analytica chimica acta 606 (2008) 223–229

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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 ±2% of oxygen concentration and ±1 °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.

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. O_2, 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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0003-2670/$ – see front matter
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 problematic 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]:

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}\,[O_2] \tag{1}$$

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