Optimization of Optical Fiber Oxygen Sensors based on Metalloporphyrins Following Layer-by-Layer method

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Sensors based on the luminescent complex platinum tetrakis pentrafluorophenyporphine (PtTFPP) have been prepared by depositing this material onto a plastic-clad silica (PCS) optical fiber. The construction is performed in terms of Layer-by-Layer (LbL) method: the features of the sensors are studied in terms of the concentration of the sensing material and the thickness of the sensing film. The sensors are illuminated with a LED centered at 400 nm, so that the emission of the sensing compound (at 648 nm) is recorded by a spectrometer. A tradeoff is required between the concentration and thickness of the sensing layer, looking for both the sensitivity and kinetics of the response are optimal. The best results obtained offer a signal change around 8 times when the O_2 concentration varies from 0% up to 21 %, with a response time of 24 seconds and a recovery time of 6 seconds.

Motivation and results

The detection and quantification of oxygen sensing is relevant in several fields such as food industry or biomedicine. On the other hand, the features that optical fiber sensors show for gas sensing applications have focused the attention of many researches to this topic. In this background, Layer-by-Layer technique (LbL) offers good results to deposit reagents: the parameters of the construction process can be set to meet the requirements of the final application. Metalloporphyrins are materials used to detect oxygen: they have a high chemical and thermal robustness [2]. This product is not soluble in water, which is a requirement in the LbL method. This inconvenience is overcome by preparing an emulsion of the sensing material with a surfactant that preserves its optical properties [3] (see Figure 1.A). In this manner, it can be deposited with LbL.

This work studies both the sensitivity and kinetics of sensors with different two different concentration of the sensing material: 0.04 mg/mL (concentration A) and 0.8 mg/mL (concentration B). The sensors are prepared with a cleaved ended PCS fiber, onto which the material is deposited [4]. The LbL is an iterative procedure: a construction cycle is known as bilayer, so that the thickness of the sensing film (in the nanometer scale) is expressed in terms of the number of bilayers deposited.

Figure 1.B illustrates the emission peak (21% O_2) registered for the two concentrations and the different number of bilayers: in the case of concentration A, the signal increases with the thickness, which is not the observed case with concentration B. For the first concentration, the sensing material density is lower, so with more layers, more luminescence is couple into the fiber. However, for concentration B the peak decreases along the process: it is because the film gets too thick and optical losses increases significantly. The higher signal level is recorded with 2 and 4 bilayers for concentration B.

In order to check the performance of the sensors, they were exposed to cycles of O_2concentrations between 0% and 21%. The emission peak was registered to evaluate the sensitivity and kinetics of the distinct devices. Results are exposed in Figure 2. It is important to highlight that in every case the response is repetitive and the base line level is recovered. Results are summarized in Table 1 and in Table 2. In the case of concentration A, the sensitivity increases with the number of bilayers; response and recovery times are not affected by the number of bilayers, so the thickness is so low that does not affect it. In the case of concentration B, the highest sensitivity is observed with 4 bilayers. The kinetics get worse with more deposited bilayers: the sensing film is too thick and the oxygen needs more time to get adsorpted de adsorpted. Anyway, the best device in terms of sensitivity and response / recovery times is the one obtained with concentration B and 4 bilayers. This work highlights the great potentiality of LbL method to prepare oxygen sensors even with immiscible products, and show how the construction parameters define the response of the final device.

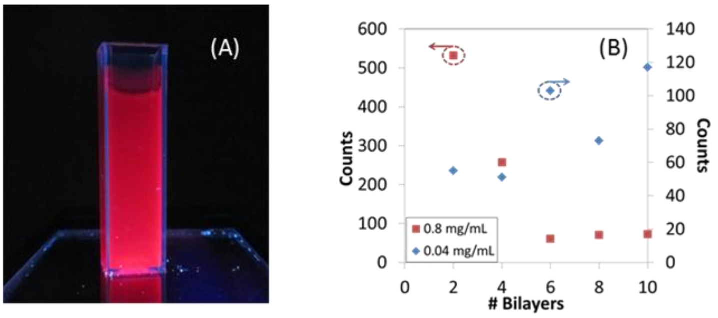

Figure 1. (A) Emission of the metalloporphyrin emulsion when illuminated with an UV lamp; (B) Characteristic spectrum of the material deposited onto the fiber and interrogated with a LED at 400nm.

References

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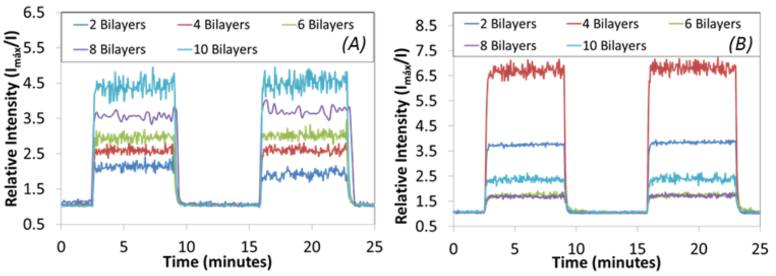

Figure 2. Dynamic responses of the sensors depending on the number of bilayers deposited with concentration (A) and (B). Cycles are set between 0% O_2 (baseline) and 21% O_2.

Concentration A (0.04 mg/ml Pt-TFPP)				
#Bilayers	I_{max} (counts)	Dynamic Range	$T_{response}$ (s)	$T_{recovery}$ (s)
2	54.68	2.18	30	9
4	51.01	2.57	27	9
6	103.16	2.98	27	6
8	73.76	3.56	24	12
10	117.91	5.11	24	6

Table 1. Response parameters of the sensors prepared with Concentration A depending on the number of bilayers deposited onto the fiber.

Concentration B (0.8 mg/ml Pt-TFPP)				
#Bilayers	I_{max} (counts)	Dynamic Range	$T_{response}$ (s)	$T_{recovery}$ (s)
2	532.22	4	18	9
4	258.31	7.55	24	6
6	61.29	1.91	39	18
8	71.53	1.86	27	27
10	73.29	2.65	39	33

Table 2. Response parameters of the sensors prepared with Concentration A depending on the number of bilayers deposited onto the fiber.