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ساخت و مشخصه یابی لایه لومینوفور حساس به اکسیژن

فاطمه آبشاری، سارا دربای

دانشکده فنی مهندسی دانشگاه تربیت مدرس

چکیده- در این کار تحقیقاتی روش ساخت لایه لومینوفور برای حسگر نوری گاز اکسیژن پیشنهاد شده و مورد بررسی قرار می‌گیرد. در این روش تلاش شده تا بیشترین نفوذپذیری ملکول های اکسیژن در لایه حسگر متخلخل و بهترین عملکرد خاموش‌سازی نشانگرهای نوری اکسیژن بدست آید. تصاویر FE-SEM ثبت شده از لایه حسگر پیشنهادی نشان می‌دهد که روزنه هایی با قطر متوسط ۱,۸ میکرومتر بصورت یکنواخت در سرتاسر لایه ایجاد شده است. همچنین اندازه‌گیری طیف نشری فتولومینسانس از لایه ایجاد شده در حضور و عدم حضور اکسیژن نشان‌دهنده کاهش قابل توجه شدت طیف نشری در محدوده نور قرمز در اثر حضور گاز اکسیژن است. در واقع حضور گاز اکسیژن باعث خاموش‌سازی نشان‌گرهای نوری موجود در لایه حسگر می‌گردد.

کلید واژه- فتولومینسانس، حسگر نوری گاز اکسیژن، عملکرد خاموشی، ماتریس پلیمری متخلخل.

Fabrication and Characterization of Oxygen Sensitive Luminophore Layer

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Abstract- In this paper we propose a method to fabricate the luminophore layer for an optical oxygen sensor to gain the maximum permeability of oxygen molecules into the sensing layer as well as the optimum quenching mechanism by selecting the appropriate matrix layer and the Oxygen Sensing Probe (OSP). We show the FE-SEM images of the resulting sensing layer that indicate the porosity of the layer with average pore diameter of ≈1.8 µm. Furthermore, we measure the Photoluminescence (PL) emission of the resulting sensing layer either in the presence or in the absence of O_2, which shows a significant reduction in the PL emission peak intensity that is attributed to the quenching mechanism due to the presence of oxygen.

Keywords: Photoluminescence, Optical oxygen sensor, Quenching mechanism, porous polymer matrix

1. Introduction

Oxygen sensing have become an interesting topic of recent studies due to its vast applications in different industries, e.g. to adjust the combustion process and improve the efficiency in power plants, or to reduce the possibility of explosion in coal mines. Moreover, oxygen concentration plays a crucial rule in human health and lack of oxygen in living environment can cause damage to the lives of all living creatures. According to the standards, the allowable range of oxygen concentration in the environment is 10%-20%. Thus, acceptable degree of sensitivity for the designed oxygen sensors is of great importance.

The early oxygen detecting systems were mostly zirconia electrochemical sensors, which are still commonly used in industry. The major drawback of these kinds of sensors is their limited operating lifetime and high cost of maintenance and calibration. In contrast, optical oxygen sensors take advantage of higher accuracy and longer lifetime without the need for maintenance [1]. Moreover, it is possible to build them in very small dimensions, e.g. on an optical fiber. Among optical methods of oxygen sensing, luminescent oxygen sensors based on quenching mechanism of oxygen sensitive probes (OSPs) have gained much attention recently [2-6].

In luminescent oxygen sensors, the luminophore layer is composed of an oxygen-sensitive probe (OSP) whose luminescence properties change in the presence of O_2, and a polymer matrix that acts as a host to the probe and determines the permeability of oxygen molecules. In this work, we propose a method of fabricating the luminophore layer to gain the maximum permeability of oxygen molecules in the matrix as well as the optimum quenching mechanism by selecting the appropriate matrix layer and the OSP.

2. Experimental Methods

2.1. Materials and Fabrication of the Luminophore Layer

PtOEP (98%), polystyrene (Mw~192,000) and chloroform (≥99.5%) were used as the OSP, the polymer matrix and the solvent, respectively. The solid sensing layer was prepared by mixing PtOEP and PS with a weight ratio of 1:40. To prepare a porous sensing layers, PEG (Mw ~1000 from Alfa Aesar, USA) was added into the mixtures of PtOEP and PS to obtain 1:36:4 PtOEP-PS-PEG weight ratios. Then, the prepared polymer was dissolved in chloroform to obtain solutions with a concentration of 2.68 (wt%).

The schematic description of the casting process of the oxygen sensing layer is depicted in Fig. 1. The prepared polymer solution was dispensed in 60 mm × 15 mm glass petri dish and then was dried inside a fume hood under ambient air conditions for about 20 min. After this step, the flexible layer was immersed in deionized (DI) water and placed in an ultrasonic bath to remove the remaining PEG. Finally, the resulting sensing layer, together with their glass mold, was put in the refrigerator for about 12 hours to be stabilized.

2.2. Measurement Instruments

Field-emission scanning electron microscopy (FE-SEM) was used to analyse the thickness and morphology of the resulting oxygen layers. The transmittance of the sensing layer was measured using a fiber-coupled UV–Vis-NIR spectrophotometer. For this purpose, the light emitted from a green laser with peak wavelength at 532 nm is illuminated onto the layer as the excitation light source, and the transmitted light was collected at the other side of the layer using a fiber. The sensing layer is placed inside a chamber that can either be vacuumed or filled with different gases. Fig. 2 shows the designed chamber

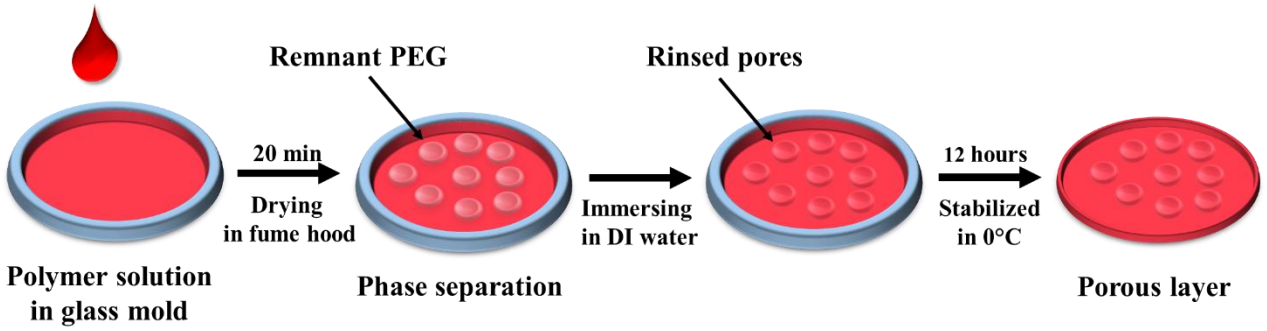

Fig. 1: Schematic description of oxygen sensing layer fabrication

with two optical ports for laser and detector, and two vents to apply gas flow.

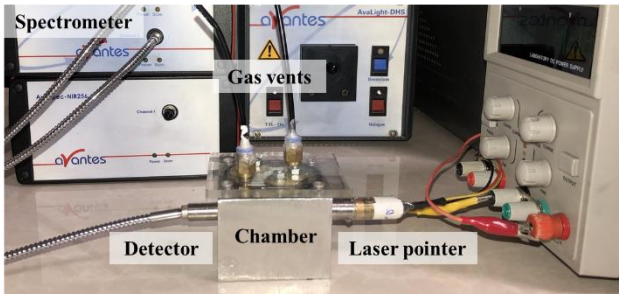

Fig. 2: Optical setup for PL measurements

3. Results and Discussion

3.1. Morphology of the sensing layer

The top views of the resulting porous sensing layer, imaged by FE-SEM with ×1000 and ×6000 magnification factors are shown in Fig. 3(a) and 3(b). It is observable from these figures that the porous layer is successfully achieved with average pore diameter of ≈1.8 µm. The cross sections of the same layer with ×1500 and ×10000 magnification factors are also shown in Fig. 3(c) and 3(d). The layer thickness of about 50 µm can be estimated using Fig. 3(c). Moreover, an oblique top view of the resulting porous layer is shown in Fig. 3(e) that gives us a better vision of the surface porosity.

3.2. Optical properties of the sensing layer

PtOEP, which is utilized as the photosensitive dye in the sensing layer, has a light absorption peak at 535 nm and an emission peak at 645 nm [7]. The photoluminescent (PL) emission of PtOEP is effectively quenched in the dynamic range of O_2 density. This property is utilized in our proposed optical sensor to detect the presence and concentration of oxygen in a chamber.

The PL emission of the resulting sensing layer is measured in several different cases: 1) N_2 flew in the sealed chamber with a flow of ≈150 cc/min for 2 minutes, then the inlet and outlet of the chamber are closed. Thus, the sealed chamber is filled with stagnant N_2. 2) N_2 and O_2 flew simultaneously in the sealed chamber, each with a flow of ≈150 cc/min for 2 minutes, then the inlet and outlet of the chamber are closed. Thus, the sealed chamber is filled with stagnant N_2 and O_2.

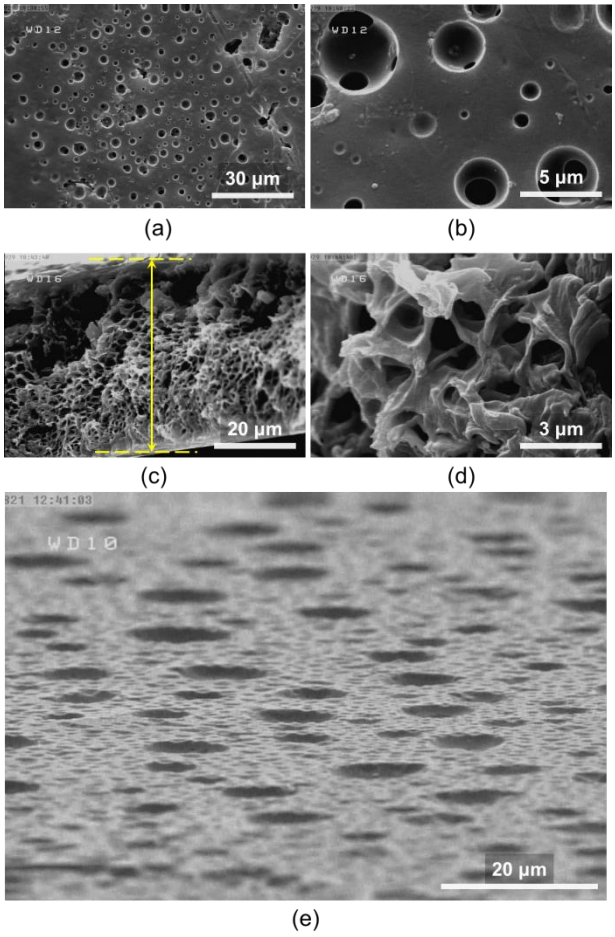

Fig. 3: Top views (a,b) and cross sections (c,d) of the resulting porous sensing layer, imaged by FE-SEM with different magnifications. (e) Oblique top view of the resulting porous layer.

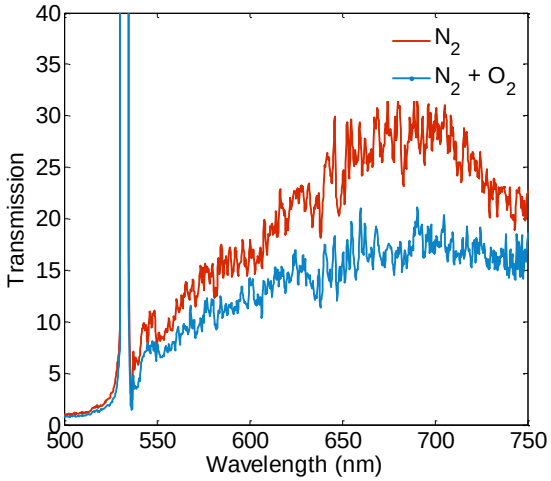

Fig. 4: The measured PL emission spectra of the sensing layer when the chamber is filled with a) N_2, b) N_2 and O_2

The measured PL emission spectra of the mentioned cases are shown in Fig. 4. As can be observed in this figure, the PL emission peak intensity in the red region (λ_{peak}=) is larger for case 1 compared with the other case. The amount of PL emission peak intensity is reduced in cases 2 due to the quenching mechanism that is attributed to the presence of oxygen in the chamber.

4. Conclusion

We have presented a method to enhance the permeability of oxygen molecules in the luminophore layer of optical oxygen sensors by morphological modification. Furthermore, the degree of light trapping was improved due to the porosity of the sensing layer, leading to a higher sensitivity. In this work, we have used a laser pointer as the excitation light source. In order to improve the PL measurement results, we can use LEDs instead of laser.

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