Pyrene Chemisorption Film on an Alumina Plate as an Optical Oxygen-Sensing Material

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An optical oxygen sensor based on the fluorescence quenching of pyrene-1-butyric acid (PBA) chemisorption film onto an alumina plate was developed. The fluorescence intensity of PBA film decreased with increasing oxygen concentration. The PBA film sensor is calibrated by a modified Stern–Volmer equation.

A determination of the oxygen concentration is important in various fields of chemical, clinical analysis and environmental monitoring.[1–3] The most successful oxygen-detection method has been the oxygen-electrode method.[4] 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 the luminescence quenching of organic dyes, polycyclic aromatic hydrocarbons immobilized in an oxygen-permeable polymer (silicon polymer, polystyrene and so on) were developed to measure the oxygen concentration.[5–7] Because organic dyes interact with polymer molecules directly, the properties of sensing films strongly depend on the properties of polymer matrices. To overcome these problems, chemisorption film has been exploited. Chemisorption films are formed using spontaneous binding between the mercapto group and the metal surface (Au, Ag, or Pt) or between the carboxyl group and the metal oxide surface (Al_2O_3, Fe_2O_3, TiO_2 etc.). Because the chemisorption film technique is very convenient, this film is widely used for both optical and optoelectronic devices.[8–10] Among a number of chemisorption film techniques, the use of compounds with a carboxyl functional group is most prevalent in preparing chemisorption films of organic compounds on metal aluminum oxide. Because the sensing dyes are arranged on the solid surface directly using this technique, a highly sensitive device for oxygen sensing will be accomplished by using chemisorption film. On the other hand, among polycyclic aromatic hydrocarbons, pyrene derivatives display strong fluorescence with a high quantum yield and a long lifetime. Among pyrene derivatives, pyrene-1-butyric acid (PBA) is suitable for optical oxygen-sensing devices using a chemisorption film, because of the formation of a stable film on alumina and a carboxyl group of PBA.

In this paper we describe the fabrication of PBA as a fluorescence probe for oxygen sensing, a chemisorption film onto an alumina plate and the optical oxygen sensing properties of PBA film.

PBA chemisorption film showed fluorescence at 376, 396 and 474 nm when excited at 365 nm, as shown in Fig. 1. The fluorescence spectra shape of the PBA film was almost the same as that in an ethanol solution (0.1 mmol dm^{-3} PBA). The emissions of PBA monomer (376 and 396 nm) and excimer between PBA molecules (474 nm) were observed. From Fig. 1, the fluorescence intensity of the film at 376, 396 and 474 nm depended on the oxygen concentration. The intensity at 474 nm decreased along with an increase in the oxygen concentration, as shown in the inset of Fig. 1. This result indicates that the fluorescence of PBA film was quenched by oxygen. The ratio I_0/I_{100} is used as the sensitivity of the sensing film, where I_0 and I_{100} represent the detected fluorescence intensities at 474 nm from a film exposed to 100% argon and 100% oxygen, respectively. In general, a sensor having an I_0/I_{100} ratio of more than 3.0 is a suitable oxygen-sensing device.[11] The I_0/I_{100} value of PBA film is estimated to be 6.14. On the other hand, the I_0/I_{100} value of pyrene immobilized in poly(dimethylsiloxane) film has previously been reported to be 1.5.[6] These results indicate that PBA film is a highly sensitive device for oxygen. Figure 2 shows a Stern–Volmer plot between the fluorescence intensities of PBA film at 474 nm attributed to PBA excimer emission and the oxygen concentration. At higher PBA concentrations, the emission of the PBA excimer is sensitized by energy transfer from the PBA monomer. The fluorescence of the PBA monomer observed at 376 and 396 nm was also quenched by oxygen (Fig. 1). There are two processes in quenching PBA monomer emission: one is due to direct

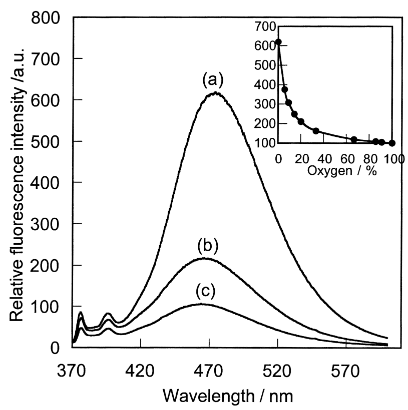

Fig. 1. Fluorescence spectrum change of PBA chemisorption film under various oxygen concentrations excited at 365 nm. (1) argon saturated, (2) air saturated and (3) oxygen saturated conditions. The inset shows the relative fluorescence intensity change of PBA chemisorption film under various oxygen concentrations. Excitation and emission wavelength were 365 and 474 nm, respectively.

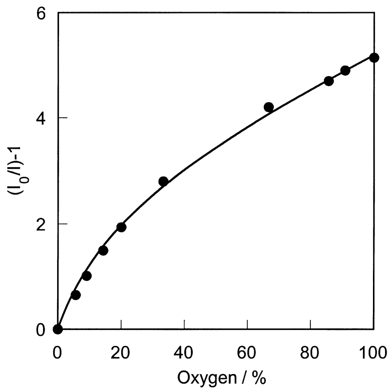

Fig. 2. Stern–Volmer plot for PBA chemisorption film. The solid line is a fitting curve using Eq. 1. Excitation and emission wavelength were 365 and 474 nm, respectively.

quenching by oxygen; the other is due to energy transfer to the PBA excimer. However, a Stern–Volmer plot between the fluorescence intensities of PBA film at 376 nm, attributed to PBA monomer emission and oxygen concentration, exhibits considerable linearity, and the Stern–Volmer quenching constant is estimated to be 0.0070%$^{-1}$. Thus, the fluorescence quenching process of the PBA monomer only is due to direct quenching by oxygen. On the other hand, a Stern–Volmer plot between the fluorescence intensities of PBA film at 474 nm, attributed to the PBA excimer emission and the oxygen concentration, exhibits considerable linearity at lower oxygen concentrations (within 40%). At higher oxygen concentrations, on the other hand, Stern–Volmer plot of the film is nonlinear because of the simultaneous presence of some different oxygen-accessible sites. Demas et al. reported a multi-site model in which the oxygen-sensing film has some different oxygen-accessible site.[12] According to this model, the site has its own individual characteristic quenching constant. Because the observed fluorescence intensity was the sum of the emission from different oxygen-accessible sites with its own characteristic quenching constant, the Stern–Volmer relationship is given by

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

where n is an integer; f_n is the fractional contributions to each oxygen-accessible site; and K_{SVn} is the quenching constant for each accessible site. The best-fit curve was obtained when n was equal to 2, as shown in Fig. 2. The correlation factor of the plots, r^2, as estimated to be 0.998 by the least-squares method, indicating that the PBA film sensor is calibrated by the modified Stern–Volmer equation (Eq. 1). Thus, there are two oxygen-accessible sites in sensing films: one is an oxygen-accessible site ($K_{sv1} = 0.21\%^{-1}$, $f_1 = 0.820$), and the other is an oxygen difficult accessible site ($K_{sv2} = 0.0065\%^{-1}$, $f_2 = 0.180$). The K_{SV1} value of pyrene in poly(dimethylsiloxane) film has previously been reported to be 0.014%$^{-1}$.[6] These results indicate that the PBA chemisorption film is a highly sensitive device for oxygen compared to the other oxygen sensor using pyrene. An important factor for applying the PBA film as an optical oxygen-sensing material is its photostability. To characterize the photostability of the PBA film, the reflectance spectrum of the film was measured after continuous irradiation using a 150 W tungsten lamp on the film for 24 h. Only a small spectrum change was observed, indicating that the PBA film is stable against irradiation.

Experimental

An alumina plate was prepared by the anodic oxidation of an aluminium plate (1.2 × 4.0 cm) in dilute sulfuric acid. A PBA chemisorption film was prepared as follows. An alumina plate was dipped into 0.1 mmol dm^{-3} PBA in an ethanol solution at room temperature for 10 min. After dipping, the plate was washed with water and ethanol several times. After PBA physically adsorbed onto alumina was removed by ultrasonication, the film was dried under vacuum overnight. The fluorescence spectra of the films were measured using a Shimadzu RF5300-PC fluorescence spectrometer with a 150 W xenon lamp as a visible excitation light source. The excitation and emission bandpasses were 5.0 nm. The sample film was mounted at a 45° angle in the quartz cell to minimize the light scatter from the sample and substrate. The oxygen-sensing properties of the PBA film were characterized by the Stern–Volmer quenching constant, K_{SV}, obtained from the following equation: $(I_0/I) - 1 = K_{SV}\,[O_2]$. The K_{SV} value was obtained from a linear plot of $(I_0/I) - 1$ versus $[O_2]$. The experimental details are described in the literature.[13]

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