Fabrication of the Silica Rod by Inner Sol–Gel Transcription

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The rod-like silica structure was obtained by inner sol–gel polymerization of BTEB using the organic tube **1** as a template, and its gas-absorption property was characterized. The organic silica rod-like material absorbed 0.68 wt % of hydrogen at 78 K.

The mesoporous inorganic nanomaterials have attracted much attention because of their widely used application as adsorbents for environmentally hazardous chemicals, reaction catalysts, catalyst supports, chemical sensors, and electrical and optical devices.[1] The mesoporous transition-metal oxides are of increased interest as possible materials for hydrogen-storage applications.[2] These materials possess the high surface area and porosity of nanotubes and framework structures, with accessible variable oxidation states that may be important in adsorption of hydrogen.

Inorganic materials can be shaped into a variety of structures using organic supramolecular assemblies as templates.[3] Vesicles,[4] organic crystals,[5] and surfactants[6] are some of the organic templates that have been successfully employed to create interesting silica structures. In addition, we have found that superstructures formed by organogelators act as excellent templates because of their stable "solid-like" aggregation behavior.[7] For example, the azacrown-appended organogelator **1** (see Graphical Abstract) is well known for formation of tubular structures in organic solvents by self-assembly.[7] This organogel tube produced hollow structures of the inorganic nanomaterials by sol–gel transcription, because the sol–gel polymerization of a precursor occurs selectively on the outside surface of the organogel tube.[7] In contrast, sol–gel reactions have never been observed selectively inside of organogel tubes. If we could control the absorption site of the inorganic precursor in sol–gel reactions, a variety of shapes of inorganic nanomaterials should be obtained using the same organogel template.

To test the feasibility of our idea, the sol–gel transcription was conducted to make rod-like silica structures using the organic tube **1** as a template (see Graphical Abstract). We successfully obtained the rod-like silica structure by the sol–gel reaction which occurred selectively inside of the organogel tube. Herein, we describe the inner sol–gel transcription into the rod-like silica by organogel **1** as a template and its gas-adsorption (nitrogen and hydrogen) properties. The result is a rare example for sol–gel reaction of 1,4-(bis(triethoxysilyl)benzene) (BTEB) by an organogel template.

First, we carried out the sol–gel polymerization of BTEB as the organic silica precursor using **1** in 1-butanol. For example, **1** (5–10 mg) was dissolved in a medium for sol–gel polymerization: water (10–20 mg)/BTEB (100–300 mg) or TEOS (100–300 mg)/benzylamine (10–20 mg). The sample was sealed in a glass tube and left at ambient temperature for 1 week. Subsequently, a template was removed by washing with THF in reflux condition.

Figure 1 shows SEM pictures of the silica obtained from the azacrown-appended cholesterol organogel **1** before and after washing with THF. Before washing with THF, the resultant silica reveals a fiber structure of ≈320 nm in diameter. This silica structure is quite different from that of silica obtained from sol–gel polymerization of tetraethyl orthosilicate (TEOS). Interestingly, after washing with THF, the silica shows the same structure with ≈300 nm of diameter but only reduced the diameter (Figure 1b). The result suggests that the oligomeric silica species are adsorbed onto these wide aggregates mainly by hydrogen-bonding interaction between gelator and the BTEB.

To further corroborate the action of the organogel superstructure as a template for the growth of the silica structure, we obtained TEM pictures after removal of **1** by washing. Figure 2a shows a TEM image of the silica obtained from the organogel **1**. Interestingly, the silica shows a fiber structure of ≈300 nm in diameter and several micrometers in length. However, the obtained silica did not reveal a hollow inner cavity, but, rather, a rod-like structure suggesting that the sol–gel reaction of BTEB proceeded only inside of the organogel tubes and not on the outer surface. We also performed elemental mapping of the organic silica nanostructure with energy dispersive X-ray

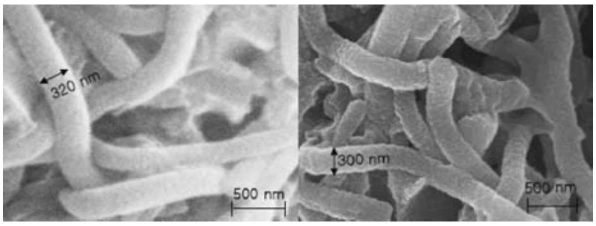

Figure 1. SEM images of the silica obtained from the azacrown-appended organogel **1** (a) before and (b) after washing with THF.

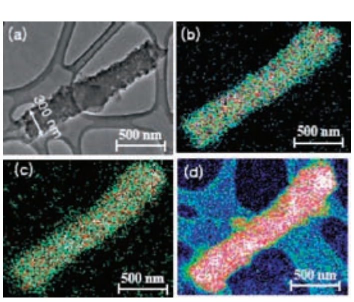

Figure 2. (a) Bright-field TEM image of silica rod after complete removal of the template with THF. (b) Elemental Si mapping, (c) elemental O mapping, and (d) elemental C mapping.

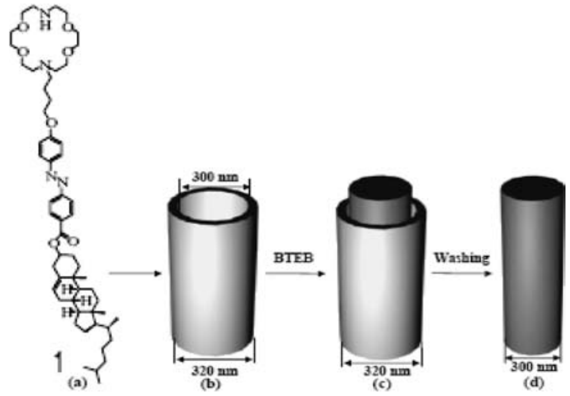

Figure 3. Mechanism for the formation of the silica rod-like structure from the organogel **1** by inner sol–gel reaction. (a) Organogel **1**, (b) the self-assembled organogel tube, (c) sol–gel polymerization of BTEB, and (d) the rod-like silica obtained from sol–gel reaction after washing with THF.

spectroscopy as shown in Figures 2b–2d. After complete removal of the template with THF (Figure 2a), silicon (Figure 2b), oxygen (Figure 2c), and carbon (Figure 2d) were identified. The result implies that the organogel structure is finely transcribed into the silica structure.

We considered the differences between the sol–gel reactions of BTEB and of TEOS. Generally, BTEB is more hydrophobic than TEOS. Therefore, the result reveals that if the sol–gel reaction of BTEB is performed in hydrophilic solvents such as alcohols or water, the sol–gel reaction of hydrophobic BTEB at the inner side of the organic tubes should be favored, owing to the high hydrophobicity of the inner side of the organic tube. On the other hand, if the sol–gel reaction of BTEB is performed in a hydrophobic solvent such as cyclohexane, the reaction of the hydrophobic BTEB should occur at the outer surface of the organogel tube, owing to the high hydrophobic property of the outside surface of the organic tube.

To test the feasibility of our idea, we carried out the sol–gel polymerization of BTEB in cyclohexane as the hydrophobic solvent. As expected, the resultant silica revealed the hollow tubular structure with inner diameter of 300 nm (Supporting Information: Figure S1). The foregoing result strongly supports the view that the oligomeric BTEB is adsorbed onto the outer surface of the organic tube and that the organic tubular structure is finely transcribed into the silica mainly by the intermolecular hydrogen-bonding interactions.

We propose the mechanism for the formation of the silica rod-like structure from the organogel **1** by inner sol–gel reaction (Figure 3). The gelator **1** forms the tubular structure in 1-butanol (Figure 3b). Oligomeric organic silica species are adsorbed inside of the tubular structure of **1** (Figure 3c), because of the hydrophobic interaction between the organic tube and BTEB, and the polymerization further proceeds to create a rod-like structure. This propagation mode eventually yields the novel rod-like silica structure, which is isolated after removal of gelator by washing with organic solvents (Figure 3d).

To confirm characterization of the rod-like silica for gas adsorption, the nitrogen adsorption–desorption isotherms of the organic rod-like silica is shown in Figure S2 (Supporting Information). The organic rod-like silica had a Brunauer–Emmett–Teller (BET) surface area of 615 m^2/g and a Langmuir surface area of 823 m^2/g. These values are much higher than that of general carbon nanotubes, but lower than those of mesoporous silica. We also measured the hydrogen-adsorption abilities for the novel organic rod-like silica (BTEB) and inorganic silica tube (TEOS) as reference. We initially suspected that the organic moieties played an important role in hydrogen adsorption. The hydrogen-adsorption value of the organic silica material (BTEB) at 78 K and 600 Torr was 0.68 wt % (obtained volumetrically, Figure 4a), whereas the hydrogen adsorption ability of the inorganic silica tube (TEOS) was less than 0.1 wt % (Figure 4b). The ≈sevenfold increased hydrogen capacity of the organic silica rod-like material at 78 K was likely due to the preferred adsorption of hydrogen onto carbon. In addition, the polarizable π-electron clouds of the benzene rings in the organic–silica material would be expected to have some affinity for hydrogen.[8]

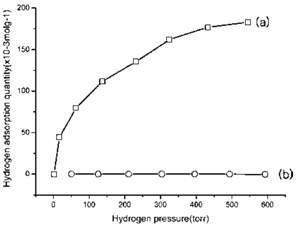

Figure 4. Hydrogen-adsorption isotherms of the organic silica material (curve a) and the inorganic silica (curve b).

In conclusion, sol–gel polymerization of BTEB in the organogel phase supported by an azacrown-appended cholesterol gelator results in unique rod-like silica. This is a rare example of a sol–gel reaction and illustrates the versatility of the template method for the creation of various silica structures. Also, since the hydrogen-absorption capacity of the organic silica possessing a benzene moiety was higher than that of inorganic silica, we believe that the present silica would be useful as a gas-absorption material.

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