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A new portable optical sensor for dual sensing of temperature and oxygen

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ABSTRACT

A new simple, low-cost technique for the fabrication of a portable optical sensor for the dual sensing of temperature and oxygen is described. The sensing film is based on the oxygen sensing dye platinum tetrakis pentrafluoropheny porphine (PtTFPP) and 7-amino-4-trifluoromethyl coumarin (AFC) embedded in tetraethylorthosilane (TEOS)/*n*-octyltriethoxysilane (Octyl-triEOS) composite xerogels. The feasibility of coating a color sensor with the sensing film to fabricate a portable optical dual sensing device is investigated. The temperature and oxygen indicators can both be excited with an LED at a wavelength 405 nm. The portable optical dual sensor has been tested with regard to monitoring different temperatures and oxygen concentrations, the oxygen response of which is quantified in terms of the ratio I_{N_2}/I_{O_2}, where I_{N_2} and I_{O_2} represent the detected phosphorescence intensities in pure nitrogen and pure oxygen environments, respectively. The experimental results reveal that the portable optical oxygen sensor has a response of $I_{N_2}/I_{100O_2} = 1.75$. In addition, our results show that the luminescence properties of the temperature sensor are independent of the presence of the oxygen sensor, and have a uniquely good linear response in the 25–65 °C range. Finally, the oxygen sensing scheme presented in this work is intended for use in temperature compensation, and the portable optical dual sensor is a cost-effective alternative to traditional electrochemical-based temperature and oxygen sensors and provides a platform for other optically based sensors.

1. Introduction

The determination of multiple parameters simultaneously can be approached by optical sensors, which have advantages over other sensing principles [1]. One interesting example of multianalyte sensing is offered by temperature and oxygen because it is important to know the temperature in the luminescent sensing of oxygen, since quenching by oxygen always is highly temperature dependent [2]; consequently, there is a need for optical sensors that measure both oxygen and temperature.

In optical oxygen sensors, oxygen concentration is evaluated based upon the reduction in luminescence intensity caused by oxygen quenching of the emitting state. Optical oxygen sensors consist of an oxygen-sensitive dye embedded in a matrix with a high permeability to oxygen. Many researchers have reported that sol–gel derived glass is a suitable matrix material for oxygen, since it has high oxygen permeability, good mechanical and chemical stability, and superior optical clarity [3–5]. Furthermore, it has been shown that the use of organically modified silicate (ORMOSIL) matrixes improves the response and sensitivity of ruthenium-based oxygen sensors [6–8]. ORMOSILs can accommodate and disperse analyte-sensitive dyes, and also have a porous structure, which is essential for improving the sensor response. On the other hand, longer-lived, fluorescent oxygen-sensitive dyes are needed to improve the sensitivity of oxygen sensors. Phosphorescent porphyrins of platinum [9–11] such as platinum tetrakis pentrafluoropheny porphine (PtTFPP), have the desirable features of longer lifetimes, convenient excitation and emission wavelengths with large Stokes shifts (100–170 nm), and a reasonable luminescence quantum yield. Recently, our lab developed fiber-optic oxygen sensors based on 3,3,3-trifluoropropyltrimethoxysilane (TFP-TriMOS) or *n*-propyltrimethoxysilane (*n*-propyl-TriMOS)/tetraethylorthosilane (TEOS)/*n*-octyltriethoxysilane (Octyl-triEOS) composite xerogel doped with platinum complexes. The resulting fiber-optic oxygen sensors have linear Stern–Volmer plots and show better performance than existing oxygen sensors based on ruthenium dye immobilized in various sol–gel matrixes [12].

Fluorescent temperature sensing and luminescence quenching are two common approaches for the optical determination of temperature [13–15]. In the latter approach, an excited fluorophore

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Table 1
Comparison between various optical dual sensors reported in the literature and the one proposed in this work.

Temperature probe	OXYGEN probe	λ_{ex} (nm)	λ_{em} (nm)	T range	O_2 range	signal	Sensor Type	Ref.
$La_2O_2S:Eu^{3+}$ phosphor	PtTFPP	337	650 (Pt complex) 514 (T phosphor)	5–50 °C	0–20%	Luminescence decay time	Polymer film	[16]
Ru-phen microbeads	PtTFPP	465	580 (Ru complex) 650 (Pt complex)	10–50 °C	0–20%	Luminescence intensity	Polymer film	[17]
Magnesium fluoro-germanate	$Ru(dpp)_3^{2+}$	470	610 (Ru complex) 650 (T phosphor)	25–65 °C	0–100%	Luminescence decay time	Ormosil film	[18]
Eu-β-diketonate complex	PtTFPP lactone	390	615 (Eu complex) 738 (Pt complex)	5–45 °C	0–20%	Luminescence intensity and decay time	Polymer film	[19]
Europium (III) microbeads	PdTFPP microbeads	405	615 (Eu complex) 670 (Pd complex)	1–70 °C	0–20%	Luminescence decay time	Hydrogel film	[20]
Eudapt	Rudpp	400	610 (Ru complex) 615 (Pt complex)	10–70 °C	0–21%	Luminescence decay time	Polymer film	[21]
$Eu(tta)_3dpbt$ microbeads	PtTFPP microbeads	405	615 (Eu complex) 650 (Pt complex)	1–50 °C	1–40%	Luminescence intensity and decay time	Hydrogel film	[22]
Ru-phen in PAN film	C_{70} in EC/OS film	470	580 (Ru complex) 670-70 (C_{70})	0–120 °C	0–0.005%	Luminescence intensity and decay time	Polymer film	[23]
Epoxy glue	PtTFPP	380	497 (Epoxy glue) 650 (Pt complex)	22–73 °C	0–100%	Luminescence Intensity	Optical fiber	[24]
Core–shell CdSe QDs-silica nanoparticles	PtTFPP	409	532 (CdSe QDs) 648 (Pt complex)	0–100 °C	0–100%	Luminescence Intensity	Optical fiber	[25]
CF	PtTFPP	405	532 (CF) 650 (Pt complex)	25–66 °C	0–100%	Luminescence Intensity	Optical fiber	[26]
Ru-phen microbeads	PdTFPP microbeads	470 (Ru) 525 (Pd)	580 (Ru complex) 670 (Pd complex)	1–60 °C	0–100%	Luminescence decay time	Hydrogel film	[27]
Ru-phen microbeads	PtTFPP	475 (Ru) 505 (Pt)	580 (Ru complex) 650 (Pt complex)	0–50 °C	0–20 kPa	Luminescence decay time	Optical fiber	[28]
AFC	PtTFPP	405	487 (AFC) 650 (Pt complex)	25–66 °C	0–100%	Luminescence Intensity	Color sensor	Present Study

molecule can drop back to its ground state through radiation emission (luminescence) or through collision with another molecule. The luminescence emission and collision processes are in equilibrium for a system at a certain temperature. A change in temperature alters the frequency of collision, and thus shifts the equilibrium of the two processes, resulting in changes in the luminescence intensity and lifetime, which has allowed for optical temperature sensors to be developed based on this characteristic [13–15].

Most dual sensors of oxygen and temperature reported so far have the following attributes in common: a single excitation wavelength [16–26] or two different wavelengths [27,28] in the visible region, luminescence intensity or decay time as the analytical signal, a signal matrix to disperse both temperature and oxygen probes, and working rages from 0 to 120 °C over oxygen concentration in the 0–100% range (refer to Table 1). Although these optical dual sensors of oxygen and temperature (O_2/T) have been successfully developed, they are still relatively large which make them inconvenient for field use. In addition, the cost and complexity of these sensing systems are higher since software and personal computers are required for the control and data acquisition. As such, the development of simple, low-cost and portable optical temperature and oxygen sensors is still needed. In this work, we report on the development of a new simple, small and low cost portable optical dual sensor. Our sensing platform is based on PtTFPP/AFC sequestered within a porous sol–gel-derived film that is coated directly onto the active area of the color sensor. The sensing film is excited by an LED, after which the PtTFPP and AFC emissions are directly detected with an inexpensive color sensor. The proposed portable optical dual sensor enables stable luminescence via a simple technique at low cost, for temperature and oxygen in the gaseous phase.

2. Theory section

The mechanism successfully applied in fluorescence intensity and decay-time sensing is fluorescence quenching. This well-known phenomenon is employed in many conventional fluorescence sensors, in which the interaction of the analyte with the indicator occurs when the latter is in the excited state. The effect of the interaction is a radiationless relaxation of the indicator to its ground state. Thus the presence of the analyte quenches the fluorescence emission, giving a lower intensity, but also a shorter decay time. Commonly, the luminophore quenching effect depends on several factors; however, in the simplest scenario of a luminophore in a homogeneous microenvironment, quenching takes place in accordance with the Stern–Volmer equation [29]:

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

where I_0 and I represent the steady-state luminescence intensities in the absence and presence, respectively, of the quencher (O_2 in the current case); K_{SV} is the Stern–Volmer quenching constant; and $[O_2]$ is the oxygen concentration. In the ideal case, a plot of I_0/I versus $[O_2]$ is linear with a slope equal to K_{SV} and an intercept of unity, allowing the application of a simple single-point sensor calibration scheme. Thus, by monitoring the luminescence intensity, one can determine the amount of oxygen present in a given sample.

Eq. (1) describes the idealized behavior of a luminophore with a single excited-state lifetime in a homogeneous environment undergoing dynamic quenching. The Stern–Volmer plot of luminescence quenching of the actual sensor is nonlinear due to the presence of both static and dynamic quenching. Demas et al. reported a multisite model for a sensing film with various oxygen-accessible sites [30]. In this model, the oxygen molecule can exist at