

## Sol-gel Transcription of Novel Low-molecular-weight Hydrogel Assembly Based on 2'-Deoxyuridine into the Silica Structure

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The use of organic molecules, assemblies, and supramolecular systems in the development of novel inorganic materials continues to offer new and exciting alternatives to conventional synthetic strategies.<sup>1</sup> As possible templates, protein, multicellular superstructures, surfactants, and DNA have been utilized to create novel structures of inorganic materials.<sup>2</sup> Recently, increasing attention has been paid to low molecular-weight compounds that can efficiently gelate various organic solvents.<sup>3-9</sup> The organogels were applied as novel media to produce various structures of the silica such as linear,<sup>8</sup> lamellar,<sup>9a</sup> and helical<sup>9b</sup> fibrous structures by sol-gel polymerization. It has been shown that the presence of some attractive force between the superstructures and tetraethoxysilane (TEOS) is indispensable for efficient sol-gel transcription.<sup>8,9</sup> Up till now, transcription into silica *via* TEOS polymerization has been limited to superstructures of molecules that possess a cationic charge in form of metal cations,<sup>8,9</sup> and molecules that possess a H-bonding site in the form of primary amines or combinations of primary and secondary amines.<sup>10</sup> The design of new gelators for organogel/hydrogel transcription into silica has, therefore, been strongly limited to molecules containing either positive charges or amine groups.

In this paper we show the rare example for the hydrogel assembly based on 2'-deoxyuridine<sup>11</sup> that can be successfully transcribed into the silica structure by sol-gel polymerization of TEOS although it does not possess either directly positive charge or efficient H-bonding amine group. The amide-type

NH group of **1** is quite difficult to act as a direct driving force to sol-gel transcription,<sup>12</sup> because the amide-type NH group forms the intermolecular hydrogen-bonding interaction between gelator **1** and the protonation of acidic proton at amide-type NH group is more difficult than that of free amine. We have found that acidic proton can protonate at the molecular aggregates **1** in the gel fibers, thus providing the driving force necessary for the transcription process.

In water, gelator **1** forms a clear gel consisting of linear fibers with 700-2000 nm of diameters and several micrometers lengths in acidic condition (Fig. 1). It is known that  $pK_b$  values of triazole derivatives are relatively high<sup>13</sup> and the nitrogen atoms of triazole group of the gelator **1** should partially protonate in acidic condition. On the other hand, when the small amount of benzyl amine as base was added to the hydrogel **1**, the gel structure immediately disappeared. These results indicate that the gelation ability of **1** was sensitively influenced at pH condition.

Hence, we carried out sol-gel polymerization of TEOS using **1** in acidic and neutral condition according to the method described previously.<sup>8,9</sup> Figure 2 shows SEM pictures of the silica obtained from the hydrogel **1** before and after calcinations. Before calcination, the template effect does not reveal from the resultant silica particle, but shows crystal-like the particle shape (Fig. 2a). On the other hand, after calcination by which organic compounds are removed

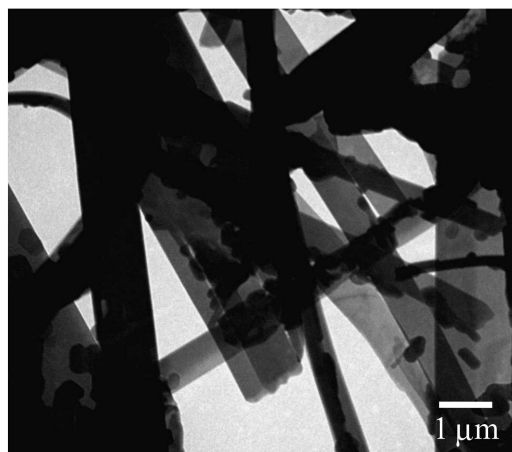
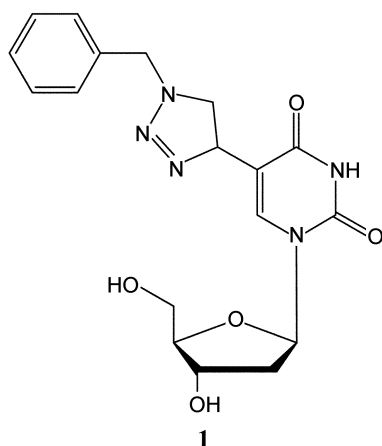
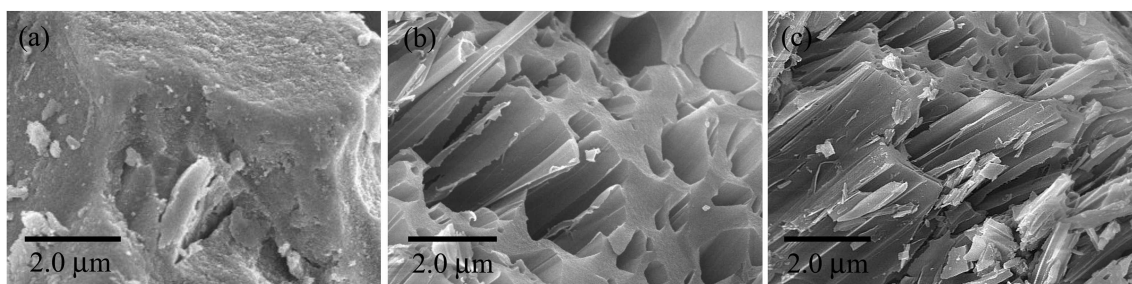


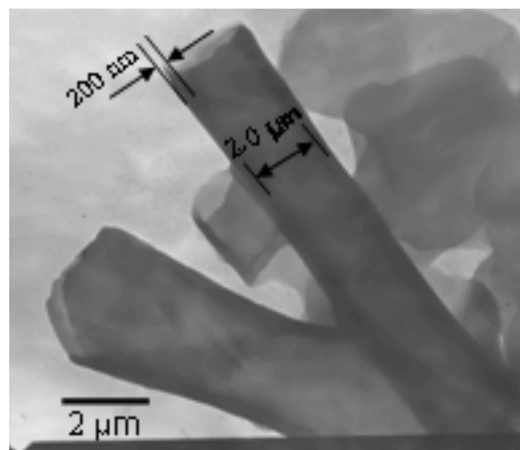
Figure 1. TEM image of the hydrogel **1** in acidic condition.



**Figure 2.** SEM images of the silica structures obtained from **1** in acidic condition (a) before and (b and c) after calcination.

by combustion, very interestingly, the resultant silica reveals the pore structures with 700-2500 nm of pore diameters in acidic condition (Figs. 2b and 2c). The yield for porous-type silica structure obtained from **1** was almost 90%. The results suggest that the oligomeric silica species are adsorbed onto these wide aggregates mainly by the electrostatic interaction between negative charge of TEOS and ammonium charge groups of the gelator by protonation. The porous-type silica structure obtained from **1** in acidic condition is quite different from those of obtained from general sol-gel transcription in basic condition. This finding indicates that the surface group of silica prepared from acidic condition had much higher reactivity than that obtain from basic condition. In contrast, the resultant silica prepared in neutral condition revealed the conventional granular structure, indicating that the cationic charge interaction is necessary for the sol-gel polymerization in order to adsorb "anionic" silica particles onto the organic molecular assemblies.

To further corroborate that the hydrogel superstructure really acts as a template for the growth of the silica structure, we took the TEM picture after removal of **1** by calcination. Figure 3 shows TEM image of the silica obtained from the hydrogel **1** in acidic condition. Observation of the thick porous-type silica structure by TEM is very difficult due to limitation of electron-beam transmission. Thus, we observed TEM image for the isolated single tubes of the silica even though the morphology of the silica is slightly different from that of shown in Figure 2. The silica tube possesses 700-2000 nm inner diameter and 200-300 nm thickness. The



**Figure 3.** TEM image of the silica structure obtained from **1** in acidic condition.

foregoing results consistently support the view that the hydrogel structure is finely transcribed into the silica mainly due to the electrostatic interaction, and oligomeric silica species are adsorbed onto the gelator surface.

In conclusion, we have shown that the hydrogel of a compound which does not contain directly positive charge or an amino group can still be transcribed into a silica structure, as long as the acidic proton for the polymerization process can interact with the gelator molecules. Preliminary results using other gelators that do not contain positive charges or amino groups either, indicate that this phenomenon is of a general nature. As a consequence, the transcription of a much broader range of TEOS can now be taken into consideration. Being able to transcribe such entities will undoubtedly lead to a greater variety of inorganic materials with interesting new shapes and properties.

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