An Efficient Synthesis of Helical Mesoporous Silica Nanorods

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Helical mesoporous silica nanorods have been synthesized with high efficiency by the addition of 1-alkanol or 1-aminoalkane with proper carbon chain length (C_4–C_8) as a cosurfactant of cetyltrimethylammonium bromide (CTAB) during the synthesis of MCM-41 in a dilute synthesis gel containing CTAB, tetraethyl orthosilicate, ammonium hydroxide, and water.

Inorganic materials with helical pores have attracted much attention because they may exhibit peculiar advantages of shape selectivity in adsorption, separation, and heterogeneous catalysis.[1] Thus far, only very scattered reports have succeeded in the synthesis of this kind of materials. Usually, complicated structure-directing agents with chiral property have to be applied, e.g., chiral ligand or chiral metal complex for microporous materials, chiral organic templates for mesoporous materials.[2,3] A recent paper showed that the use of an achiral ionic liquid as the template could yield helical mesoporous silica.[4] Here, we report a new route for the synthesis of inerratic helical channel architecture in mesoporous silica nanorods with high efficiency by using primary alcohol or amine as a cosurfactant. The current study offers a possibility of simply fabricating mesoporous materials with regular helical channels.

MCM-41, one of the most widely studied ordered mesoporous materials, was synthesized by the self-assembly of organic template molecules and inorganic silicate ions into an organic–inorganic hybrid as a precursor.[5] It can be expected that the channel architecture and the morphology of the mesoporous materials synthesized by this approach are largely dominated by the assembling behavior of the template molecules. Many pioneer researches have provided several interesting morphologies of mesoporous silica under specific synthetic conditions or in the presence of an additive.[6–16] The formation of mesoporous silica nanofibers with either circular or longitudinal pore architecture was observed by the addition of concentrated inorganic salts to an acidic synthesis gel.[8] Organic additives such as decane[14] and ethylacetate[15] were also reported to be capable of changing the morphology of mesoporous silica from sphere to tube or rod. However, there are only a few reports on the synthesis of mesoporous materials with inerratic helical channels with high efficiency.[3]

Recently, we discovered that helical mesoporous silica nanorods could be formed with high yields by simply modifying the synthesis procedure using C_4–C_8 primary alcohol or amine as a cosurfactant of CTAB. In a typical synthesis, the surfactant (CTAB) was first dissolved in deionized water. After the adjustment of pH value of the solution with ammonium hydroxide, 1-hexanol, and TEOS were added, and the mixture with a molar ratio of CTAB:TEOS:NH_3:H_2O being 0.11:1:10:525 was allowed to react at temperatures of 35–95 °C under continuous stirring for 2 h. The product was recovered by filtration followed by washing and drying. The organic molecules were removed by calcination in air at 550 °C for 8 h.

Figure 1 shows the SEM micrographs of the samples after the addition of 1-hexanol as a cosurfactant of CTAB at a reaction temperature of 80 °C. The particles prepared from the gel without 1-hexanol were spheres with diameters of 150–300 nm. By adding 1-hexanol, the spheric particles elongated in one direction, and gradually developed into nanorods as the molar ratio of 1-hexanol/CTAB increased to 1/1. Further increases in the ratio to 2/1 led to the formation of small spheric particles again with diameters of ca. 80 nm. Finally, irregular hollow par-

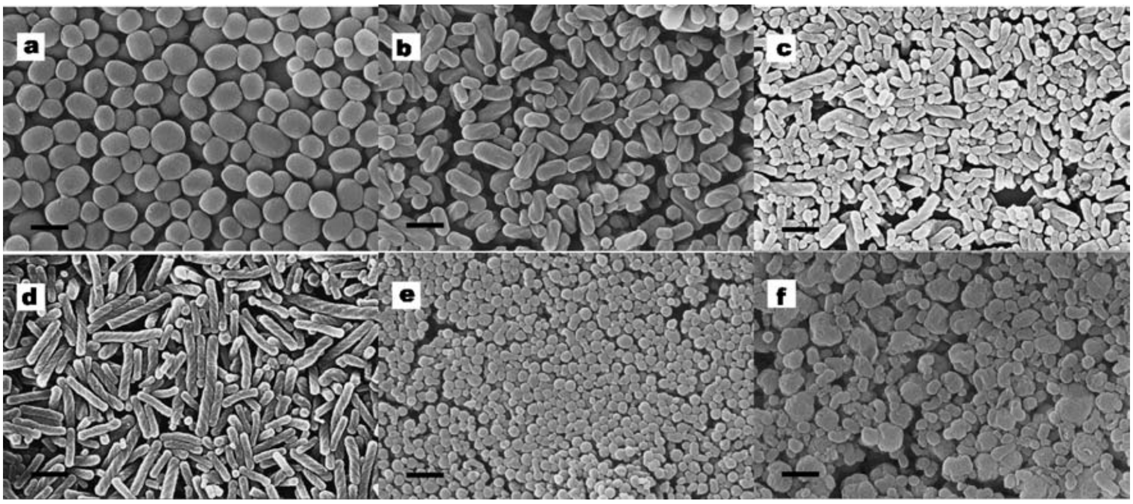

Figure 1. SEM images of mesoporous silicas prepared at 80 °C with and without 1-hexanol co-surfactant. The molar ratios of 1-hexanol/CTAB are: (a) 0/1, (b) 0.25/1, (c) 0.5/1, (d) 1/1, (e) 2/1, and (f) 7/1. The black bar in each micrograph denotes 400 nm.

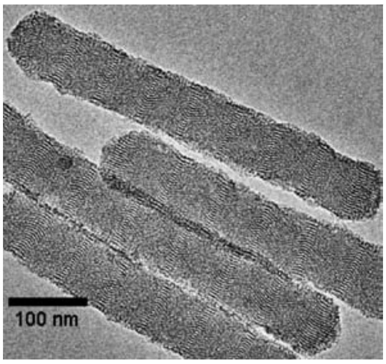

Figure 2. TEM image of the mesoporous silica nanorods prepared at 80 °C in the presence of 1-hexanol with 1-hexanol/CTAB = 1/1.

ticles appeared as the 1-hexanol/CTAB increased to 7/1.

The SEM image in Figure 1d for the rodlike sample showed equidistant lines going diagonally across the external surfaces, revealing that the sample possessed perfect helical morphology. The proportion of this morphology was almost 100%. These helical silica rods were 70–120 nm in diameter and 400–1000 nm in length.

Figure 2 shows the TEM micrograph of this sample. A clear and well-ordered sinuated pattern of mesoporous channels was observed equidistantly along the rod direction. Similar TEM images were recently reported for a mesoporous silica with chiral channels synthesized using a very complex chiral template.[3,17] We speculate that each of our helical rods also contains chiral channels along the rod direction. From the SEM image, we could clearly find two kinds of handedness of helical surface stripes. By counting the helical peculiarity of ca. 200 randomly chosen samples, we estimated that the ratio of the left/right handed helical rods was ca. 5.06/4.94.

XRD measurements revealed that the larger spheric particles or the shorter rods observed in Figures 1a and 1b exhibited three well-resolved diffraction peaks at 2–6° (2θ degrees) ascribed to (100), (110), and (200) reflections of MCM-41. For the rodlike samples synthesized with 1-hexanol/CTAB ratios of 0.5/1 and 1/1, the diffraction peaks became broad and only the peak of (100) could clearly be identified. For both the spheric and rodlike samples, the N_2 adsorption/desorption isotherms measured by N_2-sorption at 77 K showed a shape of type IV, typical for mesoporous materials. The pore diameters were evaluated to be ca. 3.0 nm by the BJH method, and the BET surface areas and pore volumes were 970–1030 $m^2\,g^{-1}$ and 0.80–1.01 $cm^3\,g^{-1}$, respectively.

Other additives such as 1-alkanols, 1-aminoalkanes, *n*-alkanes, alkyl acids, and alkyl halides have also been investigated as the cosurfactants of CTAB for the synthesis of mesoporous silica. 1-Alkanols and 1-aminoalkanes with carbon numbers of C_4–C_8 showed similar effects to 1-hexanol, but the dimensions of the helical nanorods were different. It was clarified that the length of the silica rods increased with an increase in the carbon chain length of the organic additive. However, the use of alkane, alkyl acid, or alkyl halide as the cosurfactant could not give helical silica nanorods. Thus, the additive molecules may interact with the CTAB molecules by the polar hydroxyl or amine group, and this interaction could be very crucial in the formation of helical rodlike morphology.

In conclusion, we have discovered a simple route for the synthesis of helical mesoporous silica nanorods with high efficiency by using alkyl alcohol or alkylamine as a cosurfactant of CTAB in a dilute synthesis gel containing CTAB, TEOS, ammonium hydroxide, and H_2O. The nature of the cosurfactant and the ratio of the cosurfactant to CTAB are key factors influencing the morphology. The current route may also be applicable to the syntheses of other nonsilica helical mesoporous materials, which may be useful for shape-selective adsorption, separation, and catalysis. Researches on this direction and the elucidation of the formation mechanism are underway in our laboratory.

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