# Photochromism of Titanium Oxide Gels Prepared by the Salt-Catalytic Sol-Gel Process

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Photochromism for the monolithic gel of titanium oxide prepared by the catalytic sol-gel process was observed. When hydrazine monohydrochloride was used as a catalyst, an intense blue color development was observed with the formation of $Ti^{3+}$ on the irradiation of UV light (< ca. 350 nm). The degree of coloration and the recovery time were strongly affected by a kind of salt catalysts although the color was independent. Presence of active salt catalysts in the gel was indispensable for color development.

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Colloidal titanium oxide particles dispersed in thin films such as polyvinyl alcohol or in an alcohol exhibited light-induced blue coloration.[1-6] The colored particles reversely bleached after the irradiation stopped. The coloration is attributable to the formation of colored species $Ti^{3+}$ via the reduction of $Ti^{4+}$ cation in a $TiO_2$ lattice with a photogenerated conduction-band electron. Scavenging of a photogenerated hole by the alcohol prevents it from recombining with the electron and facilitates the accumulation of electrons. The fading of the blue color is due to the oxidation of $Ti^{3+}$ with oxygen.

On the other hand, photochromism was hardly observed in bulky titanium oxide particles.[7-9] However, by using photoacoustic spectroscopy (PAS), the photochromic change which consisted of charge separation followed by recombination was observed.[10, 11] The colored species $Ti^{3+}$ was formed only on the inside of particles. Electrons are drifted into the bulk while holes are drifted to the surface according to the Shottky barrier theory.

Although photochromism has been widely observed for iron-doped rutile particles,[7-9, 12-15] the pinkish-brown coloration was not due to $Ti^{3+}$ but due to the $Fe^{2+}$□ color center. Clark and Broadhead[15] have demonstrated that the $Fe^{2+}$□ center trapped a photogenerated electron in the $TiO_2$ particles (□ signifies an iron-adjacent anion vacancy).

We have previously demonstrated that a salt catalyst effectively accelerates the polycondensation of titanium alkoxide in sol-gel process and allows the titanium alkoxide solution to transform into monolithic gel of titanium oxide.[16-18] The microstructure of titanium oxide gel was controlled by the kind of catalysts. The spongy structure of the transparent gel was prepared with 1,10-phenanthroline hydrochloride while the stacking sheet structure of the opaque gel was obtained with ammonium acetate.[17]

In this study, photochromism for the monolithic gel of titanium oxide prepared by the catalytic sol-gel process with a variety of catalysts was investigated concerning the degree of coloration and the recovery time.

In nitrogen atmosphere, 10 mL of the 1-butanol solution containing 5 mmol of titanium tetra-*n*-butoxide and 12.5 mmol of diethylene glycol (DEG), and 15 mL of another 1-butanol solution containing 0.025 mmol of a salt catalyst and 31.25 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 mol $dm^{-3}$, $H_2O$: 1.25 mol $dm^{-3}$ and a salt catalyst: 0.01 mol $dm^{-3}$) in the optical glass cell (path length: 1 cm). The reaction temperature was kept at 25 °C. The resultant gel was not dried. It has the same volume as the starting solution. After the gel was sufficiently formed, it was irradiated by the 150 W xenon lamp with a sharp cut filter.

Figure 1 shows transmission curves before and after the irradiation at $\lambda_{ex}$ for titanium oxide gels prepared with hydrazine monohydrochloride[18] as a catalyst. The deep lowering of transmittance was observed at $\lambda_{ex}$ > 300 nm with a blue color development, while a little change and no change were observed at $\lambda_{ex}$ > 350 and 420 nm, respectively. It suggests that this coloration is induced by the absorption in the range of below ca. 350 nm, which is assignable to a charge transfer band of titanium oxide. The color development occurred only at the irradiated surface of gel by 5-min irradiation ($\lambda_{ex}$ > 300 nm). Most of the UV light would absorbed at the surface. The $Ti^{3+}$ signal[11, 19-22] was observed in the ESR spectrum obtained only for colored gels. Colored species would be $Ti^{3+}$ formed by a photogenerated conduction-band electrons. This color development recovered (discolored) after the retention in the dark for 4 h. The discolored gel was recolored by irradiation.

Table 1 summarizes the photochromic behavior of titanium oxide gels prepared with a variety of salt catalysts. The degree

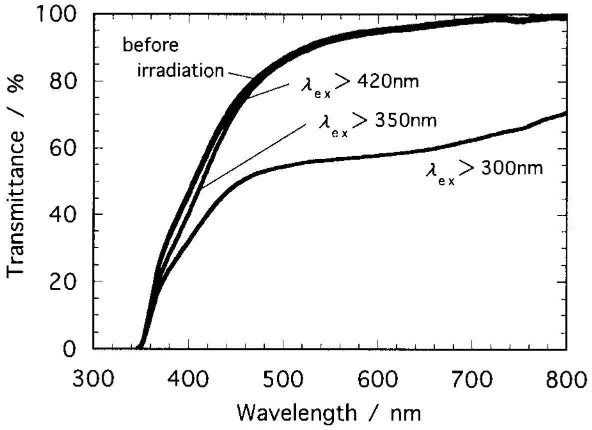

**Figure 1**. Transmission curves for titanium oxide gels before and after the irradiation for 5 min at $\lambda_{ex}$. Curves "before irradiation" and "$\lambda_{ex}$ > 420 nm" were overlapping each other. Ranges of $\lambda_{ex}$ are shown in this figure. $[Ti(OC_4H_9)_4]$ = 0.2 mol $dm^{-3}$, $[H_2O]$ = 1.25 mol $dm^{-3}$ and [DEG] = 0.5 mol $dm^{-3}$ in the precursor solution. The catalyst was 0.01 mol $dm^{-3}$ hydrazine monohydrochloride.

**Table 1.** Photochromic characteristics of titanium oxide gel prepared with salt catalysts

| | Before the Irradiation (Initial) | | After the Irradiation for 5 min at $\lambda_{ex} > 300$ nm | | |
|---|---|---|---|---|---|
| Salt Catalyst | Color and Transparency | $T_{700nm}$ / % | Coloration | $-\Delta T_{700nm}$ / %$^a$ | $t_{dis}$ / min$^b$ |
| Hydrazine Monohydrochloride | Yellowish, Transparent | 97 | Deep blue | 37 | 240 |
| 1-Benzyl-1-phenylhydrazine Hydrochloride | Yellowish, Transparent | 96 | Deep blue | 39 | 60 |
| Hydroxylamine Hydrochloride | Colorless, Transparent | 99 | Deep blue | 13 | 60 |
| Acetamidine Hydrochloride | White, Opaque | 18 | Deep blue | 4 | 90 |
| 1,10-Phenanthroline Hydrochloride | Yellowish, Transparent | 98 | No change | - | - |
| Ammonium Acetate | White, Opaque | 2 | No change | - | - |

$^a$ The decrease in transmittance of the gel just after the irradiation. $^b$ Retention time in the dark for discoloration.

of coloration of the gel prepared with 1-benzyl-1-phenylhydrazine hydrochloride was almost the same as that in the case of hydrazine monohydrochloride, but the recovery time was shorter. For the gel prepared with hydroxylamine hydrochloride, color development was not so remarkable. The opaque gel prepared with acetamidine hydrochloride[18] showed significant coloration in spite of small -$\Delta T$. On the other hand, no color change was observed for either the transparent gel prepared with 1,10-phenanthroline hydrochloride[17] or the opaque gel prepared with ammonium acetate.[16, 17]

Figure 2 shows changes in the solution viscosity during the sol-gel process which converts titanium butoxide into titanium oxide gels with each catalyst. Since titanium oxide growth is followed by the solution viscosity,[16, 18, 23, 24] the gel attained to the high viscosity when the catalyst used for the sol-gel process was active for titanium oxide growth. The catalyst used for the preparation of the photochromic gel is much more active for the titanium oxide growth than that used for the gel which exhibited no photochromism.

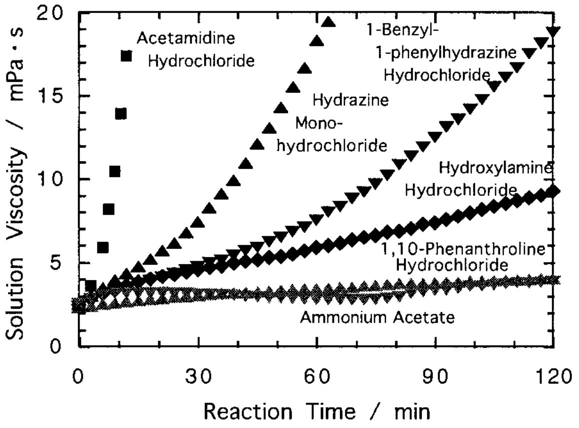

**Figure 2.** Time course of the solution viscosity and its dependence on the variety of the salt catalyst. $[Ti(OC_4H_9)_4]$ = 0.2 mol dm$^{-3}$, $[H_2O]$ = 1.25 mol dm$^{-3}$, [DEG] = 0.5 mol dm$^{-3}$ and [salt catalyst] = 0.01 mol dm$^{-3}$ in the precursor solution. Varieties of salt catalyst are shown in this figure.

The degree of coloration and the recovery time were strongly affected by the kind of salt catalysts although the color was indepedent. We have previously demonstrated that the microstructure of a resultant titanium oxide gel depended on the catalyst for the titanium oxide formation. However, the appearance of photochromism was independent of the transparency of the gel which affected its microstructure. The active salt catalyst located around Ti ions enhanced the formation of the color center, $Ti^{3+}$. Photochromism was not observed for a dried gel. The mobility of proton through the active salt catalyst[18] would be indispensable for color development. The titanium oxide gel with photochromism can be applied for light-regulating optical devices and photochemical sensors although further investigations are required for revealing the mechanism of the photochromism.

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