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Dual sensing of oxygen and temperature using quantum dots and a ruthenium complex

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ARTICLE INFO

Article history:

Received 4 August 2007

Received in revised form

30 October 2007

Accepted 2 November 2007

Published on line 26 November 2007

Keywords:

Quantum dots

Luminescence

Optical fiber

Oxygen sensors

Temperature

ABSTRACT

A scheme for the simultaneous determination of oxygen and temperature using quantum dots and a ruthenium complex is demonstrated. The luminescent complex [Ru(II)-tris(4,7-diphenyl-1,10-phenanthroline)]²⁺ is immobilized in a non-hydrolytic sol-gel matrix and used as the oxygen sensor. The temperature information is provided by the luminescent emission of core-shell CdSe-ZnS semiconductor nanocrystals immobilized in the same material. Measurements of oxygen and temperature could be performed with associated errors of $\pm 2\%$ of oxygen concentration and $\pm 1^\circ\text{C}$, respectively. In addition, it is shown that while the dye luminescence intensity is quenched both by oxygen and temperature, the nanocrystals luminescent emission responds only to temperature. Results presented demonstrate that the combined luminescence response allows the simultaneous assessment of both parameters using a single optical fiber system. In particular, it was shown that a 10% error in the measured oxygen concentration, induced by a change in the sample temperature, could be compensated using the nanocrystals temperature information and a correction function.

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1. Introduction

Luminescence based techniques can provide a fast and sensitive detection of a variety of parameters and are a preferred tool for biochemical sensing applications [1,2]. Recent technological advances in different areas have concurred for the feasibility of performing luminescence spectroscopy in the tip of an optical fiber. In this context, advanced analytical tools for remote and real time detection, with minimum intrusion and immunity to electromagnetic interference can be fabricated. Presently, luminescent optical fibers sensors have been demonstrated for a wide variety of chemical and biological species [2,3]. Some of these devices can even be found as commercial products (e.g. O₂, pH). However, in spite

of great advances, some limitations still arise. In particular, luminescence mechanisms are temperature dependent and, therefore, the univocal determination of the analyte is only possible if temperature is known at the measurement site. Although in many cases standard electronic methods can be used to provide the optical sensor with a temperature reference, this situation must often be avoided when operation takes place in remote locations, in explosive environments or in the presence of high magnetic fields. In such cases, an all-optical configuration must be applied. While the use of luminescence to measure temperature is a well-established technique, the simultaneous detection of a chemical species and temperature, using two luminescent indicators, is not an easy task. Cross sensitivity and spectral overlap can

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doi:10.1016/j.aca.2007.11.008

strongly increase system complexity and hinder its performance [4–6].

Liao et al. used the excited state lifetimes of the phosphorescence emission of an alexandrite crystal together with platinum tetraphenylporphyrin to detect oxygen and temperature with the same fiber probe. By using a frequency domain signal processing scheme they were able to separately acquire both parameters with good accuracy and reduced cross sensitivity [7]. In this scheme, however, at least one order of magnitude difference in lifetime is needed to decode the two combined luminescent responses in the frequency domain. In addition, interference filters must be used to reject excitation noise. A diversity of other dual sensing solutions have been reported; the field of luminescent pressure sensitive paints, where a strategy is needed to discriminate pressure changes from temperature changes in wind tunnel applications, for instance, has been particularly productive in producing dual sensing strategies [8–13]. The important problem of multiple parameter chemical sensing has also been recently reviewed by Wolfbeis et al. [14].

Some interesting examples of recent solutions include the synthesis of a new composite luminescent material allowing dual sensing of oxygen and temperature by lifetime methods [15]. A temperature sensing dye, Ru(II)-tris-1,10-phenantroline, was made oxygen insensitive by being incorporated in microparticles of poly(acrylonitrile), a polymer with extremely low permeability to this gas. For sensing oxygen, on the other hand, microparticles of poly(styrene-co-acrylonitrile), with high oxygen permeability, were doped with fluorinated palladium(II) tetraphenylporphyrin. Samples of both microparticles were finally suspended in polyurethane hydrogel producing a dual parameter sensing membrane. The authors demonstrated that simultaneous and independent measurement of oxygen and temperature could be performed using the new composite material both in the intensity and lifetime domains. In spite of good results, the system optimal performance required a complex combination of excitation and emission filters. In addition, the chemical procedures for fabrication of membranes are relatively complex. The application of this technique with different indicators may require completely different immobilization procedures. In a different approach, MacCraith et al. took advantage of sensor cross sensitivity to implement dual parameter sensing [16]. By incorporating the same sensing dye in sol-gel matrices with different oxygen permeability, membranes with a differentiated oxygen and temperature sensitivities could be obtained. By numerical methods the information of both parameters could then be discriminated. Such an approach introduces interesting possibilities but it requires a very accurate control of the membrane fabrication processes. In spite of great progresses, most commercial sensors still rely on conventional technologies for temperature measurement and, therefore, all-optical solutions for simultaneous detection of temperature and a biochemical parameter are highly desirable.

Quantum dots (QD), are nanometer sized particles of semiconductor material with potential to solve many problems of luminescence based sensors [17]. Due to quantum confinement of the charge carriers, a strong enhancement of their luminescent properties is observed which can be tuned by simply controlling the size of the nanocrystals. When

compared with traditional dyes, QD show narrow emission spectrum, a broad absorption band, high quantum yields, increased photostability and the ability to tune their properties by changing the nanocrystals size or composition [18,19]. Available in a wide range of wavelengths, from blue to infrared, they have a great potential for multiplexing applications [20]. Their outstanding properties have been explored in a variety of biochemical sensing and imaging applications [21–23]. QD have recently been reported as suitable luminescent temperature probes. The luminescence intensity, peak emission wavelength and spectral width, change proportionally and reversibly with temperature making them a versatile solution for sensing applications [24].

The dynamic quenching of luminescence is the most widely used optical oxygen sensing mechanism. When excited by blue LEDs, organometallic ruthenium complexes present luminescence emission which is strongly quenched by oxygen. Their immobilization in sol-gel hosts is straightforward, making them suitable for optical fiber sensing applications [25–27]. The behavior of both the luminescence intensity, I , and the excited state lifetime, τ , of these sensing dyes in the presence of oxygen can be described by the Stern–Volmer (SV) equation [28]:

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV} [O_2] \quad (1)$$

where I_0 and τ_0 are the unquenched luminescence intensity and lifetime, respectively, K_{SV} is the SV constant, and $[O_2]$ is the oxygen concentration. This equation establishes a linear relation between I_0/I and $[O_2]$, which can be used for calibration purposes. When the sensing dye is immobilized in a solid material, however, heterogeneous distribution within the host matrix can lead to deviations from this behavior due to the existence of sites with different oxygen accessibilities. Such situations must be described by a two site-model [28].

Temperature has a dual effect on the sensor calibration function. Increasing temperature introduces higher probability of non-radiative transitions, thus decreasing the luminescence yield and the excited state lifetime. This behavior can be accurately described by an Arrhenius type model [29]. In the physiological temperature range, however, a good approximation can be obtained using a linear transfer function [30]. In addition, temperature also affects the quenching dynamics by changing the diffusion coefficient of oxygen into the sensing membrane. Therefore, K_{SV} is also temperature dependent. Typically, increased temperature results in higher quenching efficiency and, therefore, higher values of K_{SV} . This way, an independent temperature measurement is needed, in order to univocally retrieve the oxygen concentration from luminescence measurements.

In this work, we propose the combination of luminescent CdSe–ZnS nanocrystals with an oxygen sensitive dye to obtain a sensor whose spectral characteristics allows simultaneous measurement of oxygen and temperature. The temperature dependent spectral shift of the QD emission allows to perform self-referenced intensity based temperature measurements. Results are presented demonstrating the feasibility of this concept. Due to the ability of tuning the QD emission wavelength by simply changing the nanocrystals size, this scheme

can be applied in combination with any luminescent indicator, avoiding spectral overlap and using the same immobilization chemistry.

2. Experimental

2.1. Materials

CdSe–ZnS core–shell nanocrystals, were purchased from Nanoco, and [Ru(dpp)]-tris(4,7-diphenyl-1,10-phenanthroline)chloride hexahydrate was purchased from Sigma. QD with peak emission around 520 nm were chosen to avoid overlap with the Ru(dpp) luminescence (595 nm). According to the manufacturer, the nanocrystals average size was 2.4 nm with a size dispersion of 5%. This was in agreement with the observed peak emission at 520 nm and FWHM of 30 nm. The nanocrystals were used to dope a solution of a non-hydrolytic sol–gel with a concentration of 5 mg/ml. Details of sol–gel preparation and coating procedures are described elsewhere [31]. After stirring for 6–8 h, to obtain a homogeneous mixture, the solution was filtered through a 0.1 μm filter. Thin films and bulk samples with different thickness were made by spin coating (1500 rpm) or molding in silicone. All the samples were subject to thermal annealing under a nitrogen flux. The exact baking times and temperatures (ranging from 120 °C to 200 °C) depended on the sample thickness. After the thermal treatment, a dense glass material was formed that provided the QD further protection from oxidation.

A similar procedure was used to encapsulate Ru(dpp) (doping concentration of 2.5 g/L) in the same non-hydrolytic sol–gel. Thin films with thickness of 50 μm were obtained by spin coating. Curing was performed at lower temperature (<100 °C) to obtain membranes with higher oxygen permeability in comparison with the QD films.

2.2. Instrumentation

To demonstrate the feasibility of the proposed concept, oxygen sensing membranes doped with Ru(dpp) and reference membranes doped with QD were interrogated using the setup of Fig. 1. A silica optical fiber coupler, with 50/50 coupling ratio, core/cladding diameter of 550/600 μm , respectively, was used to perform excitation and collection of luminescence. A blue LED (470 nm from Nichia) followed by a short pass filter (cutoff 500 nm), was used as excitation source. The sensing samples were placed on top of a peltier cooling device, which allowed changing their temperature, inside a gas chamber with controlled atmosphere. Collection of luminescence was performed by the distal ends of the coupler outputs. Detection was then made using a CCD spectrometer (USB 2000 Ocean Optics) with additional filtering (long pass, cutoff 500 nm).

2.3. Procedures

We applied QD to provide an independent temperature measurement. In order to render the nanocrystals emission independent from oxygen concentration, core shell QD were immobilized in a non-hydrolytic sol–gel material with low oxygen permeability. Core–shell nanoparticles are made of a

CdSe core coated with a layer of ZnS. By coating the dots with a semiconductor material of higher bandgap, passivation of surface defects is achieved, resulting in increased quantum yields [32]. In addition, the protective shell also prevents irreversible oxidation. The resulting sensing membrane displays a luminescence emission which is independent of oxygen concentration. Conversely, it has been shown that both the luminescence intensity and the peak emission wavelength of QD, have a linear and reversible dependence on temperature in the environmental range. When temperature is increased, luminescence intensity decreases, due to increase of non-radiative transitions. The peak wavelength, on the other hand, is shifted towards longer wavelengths, due to expansion of the crystalline lattice inducing a decrease in the material bandgap energy [33]. Either effect can be used to obtain temperature information. However, simple intensity measurements are prone to error due to optical power fluctuations. In a previous work we have demonstrated a detection scheme allowing self-referenced temperature measurements with QD [34]. It involves detection of two signals, A and B, corresponding to two narrow spectral windows on opposite sides of the emission spectrum, and subsequent processing according to $S_{\text{QD}} = (A - B)/(A + B)$. Due to the presence of a wavelength shift S_{QD} is proportional to temperature and independent of the system optical power level.

Dedicated software allowed implementation of signal processing on the detected spectral outputs. In particular, it was possible to define which spectral windows were acquired. This way, for detection of the Ru(dpp) luminescent emission, the CCD output ranging from 560 nm to 650 nm was integrated. For detection of the QD luminescence emission, the interval 510–540 nm was considered instead. Finally, for detection of signals A, and B, the intervals 510–515 and 535–540 nm, were considered, respectively. The setup in Fig. 1 was used to submit the samples to controlled changes of temperature and oxygen concentration. After sensor calibration, and adequate signal processing, which will be described in the next section, it was possible to perform simultaneous measurement of both parameters.

3. Results and discussion

In order to obtain the sensor calibration curves, two samples were subjected to controlled and alternate changes of oxygen concentration and temperature. For oxygen sensing, a glass slide coated with a 50 μm thick thin film doped with Ru(dpp) was used. The temperature reference was provided by a 1 mm thick bulk glass sample, doped with CdSe–ZnS QD. Both samples had approximately 1 cm \times 1 cm. The sensors were placed in closed vicinity and on top of the peltier, and were excited/interrogated by the fiber coupler outputs as depicted in Fig. 1.

In Fig. 2, the spectral outputs of the combined response can be observed. Fig. 2a shows the behavior of QD and Ru(dpp), at a constant temperature, when subjected to different atmospheres (oxygen content ranging from 0% to 100%). Conversely, in Fig. 2b, it is shown the behavior of the same samples, in a 20.9% oxygen atmosphere, when subjected to temperatures ranging from 16 °C to 40 °C.

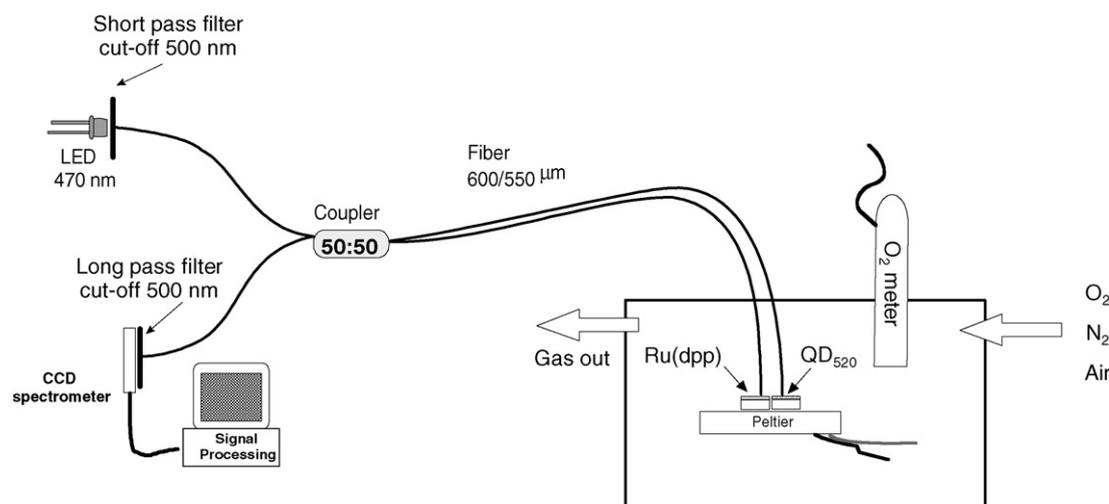


Fig. 1 – Experimental setup used for simultaneous determination of oxygen and temperature.

It can be observed that while oxygen strongly quenches the luminescence of Ru(dpp), it has no effect on the QD luminescence. This was the case when the relative luminescence intensities of Ru(dpp) and QD were similar. However, in situations where Ru(dpp) has a much stronger signal, the

small spectral overlap can originate crosstalk. In the present scheme, this situation was avoided by balancing the luminescent outputs of both samples, controlling film thickness and doping concentrations. Temperature, on the other hand, strongly affects both luminescence signals. Both samples are strongly quenched, with a wavelength shift being observed in the QD emission. From these results, the sensor calibration curves could be obtained. The regression analysis data, corresponding to the different linear fits used for calibration, are given in Table 1.

The obtained SV plot is slightly non-linear. Nevertheless, a reasonable linear fit could be obtained given by

$$\frac{I_0}{I([O_2])} = 1.01 + 0.008 [O_2] \quad (2)$$

which was used as an approximation ($R^2 = 0.997$, additional regression data is given in row (i) of Table 1). Both the luminescence intensity and peak wavelength of the QD have shown to be insensitive to O_2 concentration; fluctuations observed over the full concentration range were smaller than 0.6% for the intensity response, and smaller than 3% for the wavelength response (corresponding to the processed output S_{QD}). These residual fluctuations are partly due to a small thermal drift, which took place during the tests. Both samples showed a linear dependence on temperature which is compared in Fig. 3 (the corresponding regression data can be seen in Table 1, in row (ii) for Ru(dpp) and in row (iii) for QD).

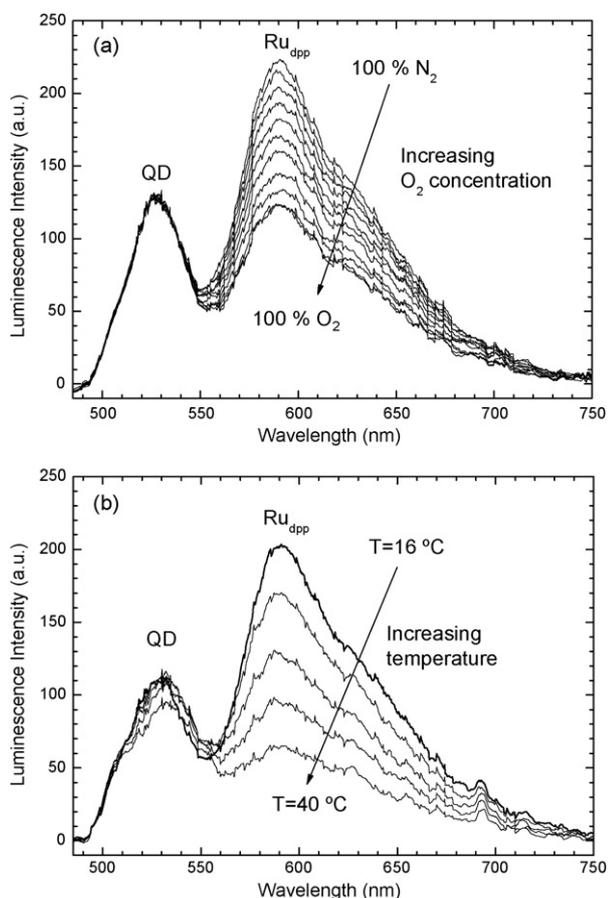


Fig. 2 – Spectral response of sensing samples subjected to (a) changes of oxygen concentration and (b) temperature changes.

Table 1 – Regression analysis data corresponding to the linear fits used in the calibration of the dual sensor

	m	Δm	b	Δb	R^2
(i) $I_0/I [O_2]$	0.0080	0.0001	1.01	0.01	0.997
(ii) $I_{Ru} [T]$	-0.032	0.001	1.65	0.03	0.988
(iii) $S_{QD} [T]$	0.0068	0.0002	-0.21	0.01	0.992

(i) Stern–Volmer response of Ru(dpp); (ii) temperature response of Ru(dpp); (iii) wavelength response of QD.

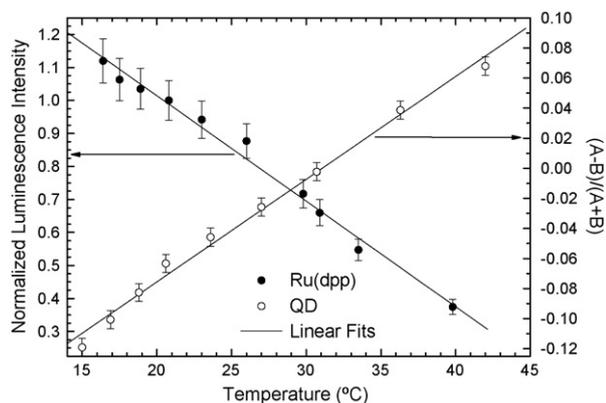


Fig. 3 – Response of the QD and Ru(bpy) signals to changes in temperature.

From the statistical data obtained with the regression analysis of the calibration curves the resolution of both oxygen and temperature sensor could be estimated. The oxygen measurements had an associated error of $\pm 2\%$ for oxygen concentration while for temperature this value was $\pm 1^\circ\text{C}$. These results may seem poor as compared with previous achievements; nevertheless, the poor performance is mainly related with the reduced signal-to-noise-ratio (SNR). The main reason for this was due to the fact that the luminescence collecting efficiency of the extrinsic configuration used is very small. In previous works, the use of the same sensing materials applied to intrinsic fiber probes or large fiber bundles allowed us to increase SNR and obtain a minimum detectable variation of 0.1% oxygen concentration [35] and 0.3°C [34]. Therefore, there is room for improvement using intrinsic fiber probes and laser excitation. Nevertheless, the results obtained with the extrinsic probes are acceptable for the purpose of demonstrating the principle of

simultaneous oxygen and temperature measurement using QD.

By using the calibration data, a simple test was made to assess the capability of the system for simultaneous measurement. The sensing samples were subjected to successive cycles of air and nitrogen. Initially this was done at a slightly elevated temperature (around 24°C), at $t = 360\text{ s}$, however, the temperature was lowered to room values (around 20°C). The resulting measurements can be seen in Fig. 4. Fig. 4a shows the oxygen concentration as measured by the luminescence of Ru(dpp). While at ambient temperature accurate oxygen concentrations of 20.9% (air) and 0% (N_2) were measured, at a higher temperature, the retrieved oxygen concentrations are of 30% (air) and 10% (N_2) showing the deleterious effect of temperature. Fig. 4b gives the temperature information recovered by the QD processed signal, clearly showing the applied temperature step and some thermal drift of the peltier. In order to obtain an accurate oxygen measurement, this information was then used to correct the measured luminescence intensity of Ru(dpp) for the effect of temperature.

The signal processing steps to obtain the corrected oxygen and temperature measurements can be described as follows: in a first step, the calibration functions given in Table 1, were used to obtain the raw oxygen and temperature values. While the temperature obtained from the QD wavelength shift yielded a correct value, the same was not true for the measured oxygen concentration. Accurate oxygen concentrations could only be obtained if the temperature of the sample coincided with the temperature at which the sensor was calibrated (approximately 20°C). This way, at higher or lower temperature a second step was necessary to obtain the corrected oxygen concentrations. In this second step, the temperature value retrieved by the QD was inserted into the calibration curve for the Ru(dpp) temperature response (given in row ii of Table 1) allowing to obtain a temperature compensated luminescence intensity value. Finally, in a third step, by introducing

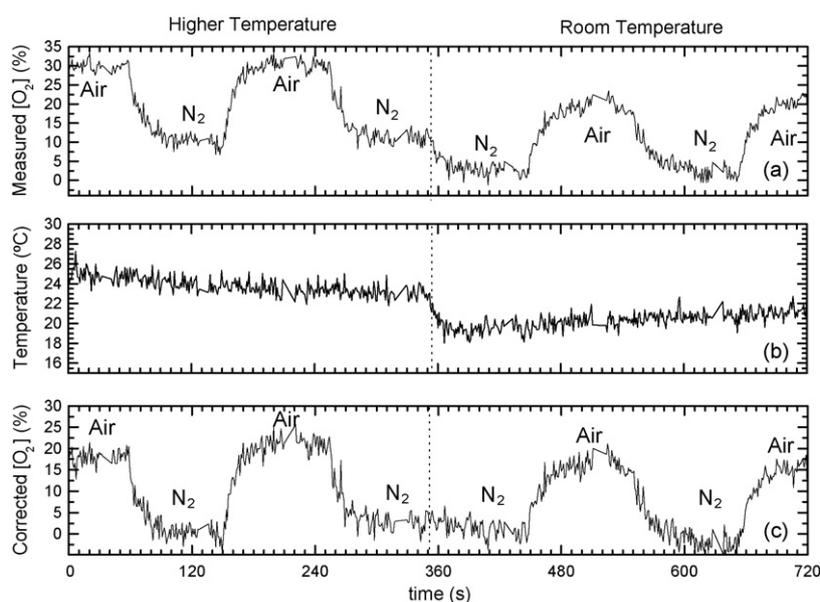


Fig. 4 – Sensor output when subjected to simultaneous change of oxygen and temperature: (a) O_2 measured by Ru(dpp); (b) temperature measured by QD; (c) temperature compensated O_2 measurement.

the corrected intensity value in the SV calibration function, an accurate oxygen measurement could then be obtained in the whole temperature range (Fig. 4c).

Due to the use of extrinsic probes combined with LED excitation, the system SNR was very poor and in the present configuration this system cannot compete with existing single sensors in terms of precision, accuracy, and resolution. Nevertheless, as previously discussed, using intrinsic probes together with laser excitation will improve significantly the system performance, making it an interesting solution.

Because a small temperature step was applied, for simplicity the effect of temperature in the value of K_{SV} was not accounted for, and the value of the SV constant obtained at 20 °C was used on all tests. Due to this approximation, and to the non-homogeneous heating of the test chamber, a small temperature induced drift can still be observed in the corrected signal. Nevertheless, full characterization of $K_{SV}(T)$, together with optimization of the temperature control system will surely allow for temperature independent oxygen sensing in a broader temperature range. In this regard, it has been shown, in previous works, that QD are responsive to temperature in a very large temperature range [24] that goes from a few Kelvin to slightly below their synthesis temperature (200–300 °C). The sol-gel matrix, on the other hand, can cope with most of this range as it was cured at 200 °C. Therefore, the limitation on the operation range of this scheme would be imposed by the organic dye. Nevertheless, it has been shown that some sol-gel immobilized ruthenium dyes can operate in a broad range of temperatures that goes up to 300 °C [36].

Another potential problem is related with the instability of some sol-gel matrices that can induce changes in the observed SV constants and, therefore, compromise long-term validity of calibration curves. In this particular case, the use of non-hydrolytic sol-gel materials together with relatively high annealing temperatures contributed to an enhanced stability [31]. Nevertheless, no long-term studies were performed so far. While stability problems can be circumvented by sensor recalibration prior to each use, this is not a desirable situation in long-term applications. Therefore, the study of long-term behavior of these sensing materials will be addressed in future works.

The proposed scheme cannot account for photobleaching of the sensing dye. However, because a low permeability matrix was used, photodegradation of the Ru(dpp) was very small. It has already been demonstrated that, in spite of introducing a reduced sensitivity, doped non-hydrolytic sol-gel matrixes can provide for very photostable oxygen and temperature sensors [34,37].

When higher sensitivity is necessary, more permeable hydrolytic membranes can be used instead. In such cases, the effect of photodegradation on the Ru(dpp) emission can be avoided using well known lifetime based methods [38]. Preliminary results have shown that the sol-gel encapsulated nanocrystals have a lifetime in the 10–20 ns range, meaning that the lifetime response of QD can be well discriminated from the microsecond lifetimes of ruthenium complexes. Therefore, in principle, the temperature compensation scheme proposed here can also be applied using frequency domain interrogation.

4. Conclusion

An all-optical scheme for simultaneous determination of oxygen and temperature was demonstrated. Results obtained showed the feasibility of using QD in combination with a ruthenium dye, both immobilized in a sol-gel host, to design dual parameter sensing membranes. Due to the versatility of QD and the sol-gel process, the demonstrated principles can be applied to any luminescence-based sensor, using the same coating chemistry. Presently, the coating of single fiber probes with these sensing membranes is under investigation. This will allow the implementation of miniaturized multiparameter sensing heads with great potential for medical and environmental use.

Acknowledgments

César Maule acknowledges the support from the Marie Curie Early stage research training network, funded by European Commission under the contract MEST-CT-2005-020353. The financial support of FCT is also acknowledged (POCI/AMB/56132/2004).

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