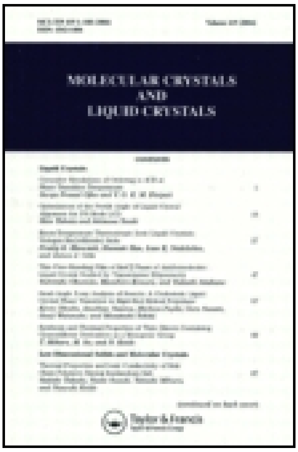

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Organic Dye-Doped Silica Films by the Liquid Phase Deposition Method as Potential New Hybrid Materials for Photonics

Toshihiko Nagamura [a] & Hisahiro Shimizu [a]

[a] Crystalline Films Laboratory, Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu, 432, JAPAN

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ORGANIC DYE-DOPED SILICA FILMS BY THE LIQUID PHASE DEPOSITION METHOD AS POTENTIAL NEW HYBRID MATERIALS FOR PHOTONICS

TOSHIHIKO NAGAMURA AND HISAHIRO SHIMIZU
Crystalline Films Laboratory, Research Institute of Electronics,
Shizuoka University, 3-5-1 Johoku, Hamamatsu 432, JAPAN.

Abstract Silica films doped with malachite green (MG) or uranine (UR) were deposited on the surface of a glass slide at 35°C from saturated hydrofluorosilicic acid solution containing these dyes. The steady fluorescence of MG was observed in silica films, which was absent in aqueous solutions. The fluorescence lifetime of MG in silica films was about 60 times longer than that in aqueous solutions. No absorption changes of MG-doped silica films by the LPD method were observed after storing 24 h in 25% ammonia solution, while those prepared by the sol-gel method showed changes immediately after immersion. The absorption and fluorescence spectra varied slowly by the heat treatment and by the immersion in hydrochloric solutions, indicating the deprotonation and protonation of MG. The delayed fluorescence of UR was observed in silica films. All these results indicated organic dyes were fixed rigidly in silica films prepared by the present LPD method.

INTRODUCTION

Organic compounds have attracted much interest in view of their potential applicability to future electronics and photonics. As a few examples we have reported novel photochromism (photoinduced electrochromism) in microcrystals, Langmuir-Blodgett (LB) films, and polymer films which occurred in less than 20 ps and was due only to the photoinduced electron transfer reaction via the excited state of specific ion-pair charge-transfer (IPCT) complexes[1-15]. We have also achieved amplified fluorescence quenching in LB films, molecular control of photoelectric responses in LB films, optical control of second order nonlinear optical responses in LB films and microcrystals[16-19].

In order to make full use of superior functionalities of organic molecules for a long period, we will have to develop new robust yet optically transparent microenvironments around organic molecules. The fixation of organic compounds into inorganic materials such as silica will be one of the most promising approaches especially in photonic applications. The sol-gel method is very popular in preparing silica thin films containing organic dyes and has contributed a great deal to increase the stability and the physical properties of organic compounds. But there remain some problems such as micro pores, less etching resistance, organic impurities, or a heating process. Recently the liquid phase deposition (LPD) method was developed as a new means to prepare silica films with highly dense structure and very low impurities near room temperature[20]. This method has been applied to dope and fix various organic molecules into silica films[21,22]. In the present paper the fixation of some organic dyes into silica by this method and the spectroscopic characterization will be reported in search for new hybrid materials for future photonics.

EXPERIMENTAL

Silica films doped with malachite green oxalate (MG) or uranine (UR) were deposited on the surface of a glass slide at 35°C by immersing it for appropriate times (ca. 16 h) in hydrofluorosilicic acid solution, which contained organic dye molecules and were supersaturated with silica gel. The procedure is summarized in Fig. 1, where aluminium was dissolved to shift following equilibria to the right side (formation of silica).

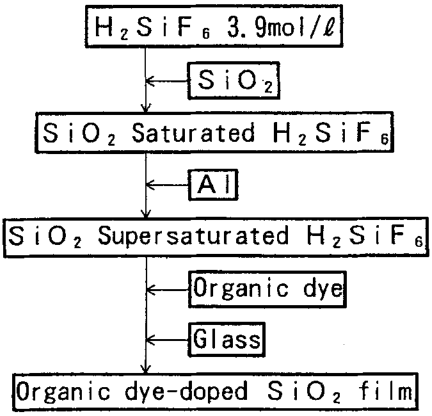

Fig. 1 A schematic representation of the LPD process for deposition of silica films.

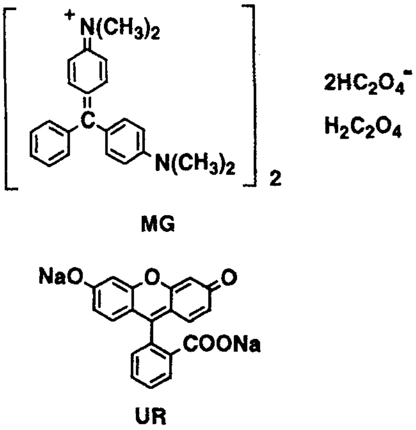

Fig. 2 The structure of MG and UR.

$$H_2SiF_6 + 2H_2O \rightleftharpoons SiO_2 + 6HF \quad (1)$$

$$4HF + 4H_2O + Al^{3+} \rightleftharpoons AlF_4^- + 4H_3O^+ \quad (2)$$

The structures of organic dyes employed in the present experiment are shown in Fig. 2. These films were characterized by absorption and fluorescence spectroscopies, and fluorescence lifetime measurements. The fluorescence lifetime was measured with a Hamamatsu C4334 streak scope upon excitation with a dye laser (420 nm) pumped by a nitrogen laser. The decay of long-lived emission of UR in a silica film was measured with a digital memory using an Ar^+ laser (457.9 nm) as a light source. The anisotropy ratio **r** of fluorescence was determined by $(I_\parallel - I_\perp)/(I_\parallel + 2I_\perp)$, where $I_\parallel$ and $I_\perp$ are the parallel and perpendicular component of fluorescence intensity. Spectral changes by heat treatment and by immersion in ammonia or in hydrochloric acid solutions were also studied.

RESULTS AND DISCUSSION

The absorption spectra of MG in a thin silica film prepared by the LPD method (A) from a 0.1 mM solution in saturated hydrofluorosilicic acid and that of a 1μM aqueous blue solution (B) are shown in Fig. 3. MG-doped silica films were green and the absorption peak at 455 nm increased as shown in Fig. 3. It was attributed to the protonation of MG

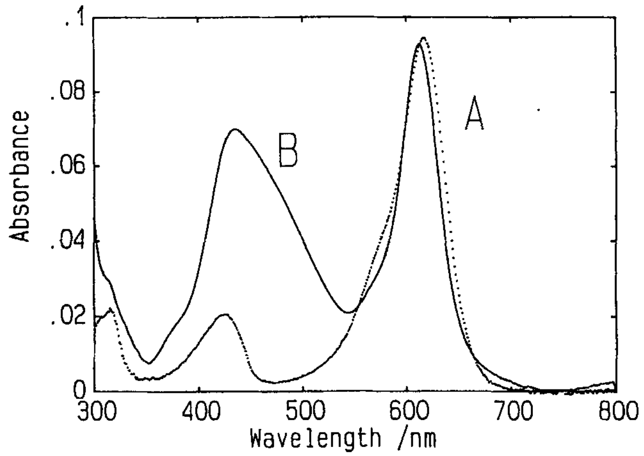

Fig. 3 The absorption spectra of MG in a silica film prepared by the LPD method (A) from a 0.1 mM solution in saturated hydrofluorosilicic acid and that in a 1μM aqueous blue solution (B).

in saturated hydrofluorosilicic acid solution for the LPD process from comparison of Fig. 3 with the pH dependences of absorption spectra of MG in aqueous solutions shown in Fig. 4. Similar protonation was also observed in the case of UR as mentioned below. The gradual increase of absorbance at 613 nm and concomitant decrease at 460 nm were observed during heat treatment of a MG-doped silica film at 50 °C. The absorption spectrum after heat treatment for 214 h at 50 °C returned to that of an aqueous solution as shown in Fig. 3(B). Immersion of this heat-treated silica in 1M hydrochloric acid solution (pH 0) gradually caused opposite spectral changes and reverted after 24 h the absorption spectrum before heat treatment. The spectral changes during heat treatment and immersion in acidic solutions corresponded to those in Fig. 4. These results can thus be explained by the thermally activated slow deprotonation and subsequent protonation of MG doped in silica films. Recently it was reported that MG-doped silica films prepared by the sol-gel method showed considerable changes of absorption and fluorescence spectra after immersing in 25% ammonia solution[23]. The present MG-doped silica films by the LPD method showed completely no changes after immersion for 24 h in a 25% ammonia solution. This results clearly indicates that MG-doped silica films have much more dense structure than those by the sol-gel method as reported by the etching resistance[21]. Protons can pass through our silica films, but hydroxide ions cannot.

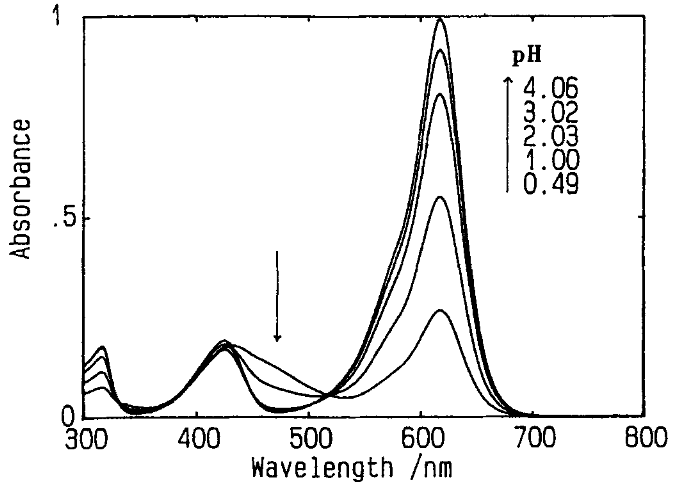

Fig. 4 The pH dependences of absorption spectra of MG in aqueous solutions.

The steady fluorescence of MG was observed in silica films at room temperature, which was absent in aqueous solutions due to the extremely rapid deactivation by rotation of phenyl rings[24]. The fluorescence of MG in silica films showed a single exponential decay with a lifetime of 134 ps, which was about 60 times longer than that in aqueous solutions[24]. This result indicated MG molecules were held so rigidly that rapid rotation of phenyl ring around C-C bonds was almost prohibited.

The absorption spectra of UR in silica films, abbreviated to UR-A and UR-B, prepared from 53 μM and 349 μM solution, respectively, in saturated hydrofluorosilicic acid showed a peak at 437 nm, which indicated the protonation of UR. The fluorescence spectra of UR-A showed a peak at 460 nm, while UR-B showed a peak at 500 nm and a shoulder at about 460 nm. These fluorescence spectra were similar to those in hydrochloric solutions at corresponding concentrations. The peak at 460 nm was attributed to the monomer fluorescence and that at 500 nm to the aggregates. The fluorescence decay was single exponential for the UR-A sample with a lifetime of 2.5 ns equivalent to that in dilute aqueous solutions. The UR-B sample showed double exponential decay with lifetimes of 488 ps (52%) and 2.8 ns (48%). The anisotropy ratio of fluorescence of UR-A and UR-B were 0.38 and 0.24, respectively. The former value is close to the value (0.4) expected for chromophores randomly dispersed and rigidly fixed. These results indicated the interactions of excited UR molecules both in solutions and silica films at higher concentration and that UR molecules were fixed in silica films in almost the same microenvironments as in solutions.

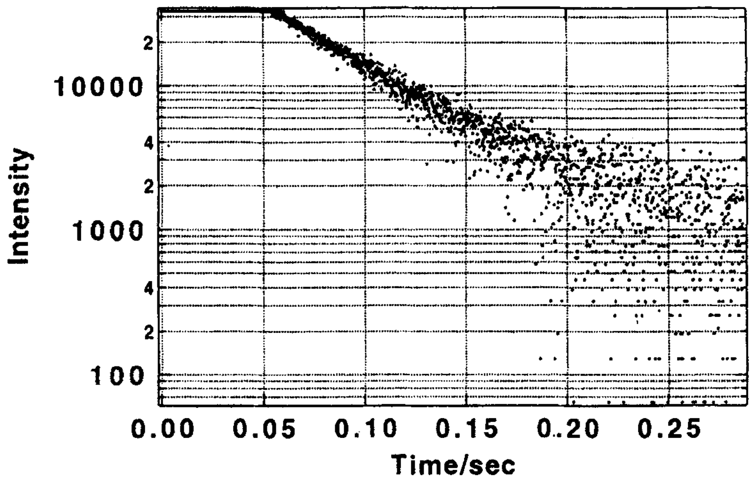

Fig. 5 A logarithmic plot of the decay of long-lived emission of UR in a silica film.

Fairly strong and long-lived emission of UR was observed in silica films, which could be easily seen by naked eyes. The decay was single exponential as shown in Fig. 5 with the lifetime of 51 ms at room temperature. The observed emission could be attributed to the delayed fluorescence or phosphorescence of UR rigidly fixed in silica matrices. This is another indication that the LPD method is useful to fix organic dye molecules in silica films rigidly and homogeneously dispersed. Investigations are under way to study the specific properties of organic dye-doped silica films and to apply them to photonics.

CONCLUSION

The present results indicated that the LPD method is very useful to dope and fix organic dye molecules in silica films rigidly and homogeneously. The deactivation of excited dye molecules by various nonradiative processes can be considerably suppressed in silica films prepared by this method, which will contribute to open new physics and applications of organic molecules. The present method will also increase a long time stability of organic dyes against oxidation, moisture, and other causes.

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