Characterization of Erythrosin B-Doped Sol-Gel Materials for Oxygen Sensing in Aqueous Solutions

M. A. Chan,[1] S. K. Lam,[2] and D. Lo[1,2]

We have studied the luminescence and spectroscopic properties of erythrosin B-doped sol-gel silica in aqueous solutions. Stern-Volmer plot was obtained for the phosphorescence intensity as a function of the dissolved oxygen content. Leaching of the dye molecules from the sol-gel matrix was examined by absorption spectroscopy. That acid-catalysed sol-gel materials leach slowly and based-catalysed sol-gel materials leach rapidly was revealed. Absorption data of the sol-gel materials indicated the existence of two leaching rate constants. Finally we demonstrated that the sol-gel oxygen sensor had a response time faster than 30 ms.

INTRODUCTION

Much research activity has been generated recently in the development of fiberoptic oxygen sensors based on luminescence quenching by oxygen. Most of the optical oxygen sensors make use of fluorophore such as transition-metal complexes (e.g., ruthenium [II] etc.) embedded in polymeric or sol-gel matrices [1–4]. The luminescence lifetime of these transition-metal complexes typically lasts hundreds of ns [3]. Such a short lifetime reduces the sensitivity of the sensor and requires the use of high-speed electronics for signal processing. In this connection, sensors that make use of phosphorescence quenching may allow for higher sensitivity detection and low-cost electronics.

We observed room temperature phosphorescence for a number of dye molecules embedded in sol-gel silica. The phosphorescence lifetime of these dye-doped sol-gel materials lasted for a good fraction of a ms [5]. The phosphorescence quantum yield was 2% [6]. We developed a fiberoptic oxygen sensor based on erythrosin B trapped in sol-gel silica [7]. The oxygen sensing characteristics were studied over the oxygen pressure range from 10^{-6} to 1000 mbar and over a temperature range from -173 to 200°C in gaseous environment [8]. A Stern-Volmer ratio of 123 was observed [8]. Quenching by gaseous oxygen was significant throughout. To meet the application needs of biological and environmental monitoring that require the sensor probe to be in constant contact with aqueous solutions, complete performance characterization in liquids is clearly needed. Performance characterization including leaching study and luminescence quenching for oxygen sensors based on transition-metal complexes in polymer for the detection of dissolved oxygen has been reported [9–11]. However, there appears to be little published result on the performance of phosphorescence oxygen sensors based on sol-gel materials in aqueous solutions. In this paper, we examine the oxygen quenching effect and the leaching of dye molecules of our phosphorescence oxygen sensor in liquid environment.

Using laser excitation, we measured the phosphorescence intensity as a function of the dissolved oxygen in water at room temperature. The Stern-Volmer plot was obtained. In measuring dissolved oxygen in liquids, the sol-gel silica probe was immersed in aqueous solution.

[1] C & C Authentication Laboratory Limited, Hong Kong SAR, China.
[2] Physics Department, The Chinese University of Hong Kong, Shatin, Hong Kong SAR, China.

Because of the porosity of the sol-gel matrix, there is obvious concern over the leaching of the erythrosin B out of the sol-gel silica. With the aim to minimize leaching, samples of erythrosin B trapped in sol-gel silica with different recipes were prepared. A comparison study based on the data from absorption spectroscopy was performed to reveal their leaching rates and the final amount of leaching. The high porosity of the sol-gel matrix gives rise to leaching. At the same time, it reduces the response time of the oxygen sensor. A measurement of the response time of the oxygen sensor using a solenoid valve was made. The phosphorescence quenching was measured to be 30 ms, which was faster than the read-out from a commercial pressure gauge.

PREPARATION OF ACID-BASED AND BASE-BASED OXYGEN SENSOR PROBES

TMOS (tetramethoxysilane), methanol, DI water, and NaOH were mixed under magnetic stirring at room temperature for the preparation of base-catalyzed sensor probes. NaOH was replaced by HCl for acid-catalyzed sensor probes. Details of the sol-gel process can be found in [5,6]. The erythrosin B dye was added to the mixture, and the resulting solution (sol) was casted in acrylic cuvettes, which were then sealed. The concentration of the erythrosin B in the starting solution was 5×10^{-3} mol/L. After the sol gelled, dried and shrunk at room temperature for 2 weeks, they were then baked at 200°C for 24 hr. The ends of multi-mode optical fiber were cleaved and bonded to the silica gel by using PMMA as adhesive, resulting in a fiberoptic sensor probe [8].

EXPERIMENTAL SET-UP

The performance of the oxygen sensor in water was studied with the experimental setup shown in Fig. 1. A pump was used to circulate the water between the test cell and the water bulb. A gas mixture of high-purity nitrogen (99.9%) and high-purity oxygen (99.95%) was injected continuously into the water during the experiment. The desired oxygen content of the water was obtained by controlling the flow rates of the nitrogen and oxygen with the respective mass flow controllers. Both mass flow controllers can control the flow rate over a range from 80–500 standard cubic centimeters per minute (sccm), and the total flow rate was set to be about 400 sccm. When the flow was pure oxygen, the oxygen content in water reached its maximum (100% oxygen saturation), which was determined by the solubility of oxygen

in water at room temperature. Mixed gas flow led to lower dissolved oxygen content. Deionized (DI) water was used for our study, at room temperature, which varied from 21°C to 22°C in all experiments. The optical arrangement and measurement of the photoluminescence were identical with those given in our previous papers [5,6]. A frequency-doubled pulsed Nd-Yag laser was used for excitation. The time-integrated luminescence spectra were taken using an intensified charge-coupled device (ICCD) detector mounted on a 0.3 M spectrograph. A Hitachi spectrophotometer was used for the absorption spectroscopic measurement.

RESULTS AND DISCUSSION

A base-catalysed oxygen probe was placed inside a glass bulb filled with water. The base-catalyzed oxygen probe was preleached (having soaked in water for 3–4 days) before the measurements were taken. Nitrogen flowed continuously into the glass bulb to drive out all the oxygen content inside. Oxygen was then flowed into the bulb to achieve the particular oxygen concentration of the fluid. The ratio of oxygen to nitrogen concentration in the bulb was controlled by the oxygen flow rate. Oxygen was bubbled into the bulb for several hours to attain the desired oxygen concentration. The DI water in the glass bulb of a predetermined dissolved oxygen level was then pumped to the test cell for optical measurement. Delayed luminescence spectra of the oxygen probe at various dissolved oxygen concentrations were taken. The intensity of phosphorescence (at 680 nm) dropped as the oxygen concentration increased (Fig. 2). The flow rate of oxygen used in obtaining the spectra in Fig. 2 was slow (about 50 sccm) so that after 2.5 hr of bubbling the oxygen content was about 5%. Such slow rate was necessary for presenting three spectra on the same scale (Fig. 2). To increase the oxygen content at a fixed time, one needed only to increase the flow rate. A Stern-Volmer (S-V) plot of the phosphorescence is taken against oxygen concentration (in % of oxygen saturation; Fig. 3). The S-V plot shows a mildly non-linear dependency on dissolved oxygen concentration. The S-V ratio is calculated by taking the intensity of phosphorescence peak of the nitrogen saturated DI water as Io. The usefulness of the sol-gel sensor for dissolved oxygen was demonstrated.

In applications in which the probes are immersed in liquids, concern over the leaching of dye out of the probes arises. Leaching tests were thus conducted to investigate the extent of leaching and the effects of leaching on the probes' sensitivity. Two types of probes were fabricated for comparison in the leaching study—the acid-catalyzed
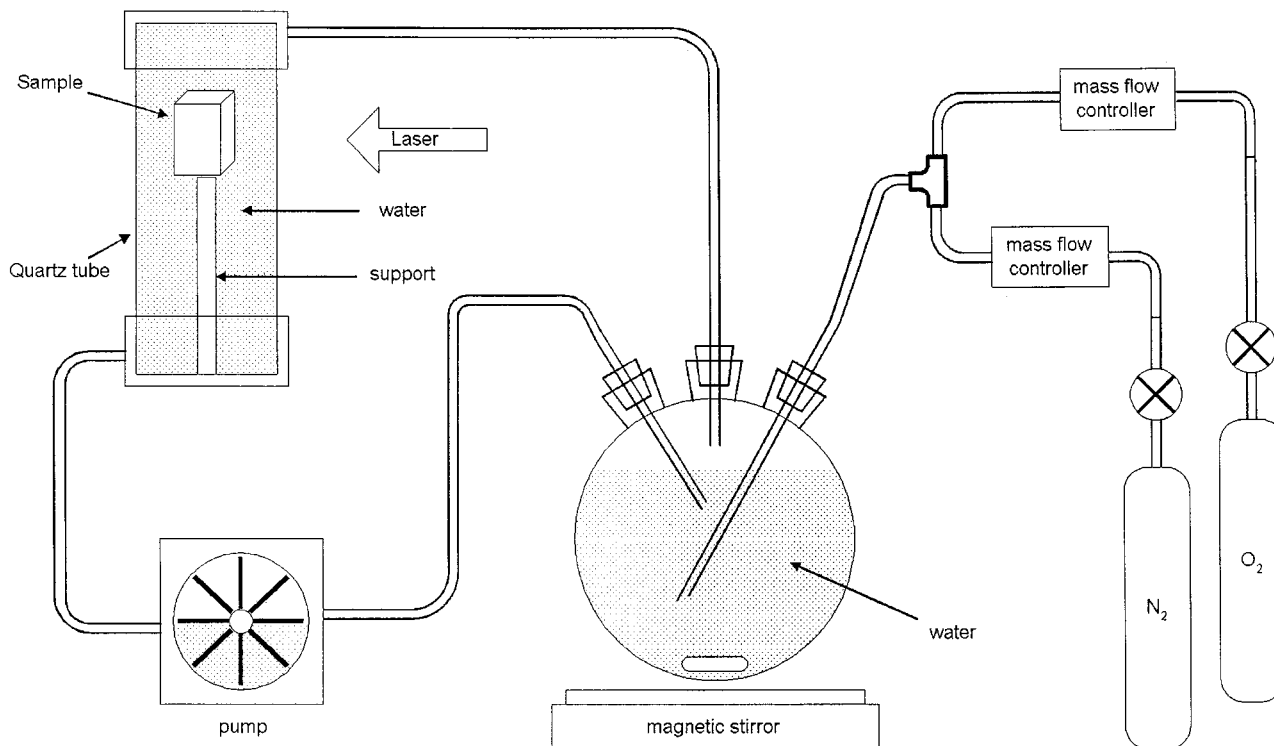
Fig. 1. Experimental setup for sol-gel optical oxygen sensor characterization in aqueous solution.

(pH 1–3) and the base-catalyzed (pH ~11) sol-gel probes. Both types were immersed in 10 mL of DI water and absorption spectra were taken at regular intervals. Fig. 4 shows the absorption spectra of acid-catalyzed probes at four time intervals. The 0-min curve (without immersion in liquid) serves as the baseline. Leaching of dye in acid-catalyzed samples was not significant. After 1 month of soaking in DI water, the magnitude of the absorption peak changed very little. The absorption spectrums showed a two-peak characteristic. The first peak (at wavelength 466 nm) kept fairly constant, but the second peak (at wavelength 491 nm) mildly grew in magnitude with the time of immersion in water. A plot of the peaks as a function of time is shown in Fig. 5. Both peaks showed
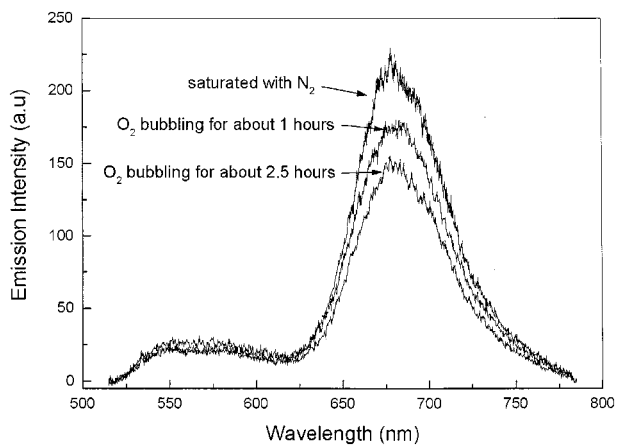

Fig. 2. Luminescence spectra (fluorescence at 550 nm and phosphorescence at 680 nm) of the sol-gel optical oxygen sensor in water at different dissolved oxygen levels.
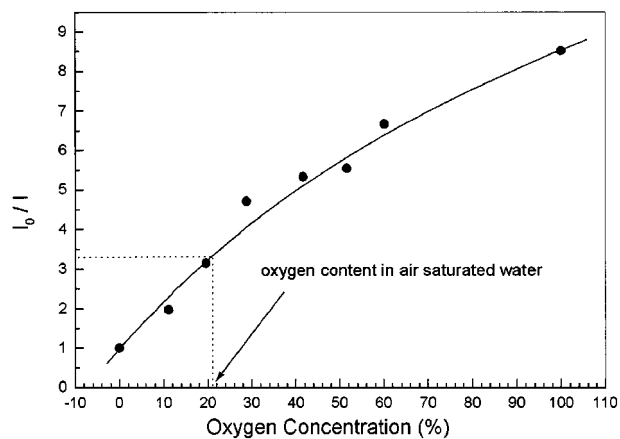

Fig. 3. Stern-Volmer plot of the phosphorescence intensity (at 680 nm) as a function of the percentage of oxygen saturation in water at room temperature.
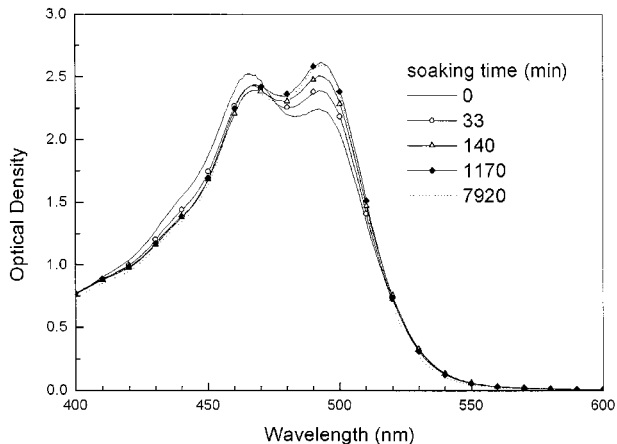
Fig. 4. Absorption spectra of acid-catalyzed sensor probes at various leaching time intervals.

Fig. 6. Absorption spectra of base-catalyzed sensor-probes at various leaching time intervals.

significant change during the first 10 hr of immersion and then plateaued. A shift of the relative magnitude of the two peaks may indicate change in the polarity/polarizability of the microenvironment surrounding the dye molecules.

In contrast to the acid-catalyzed probes, the absorption spectra of the base-catalyzed probes exhibited a single-peak structure. The magnitude of the absorption peak also dropped much more rapidly and the peak position shifted as a function of time. The decrease in the absorption was obviously caused by dye molecules being leached out of the sol-gel matrix. The difference in the observed leaching rates in the acid-catalyzed and in the base-catalyzed sol-gel samples should be correlated to the difference in porosity of the sol-gel samples of different initial pH [12,13]. The peak was red-shifted (from
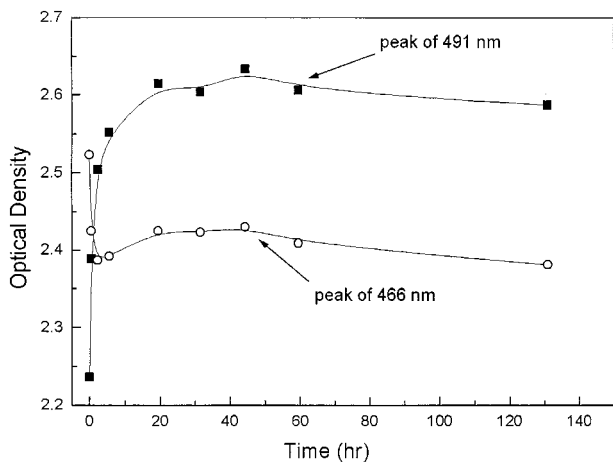
530 nm to 544 nm) as the soaking time of the probes increased (Fig. 6). The shifting of the absorption peak was plotted as a function of soaking time for two sol-gel samples (Fig. 7). Significant shifting occurred after 100 min. of soaking. No shift in wavelength was observed for soaking time over 10000 min. The absorption data for the 530-nm peak was plotted as a function of time in Fig. 8. A double exponential decay function (solid line) provides very good fit for the absorption data (solid squares). Two leaching rate constants can be obtained by fitting the absorption data with a double exponential function with two rate constants: a fast leaching rate, κ_1, of 4353.5 OD/min and a slow leaching rate, κ_2, of 319.1 OD/min. The existence of two decay rate constants suggests that there are two leaching processes, one fast and one slow.

The sol-gel–derived silica matrix has a high porosity. When dye is introduced into the porous structure,

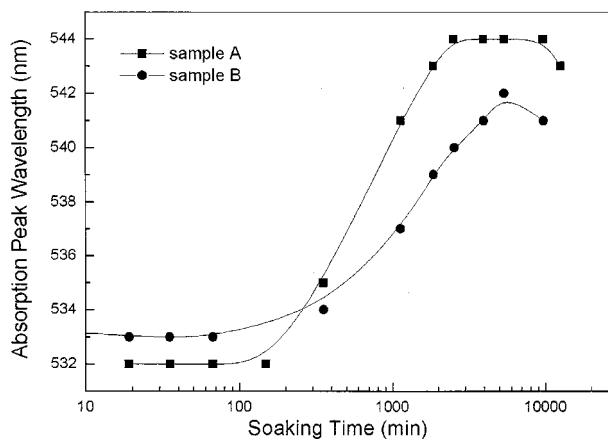**Fig. 5.** Absorption peaks of acid-catalyzed sensor-probes as a function of soaking/leaching time.

Fig. 7. Red-shifting of the absorption peak of the base-catalyzed sensor probes.
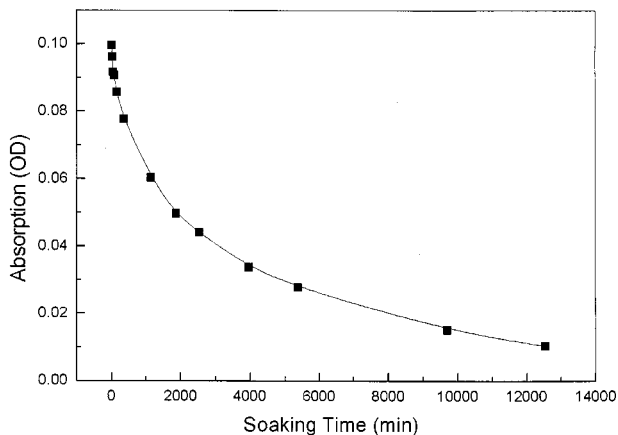
Fig. 8. Plot of the peak of absorption (in optical density O.D.) as a function of time for base-catalysed sensor-probes

some of the dye molecules may become chemically bonded with the sol-gel matrix. Other dye molecules may simply diffuse into and become lodged inside the pores of the matrix. When the oxygen probes are immersed in water, dye lodged in porous structure of the sol-gel will be leached out faster and those that are chemically bonded to the sol-gel matrix may be leached out more slowly. The time derivative of Fig. 8 (Fig. 9) reveals the leaching rate of base-based oxygen probes. Leaching was rapid initially but slowed quickly as time progressed. Leaching was hardly detectable after 100 hr. The final optical density at 0.01 indicated that there was still a sufficient concentration of dye in the sol-gel matrix for oxygen detection. Leaching ceased when an equilibrium between the leaching and diffusion processes in the dye/sol-gel silica/water composite system was established. The important point is that the leaching rate decreases as time
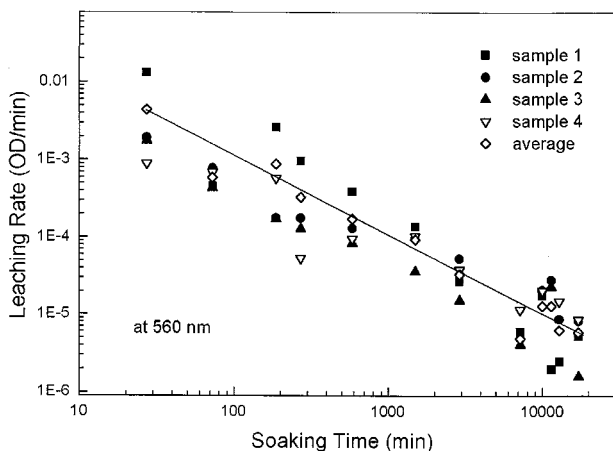

Fig. 9. Leaching rate of base-catalyzed sensor probes as a function of time. The solid line is a linear fit of the data.

increases and the leaching eventually ceases. Therefore, the negative effect of leaching on the sensor performance can be neutralized by presoaking the probes in water before actual measurements are taken. In applications in which the oxygen probe is required to remain in liquid for extended periods of time or high-sensitivity sensing is needed, acid-catalyzed oxygen probes may be more suitable. However base-catalyzed sol-gel is still of interest because the strong absorption in the green (see Fig. 6) allows the use of inexpensive light sources. By contrast, acid-catalyzed sol-gel has strong absorption in the blue range (see Fig. 4). A more expensive blue light source will be needed.

We wish to point out that in a previous study [7], the Stern-Volmer (S-V) plot of the phosphorescence data over the pressure range of 10^{-6} to 1000 mbar also show a non-linear dependence on oxygen pressure. Fitting by the two-site model [14,15] showed very good agreement with experimental data [7]. It was concluded that the dye molecules resided in two quenching sites. In the present study, the two leaching rate constants observed in our absorption experiments may add further evidence to the S-V data that indicated the dye molecules indeed resided in two sites.

In a previous work [8] we made a rough estimate of the response time of our oxygen sensor. Oxygen was introduced into the chamber by manually turning on a mechanical valve. The result of the experiment showed that the response time of our oxygen sensor was approximately 1 sec. In this study, a SMC VX3115 electrical solenoid valve with a switching time (on) of about 30 ms was employed to create a step change in oxygen concentration. A continuous wave argon ion laser operating at 514 nm was used to irradiate the sensor probe. The luminescence near the peak position ($\sim$695 nm) was monitored with a photomultiplier in combination with a digital oscilloscope. The pressure of the chamber was about 10^{-5} mbar before the valve was switched on. The steady state pressure of the chamber was set to be about 2 mbar after the valve was switched on. For comparison, a commercial pressure gauge was also installed on the chamber to monitor the variation of the pressure. The responses of this gauge and our optical sensor were measured simultaneously and plotted in Fig. 10. Our optical oxygen sensor clearly had a quicker response than the readout from the commercial pressure gauge. The change of the phosphorescence signal (from 0 to 80%) in response to the abrupt change in oxygen concentration was 30 ms, which was in fact the switching time of the solenoid valve.

In this study we characterized our oxygen sensor in liquid environment. It was demonstrated that our oxygen
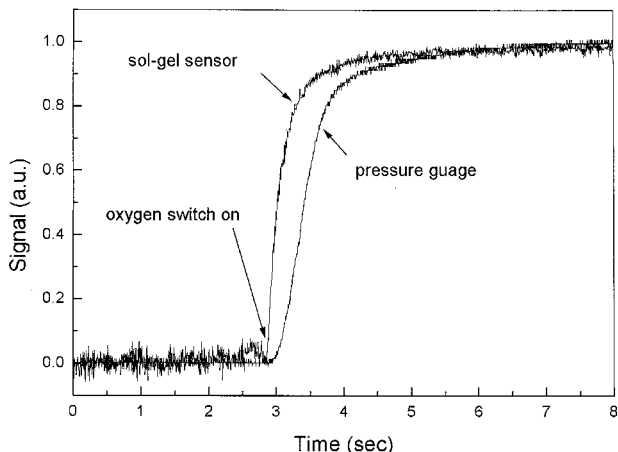
Fig. 10. Time response of the sol-gel optical oxygen sensor and the pressure gauge.

sensor was capable of detecting dissolved oxygen. When oxygen in liquid diffused into our dye-doped silica gel probe, it quenched phosphorescence. A Stern-Volmer plot of the phosphorescence signal was obtained. Leaching of dye from the probes was investigated to determine the suitability of the probes for oxygen measurements in liquid. Acid-catalyzed and base-catalyzed sol-gel probes were fabricated and their characteristics were compared. Last but not least, the response time of the oxygen sensor was measured and was found to be faster than a commercially available pressure gauge.

ACKNOWLEDGMENT

REFERENCES

1. I. Kilmant, M. Kuhl, R. N. Glud, and G. Holst (1997) Optical measurement of oxygen and temperature in microscale: strategies and biological applications, *Sensors Actuators B* **38–39**, 29–37.
2. B. D. MacCraith, C. M. McDonagh, G. O'Keefe, A. K. McEvoy. T. Butler, and F. R. Sheridan (1995) Sol-gel coatings for optical sensors and biosensors, *Sensors Actuators B* **29**, 51–59.
3. P. Hartmann and W. Trettnak (1996) Effects of Polymer Matrices on calibration functions of luminescent oxygen sensors based on porphyrin ketone complexes, *Anal. Chem.* **68**, 2615–2620.
4. A. Mills (1999) Response characteristics of optical sensors for oxygen: a model based on a distribution in τ_0 and k_q, *Analyst* **124**, 1309–1314.
5. S. K. Lam and D. Lo (1997) Time-resolved spectroscopic study of phosphorescence and delayed fluorescence of dyes in silica-gel glasses, *Chem. Phys. Lett.* **281**, 35–43.
6. S. K. Lam, E. Namdas, D. Lo (1998) Effects of oxygen and temperature on phosphorescence and delayed fluorescence of erythrosine B trapped in sol-gel silica, *J. Photochem. Photobiol. A Chem* **118**, 25–30.
7. S. K. Lam, M. A. Chan, D. Lo (2001) Characterization of phosphorescence oxygen sensor based on erythrosine B in sol-gel silica in wide pressure and temperature ranges, *Sensors Actuators B* **73**, 135–141.
8. M. A. Chan, J. L. Lawless, S. K. Lam, and D. Lo (2000) Fiber optic oxygen sensor based on phosphorescence quenching of erythrosine B trapped in silica-gel glasses, *Anal. Chim. Acta* **408**, 33–37.
9. O. Wolfbeis (1991) *Fiber Optic Chemical and Biosensors*. Vol. 2. CRC Press, Boca Raton, FL.
10. P. C. Hauser and S. S. Tan (1993) All solid state instrument for fluorescence-based chemical sensors, *Analyst* **118**, 991–995.
11. Z. Rosenzweig and R. Kopelman (1995) Development of a submicrometer optical fiber oxygens sensor, *Anal. Chem.* **67**, 2650–2654.
12. M. Yamane (1988) in *Sol-gel Technology for Thin Films, Fibers, Preforms, Electronics and Specialty Shapes* Chapter 10. L. C. Klein (Ed.) Noyes Publications, Park Ridge, New Jersey.
13. K. S. Lam, D. Lo, and K. H. Wong (1995) Sol-gel silica laser tunable in the blue, *Appl. Optics* **34**, 3380–3383.
14. E. R. Carraway, J. N. Demas, B. A. Degraff, and J. R. Bacon (1991) Photophysics and photo-chemistry of oxygen sensors based on luminescent transitional metal complexes, *Anal. Chem.* **63**, 337–342.
15. L. Sacksteder, J. N. Demas, and B. A. Degraff (1993) Design of oxygen sensors based on quenching of luminescent metal complexes–effect of ligand size on heterogeneity, *Anal. Chem.* **65**, 3480–3483.