Racemic Helical Mesoporous Silica Formation by Achiral Anionic Surfactant

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Received September 16, 2005
Revised Manuscript Received December 12, 2005

The self-assemblies of small molecules into helical architectures can be found throughout nature: from simple molecules,[1] polymers,[2] surfactants,[3] and amphiphilic molecules[4] to biological supramolecular assemblies.[5] Generally, the chirality of supramolecular systems can be generated through the assembly of chiral molecules or a combination of chiral and achiral molecules. However, the finding of spontaneous chiral supramolecular formation from an achiral molecule assembly has attracted great attention.[6] Understanding the expression of molecular information at the macroscopic level to construct helical structure is of fundamental importance.

The assembly of surfactants and amphiphilic molecules is of particular interest, as chirality within the individual molecule can be expressed in the superstructure by the formation of helices and twisted bilayers.[4,5] We recently discovered a templating route for preparing well-ordered mesoporous silica based on the self-assembly of chiral anionic surfactants and inorganic precursors by using aminosilane or quaternized aminosilane as a co-structure-directing agent (CSDA).[7] On the basis of this templating route, we have achieved the formation of a chiral mesostructure by using *N*-miristoyl-L-alanine sodium salt and *N*-trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride (the cation denoted here as TMAPS) or 3-aminopropyltrimethoxysilane.[8] Unexpectedly, we have now found that achiral surfactant sodium dodecyl sulfate (SDS) can form ordered racemic helical mesoporous silica by its self-assembly in the presence of TMAPS. To the best of our knowledge, this is the first report on the formation of templated helical structure from an achiral surfactant assembly.

Helical ordered mesoporous silica was synthesized by using achiral surfactant SDS as the template, TMAPS as the CSDA, and tetraethyl orthosilicate (TEOS) as the silica source. The chemical composition (mole ratios) of the reaction mixture was 1:0.46:5.5:1611 SDS/TMAPS/TEOS/H_2O. The mixture of the SDS, TMAPS, and TEOS was stirred at room temperature for 10 min and allowed to react at 100 °C for 20 h under static conditions. The pH value of the synthesis gel was about 7.5. The products were recovered by filtration and dried at 100 °C. Both the anionic surfactant and the organics of the TMAPS used were removed by calcination at 650 °C for 6 h. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2000 powder diffractometer equipped with Cu Kα radiation (40 kV, 20 mA) at the rate of 1.0°/min over the range of 1.5−10.0° (2θ). The microscopic features of the sample were observed with scanning electron microscopy (SEM; Hitachi, S-5200). The samples were observed without any metal coating for SEM. Using a low accelerating voltage, we were able to obtain the SEM images of the samples without metal coating and therefore selective information from the genuine surface region. High-resolution transmission electron microscopy (TEM) images were taken on a JEM-3010 microscope operated at an accelerating voltage of 300 kV. For TEM measurements, all samples were dispersed in ethanol and deposited on a microgrid. The N_2 adsorption−desorption isotherms were measured at −196 °C on a Micromeritics ASAP 2010 volumetric adsorption analyzer.

Figure 1a shows the XRD pattern of a calcined helical mesoporous silica synthesized with a TMAPS/SDS $= 0.5$ molar ratio. This sample showed three well-resolved peaks in the range $2\theta = 1-6°$, which were indexed as 10, 11, and 20 reflections on the basis of the two-dimensional hexagonal *p*6*mm* unit cell (which was also confirmed by TEM) with the unit cell constant $a = 4.5$ nm, indicating that this

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10.1021/cm052085e CCC: $33.50

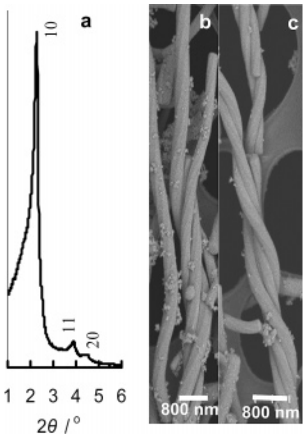

Figure 1. XRD pattern (a) and SEM images (b and c) of racemic helical mesoporous silica.

mesoporous silica has a highly ordered hexagonal mesoscopic structure. The nitrogen adsorption−desorption isotherm (see Figure S1, Supporting Information) shows type IV features, which also confirmed the existence of uniform mesopores with a BJH (Barrett−Joyner−Halenda) pore diameter of 2.5 nm. The BET (Brunauer−Emmett−Teller) surface area and mesopore volume were 678 $m^2\ g^{-1}$ and 490 $mm^3\ g^{-1}$, respectively.

SEM images (Figure 1b,c; see also Figure S2, Supporting Information, for a low-magnification SEM image) reveal that this material has a twisted rodlike morphology with a hexagonal cross section. They are usually twisted in bundles with two, three, or four single strands, forming superhelices. The chirality of superhelices was observed by the TEM images as briefly discussed later to be right-handed from right-handed strands or left-handed from left-handed strands. This is different from that of supercoiled DNA or ropes. It is well-known that the left-handed DNA helices determined by the molecular helicity coil up to form large right-handed superhelices[9] and the handedness of the rope must be opposite to the handedness of the several strands it is composed of, to avoid spontaneous unwinding to release twist tension. Figure 2a is a TEM image which shows two chiral rods twisted together, and Figure 2b is an enlargement of the rectangular area in Figure 2a. It can be seen that the fringes correspond to the interplanar space (10) indicated by arrows bent to an opposite direction in these two rods. As explained in our previous letter,[8] the (10) fringes will curve when the rod is not precisely perpendicular to the electron beam. The rods of right- and left-handedness will have opposite curve directions when they are tilted to the same direction relative to the electron beam. As for one rod, the (10) fringes will change their curve directions to the opposite when the rod is tilted up or down to the electron beam. In Figure 2b, one of the two rods has an up direction relative to the electron beam and the other has a down direction, so if these two rods have the same handedness, the (10) fringes would curve in an opposite way just as observed. Therefore, TEM observation also confirmed that the rods with the same handedness twist together.

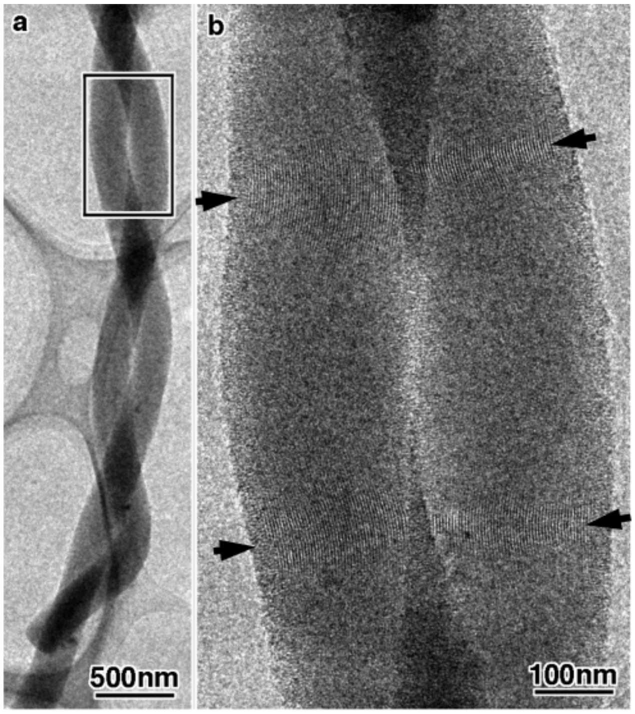

Figure 2. TEM images with different enlargements of two twisted single strands. (a) TEM image shows two chiral rods twisted together and (b) an enlargement of the rectangular area in part a.

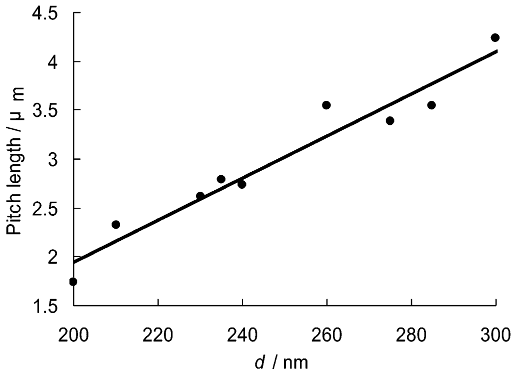

Figure 3. Pitch length of chiral mesoporous silica with different rod diameters.

Depending on the synthesis conditions, twisted rods with outer diameters ranging from 200 to 400 nm and lengths from a few micrometers up to several tens of micrometers were obtained. From six distinct outer surfaces of the rods, the helical pitches along the rod axis were estimated to be ∼1.6−4.0 μm. Interestingly, as illustrated in Figure 3, the larger the helical rod diameter the longer the helical pitch, indicating that the curvatures of the channels within thinner rods and thicker rods are different when the channels are at the same distance from the center of the rods. The curvature is decreased with increasing aggregation number of rodlike micelles. This was confirmed by the TEM image shown in Figure 4. In a manner similar to our samples reported previously,[8] the fringes indicated by arrows correspond to the interplanar space of (10). Between two sets of (10) fringes, the rod twists by 60°, which means that the distance between two sets of (10) fringes is one-sixth of one pitch. The distance between two sets of (10) fringes in the thicker rod is obviously larger than that in the thinner rod. It has been found that the pitch length was decreased with

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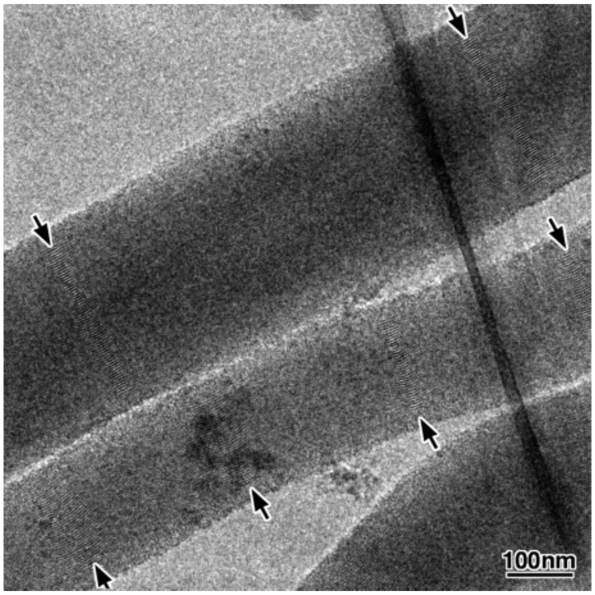

Figure 4. TEM image showing different helical pitches of two rods with different diameters.

increasing temperature, with decreasing pH value and salt additives.

Handedness of this porous material was estimated by counting characteristic morphologies of 500 randomly chosen crystals from SEM images, and left- to right-handed ratio was proved to be ∼1:1. The achiral organic molecule can form a racemic nematic phase in the presence of proper amounts of CSDA, indicating that the effective cross-sectional area at the aggregate interface has been changed by controlling of the interaction between surfactant SDS and CSDA. The formation of chiral mesostructure was found to be very sensitive to composition, reaction temperature, and time, indicating that the headgroup orientation of the helical micelle is elaborately controlled not only thermodynamically but also kinetically. The yield of the product based on the TEOS was in the range 20−60% depending on the synthesis conditions. The neutral pH value of the synthesis gel would be an important factor that affects the silica framework condensation and, as a result, lowers the silica yield. At present the origin of the helical morphology of mesoporous materials formed from achiral surfactant is not very clear. We are working on elucidating the mechanism of helical mesostructure formation by achiral and chiral surfactant self-assembly.

In our previous work,[8] the maximum left- to right-handed ratio was found to be only 3:1, despite the pure left-handed surfactant being used, indicating that competing driving forces for the formation of chiral structure exist, other than the chiral surfactant packing. It is not doubtful that the formation of racemic helical mesostructure with achiral surfactant gave us key information of the driving force existing in these synthesis systems. Understanding the mechanism for the construction of helical structure by achiral surfactant and the driving force of the formation of racemic helical mesostructure with achiral surfactant is fundamentally important, which will enable us to design and construct enantiomerically pure mesostructure or new functional helical architecture.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grant 20425102), the China Ministry of Education and Shanghai Science Foundation (0452nm061). S.C. thanks Prof. Takashi Tatsumi (Catalytic Chemistry Division, Chemical Resources Laboratory, Tokyo Institute of Technology) for scientific discussion. O.T. thanks Swedish Science Research Council (VR) and Japan Science and Technology Agency (JST) for financial support.

Supporting Information Available: N_2 adsorption and desorption isotherms and pore size distribution as well as SEM images of racemic helical mesoporous silica (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM052085E