Preparation of a UV-absorbed Transparent Monolithic Titanium Oxide Gel by the Catalytic Sol-Gel Process with a Phenanthroline Hydrochloride Catalyst

Taki Matsumoto,* Yasushi Murakami, and Yoshio Takasu
Department of Fine Materials Engineering, Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda 386-8567

(Received November 16, 1998; CL-980869)

UV-absorbed transparent monolithic titanium oxide gels were prepared by the catalytic sol-gel process with 1,10-phenanthroline hydrochloride and n-butylamine. When 1,10-phenanthroline was added to the precursor solution, transmittance of the gels increased. The higher the content of 1,10-phenanthroline hydrochloride and the lower content of water, the more transparent gel was formed. The transparent titanium oxide gels were obtained by reducing hydrolysis and promoting polycondensation.

Titanium oxides have been widely used for pigment and opacifiers in paints,[1-3] make-up foundations in cosmetics,[4] and coatings of various substrates as a UV-absorbed,[5] photocatalytic,[6] antibacterial,[7] or light-induced amphiphilic[8] material. Most of titanium oxides are white because of the light scattering of particles. However, to make use of the color of substrates, both UV-absorbing power and transparency are required for the UV-absorption materials. So the transparent titanium oxide gel can open it's new application fields. A monolithic bulk gel has an advantage over a colloidal gel in reducing the light scattering. However, the preparation of polymer macromolecules and the monolithic bulk gel of titanium oxides is more difficult than that of their colloidal particles and colloidal gel. Doeuff et al.[9] have found that monolithic gels can never be prepared from the low-concentration (< 0.15 M) titanium alkoxide solution in ambient conditions even by introducing acetic acid. They found that the titanium alkoxide exhibits a low reactivity for gelation. We have previously reported that the "salt" catalysts, containing basic anions and acidic cations such as ammonium acetate, made it possible to form the monolithic gel from the low concentration of titanium tetra-n-butoxide solution (0.05 M) in several hours and were more effective for the polycondensation than conventional acid catalysts such as HCl, HNO_3 or CH_3COOH.[10,11] However, we have only obtained opaque gels by using ammonium acetate. The opacity was caused by the formation of stacks of sheet-like particles. Doeuff et al.[9] have observed that transparency of a monolithic gel is obtained from a higher concentration of tetra-n-butoxide solution (~ 0.8 M). More effective catalysts were required for the preparation of the transparent bulk gel from the low-concentration titanium alkoxide solution. And we found a new effective catalyst in promoting polycondensation.

In nitrogen atmosphere, 10 ml of the 1-butanol solution containing 5 mmol of tetra-n-butoxide with or without 12.5 mmol of 1,10-phenanthroline, and 15 ml of another 1-butanol solution containing 1.25 mmol of 1,10-phenanthroline hydrochloride, 12.5 mmol of n-butylamine and 12.5 mmol of water were prepared. The sol-gel reaction started when both the 1-butanol solutions were mixed to be a total of 25 ml of the solution (tetra-n-butoxide: 0.2 M, H_2O: 0.5 M and a *salt* catalyst: 0.05 M) in the optical glass cell (path length: 1 cm). The reaction temperature was kept at a constant 25 °C.

Figure 1a shows transmission curves for titanium oxide gels prepared with ammonium acetate as a catalysts. Transmittance was almost 0% in the whole range of wavelength. This opaque gel consisted of stacking sheet-like particles as shown in Figure 2a. These particles had a width of several micrometers. Because the particle width exceeded the wavelength of visible light, the light was scattered by particles, causing opacity of the gel. A yellowish gel prepared in the presence of 1,10-phenanthroline hydrochloride and n-butylamine as catalysts absorbed a UV band (< 350 nm) and was translucent to visible light (Figure 1b).

When 1,10-phenanthroline was further added (0.5 M), transmittance of the gel increased (80% at > 500 nm) as shown in Figure 1c. As shown in Figure 2b, the transparent gel had a spongy structure with ultrafine pores which had a diameter of several nanometers. Because the cell/pore size was smaller than the wavelength of visible light, the light passed through the gel without scattering. The amount of 1,10-phenanthroline bonding to titanium ion was evaluated by thermal analysis of dried gel. The sharp exothermic peak at ~520 °C increased in area with the addition of 1,10-phenanthroline. The peak may be due to the release of 1,10-phenanthroline bonding to titanium ion. By adding 1,10-phenanthroline, the coordination of 1,10-phenanthroline to titanium ion was promoted and thereby hydrolysis was reduced. This research suggest that reducing hydrolysis will probably be required for the preparation of the transparent gel. Changing the

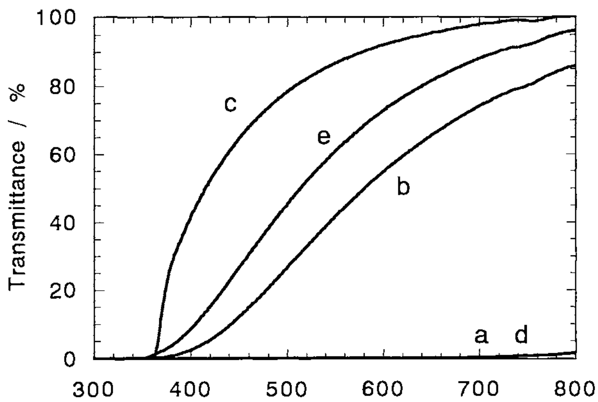

Figure 1. Transmission curves for titanium oxide gels. Curves a and d were overlapping each other. Preparation condition: Reactants were 0.2 M tetra-n-butoxide, and 0.5 M(a-c, e) or 1.0 M(d) H_2O. The catalyst in the sol-gel process was 0.05 M ammonium acetate(a), or 0.05 M(b-d) or 0.005 M(e) 1,10-phenanthroline hydrochloride with 0.5 M butylamine(b-e). 0.5 M 1,10-phenanthroline was further added(c-e).

molarity of water from 0.5 M to 1.0 M in the preparation, transmittance of the resulting gel decreased remarkably (Figure 1d). By increasing water, hydrolysis was promoted to form the opaque gel.

When the molarity of 1,10-phenanthroline hydrochloride was lowered from 0.05 M to 0.005 M in the preparation, transmittance of the resulting gel decreased (Figure 1e). The low concentration of the catalyst will probably accelerate polycondensation insufficiently for the preparation of the transparent gel. When either 1,10-phenanthroline hydrochloride or n-butylamine was used alone, a gelation was not observed. It is likely that not only 1,10-phenanthroline hydrochloride but also n-butylamine acts as a catalyst for polycondensation. We have reported that in the case of ammonium acetate, ammonium cation acts as an acid catalyst while acetate anion acts as a base catalyst.[10,11] In this system, 1,10-phenanthrolinium cation and n-butylamine should act as an acid catalyst and a base catalyst, respectively. Both reducing hydrolysis and promoting polycondensation should be required for the preparation of a transparent gel which has a low-dimensional structure such as a sponge. The low-dimensional structure with small cell/pore size was formed by the catalytic sol-gel process with 1,10-phenanthroline hydrochloride and n-butylamine to allow the light to pass through the gel.

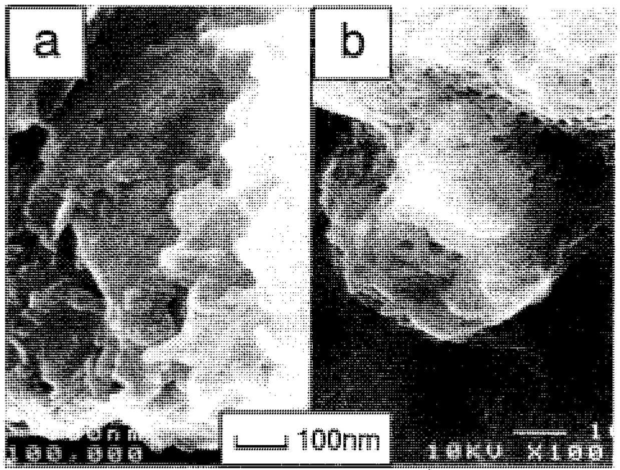

Figure 2. High resolution SEM images of titanium oxide gels. Preparaton conditions of a and b were described in the caption of Figure 1a and c, respectively.

References and Notes

1 G. Winter, *J. Oil Colour Chem. Assoc.*, **36**, 689 (1953).
2 E. S. Thiele and R. H. French, *J. Am. Ceram. Soc.*, **81**, 469 (1998).
3 R. W. Johnson, E. S. Thiele, and R. H. French, *Tappi J.*, **80**, 233 (1997).
4 R. G. Harry, in "Harry' s Cosmeticology," 7th ed, ed by J. B. Wikinson and R. J. Moor, Gorge Godwin, London (1982), Chap. 15, p. 231
5 T. Kyprianidou Leodidou, P. Margraf, W. Caseri, U. W. Suter, and P. Walther, *J. Polym. Adv. Tech.*, **8**, 505 (1997).
6 T. Inoue, A. Fujishima, S. Konishi, and K. Honda, *Nature*, **277**, 637 (1979).
7 T. Watanabe, A. Kitamura, E. Kojima, C. Nakayama, K. Hashimoto, and A. Fujishima, in "Photocatalytic Purification and Treatment of Water and Air," ed by D. E. Ollis and H. Al-Ekabi, Elsevier (1993), p. 747
8 R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigashi, and T. Watanabe, *Nature*, **388**, 431 (1997).
9 S. Doeuff, M. Henry, C. Sanchez, and J. Livage, *J. Non-Cryst. Solids*, **89**, 206 (1987).
10 Y. Murakami, T. Matsumoto K. Yahikozawa, and Y. Takasu, Jpn. Kokai Tokkyo Koho, JP 09-1001249
11 Y. Murakami, T. Matsumoto, and Y. Takasu, *J. Phys. Chem.*, submitted for publication.