Application of a Water Soluble Alkoxysilane for the Formation of Mesoporous Silica from Nonionic Surfactant Micelles Bearing Cholesterol

Shun Takahashi,[1] Yasunari Ikkai,[2] Carlos Rodriguez-Abreu,[3] Kenji Aramaki,[2]
Tetsu Ohsuna,[4] and Kazutami Sakamoto*[1]
[1]*Shiseido Research Center, 2-2-1 Hayabuchi, Tsuzuki-ku, Yokohama 224-0025*
[2]*Graduate School of Environment and Information Science, Yokohama National University,*
79-7 Tokiwadai, Hodogaya, Yokohama 240-8501
[3]*Departamento de Química Física, Facultad de Química, Universidad de Santiago de Compostela,*
E-15782, Santiago de Compostela, Spain
[4]*CREST, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi 332-0012*

(Received September 25, 2006; CL-061109; E-mail: kazutami.sakamoto@to.shiseido.co.jp)

A water soluble silica precursor, tetrahydroxyethyl orthosilicate (THEOS), was used for the synthesis of mesoporous silica from micellar solutions of a nonionic surfactant bearing cholesterol moiety ($ChEO_{10}$), which also forms a variety of lyotropic liquid crystal (LLC) structures. The resulting mesoporous silica showed ribbon-like structures, both in µm and nm scale, corresponding to the rectangular LLC phase of $ChEO_{10}$. We propose the use of THEOS as a novel silica precursor for the investigation of tailored imprinting of LLC topology into the mesoporous silica.

Mesoporous silica with nanometer-scale well-ordered pores in size and connectivity is of interest for catalysis, chromatography and other applications. Origin of such organized structures of the mesoporous silica is attributed to the topology of the surfactant self-organization as a template imprinted by the condensation of silica precursor such as tetraethyl orthosilicate (TEOS); $Si(OCH_2CH_3)_4$, tetramethyl orthosilicate (TMOS); $Si(OCH_3)_4$.[1] TEOS and TMOS are insoluble in water and require acidic or alkaline conditions for the hydrolysis to generate reactive monomers. Under these conditions, it is difficult to design and control the topology of the mesoporous silica. We have utilized a novel silica precursor tetrahydroxyethyl orthosilicate (THEOS); $Si(OCH_2CH_2OH)_4$, which is soluble in water and hydrolyses to form silicic acid at the neutral conditions.[2] Upon dissolution in water, THEOS easily hydrolyses and yields ethylene glycol, which barely affects the self-organized structures in the surfactant solution, therefore we could utilize the readily available aqueous phase diagram of selected surfactant for the investigation.

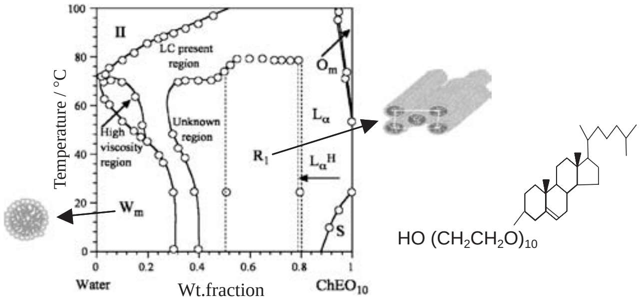

Figure 1. Phase diagram of $ChEO_{10}$/water system[3] as a function of temperature and surfactant weight fraction. Wm, R_1, $L\alpha^H$, $L\alpha$, and Om denote micellar, intermediate ribbon, distorted lamellar, lamellar, and reverse micellar phases, respectively. S is a solid-present region, and II indicates a two-phase region.

We have chosen a non-ionic surfactant bearing cholesterol moiety ($ChEO_{10}$), which provides a variety of lyotropic liquid crystal (LLC) phases as shown in Figure 1.[3] Ion-exchanged water (270 g) and non-ionic surfactant ($ChEO_{10}$) (15 g) were mixed thoroughly to obtain a clear solution at room temperature. Thereafter, THEOS (15 g) was added into $CHEO_{10}$/water solution and was stirred for 24 h at 60 °C. After the reaction, the solution was dried up at 90 °C for 24 h to remove solvent. Residual solids were washed by ethanol to remove ethylene glycol, then filtered and dried at 80 °C for 5 h.[4]

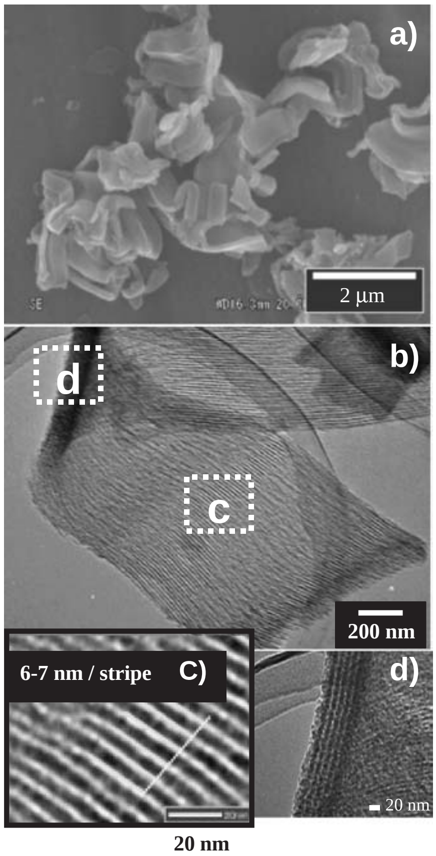

Figure 2. Morphological images by SEM (a) and TEM (b) of the white solid obtained from $ChEO_{10}$/water/THEGS mixture. The magnified image of surface (c) and bend of the sheet (d).

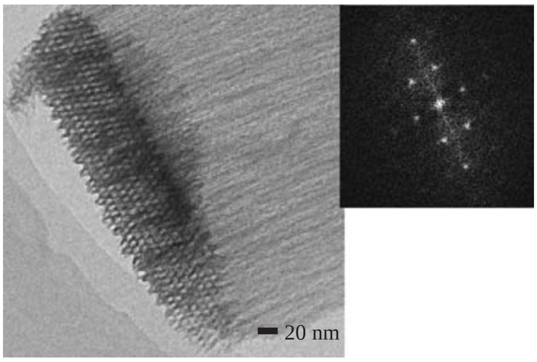

Figure 3. TEM image by adjusting beam angle to the sample, regularly arrayed pores with rectangular structure. The right image is the Fourier transforms of the TEM image.

Morphological images by SEM and TEM of the white solid obtained from $ChEO_{10}$/water/THEGS mixture are shown in Figure 2. SEM image of the sample exhibited a bending ribbon-shaped morphology as an individual sheet or lumped mass (Figure 2a).

The TEM image also shows a bending ribbon-shaped structure with striped pattern along the longitudinal direction with constant interval which reveals the ordered pore structure (Figure 2b). The interval of these stripes is found to be ca. 6 to 7 nm from the magnified image (Figure 2c). At the largest bend of the sheet, one can also observe a regularly assembled pattern with constant periodic distances (Figure 2d). From these images the mesoporous structure of the sample was confirmed.[5] Further investigation of TEM by adjusting beam angle to the sample along with the Fourier transforms of the TEM image (Figure 3) confirmed regularly arrayed pores with rectangular structure. To our knowledge, this is the first example of ribbon-shaped mesoporous silica built up from layered ribbon-shaped topology, which would have practical advantages for nano-composite fillers or surface fabrications because of such unique thin layered structures.

Figure 4 shows the SAXS spectra for the mesoporous silica with embedded surfactant and for the LLC of $ChEO_{10}$/water system. The miller indices of the diffraction peaks for both mesoporous silica (Figure 4a) and LLC (Figure 4b), indexed as 02, 11, 13, 20, and 22, indicate a rectangular structure in which five infinite cylinders with elliptical cross section are packed in a rectangular lattice.[3] Upon calcination of the silica/surfactant composite there were neither changes for SEM and TEM morphology nor differences of SAXS spectra, which indicates preservation of mesopore structures after heat treatment.[4]

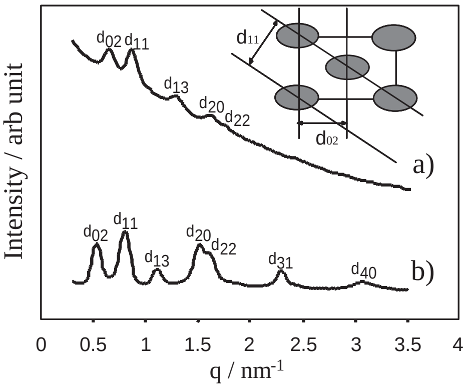

Figure 4. SAXS spectra of the mesoporous silica (a) and lyotropic liquid crystal (b) of $ChEO_{10}$/water system.

The concordance of crystallographic structures between mesoporous silica and LLC of $ChEO_{10}$/water system suggests that the condensation of silicic acid at the micelle surface might have propagated to the rectangular LLC structure which eventually fixed in the mesoporous silica structure. It is important to point out that we can directly compare the topology of mesoporous silica with that of the LLC of the surfactant/water system because THEOS is soluble in water and sol–gel transformation of silicic acid in the present system proceeds in the neutral aqueous phase. On the contrary, the traditional process involves solvents such as ethanol to dissolve TEOS in the system and catalyst such as hydrochloric acid to generate silicic acid; all of these additives seriously affect and deform the surfactant phase diagram, hence the process becomes a black box for the determination of mesoporous silica topology.

Assignment of crystallographic structures for the surfactant/water phase diagram is not always easy because of their fluid nature for the SAXS and other physical measurements. Utilization of THEOS could be a useful tool for the investigation of such vulnerable phase behaviors in the surfactant/water system. Upon imprinting to mesoporous silica from LLC, we could have a powder sample which would be easily investigated by TEM or SAXS to conduct detailed structural study. So we propose it as a novel and effective way to determine the LLC of surfactant/water system with THEOS as silica monomer by imprinting LLC structure to mesoporous silica. We are currently investigating the direct imprinting by adding THEOS to the original surfactant LLC.

In conclusion, we found the usefulness of THEOS as a novel silica precursor for the investigation of tailored imprinting of LLC topology as a template to the mesoporous silica. Further detailed investigation on the mechanism of silicic acid condensation and formation of hierarchical LLC structures must be done in order to establish the effective procedure to determine the topology of LLC by imprinting its structure to the mesoporous silica.

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References and Notes

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4 Upon calcination of residual solid (mesoporous-silica/surfactant composite), ca. 15% weight reduction corresponding to the decomposition of $ChEO_{10}$ was found at around 300 °C as shown in the Supporting Information. TEM images and SAXS spectra before and after calcinations are also included in the Supporting Information. http://www.csj.jp/journals/chem-lett/index.html.
5 Mesoporous structure was also confirmed by nitrogen adsorption–desorption experiment as shown in the Supporting Information.

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