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Development and Characterization of Optical Dissolved Oxygen Sensor based on the Fluorescence Detection

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형광검출기반 광학식 용존산소 측정센서 개발 및 특성 분석

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Abstract We developed and evaluated a fluorescence-based optical DO sensor (OS-100, Global Optical Communication Ltd., Korea) for long-term monitoring of the dissolved oxygen concentration in waste water treatment. Fluorescent sensing membrane containing $Ru(Dpp)_3^{2+}$ (tris(4,7diphenyl-1, 10-phenanthroline) ruthenium(II)) was prepared with GA sol-gel matrix and coated on a quartz plate by sprayed method. Properties of sensor film exhibit deviation about ±1% under wide range of DO concentration from 3 to 10. The developed optical DO sensor was actually mounted in waste water from dyeing industry and successfully applied for on-line DO monitoring. Online monitoring results showed the changes of DO concentrations in wastewater treatment processes with accuracy better than ±2% during the 6 months measurements period in vicious environmental conditions.

요 약 오폐수 처리에 있어서 용존산소량을 장기간, 연속측정이 가능한 DO 센서의 개발이 요구되어, 형광검출 특성을 이용한 광학식 DO 센서를 개발하고 특성을 분석하였다 (OS-100, 글로벌광통신주식회사). 형광 센서막은 GA를 이용하여 졸-겔 방법을 이용하여 $Ru(Dpp)_3^{2+}$ (tris(4,7diphenyl-1, 10-phenanthroline) ruthenium(II)) 형광물질을 제작하였고, 용액과 혼합하여 스프레이 방법으로 석영기판위에 증착하였다. 증착된 형광막은 용존산소 농도 3 mg/L에서 10 mg/L 사이의 넓은 영역에서 ± 1% 이하의 오차를 보였다. 제작된 광학식 DO 센서의 성능평가를 위하여 대구염색단지의 오폐수처리장 폐수의 실시간 용존산소를 장기간 측정하였다. 6개월간의 장기간에 걸쳐 실시간 측정된 용존산소의 결과는 염색공단 폐수의 악조건 하에서도 ± 2% 이하의 오차를 나타내었다.

Key Words : Dissolved; oxygen, Fluorescence detection, On-line monitoring, Optical sensor

1. Introduction

Monitoring and controlling of dissolved oxygen (DO) concentration in water treatment is the most important parameter for determining the effectiveness and quality of water treatment. [1] Among the developed DO sensors, such as titration sensor, amperometric sensor, chemi-luminescence sensor, and thermo-luminescence

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sensor, amperometers based on the Clark electrodes are widely used in the biological, environmental, and industrial areas due to their ideal response to oxygen concentration in solution. [2,3] However, these electrode type sensors have several drawbacks such as sluggish response, difficult to miniaturize, electromagnetic interferences with other sensors, etc. Over the past decades, the development and applications of optical sensors have grown rapidly because of their fast response, good sensitivity and selectivity, and long-term stability. Optical DO sensors are based on oxygen dependent changes of the luminescence of certain indicator molecules in certain solid substrates. However, the leaching of the indicators, the substrates and the linking bonds between the indicators and substrates are serious problems for operating sensors in vicious condition.

We developed optical DO sensor using optical fiber method with oxygen sensitive fluorophore $[Ru(dpp)_3]^{2+}$ film. Oxygen sensor xerogels were prepared using the mixture of organosilicone precursor and solution of $[Ru(dpp)_3]^{2+}$. Oxygen existence in solution quench the excited-state lifetime of the luminophore $[Ru(dpp)_3]^{2+}$. [4,5] The quenching process is described by the Stern-Volmer equation.

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}[pO_2] = 1 + k_q\tau_0[pO_2]$$

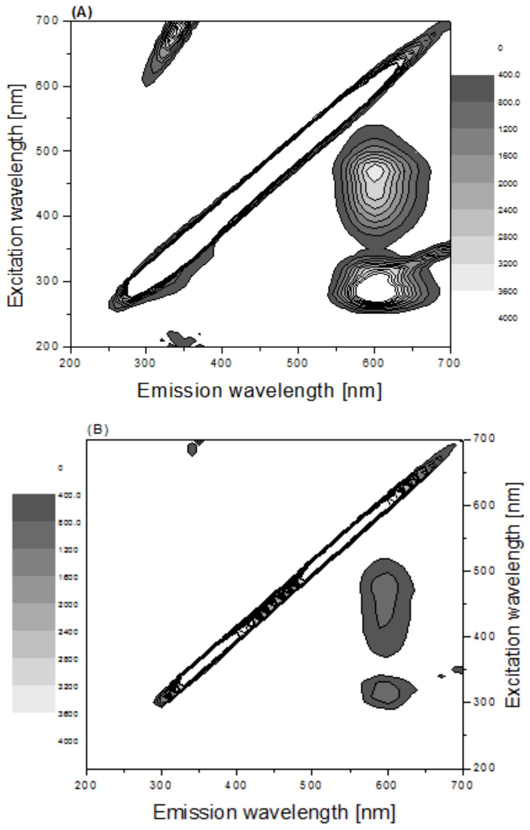
Where I_0 and τ_0 are the fluorescence intensity and decay time of the luminophore in the absence of oxygen, respectively. K_{SV} is the sensor sensitivity by Stern-Volmer constant, pO_2 is the partial pressure of oxygen, and k_Q is the quenching constant, which incorporates the oxygen diffusion coefficient for the matrix.

Oxygen sensitive sensor film was prepared by sprayed coating of oxygen sensitive xerogel on the quartz plate. Covalent immobilization of $Ru(dpp)_3$ in the sol-gel matrix was accomplished by the reaction of the $Ru(dpp)_3$ linked sol-gel precursor with atetraethyorthosilicated (TEOS) under acid conditions. The developed DO sensor equipped with a blue LED for excitation of luminescent sensor film and silicon photodiode for the detection of the oxygen sensitive luminescent signal. In this paper, we report on the result of measurement of dissolved oxygen in factory wastes under vicious environmental condition during the 6 months period without calibration. Optical DO sensor with $[Ru(dpp)_3]^{2+}$ doped xerogels film reported here is suitable for industrial and environmental applications such as service water, sewage, wastewater, and seawater, where the key sensor characteristics are :enhanced oxygen sensitivity and insensitivity to hydrogen presence, long-term stability, and fast response.

2. Discussion

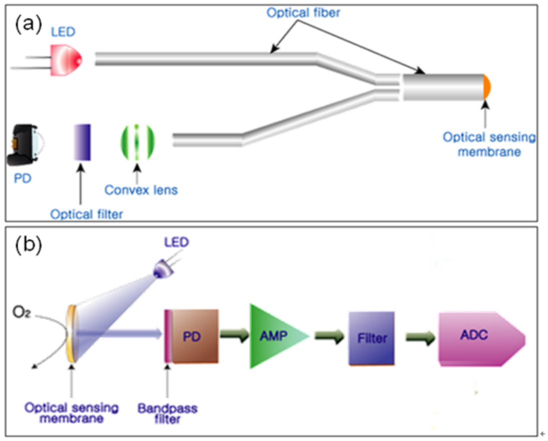
2.1 Experimental

The covalent immobilization of dissolved oxygen sensitive luminophore tris(4,7diphenyl-1,10-phenanthroline) ruthenium(II) complex $Ru(Dpp)_3^{2+}$ in the sol-gel matrix was accomplished with a sol-gel solution containing tetraethyorthosilicated (TEOS) under acidic conditions. The sensing membrane was obtained by spraying method with homemade spray device onto a quartz glass of 9 mm diameter and 1mm thickness. For uniform and firm coating, GPTMS (3-glycidoxypropyl trimethoxy silane) and APTMS (3-aminopropyl triethoxy silane) were dissolved in 99% purity ethanol and adding 35% HCl. [6] Prepared mixture with G:A:Et-OH:DW:HCl = 1.25 mL:625 µL:2.708 mL:5.417 mL:400 µL was left under stirring at room temperature for 3 hrs for forming GA sol-gel. [7] Then oxygen indicator luminophore was added into the mixture and was sprayed onto the quartz glass. The sprayed homogeneous indicator-doped mixture on the quartz was dried 24 hrs and finally heated at 60 ℃ for 48 hrs. Fluorescence intensity of 590 nm of the synthesized membrane did not change during the test period of 6 months in distilled water. These results demonstrate no dye leaching from the membrane by their covalent immobilization in gel. Fig. 1.a shows the 2D fluorescence spectra of the covalently immobilized sensing membrane. This membrane exhibits a strong fluorescence emission at 590 nm when excited by 470 nm radiation in aqueous media deaerated by bubbling N2 gas. Fluorescence emission intensity was reduced by the quenching process of dissolved oxygen in liquid as shown in Fig. 1.b.



[Fig. 1] 2D-fluorescence spectra of optical sensing membrane, (A) 0% dissolved oxygen, (B) 100% dissolved oxygen.

Fig. 2 shows the instrumental setup realized to interrogate the sensing probe. Sensing probe at the tip of the optical fiber is illuminated by 470 nm blue light and luminescence 590 nm reflected beam is collected. It consists of a 470 nm high brightness LED (LB520, Seoul Semiconductor Co., Ltd., Korea), 2 mm dual branch plastic optical fiber (SH-8001, Mitsubishi Co., Japan), and silicon photodiode (OPT301M, Texas Instruments Co., USA). In this optical system, we adopted condensing lens and 600 nm bandpass filter for minimize the interference by the external light and for amplifying the low intensity of luminescence beam by the effect of dissolved oxygen. Generated electric signal is modulated by typical optoelectronic circuit as shown in Fig. 2 b.



[Fig. 2] (A) Set-up of optical components and (B) optoelectronics

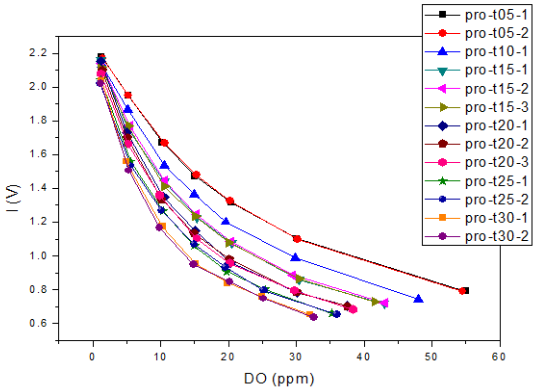
2.2 Results and Discussion

Typically, experimental results on the luminescent properties of oxygen sensitive luminophores based on the ruthenium, iridium and palladium complexes have shown an excited state lifetime dependence on the temperature. [8] Fig. 3 shows the decreasing output signals of fluorescence intensities depend on the temperature at different amount of dissolved oxygen in water. Based on this observation, we used following equation for compensation. In this experiment, we used the method of KS I ISO 5813 (Winkler-Azide modification) for finding compensation values.

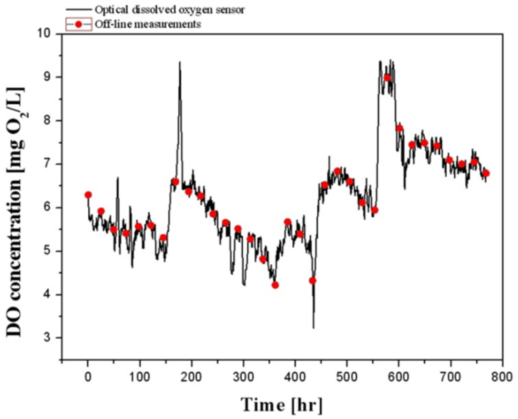
$$\frac{(T-T_L)O_{2H} + (T_H-T)O_{2L}}{T_H - T_L} = O_2$$

Where T is the measured temperature of solution by temperature sensor, T_H and T_L are the high and low values of compensation range of temperature. And O_{2H} and O_{2L} are concentrations of dissolved oxygen at those temperature ranges. In our measurement system, we used the compensation coefficient by 5℃ between the ranges of water temperature from 5℃ to 50℃.

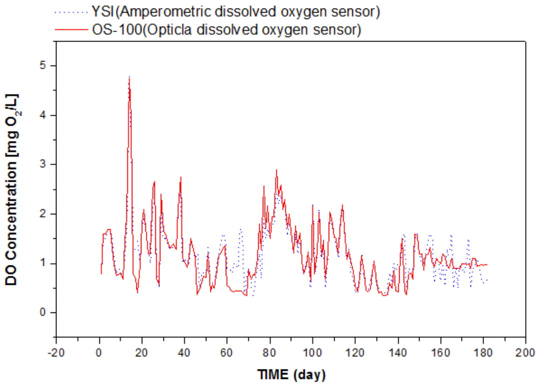
For characterizing our device in actual situation, we did comparative test between an amperometric sensor (YSI-550A, YSI Co., USA), often considered the reference for online oxygen measurement, and OS-100 sensor (Global Optical Communications Co., LTD., Korea) in different conditions. Fig. 4 illustrates comparative test results in phosphate buffer solution with pH 3 to pH 10. In this experiment, the OS-100 optical sensor is shown to measure with a less than 1% measurement error under the external ionic strength from 25 mM to 200 mM. Also, it shows that the developed DO sensor does not influence by the presence of hydrogen ion. Fig. 5 shows 6 months period experimental data of DO concentration at wastewater treatment plant at Daegu Dyeing Industrial Center. The wastewater from dyeing industry has deteriorated condition such as high temperature, contains high alkaline substances compare to the typical wastewater or sea water. In this case, the OS-100 optical sensor is still shown to measure with ±2% measurement error.



[Fig. 3] Effect of water temperature on the measurement of dissolved oxygen concentrations based on the ruthenium(II)-complex



[Fig. 4] Long-term on-line measurements of DO concentrations with OS-100 sensor and comparison with off-line measurements



[Fig. 5] Comparative test of an OS-100 and YSI-550A in wastewater treatment plant (Daegu Dyeing Industrial Center, Korea)

3. Conclusion

We developed a fluorescence-based optical DO sensor for on-line monitoring of dissolved oxygen in wastewater. Oxygen sensitive sensor matrix was prepared using the mixture of organosilicon precursor and solution of $[Ru(dpp)_3]^{2+}$ and was sprayed on quartz plate. Properties of sensor film exhibit deviation less than ± 1% under the wide range of DO concentration from 3 to 10 with temperature range of 4℃ and 50℃. The developed optical DO sensor was actually mounted in wastewater at wastewater treatment plant on dyeing industry. We did online monitoring of DO concentration for 6 months in this vicious environmental condition. Experimental results showed the changes of DO concentrations in wastewater treatment processes with accuracy better than ± 2% during the 6 months measurements period. This sensor exhibits advantages over many existing optical DO sensors including wider dynamic DO concentration range, ease of fabrication and long-term stability in vicious condition. The application of this sensor for DO concentration monitoring of industrial processes is in progress in our laboratory.

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