CHEMISTRY LETTERS, pp. 1029-1032, 1994.

The Characteristics of the Fluorescence Spectra of Rhodamine B Molecules Doped in Si-Ti Binary Oxide System by the Sol-Gel Method

Nobuaki NEGISHI, Hiromi YAMASHITA, and Masakazu ANPO*
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Gakuen-cho 1-1, Sakai, Osaka 593

The characteristics of the fluorescence spectra of Rhodamine B (RhB) doped in Si-Ti binary oxide by the sol-gel method were measured as a function of Ti-content in the binary oxides. The RhB fluorescence in the Si-Ti binary oxide was only from the excited state of the monomer when the Ti-content in the Si-Ti binary oxide was low. On the oter hand, the RhB dimer fluorescence was observed when the Ti-content in the Si-Ti binary oxide was high.

The fluorescence spectra of luminescent dye molecules adsorbed on solid surfaces provide useful information not only on the electronically excited states but also on the chemical properties of solid surfaces. Rhodamine B (RhB) molecules are often used as probe molecules because of various unique properties such as concentration dependence in the fluorescence yield1) and changes in its molecular structure with the environmental polarity.2) It is especially known that the fluorescence yield of RhB is drastically decreased by their dimerization,1) therefore, the dimerization of RhB molecules should be avoided to use a dye laser medium.3) On the other hand, solid matrices prepared by the sol-gel method are potentially useful for optical functional materials.4) Dye molecules doped in binary oxide matrices by the sol-gel method can be expected to have various optical functions, however, the studies on their behavior have not yet been fully carried out.5) In the present study, the mechanism of the structural transformation of RhB molecules doped in the Si-Ti binary oxide systems has been investigated by measuring the fluorescence spectra of RhB during the sol to gel to xerogel transition and the changes in their structure as a function of the Ti-content in the binary oxides.

The starting reagent was a mixture of tetraethoxysilane (TEOS), tetra-*i*-propoxy titanium (TPOT), and a RhB/ethanol solution (1×10^{-4} M). Three kinds of mixtures were used, TEOS:TPOT=99:1 (system I), 50:50 (system II), and 10:90 (system III). The fluorescence spectra were recorded on a Shimadzu RF-5000 spectrofluorophotometer. Observation of the fluorescence decay curves was carried out using a Hamamatsu C-4334 streak scope with a N_2 dye laser.

Figure 1 shows the changes in the fluorescence spectra of RhB included in the system I during the sol to gel to xerogel transitions. The peak of the fluorescence spectra of the starting solution at 567 nm is attributed to the presence of the zwitterion form of RhB (Z) in neutral solutions.[2)] The intensity of the fluorescence spectra of RhB increased about 2 times during the sol to gel transitions, and slight spectral shift from 567 nm to 577 nm was observed during the gel to xerogel transition of system I.[2)] These results suggest the following: 1) Z is in equilibrium with the non-fluorescent lactone form of RhB (L) in the starting mixture solution; 2) this Z$\rightleftharpoons$L equilibrium changes to the equilibrium between Z and cation form of RhB (C) as formation of TiOH after the gelation; 3) C is generated in the xerogel stage by their interaction with the TiOH sites on the gel surfaces after the evaporation of the solvent.

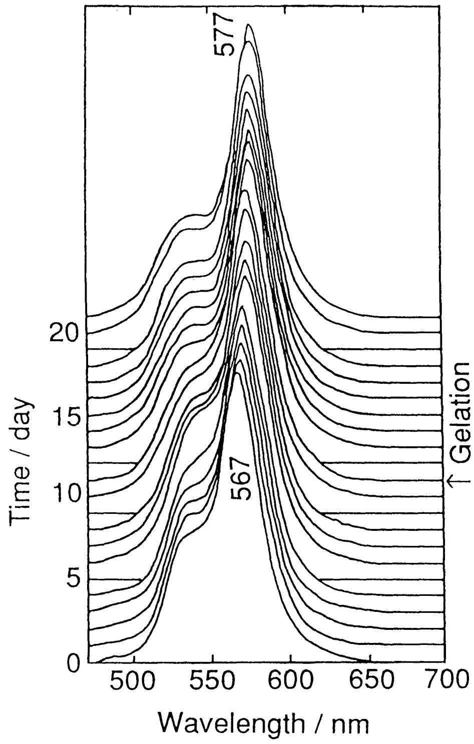

Fig. 1. The changes in the fluorescence spectra of RhB (normalized) in the system I (Si:Ti=99:1) during the transition of the system from sol to gel to xerogel. Excitation wavelength is 470 nm.

Figure 2 shows the changes in the fluorescence spectra of RhB included in the system II during the sol to gel to xerogel transitions. The fluorescence band of RhB was observed at 567 nm in the starting solution and shifted to 576 nm after gelation in a similar manner as observed in the system I. However, the fluorescence intensity of the system II in the xerogel stage was lower than that of the system I (ca. 89 %). This result suggests the formation of RhB dimer in the system II.

Figure 3 shows the changes in the fluorescence spectra of RhB included in the system III during the sol to gel to xerogel transition. The fluorescence band was observed at 568 nm in the starting solution. However, the RhB fluorescence band shifted to 595 nm in the xerogel stage. It is known that the RhB dimer formed on solid surfaces exhibits a fluorescence spectrum different from that of an aqueous system. Kemniz et al. have reported that the fluorescence band at 595 nm is identified as a typical RhB dimer species generated onto the solid surface as a monolayer.[6)] The fluorescence intensity of system III in the xerogel stage was lower than that of the system I (ca. 42 %)

Figure 4 shows the fluorescence decay curve of RhB in the systems I, II, and III. As shown in Fig. 4-A, the decay curve in the system I was a single exponential form with a lifetime of τ_1=3.33 ns, indicating that the RhB dimer was scarcely formed.[5,7)] This result agrees with that obtained from the fluorescence spectra in Fig. 1. On the other hand, as

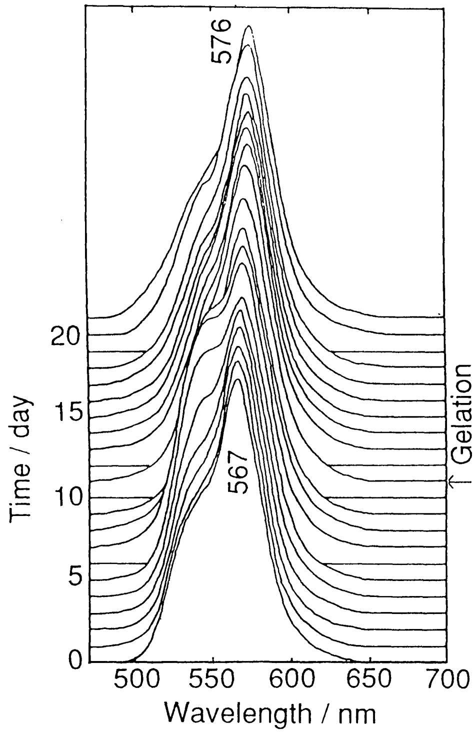

Fig. 2. The changes in the fluorescence spectra of RhB (normalized) in the system II (Si:Ti=50:50) during the transition of the systems from sol to gel to xerogel. Excitation wavelength is 470 nm.

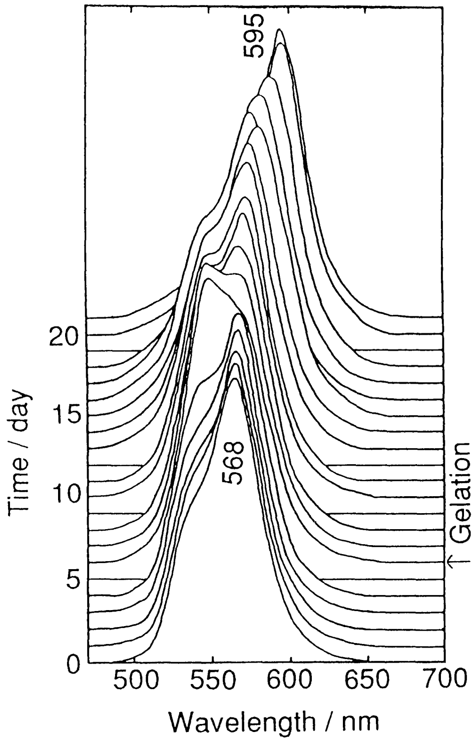

Fig. 3. The changes in the fluorescence spectra of RhB (normalized) in the system III (Si:Ti=10:90) during the transition of the systems from sol to gel to xerogel. Excitation wavelength is 470 nm.

shown in Fig. 4-B, the decay curve of RhB in the system II was a double exponential form with a lifetime of τ_1=1.18 ns and τ_2=4.25 ns. As shown in Fig. 4-C, the decay curve of RhB in the system III was the same double exponential form as that of the system II. The short lifetime species can be assigned to the RhB dimer, and the species with long lifetime can be assigned to the RhB monomer.[5-8] These results show that two types of RhB forms exist in the system with a high Ti content, but one form exists in the system with a lower Ti-content.

In the systems I and II, C is formed by the interaction between Z and H^+ supplied from TiOH groups on the gel surfaces ($Z+H^+ \rightarrow C$). In the system I, isolated TiOH sites on the gel surfaces can make the RhB molecule as a monomer. In the system II, although the Ti content was large enough to form TiO_2 particles, the gel kept its glass-like structure, indicating that these TiO_2 particles were capsulated in the pore of the gel. Therefore, it is considered that the RhB monomer exists in the system II by the interaction with TiOH sites on the gel surfaces, while the RhB dimer exists by the adsorption onto the TiO_2 particles.[9] The weak fluorescence band of the RhB dimer can not be observed in Fig. 2 but the strong fluorescence band of the RhB monomer is observed in spite of the existence of both RhB monomer and dimer in the system II. The gel of the system III is no longer in the glass-like structure but in powder form, indicating that the aggregation of TiO_2 particles proceeded considerably. For lack of isolated TiOH sites, RhB molecules may aggregate on the TiO_2 particles in the system III to form dimer species as shown in Fig. 3.

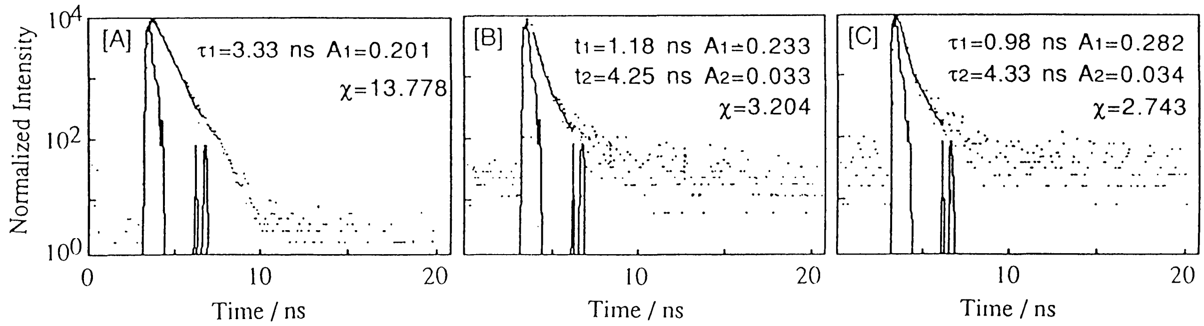

Fig. 4. The fluorescence decay curves of the RhB doped in the Si-Ti binary oxide matrices. [A]: system I (Si:Ti=99:1), [B]: system II (Si:Ti=50:50), [C]: system III (Si:Ti=10:90).

In summary, the adsorption mechanism of RhB molecules depends on the types of adsorption surface sites. RhB molecules exist as monomers in the system I. RhB monomers and dimers exist in the systems II and III, the dimer is the main species in the system III.

References

1) J. E. Selwyn and J. I. Steinfeld, *J. Phys. Chem.*, **76**, 762 (1972).
2) D. A. Hinckley, D. G. Seybold, and D. P. Borris, *Spectrochimica Acta*, **42A**, 747 (1986); D. A. Hinckley and D. G. Seybold, *ibid.*, **44**, 1053 (1989); T. L. Chang and H. C. Cheung, *J. Phys. Chem.*, **96**, 4874 (1992); M. Barra, J. J. Cosa, and R. H. Rossi, *J. Org. Chem.*, **55**, 5850 (1990).
3) F. Wakai, Y. Kodama, and S. Sakaguchi, *J. Am. Ceram. Soc.*, **73**, 457 (1990); A. Makishima and T. Tani, *J. Am. Ceram. Soc.*, **69**, C-72 (1986).
4) N. Negishi, M. Matsuoka, H. Yamashita, and M. Anpo, *J. Phys. Chem.*, **97**, 5211 (1993).
5) D. Avnir, V. R. Kaufman, and R. Reisfeld, *J. Non-Cryst. Solids*, **74**, 395 (1985); J. M. McKiernan, S. A. Yamanaka, B. Dunn, and J. I. Zink, *J. Phys. Chem.*, **94**, 5652 (1990).
6) K. Kemniz, N. Tamai, I. Yamazaki, N. Nakashima, and K. Yoshihara, *J. Phys. Chem.*, **90**, 5094 (1986).
7) H. Böttcher, O. Hertz, and M. A. Fox, *Chem. Phys. Lett.*, **160**, 121 (1989).
8) Y. Liang and A. M. P. Goncalves, *J. Phys. Chem.*, **89**, 3290 (1985).
9) N. Negishi, T. Fujii, and M. Anpo, *Langmuir*, **9**, 3320 (1993).

(Received February 1, 1994)