Research News

Surfactant-Mediated Fabrication of Silica Nanotubes

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Hollow nanotubes are attracting a great deal of attention in both fundamental and industrial studies.[1–3] They have novel properties, and could be used to study the physical and chemical properties of molecules confined in their inner and outer spaces. They also have potential applications in fields such as electronics, optics, advanced catalysis, and energy storage/conversion, and could be designed to mimic biological channels. Thus, methods must be developed to fabricate hollow nanotubes and modify the properties by filling and coating the tubes for particular applications.

Inorganic hollow tubes that have been fabricated so far include those composed of carbon,[4,5] boron nitride,[6] silica,[7] and vanadium oxide.[8] Apart from vanadium oxide, these inorganic nanotubes have been synthesized under high temperature reaction conditions. For example, carbon nanotubes are produced by arc-discharge evaporation of carbon. On the other hand, recent advances in molecular biology have shown us that nature uses molecular self-assembly to construct microstructures of biomaterials.[9] The bio-inspired method is another important route to the fabrication of nanotubes. The Mobil research group has synthesized ordered nanotubes in condensed forms, i.e., mesoporous materials (the so-called M41S family) using surfactant-mediated template mechanism and the method for controlling the geometry of the tubes.[19,20] The strategy of fabricating single nanotubes is as follows: Surfactants such as alkyl ammonium salts self-organize into micelles of various shapes in the equilibrium state. The factor that determines the shape is the packing index, \( P = V_c/(2l_c) \), which cannot be expected for condensed materials such as the M41S family.

Here, we describe the sol–gel method for fabricating single silica nanotubes or bundles of a few tubes by the surfactant-mediated template mechanism and the method for controlling the geometry of the tubes.[19,20] The strategy of fabricating single nanotubes is as follows: Surfactants such as alkyl ammonium salts self-organize into micelles of various shapes in the equilibrium state. The factor that determines the shape is the packing index, \( P = V_c/(2l_c) \). For spheres, \( P < 1/3 \); for cylinders, \( 1/3 < P < 1/2 \); and for bilayers, \( 1/2 < P < 1 \). Here, \( V_c \) and \( l_c \) represent the volume and effective length, respectively, of the hydrocarbon chain attached to a surfactant polar head, whose area is \( \Sigma \). In the sol–gel process under acidic conditions, silicon alkoxide is first hydrolyzed, and then the condensation reaction proceeds to yield silica polymer. When the hydrolysis reaction is fast compared with the condensation reaction, combined molecules composed of the surfactant and hydrolyzed alkoxide are formed. They have an amphiphilic nature and self-organize into cylindrical aggregates if the \( P \) value for the combined molecules becomes 1/3 to 1/2. Thereafter, the condensation reaction slowly proceeds on the aggregate surface, resulting in the formation of single cylindrical aggregates covered by silica. The resultant aggregates are converted to nanotubes by calcination. The essential points in the formation of nanotubes are as follows: 1) The combined molecules self-organize into cylindrical assemblies in a quasi-equilibrium state. 2) Deformation of the generated aggregates does not occur during the condensation reaction, i.e., no mismatch of the array occurs between the surfactant molecules and silica units on the aggregate surface during the condensation reaction.

We selected a laurylamine hydrochloride (LAHC)/tetraethoxysilane (TEOS) system.[19] The experimental procedure is as follows: TEOS was added to 0.1 M LAHC aqueous solution (pH 4.5), and the reaction was started in a stirred cell at 313 K. The TEOS-to-LAHC molar ratio was adjusted to 4–12. TEOS does not dissolve in water to yield an emulsified solution in the early stages of the reaction. After 2–3 h, TEOS completely dissolved in the aqueous solution due to hydrolysis, and the solution became transparent. After 13–14 h, the solution turned into a homogeneous gel state.
The formation processes of silica nanotubes were elucidated by monitoring the evolution of the shape and size of the molecular aggregates composed of surfactant and silicate with small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), \( \mathrm{N}_2 \) adsorption isotherm, and \( \textsuperscript{29}\text{Si} \) NMR. The formation processes of the silica–surfactant aggregates in dilute solution of LAHC at pH 4.5 are summarized in Figure 1.\(^{[20]} \) The surfactant tends to take on a lamellar structure at higher concentrations (\( P = 0.63 \)), whereas in dilute solutions it becomes a finely divided bilayer-like assembly. Partially hydrolyzed TEOS penetrates into the assembly and converts it to globular aggregates (\( P = 0.33 \)). Then the condensation reaction of TEOS proceeds on the surface of the aggregates, converting the aggregates to the cylindrical form (\( P = 0.45 \)). Geometrical matching was observed for the array of the surfactant molecules and \( \text{SiO}_2 \) elements, i.e., four \( \text{SiO}_2 \) units per surfactant molecule. This matching enabled the flat surface of surfactant cylindrical aggregates to be covered with \( \text{SiO}_2 \) units without deforming the shape. Whereas, in the spherical end caps of the cylindrical aggregates, some mismatch of the array exists. Thus, the cylindrical aggregates were connected with each other at the end caps to elongate the cylinder length. The rate of the increase in length is nearly constant until 9 h reaction time. Some long cylinders combine and generate bundles composed of several to dozens of single cylindrical nanoaggregates. The elongation of the cylinders makes a network structure that converts the solution a gel state. The processes observed above indicate that the selected system satisfies the conditions necessary for the formation of nanotubes.

The TEM image of the dried gel indicates the presence of single cylindrical nanoaggregates (shown by the arrow in Fig. 2a). The diameter of the nanoaggregates was around 5 nm. The central part of the cylindrical aggregate is white and the two peripheries are black, indicating the formation of single silica nanotubes in which the hydrocarbon chains are filled. We can also see bundles of several cylindrical aggregates on the upper side of Figure 2a. Figure 2b is the TEM image of the materials obtained by calcination of the dried gel at 773 K. This figure shows the presence of long bundles of silica nanotubes in random configuration.

There exist silanol groups on the surfaces of single cylindrical aggregates. They are in contact with each other, and the condensation reaction occurs between different aggregates to yield their network. If the silanol groups are deactivated, the cylindrical aggregates may be elongated. We tried to deactivate the silanol groups using trimethylsilylation:

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\text{Si} \equiv \text{OH} + (\text{CH}_3)_3\text{SiCl} \rightarrow \text{Si} \equiv \text{O} \equiv \text{Si}(\text{CH}_3)_3 + \text{HCl} \quad (1)
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The trimethylsilylation procedure is as follows:\(^{[23]} \) First, we prepared the solution containing the silica cylindrical aggregates in the way mentioned previously. After 9 h, we drew out 10 cm\(^3\) of the solution. This solution was added to a mixture composed of trimethylchlorosilane (60 cm\(^3\)), isopropyl alcohol (50 cm\(^3\)), and water (50 cm\(^3\)). The resultant solution was kept for 2 days at room temperature under stirring. The solution was separated into two phases, i.e., alcohol-rich and water-rich phases, after stopping the stirring. The silica produced was extracted into the alcohol-rich phase and then dried at 313 K.
The TEM image of the trimethylsilylated dry silica is shown in Figure 3. The cylindrical aggregates are markedly elongated beyond the micrometer. The diameter is about 10 nm, indicating the presence of bundles of single cylindrical nanoaggregates. Nitrogen adsorption isotherm of the dried silica showed the formation of hollow silica tubes. This result indicates that the trimethylsilylation treatment removed the surfactants from the silica–surfactant aggregates leaving silica nanotubes at room temperature.

The diameter of the nanotubes can be easily controlled using a different length of alkyl chain of surfactant as shown by Beck et al.\(^{[11]}\) When the surfactant with alkyl chain carbon number \(n = 18\) was used in place of LAHC \((n = 12)\), the diameter increased from 5.0 nm to 6.25 nm. This increase in diameter corresponds to that of the surfactant–silica aggregate core, in which the hydrocarbon chains are filled. These results show that the geometric structure of the silica nanotubes can be easily controlled by simple procedures.

In conclusion, single silica nanotubes, or bundles of them, can be fabricated by a surfactant-mediated procedure. This procedure may be applicable to the fabrication of nanotubes composed of other inorganic species, e.g., titania.

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\[9\] Biomimetic Materials Chemistry (Ed: S. Mann), VCH, Weinheim 1996.

