

THE INFLUENCE OF SOL-GEL COATED LENGTH AND WITHDRAWAL RATE ON PLASTIC OPTICAL FIBER CORE TOWARDS OXYGEN GAS SENSING SENSITIVITY

Article history

Received

15 August 2015

Received in revised form

15 November 2015

Accepted

30 December 2015

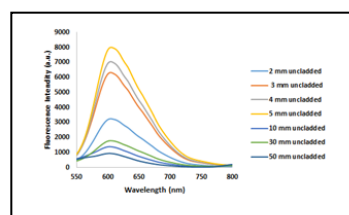
Maizatul Zolkapli^{a*}, Suhairi Saharudin^b, Sukreen Hana Herman^a, Wan Fazlida Hanim Abdullah^a

*Corresponding author
maizatulu544@salam.uitm.edu.my

^aFaculty of Electrical Engineering, University Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

^bDepartment of Photonics, MIMOS Berhad, 57000 Technology Park Malaysia, Kuala Lumpur, Malaysia

Graphical abstract



Abstract

The fabrication and characterization of an optical fiber oxygen sensor based on oxygen fluorescence quenching are described. The sensors are prepared by coating the oxygen sensitive indicator (tris-BP ruthenium (II) chloride and platinum octaethylporphyrin) that is immobilized by the sol-gel route onto the uncladded middle portion of a multimode plastic optical fiber. A design of experiment based on two parameters which are the uncladded coated length and withdrawal rate was carried out in order to identify the optimum setting that gives the highest fluorescence emission which leads to better sensitivity. The sensitivity of the optical oxygen sensor is quantified in terms of the ratio I_0/I where I_0 and I represent the fluorescence intensities in pure nitrogen and pure oxygen environments, respectively. Both ruthenium and platinum coated fiber produced a linear Stern-Volmer relationship which indicate the homogeneous environment of the luminophore. The experimental result reveals that the optimized setting for ruthenium sol-gel coated fiber is 5 mm decladded length and 120 mm/min withdrawal rate while for platinum sol-gel coated fiber is 8 mm decladded length and 160 mm/min withdrawal rate.

Keywords: Ru(dpp)₃Cl₂, PtOEP, POF, oxygen sensing, sol gel

Abstrak

Fabrikasi dan pencirian sensor oksigen gentian optic berdasarkan pendarfluor oksigen pelindapkejutan diterangkan. Sensor disediakan dengan salutan bahan peka oksigen (tris-BP ruthenium (II) chloride and platinum octaethylporphyrin) menggunakan kaedah sol-gel di bahagian tengah gentian optik plastik. Eksperimen berdasarkan dua parameter iaitu panajang gentian yang bersalut dan kelajuan rendaman telah dijalankan untuk mengenal pasti tetapan optimum yang memberikan pelepasan pendarfluor palaing tinggi yang membawa kepada kepekaan yang lebih baik. Hasil eksperimen menunjukkan penetapan optimum bagi ruthenium ialah kombinasi 5 mm panjang kawasan bersalut pada kadar kelajuan 120 mm/min, manakala bagi platinum pula ialah kombinasi 8 mm panjang kawasan bersalut pada kadar kelajuan 160 mm/min.

Kata kunci: Ru(dpp)₃Cl₂, PtOEP, POF, kepekaan oksigen, sol gel

© 2016 Penerbit UTM Press. All rights reserved

1.0 INTRODUCTION

In the last few decades, there are lots of work done in developing oxygen sensor based on optical sensing technologies [1-5]. Optical fiber received considerable attention attributes to its being passive and lightweight apart from its ability to act as sensor as well as the medium of communication on one platform in a distributed manner.

The sensing of oxygen is based on the photoluminescence principle. Quenching of oxygen will decrease the fluorescence signal of the fluorescence dye and this degree of decreasing fluorescence correlates to the partial pressure of oxygen around the sensing material [6–8]. The greater the quencher's concentration, the lesser fluorescence intensity will be. The sol-gel process has been the most preferred method to immobilize the oxygen-sensitive dye on the plastic optical fiber (POF) surface and investigate its sensing performance.

In this work, the effect of varying the length of the coated fiber and the withdrawal rate of dip coating process towards oxygen sensing performance was studied. Findings of this study will be used as the basis to further develop the quasi-distributed fiber optic oxygen sensor.

2.0 EXPERIMENTAL

2.1 Preparation of Optical Fiber Oxygen Sensor

TetraethylorthosilicateSi (OC₂H₅)₄ (TEOS) and Octyl-triEOS were used as the precursor liquid to prepare the pure silica thin film on fiber. A porous silica glass film with a refractive index of less than that of the fiber core ensures that the wave guidance condition is met [9]. The silica sol was prepared by dissolving TEOS (99.999% Aldrich) in ethanol (EtOH) as TEOS is initially immiscible and require alcohol to form a homogeneous mixture. Then Octyl-triEOS, HCl (0.1 M) and triton X-100 were added to the mixture to stimulate hydrolysis and prevent cracks in the sol-gel film. The composition of the prepared sol solution is as described in Table 1. The mixture was magnetically stirred for 1 hour at ambient temperature to obtain a stable silica sol.

Table 1 Composition of the prepared sol solution

TEOS (ml)	EtOH (ml)	Octyl-triEOS (μl)	HCl (μl)	Triton X-100 (μl)
4	1.25	40	400	40

Tris (4, 7-diphenyl-1, 10-phenanthroline) ruthenium (II) dichloride (Ru(dpp)₃Cl₂) and platinum octaethylporphyrin (PtOEP) were used as the oxygen sensing dye in this study. The dye solution for Ru(dpp)

was prepared by dissolving it in EtOH, whilst PtOEP was dissolved in tetrahydrofuran (THF). Each dye solution was then stirred under ambient temperature for 1 hour as described in Table 2. Subsequently, the luminophore-doped sol solution was prepared by mixing the Ru/EtOH solution or PtOEP/THF solution into the sol solution and followed by 2 hours of magnetic stirring at room temperature to ensure the formation of homogeneous sol-gel polymer.

Table 2 Composition of the prepared dyeol solution

Ru(dpp) (mg)	EtOH (ml)	PtOEP (mg)	THF (ml)
2	2	2	2.5

A multimode plastic optical fiber (Mitsubishi Rayon Co. LTD.) with a core diameter of 1000 μm was used in the experiment. Using a hot knife, the central portion POF cladding was removed to expose the core region for sol-gel coating. The sensing part is placed at the middle portion since it will be applied for quasi-distributed later. The length is varied from 2 mm to 50 mm as shown in Figure 1. They were then wiped with EtOH and rinsed with DIW to ensure the cladding was completely removed prior to the dip coating process. Finally, the sol-gel was coated on the uncladded POF fiber using a computer-controlled dip-coating apparatus at a speed of 80, 120 and 160 mm/min. These fibers were then kept for 7 days in dark environment at atmospheric pressure and room temperature for stabilization of dyes in the host matrix.

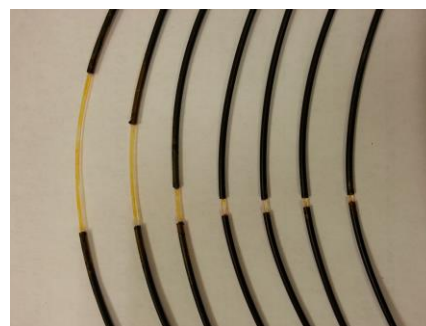


Figure 1 POF fiber coated with Ru sol-gel for various declad region

2.2 Instrumentation

Figure 2 shows a schematic illustration of the experimental arrangement used to characterize the performance of the optical fiber oxygen sensor. In the sensing experiment, the fluorescence excitations are provided by LED (LED3C_SMA, Doric) with a central wavelength of 385 nm and 465 nm driven by a programmable LED driver (LEDRV4_4ch_1000). The wavelength was as such because they are the

excitation wavelength for each of the indicator. In fluorescence analysis, a correct generation of the excitation waveform is very important because this waveform will be used in the final processing.

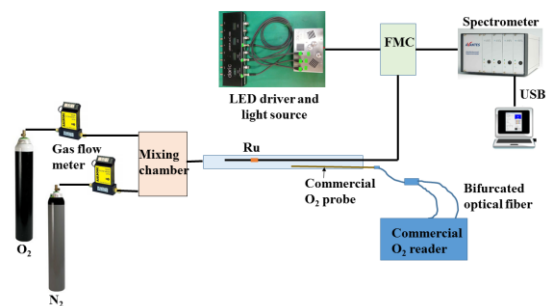


Figure 2 Experimental setup to measure the spectral response of the fiber optic oxygen gas sensor

The optical oxygen gas sensing system consists of a coated plastic optical fiber (Mitsubishi Rayon Co. LTD., core diameter 1000 μm) connected to the bandpass filter (fluorescence mini cube, FMC, Doric). A bifurcated optical fiber is used to connect the commercial oxygen probe as a reference gauge to measure the oxygen concentration in the chamber. The emission is measured using Avaspec multichannel fiber optic spectrometer (Avantes). A USB cable then connects the spectrometer to a computer to display the spectral of the modulated light in the probe performance in various oxygen concentration which is obtained by mixing oxygen and nitrogen, of which the process is controlled by gas flowmeters.

3.0 RESULTS AND DISCUSSION

3.1 Optical Properties of Ruthenium and PtOEP-Doped Oxygen Sensor

Figure 3 (a) and (b) shows the absorption spectrum of ruthenium and platinum sol-gel which peaks at 463 nm and 380 nm respectively. This confirms that LED with central wavelength of 465 nm and 385 nm, available in the lab can be used as the excitation source for the oxygen sensing probe. Photoluminescence measurement was then carried out based on the obtained excitation length to identify the emission wavelength for each dye. Figure 4(a) and (b) show the emission wavelength for ruthenium and platinum is at 604 nm and 644 nm respectively.

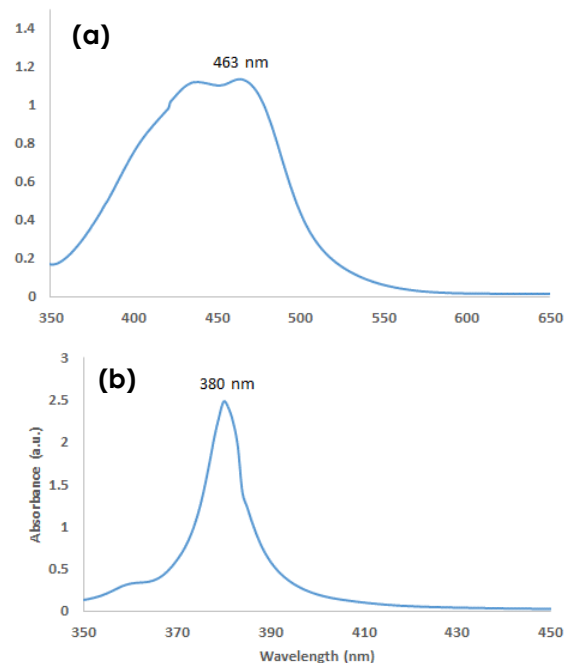


Figure 3 UV-VIS absorption spectra: (a) $\text{Ru}(\text{dpp})_3\text{Cl}_2$ and (b) PtOEP

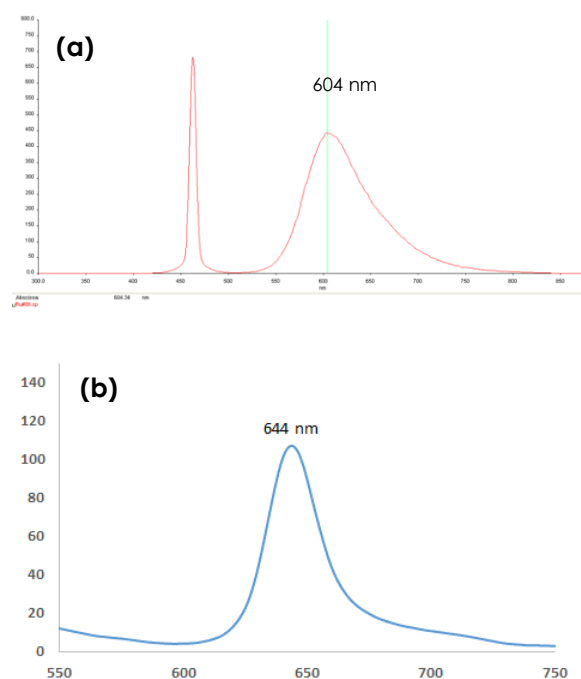


Figure 4 Emission spectra from photoluminescence scan: (a) $\text{Ru}(\text{dpp})_3\text{Cl}_2$ at 604 nm and (b) PtOEP at 644 nm

3.2 Sensing Analysis

Figure 5 presents the emission intensity of ruthenium coated POF for various declad length. The intensity is higher for declad length less than 10 mm. Hence, further studies focusses on declad length of 5 mm and below.

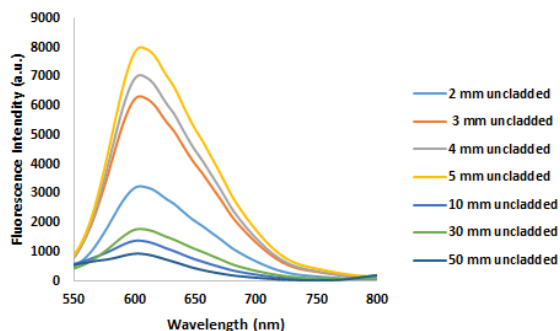


Figure 5 Ru(dpp)₃Cl₂ emission intensity in air for declad length 2 – 50 mm

The intensity check for each declad length and withdrawal rate combination for both Ru(dpp)₃Cl₂ and PtOEP were carried out in air at room temperature. Figure 6(a) and (b) show that the highest intensity for Ru(dpp)₃Cl₂ is observed for combination of 2 mm declad length at 160 mm/min withdrawal rate while for PtOEP is from the combination of 5 mm declad length at 80 mm/min withdrawal rate.

At this point, a conclusion cannot be made based on the intensity alone as it is important to check for the sensitivity of the sensor. Hence, the sensing probe was tested in various oxygen concentration and the Stern-Volmer analysis was carried out to further confirm the results. The relation is described as follows:

$$I_0 / I = 1 + K_{sv}[O_2] \quad (1)$$

where I_0 and I are the fluorescence intensity in the absence and presence of O₂ respectively, K_{sv} is the Stern-Volmer quenching constant, and [O₂] is the oxygen concentration.

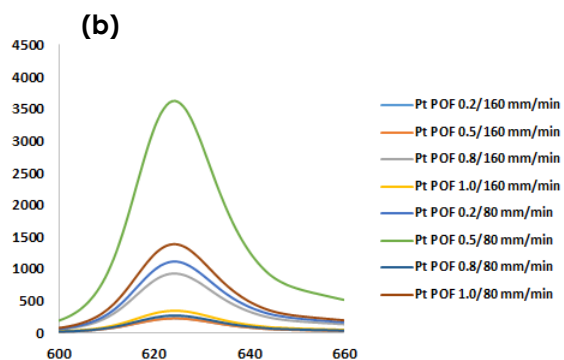
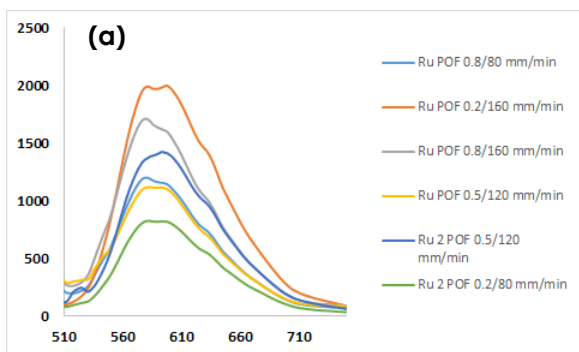


Figure 6 Emission spectra of optical fiber sensor under different declad length and withdrawal rate: (a) Ru(dpp)₃Cl₂ at 604 nm and (b) PtOEP at 644 nm

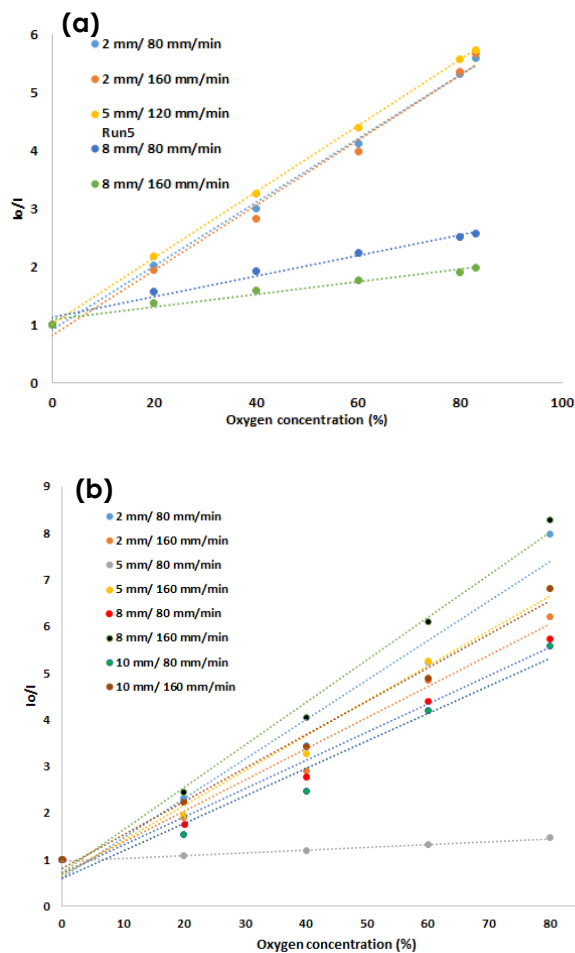


Figure 7 Stern-Volmer plot for various coated length and withdrawal rate: (a) Ru(dpp)₃Cl₂ and (b) PtOEP

Plots of I_0/I against the O_2 concentration for $Ru(dpp)_3Cl_2$ and PtOEP are shown in Figure 7(a) and (b) respectively. Stern-Volmer plots for $Ru(dpp)_3Cl_2$ as shown in Figure 6(a) indicates highest sensitivity from a combination of 5 mm coated length and 120 mm/min withdrawal rate with R^2 value of 0.9999. However, the combination that gives the highest sensitivity for PtOEP is from 8 mm coated length and 160 mm/min withdrawal rate with R^2 value of 0.9919 as shown in Figure 6(b). These findings indicates that intensity results alone is insufficient to draw a conclusion.

Figure 8(a) and (b) show the fluorescence emission spectra of the oxygen sensitive coating towards various oxygen concentrations. As shown in the graphs, the fluorescence intensity decreases as more oxygen flows into the container until it is at its lowest intensity when the container is being occupied with 100% oxygen concentrations. This result is in agreement with the work done by C.S. Chu et al. [3-4] which explains the O_2 quenching. The fluorescence intensity is efficiently quenched by molecular O_2 .

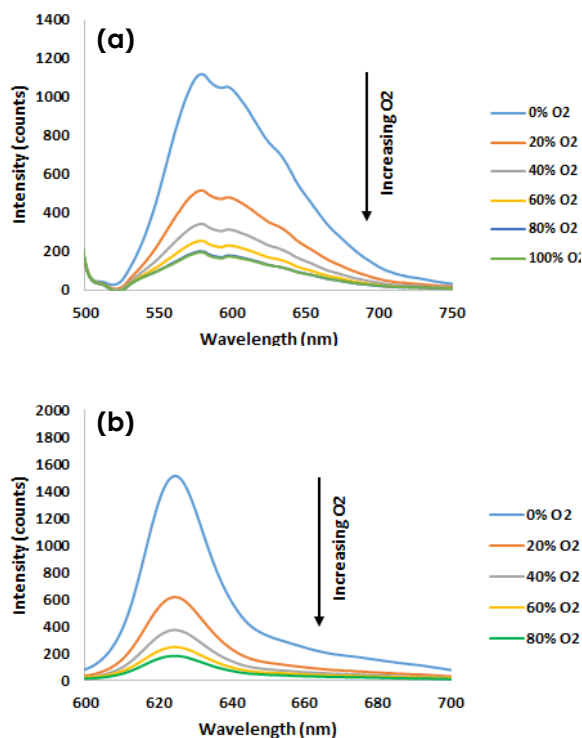


Figure 8 Emission spectra of optical fiber sensor when subjected to various oxygen concentration: (a) $Ru(dpp)_3Cl_2$ and (b) PtOEP

4.0 CONCLUSION

In this work we successfully presented a simple, low cost technique to fabricate a plastic optical fiber sensor for oxygen sensing via sol-gel process. The work compares the performance of the optical fiber sensor based on two parameters which are the core coated length and dip coating withdrawal rate for oxygen sensitive dyes; $Ru(dpp)_3Cl_2$ and PtOEP. The

coated length is varied from 2 mm to 50 mm while withdrawal rate is varied from 80 to 160 mm/min. It is concluded that the optimized combination for $Ru(dpp)_3Cl_2$ is 5 mm coated length and 120 mm/min withdrawal rate, while for PtOEP the optimized combination is from 8 mm coated length and 160 mm/min withdrawal rate. These results will be the basis for the development of quasi-distributed optical oxygen sensor.

Acknowledgement

The authors wish to thank the Ministry of Science, Technology and Innovation (MOSTI) and Ministry of Education (MOE), Malaysia for funding the research project through the e-science and Niche Research Grant Scheme [Ref. No. 600-RMI/NRGS 5/3 (2013)], as well as MIMOS Berhad and Research Management Institute (RMI) Universiti Teknologi MARA (UiTM) for the facilities and administrative support.

References

- [1] Quaranta, M., Borisov, S. M. and Klimant, I. 2012. Indicators for Optical Oxygen Sensors. *Bioanalytical Reviews*. 4: 115-157.
- [2] Kocincova, A. S., Borisov, S. M., Krause, C. and Wolfbeis, O. S. 2007. Fiber-Optic Microsensors for Simultaneous Sensing of Oxygen and Ph, and of Oxygen and Temperature. *Analytical Chemistry*. 79(22): 8486-93.
- [3] Chu, C. S. 2013. Optical Fiber Oxygen Sensor based on Pd(II) Complex Embedded in Sol-Gel Matrix. *Journal Of Luminescence*. 135: 5-9.
- [4] Chu, C. S. and Chuang, C. Y. 2014. Highly Sensitive Fiber-Optic Oxygen Sensor based on Palladium Tetrakis (4-Carboxyphenyl) Porphyrin Doped in Ormosil. *Journal of Luminescence*. 154: 475-478.
- [5] Chu, C. and Lin, C. 2014. Optical Fiber Sensor for Dual Sensing of Temperature and Oxygen based on PTFPP/CF Embedded In Sol - Gel Matrix. *Sensors and Actuators B: Chemica*. 195: 259-265.
- [6] Mahmud, Z., Herman, S. H., Noor, U. M. and Saharudin, S. 2013. Effect of Catalyst on the Fluorescence Quenching of [Tris (4, 7-Diphenyl-1, 10-Phenanthroline) Ruthenium (II) Dichloride] for Dissolved Oxygen Detection. *Proceedings Of The IEEE Regional Symposium on Micro and Nanoelectronics*. 360-362.
- [7] Choi, M. M. F., Xiong, X. and Xiaoa, D. 2006. Dissolved Oxygen Sensor based on Fluorescence Quenching of Oxygen-Sensitive Ruthenium Complex Immobilized on Silica-Ni-P Composite Coating. *Sensors Actuators B*. 117: 172-176.
- [8] Chen, R., Farmery, A. D., Obeid, A. and Hahn, C. E. W. 2012. A Cylindrical-Core Fiber-Optic Oxygen Sensor based on Fluorescence Quenching of a Platinum Complex Immobilized in a Polymer Matrix. *IEEE Sensors Journal*. 12(1): 71-75.
- [9] Gupta, B. D. and Sharma, S. 1998. A Long-Range Fiber Optic Ph Sensor Prepared by Dye-Doped Sol-Gel Immobilization Technique. *Optics Communications*. 154(5-6): 282-284.