

## Preparation of TiO<sub>2</sub> Hollow-Fibers Using Supramolecular Assemblies

Satoshi Kobayashi, Kenji Hanabusa,\*  
Nobuhiro Hamasaki, Mutsumi Kimura, and  
Hirofusa Shirai

Department of Functional Polymer Science, Faculty of  
Textile Science and Technology, Shinshu University,  
Ueda, Nagano 386-8567, Japan

Seiji Shinkai

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

Received February 1, 2000

Revised Manuscript Received April 13, 2000

Porous, nanostructured materials have attracted considerable attention because of their potential applications as sorption media,<sup>1</sup> molecular sieves,<sup>2</sup> supports,<sup>3</sup> and catalysts.<sup>4</sup> In particular, nanostructured TiO<sub>2</sub> materials are of great interest for possible applications to photovoltaic cells,<sup>5</sup> catalysts,<sup>4</sup> and semiconductor devices.<sup>6</sup> Despite their well-defined utility, the morphological control of the nanostructures of inorganic materials is quite difficult. Nanostructured inorganic materials have been synthesized by postsynthetic removal of surfactant assemblies,<sup>7</sup> and liquid-crystalline molecules<sup>8</sup> from inorganic–organic mesostructures. In such syntheses, the morphology is determined by the cooperative organization of inorganic and organic species into a three-dimensional mesostructure. On the other hand, a replica process,<sup>9</sup> a chemical process,<sup>10</sup> and a template approach<sup>11</sup> have been reported as the procedures for the preparation of nanotubes. Recently,

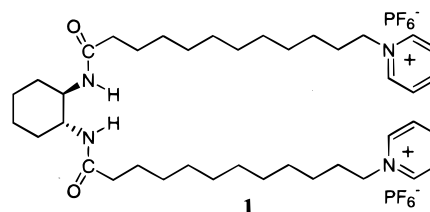
Table 1. Results of Gelation Tests of **1** at 25 °C<sup>a</sup>

organic/organometallic fluid	
Ti[OCH(CH <sub>3</sub> ) <sub>2</sub> ] <sub>4</sub>	gellike
Ti(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>4</sub>	gellike
Si(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>4</sub>	gellike
ethanol	gellike
2-propanol	insoluble
<i>n</i> -butanol	gel (20)
pyridine	solution

<sup>a</sup> Value means the minimum gel concentration (mg mL<sup>-1</sup> 1/fluid).

one of the authors reported the preparation of a hollow-fiber silica by using organogelators.<sup>12</sup> Organogelators are low molecular weight compounds that can gel solvents at low concentrations.<sup>13</sup> The gelling phenomenon has been attributed to the formation of a three-dimensional network based on fibrous aggregates in organic fluids. The self-assembled organogelators interacted with inorganic species and acted as a template in the sol–gel polymerization process.<sup>14</sup>

In the present paper, we report the preparation of a novel TiO<sub>2</sub> material with a hollow-fiber structure like “macaroni” by using self-assembly to form a template. We designed an amphiphilic compound **1** containing cationic charge moieties with the expectation that the self-assembled compound **1** would electrostatically interact with titania species in the sol–gel polymerization process of Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>. *trans*-(1*R*,2*R*)-1,2-Cyclohex-



\* To whom correspondence should be addressed. Phone: +81-268-21-5487. Fax: +81-268-24-7248. E-mail: hanaken@giptc.shinshu-u.ac.jp

(1) Lopez, N.; Illas, F.; Pacchioni, G. *J. Am. Chem. Soc.* **1999**, *121*, 813.

(2) (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710. (b) Bagshaw S. A.; Pinnavia, T. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1102.

(3) (a) Feng, X.; Fryxell, G. E.; Wang, L.-Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science* **1997**, *276*, 923.

(4) (a) Tian, Z.-R.; Tong, W.; Wang, J.-Y.; Duan, N.-G.; Krishnan, V. V.; Suib, S. L. *Science* **1997**, *276*, 926. (b) Kisch, H.; Zang, L.; Lange, C.; Maier, W. F.; Antonius, C.; Meissner, D. *Angew. Chem., Int. Ed.* **1998**, *37*, 3034. (c) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. *Adv. Mater.* **1998**, *10*, 135.

(5) (a) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49. (b) Bach, U.; Lupo, D.; Comte, P.; Moser, J. E.; Weissörtel, F.; Salbeck, J.; Spreitzer, H.; Grätzel, M. *Nature* **1998**, *395*, 583.

(6) Vinodgopal, K.; Hotchandani, S.; Kamat, P. V. *J. Phys. Chem.* **1993**, *97*, 9040.

(7) (a) Hou, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317. (b) Bagshaw, S. A.; Pinnavaia, T. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1102. (c) Imhof, A.; Pine, D. J. *Adv. Mater.* **1999**, *11*, 311.

(8) (a) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834. (b) Göltner, C. G.; Henke, S.; Weissenberger, M. C.; Antonietti, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 613.

(9) Hoyer, P. *Langmuir* **1996**, *12*, 1411.

(10) Kasuga, T.; Hiramatsu, M.; Hoson, Akihiko; Sekino, T.; Niihara, K. *Adv. Mater.* **1999**, *11*, 1307.

anedi(11-aminocarbonylundecylpyridinium) hexafluorophosphate (**1**) was prepared by the quaternization of *trans*-(1*R*,2*R*)-1,2-cyclohexanedi(11-aminocarbonylundecyl bromide) and pyridine, followed by the exchange of the counteranion with KPF<sub>6</sub>.<sup>15</sup>

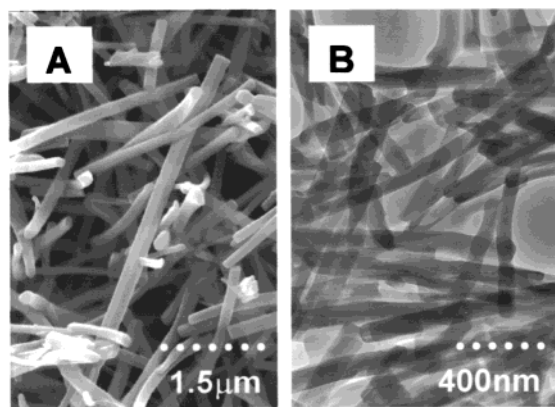
The results of gelation tests for **1** are summarized in Table 1.<sup>16</sup> Compound **1** gelled *n*-butanol and the minimum gel concentration necessary for the gelation was 20 g L<sup>-1</sup>. The solution of **1** often afforded a highly viscous fluid instead of gels on cooling at 25 °C. The term “gellike” in Table 1 indicates the formation of a highly viscous fluid. Actually, compound **1** formed turbid viscous fluids of sol–gel sources consisting of titanium alkoxides and alcohols. Previously, we reported the formation of a supramolecular assembly of *trans*-(1*R*,2*R*)-

(11) (a) Martin, C. R. *Science* **1994**, *266*, 1961. (b) Hulteen, J. C.; Jirage, K. B.; Martin, C. R. *J. Am. Chem. Soc.* **1998**, *120*, 6603.

(12) (a) Ono, Y.; Nakashima, K.; Sano, M.; Kanekiyo, Y.; Inoue, K.; Hojo, J.; Shinkai, S. *Chem. Commun.* **1998**, 1477. (b) Ono, Y.; Nakashima, K.; Sano, M.; Hojo, J.; Shinkai, S. *Chem. Lett.* **1999**, 1119.

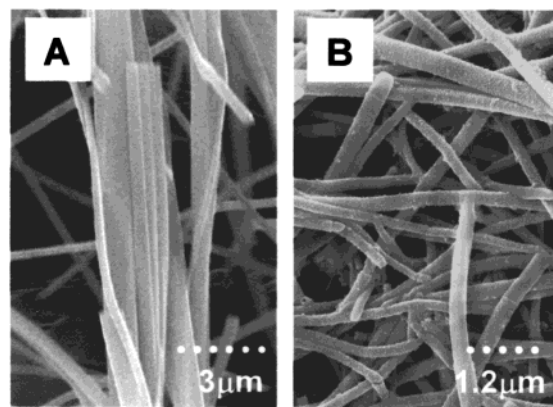
(13) (a) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133. (b) Hanabusa, K.; Hiratsuka, K.; Kimura, M.; Shirai, H. *Chem. Mater.* **1999**, *11*, 649.

(14) Kobayashi, S.; Hanabusa, K.; Suzuki, M.; Kimura, M.; Shirai, H. *Chem. Lett.* **1999**, 1077.



**Figure 1.** SEM (A) and TEM (B) images of self-assembled structure formed by **1** in ethanol.

1,2-di(undecylcarbonylamino)cyclohexane and the gelation mechanism in organic fluids.<sup>17</sup> Considering the self-assembling behavior of *trans*-(1*R*,2*R*)-1,2-di(undecylcarbonyl-amino)cyclohexane in organic fluids, it can be assumed that compound **1** will also form three-dimensional fibrous networks which are stabilized by intermolecular hydrogen-bonding through the amide groups in sol-gel sources. In fact, the self-assembled rods of **1** could be observed in electron microscopy. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the self-assembled rods in ethanol are shown in Figure 1. The figure reveals extended fibrous rods whose diameters are 50–300 nm. From the fact that the diameter of the smallest fibril in Figure 1 is several tens of nanometers, we presume that



**Figure 2.** SEM images of the dried samples prepared under acidic (A) and basic (B) conditions.

the rods were formed from the numerous molecules of **1** by intermolecular hydrogen-bonding, and then they were juxtaposed to form the large aggregates.

A precursor solution of the typical sol-gel polymerization under basic conditions was composed of Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (0.1 mL, 0.34 mmol), **1** (31 mg, 0.034 mmol), ethanol (1.5 mL), and 25% ammonium hydroxide aqueous solution (5.4 × 10<sup>-3</sup> mL). For the polymerization under acidic conditions, 2 M HCl aqueous solution (1.3 × 10<sup>-3</sup> mL) was used instead of NH<sub>3</sub> solution. First, Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> and **1** were added to half of the prescribed amount of ethanol. The other half was mixed with 25% ammonium hydroxide aqueous solution or 2 M HCl aqueous solution as a catalyst, and the mixture was added dropwise to the former solution under ice-cooled conditions with stirring. The mixture was then heated at 80 °C, and the resultant homogeneous solution was slowly cooled to 25 °C. In the cooling process, the viscosity of the solution increased and a white precipitate appeared. To obtain a *dried sample*, the solution was dried at 25 °C for 10 days, followed by heating at 50 °C for 5 h in a vacuum. To make a *calcined sample*, the dried sample was further heated at 200 °C for 2 h. Finally, it was calcined at 450 °C for 2 h to remove organic components and completely convert into TiO<sub>2</sub>. Consequently, calcined samples could be obtained. FT-IR spectra confirmed that all organic components could be removed thoroughly from the calcined samples.

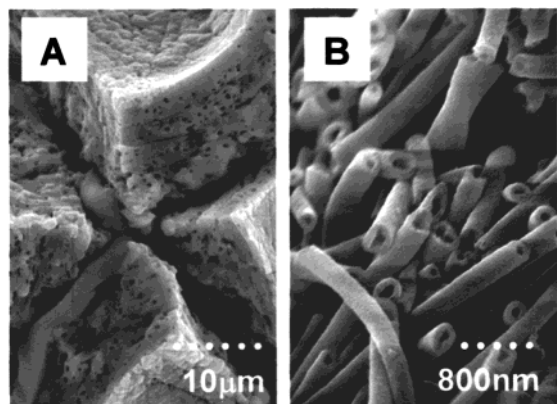
Figure 2 shows SEM images of dried samples prepared under acidic and basic conditions. The fully grown fibrous aggregates of **1**, whose diameters are 150–600 nm, form an extensive network structure under both conditions. The surface of the fiber prepared under basic conditions is rough (Figure 2A), whereas the sample under acidic conditions has a very smooth surface (Figure 2B). The rough surface under the basic condition may have been the result of the adhesion of the TiO<sub>2</sub> particles to fibrous aggregates.

Figure 3 shows SEM images of calcined samples after calcination at 450 °C. No fibrous structure was observed for the samples prepared under acidic conditions; in contrast, the fibrous structure under basic conditions was completely preserved after calcination. When sol-gel polymerization is carried out under basic conditions, the propagation species is considered to be anionic.<sup>7a</sup> Hence, the oligomeric titania species are adsorbed onto cationic aggregates of **1** and the polymerization further proceeds along these aggregates. The titania fibers of

(15) *trans*-(1*R*,2*R*)-1,2-Cyclohexanedi(11-aminocarbonylundecyl bromide). 12-Bromododecanoyl chloride (10.7 g, 3.60 mmol) was dissolved in 30 mL of tetrahydrofuran (THF). A mixture of 8.0 mL (57.4 mmol) of triethylamine and 2.05 g (1.80 mmol) of *trans*-(1*R*,2*R*)-1,2-diaminocyclohexane in 50 mL of THF was added dropwise to the above solution and stirred overnight at 60 °C. After evaporation, the crude product was dissolved in 200 mL of hot ethanol and cooled to room temperature. The formed gel was filtered with suction and dried. This purification procedure with ethanol was repeated. Yield: 7.4 g (65%). *trans*-(1*R*,2*R*)-1,2-Cyclohexanedi(11-aminocarbonylundecylpyridinium) bromide. *trans*-(1*R*,2*R*)-1,2-Cyclohexanedi(11-aminocarbonylundecyl bromide) (0.50 g, 0.785 mmol) was dissolved in 30 mL of pyridine and refluxed for 12 h. After evaporation, the residue was dissolved in a minimum volume of ethanol. Acetone was added dropwise to the ethanol solution with stirring until white precipitation was generated. The solution was cooled at 0 °C, and then the gellike matter was filtered with suction and dried. Yield: 0.65 g (90%). *trans*-(1*R*,2*R*)-1,2-Cyclohexanedi(11-aminocarbonylundecylpyridinium) hexafluorophosphate (**1**). To a solution of 0.50 g (0.63 mmol) of *trans*-(1*R*,2*R*)-1,2-cyclohexanedi(11-aminocarbonylundecylpyridinium) bromide in 50 mL of distilled water was added 0.46 g (2.5 mmol) of potassium hexafluorophosphate in 50 mL of distilled water, followed by stirring for 3 h. The precipitated matter was filtered off, washed with water, and dried in a vacuum. Yield: 0.55 g (92%). <sup>1</sup>H NMR (400.1 MHz, CD<sub>3</sub>CN): δ 1.26–1.67 (m, 36 H, CH<sub>2</sub>), 1.93 (t, 4 H, COCH<sub>2</sub>), 1.94–2.05 (m, 8 H, cyclohexane), 3.49 (d, 2 H, cyclohexane), 4.50 (t, 4 H, CH<sub>2</sub>), 6.53 (s, 2 H, NH), 8.03 (t, 4 H, pyridine), 8.50 (t, 2H, pyridine), and 8.66 (d, 4H, pyridine). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN): δ 24.17, 25.23, 28.26, 28.59, 28.66, 28.77, 28.83, 30.54, 31.57, 35.81, 53.05, 61.52, 128.08, 144.07, 145.39, and 172.78. FT-IR (KBr): 3282 (ν NH) and 1637 cm<sup>-1</sup> (ν C=O). Element analysis calculated for C<sub>40</sub>H<sub>66</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>F<sub>16</sub>: C 51.9, H 7.2, N 6.1; found: C 52.2, H 7.4, N 6.1.

(16) The gelation testing procedure was as follows: A weighed sample was mixed with an organic liquid (2.0 mL) in a test tube with a screw cap (inside diameter 14 mm), and the mixture was heated until the solid dissolved. The resulting solution was cooled to 25 °C for 2 h and then the gelation was checked visually. When no fluid ran down the wall of the test tube upon inversion of the tube, we judged it to be a "gel". A highly viscous solution was distinguished from a gel as a "gellike". The gel-forming ability was evaluated by the minimum gel concentration (MGC), which is the minimum concentration of gelator necessary for gelation at 25 °C.

(17) Hanabusa, K.; Yamada, M.; Kimura, M.; Shirai, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1949.

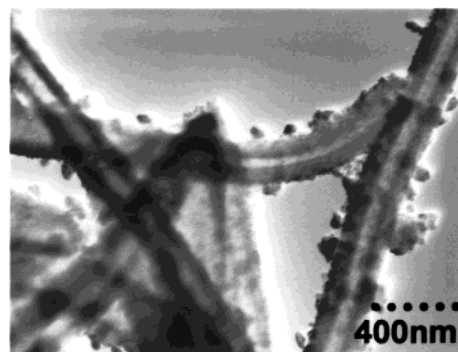


**Figure 3.** SEM images of the calcined samples prepared under acidic (A) and basic (B) conditions.

the calcined samples possessed hollow structures with outer diameters of 150–600 nm (Figure 3B), and the maximum length of the titania fiber was  $\sim 200 \mu\text{m}$ . A comparison of the SEM images of the dried sample (Figure 2B) and the calcined one (Figure 3B) revealed no difference in outer diameter.

It is also clarified from a TEM image (Figure 4) that the  $\text{TiO}_2$  fibers have a hollow structure. In the figure, the inner diameters of the  $\text{TiO}_2$  fibers are 50–300 nm, which are compatible with the diameter size of the self-assembled rods of **1** observed in Figure 1B.

The crystal structures of the resultant  $\text{TiO}_2$  fibers were analyzed by X-ray diffraction using  $\text{Cu K}\alpha$  radiation. The X-ray diffraction patterns showed that the  $\text{TiO}_2$  fibers crystallized into anatase structures after calcination at  $450^\circ\text{C}$  for 2 h. Nanostructured anatase  $\text{TiO}_2$  has been employed in a variety of photoelectric devices. Therefore, this hollow-fiber  $\text{TiO}_2$  material has excellent potential for applications as photovoltaic solar



**Figure 4.** TEM image of the calcined sample prepared under basic conditions.

cells, photocatalytic devices, and rechargeable lithium ion battery electrodes.

In summary, the sol–gel polymerization of  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$  using compound **1** as a self-assembled template afforded fibrous  $\text{TiO}_2$  materials with a “macaroni”-like structure. The unique structure of  $\text{TiO}_2$  could be created by the formation of a fibrous self-assembled aggregate and electrostatic interaction between anionic titania species and cationic **1** under basic conditions.

**Acknowledgment.** This work was supported by Grant-in-Aid for COE Research (10CE2003) by the Ministry of Education, Science, Sports, and Culture of Japan.

**Supporting Information Available:** The distribution of cross-sectional diameter for the fibrous structures and sample preparation for electron microscopy. This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM0000907