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Optical Oxygen Sensing Properties of Tris(4,7'-diphenyl-1,10'-phenanthroline) Ruthenium (II)-Polyacrylic Acid Complex Thin Film

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Oxygen sensors are extensively used in various fields to determine the oxygen concentration.^{1–3} The amperometric method using an oxygen electrode has been the most popular technique among various oxygen-sensing systems.⁴ This system, however, is limited by the stability of the electrode surface and instabilities in the oxygen diffusion barrier. Recently, much attention has been given to optical oxygen-sensing methods based on the luminescence quenching of an indicator by oxygen. Indicators available for this sensor are luminescent and oxygen-quenchable organic dyes, such as polycyclic aromatic hydrocarbons (pyrene and its derivatives),^{5–11} platinum and palladium porphyrins^{12–15} and transition-metal complexes.^{16–25} Many optical oxygen sensors are composed of organic dyes immobilized in an oxygen permeable polymer (silicon polymer, polystyrene and so on). Especially, ruthenium complexes among luminescent dyes display strong luminescence with high quantum yield and long natural lifetime.²⁶ Therefore, these compounds have been frequently utilized as oxygen sensitive dyes. Among ruthenium complexes, tris(4,7'-diphenyl-1,10'-phenanthroline) ruthenium (II) (Ru (ph₂phen)₃) is widely used for oxygen sensing dye.¹⁹ Many optical oxygen sensors based on luminescence change of Ru (ph₂phen)₃ immobilized in organic, inorganic polymers (polystyrene,²³ silicone polymer, sol-gel glass²⁴ and so on) and zeolite matrix²⁵ have been reported. As organic dyes interacted with polymer molecules, the properties of sensing films strongly depend on the properties of polymer matrices in the optical oxygen sensing systems using organic dyes immobilized in polymer films. To overcome these problems chemisorption films of organic compounds on the metal oxide surface (Al₂O₃, Fe₂O₃ and so on) have been exploited.^{27–29} Among a number of chemisorption film techniques, the use of compounds with carboxyl functional group is most prevalent in preparing the chemisorption of organic compounds on the metal oxide surface. As the thin film, the sensing dyes are arranged on the solid surface, are made by using this technique, highly sensitive device for oxygen sensing will be accomplished. Thus, Ru (ph₂phen)₃ immobilized polymer with carboxyl group will be suitable for optical oxygen sensing device using the chemisorption technique, be-

cause of formation of a stable film by surface on alumina *via* the carboxyl group of polymer which forms a chemisorptive ester bond. As polyacrylic acid is the anionic polymer with carboxyl group, positively charged Ru (ph₂phen)₃ is immobilized in polyacrylic acid by an electrostatic effect and a stable chemisorption film will be formed by the surface on alumina and carboxyl group of polyacrylic acid.

In this paper we hope to describe the fabrication of Ru (ph₂phen)₃-polyacrylic acid polyion complex chemisorption thin film onto alumina plate and optical oxygen sensing properties of this sensing film.

EXPERIMENTAL

Materials

Tris(4,7'-diphenyl-1,10'-phenanthroline) ruthenium (II) (Ru (ph₂phen)₃) was purchased from GFS Chemicals Inc. Polyacrylic acid (M.W. 25000) was purchased from Wako Pure Chemicals Co. Ltd. A silicone polymer (GP 197, polydimethylsiloxane) was obtained from Genesee Polymer Co. All the other chemicals were obtained from Wako Pure Chemicals Co. Ltd.

Formation of Polyion Complex with Ru (ph₂phen)₃ and Polyacrylic Acid

Ru (ph₂phen)₃-polyacrylic acid complex solution was prepared from 2.0×10^{-4} mol dm⁻³ Ru (ph₂phen)₃ and 1.0×10^{-2} mol dm⁻³ (monomer unit) polyacrylic acid in 50 mmol dm⁻³ Tris-HCl buffer (pH=7.5). Polyion complex formation was observed using UV spectrum.

Preparation of Ru (ph₂phen)₃-Polyacrylic Acid Complex Film

Ru (ph₂phen)₃-polyacrylic acid complex film was prepared as follows. Alumina plate was dipped into Ru (ph₂phen)₃-polyacrylic acid complex in 50 mmol dm⁻³ Tris-HCl buffer solution at room temperature for 24 h. After dipping, the plate was washed with water and ethanol several times. Ru (ph₂phen)₃-polyacrylic acid complex physically adsorbed onto alumina was removed by ultrasonication and then the film was dried under vacuum overnight. Ru (ph₂phen)₃-GP197 film was prepared onto alumina plate as the reference. The film was prepared by casting a solution of Ru (ph₂phen)₃ (2.0×10^{-4} mol

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Figure 1. Absorption spectra of Ru (ph₂phen)₃-polyacrylic acid complex (solid line) and Ru (ph₂phen)₃ (dash line) in 50 mmol dm⁻³ Tris-HCl buffer solution.

dm⁻³) and GP197 in ethanol. The films were dried at room temperature and stored in dark prior to use.

Spectroscopic Measurement

Absorption spectrum was recorded using a Shimadzu U-2400PC spectrometer. Steady state phosphorescence spectra and excitation spectra were measured using a Shimadzu F-5300PC spectrofluorophotometer with a 150 W Xenon lamp as the visible excitation light source. Excitation and emission bandpasses were 5.0 nm. All samples were excited at 470 nm attributed to the absorption band of Ru (ph₂phen)₃, the wavelength producing maximum luminescence intensity at 610 nm.

Oxygen Sensing System

Oxygen sensing was carried out using a spectrofluorophotometer with a 150 W Xenon lamp as the visible excitation light source. Sample film was mounted at 45° angle in the quartz cell to minimize light scatter 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 the mixing chamber. Total pressure was maintained at 760 Torr by the method mentioned elsewhere.³⁰ All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Absorption Spectrum of Ru (ph₂phen)₃-Polyacrylic Acid Complex Solution

Figure 1 shows the absorption spectra of Ru (ph₂phen)₃-polyacrylic acid complex (solid line) and Ru (ph₂phen)₃ (dash line) in 50 mmol dm⁻³ Tris-HCl buffer solution. Absorption peaks of Ru (ph₂phen)₃-polyacrylic acid complex are 443 and 470 nm in visible region. On the other hand, absorption peaks of Ru (ph₂phen)₃ are 435 and 461 nm. In comparison with the spectrum in Ru (ph₂phen)₃ solution, the red shift of absorption peak was observed. This result suggests that complex is formed due to electrostatic force between positively charged Ru

Figure 2. Luminescence spectrum change of Ru (ph₂phen)₃-polyacrylic acid complex film (a) and Ru (ph₂phen)₃-GP197 film (b) by oxygen.

(ph₂phen)₃ and negatively charged polyacrylic acid.

Luminescence Spectrum Change of Ru (ph₂phen)₃-Polyacrylic Acid Complex Film by Oxygen

Ru (ph₂phen)₃-polyacrylic acid complex film showed strong luminescence at 610 nm when excited at 470 nm attributed to the absorption band of Ru (ph₂phen)₃, as shown in Figure 2a. Figure 2b shows the luminescence spectrum of Ru (ph₂phen)₃-GP197 film. In both cases, the luminescence intensity of the film depended on oxygen concentration. The intensity decreased with increase of oxygen concentration. This result indicates that these films can be used as an optical oxygen sensing device based on luminescence quenching by oxygen. The ratio I_0/I_{100} is used as a sensitivity of the sensing film, where I_0 and I_{100} represent the detected luminescence intensities from a film exposed to 100% argon and 100% oxygen, respectively. In general, the sensor having the ratio I_0/I_{100} more than 3.0 is a suitable oxygen sensing device.²⁴ The I_0/I_{100} of Ru (ph₂phen)₃-polyacrylic acid complex film and GP197 film are estimated to be 3.7 and 2.7, respectively. In previous reports, on the other hand, I_0/I_{100} of Ru (ph₂phen)₃ immobilized in polystyrene film,

Figure 3. Stern-Volmer plot for Ru (ph₂phen)₃-polyacrylic acid complex film (■) and Ru (ph₂phen)₃-GP197 film (●). Excitation and emission wavelengths were 470 and 610 nm, respectively.

in zeolite matrix and in sol-gel glass film are 2.5,²³ 3.0²⁴ and 2.6,²⁵ respectively. As the thickness of Ru (ph₂phen)₃-polyacrylic acid complex chemisorption film is thinnest among the other polymer films, the effective oxygen quenching the luminescence of Ru (ph₂phen)₃ in polyacrylic acid complex film occurs. Thus, Ru (ph₂phen)₃-polyacrylic acid complex film is useful device for oxygen sensor.

Oxygen Sensing Properties of Ru (ph₂phen)₃-Polyacrylic Acid Complex Film

Figure 3 shows a plot of the luminescence intensities of Ru (ph₂phen)₃-polyacrylic acid complex film as a function of oxygen concentration (Stern-Volmer Plot, $I_0/I = 1 + K_{SV}[O_2]$; where I_0 and I are luminescence intensities in the absence and in the presence of oxygen, respectively; K_{SV} is the Stern-Volmer quenching constant; $[O_2]$ is oxygen concentration). At lower concentration, the intensities from the photoexcited of Ru (ph₂phen)₃-polyacrylic acid complex film are quenched by oxygen according to Stern-Volmer equation as well in homogeneous system. At higher concentrations, on the other hand, Stern-Volmer plots of sensor based on phosphorescence quenching is nonlinear, because of the simultaneous presence of static and dynamic quenching. Demas *et al.* reported a multi-site model that sensing film has some different oxygen-accessible site.³¹ According to this model, the site has own individual characteristic quenching constant. As the observed luminescence intensity was a sum of emission from different oxygen-accessible site with its own characteristic quenching constant, Stern-Volmer relationship is given by

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

where f_n is the fractional contributions to each oxygen accessible site. K_{SVn} is the quenching constant for each accessible site. When n was equal to 2, the best-fit curve was obtained. In Figure 3, the solid line is the best-fit using above equation ($n=2$). Thus, there are two oxygen

Figure 4. Response time, relative luminescence intensity changes for Ru (ph₂phen)₃-polyacrylic acid complex film on switching between 100% argon (1) and 100% oxygen (2). Excitation and emission wavelength was 470 and 610 nm, respectively.

accessible sites in the sensing film; one is an oxygen easily accessible site ($K_{SV1} = 0.162\%^{-1}$, $f = 0.722$) and the other is an oxygen difficult accessible site ($K_{SV2} = 0.00223\%^{-1}$, $f = 0.278$). In the case of GP197 film, on the other hand, K_{SV1} and K_{SV2} are 0.0621 ($f = 0.615$) and 0.00366 ($f = 0.385$), respectively. Stern-Volmer constant of oxygen accessible site (K_{SV1}) of Ru (ph₂phen)₃-polyacrylic acid complex film is larger than that of GP197 film. Thus, the oxygen easily accessible site is attributed to dynamic quenching of luminescence of Ru (ph₂phen)₃ by oxygen. In both cases, the K_{SV2} is very low value ($0.00223\%^{-1}$ for Ru (ph₂phen)₃-polyacrylic acid complex film and 0.00366 for GP197 film) and low contribution compared with K_{SV1} , indicating that oxygen difficult accessible site is attributed to static quenching of luminescence of Ru (ph₂phen)₃. The K_{SV1} of Ru (ph₂phen)₃-polyacrylic acid complex film is larger than that of GP197 film. In previous reports, K_{SV1} values of Ru (ph₂phen)₃ immobilized in polystyrene film, in zeolite matrix and sol-gel glass film are approximately to be 0.050,²³ 0.075, and 0.050 (estimated from data in references 24 and 25), respectively. Thus, Ru (ph₂phen)₃-polyacrylic acid complex film is a highly sensitive device for oxygen.

Response Time of Ru (ph₂phen)₃-Polyacrylic Acid Complex Film

Figure 4 shows the typical dynamic response of the sensor of Ru (ph₂phen)₃-polyacrylic acid complex film when switching between fully oxygenated and fully deoxygenated atmospheres. The response times of the sensor are 4.6 s on going from argon to oxygen and 48 s on going from oxygen to argon. The signal changes were fully reversible and measurement hysteresis was not observed. On the other hand, the response times of Ru (ph₂phen)₃ immobilized in polystyrene film, in zeolite matrix and sol-gel glass film are approximately to be 30, 10, and 10 s on going from argon to oxygen and approximately to be 100, 60, and 40 s on going from oxygen to argon, respectively and measurement hysteresis was observed in polystyrene film²³ and zeolite matrix.²⁵ As oxygen diffusion rate in Ru (ph₂phen)₃-polyacrylic acid com-

plex chemisorption film may be rapid compared with the other sensor films, the fast responses for changes of argon to oxygen saturated condition and of oxygen to argon saturated condition were observed. The stability of Ru (ph₂phen)₃-polyacrylic acid complex film against irradiation was measured by the luminescence intensity change at 610 nm before and after irradiation with 470 nm light. A little luminescence intensity change of the film was observed before and after irradiation for 10 h. On the other hand, the luminescence intensity changes of Ru (ph₂phen)₃ immobilized in polystyrene film and GP 197 films were observed by the irradiation. These results show that little decomposition of Ru (ph₂phen)₃-polyacrylic acid complex film is observed. Thus, Ru (ph₂phen)₃-polyacrylic acid complex film was stable against irradiation.

CONCLUSION

An optical oxygen sensing technique was prepared using the Ru (ph₂phen)₃-polyacrylic acid complex film onto alumina plate. The ratio I_0/I_{100} as a sensitivity of the Ru (ph₂phen)₃-polyacrylic acid complex film is estimated to be 3.7, showing that this film is highly sensitive for oxygen. This sensing film was good linearity using two-site model (oxygen-accessible site and oxygen-difficult accessible site) Stern-Volmer plots in total oxygen concentration region and possesses good operational stability and a fast response. These results show that Ru (ph₂phen)₃-polyacrylic acid complex film can be developed for a highly sensitive device for oxygen sensing.

The effects of the composition ratio of Ru (ph₂phen)₃ to polyacrylic acid and temperature change on oxygen sensing are now being studied.

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