Preparation of TiO_2 Fiber in a Sol-Gel System Containing Organogelator

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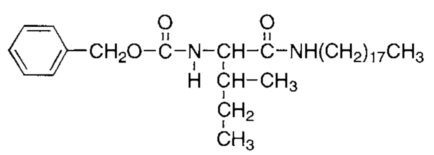
Porous titania with fibrous structure has been prepared, via sol-gel method, from a physical gel of titanium tetraisopropxide by a low molecular weight organogelator.

The synthesis of inorganic materials with specified and organized pore networks have received special attention in the field of catalysis,[1] separation technology,[2] and biomaterials engineering.[3] In particular, porous TiO_2 is of great interest for potential applications to photovoltaic cell,[4] electrochemical photolysis of water,[5] and semiconductor.[6] Ordered arrangements of porous structure of inorganic materials have been produced by post-synthetic removal of surfactant assemblies or organogelator-fibers as supramolecular templates from inorganic-organic mesostructure.[7,8] These studies have suggested that ionic charge density along the template aggregates was an important factor of the template effects.[7,8] On the other hand, it have been reported that unique morphology of inorganic materials was prepared by the sol-gel system of organic polymers with hydrogen bonding units.[9] It suggests that three-dimensional structure of inorganic materials can be controlled using the hydrogen bonding interaction between the organic template and inorganic materials. We have developed organogelators which can gel up several solvents with mainly hydrogen bonding interactions.[10,11] Especially, N-carbobenzyloxy-L-isoleucylaminooctadecane, which is referred to as Z-L-Ile-$NHC_{18}H_{37}$, is an excellent gelator which can harden a wide variety of organic fluids.[10] It is assumed that organogelators form three-dimensional networks based on fibrous aggregates in organic fluids. The macromolecule-like aggregates formed through non-covalent interactions are responsible for the gelation and these fibers form a three-dimensional network encapsulating the solvent.[10-12] Recently, Ono and co-workers reported that the sol-gel polymerization of tetraethoxysilane (TEOS), gelled by cholesterol-based gelators with cationic density, gave novel silica with a hallow fiber.[7] The system succeeded in building up unique morphology of silica using electrostatic interactions.



Z-L-Ile-$NHC_{18}H_{37}$

In the present paper, we report that the porous TiO_2 with fibrous structure is formed by the sol-gel polymerization of titanium tetraisopropoxide $Ti[OCH(CH_3)_2]_4$ gelled by Z-L-Ile-$NHC_{18}H_{37}$ through hydrogen bonding interaction.

Gelation ability of Z-L-Ile-$NHC_{18}H_{37}$ was examined in the sol-gel sources, $Ti[OCH(CH_3)_2]_4$, $Ti(OCH_2CH_3)_4$, and $Si(OCH_2CH_3)_4$ at 25 °C. The amount of Z-L-Ile-$NHC_{18}H_{37}$ necessary to solidify 1 cm^3 of $Ti[OCH(CH_3)_2]_4$, $Ti(OCH_2CH_3)_4$, and $Si(OCH_2CH_3)_4$ are 6, 4, and 7 mg, respectively. We are convinced that Z-L-Ile-$NHC_{18}H_{37}$ was an excellent gelator for sol-gel sources. Sol-gel polymerization was carried out under acidic condition as follows: A mixture of $Ti[OCH(CH_3)_2]_4$ ($3.4x10^{-4}$ mol), H_2O ($2.6x10^{-4}$ mol), HCl ($1x10^{-5}$ mol), ethanol ($3.2x10^{-2}$ mol), and Z-L-Ile-$NHC_{18}H_{37}$ ($3.4x10^{-4}$ mol) was used as a common precursor solution. First, $Ti[OCH(CH_3)_2]_4$ was dissolved in half of the prescribed amount of ethanol. The other half was mixed with 2 mol dm^{-3} HCl as catalyst, and the mixture was added dropwise to the former solution under ice-cooled condition with stirring. Then, Z-L-Ile-$NHC_{18}H_{37}$ was added and dissolved in the solution at 80 °C. The resultant hot solution was slowly cooled at room temperature to form gels. The gels were dried at 25 °C for 10 days, followed by heated at 50 °C for 5 h *in vacuo* to remove residual liquid. Figure 1A shows a scanning electron microscopy (SEM) image of the dried gel. It is clarified that the well-grown gelator fibers, whose diameter is 300-1500 nm, form a three-dimensional network structure. The dried gel aggregates is assumed to be formed by gelator-fibers surrounded by TiO_2. The dried gels were further converted to the corresponding calcined gels by heating at 200 °C for 2 h, followed by at 450 °C for 1 h in air. It is confirmed by FT-IR spectra that the gelator molecules were removed completely from the obtained calcined gels. A SEM image of the calcined gel is shown in Figure 1B. The calcined gel from sol-gel polymerization of $Ti[OCH(CH_3)_2]_4$ gelled by Z-L-Ile-$NHC_{18}H_{37}$ reveals the gathering of fibrous structure. It should be mentioned that SEM images of calcined gels of the ordinary sol-gel polymerization of $Ti[OCH(CH_3)_2]_4$ solution without the gelator exhibit smooth surfaces. Considering the fact that the diameter of the titania fiber of the calcined gel is 200-1200 nm, the shrinkage of fibrous aggregates seems to occur during the heat treatment process. The transmission electron micrograph (TEM), which can reflect the small scale structure of the TiO_2 fiber as compared with the SEM, of the

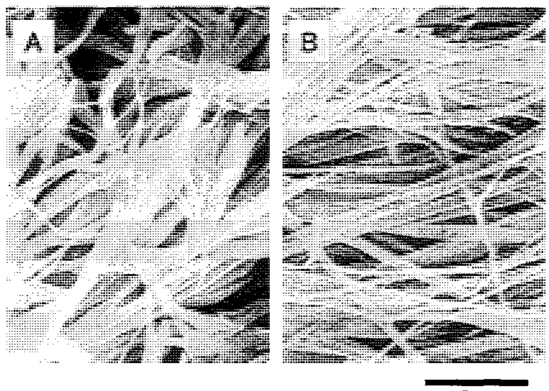


Figure 1. SEM images of TiO_2 fibers (A) before and (B) after calcination at 450 °C.

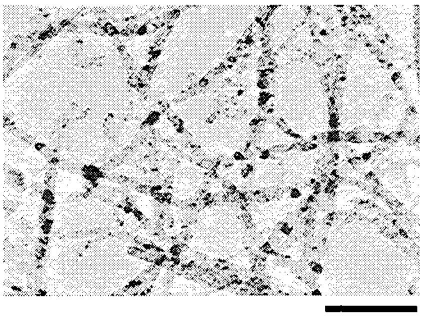


Figure 2. TEM image of the calcined gel by heat treatment at 450 °C.

calcined gel shows several width of filaments whose diameter is 15-150 nm (Figure 2). These filaments consist of TiO_2 particles of 15-30 nm. We presume that the aggregate are formed from numerous gelator molecules by intermolecular hydrogen bonding, then they are juxtaposed and interlocked to form the wide aggregates, and the oligomeric titania species are adsorbed onto these several wide aggregates by the hydrogen bonding interaction between titania and amide units of the gelator. The crystal structures of the resultant calcined gels were analyzed by powder X-ray diffraction (Figure 3). The calcined gel without

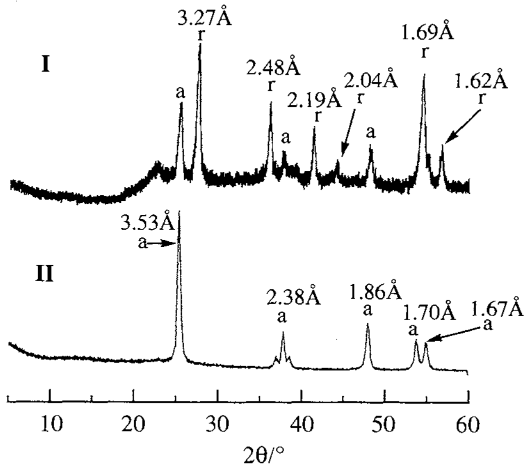


Figure 3. Powder X-ray diffraction patterns of TiO_2 calcined at 450 °C for 1 h with Z-L-Ile-$NHC_{18}H_{37}$ (I) and without the gelator (II). a: antase type, r: rutile type.

the gelator has crystallized into the anatase crystal structure, while the calcined TiO_2 in the presence of the gelator consists of the anatase and rutile ones.[13] This means that the rutile TiO_2 was formed with the help of Z-L-Ile-$NHC_{18}H_{37}$ molecules, suggesting the presence of the interaction with titania molecules and the gelator molecules. Since Z-L-Ile-$NHC_{18}H_{37}$ has no charge, it is unlikely that titania ion species are adsorbed onto the gelator fibrers by electrostatic interaction during polymerization. However, the formation of the titania fibrer and the presence of the rutile crystal structure indicate the interaction of gelator fibers and oligomeric titanias. It is thought that the oligomeric titanias were gathered around the frameworks of gelator aggregate in a similar fashion to the hydrogen bonding interaction between amino acid derivatives and titania.[14] Then, the calcination may result in the formation of titania fiber.

In summary, SEM and TEM observations of the calcined gel of $Ti[OCH(CH_3)_2]_4$ with Z-L-Ile-$NHC_{18}H_{37}$ revealed that sol-gel polymerization of the metal alkoxide using the gelator affords the well-grown fibrous structure of TiO_2. The unique structure of TiO_2 may be created by the hydrogen bonding interaction of the fibrous gelator aggregates and the oligomeric titanias.

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