer synthesis time resulted in the evolution of a platelike morphology at the expense of the helical morphology.

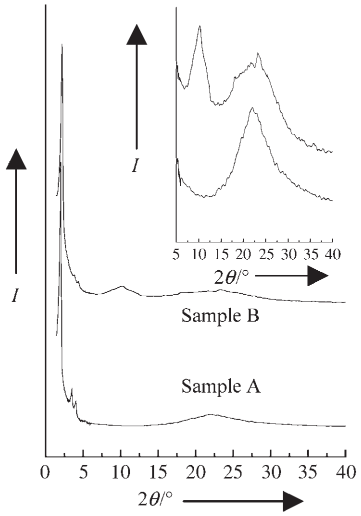

Figure 2. XRD patterns of samples A and B. The inset shows magnifications of these patterns in the wide-angle region (5° < 2θ < 40°).

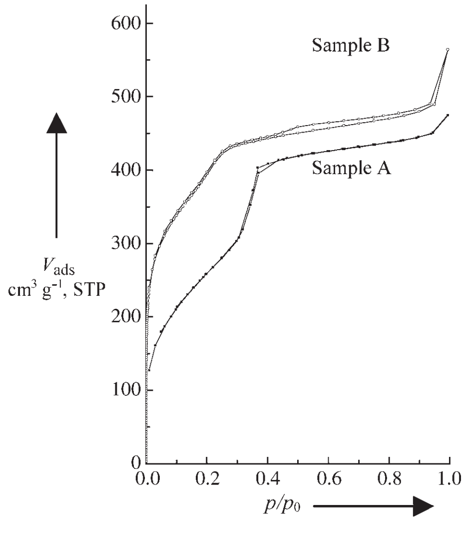

Figure 3. N_2 adsorption isotherms of samples A and B.

The XRD patterns of sample B in the region 6–40° exhibited two resolved peaks and an unresolved one, with *d* spacings of 0.85, 0.42, and 0.22 nm, respectively (Figure 2); these diffraction peaks could be explained by the existence of a periodic structure with a spacing of about 0.85 nm. An enlarged transmission electron microscopy (TEM) image revealed lattice fringes that were stacked along the channel's axis with a relatively uniform spacing of about 0.85 nm on the mesopore walls (Figure 4).

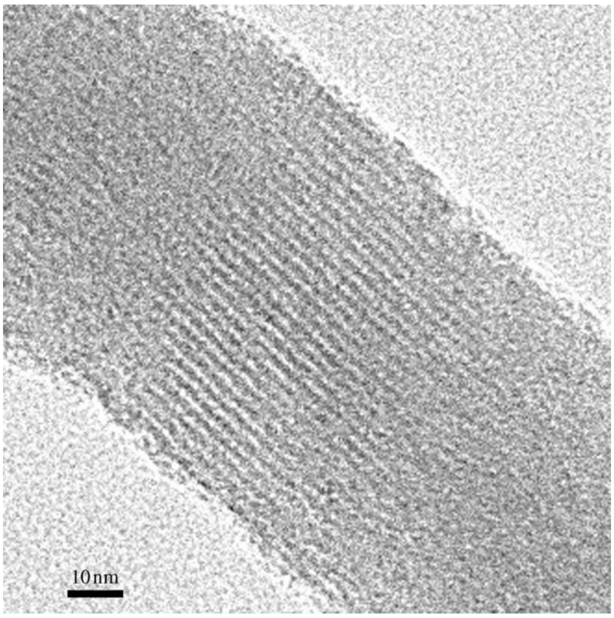

Figure 4. Enlarged TEM image of sample B, which corresponds to the selected area in Figure 7 of the Supporting Information.

Sample B, which exhibits a spiral-nanorod morphology, can be distinguished from the platelike particles reported previously during the synthesis of PMOs with a crystal-like wall by using BTEB.[10] This sample showed a relatively large molecular-scale periodicity (namely, 0.85 nm). Additionally, it was difficult to observe a layered structure—stacked along the channel axes—over the whole region, and this is the result of badly resolved reflections in the wide-angle XRD patterns, which can be attributed to an incomplete condensation and a loosely self-assembled framework. These results were confirmed by the ^{29}Si NMR spectra. Inagaki et al.[10] have claimed that a similar molecular-scale periodicity could be observed in mesoporous ethylene–silica; however, we did not find such a layered structure in the case of sample A (prepared from BTEE).

The handedness of the PMOs was determined by counting the characteristic morphologies from 400 randomly chosen crystals in the scanning electron microscopy (SEM) images.[3,4] The number of left-handed particles was almost equal to that of right-handed ones (for both samples), thus indicating racemic mixtures. However, it should be noted that the left-to-right-handed ratio could be increased to 55/45 by adding a small amount of sodium L-tartrate during the preparation procedure. Such results suggest that the driving forces for the formation of helical structures come from the addition of fluorinated surfactants, and that the use of appropriate chiral additives may enhance the enantiopurity of the final products.

The synthesis of chiral mesoporous silica without using chiral additives has recently gained great attention,[4,5] and a reduction of the surface free energy has been proposed as the main driving force for the formation of the chiral structure,[5] which can explain our results very well. In the case of a rodlike morphology, decreases in the particle size and increases in the surface area are energetically favorable for reducing the surface free energy, which results in the formation of a chiral PMO.[5] However, when an inorganic silica source—such as TEOS—is employed, amorphous products are formed rather than chiral mesoporous materials. Therefore, this method can only be applied when organosilica compounds are used as the starting materials. The formation mechanism on the molecular level and the control of the enantiopurity are still being studied.

The addition of crystallinity to the pore wall of mesoporous materials has long been sought after and represents an important development in materials science. Organic-bridged mesoporous materials with crystal-like periodic pore walls may have important potential applications as adsorbents for separations, electrolytes for fuel cells, and highly selective and active catalysts for liquid- and gas-phase reactions. The control of the pore architecture of mesoporous materials is another interesting topic in this research field, and the preparation of mesoporous materials exhibiting chirality is also an attractive goal, because of its possible applications in materials science, chemical sensing, and enantioselective catalysis. To our knowledge, this is the first report on the synthesis of a periodic mesoporous organosilica sample with crystal-like walls and chiral mesochannels. We believe that this result will enable us to dispose silanol or other functional groups on the silica wall in a chiral arrangement. Further developments of these materials could lead to wide-ranging applications that include the manufacture of enantiopure chemicals and pharmaceuticals by using the chiral microenviroments as catalysts and separation media with both shape specificity and enantioselectivity.

Experimental Section

Chiral mesoporous ethylene–silica (sample A) was synthesized from BTEE in the presence of FC-4911 and CTAB as co-templates. In a typical synthesis, FC-4911 (0.105 g) was dissolved in deionized water (60 g) upon stirring at room temperature before adding CTAB (0.1 g) and 2 M NaOH (0.35 g). The system was kept at a constant temperature of 80 °C, and BTEE (0.463 g) was added upon vigorous stirring. After 2 h, the as-synthesized products were collected by filtration, washed, and dried. To remove the templates, the products were finally heated under reflux in a mixture of ethanol and HCl for 24 h at 70 °C.

Chiral mesoporous benzene–silica (sample B) was prepared from BTEB following the same procedure described above but using 0.9 g of FC-4911 and 0.529 g of BTEB.

The XRD patterns were recorded on an MAC Science M3X 1030 X-ray diffractometer with $Cu_{K\alpha}$ radiation (40 kV, 20 mA). The isotherms of nitrogen were measured using a Micromeritics ASAP 2010M system, with the samples being out-gassed for 10 h (at 100 °C) before the measurements. SEM experiments were performed on a Hitachi S-5200 electron microscope, and TEM studies were carried out on a high-resolution field-emission transmission electron microscope (JEM-2010F, JEOL) operating at 200 keV. The ^{29}Si magic-angle spinning (MAS) NMR measurements were performed on a JEOL LA400WB 400 MHz nuclear magnetic resonance spectrometer at ambient temperature.

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