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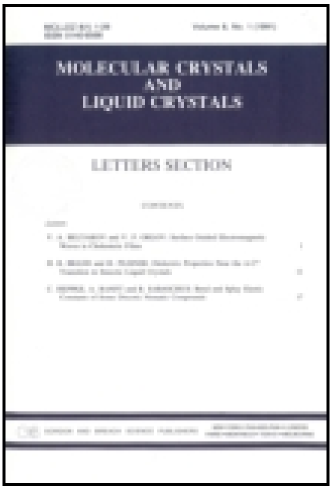

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# Improved Photoluminescence Lifetime of Organic Emissive Materials Embedded in Organic-Inorganic Hybrid Thin Films Fabricated by Sol-Gel Method Using Tetraethoxysilane

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*We fabricated organic-inorganic hybrid films by a sol-gel method using Tetraethoxysilane (TEOS). It is found that water-soluble organic emissive materials should be used, because water must be added to TEOS for a sol-gel reaction. The acid catalyst is better than the base catalyst when TEOS is used. The organic-inorganic hybrid films reveal a fine antioxidant effect, because most of the organic emissive materials are surrounded by* $SiO_2$*. This means that hybrid films have fine resistance to moisture and an antioxidant effect. Consequently, they lead to a strong sealing effect, resulting in the long operation lifetime of photoluminescence (PL) emissions.*

**Keywords** Organic-inorganic hybrid films; sol-gel; TEOS; photoluminescence

## 1. Introduction

Recently, organic light emitting diodes (OLEDs) have been actively investigated for applications to flat panel displays [1–6] and novel illumination light sources [7–13] because they have various advantages in comparison with inorganic LEDs. However, since OLEDs are greatly damaged by moisture and the oxidant effect, their operation lifetime is shorter than inorganic LEDs [14]. Very recently, we successfully fabricated by the sol-gel method organic-inorganic hybrid thin films that contain organic emissive materials and applied them to the active layers of OLEDs [15–18]. Consequently, the fabricated OLEDs emitted light by current injection and revealed much longer operation lifetime without the sealing process, because the organic emissive materials were protected against the oxidant effect by the sealing effect of the inorganic material $SiO_2$. In this case, we used perhydropolysilazane (PHPS) as the reactant for sol-gel reaction, which is soluble in nonpolar solvents. In this paper, we used Tetraethoxysilane (TEOS) as the reactant for sol-gel reaction because it is soluble in polar-solvents and requires water to accelerate the sol-gel reaction. Thus, the organic emissive material must be water-soluble. We evaluated the flatness of the surface of the fabricated films and the lifetime of the photoluminescence (PL) emissions.

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## 2. Experimental

### *2.1 Sample Fabrication*

We fabricated the sol-solution using TEOS as follows: First, the emissive material (1wt%) was added to the ethanol solution. Then TEOS, pure water, and a catalyst were added in the ethanol solution as the following mole fractions:

TEOS: $H_2O$: ethanol: catalyst = 1.0: 4.5: 5.0: 1.0.

We used two organic emissive materials; rhodamine 6G and poly[2-méthoxy-5- (2-éthyl-hexyloxy)-1,4-phénylène-vinylène] (MEHPPV). Rhodamine 6G is soluble in water and ethanol, but MEHPPV is only soluble in ethanol. In addition, we used two catalysts, HCl and NaOH to determine the more suitable catalyst for fabricating samples using TEOS. Note that HCl is an acid catalyst, and NaOH is a base catalyst. The concentration of HCl is 36%, and the concentration of NaOH is 1 mol/L.

The fabricated sol-solutions were dropped on cleaned glass substrates. Then we fabricated a thin film using the spin-coating method. To accelerate the sol-gel reaction, they were baked at 70 degree Celsius for two hours.

### *2.2 Experimental Setup*

The surface roughness of the films was observed using an atomic force microscope (AFM; SII, Nanocute). Fourier-transform infrared (FT-IR) spectroscopy was performed on a JASCO FT/IR-4100. The PL spectra were recorded using a multi-channel spectroscope (Ocean Optics USB-2000), and a pulsed $N_2$ laser was used to photoexcite the samples. The thicknesses of the fabricated films were measured using a step profiler (AMBIOS XP-1). All measurements were performed in the atmosphere and at room temperature.

## 3. Results and Discussion

### *3.1 Comparison of Acid and Base Catalysts*

Figure 1 shows the AFM images of the sample before and after the sol-gel reaction when the HCl catalyst was used. In this case, the organic emissive material was rhodamine 6G. The thickness of the film after the sol-gel reaction was about 50 nm. In addition, the surface roughness became smoother after the sol-gel reaction. The averaged surface roughness was about 1 nm. Thus, the HCl catalyst, which is an acid catalyst, is suitable to fabricate hybrid films using TEOS. When we used another organic emissive material (MEHPPV), it was impossible to fabricate fine thin films. MEHPPV was precipitated in the solution because it dose not dissolve in water: TEOS needs water for the sol-gel reaction. This indicates that water-soluble organic materials are compatible with the sol-gel reaction using TEOS. Thus, we only used rhodamine 6G in the following measurements.

When the NaOH catalyst was used to fabricate the sol-solution, the sol-gel reaction started just after the TEOS was added. Figure 2 shows the sol-solution using the NaOH catalyst just after the TEOS was added. The white-color deposits are the generated gel. This means that the speed of hydrolysis depends on the type of the catalyst; the sol-gel reaction was very fast using a base catalyst, NaOH. These results indicate that the HCl catalyst is better than NaOH, because the sol-gel reaction using the HCl catalyst is gently accelerated. The acid catalyst HCl is easier to use for the sol-gel reaction with TEOS. Therefore, in

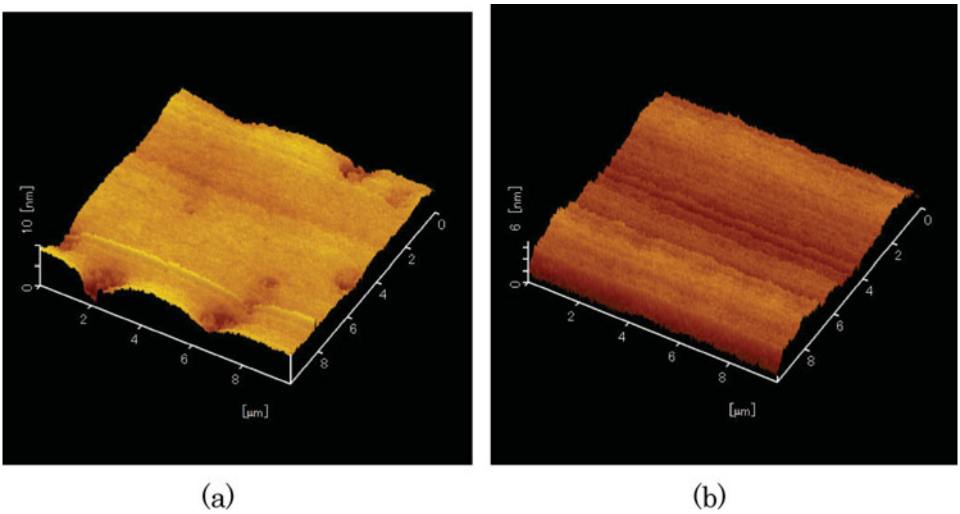

**Figure 1.** AFM images of the sample surfaces (a) before sol-gel reaction and (b) after it when HCl catalyst was used.

the following measurements, we used rhodamine 6G as an emissive material and HCl as a catalyst.

### 3.2 Evaluation of Sol-Gel Reaction Using FT-IR Spectroscopy

Figure 3 shows the IR absorption spectra of the hybrid films recorded just after starting the sol-gel reaction and after one, two, and three hours. In addition, the assigned IR absorption

**Figure 2.** Sol-solution using NaOH catalyst just after TESO was added.

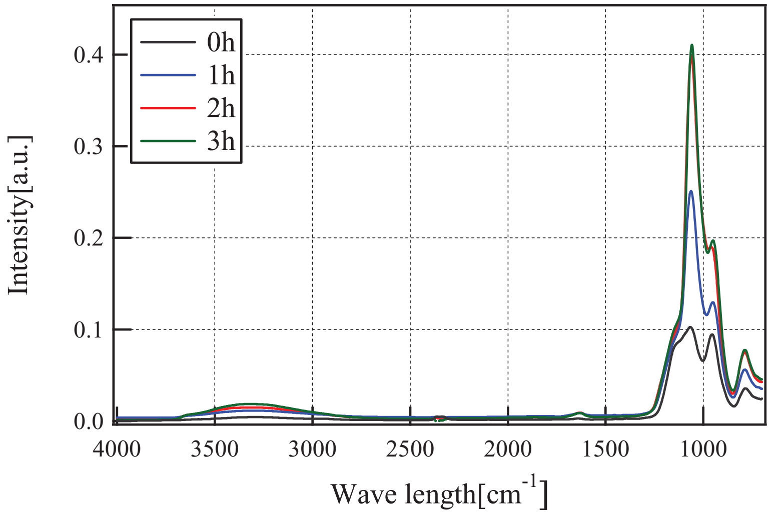

**Figure 3.** IR absorption spectra of the hybrid films just after starting the sol-gel reaction (black line), after one hour (blue line), two hours (red line), and three hours (green line).

signals derived from Fig. 3 are listed in Table 1. The Si—O—Si, Si—O, and Si-OH signals from 770 to 1050 cm$^{-1}$ gradually increased by the acceleration of the sol-gel reaction. This means that $SiO_2$ was generated by the sol-gel reaction. On the other hand, the —OH signal from 3000 to 3500 cm$^{-1}$ also increased. The fabricated hybrid films contain moisture, revealing their moisture-absorption characteristic.

### *3.3 Lifetime of PL Emissions*

Since the organic-inorganic hybrid films are expected to reveal a strong sealing effect [15–18], we evaluated the lifetime of the PL emissions. Figure 4 shows the PL spectra of four samples. Sample A was recorded before the sol-gel reaction, sample B was recorded just after the sol-gel reaction, sample C was exposed in air for three days after it, and sample D was a film containing only rhodamine 6G exposed in air for three days without it. The PL intensity of sample C did not decrease, and sample D did not emit light at all. This indicates that the rhodamine 6G in sample C was not destroyed by the oxidant effect because it was surrounded by $SiO_2$ in the hybrid film. The fabricated organic-inorganic hybrid films reveal a fine antioxidant effect, increasing the operation lifetime of the PL emission. In addition, the PL peaking wavelengths of samples B and C were slightly red-shifted. This is most likely caused by the interference effect in thin films, because the emission wavelengths

**Table 1.** Assigned IR absorption signals derived from Fig. 3

| | Wave number |
|---|---|
| Si—O bending | 770 cm$^{-1}$ |
| Si—OH stretching | 950 cm$^{-1}$ |
| Si—O—Si stretching | 1050 cm$^{-1}$ |
| —OH stretching | 3000 cm$^{-1}$~3500 cm$^{-1}$ |

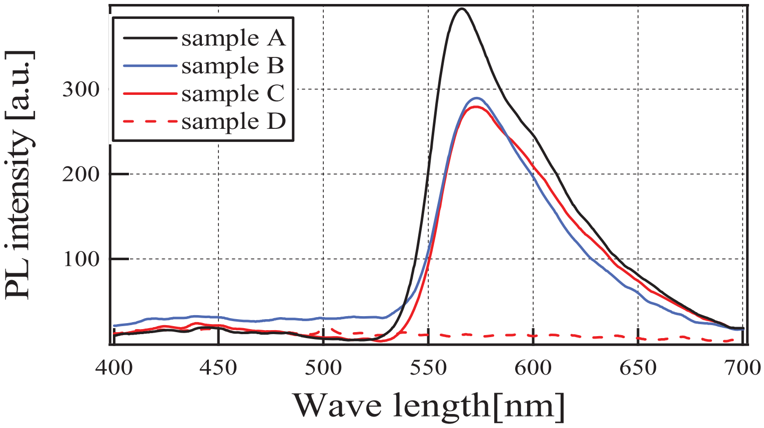

**Figure 4.** PL spectra of four samples. Sample A was recorded before the sol-gel reaction (black line), sample B was recorded just after the sol-gel reaction (blue line), sample C was exposed in air for three days after the sol-gel reaction (red line), and sample D was a rhodamine 6G film exposed in air for three days without the sol-gel reaction (red broken red line).

depend on the thickness of the films. The density of TEOS is 0.932 g/cm$^3$, while $SiO_2$ is 2.65 g/cm$^3$. This means that the thicknesses of the fabricated films were changed due to the sol-gel reaction. Thus, to identify the cause of the blue-shifted PL signals, precise PL measurement of the thickness dependence is necessary.

### *3.4 Water Resistant Properties*

To evaluate the water resistant properties of the hybrid films, we observed the PL spectra of the sample after dripping some water on the film after the sol-gel reaction. Figure 5 shows the PL spectra of the two samples. Sample E was recorded after dripping water on

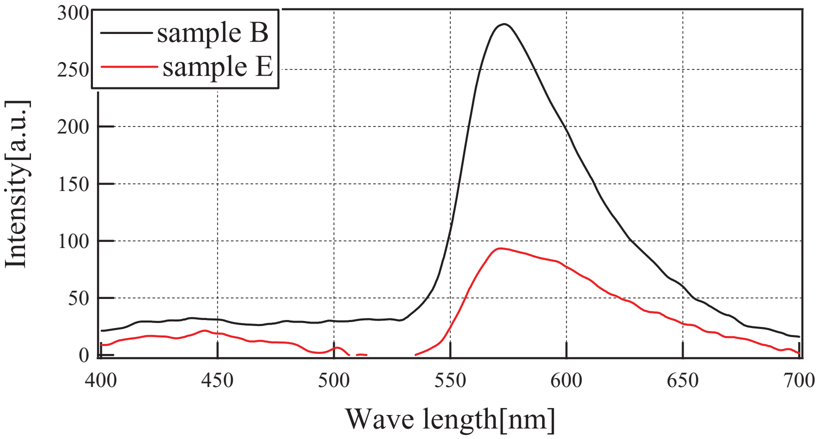

**Figure 5.** PL spectra of two samples: Sample B was recorded just after the sol-gel reaction, which is the same spectrum shown in Fig. 4 (black line). Sample E was recorded after dripping some water on the film after the sol-gel reaction (red line).

**Figure 6.** Picture of two samples. Since water was dropped on the film on the right side, the film came off the glass substrate. Another hybrid film on the left side without water was not destroyed, although it exposed in air for the same duration.

the film after the sol-gel reaction. Sample B, which has the same spectrum shown in Fig. 4, is displayed here for comparison with sample E. Obviously, the PL intensity of sample E drastically decreased. This means that the silica hybrid film with rhodamine 6G might be broken by dropped water. Figure 6 shows two samples. Note that the hybrid film on the right was removed from the glass substrate by the water, but another hybrid film on the left without water was not destroyed, even though it was exposed in air for the same duration. This result suggests that fabricated hybrid films using TEOS have fine water resistant characteristics.

## 4. Conclusion

We fabricated organic-inorganic hybrid films containing organic emissive materials were fabricated by the sol-gel method using TEOS. Water-soluble organic emissive materials are suitable for the sol-gel reaction using TEOS, because water must be added to TEOS to accelerate the sol-gel reaction. In addition, acid catalysts are more suitable for the sol-gel reaction using TEOS than base catalysts because the sol-gel reaction using acid catalysts is gently accelerated. The lifetime of the PL emissions was drastically improved because most of the organic emissive materials were not exposed in air, and thus they are protected against the oxidant effect. However, they have a water resistant characteristic, which should be improved to realize a stronger sealing effect of the hybrid films.

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