Highly Sensitive Optical Oxygen Sensing Material: Thin Silica Xerogel Doped with Tris(4,7-diphenyl-1,10-phenanthroline)ruthenium

Sang-Kyung Lee*, Yong Beom Shin, Hyeon-Bong Pyo, and Seon Hee Park
Telecomnunication Basic Research Laboratory, Electronics and Telecommunications Research Institute, 161 Kajong-Dong, Yusong-Gu, Taejon 305-350, Korea

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A highly sensitive optical sensor based on the luminescence quenching of tris(4,7-diphenyl-1,10-phenanthroline)-ruthenium (II) complex (Rudpp) immobilized in a sol–gel-based thin silca xerogel was fabricated. Sensor material was prepared by entrapping it in chemically inert silica using the sol–gel process. The sensor showed good linearity from the modified Stern–Volmer plot. The dynamic response result demonstrated the fast response time of the sensor, less than 10 s. Largely enhanced photostability of the material was also one of the sensor's most promising properties.

For a long time, luminescent transition metal complexes have been used in a variety of areas such as solar energy conversion,[1] electron transfer studies,[2] chemi- and electroluminescent systems,[3,4] binding dynamics of heterogeneous media,[5] and probes of macromolecular structure.[6] Recently, ruthenium(II) complexes are gaining considerable interest as oxygen-sensitive materials in analytical chemistry due to strong visible absorption, efficient luminescence and quenching by oxygen, and relatively long-lived metal to ligand charge transfer (MLCT) excited states.[7,8] For sensor fabrication, the luminescent reagents usually should be immobilized in a matrix in order to prevent a reaction from occurring between the luminescent reagent and the species in the measuring environment. So far, a variety of studies have concentrated on polymer as an optical oxygen sensor matrix.

The sol–gel process, a low-temperature preparation method of ceramic material, is gaining considerable interest because it provides a convenient way to incorporate organic molecules into porous ceramic matrices.[9–11] The relative simplicity of the sol–gel process is also partially responsible for its rapid proliferation. Inorganic supports such as silica offer several advantages over polymer matrices, including chemical inertness, high thermal and photochemical stability as well as negligible swelling, excellent transparency, and low intrinsic luminescence.[12]

More recently, McDonagh et al. have studied ruthenium(II) complex as a sensing reagent for oxygen sensors.[13] They prepared the sensing film by soaking a substrate in a silica sol of ruthenium complex and coating it on a glass substrate. In this letter, we describe a highly sensitive oxygen sensing material, tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) complex (Rudpp)-doped silica xerogel and its optical sensing characteristics.

The dichloride hexahydrate salt form of Rudpp was synthesized by the reported method.[14] Preparation of undoped silica sol was performed by addition of 30 mL (0.135 mol) of tetraethyl orthosilicate (TEOS) to 31 mL of ethanol (0.53 mol). After vigorous stirring for 2 min, a mixture of H_2O and a catalytic amount of nitric acid was added, then stirred for an additional 4 h. The Rudpp-doped silica sample was prepared from the mixture of undoped silica sol and Rudpp aqueous solution (0.01 g of Rudpp in 5 mL of DI water). The final mixture was stirred for an additional 12 h at room temperature and transferred to a home-made acrylate mold (ca. $0.15 \times 1.2 \times 3$ cm^3). At this point, a drop of Triton-X 100 was also added in order to improve homogeneity of silica sol and created a crack-free thin monolith. After a long gelation time of about 2 weeks, the wet gel was aged in the air at room temperature for more than 3 weeks, until 80 % shrinkage occurred, and kept in the dark until use.

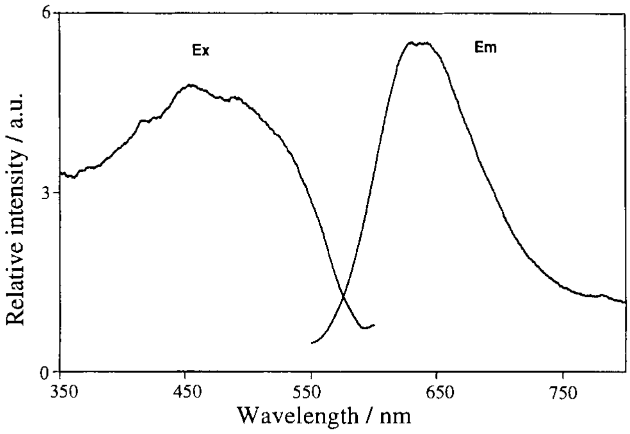

Figure 1. Excitation and emission spectra of Rudpp-doped silica xerogel.

Figure 1 shows the excitation and emission spectra of Rudpp-doped silica monolith. Absorption peak is detected at 454 nm for the silica and is attributed to the MLCT state of Rudpp. The emission band has a maxium of 624 nm. The spectra of aqueous solution and doped xerogel are almost the same, indicating no or very little interaction between Rudpp and silica xerogel matrix. The addition of Triton X-100 also did not affect the optical spectra. The luminescence intensity of the doped sample decreased significantly with the increase of oxygen concentration, indicating that this can be used as a highly sensitive optical oxygen sensing material based on the luminescence quenching by oxygen. In many cases, I_0 / I_{100} (where I_0 and I_{100} are the detected luminescence intensities from the material exposed to 100% nitrogen and 100% oxygen, respectively.) has been an indicative of the degree of luminescence quenching by oxygen and also a simple sensitivity measure for oxygen sensors. The typical I_0 / I_{100} value of Rudpp-doped monolith was > 26, as known from Figure 2. This is one of the best results in the many reports where Rudpp was immobilized in a wide variety of organic and inorganic matrices; the I_0 / I_{100} values of Rudpp immobilized in polystyrene[15], ethylcellulose[15], PVC[15], silicone polymer[15], zeolite[16], silica[16] and sol–gel film[13] are ~ 2.0, 3.0, 3.6, 4.3, 3.5, 4.3 and 8, respectively. It is obvious that the origin of high sensitivity comes from higher porosity of the resulting sol–gel samples than that of the polymer matrices. Compared to the thin film-type materials, the higher luminescence intensity of the samples appears to be easily quenched by oxygen at the expense of response times.

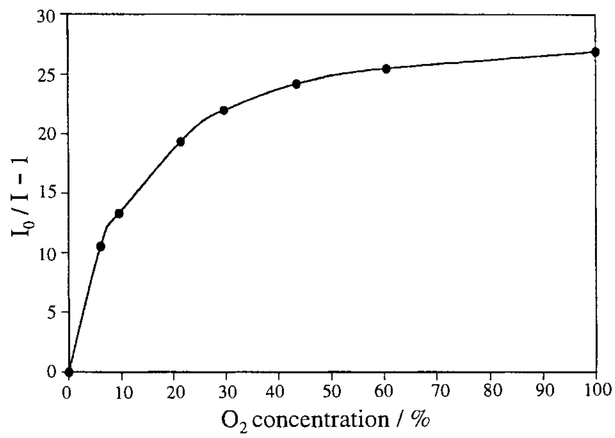

Figure 2. Stern–Volmer plot for Rudpp-doped thin silica xerogel.

Figures 2 is the Stern–Volmer plot,

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

where I_0 and I are luminescence intensities in the absence and in the presence of oxygen concentration, $[O_2]$, respectively and K_{SV} is the Stern–Volmer quenching constant. Like in all of the other reports on optical oxygen sensoring, the Stern–Volmer plots show downward-curvature. In explaining the downward curvature of the Stern-Volmer plot, the possibility of existence of static quenching process was ruled out by the theoretical reason. In this case, the overall quenching accompanied by either static quenching or a transient component in dynamic quenching can result in a quadratic dependence of I_0 / I with $[O_2]$. However, quadratic form from this hypothesis will result in a positive (i.e. upward) curvature. This result may indicate site heterogeneity in which one site is more heavily quenched than the other. According to the two-site model, it is believed that there are heterogeneities in the dye environment i.e., two or more sites with different quenching constants occupied by the Rudpp molecules: quencher-easy accessible and quencher-difficult accessible sites. Therefore, in a case of condensed system the Stern–Volmer plot deviates from linearity because of the different relative contributions which originate from different quenching sites. Hence, the dependence of I_0 / I on the oxygen concentration differs from eq (1):

$$I_0 / I = 1 / [\,\Sigma\{f_i / (1 + K_{SV\,n} [O_2])\}] \qquad (2)$$

where f_i is the fractional contributions to each oxygen accessible site. $K_{SV\,n}$ is the quenching constant for each accessible site. Assuming that there are *k* accessible molecules with the same K_{SV}, then eq (2) can be

$$I_0 / (I_0 - I) = 1 / (f K_{SV}[O_2]) + 1 / f \qquad (3)$$

where, $f = f_i$, for *k* addition. This is the maximum mole fraction of dye molecules that are accessible to oxygen. If only a single class of dye molecules with the same accessibility to oxygen is present, $1/f$ in eq (3) should be 1.

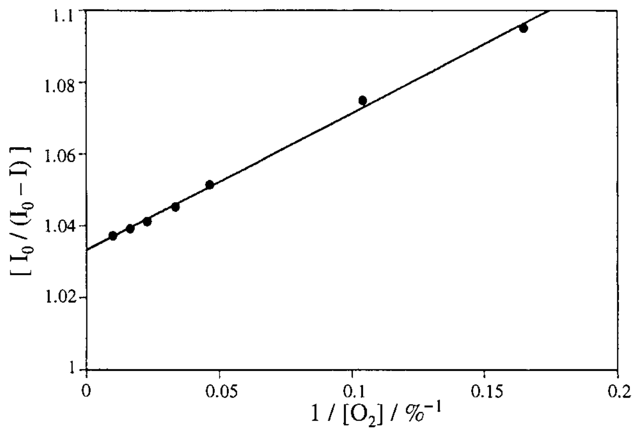

Figure 3. The modified Stern–Volmer plot for Rudpp-doped thin silica xerogel using equation (3).

Figure 3 shows the modified Stern–Volmer plots for the silica-based Rudpp plotted using eq (3). $I_0 / (I_0 - I)$ against $1 / [O_2]$ showed good linearity, which was highly enhanced compared with plot of I_0 / I against $[O_2]$. Regression values, r^2 were > 0.997. In order to obtain the *f* value, the regression line was extrapolated to $1 / [O_2] = 0$. The *f* values are close to unity (0.913) for the silica-based Rudpp.

We also investigated other sensing characteristics of the materials. The response times (t_{90}; 90% of total intensity change to occur) of the samples were within 10 s on going from oxygen to nitrogen and 5 s on going from nitrogen to oxygen. Although it shows response time which is a little slow in comparison with those of the thin film-type sensors, it has high fluorescence intensity and quenching properties by oxygen. Also it still remains the high degree of porosity, making it useful as an optical oxygen sensor. The signal changes were fully reversible and measurement hysterisis was not observed. Little luminescence intensity was decreased by long-term irradiation during measurement (> 12 h).

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