PYRENE-1-BUTYRIC ACID–DOPED POLYANILINE FOR FLUORESCENCE QUENCHING-BASED OXYGEN SENSING

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Abstract–The synthesis of pyrene-1-butyric acid (PBA)-doped polyaniline (PANI) and its oxygen sensing properties, through fluorescence quenching, are reported. The structures of both undoped PANI (emeraldine) and PBA-doped PANI are investigated by means of Fourier Transform InfraRed (FT-IR) spectroscopy. The O_2 sensing capability of the synthesized layer is demonstrated through fluorescence spectroscopy performed at different air pressure values. PBA-doped PANI is expected to lead to a fluorophore with better stability and reliability than free PBA. This could bring real benefits to the overall functioning of industrial O2 sensors based on fluorescence quenching.

Keywords: O_2 sensor, polyaniline, fluorescence quenching, pyrene – 1 - butyric acid.

1. INTRODUCTION

Measuring the oxygen concentration is important in various fields, such as automotive, medical (i.e., anesthesia monitors), and environmental monitoring [1]. Among the traditional oxygen sensing techniques, one can enumerate: amperometric, titration, thermoluminescence, chemiluminescence, etc. [2].

Molecular oxygen (O_2) is an efficient quencher of fluorescence due to its unusual triplet ground state. Recently, a lot of devices based on the fluorescence quenching of organic and inorganic fluorescent molecules in the presence of O_2 were developed as oxygen sensors [1, 2].

The most used fluorophores for O_2 sensing are: pyrene and its derivatives (pyrene-1-acetic acid, pyrene-1-butyric acid, pyrene-1-decanoic acid, pyrene-1-dodecanoic acid), quinoline, decacyclene and its derivatives, phenantrene, erythrosine B, aluminum 2, 9, 16, 23, tetraphenoxy-29H, 31H-phthalocyaninehydroxide, metal complex organic dyes (ruthenium, osmium, iridium, rhodium and lanthanide complexes,

metalloporphyrins) [1-6].

However, such fluorophores have reduced adhesion to the substrate (e.g. glass), thus leading to low stability and low reliability sensors. In order to overcome these issues, supporting materials (such as silicones, polystyrene, ethyl cellulose, Al_2O_3, ZrO_2, Fe_2O_3, Sb_2O_3 [7-10]) are required. These supporting materials, which are selectively permeable to oxygen and adhere better to the substrate, are bonded to the fluorophore. This bonding and the stability of the fluorophore are crucial for the sensors reliable and stable operation.

If a polymer is used as supporting material, the fluorophore molecule could crystallize in the polymer due to its poor solubility. In order to prevent aggregation and crystallization, the fluorophore can be immobilized in the polymeric substrate through covalent bonding [11]. However, the covalent bonding might reduce the fluorescent properties of the fluorophore.

In this paper, we demonstrate the fluorescence quenching-based O_2 sensing capabilities of a layer fabricated by doping polyaniline (PANI – supporting material) with pyrene-1-butyric acid (PBA - fluorophor). The O_2 sensing capability of the synthesized layer is proven by fluorescence spectroscopy performed at different air pressure values.

2. EXPERIMENTAL

Ammonium peroxydisulfate, hydrochloric acid, PBA, ammonium hydroxide and deionizated water, dimethylformamide, tetrahydrofurane were purchased from Sigma-Aldrich and used as purchased. Aniline, purchased from Sigma-Aldrich, was vacuum distilled before chemical polymerization.

The synthesized compounds (emeraldine and PBA-doped PANI) were characterized by

means of Fourier Transform InfraRed (FT-IR) spectroscopy using a Bruker Vertex 70 spectrometer. Their fluorescence properties were analyzed using the experimental set-up presented in Fig. 1. The samples were excited with a monochromatic radiation generated by a 150 Xe lamp and the fluorescence emission spectrum was analyzed with another monochromator and a photomultiplier (EMI 9658QB). The low level signal was amplified using a lock-in amplifier (SR810) and recorded by a PC, used also for controlling both monochromators.
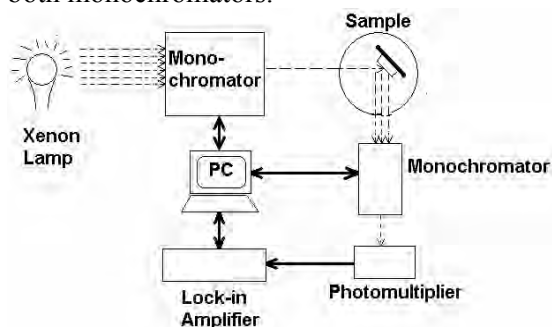

Fig. 1. Diagram of the experimental set-up.

The measurements were performed for an excitation wavelength of 380nm (maximum absorption wavelength for PBA [2]), and the fluorescence was recorded between 400nm and 800nm.

2.1. Synthesis of PANI (Emeraldine)

Undoped PANI (free base) was prepared by chemically oxidizing aniline with ammonium peroxydisulfate (Fig. 2), according to [12, 13]. The aniline (9.32 g, 0.1 mol) was dissolved in 200 ml of water. 40 ml of 37.5% hydrochloric acid were then added in the solution. The mixture was stirred in an ice bath for two hours. After the addition of ammonium peroxydisulfate (22,8g, 0.1 mol), the new mixture was covered and placed in a refrigerator at 4°C, for six hours.
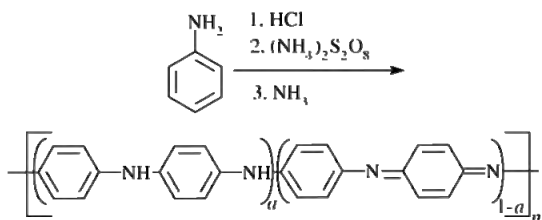

Fig. 2. Synthesis of PANI as a free base (emeraldine).

Afterwards, the mixture was diluted in water, the PANI precipitate was filtered, washed with 1l of distilled water, washed again with a solution of 30% ammonium hydroxide and, finally, washed for a second time with distilled water. The powder was dried in an oven, at 80°C, for six hours.

2.2. Doping of Emeraldine

Pyrene-1-butyric acid (PBA) (Fig. 3) was chosen as doping agent for PANI [14]. The doping of emeraldine was performed as described in [12]. PANI−in the emeraldine form (0.5 g)−was placed in 200ml dimethylformamide, which contained 0.3g of PBA, and stirred for 24 hours at room temperature. After that, the doped PANI was filtered and rinsed with water and tetrahydrofurane in order to remove the unreacted PBA. The scheme for doping of emeraldine with PBA is presented in Fig. 4.
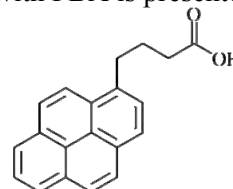

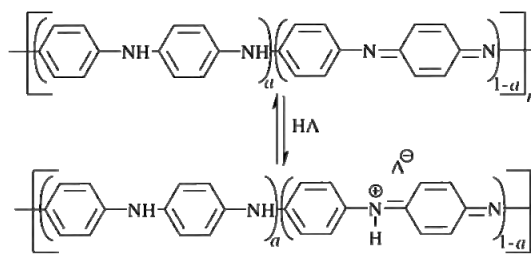
Fig. 3. The structure of PBA.

Fig. 4. Synthesis of doped PANI, where the doping agent (HA) is PBA.

3. RESULTS AND DISCUSSIONS

The emeraldine FTIR spectrum (Fig. 5, bottom) features two distinctive lines: one at 1303 cm^{-1}, assigned to the vibration stretch of C-N bond in the secondary aromatic amines, and the other at 827 cm^{-1}, corresponding to aromatic C-H bond. In good agreement with [15], the 1589 cm^{-1} and 1495 cm^{-1} vibration modes from undoped PANI (Fig. 5, bottom) exhibit a small shift (8-10 cm^{-1}) in doped PANI (Fig. 5, top). PBA-doped PANI exhibits typical bands for PBA centered at 1687cm^{-1} and 2942 cm^{-1} (Fig. 5, top). These

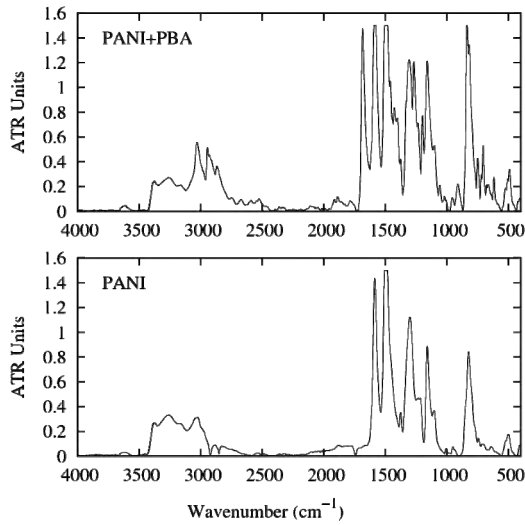results validate the synthesis we have performed.

Fig. 5. IR spectra for PANI (top) and PBA-doped PANI (bottom).

We have chosen PBA as fluorophore for oxygen sensing and PANI as supporting material based on the following reasons:

• PBA exhibits strong fluorescence with high quantum yield;

• PANIs are polymers with good environmental stability, low cost and mature fabrication process.

• The O_2 sensing layer is synthesized by doping the supporting material (undoped PANI) with the fluorophore (PBA) via the non-covalent immobilization of the dopant. This type of immobilization has the advantage that it leads to a minimum change in the molecular structure of the dopant and, as a consequence, it does not diminish its fluorescent properties.

• It is well-known that the size of the dopant is of paramount importance for the stability of doped-PANI [16-17]. PBA is a counter-ion large enough to suppress the de-doping of PANI. Thus, the stability of the PBA-doped PANI film is expected to be significantly higher than that of PANI films doped with other ions.

The photoluminescence spectra for both free PBA and PBA-doped PANI, presented in Fig. 6, show that the PBA fluorescence peak configuration changes when using the acid for PANI doping, thus confirming the efficiency of the doping.
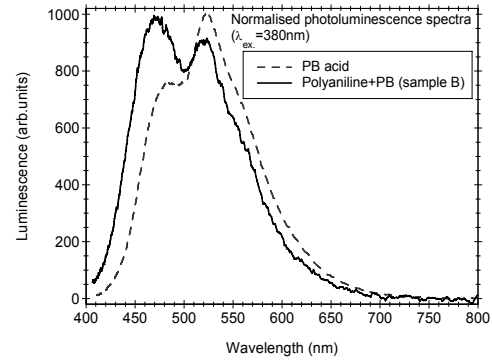

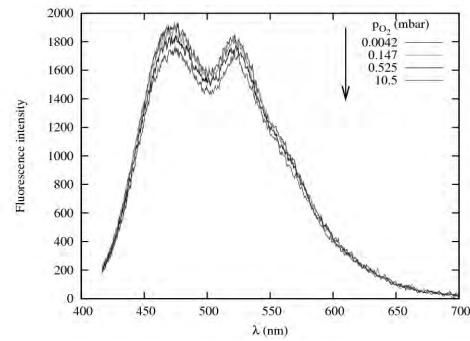**Fig. 6.** Fluorescence spectra for PBA and PBA-doped PANI.

Fig. 7. Photoluminescence spectra for PBA-doped PANI at various air pressure values.

The oxygen sensing properties of the PBA-doped PANI sample were assessed by measuring the fluorescence intensity for 380 nm excitation wavelength at different values of the environmental pressure. The samples were placed in a sealed enclosure and the pressure was lowered below 1 mbar in the enclosure using a vacuum pump. Using a manual valve, the pressure was then slowly brought back to the atmospheric value, while measuring the fluorescence spectrum. The experimental curves are presented in Fig. 7.

The fluorescence intensity I, calculated as the integral of each spectrum curve between 430 nm and 700 nm, was fitted to a modified Stern-Volmer equation [8]:

$$\frac{I_0}{I_0 - I} = \frac{1}{f} + \frac{1}{f K_{SV} p_{O_2}}$$

where: f=0.097±0.007 is the fraction of fluorescent sites accessible to oxygen, and K_{SV}=1.32±0.09 is their (common) quenching constant. I_0 is the fluorescence intensity at zero oxygen pressure. It has been obtained from the fit, as well, and it is very close to the

intensity measured at the lowest air pressure of 0.02 mbar.

The Stern-Volmer plot, both the data and the fitted curve, are presented in Fig. 8, and it is similar to the one for PBA on alumina proposed for fluorescence quenching oxygen sensor [8].
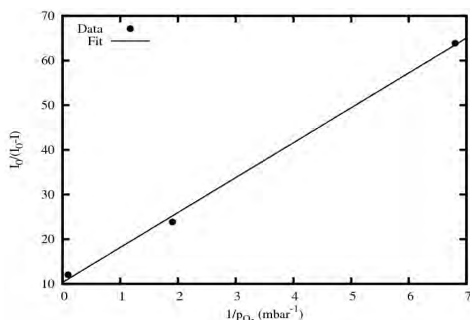

Fig. 8. The relative change in fluorescence intensity for PBA doped PANI, when the air pressures increases from below 1mbar to 50 mbar.

4. CONCLUSIONS

A new sensing material for oxygen sensors working on fluorescence quenching principle has been demonstrated by spectroscopic and functional tests. Synthesis of a new type of pyrene-1-butyric acid–doped polyaniline is reported. The structures of both polyanilines (emeraldine and doped polyaniline) were investigated by FT-IR spectroscopy. A comparison of fluorescence properties of pyrene-1-butyric acid (free and immobilized in polyaniline) was performed for showing the suitability of the polyaniline as supporting material. The oxygen sensing properties of the PBA-doped polyaniline sample were assessed by measuring the fluorescence quenching at different air pressure values. These functional tests prove that the novel sensing layer obtained by doping the polyaniline with PBA is strong candidate for next generation O_2 sensors based on fluorescence quenching.

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