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Quasi-distributed sol-gel coated fiber optic oxygen sensing probe

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ABSTRACT

In the field of aquaculture, optical sensor technology is beginning to provide alternatives to the conventional electrical sensor. Hence, the development and characterization of a multipoint quasi-distributed optical fiber sensor for oxygen measurement is reported. The system is based on 1 mm core diameter plastic optical fiber where sections of cladding have been removed and replaced with three metal complexes sol-gel films to form sensing points. The sensing locations utilize luminophores that have emission peaks at 385 nm, 405 nm and 465 nm which associated with each of the sensing points. Interrogation of the optical sensor system is through a fiber optic spectrometer incorporating narrow bandpass emission optical filter. The sensors showed comparable sensitivity and repeatability, as well as fast response and recovery towards oxygen.

1. Introduction

In the past few decades, significant efforts have taken place to enhance the performance of oxygen sensors based on optical fiber via incorporating oxygen sensitive nano-materials into their structure [1–10]. At present, the majority of work in the field of optical oxygen sensors has been devoted to coating the luminescent nanomaterials on the tip of optical fiber [2,5,11–15], whilst the number of reports on the sensing properties of quasi-distributed optical oxygen sensor based on evanescent wave, are significantly lower [16–19]. This may be due to the fact that the preparation of quasi-distributed or multipoint sensor involves tedious and complicated fabrication techniques. Moreover, such configuration requires sensing region to be arranged at different points along an optical fiber.

A variety of techniques have been reported such as tapering the optical fiber [20], etching the optical fiber to form a D-shape fiber [21,22], bending the fiber into U-shape fiber [23,24], and stripping to remove a region of cladding from the fiber [16,25,26]. In most cases, a reduction of the cladding thickness is required to provide effective evanescent field interaction, especially if short wavelengths are planned to be used for sensor excitation. Hence, resulting in a very fragile filament that requires additional care as compared to single point sensing where the luminescent material is immobilized on the tip of the optical fiber. Despite of the difficulty, such arrangement is favored for simultaneous measurement of two or more parameters in complex media and processes. Substantial research has reported various evanescent wave sensing scheme [27–29] for oxygen measurement [30–34], but sensing element arranged in quasi-distributed configuration is very minimal. Our goal in this work is to demonstrate that by capitalizing the evanescent wave phenomenon, a multi-position oxygen sensing element can be fabricated in a single optical fiber for real-time and simultaneous measurements. This is particularly important especially in aquaculture for example where dissolved oxygen concentration varies at different depth and location in the water. By having a quasi-distributed optical fiber dissolved oxygen sensor a large area of the pond can be covered and can be monitored within a single system. The measurement of dissolved oxygen at diverse locations and depths can be made possible depending on how the sensor is placed. If the fiber optic is deployed horizontally, it can measure the dissolved oxygen levels at various locations. If it is deployed vertically, it can measure the oxygen levels at different depths of the pond. Optical sensor technology addresses the weaknesses of the conventional electrical sensor as it is capable of measuring the parameter for a long period of time with minimal measurement drift and without cleaning the sensing head regularly as in the electrochemical based sensor [35–37]. These attributes combined with less maintenance and calibration requirement in optical dissolved oxygen technique has appealed more and more usage of such sensor in the aquaculture sensor.

In this paper, the development of a quasi-distributed sol-gel coated fiber optic oxygen sensor based on direct measurement of luminescence intensity is demonstrated. To achieve this, a simple, low cost technique to fabricate a plastic optical fiber sensor for the sensing of oxygen is presented. A narrow bandpass emission optical filter is utilized to capture the emission signal from the three sensing points. Each point consists of a section of sol-gel coated uncladded fiber with a selected length as mentioned in the previous publication [38]. The performance

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characteristics, such as quenching behavior, sensitivity, repeatability and response time of the sensing system are reported.

2. Experimental work

2.1. Preparation of the oxygen sensing fiber

A multimode plastic optical fiber (Mitsubishi Rayon Co. Ltd.) with a core diameter of 1 mm was used in the experiment. The large core size makes it easy to couple lots of light from the light source and connectors do not need to be high precision [39]. In an attempt to make a quasi-distributed sensor, the multiple sensing region needs to be created along the optical fiber line and placed 15 cm apart from each other. Hence, using sol-gel technique the oxygen sensitive material will be coated at the pre-determined middle sections of the fiber. With the aid of a retractable blade utility knife, a small section about 5 mm length of the POF jacket was removed exposing the core-cladding. This is the optimum size for the sensitive sections that gives high sensitivity as reported in earlier study [38]. The cladding was then chemically etched with acetone leaving the core region to be coated with sol-gel. To access whether the cladding was completely removed, the diameter of the fiber was measured using a digital Vernier caliper (Mitutoyo). Fig. 1 shows the FESEM images of the POF core-cladding surface before and after chemical etching. This is to inspect that the cladding has been completely removed prior to sol-gel dip coating step. Prior to the dip coating process, the POF was wiped with EtOH and rinsed with copious amounts of de-ionized water and left to dry at room temperature for one hour. In order to verify the reproducibility of the sensor performance, three samples were fabricated for each dye and the average values were obtained.

2.2. Preparation of film coatings

The synthesis of sol-gel was done by adapting the procedure used by Yeh et al. [11] with some modification. The optimized recipe used in this work is based on characterization work performed by the team [40,41]. For this study three types of oxygen sensitive luminescence dyes namely Tris (4,7-diphenyl-1,10-phenanthroline) ruthenium (II) dichloride ($Ru(dpp)_3Cl_2$)/$Ru(dpp)_3^{2+}$), platinum octaethylporphyrin (PtOEP) and 5,10,15,20-tetrakis (pentafluorophenyl) 21*H*,23*H*-porphine palladium (II) (PdTFPP) were used. These dyes which upon excitation, responds to different spectral wavelength unique to each material has been widely used as a probe for luminescent detection and quantification of oxygen [3,11,13,42–44]. Silica sol was prepared by mixing tetraethylorthosilicate (TEOS, 99.999% Aldrich) and octyl-triEOS together to form precursor solutions. Ethanol (EtOH) was then added to the sol solution to form a homogeneous solution. Then HCl and triton X-100 were added with constant stirring to accelerate hydrolysis and prevent cracks in the sol-gel film. This mixture was magnetically stirred for 1 h at ambient temperature to get a stable silica sol. To prepare the dye solution, each dye was dissolved separately with its solvent and the solutions were stirred under ambient temperature for 1 h. EtOH was the solvent for $Ru(dpp)_3^{2+}$, while THF was the solvent for PtOEP and PdTFPP. Eventually, to prepare the luminophore-doped sol-gel, the prepared sol solution was mixed with the dye solution. The sol mixtures were capped and stirred for another 2 h at room temperature to ensure the formation of a homogeneous sol-gel. The process was repeated for all dyes. The composition of the prepared solution is tabulated in Table 1.The sol-gel was coated on the core POF using a computer-controlled dip coating apparatus at a speed of 120 mm/min. This will result in about 10 nm thickness of sol-gel which has been characterized earlier [40]. These fibers were dried in the oven at 70 °C for 24 h for stabilization of dyes in the host matrix as shown in Fig. 2. The dried coatings were then washed with de-ionized water to remove the excess and unbound dye.

Table 1
Composition of the prepared sol and dye solution.

Sol solution	TEOS (ml)	EtOH (ml)	Octyl-triEOS (µl)	HCl (µl)	Triton X-100 (µl)
	4	1.25	40	400	40
Dye solution	PtOEP (mg)	PdTFPP (mg)	$Ru(dpp)_3^{2+}$ (mg)	EtOH (ml)	THF (ml)
	2	2	2	5	10

2.3. Experimental setup

Figs. 3 and 4 illustrate the experimental setup used to characterize the performance of the quasi-distributed fiber optic oxygen sensor in gas and aqueous media. The same optical setup was used for both gas and aqueous except that the test chamber was different for each condition. The sensor was characterized in two different salinity which are 0.1 ppt and 35 ppt (salinity of water and salt water respectively) at three different temperatures; 10 °C, 25 °C and 40 °C. One end of the sensor probe was fed to the fluorescence mini cube (FMC) filter. Excitation energy was provided by the Doric LED3C_SMA (385 nm, 405 nm and 465 nm wavelength) which each wavelength was the excitation suitable for each luminescent indicator. The excitation light was transmitted to the sensors through a fiber optic cable. When the excitation light from the source reached the luminescence materials on the sensor, a molecular excitation occurred and a new colour was emitted. This emission was then carried back to the FMC filter. The FMC filter was used to split the emission of the indicator so that it can be analyzed separately. The remaining 3 ports from the FMC filter were

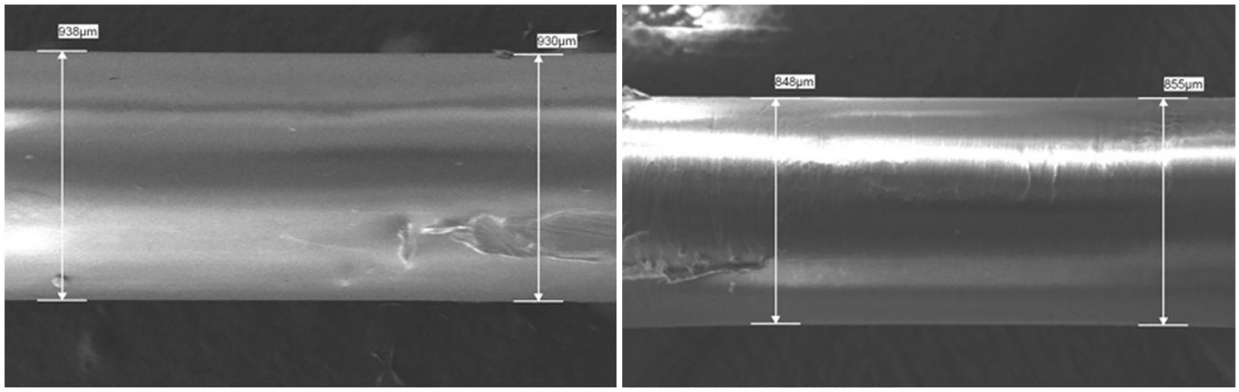

Fig. 1. The structure and the dimension of SK-4001 POF at 50× magnification (a) before etching and (b) after etching with acetone at two different locations along the sample.