Photoluminescent Oxygen Sensing Using Tris(acethylacetonato) 1,10-Phenanthroline Terbium(III) Complex Doped on Alumina Film

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A new photoluminescent oxygen sensor based on the luminescence intensities of tris(acethylacetonato) 1,10-phenanthroline terbium(III) complex ($Tb(acac)_3phen$) doped in alumina film was developed. The luminescence intensity of the $Tb(acac)_3phen$ film decreased with increasing the oxygen concentration. $Tb(acac)_3phen$ film sensor is calibrated by the modified Stern–Volmer equation.

Determination of oxygen concentration is important in various fields of chemical, clinical analysis and environmental monitoring.[1–3] Several oxygen detection systems have been reported i.e., some based on titration,[4] amperometric,[5] chemiluminescence,[6] or thermoluminescence.[7] The most successful method has been the oxygen electrode method. However, it is limited by the stability of the electrode surface and by instabilities in the oxygen diffusion barrier, because it measures the rate of diffusion of oxygen to the cathode. Recently, a variety of devices and sensors based on luminescence quenching of organic dyes were developed to measure oxygen pressure. Many optical oxygen sensors are composed of organic dyes, such as polycyclic aromatic hydrocarbons (pyrene and its derivatives)[8,9] and organometallic compounds[10–13], immobilized in oxygen permeable polymer (silicon polymer, polystyrene and so on). The essential demands for the organic dyes are strong luminescence with high quantum yield and have long lifetime. Recently, much attention has been given to the photochemical and photophysical properties of lanthanide complexes.[14] Terbium(III) and europium(III) complexes display remarkably strong luminescence with high quantum yield and have long lifetime.[14] Thus, terbium(III) and europium(III) complexes are attractive candidates as novel optical oxygen sensing materials. We have previously reported the development of oxygen sensitive optical sensor based on the luminescence intensity change of thenoyltrifluoroacetonato 1,10-phenanthroline europium(III) complex ($Eu(TTA)_3phen$) immobilized in polystyrene-trifluoroethylmethacrylate copolymer film.[15]

In this letter we describe a new photoluminescent oxygen sensing material, tris(acethylacetonato) 1,10-phenanthroline terbium(III) complex ($Tb(acac)_3phen$) doped in alumina film, and its oxygen sensing properties.

$Tb(acac)_3phen$ was prepared by adding 40 mL of a warm ethanolic solution of 1,10-phenanthroline (1 mmol) to an ethanolic solution containing 1 mmol of tris(acethylacetonato) terbium(III) (obtained from Aldrich) at 70°C for 5 h. $Tb(acac)_3phen$ was characterized by the UV–vis absorption spectrum. During the synthesis of $Tb(acac)_3phen$, the intensity of absorption band at 268.1 nm attributed to coordination of 1,10-phenanthroline increased. The precipitate was filtered, washed with ethanol and dried in vacuum. Purification was performed by recrystallization from ethanol–water (1:2) mixture. $Tb(acac)_3phen$ doped in alumina film was prepared as follows. Alumina plate (for TLC) was dipped into 0.1 mmol dm^{-3} $Tb(acac)_3phen$ in water solution at room temperature for 30 min. After dipping, the plate was washed with water and ethanol several times. The films were dried at room temperature and stored in the dark prior to use.

Oxygen sensing was carried out by using a spectrofluorophotometer with a 150 W Xenon lamp as the excitation light source. The sample film was mounted at a 45° angle in the quartz cell to minimize light scattering from the sample and substrate. Different oxygen standards (in the range 0–100%) in a gas stream were produced by controlling the flow rates of oxygen and argon gases entering a mixing chamber. The total pressure was maintained at 760 Torr (1 Torr =133.322 Pa). All the experiments were carried out at room temperature. The oxygen sensing properties of $Tb(acac)_3phen$ film was characterized by the Stern–Volmer quenching constant, K_{SV}, obtained from the following equation (1):

$$(I_0 / I) - 1 = K_{SV}[O_2] \quad (1)$$

where I_0, I and $[O_2]$ are the luminescence intensities in the absence and presence of oxygen and oxygen concentration, respectively. The K_{SV} value was obtained from a linear plot of $(I_0/I) - 1$ versus $[O_2]$.

$Tb(acac)_3phen$ film showed strong luminescence at 490, 546, 580 and 620 nm as shown in Figure 1. The excitation wavelength was 350 nm. At 100% argon condition, the luminescence quantum yield was ca. 11% determined by standard procedures using an integral sphere.[16] The luminescence intensity of the film depended on the oxygen concentration. The intensity decreased with increasing the oxygen concentration. The intensity at 546 nm changed as shown in Figure 2. The

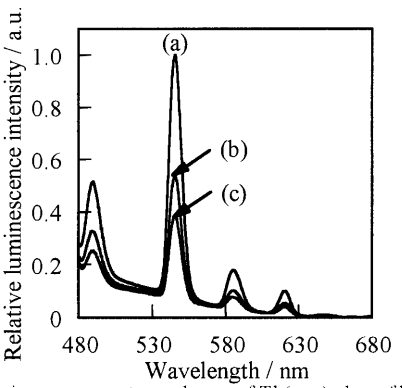

Figure 1. Luminescence spectrum change of $Tb(acac)_3phen$ film by oxygen. Excitation wavelength was 350 nm. $[O_2]$=0 (a), 20 (b) and 100% (c).

ratio I_0 / I_{100} is used as a measure of the film sensitivity, where I_0 and I_{100} represent the detected luminescence intensities from the film exposed to 100% argon and 100% oxygen, respectively. The I_0 / I_{100} value of Tb(acac)$_3$phen film is estimated to be 2.68. This result indicates that the luminescence of Tb(acac)$_3$phen in alumina film is quenched by oxygen, and that this film can thus be used as an optical oxygen sensing device by employing its oxygen-induced luminescence quenching ability as an indicator of oxygen concentration.

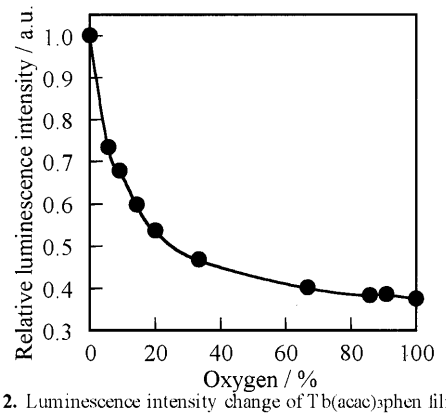

Figure 2. Luminescence intensity change of Tb(acac)$_3$phen film by oxygen. Excitation and emission wavelengths were 350 and 546 nm, respectively.

Figure 3 shows a Stern–Volmer plot for the Tb(acac)$_3$phen film. The plot exhibits considerable linearity at the lower oxygen concentration, although the curvature decreases at higher oxygen concentrations. At lower oxygen concentration, the intensities from the Tb(acac)$_3$phen film are quenched by oxygen according to Stern–Volmer equation as well as in homogeneous system. At higher concentrations, on the other hand, Stern–Volmer plot of the Tb(acac)$_3$phen film is nonlinear because of the simultaneous presence of static and dynamic quenching. We reported that palladium tetrakis(4-carboxyphenyl)porphyrin chemisorption film on alumina plate has some different oxygen-accessible site due to static and dynamic quenching.[17] There are two oxygen accessible sites in the sensing film; one is an oxygen easily accessible site due to dynamic quenching and the other is an oxygen difficult accessible site due to static quenching. Demas et al. also reported that multisite model; oxygen-accessible site and oxygen-difficult accessible site, respectively.[18] In this model, the sensor molecule can exist in two or more sites each with its own characteristic quenching constant. Stern–Volmer plot becomes as follows;

$$I_0/I=[\Sigma(f_n/(1+K_{SVn}[O_2]))]^{-1} \quad (2)$$

Where, the f_n is the fractional contributions to the oxygen accessible site or oxygen-difficult accessible site. K_{SVn} is the quenching constant for each accessible site. The best-fit curve was obtained when n was equal to 2, supported by the correlation factor, r^2, estimated to be 0.994 by the least squares method. In Figure 3, the solid line is the best fit using the above equation (n = 2). Tb(acac)$_3$phen film sensor is calibrated by the modified Stern–Volmer equation (equation (2)). Thus, there are two oxygen accessible sites for Tb(acac)$_3$phen film; one is an oxygen accessible site due to dynamic quenching (K_{SV1}=0.141%$^{-1}$, f_1=0.910) and the other is an oxygen difficult accessible site due to static quenching (K_{SV2}=0.00216%$^{-1}$, f_2=0.090).

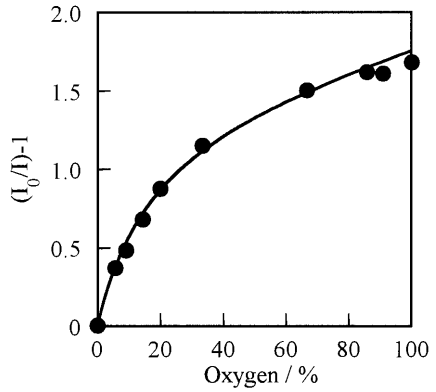

Figure 3. Stern-Volmer plot of Tb(acac)$_3$phen film. The solid line is the best fit using equation (2) (n=2).

An operational stability test was conducted by reading the luminescence intensity signal while oxygenated and deoxygenated gases were switched for 200 s. The response times of the Tb(acac)$_3$phen film were 7.3 s for switching from argon to oxygen, and 70 s for switching from oxygen to argon. The signal changes were fully reversible and hysterisis was not observed during the measurements. An important factor for application of the Tb(acac)$_3$phen film as an optical oxygen sensing material, is its photostability. To characterize the photostability of the Tb(acac)$_3$phen film, the reflectance spectrum of the film was measured after continuous irradiation using a 150 W tungsten lamp on the film for 24 h. No spectrum change was observed, indicating that the Tb(acac)$_3$phen film is stable against irradiation.

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