

## Preparation of Helical Transition-Metal Oxide Tubes Using Organogelators as Structure-Directing Agents

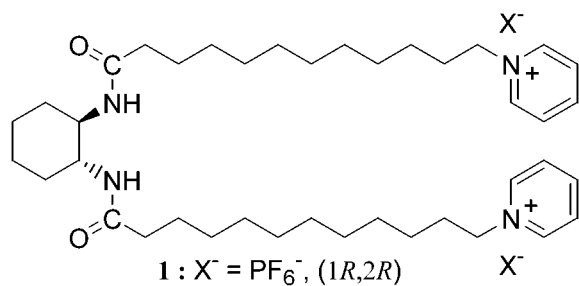
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Nanostructured materials have attracted considerable attention because of their novel properties and applications unlike those of conventional macroscopic materials. In particular, nanostructured transition-metal oxides such as tantalum, titanium, and vanadium oxides are generally accepted as the next-generation materials in fields such as electronics<sup>1</sup> and advanced catalysts.<sup>2</sup> Many efforts have been made to control nanostructures of transition-metal oxides using replication process,<sup>3</sup> chemical process,<sup>4</sup> and template technique.<sup>5</sup>

Recently, Shinkai et al. reported the preparation of a helically structured silica by a sol-gel transcription in chiral organogel systems.<sup>6</sup> Their studies suggested that the unique superstructure of the organogel fiber can be transcribed in the silica structure. Organogelators are low-molecular weight compounds that can gelate organic fluids at low concentrations.<sup>7</sup> Especially, *trans*-(1*R*,2*R*)- or *trans*-(1*S*,2*S*)-1,2-di(undecylcarbonylamino)cyclohexane are excellent gelators that can harden a wide variety of organic fluids.<sup>8</sup> This gelling phenomenon has been attributed to the formation of a three-dimensional network based on fibrous aggregates in organic fluids. Further, the *trans*-(1*R*,2*R*)- and *trans*-(1*S*,2*S*)-1,2-diaminocyclohexane derivatives self-assemble into left-handed and right-handed helical fibers which are stabilized by intermolecular hydrogen-bonds through amide groups, respectively. The chiral self-assemblies based on these organogelators would provide an excellent template for the creation of inorganic materials having a chiral nanostructure.



Previously, we reported that organogelator **1** formed a supramolecular assembly with a rodlike fibrous structure in ethanol, and the sol-gel polymerization of  $Ti[OCH(CH_3)_2]_4$  using **1** as a structure-directing agent afforded  $TiO_2$  material with a hollow-fiber

structure.<sup>9</sup> Recently, it was found that organogelators **2a** and **2b** containing  $ClO_4^-$  as the counteranion formed chiral fibrous aggregates in ethanol. The chiral aggregate of **2** should act as a chiral template in the sol-gel polymerization process of metal alkoxide.

This contribution describes the preparation of chiral, helical tubes of transition-metal (Ti, Ta, V) oxides by the sol-gel polymerization of the metal alkoxides using the chiral aggregates of **2a** and **2b** as the structure-directing agents.

Compounds **2a** and **2b** were synthesized according to the method described previously<sup>9</sup> and identified by IR, <sup>1</sup>H NMR, mass spectroscopy, and elemental analysis. The gelation ability of **2a** was tested for several organic fluids and water.<sup>10</sup> Compound **2a** could gel up four alcohols and water at 25 °C. The amounts of **2a** necessary to harden 1 mL of ethanol, 1-propanol, 2-propanol, 1-butanol, and water were 17, 11, 12, 11, and 3 mg, respectively. It is noteworthy that the gelation ability of **2a** for the polar solvents is better than that of **1** containing  $PF_6^-$  as the counteranion.<sup>9</sup>

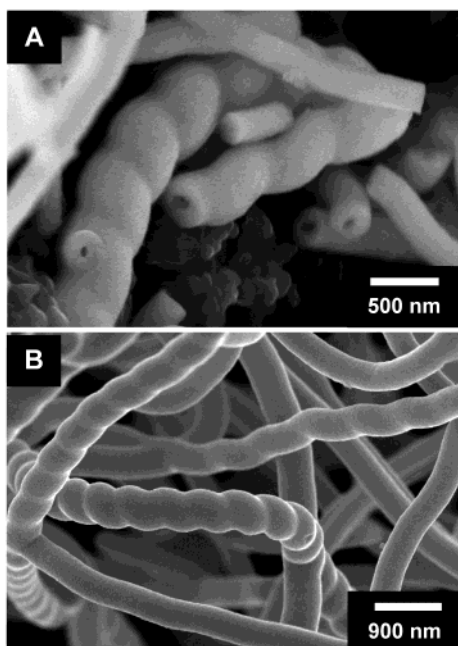
Superstructures built up with enantiomers **2a** and **2b** in ethanol were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electron micrographs revealed that **2a** and **2b** self-assembled into numerous intertwined, helical fibers with widths of 30–160 nm. However, the chiralities of the helical fibers of **2a** and **2b** were uncertain in the electron micrographs. To study the chiralities of the aggregates, circular dichroism (CD) spectra of loose gels (3 mM) in water were measured. The CD spectrum of **2a** at 20 °C exhibited significant negative peaks at 205, 260 nm, and a positive peak at 220 nm. These peaks decreased with increasing temperature and disappeared at 60 °C as the loose gel was transformed to an isotropic solution. The disappearance of the CD signal in the isotropic solution indicated that the CD bands arose from the formation of a chiral aggregate, but not from a chiral conformation of **2a**. On the contrary, CD spectra of the *S,S*-enantiomer **2b** were opposite those of the *R,R*-enantiomer **2a**. The observed CD spectral data exhibited that the aggregates of **2a** and **2b** were organized into helical structures with opposite chiralities. However, we find it ambiguous at best to settle on the helical senses of the aggregates for **2a** and **2b** from the TEM images and CD spectra. We shall later revisit this issue (see below).

We succeeded in clearing the helices by a sol-gel polymerization of metal alkoxides using the chiral aggregates of **2a** and **2b**. The sol-gel polymerization of metal alkoxides was carried out using the method which is similar to that described previously.<sup>9</sup> In a typical synthesis,  $Ta(OC_2H_5)_5$ ,  $Ti[OCH(CH_3)_2]_4$ , and  $O=V[OCH(CH_3)_2]_3$  were used as metal alkoxides. A mixture containing molar ratio of 1 (**2a** or **2b**):5 (metal alkoxide):2.5 ( $H_2O$ ):0.4 ( $NH_4OH$ ): ca. 350 (ethanol) was vigorously stirred in an ice-cooled condition

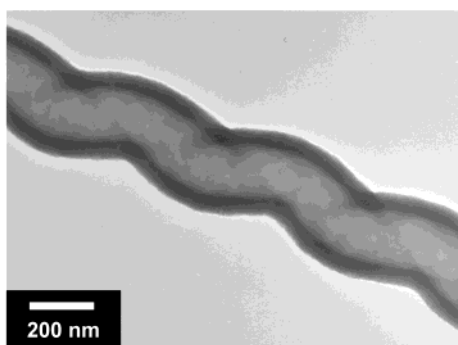
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**Figure 1.** SEM images of tantalum oxide fibers obtained from (A) (*R,R*)-enantiomer **2a** and (B) (*S,S*)-enantiomer **2b**.



**Figure 2.** TEM image of left-handed helical fiber of tantalum oxide obtained from (*R,R*)-enantiomer **2a**.

and then heated at 80 °C until a transparent solution was obtained. The solution was slowly cooled to 25 °C. In the cooling process, a turbid gel was formed. The gel was dried at 25 °C for 10 days, followed by heating at 50 °C for 5 h in vacuo. To remove the organogelator, the dried gel was washed with acetonitrile and then dried in vacuo. Finally, the organogelator was completely removed by calcination at 200 °C for 2 h and then at 450 °C for 2 h. Exceptionally, the vanadium oxide sample was heated at 180 °C for 2 h.

Figure 1 shows SEM images of tantalum oxide prepared using **2a** and **2b** as the structure-directing agents. These images reveal that the tantalum oxide materials have helical fiber structures with an outer diameter of 100–600 nm and a maximum length of ca. 30  $\mu$ m. The helices are always left-handed for the tantalum oxide fibers from the *R,R*-enantiomer **2a**, and right-handed in the case of ones from the *S,S*-enantiomer **2b**. The helical sense of the tantalum oxide tubes is the same as that of the helical silica tube system.<sup>6b,c</sup>

Figure 2 shows a TEM image of the left-handed tantalum oxide fiber obtained from **2a**. It is apparent from the TEM image that the tantalum oxide fibers have a hollow structure. The inner diameters of the tantalum oxide fibers are 30–180 nm, which are compatible with the diameter size of the self-assemblies of **2a**. Furthermore, the cavities of the fibers have a left-handed helix structure. These results indicate that the chiral nanostructures of

the organogel aggregates were completely transcribed into a tantalum oxide structure. Now we say that the helices of the aggregates of **2a** and **2b** were left-handed and right-handed, respectively.

Similar results were obtained in sol–gel polymerization systems of titanium and vanadium alkoxides. The resulting titanium and vanadium oxides also had helical tubular structures, whose helices were always left-handed for the *R,R*-enantiomer **2a** and right-handed for the *S,S*-enantiomer **2b**.

In summary, the sol–gel polymerization of metal (Ti, Ta, V) alkoxides using organogelators **2a** and **2b** as templates afforded tubular helical fiber materials of transition-metal (Ti, Ta, V) oxides. The helices of metal oxide fibers were always left-handed in the sol–gel system of the *R,R*-enantiomer **2a**, and right-handed in the case of the *S,S*-enantiomer **2b**. The chiral structures of metal oxide fibers can be created by the formation of chiral self-assemblies constructed by the organogelators and by the transcription of the organogel superstructures into metal oxides. Because of the unique nanostructures and the properties of transition-metal oxides, the resulting chiral helical tubes have a variety of promising applications, for example, in electronics, as optically functional materials, and as chiral- and photocatalysts.

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**Supporting Information Available:** CD spectral data of **2a** and **2b**, gelation ability of **2a**, electron micrographs of self-assemblies formed by **2a** and **2b**, SEM images of titanium and vanadium oxide fibers obtained from **2a** and **2b** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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

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