Preparation and Characterization of Dye-Doped Zirconia Gel Films from Zirconium Tetra-*n*-butoxide Stabilized with Diethanolamine or Acetoin

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Zirconia gel films were prepared by a dipping method from a 2-propanol solution of zirconium tetra-*n*-butoxide (ZTNB) stabilized with diethanolamine (DEA) and acetoin. In the case of the ZTNB–DEA system, crystallization to zirconia occurred at 480 °C, while in the case of the ZTNB–acetoin system it occured at 380 °C. The density of gel film prepared from the ZTNB–DEA system was higher than that from the ZTNB–acetoin system. Neutral acetoin could act as a good stabilizer for dye-doped ZTNB gel films. The photostability of dyes depended on the combination between dyes and stabilizers. DEA could act as an anti-oxidizing reagent and an electron donor to depress and accelerate the photo-decomposition of the dyes, respectively.

Much attention has been paid to the preparation and properties of inorganic-organic hybrids due to their applications as functional materials.[1,2] Since fluorescent dyes have been used as sensors and laser dyes, many papers on the preparation and photostability of dye-doped gel films and bulks have been reported.[3–10] The host matrices have been limited to silica or organically modified silicates (ORMOSILs). However, silicon alkoxides are easy to handle and the formed matrices are very stable against UV irradiation. Zirconia can also be expected to serve as stable host matrix for dyes, based on an optical study of Rhodamine 6G doped in zirconia.[11] However, compared with silicon alkoxides, because transition-metal alkoxides are usually too unstable to handle in air, some stabilizers or modifiers are required to stabilize them. Recently, we found that alkanolamines and α-hydroxyketones can very effectively stabilize the alkoxides of transition metals, including titanium and zirconium, to afford very stable solutions of them.[12–16] Using these solutions, very uniform gel films of the corresponding metal oxides could be dip-coated; also, very uniform metal oxide films were prepared by heating the gel films above 500 °C in air. As an extension of this study, we have examined the applicability of gel films obtained from the solutions as host matrices for various dyes. Since the properties of pure oxide films were already studied,[16] the properties of zirconia gel films, which were selected as host matrices of dyes; the behaviors of dyes encapsulated in the gel matrices are described in this paper. The ZTNB–DEA and -acetoin solution systems were selected for the dip-coating of zirconia oxide gel films.

Experimental

Instruments. The thickness and refractive index of films were measured by a Mizoziri Kogaku ellipsometer equipped with a Helium-Neon laser (632.8 nm). Thermogravimetric differential thermal analysis (TG-DTA) was performed with Shimadzu TGA-50 and DTA-50 instruments. UV-vis and fluorescence spectra were measured with Hitachi U-3500 and F-4500 spectrometers, respectively. Photo-irradiation was carried out with a 500-W super high-pressure mercury lamp (Ushio Denki Co., Ltd.) through a filter (Toshiba Glass UV-31, $\lambda > 310$ nm).

Materials. Coumarin 30, Rhodamine B, and acetoin were purchased from Tokyo Kasei Co., Ltd. Fluorescein was obtained from Katayama Chemicals Co., Ltd. Diethanolamine (DEA), tetraethyl orthosilicate (TEOS), concentrated hydrochloric acid, and 2-propanol were purchased from Wako Pure Chemical Industries. ZTNB was obtained from Mitsuwa's Pure Chemicals. 2-Propanol was distilled before use. Glass (Corning #7059) and quartz glass (Nippon silica glass) were defatted with acetone under sonication before a sol-gel coating process.

Preparation of Zirconia Gel Films. Zirconia gel films were prepared as shown in Fig. 1. 2-Propanol solution of ZTNB (1.6 cm^3) and either DEA (0.77 cm^3) or acetoin (1.4 cm^3) were stirred overnight at room temperature. When DEA was used, water (0.14 cm^3) was added to the mixture and stirred for another 24 h to prepare a homogeneous zirconia gel film. The volume of the sol was adjusted to 20 cm^3, corresponding to zirconium atom concentrations of 0.2 mol dm^{-3} in both of the sols. The gel films were prepared by a dipping method (withdrawing rate, 60 mm min^{-1}). The wet films were then dried and heated under an air atmosphere. In the case of dye-doped gel films, the films were heated at 110 °C for 10 min under an air atmosphere. When the concentration of zirconium atoms in the ZTNB–acetoin system was higher than 0.2 mol dm^{-3}, the gel films were opaque due to the formation of cracks in the film.

Preparation of Silica Gel Films. To a 2-propanol solution (65 cm^3) of TEOS (3.1 cm^3) were added concentrated hydrochloric acid (0.014 cm^3) and water (1.5 cm^3). The total volume of the solution was adjusted to 70 cm^3. The starting sol composition in TEOS, water, and concentrated hydrochloric acid was 1:6:0.01

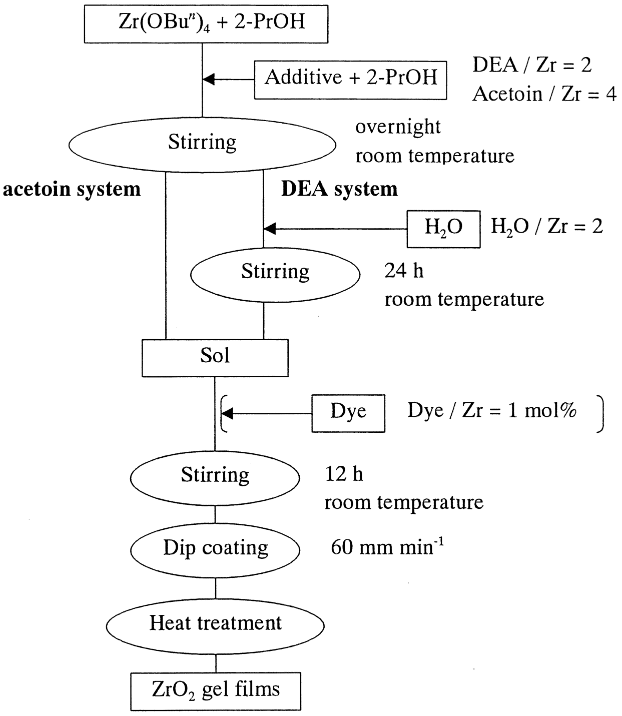

Fig. 1. Flowchart for the preparation of zirconia gel films.

molar ratio. The concentration of silicon atoms in the sol was 0.2 mol dm^{-3}. The sol was stirred overnight at room temperature. Then, a dye (Dye/Si = 1 mol%) was added to the sol and stirred for another overnight period at room temperature. The gel films were prepared by a dipping method (withdrawing rate, 60 mm min^{-1}) from the sol, which was then dried and heated under an air atmosphere.

Determination of Film Hardness. The film hardness was measured by a pencil method,[17] in which Mitsubishi Hi uni pencils (hardness: 6B–6H) were used.

Photostability Measurement of Gel Films. The dye-doped gel films were irradiated with a 500-W super high-pressure mercury lamp through a filter ($\lambda > 310$ nm) at room temperature under an air atmosphere. The sample was set up at the position (ca. 670 mm from the light source) where the photo-energy was 0.2 to 0.3 W cm^{-2}.

Results and Discussion

Formation and Properties of Zirconia Gel Films. TG-DTA thermograms of ZTNB-DEA and -acetoin gel powders are shown in Fig. 2. The sample powders were obtained by drying at 110 °C for 12 h. No change was observed in the ZTNB–DEA gel powder up to 300 °C. Then, an abrupt weight loss with large exothermic peaks was observed between 300 and 480 °C. Meanwhile, the ZTNB–acetoin gel powder showed a gradual weight loss, according to temperature rises between 120 and 450 °C, and two exothermic peaks were found at about 200 and 380 °C. The exothermic peaks observed at higher temperatures, 480 °C for ZTNB–DEA and 380 °C for ZTNB–acetoin powders, could be assigned to crystallization, which was confirmed by X-ray diffraction measurements. Above 500 °C, both the ZTNB–DEA and –acetoin gel films were completely converted to the pure crystalline oxide.

The effects of the heating temperature on the film thickness and the refractive indices of ZTNB-DEA and -acetoin gel films are shown in Fig. 3. With higher heating temperatures, the thickness of both the ZTNB–DEA and –acetoin gel films de-

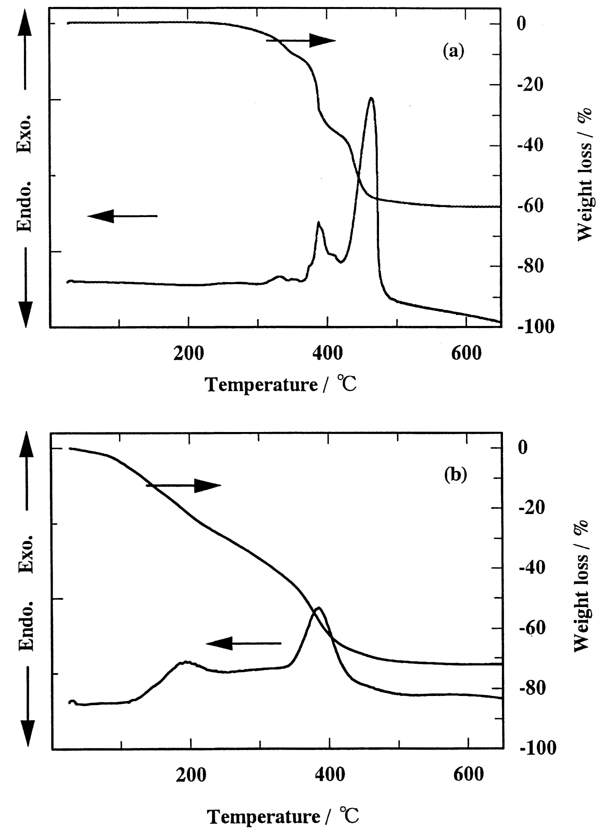

Fig. 2. TG–DTA curves of powders for (a) prepared from ZTNB–DEA system and (b) prepared from ZTNB–acetoin system. The powders (ca. 10 mg) were dried at 110 °C under air. Then, the powders were heated from room temperature to 800 °C at heating rate 5 °C min^{-1} in air.

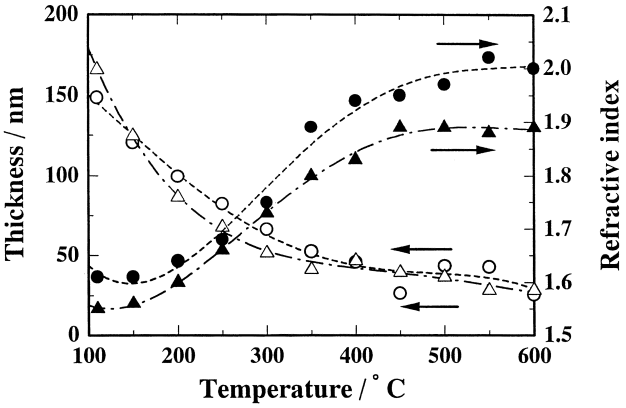

Fig. 3. Relationship among heating temperature, film thickness, and refractive index of zirconia gel films. ○: film thickness of ZTNB–DEA gel films; △: film thickness of ZTNB–acetoin gel films; ●: refractive indices of ZTNB–DEA gel films; ▲: refractive index of ZTNB–acetoin gel films. These films were dried at 110 °C for 10 min and then heated for 30 min.

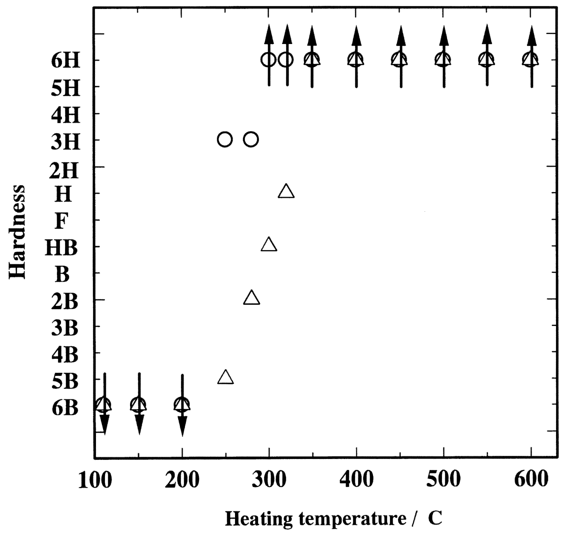

Fig. 4. Hardness of gel films. ○: ZTNB–DEA gel films; △: ZTNB–acetoin gel films. The up and down arrows show hardness of higher than 6H and lower than 6B, respectively.

creased, and became constant above 500 °C at 25 to 40 nm. The refractive indices of the gel films changed between 200 and 400 °C, and became constant above 450 °C, being 2.00 and 1.89 for the ZTNB–DEA and –acetoin systems, respectively.

Figure 4 shows the hardness of the gel films. As can be clearly seen, the ZTNB–DEA gel film was harder than the ZTNB–acetoin gel film in the temperature range 250 to 350 °C. The film was too soft below 200 °C and too hard above 350 °C to measure the hardness by the pencil method, respectively.

The porosities (p) of crystalline zirconia thin films can be calculated using the Lorentz–Lorenz equation,[18]

$$1-p = (n_f^2-1)\,(n_c^2+2)\,/\,(n_f^2+2)\,(n_c^2-1),$$

where n_f and n_c represent the refractive indices of the film and zirconia crystal, respectively. Though the crystal structure of zirconia formed around 500 °C was found to be a metastable cubic form, the n_c value was assumed to be an average of the refractive indices (2.17) of all directions for monoclinic zirconia,[19] and the porosities of zirconia gel films obtained from the ZTNB–DEA and –acetoin systems were calculated to be ca. 8 and 16%, respectively.

Thus, Figs. 3 and 4 and the calculated porosities suggest that the density of ZTNB–DEA gel film is higher than that of ZTNB–acetoin gel films. This can be ascribed to a more abrupt weight loss with larger exothermic peaks of the ZTNB–DEA system than that of the ZTNB–acetoin system. The density becomes higher as the crystallization rate increases. The difference in the density may also be attributed to the ratio of the volumes of the ligands in a dried gel film. The ratio in the ZTNB–DEA system may be less than that in the ZTNB–acetoin system, because the molar ratios of DEA/Zr and acetoin/Zr are 2 and 4, respectively.

Photostability of Dyes in Zirconia Gel Films. The fluorescent dyes used in this study are shown in Fig. 5. All of them are typical fluorescent dyes. To prepare the dye-doped gel films, the dyes were added to the sols, stirred, dip-coated, and dried.

Figure 6 shows the relationship between the heating temperature and the absorbance of fluorescein (mp, 320 °C; decomposition temperature (T_d), 480 °C) in the ZTNB–DEA, ZTNB–acetoin, and TEOS–hydrochloric acid gel films. As can be seen in all the matrices, the absorbance decreased as the heating temperature was increased. However, a rather strong absorbance was observed in the TEOS–hydrochloric acid gel film above 350 °C. In contrast, the absorbances in the ZTNB–DEA and –acetoin gel films were very small above 350 °C. Therefore, dye-doped gel films were prepared by heating at 110 °C for 10 min. This indicates that the sol modifiers used may affect the dye stability.

Table 1 shows the properties of dyes in the matrices. All of the gel films were transparent and homogeneous. The absorption maxima (λ_{max}) of gel films changed with the kinds of matrices. The λ_{max} of coumarin 30 in the TEOS–hydrochloric acid matrix showed a bathochromic shift compared to that in 2-propanol. Coumarins consist of an intramolecular charge-transfer chromophoric system.[20] The lactone and arylamino segments act as electron-withdrawing and -donating moieties, respectively. The imidazolyl nitrogen at the 3-position in coumarin 30 can be protonated by hydrochloric acid in the silica matrix, causing a bathochromic shift. In the case of Rhodamine B, no such remarkable shift of λ_{max} was observed. The λ_{max} of fluorescein in the ZTNB–DEA matrix showed a bathochromic shift compared to that in 2-propanol due to the dissociation of a hydroxy group by DEA in the matrix.

The dye-doped gel films were irradiated with a 500-W super high-pressure mercury lamp. A typical change in the absorption band during photo-irradiation is shown in Fig. 7. The absorbance of the film decreased in proportion to the irradiation time, suggesting that the dye was decomposed by photo-irradiation.

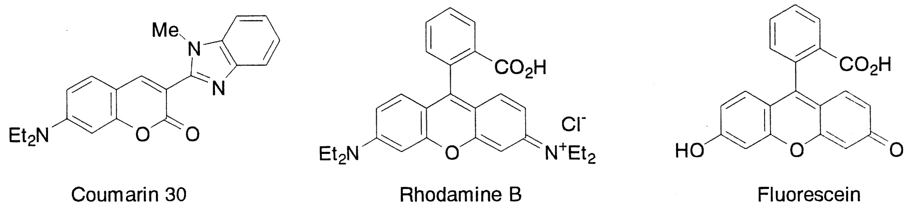

Fig. 5. Structures of fluorescent dyes.

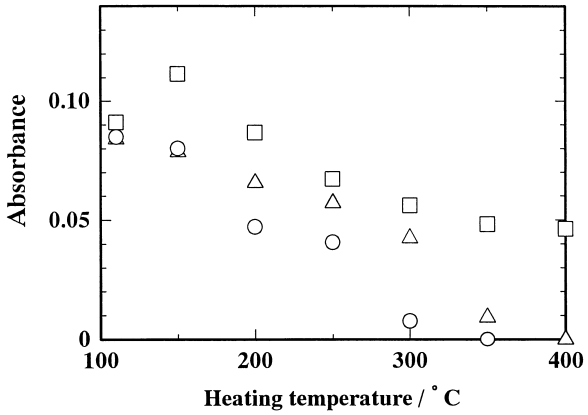

Fig. 6. Relationship between absorbance of fluorescein at λ_{max} doped in gel matrices and heating temperature. ○: ZTNB–DEA gel films; △: ZTNB–acetoin gel films; □: TEOS–hydrochloric acid gel films prepared from Si concentration of 0.8 mol dm^{-3} sol. The gel films were heated for 30 min.

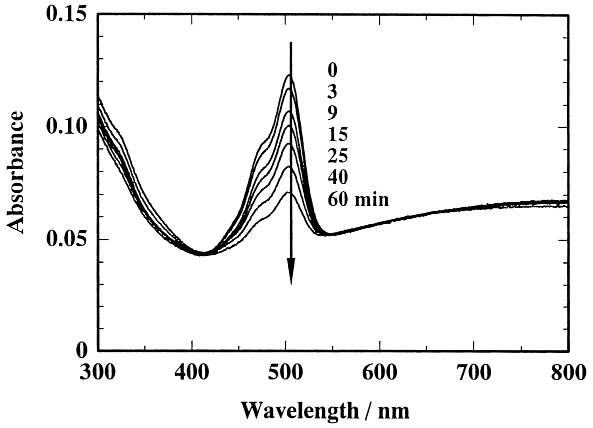

Fig. 7. Time dependence of absorption spectra of fluorescein doped in ZTNB–DEA gel film under photo-irradiation.

It is of interest to compare the photostability of dyes in different matrices. In order to evaluate the stability, two parameters, a first-order rate constant (k) in the initial stage and a remaining ratio of dyes after 30 min photo-irradiation (A_{30}/A_0), where A_{30} and A_0 represent the absorbance after 30 min and before irradiation respectively, were used. The relationship between the absorbance of fluorescein and the irradiated time is shown in Fig. 8. The first-order rate plots gave a convex curve rather than a straight line. However, by using the linear relationship in the initial stage, k was calculated to be 4.3×10^{-4} s^{-1}. The A_{30}/A_0 value was calculated to be 0.55. The k and A_{30}/A_0 values of the other dyes in the different matrices were also calculated in a similar way. The results are summarized in Table 1. In the case of coumarin 30, the k value decreased in the order of the matrices: TEOS–hydrochloric acid > ZTNB–acetoin > ZTNB–DEA. The A_{30}/A_0 value was in the order ZTNB–DEA > ZTNB–acetoin > TEOS–hydrochloric acid. Thus, these parameters can be used to evaluate the relative photostability of dyes in matrices.

Coumarin 30 doped in the ZTNB–DEA gel films was most stable among the combination of dyes and matrices examined. The oxidative degradation of 7-diethylamino-4-methylcoumarin by photo-irradiation under an air atmosphere has been reported.[19] The stability of coumarin 30 in the ZTNB–DEA matrix may be ascribed to residual DEA, which can act as an anti-oxidizing reagent. In contrast, Rhodamine B doped in the ZTNB–DEA matrix was very unstable. This would be attributed to a single-electron-transfer from residual DEA to Rhodamine B forming a 9-xanthyl radical followed by decomposition during photo-irradiation.[20] The photostability of fluorescein in the ZTNB–DEA matrix was similar to that in the ZTNB–acetoin matrix.

Thus, since DEA can act both as an anti-oxidizing reagent and an electron donor, the photostability of dyes doped in the ZTNB–DEA matrix depends on the dye structures. The photo-

Table 1. Properties of Dyes in Matrices

Dye	Matrix	λ_{max}/nm	F_{max}/nm	$k/10^{-4}$ s^{-1}	A_{30}/A_0
Coumarin 30	ZTNB–DEA	420	488	3.4	0.73
	ZTNB–acetoin	410	497	7.3	0.51
	TEOS–HCl	455	513	11	0.30
	2-PrOH	410	476	—[a]	—[a]
Phodamine B	ZTNB–DEA	553	577	12	0.38
	ZTNB–acetoin	552	588	4.9	0.53
	TEOS–HCl	557	587	4.4	0.55
	2-PrOH	550	598	—[a]	—[a]
Fluorescein	ZTNB–DEA	512	544	4.3	0.55
	ZTNB–acetoin	485	522	4.2	0.57
	TEOS–HCl	458	520	—[b]	—[b]
	2-PrOH	487	519	—[c]	—[c]

a) Since the solution abruptly discolored after an introduction period by photo-irradiation, the value was not calculated. b) The absorbance was too small to measure the photo-stability. c) Since the absorption maximum shifted by photo-irradiation, the k value was not calculated.

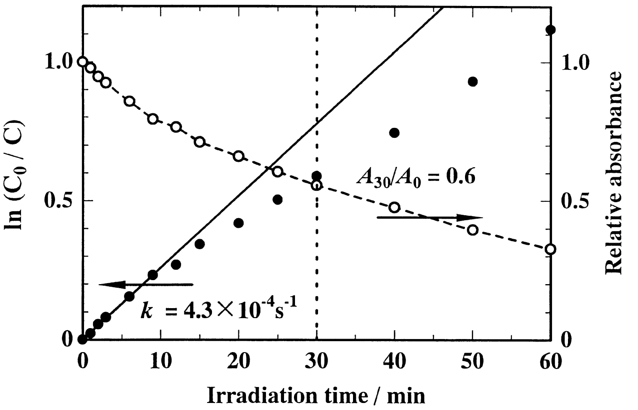

Fig. 8. Calculation of two parameters for photostability of fluorescein doped in ZTNB–DEA matrix. ○: change in relative absorbance; ●: adaptation to first-order rate kinetics.

decomposition of dyes, which can accept an electron and form active intermediates, such as triaryl and xanthyl radicals, can be accelerated in the presence of DEA. However, the photostability of dyes which can not accept an electron and can not produce active species is improved in the ZTNB–DEA system. Coumarin 30 in a ZTNB–DEA matrix is such a case, being much more stable than that in the TEOS–hydrochloric acid matrix.

Conclusions

The crystallization temperature of the ZTNB–DEA system was higher than that of the ZTNB–acetoin system. The density of gel film prepared from the ZTNB–DEA system was higher than that from the ZTNB–acetoin system. The photostability of dyes depended on the combination between dyes and stabilizers. DEA could act as an anti-oxidizing reagent and an electron donor to depress and accelerate the photo-decomposition of dyes, respectively. The photostability of coumarin 30, which can not accept an electron and can not produce active species, was improved in the ZTNB–DEA matrix.

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