

Novel preparation method for multi-layered, tubular silica using an azacrown-appended cholesterol as template and metal-deposition into the interlayer space

Jong Hwa Jung, Yoshiyuki Ono and Seiji Shinkai*

Chemotransfiguration Project, Japan Science and Technology Corporation (JST),
2432 Aikawa, Kurume, Fukuoka 839-0861, Japan

Received (in Cambridge) 29th April 1999, Accepted 3rd June 1999

Novel multi-layered 'rolled-paper-like' silica was prepared by using the aggregate of an azacrown-appended cholesterol derivative as a template for the sol-gel polymerization of tetraethoxysilane: the metal bound to the azacrown moiety was thereby deposited in the interlayer space.

Recently, exploitation of new organic gelators which can gelate various organic solvents has become an active research area of endeavour.¹⁻¹² These organogels are of particular interest in that being different from polymer gels, fibrous aggregates of low molecular-weight compounds formed by non-covalent interactions are responsible for such gelation phenomena. This is why the organogels exhibit various superstructures, reflecting the monomeric structure of each gelator. More recently, it was found that certain cholesterol derivatives can gelate even tetraethoxysilane (TEOS), which results in silica gel by sol-gel polymerization.^{12,13} Very interestingly, it was shown that sol-gel polymerization of gelated TEOS solutions followed by calcination affords novel silica with a hollow fiber structure because the organogel fibers act as a template to create an inside tube in the polymerization process.^{12,13}

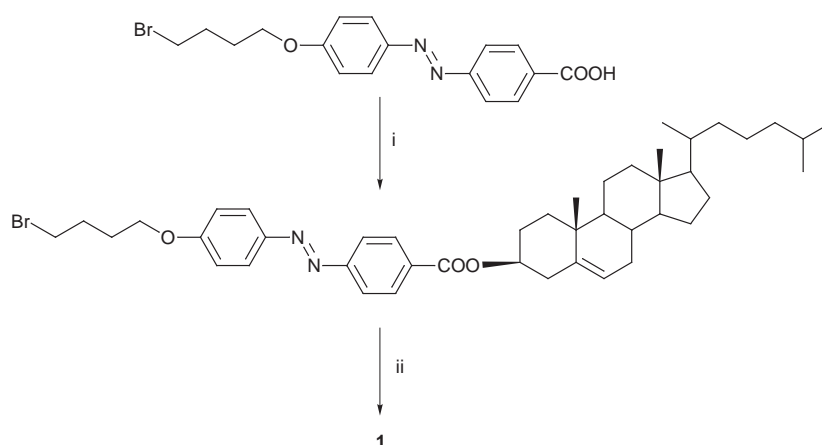
The novel finding has stimulated us to deposit metal cations inside the silica tube. It is undoubted that such metal-deposited silica is applicable as a catalyst to reactions which require size

recognition ability. To realize this intriguing idea, we synthesized the cholesterol-based gelator **1** having a cholesterol moiety as an aggregate-forming site and an azacrown moiety as a metal-binding site. If the metal-crown complexes of this gelator act as a template in the TEOS sol-gel polymerization process, it follows that metal cations are left inside the silica tube after calcination.

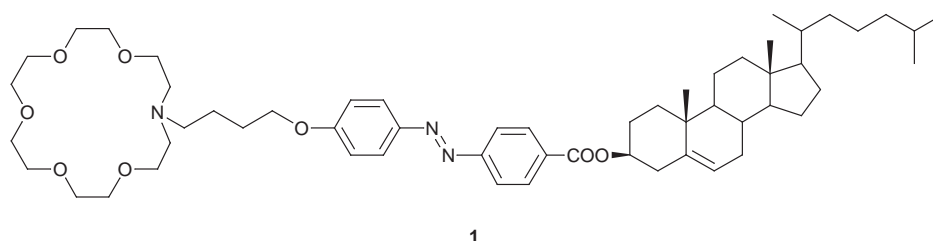
Compound **1** was synthesized according to Scheme 1 and identified by IR, ¹H NMR, ¹³C NMR, MS(SIMS) spectral evidence and elemental analysis.

Compound **1** (or its metal complexes) did not give organogels as good as those obtained in previous systems,^{12,13} but only resulted in viscous turbid solutions. Thus, the SEM pictures of the dry samples were obtained only from a few limited solutions. As shown in Fig. 1, the SEM image did not show the fibrous structure characteristic of organogel systems but rather featured film-like aggregates with 30–40 nm thickness and a few μm length, which probably consist of the lamellar structure of **1**. It is noteworthy that some films are curved (arrows in Fig. 1) to form a pseudo-cylindrical structure. Similar film-like aggregates were observed for the dry samples obtained from other solutions in the absence and the presence of AgNO₃.

We carried out sol-gel polymerization of **1** in the presence of AgNO₃ in butan-1-ol according to the method described previously.^{12,13} For example, the **1**·AgNO₃ complex (5.8×10^{-6}



Scheme 1 Reagents and conditions: i, cholesterol, dichloromethane, DCC, DMAP, 0 °C, 40%; ii, aza-18-crown-6, Na₂CO₃, butyronitrile, reflux, 45%.



mol) was prepared in THF (1.0 g). The solution was evaporated to dryness, the solid residue being dissolved in a medium for sol-gel polymerization: butan-1-ol (98 mg)-TEOS (16 mg)-water (5.7 mg)-benzylamine (5.6 mg). The sample was sealed in a glass tube and left at ambient temperature for 1 day. The SEM picture taken at this stage is shown in Fig. 2. Subsequently, the heating temperature was gradually raised up to 500 °C under a nitrogen atmosphere and then kept at 500 °C under aerobic conditions for 8 h. The SEM and TEM pictures taken after calcination are shown in Fig. 3.

It is seen from Fig. 2 that the silica before calcination already

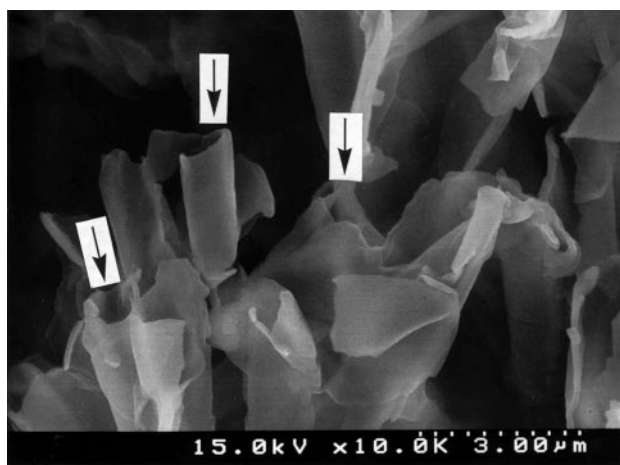


Fig. 1 SEM picture of the dry sample obtained from a **1** (5.0×10^{-5} mol dm⁻³) + cyclohexane system.

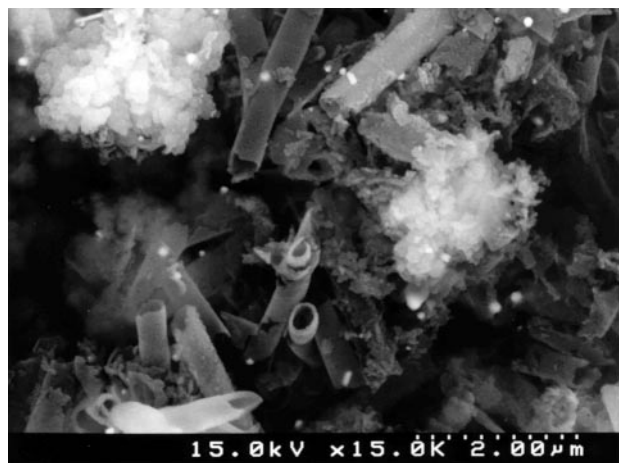
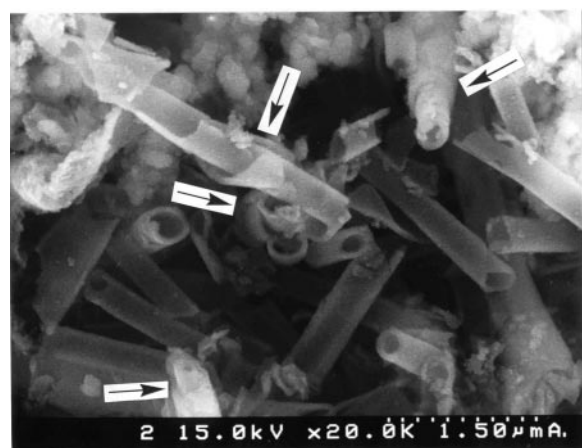
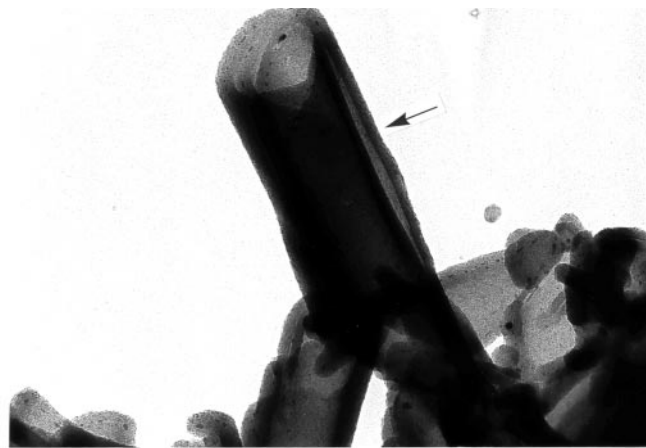


Fig. 2 SEM picture of the silica obtained from the **1**·AgNO₃ complex system before calcination.



(A)



(B)

Fig. 3 SEM (A) and TEM (B) pictures of the silica obtained from the **1**·AgNO₃ complex system after calcination.

possesses a tubular structure with 190–210 nm inner diameter and 40–60 nm wall thickness. However, the tube is apparently comprised of a single wall. After calcination by which organic compounds are removed by combustion, both the SEM and TEM pictures (Fig. 3) showed a 'rolled-paper-like' multi-layered structure (shown with arrows in the figures). The clear structural difference between Figs. 2 and 3 supports the view that the sol-gel polymerization of TEOS proceeds *via* the lamellar aggregates of **1** to grow as a tubular structure involving both the organic layer and the inorganic layer within the wall. It is not yet clear, however, how they roll up to a tubular structure although the lamellar structure is not so sharply curved.

Where has the AgNO₃ bound to the azacrown moiety gone after calcination? Careful examination of Fig. 3B reveals that there are many small dots (0.5–1 nm) on the silica wall. In some cases they aggregate into large particles (20–55 nm), which are clearly seen to be mostly deposited between the silica layers (Fig. 4). We thus believe that AgNO₃ bound to the azacrown moiety resides in the lamellar aggregates of **1** and after sol-gel polymerization followed by calcination, AgNO₃ is left as Ag between the silica layers.

In conclusion, the present paper has shown that sol-gel polymerization of TEOS in the presence of the lamellar aggregates of an azacrown-appended cholesterol derivative is useful not only to create the novel 'rolled-paper-like' silica structure but also to insert metals into the interlayer space. Previously, we found that cationic fibrous organogels act as a template of sol-gel polymerization and result in hollow fiber silica after calcination.¹² This implies that various new silica structures can be created by using various organogel structures as a template. We believe that the present system is readily applicable to designing novel catalysts featuring the metal-deposited rolled silica structure.

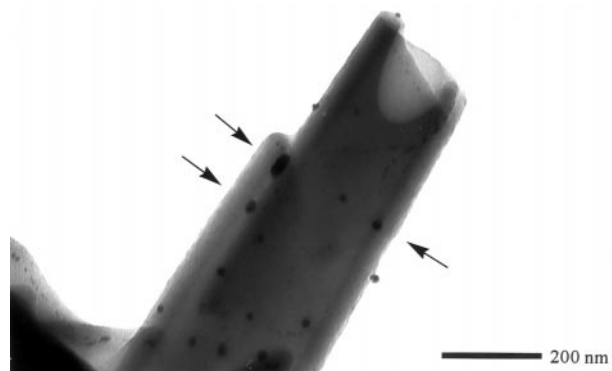


Fig. 4 Enlarged TEM picture of the silica obtained from the **1**·AgNO₃ complex system after calcination. Arrows indicate the large particles deposited into the interlayer space.

References and notes

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Communication 9/03425K