



Layer-by-Layer assembly of a water-insoluble platinum complex for optical fiber oxygen sensors



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ARTICLE INFO

Article history:

Received 5 August 2014

Received in revised form 3 October 2014

Accepted 9 October 2014

Available online 22 October 2014

Keywords:

Metallo-porphyrin

Luminescence

Layer-by-Layer

Oxygen sensing

Plastic cladding optical fiber

ABSTRACT

An optical fiber sensor to measure gaseous oxygen is presented in this work. The device is based on platinum tetrakis pentafluorophenylporphyrine (PtTFPP), a reagent that shows a luminescence at 650 nm when it is illuminated at 390 nm. The emitted signal decreases as oxygen concentrations increases. This sensing material is deposited onto a cleaved-end plastic silica cladding (PCS) fiber by means of the Layer-by-Layer method (LbL). The experimental set up has been also optimized in terms of the dimensions of the optical components in order to get the highest signal level. The response of the sensor has been studied in terms of different oxygen concentrations as well as dynamic conditions. The resulting sensor shows a reversible and linear behavior for oxygen concentrations from 0% up to 100% ($R^2 = 0.9991$). The initial inconvenience derived by the non-water solubility of PtTFPP and its challenging deposition by LbL has been overcome by preparing an emulsion.

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1. Introduction

The development of oxygen sensors has focused the working lines of many researchers due to the important applications that require them. Some of the most relevant ones belong to the fields of biomedicine, food industry, air quality or safety at work [1]. Available electronic sensors for this aim are based on electric potentials, so that a reference electrode is needed [2]; furthermore, an electric signal is required, which makes them not recommended for hazardous environments with a high inflammability risk (such as the chemical industry) [2]. This background has motivated the development of optical devices as an alternative to overcome these drawbacks. In this manner, sensing materials whose optical properties vary in the presence of oxygen have been used to implement oxygen sensors. The general working principle is based on the measurement of these parameters, such as the color, which is known as colorimetry [3]: the color is registered by a Charge-Couple Device (CCD) camera and it can be parameterized, for instance in Commission Internationale d'Éclairage L^*a^*b (CIElab) space, so that the oxygen concentration can be determined [4].

A relevant type of sensing materials used to develop optical oxygen sensors shows a luminescence emission that decreases as the target gas concentration increases: this effect is known as quenching, and it is reversible in most cases [1]. The straightforward implementation consists of monitoring this emission in time to determine the oxygen concentration [5,6]. Although there are other kinds of measurements based on the emission lifetime which are more robust, a more complex instrumentation is needed [7,8]. This type of compounds is required to show a strong luminescence emission, a significant Stokes shift, as well as photo and temporal stability. Metallo-porphyrins meet these requirements [9]: the porphyrin backbone is present in several important biomolecules such as hemoglobin or chlorophyll, both of them related with gas interaction [10]. Different materials are available: each one is characterized by the chains attached to the backbone, although the optical properties are mainly determined by the metallic atom core. The target gas gets coordinated with it, producing the transduction. Their complex chemical structure make them non soluble in water. The material used in this work is platinum tetrakis pentafluorophenylporphyrine (PtTFPP), which has been successfully used to develop oxygen sensors thanks to its excellent features such as long lifetime emission, photo stability or significant Stokes shift (around 250 nm) just to mention the most relevant ones [11].

Although colorimetry with CCD camera has been already used with metallo-porphyrins [12], the transduction could be also controlled by an optical fiber. In fact, the exciting light can be coupled into the fiber to illuminate the sensing material, as well as the

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emission signal is collected into it and guided back toward the receptor. The system can be simplified and made more robust if the compound is directly attached to the fiber, specifically onto a cleaved ended pigtail [13]. This intrinsic architecture allows taking advantage of the features that optical fiber offers [14]: low dimensions, light weight, multiplexation of different sensors, and electromagnetic immunity. Moreover, optical fiber is a passive element, so that no electrical feeding is required, which is very important in oxygen applications related to dangerous environments. The challenge when implementing this type of devices is the deposition of the sensing film onto the fiber due to its reduced dimensions and passive nature (it is made of silica). Some methods used so far are Langmuir–Blodgett [15] or dip coating [16,17], but the resulting sensors have shown a low reproducibility when the sensing material has to be deposited at the end of the fiber [18]. In this context, Layer-by-Layer (LbL) method allows films to be deposited (and even designed) at nanometric scale. This procedure is basically based on the electrostatic assembly of molecules that show opposite electrical charge densities, which is not affected either by the dimensions or geometry of the substrate. One of the standard requirements for the LbL deposition is that the material to be deposited has to be soluble in water, which initially, makes the LbL technique incompatible with many of oxygen sensing materials, for instance, PtTFPP.

In order to get advantage of the synergy between PtTFPP, optical fiber and LbL method, this work presents an oxygen sensor prepared with these three elements. The initial incompatibility between the sensing material and LbL can be overcome using a PtTFPP emulsion, which would allow the deposition of PtTFPP by LbL. To the best of our knowledge, this is the first time that PtTFPP is deposited by means of the Layer-by-Layer technique.

2. Materials and methods

2.1. Sensing material

The reagent employed in this work shows a luminescence emission that is affected by the presence of oxygen. The product belongs to the category of porphyrins, which are molecules with a metallic transition atom in its core that gets coordinated with the target gas, in this case, molecular oxygen. Typically, Ruthenium complexes have been used to detect this gas, as well as Palladium and Platinum materials. The material used has a Pt core, and its absorption spectrum shows a significant peak at 391 nm, as well as another two with lower amplitudes at 505 nm and 545 nm respectively; on the other hand, the material has a luminescence emission centered at 650 nm, so that its Stokes shift is around 260 nm, which is a relevant value. Moreover, the product offers a good temporal and chemical stability [19]. All these features make PtTFPP an excellent material to develop oxygen sensors.

Luminescence materials are divided in two groups depending on the lifetime of the emission: if it is in the ns or μ s range, the phenomenon is known as fluorescence; in the case it is longer up to ms, it is called phosphorescence. When preparing sensors, materials with long lifetime emissions are preferred, which is the case of PtTFPP [20,21]. The transduction takes place when the oxygen molecules quench the luminescence emission: once the sensing material reaches its excited state when it is illuminated at 390 nm, the gas molecules quench the emission. In this manner, the intensity, as well as the lifetime, depends on the oxygen concentration. Considering a uniform environment, the quenching effect can be modeled by Stern–Vollmer equation:

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

where I_0 is the intensity with no oxygen, I the value when the quencher is present, K_{SV} is the Stern–Volmer constant and $[O_2]$ is the gas concentration. This expression shows that there is a linear relationship between both intensities; the equation can be also expressed in terms of the emission lifetime [22].

2.2. Sensor construction process

The chemical structure of the sensing material determines its insolubility in water. Therefore, PtTFPP has been typically deposited with methods not based on water solutions. Moreover, the resulting film doped with the sensing material has to meet some requirements that allow oxygen to be properly adsorbed/deadsorbed: the film should be as thin as possible in a way that the interaction takes place close to the substrate interface; moreover, it should be porous to make easier the diffusion of the gas, and so, it should show a good oxygen permeability. Furthermore, a hydrophobic nature is also desirable in order to prevent any interaction with water vapor. So far, the methods most used to develop sensors with PtTFPP are plastic based matrices (prepared with polyvinyl chloride or polystyrene) or sol gel [23–25]. The physicochemical characteristics of this type of matrices meet the requirements exposed before, although they are difficult to combine with optical fiber due to the reduced dimensions of this substrate. Furthermore, it is difficult to obtain an acceptable reproducibility when the sensing film has to be deposited onto the extreme of a fiber.

In this context, Layer-by-Layer method is a technique firstly presented by Iler in the 1960s decade [26] and rediscovered by Decher at the 90s. It is basically based on the assembly of molecules by electrostatic attraction to construct films on the nanometric scale [27]. The procedure requires reagents that show opposite superficial electrical charge, so that they get assembled. Typically, polymers that become ions when dissolved in water are used, and therefore they are known as polyelectrolytes (polycations and polyanions respectively). The substrate has to be dipped alternately into each solution for a certain time, so that the molecules get assembled due to the electrostatic attraction, forming a bilayer. These steps can be repeated as many times as required. The density charge, known as ionization degree, affects the electrostatic attraction between polyelectrolytes and has an effect on the properties of the resulting films. There are some polymers whose ionization degree can be modified by altering the pH of the solution, which are known as weak polyelectrolytes [28,29]. In this manner, the morphology of the nanofilm can be defined depending on the degree of ionization of the polymers: important parameters such roughness or thickness of the sensing layer can be controlled depending on the final requirements. Moreover, LbL can be applied to substrates independently of their morphology: therefore, several optical fiber sensors have been developed previously following this procedure [30–33]. Finally, it is also relevant to highlight that LbL is performed at room temperature, which offers an important advantage compared to other methods.

If a sensing material is to be deposited with LbL method, it is usually added to one of the polyelectrolyte solutions: thus, the reagent has to be soluble in water and as a consequence, to show a superficial density charge as well [34]. This is not the case of PtTFPP: as it was mentioned before, it is not soluble in water due to its chemical structure. This is the reason why no sensors prepared with LbL based on this material are reported. This inconvenience has been overcome by using micelles: actually, other kinds of water non-soluble molecules have been successfully deposited with LbL following this approach [35]. The idea consists of firstly dissolving the reagent in a solvent less polar than water, such as acetone [36]; thereafter, mixture is added to a surfactant solution. In this manner, the surfactant molecules surround the sensing material ones with their polar heads pointing out, which constitutes a micelle

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