

Fabrication of TiO₂ using L-lysine-based organogelators as organic templates: control of the nanostructures†

Masahiro Suzuki,*^a Yasushi Nakajima,^a Teruaki Sato,^a Hirofusa Shirai^b and Kenji Hanabusa^a

Received (in Cambridge, UK) 20th July 2005, Accepted 10th November 2005

First published as an Advance Article on the web 7th December 2005

DOI: 10.1039/b510302a

Using uncharged or negatively charged L-lysine-based organogelators as templates, the nanostructures of TiO₂ are controllable.

Low-molecular-weight gelators, which form supramolecular organogels (organogelators) and hydrogels (hydrogelators), have been much investigated not only out of academic interest but also due to their potentially wide applications in industrial fields such as cosmetics, foods, medical science and tissue engineering.^{1–4} Although gelators are small molecules, they create a three-dimensional network by the formation of supramolecular polymers through hydrogen bonding, van der Waals and π -stacking interactions.

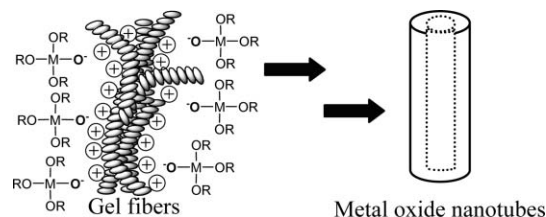
Template-directed synthesis is widely accepted as a simple and cost-effective method for the fabrication of inorganic materials through sol-gel polymerization. Since the first report by Shinkai and co-workers on the successful use of organogels as templates,⁵ the morphologies of supramolecular polymers formed by gelators have been used as organic templates for the fabrication of mesoporous polymers⁶ and nano-scaled designed inorganic materials.⁷ Because the gelators form various nanostructures such as nanofibers, nanoribbons, nanorods and nanoparticles that depend on their molecular structures, solvents, and concentrations,¹ they are recognized as good organic templates. For example, the sol-gel polymerization of tetraethyl orthosilicate, titanium isopropoxide, or tantalum ethoxide in the organogel based on the cyclohexanediamine-typed organogelators, which formed a helical supramolecular nanofiber, produced a hollow helical nanotube of SiO₂, TiO₂, and Ta₂O₅.^{7b,8} Furthermore, using other methods except sol-gel polymerization, the preparation of silver nanowires, CdS nanoribbons, and Au nanoparticles have been reported.⁹

As the sol-gel polymerization for templates, positively charged gelators are often used because their positively charged gel fibers electrostatically attract the negatively charged precursors produced in an initial stage of the sol-gel polymerization (Scheme 1); consequently, the sol-gel polymerization occurs on the gel fibers, leading to the fabrication of metal oxide nanotubes. The lengths and sizes of metal oxide nanotubes significantly depend on the nanostructure formed by a gelator. In this communication, we

describe the control of nanostructures of titanium oxide prepared in organogels based on uncharged and negatively charged gelators.

Uncharged gelator **1** and negatively charged gelator **2** (Fig. 1) were prepared from *N*^z,*N*^c-bis(hexylaminocarbonyl)-L-lysine methyl ester and *N*^c-lauroyl-L-lysine ethyl ester.¹⁰ Although these gelators have poor organogelation properties, they form the organogels in alcohols and 1,4-dioxane. Gelator **1** forms an opaque ethanol gel, translucent butanol gel, and transparent dioxane gel, and **2** forms a translucent butanol gel. The electron micrograph studies of the samples prepared from these organogels demonstrate that **1** and **2** formed the self-assembled nanofibers in their organogels; for **1**, the diameters of the nanofibers were 100–250 nm in ethanol gel, 50–100 nm in butanol gel and 10–50 nm in dioxane gel as well as 100–150 nm in butanol gel based on **2**. Therefore, the sol-gel polymerization was carried out in ethanol, butanol and 1,4-dioxane for **1** and butanol for **2** (Table 1).

Typical procedure for the sol-gel polymerization is shown in Scheme 2. Gelator, [Ti(OiPr)₄] and propylamine as a catalyst are dissolved in a solvent, and then the solution was cooled to room temperature, which leads to the formation of an organogel (A → B). The resulting gel is allowed to stand at 25 °C for 5 days



Scheme 1 Sol-gel polymerization using positively charged gelators.

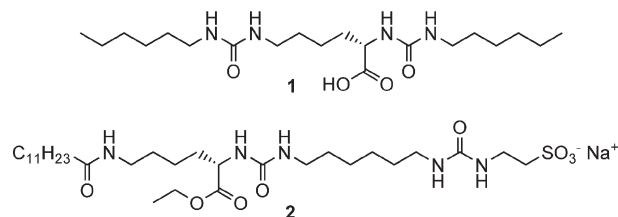
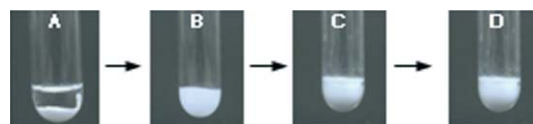


Fig. 1 Uncharged and negatively charged gelators.



Scheme 2 Typical procedure for sol-gel polymerization.

^aGraduate School of Science and Technology, Shinshu University, Ueda, Nagano, 386-8567, Japan. E-mail: msuzuki@gipstc.shinshu-u.ac.jp; Fax: +81-268-21-5608; Tel: +81-268-21-5415

^bDepartment of Functional Polymer Science, Shinshu University, Ueda, Nagano, 386-8567, Japan

† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/b510302a

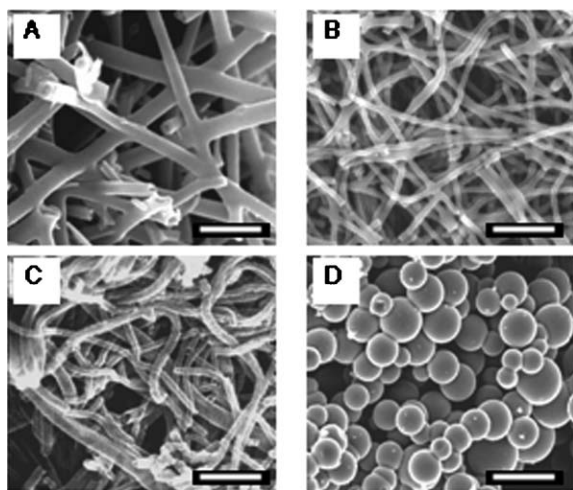


Fig. 2 FE-SEM images of TiO₂ prepared in organogels based on **1** in ethanol (A), 1-butanol (B) and 1,4-dioxane (C) and in ethanol without **1** (D). Scale bars are 1.5 μm for A and B, 300 nm for C and 6 μm for D.

(C). After washing with CHCl₃ or BuOH, the white solid is dried at 50 °C *in vacuo* overnight. The white powder of TiO₂ is obtained by calcination at 200 °C for 2 h and then 500 °C for 2 h (D).

Fig. 2 shows the SEM images of TiO₂ prepared by the sol-gel polymerization in the organogels based on **1** containing propylamine as a catalyst and ethanol (A), 1-butanol (B) and dioxane (C) and in ethanol without **1** (D). The sol-gel polymerization of [Ti(OiPr)₄] in ethanol without the gelator produced TiO₂ particles with a diameter of several micrometers (D) and their sizes were independent of solvents (ethanol, 1-butanol, dioxane). In contrast, the TiO₂ nanotubes are formed by the sol-gel polymerization in the organogels. Very interestingly, the size of TiO₂ nanotubes significantly depends on the solvents; the diameters of the TiO₂ nanotubes are 300–600 nm (ethanol gel), 150–200 nm (butanol gel), and 30–50 nm (dioxane gel). It is clear that the size of TiO₂ nanotubes reflects that of the self-assembled nanofiber formed by **1**. Namely, the size of TiO₂ nanotubes is controllable by the solvents.

As mentioned above, an electrostatic attraction between the self-assembled nanofibers and TiO₂ precursors is very important for the fabrication of TiO₂ nanotubes using the positively charged gelators. However, gelator **1** has no charge. Why can **1** play a role in a template? In our cases, propylamine is used as a catalyst for the sol-gel polymerization and partial propylamines react with the carboxy groups in **1**. Indeed, the FT-IR spectra of ethanol gel based on **1** demonstrated that the absorbance at 1780 cm⁻¹ and 1700 cm⁻¹ arising from the stretching vibration of carboxy group

Table 1 Experimental conditions for sol-gel polymerization

Gelator/mg	Ti[OCH(CH ₃) ₂]/ml	C ₃ H ₇ NH ₂ /μl	Solvent/ml	
1	0	0.15	25.1	EtOH 0.85
1	61	0.15	25.1	EtOH 0.85
1	61	0.15	25.1	BuOH 0.85
1	61	0.15	25.1	Dioxane 0.85
2	9	0.10	2.3	BuOH 1.90
2	11	0.10	2.8	BuOH 1.90
2	20	0.10	5.1	BuOH 1.90
2	30	0.10	7.6	BuOH 1.90
2	40	0.10	10.2	BuOH 1.90

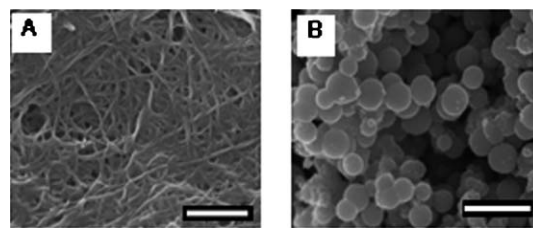


Fig. 3 FE-SEM images of dried gel prepared from butanol gel based on **2** (A) and TiO₂ prepared by sol-gel polymerization in butanol gel (B). Scale bars are 3.0 μm.

(νC=O) decreased in the presence of propylamine. The sol-gel precursors are attracted to the charged nanofibers formed by **1** and propylamine, which leads to sol-gel polymerization on the nanofibers.

On the other hand, the negatively charged gelator **2** showed a quite different result. Fig. 3 shows the FE-SEM images of the dried gel prepared from a butanol gel based on **2** (A) and TiO₂ obtained by the sol-gel polymerization in the butanol gel.¹¹ **2** creates a three-dimensional network formed by entanglement of the self-assembled nanofibers with a diameter of 100–150 nm (A). The sol-gel polymerization in the butanol gel of **2** produced TiO₂ nanoparticles, but not nanotubes. This result indicates that the nanofibers do not act as a template. Because the nanofibers formed by **2** have negative charges (negatively charged nanofibers), the polymerization on the nanofibers is inhibited due to the electrostatic repulsion between nanofibers and sol-gel precursors. Interestingly, the size of TiO₂ nanoparticles obtained was relatively uniform, compared with TiO₂ in Fig. 1D. The TiO₂ particles prepared without gelators have a wide size distribution from 500 nm to 3000 nm and the estimated average diameter is 1700 nm. In contrast, the size of TiO₂ prepared in the butanol gel of **2** is small with a distribution from 400 nm to 1400 nm and the estimated average diameter is 1200 nm. This result indicates that the sol-gel polymerization takes place in the nanospaces in the three-dimensional network formed by the self-assembled nanofibers of **2**. In the butanol gel, the three-dimensional network consisting of the negatively charged nanofibers of **2** may have relatively uniformed nanospaces. The sol-gel precursors cannot approach the nanofibers due to the electrostatic repulsion and are placed in the nanospaces as escaped from the repulsion. The sol-gel polymerization in the nanospaces produces TiO₂ nanoparticles.

In order to evaluate the sol-gel polymerization in the nanospaces, we carried out the sol-gel polymerization in butanol gels of **2** with various concentrations. The size of nanospaces will depend on the concentration of **2**; the increasing concentration of **2** decreases the nanospaces. Fig. 4 shows the FE-SEM images of TiO₂ prepared in the butanol gels with various concentrations of **2** and Table 2 lists the average diameters. As expected, the size of TiO₂ nanoparticles depended on the gelator concentrations. The size of TiO₂ nanoparticles decreases with the increasing concentration of **2** and is independent of the concentration of **2** more than 30 mg. Furthermore, the increase in the gelator concentrations produces more close packed nanoparticles. This result indicates that the sol-gel polymerization takes place in the nanospaces in the three-dimensional network and the size of the TiO₂ nanoparticles is controllable by the concentration of **2**.

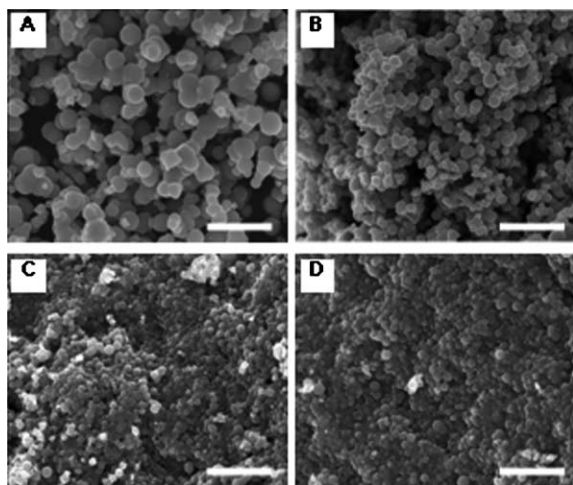


Fig. 4 FE-SEM images of TiO₂ prepared in butanol gels based on **2**. Scale bars are 7.5 μm. [2] = 9 mg (A), 11 mg (B), 20 mg (C) and 30 mg (D).

Table 2 Average diameter of TiO₂ nanoparticles

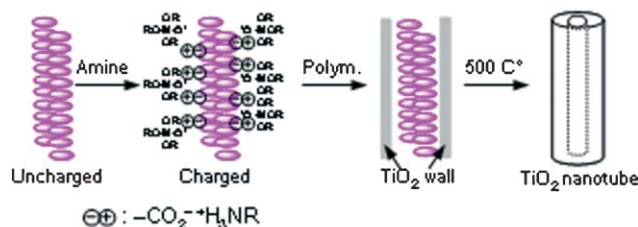
[2]	9 mg	11 mg	20 mg	30 mg	40 mg
Diameter	1500 nm	1200 nm	740 nm	550 nm	540 nm

These results led us to propose a mechanism of the fabrication of TiO₂ in the organogels as illustrated in Scheme 3. In the case of **1**, because the sol-gel precursors can readily approach the nanofibers by changing from uncharged nanofibers to charged ones by the addition of propylamine, the charged nanofibers act as a template, which leads to the fabrication of TiO₂ nanotubes. On the other hand, in the organogel based on **2**, negatively charged sol-gel precursors polymerize in the nanospaces in the three-dimensional network created by negatively charged nanofibers because of an electrostatic repulsion between the nanofiber and the precursor. After removal of nanofibers by calcination, relatively uniform TiO₂ nanoparticles are obtained.

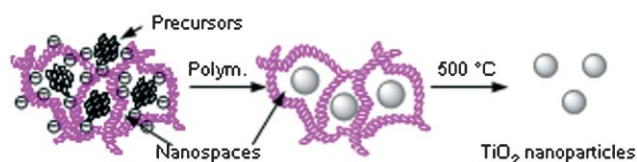
In summary, we revealed the fabrication of TiO₂ in organogels and the control of the nanostructures using organogelators self-assembling into nanofibers in organic solvents. The sol-gel polymerization in organogels based on the uncharged gelator **1** produces the TiO₂ nanotubes, while that based on negative charged gelator **2** produces the relatively uniformed TiO₂ nanoparticles. The diameter of TiO₂ nanotubes are controllable by changing of solvents; particularly, the TiO₂ nanotube fabricated in the dioxane gel has a diameter of 30–50 nm. In contrast, the size of TiO₂ nanoparticles decreases with the increasing concentration of **2**. These results indicate that the self-assembled nanofibers for **1** and the nanospaces in the three-dimensional network created by nanofibers of **2** function as a template in the sol-gel polymerization. Furthermore, it is found that the nanostructures and their sizes are controllable by suitable choice of solvents and types and concentrations of gelators.

This work was supported by a Grant-in-Aid for the 21st Century COE Program and a Grant-in Aid for Exploratory

A: gelator 1



B: gelator 2



Scheme 3 Fabrication mechanisms of TiO₂ nanotubes and nanoparticles in organogels.

Research (No. 17655049) by Ministry of Education, Culture, Sports, Science and Technology of Japan.

Notes and references

- (a) N. A. Peppas, Y. Huang, M. Tottes-Lugo, J. H. Ward and J. Zhang, *Ann. Rev. Biomed. Eng.*, 2000, **2**, 9; (b) R. Langer, *Acc. Chem. Res.*, 2000, **33**, 94; (c) K. Yong and D. J. Mooney, *Chem. Rev.*, 2001, **101**, 1869.
- (a) P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133; (b) J. H. van Esch and B. L. Feringa, *Angew. Chem., Int. Ed.*, 2000, **39**, 2263.
- L. A. Estroff and A. D. Hamilton, *Chem. Rev.*, 2004, **104**, 1201 and references cited therein.
- (a) W. Kubo, S. Kambe, S. Nakade, T. Kitamura, K. Hanabusa, Y. Wada and S. Yanagida, *J. Phys. Chem. B*, 2003, **107**, 4374; (b) T. M. Kellogg and J. van Esch, *Langmuir*, 2002, **18**, 7136; (c) A. Ajayaghosh, S. J. George and V. K. Praveen, *Angew. Chem., Int. Ed.*, 2003, **42**, 332.
- Y. Ono, K. Nakashima, M. Sano, Y. Kanekiyo, K. Inoue, J. Hojo and S. Shinkai, *Chem. Commun.*, 1998, 1477.
- M. Suzuki, Y. Sakakibara, S. Kobayashi, M. Kimura, H. Shirai and K. Hanabusa, *Polym. J.*, 2002, **34**, 474.
- (a) M. Suzuki, M. Kimura, H. Shirai and K. Hanabusa, *J. Am. Chem. Soc.*, 2002, **124**, 6550; (b) Y. Yang, M. Suzuki, M. Kimura, H. Shirai and K. Hanabusa, *Chem. Commun.*, 2004, 1332; (c) Y. Yang, M. Suzuki, M. Kimura, H. Shirai, A. Kurose and K. Hanabusa, *Chem. Commun.*, 2005, 2032.
- (a) J. H. Jung, Y. Ono, K. Hanabusa and S. Shinkai, *J. Am. Chem. Soc.*, 2000, **122**, 5008; (b) J. H. Jung, S. Shinkai and T. Shimizu, *Chem. Rec.*, 2003, **3**, 212; (c) T. Shimizu, M. Masuda and H. Minamikawa, *Chem. Rev.*, 2005, **105**, 1401.
- (a) C. L. Chan, J. B. Wang, J. Yuan, H. Gong, Y. H. Liu and M. H. Liu, *Langmuir*, 2003, **19**, 9440; (b) E. D. Sone, E. R. Z. Zubarev and S. I. Stupp, *Angew. Chem., Int. Ed.*, 2002, **41**, 1705; (c) M. Kimura, S. Kobayashi, T. Kuroda, K. Hanabusa and H. Shirai, *Adv. Mater.*, 2004, **16**, 335; (d) C. S. Love, V. Chechik, D. K. Smith, K. Wilson, I. Ashworth and C. Brennan, *Chem. Commun.*, 2005, 1971.
- (a) M. Suzuki, Y. Nakajima, M. Yumoto, M. Kimura, H. Shirai and K. Hanabusa, *Langmuir*, 2003, **19**, 8622; (b) M. Suzuki, S. Owa, H. Shirai and K. Hanabusa, *Macromol. Rapid Commun.*, 2005, **26**, 803.
- Experimental condition for fabrication of TiO₂ nanoparticles in the butanol gel based on **2**: [2] = 11 mg, Ti[OCH(CH₃)₂]₄ = 0.1 ml, propylamine = 2.8 μl and ¹BuOH = 1.9 ml.