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Preparation of Metal Oxide Nanotubes Using Gelators as Structure-Directing Agents

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Summary: Cationic gelators, capable of gelling alcohols, were developed as structure-directing agents for preparing metal oxides. The sol-gel polymerization of metal alkoxides using the gelators as templates afforded metal oxide nanotubes. The unique structure of metal oxides was created by transferring the shape of fibrous aggregates of gelator. The electrostatic interaction between cationic gelator and anionic metal oxide precursor plays an important role for acting as templates.

Keywords: gelators; metal oxides; nanotubes; sol-gel polymerization; tantalum oxide; titania; titanium oxide

Introduction

Recently nanostructured materials have received a great amount of scientific and technological interest because of their novel properties and applications unlike those of conventional macroscopic materials. Especially, nanostructured transition-metal oxides such as tantalum, titanium, and vanadium oxides are of special interest as the next-generation materials in fields as electronics[1] and advanced catalyst.[2] Many efforts have been made to control nanostructures of transition-metal oxides; for instance, hydrothermal synthesis,[3] atomic layer deposition (ALD) synthesis,[4] electrochemical anodization synthesis,[5] and template technique.[6] In the meantime we have been studying low molecular weight gelators capable of hardening organic liquids and water.[7] The driving forces of physical gelation by gelator are cooperating noncovalent interactions of gelator molecules, such as hydrogen bonding, van der Waals force, π-π interaction, and electrostatic interaction. The outstanding feature responsible for gelation is thought to rely on the formation of three-dimensional networks composed of highly intertwined fibers. The first stage of physical gelation is the self-aggregation of gelator molecules. Now we focus on gelators as structure-directing agents for preparing metal oxide nanotubes by sol-gel polymerization.

Experimental

Synthesis of Gelator 1

N-Carbobenzyloxy-L-valylaminooctadecane was prepared according to our previous method.[7a,c] A suspension of 15.0 g (28.9 mmol) of *N*-carbobenzyloxy-L-valylaminooctadecane and 2 g of 10% palladium on charcoal in 200 mL of ethanol was hydrogenated for 6 h at room temperature, during which time the formed gel was sometimes heated until the gel dissolved. The removal of carbobenzyloxy group was verified by TLC. The filtrate without catalyst was evaporated and the residue was recrystallized from ethyl acetate. L-Valylaminooctadecane was obtained in a yield of 8.98 g (82%).

To a solution of 4.18 g (11.3 mmol) of L-valylaminooctadecane and 4.68 mL of NEt_3 in 300 mL of dry THF, 2.66 g (12.5 mmol) of 6-bromohexanoyl chloride was added dropwise at 0 °C. The mixture was stirred at 0 °C

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for 1h and then at room temperature for 4h. After evaporating THF, the residue was recrystallized from ethanol. *N*-6-Bromohexanoyl-L-valylaminooctadecane was obtained in a yield of 4.12 g (67%).

Three gram (5.50 mmol) of *N*-6-bromohexanoyl-L-valylaminooctadecane was refluxed in 50 mL of pyridine under a nitrogen atmosphere overnight. The mixture was evaporated and recrystallized from a mixture of ethanol and acetone. The corresponding pyridinium bromide salt was obtained in a yield of 3.37 g (98%).

To a solution of 3 g (4.80 mmol) of the pyridinium bromide salt in a mixture of 300 mL of water and 50 mL of ethanol, 2.66 g (14.4 mmol) of potassium hexafluorophosphate in 50 mL of water was added and stirred at room temperature for 5h. The precipitated matter was filtered off and washed with water. Recrystallized from methanol gave 3.08 g (93%) of pyridinium hexafluorophosphate salt (**1**).

Synthesis of Gelator 2

Gelator **2** was prepared by the similar method described for **1**, using 11-bromoundecanoyl chloride instead of 6-bromohexanoyl chloride.

Gelation Test

Gelation test was carried out by upside-down test tube method. 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 sample dissolved. The resulting solution was cooled to 25 °C for 2h and then the gelation was checked visually. When no fluid ran down the wall of the test tube upon inversion of the test tube, we judged it it to be gel. The gelation ability was evaluated by the minimum gel concentration (MGC), which is the minimum concentration of gelator necessary for gelation at 25 °C.

Preparation of Titanium Oxide Nanotube

A mixture of 70 mg (0.102 mmol) of gelator **1**, 0.30 mL (1.02 mmol) of titanium tetraisopropoxide, 10.8 μL of 25% ammonia , and 5.70 mL of ethanol was heated at 80 °C in a test tube until a transparent solution was obtained. The solution was slowly cooled to 25 °C, which time a turbid gel was formed. The test tube forming gel was dried at 25 °C for 10 days upon exposure to the atmosphere without cap, followed by heated at 50 °C for 5 h in vacuo. To remove the gelator, the dried sample was washed with acetonitrile and then dried in vacuo. Finally, it was calcined at 200 °C for 2h and 500 °C for 2h to remove organic components and completely convert into TiO_2.

Results and Discussion

First we tried sol-gel polymerization using *N*-carbobenzyloxy-L-valylaminooctadecane which can gel many solvents, regardless of their polarity.[7a,c] Unfortunately, it didn't act as templates for sol-gel polymerization; therefore, we changed it into cationic pyridinium salts (**1** and **2**) according to Figure 1. It can be assumed that the attachment of cationic charged segments on gelators causes electrostatic interaction between gelators and metal oxide precursors. The compounds **1** and **2** were able to gel alcohols. The MGCs of **1** towards 1-propanol and 1-butanol are 12 g L^{-1} and 7 g L^{-1}, while those of **2** towards ethanol, 1-propanol, 2-propanol, and 1-butanol are 10 g L^{-1}, 12 g L^{-1}, 8 g L^{-1}, 8 g L^{-1}, respectively.

Titanium (IV) tetraisopropoxide $Ti[OCH(CH_3)_2]_4$ and tantalum (V) ethoxide $Ta(OC_2H_5)_5$ were selected as metal alkoxides and their sol-gel polymerization were carried out using a mixture of metal alkoxide and ethanol. For example, the molar ratio of gelator:metal alkoxide:-H_2O:NH_3:ethanol in the mixture was 1:10:4:1.4:960. It was vigorously stirred in an ice-cooled condition and then heated at 80 °C until a transparent solution was obtained. The solution was slowly cooled to 25 °C to form a turbid gel. The gel was exposed to moisutre in the atmosphere at 25 °C for 10 days, followed by heating at

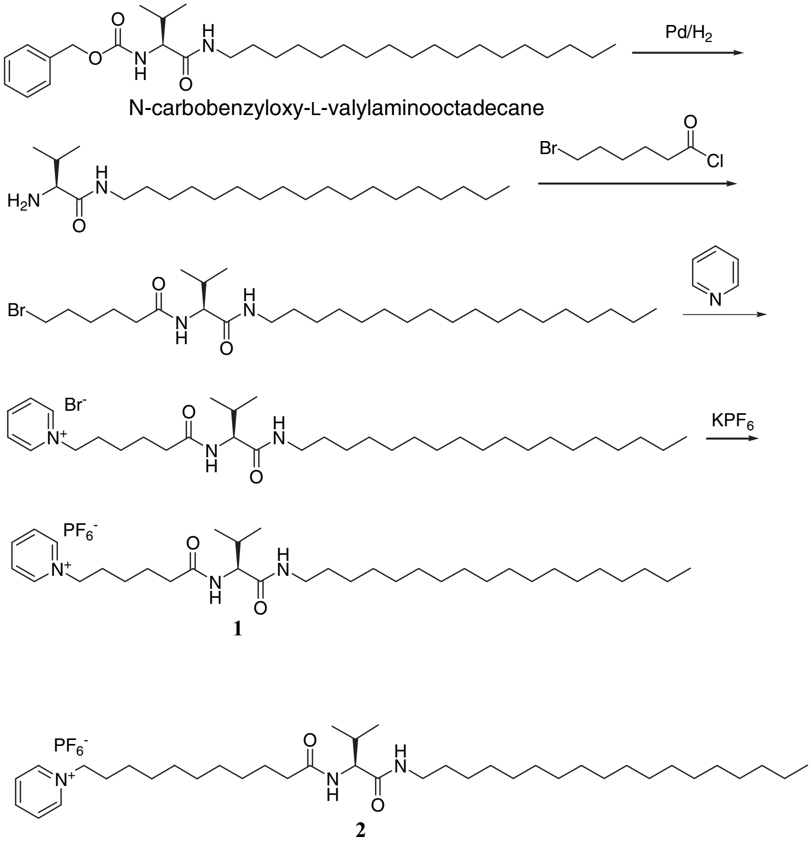

Figure 1.
Synthesis of gelator **1** and **2**.

50 °C for 5 h in vacuo. Dried sample containing gelator was obtained. To remove the gelator in the dried sample, it was washed with acetonitrile and then dried in vacuo. Finally, the calcination at 200 °C for 2h and 500 °C for 2h converted the dried sample into calcined sample of metal oxide. FT-IR spectra of the obtained metal oxides indicate that the gelators were completely eliminated by the treatment of acetonitrile washing and calcination.

Figure 2A and 2B show SEM images of TiO_2 nanotubes obtained by using gelator **1** as structure-directing agent. The average outer diameter of the TiO_2 nanotubes was 360 nm and the inner diameter ranged from 20 nm to 150 nm. It is clear from Figure 2B that the TiO_2 nanotubes have hollow structure. Figure 2C shows SEM images of the TiO_2 nanotubes obtained by using gelator **2** as templates. The average outer diameter of the TiO_2 nanotubes was 210 nm. It should be mentioned that the TiO_2 nanotubes calcined at lower than 600 °C were Anatase type, which were identified by X-ray diffraction analysis. The reason that the outer diameter of the TiO_2 nanotubes obtained with the template of gelator **2** is smaller than that with gelator **1** is probably due to the size of aggregates, which are described as bundles of gel fibers later. It is thought that the width of bundles of gel fibers of gelator **2** is small as compared with that of gelator **1**.

Tantalum oxide nanotubes were also obtained by sol-gel polymerization of tantalum (V) ethoxide. Figure 3A and 3B show SEM and TEM images of Ta_2O_5

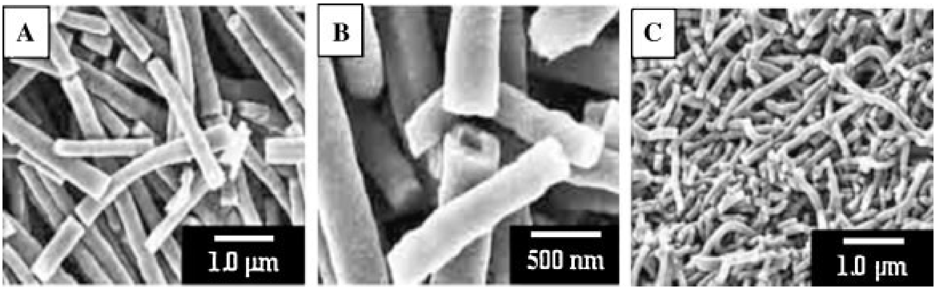

Figure 2.
SEM images of titanium oxide prepared using gelator **1** (A and B) and gelator **2** (C) as template.

nanotubes obtained by using gelator **1** as templates. The average outer diameter of the obtained Ta_2O_5 nanotubes was 365 nm. The TEM image clearly exhibits the hollow structure (Figure 3B). When the gelator **2** was used as templates, Ta_2O_5 nanotubes with the average outer diameter of 240 nm were formed (Figure 3C).

The formation process of metal oxide nanotubes is illustrated in Figure 4. First of all, slender fibrous aggregates are formed from many gelator molecules through intermolecular hydrogen bonding and van der Waals interaction. The slender fibrous aggregates are intertwined and juxtaposed to form huge and thick fibers. The huge fibers having hierarchical structure, that is to say, bundles of gel fibers act as templates for sol-gel polymerization. Having the cationic atmosphere due to pyridinium segment, the huge fibers attract anionic metal oxide precursors on their surface. Sol-gel polymerization on the surface gives metal oxide tubes, in which the huge gelator fibers still remains. Calcination of metal oxide tubes containing gelator bequeaths pure metal oxide nanotubes. We may conclude that gelator **2** is suitable as templates for preparing metal oxides nanotubes having smaller diameter.

Conclusion

Gelators having cationic charge segment were synthesized and sol-gel polymerization was carried out by using them as templates. Structurally related gelator without charged segment didn't work as templates. The sol-gel polymerization of titanium (IV) tetraisopropoxide and tantalum (V) ethoxide using gelators as templates afforded nanotubes of titanium oxide and tantalum oxide. The average diameters of nanotubes were several hundreds of nanometers, which can be moderately controlled by changing gelator. The unique structure of metal oxides was created by transferring the shape of fibrous aggregates

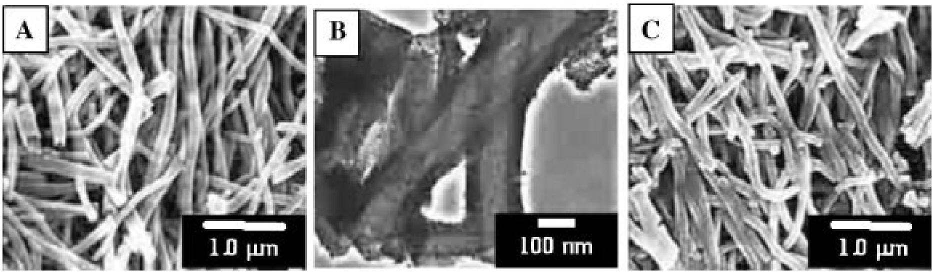

Figure 3.
SEM (A) and TEM (B) images of tantalum oxide prepared using gelator **1** and SEM (C) image of tantalum oxide prepared using gelator **2** as template.

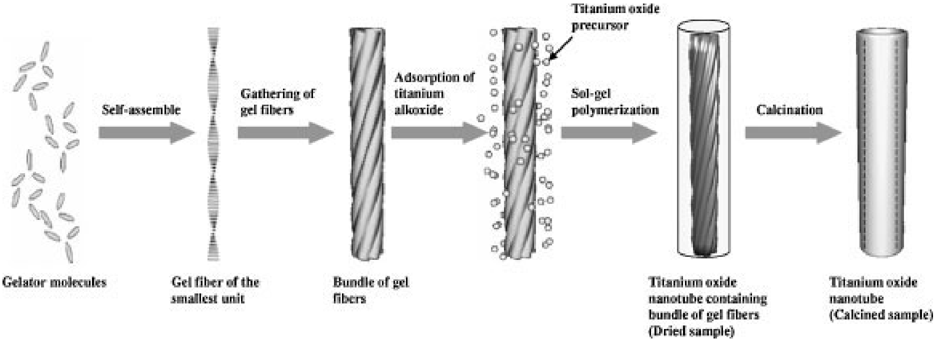

Figure 4.
Schematic illustration for formation process of metal oxide nanotube.

of gelator during sol-gel polymerization process. The electrostatic interaction between cationic gelator and anionic metal oxide precursor plays an important role for acting as templates.

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