



## Fibrous Silica Composites Fabricated Via Sol–Gel Processing Using Amino Acid Surfactant Templating

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**Abstract.** Fibrils covered by a silica shell have been fabricated by using fibrous aggregates of amino acid surfactant, *N*-dodecanoyl- $\beta$ -alanine, as a template for silicate generated in situ by sol–gel processing in an aqueous solution at pH around 6 and ambient temperature. It was shown that these conditions were inappropriate for tetraethoxysilane to generate silica. The synthesis was performed only when a new water-soluble precursor, tetrakis (2-hydroxy ethyl) orthosilicate, was applied. It is suggested that silica nucleation on the surfactant fibrils takes place via the formation of hydrogen bonds with corresponding functional groups of the amino acid residues.

**Keywords:** fibrous silica composite, sol–gel processing, amino acid surfactant, mineralization

### Introduction

The fabrication of mesoporous materials with variable pore size and structure has drawn attention owing to their potential application as catalysts, adsorbents, membranes, medical implants, etc. [1–7]. Since the discovery of the FSM-16 and M41S family of mesoporous silicates and aluminates [8–10], self-organizing surfactant assemblies are widely employed as a template to direct silica formation by sol–gel processes. The desired structural organization of material is achieved by choosing the appropriate assemblies of surfactant. As silica precursors, tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) are commonly used. Because they are poorly water-soluble compounds, it is necessary to add an organic solvent. In addition, their hydrolysis and polyconden-

sation proceed very slowly at neutral pH and room temperature. These factors impose some limitations on the preparation of hybrid materials with biopolymers and surfactants of which the solubility and phase state are sensitive to the organic solvent addition, pH and temperature.

The above-mentioned limitations can be overcome, as shown in Ref. [11], if a novel precursor, tetrakis (2-hydroxy ethyl) orthosilicate (THEOS), introduced by Mayer et al. [12] is applied. Its first advantage over TMOS and TEOS is that the THEOS is a completely water-soluble compound. Therefore, it is not necessary to add an organic solvent. This has allowed preparation of polysaccharide-silica biomaterials [11] and immobilizing labile enzymes in them [13]. The second advantage of THEOS over current precursors is a sharp acceleration of the sol–gel processes by polysaccharides. The processes can be performed at neutral pH and even reduced temperature. The polysaccharide effect, as suggested in Ref. [11], is caused by a catalysis of the sol–gel processing through hydrogen bond

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formation between hydrolytic silica products and hydroxyl groups of biopolymers.

One might therefore expect a catalytic effect for substances that bear functional groups capable of forming hydrogen bonds. To test this idea, we have taken a surfactant containing an amino acid residue as the functional group. The results obtained are presented in this communication.

## Experimental Section

The precursor tetrakis (2-hydroxy ethyl) orthosilicate (THEOS) was synthesized by using tetraethoxy silane (ABCR, Germany) as detailed in Ref. [14]. An alanine-containing surfactant, *N*-dodecanoyl- $\beta$ -alanine ( $C_{12}$ Ala), which was synthesized from alkanoyl chloride and *L*-alanine by the Schotten-Bouman method, was donated from Mitsubishi Petrochemical Co. Ltd. Doubly distilled water was used to prepare solutions.

The sol-gel processes were promoted by adding the THEOS into an aqueous solution containing 3 wt.% of surfactant which exhibited  $\sim$  pH 6.0 at ambient temperature. The mixture was stirred thoroughly to promote a homogeneous distribution of the precursor. The sol-gel processes caused gelation of the solution overnight. The gel was kept at ambient temperature for a week before examination by means of transmission electron microscopy (TEM).

TEM observation was performed with a Hitachi H 800 electron microscope at ambient temperature. The instrument was operated at an accelerating voltage of 75 or 100 kV. Specimens for the observation were prepared by placing a thin layer of the gel or a drop of the initial surfactant solution onto a carbon-coated copper grid.

## Results and Discussion

The  $C_{12}$ Ala in aqueous solutions is self-organized into infinitely long and rigid, cylindrical fibrils at 25°C and pH around 6.0 [15]. Fibrils had an average diameter of 40 nm but formed bundles by the side-by-side hydrogen bonding between them. Figure 1 presents a TEM picture of the fibrous structure formed by  $C_{12}$ Ala, as it appeared before treatment with the silica precursor. It is followed from the thickness of the fibers that there are fiber bundles, as previously shown by means of cryo-TEM technique in Ref. [15].

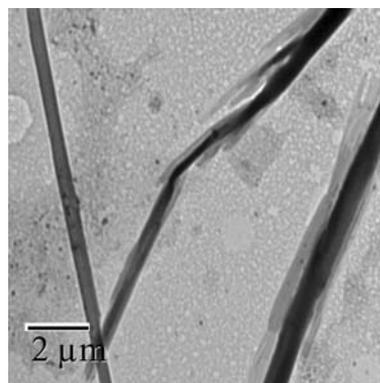


Figure 1. A TEM picture of  $C_{12}$ Ala fibers made at room temperature.

An attempt to synthesize silica in solutions of  $C_{12}$ Ala by using TEOS at pH around 6 and ambient temperature did not meet with success even after few weeks. To promote the sol-gel processes, it was necessary to heat the solution above 60°C and/or add acid or alkali. This change of the conditions brought about the disappearance of surfactant fibers because of their existence only at neutral pH and low temperature [15]. Therefore, surfactant-silica materials with fibrous architecture were not prepared, when TEOS was used.

When THEOS was introduced, sol-gel processes were performed under the conditions, at which  $C_{12}$ Ala was self-organized into the fibers. TEM pictures of hybrid surfactant-silica materials thus prepared can be seen in Fig. 2. The general view is presented in Fig. 2(a). One may see string-like entities of which the diameter is notably larger than that of fibrous surfactant aggregates in Fig. 1, suggesting that they represent the surfactant fibers coated with silica layer.

Three other TEM pictures in Fig. 2 were taken at larger magnification. They demonstrate three main morphologies that were found in  $C_{12}$ Ala solutions treated with THEOS. (i) *Fibers coated with silica particles*. A part of them is seen in a micrograph in Fig. 2(b). The fibrils of such type present the major morphology in the synthesized material. It is assumed that the particles grew out of various nucleation centers on the surface of initial surfactant fibers because of the precipitation of silica generated in situ by the sol-gel processes. (ii) *Fibers coated with a silica shell*. This morphology is obvious from Fig. 2(c). It differs from (i) by a smooth silica layer (shell) coating the surfactant fiber. Particles with sharp edges are almost absent in the shell. (iii) *Coagulated spherical particles*

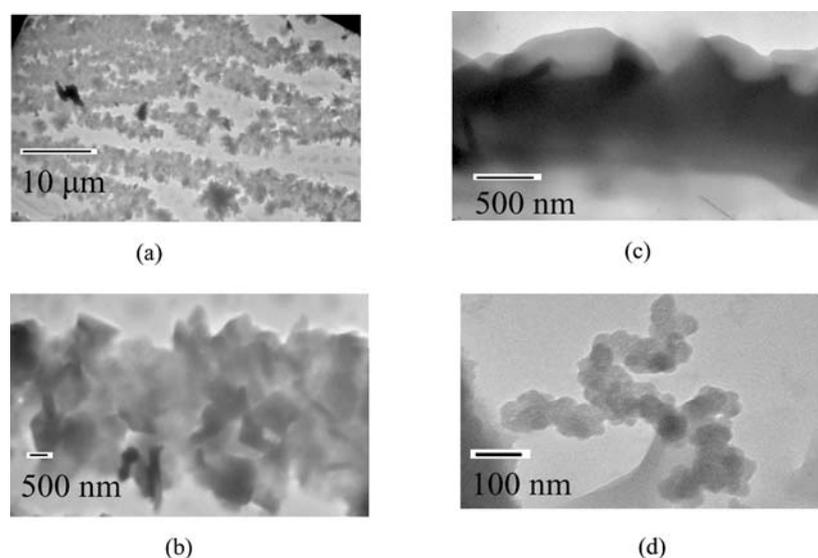


Figure 2. TEM pictures of proposed  $C_{12}Ala$  fibers covered with silica (a) General view, (b) proposed fibers coated with silica particles, (c) proposed fibers coated with silica shell, (d) proposed, coagulated spherical particles.

(Fig. 2(d)). This kind of morphology is quite common in the silica-based nanocomposite materials produced by sol–gel technique [11]. However, the amount in the material prepared here, as found from rough estimates, did not exceed a few %. This means that silica formation was related mainly to the surfactant self-assembled structures.

The foregoing results showed that only the use of THEOS as the silica precursor enabled us to prepare silica-coated fibrous structure in the  $C_{12}Ala$  solution. This occurred through silica precipitation on the surfactant fibers. Therefore, it can be inferred that fibers serve as a template for silica generated in situ by the sol–gel processes. What is also important is that this happened without addition of a catalyst. THEOS did not produce silica materials at neutral pH, when it was used alone [11, 12]. This suggests that  $C_{12}Ala$  catalyzed the sol–gel processes. By analogy with the hybrid polysaccharide-silica materials [11], it may be conceived that the catalytic effect is caused by the formation of hydrogen bonds with products of silane hydrolysis. The possible role of hydrogen-bonds was previously demonstrated with polysaccharides which accelerated sharply the sol–gel processes [11, 13]. Instead of the hydroxyl groups, the surface of the  $C_{12}Ala$  surfactant fibers is covered with carboxylic and amino groups [15] that can interact with silica through hydrogen bonding.

The lack of any silica formation by TEOS in conditions, in which the  $C_{12}Ala$  self-organizes into fibers, is probably caused by the unfavorable pH and temperature. TEOS is generally used in acidic or alkaline media with added organic solvents to increase its solubility [16–18]. Under these conditions, some authors could synthesize fibrillar and nanotubular materials. For instance, Mann et al. [19, 20] took the tobacco mosaic virus as a template for silica generated by the sol–gel process. Their report is related to the present work, because the virion surface is covered by amino acid residues, such as glutamate, aspartate, arginine, and lysine. It was believed that the amino acid residues served as nucleation sites for the silica deposition and the shell formation around tubular-like virus. Although the synthesis was performed under rather strong conditions (in ethanol/water mixture acidified up to pH 2.5), the mineralization was successfully handled only due to the stability of the virus in the acidic media. The nucleation was explained by the electrostatic interactions of anionic silica products with positively charged amino acid residues. The formation of hydrogen bonds was not mentioned, although, as believed in Refs. [17, 18], it is often responsible for the templating of silica by organic substrates.

Amino acid-containing surfactants, bis(L-leucine) dioxalamides, which can self-assemble into fibrous aggregates stabilized by hydrogen bonds in the

nonaqueous solutions, were used in the recent work [21]. When TEOS was added into a benzene solution of surfactants with small amounts of water and benzylamine, precipitated silica was found on the surfactant fibers. The sol–gel processes were provided by the good solubility of the precursor in the organic media and the presence of water in the system. It may be suggested that the amino acid residues served as nucleation centers for silica on the fiber surface. However, the reason for the mineralization processes was not considered.

The present study has demonstrated the versatility of THEOS as a silica precursor for the synthesis of inorganic-organic composites in aqueous solutions. THEOS can be applied in conditions in which commonly used TEOS is incapable of generating silicate. As shown in Refs. [11, 13], the advantage of THEOS over currently used precursors is that one may perform the sol–gel processes at any pH and reduced temperatures where organic compounds capable of hydrogen bonding formation are added to provide the catalytic effect. This has been confirmed by our study when synthesis was performed at pH  $\sim$  6 and ambient temperature ( $\sim$ 25°C).

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