

A novel sensor based on the porous plastic probe for determination of dissolved oxygen in seawater

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Abstract

A new sensor based on the porous plastic probe has been developed for the detection of dissolved oxygen. This probe was prepared by co-polymerization of monomer, cross-linking reagent, porogent and luminescent ruthenium(II)diimine complex. The porous plastic probe exhibits good response to dissolved oxygen and resistance to indicator leaching out due to its high hydrophobicity. The preparation and characteristics of the probe were investigated in detail. This porous plastic probe serves as analyte-sensitive function as well as optical wave-guide, which make it easy to assemble the fiber-optical chemical sensor (FOCS). The developed sensor has been applied to the determination of dissolved oxygen in seawater with satisfactory results compared with the standard method.

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1. Introduction

The determination of dissolved oxygen is of great importance in environmental, biomedical and industrial analysis. Considerable efforts have been devoted to the development of optic oxygen sensors. These sensors have great advantages over electrochemical devices, such as no oxygen consumption in the sensing process, no requirement for reference electrode, inertness against sample flow rate or stirring speed, and immunity to exterior electromagnetic field interference [1].

Usually, the optical film of an optical sensor consists of an analyte-sensitive dye and a support matrix. Besides being inert, suitable matrices must be able to disperse or dissolve the dye, be permeable to oxygen and hydrophobic to isolate other ions. Among the published literatures, sol–gel-based films or nanoparticles [2–9] have been proven to be promising matrices for oxygen sensing, due to their high oxygen permeability, optical transparency, and good mechanical and chemical stability. Although the sol–gel technique has been used increasingly in

the fabrication of chemical and biochemical sensors, the success of manufacturing a sol–gel film depends heavily on the rates of hydrolysis and the condensation process, both of which are greatly affected by a number of parameters including precursor type, water/precursor mole ratio, catalyst type, pH, relative humidity and temperature [2]. It is difficult to control the sol–gel process and to obtain reproducible sol–gel films. In addition, the sol–gel films are generally very brittle and easy to break upon mechanical shock [1]. Other matrices which have been addressed such as polydimethylsiloxane polymer [10], siliceous zeolite [11], mesoporous silica [12], silicone rubber [13,14], silica gel [1], polystyrene [15–18], polyvinylchloride (PVC) and ethyl cellulose (EC) [19], cellulose acetate butyrate (CAB) and poly methyl methacrylate (PMMA) [20]. In addition, a composite matrix [21–23] or co-polymer [24] has also been used.

Optical dissolved oxygen sensors are generally fabricated by spreading the dissolved sensing material on planar surfaces, dip-coating on fibers or by spin-coating technique. The film sensing membranes help oxygen diffuse from the surrounding medium into the films and result in relatively fast response times. However the thin films suffer from two drawbacks in practical application. Firstly, the sensitive dyes or indicators in the thin membranes are apt to leaching out. Secondly, the sensing mem-

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brane cannot withstand abrasive in aqueous environments and are apt to brush off from the probe over a long period of time.

Porous fiber-optic sensors are developed due to their high sensitivity and convenience for loading of reagent-phase. Glass is one of the general matrices of porous fiber-optic sensor. Zhou et al. [25] used a porous glass fiber-optic sensor for the high-sensitivity measurement of humidity. But it was very difficult to prepare and treat this kind of porous glass optical fiber, the lifetime of the probe is limited due to its crisp mechanism property, and the indicators adsorbed physically onto the porous glass matrix are easily leaked out. To overcome these problems, we developed a novel porous plastic probe [26] by copolymerization technique. This porous plastic probe serves as analyte-sensitive function as well as optical wave-guide, so it is easy to couple with the common optical fiber. Moreover, the probe exhibits good gas permeability, optical transparency, physical and mechanical properties. In this work, we fabricated a porous plastic probe for dissolved oxygen. The fluorescent ruthenium diimine complex tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II)chloride [3,7,23,27,28], $[\text{Ru}(\text{dpp})_3]\text{Cl}_2$, was chosen as the sensing reagent because of its highly emissive metal-to-ligand charge transfer state, long lifetime, high luminescence quantum yield and large Stokes shift. Furthermore, the strong absorption in the blue–green region of the spectrum is more compatible with high-brightness blue light-emitting diodes. The fabrication and characterization of the porous plastic probe were investigated in this paper, and a fiber-optical chemical sensor was developed for determination of dissolved oxygen in seawater.

2. Experimental

2.1. Chemicals

Tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II)Chloride ($[\text{Ru}(\text{dpp})_3]\text{Cl}_2$) used as an oxygen sensitive indicator was synthesized as described in Ref. [29]. Diethylene glycol dimethacrylate (DGDM), isobutyl methacrylate (IBM) and 2,2,3,3-tetrafluoropropyl methacrylate (TFPM) were all obtained from Sigma. Before polymerization, IBM and TFPM were washed with 0.5 mol L^{-1} NaOH in order to remove the inhibitor, followed by washing in double-distilled water to pH

7.0, then dried with MgSO_4 . Azobis (isobutyronitrile) (AIBN) was recrystallized from ethanol before use.

2.2. Fabrication of the porous plastic probe

IBM and TFPM were chosen as the monomers, DGDM as the cross-linking reagent, $\text{Ru}(\text{dpp})_3\text{Cl}_2$ as the indicator, toluene as the porogent and AIBN as the initiator. Monomer, cross-linking reagent, porogent, indicator and initiator were mixed equably at a proper ratio, and then the mixture was injected into a 10 cm length glass capillary (200 μm in diameter). The glass capillary was then sealed by an adhesive. When the adhesive was solidified, the glass capillary was immersed in water at about 60°C for 24 h to complete the polymerization. After polymerization, the uniform optical transparent plastic polymer was pulled out of the capillary. And then it was put in ethanol to remove the porogent and superfluous indicator. Finally the porous plastic polymer was polished and coupled with the general optical fiber to assemble the fiber-optical chemical sensor.

2.3. Instrumental setup

The instrumental setup is shown in Fig. 1A. Fluorescence intensities were collected by USB-2000 fluorescence spectrometer (Ocean Optic Inc., USA), the 470 nm excitation light from the light source LS-450 (Ocean Optic Inc., USA) was directed into one bundle of the bifurcated optical fiber QBIF600-UV-VIS (Ocean Optic Inc., USA) and reach the common end of the bifurcated fiber, with which the porous plastic probe was connected. The 610 nm light emitted from the probe was transmitted to the other bundle of the bifurcated optical fiber, which was connected with USB-2000 fluorescence spectrometer. Data acquisition and signal processing were performed using a portable computer with the OOIBase32 software (Ocean Optic Inc., USA). The probe was equipped in a flow cell (see Fig. 1B). The samples with different dissolved oxygen concentration were carried and regulated by a flow injecting apparatus model IFIS-C (Xian Remex analysis instrument Co. Ltd., China.). All measurements were performed under air-conditioned environment having a constant temperature of $25 \pm 1^\circ\text{C}$. The dissolved oxygen samples were calibrated by a Dissolved Oxygen Meter Model 850A (Orion, USA). Parts of the tests for the porous plastic probe were car-

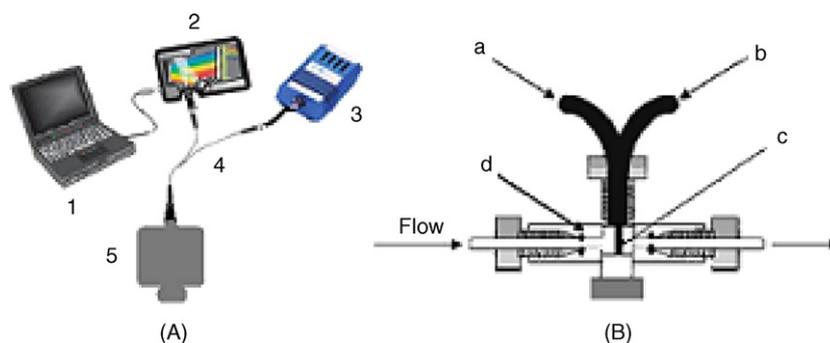


Fig. 1. Diagram of the instrumental setup (A) and design of the flow cell (B). (1) Personal computer; (2) fluorescence spectrometer (USB2000 FLG); (3) excitation source (LS/450); (4) bifurcated fiber-optic probe; (5) flow cell; (a) excitation optical fiber; (b) emission optical fiber; (c) porous plastic probe; (d) O-ring.

ried out on a fluorescence spectrophotometer model 970 CRT (Shanghai analytical instrument factory, China).

3. Results and discussion

3.1. The principle of novel porous plastic probe

The porous plastic probes were fabricated by a copolymerization technique. This procedure involved the monomer and cross-linking reagent, which can be polymerized at the presence of the porogent. Usually the porogents are inert solvents, which could not be chemically bound to the polymer network and be readily removable from the polymer to leave an interconnected porous structure. The amount of cross-linking reagent would affect the cross-linking degree of the polymer. The configuration of micro-pores could be controlled by the porogent. The indicator could be immobilized on the polymer fiber by chemical or physical method during polymerization. The polymer can be then assembled to be a fiber-optic chemical sensor by coupling with the optic-fiber based on the wave-guide technique.

The principle involved in the preparation of the porous plastic optical fiber probe for dissolved oxygen is shown in Fig. 2. This polymer fiber was of high dissolved oxygen permeability and water impermeability. Therefore, in aqueous solution dissolved oxygen would easily diffuse into the probe to react with the fluorescent indicator, while other ions would be prohibited outside of the probe. After dissolved oxygen diffuses into the fiber probe, the fluorescence of $[\text{Ru}(\text{dpp})_3]^{2+}$ was then quenched. The quenched fluorescence intensity of the indicator was related to the concentration of dissolved oxygen in solution.

3.2. Optimization of porous plastic probe

The composition of the probe would influence the physical properties as well as the sensitivity of probe for dissolved oxygen. Several monomers such as styrene, methyl methacrylate, IBM, and TFPM were tested. It was found that when IBM and TFPM were selected as monomers, the porous plastic probe for dissolved oxygen obtained the best sensitivity. The result indicates that the fluorinate polymer is a good host for oxygen sensor due to their chemical inertness, high oxygen permeability and photo-stability [8,21–23]. The ratio of IBM and TFPM also influenced the sensitivity of the probe for dissolved oxygen.

When the ratio of IBM and TFPM reached 1:1% (v/v), the $I_{\text{N}_2}/I_{\text{air}}$ value of the probe for dissolved oxygen was the highest.

The proportion of porogent and cross-linking reagent would affect the distribution of micro-pores and the optical property [26], and further affect the physical properties of the probe and the response sensitivity for dissolved oxygen. The optimal amount of DGDM was 0.05 ml in the experiment. The porogent could change the porosity in the porous plastic fiber. Since the pores could be acted as an O_2 channel to quench $[\text{Ru}(\text{dpp})_3]^{2+}$ entrapped in the polymer matrix, the increase in porosity led to an increase in the bimolecular quenching rate constant, and then resulted in enhanced sensitivity of the probe for dissolved oxygen. On the other hand, the optical diffusion increased and this would result in the block of the optical transmittance. Moreover, the excessive of porogent would decrease the porosity on the contrary and resulted in a decrease in the bimolecular quenching rate constant and sensitivity of the probe for dissolved oxygen. Toluene was tested as the porogent in the experiment, and the results showed that the optimal composition of the probe is TFPM: 25%, IBM: 25%, DGDM: 25%, toluene: 25% (v/v). A typical scanning electron microscope (SEM) image (JSM-35CF) is shown in Fig. 3. SEM verified that the porogent could not be chemically bound to the polymer network during polymerization due to its inertness and be removable from the polymer to leave an interconnected porous structure.

In contrast to the probe sensitivity, the response time was related to the diffusion and reaction equilibrium, and it is expected to depend largely upon the rate of diffusion into the encapsulating medium [30]. The diameter of the porous plastic fiber would affect the response time for dissolved oxygen. Several diameter scales of porous plastic fiber samples from 1000 to 200 μm were prepared. The result showed that the time to achieve 95% of the full response t_{95} varied from 17 to 1.5 min when the diameter of porous plastic fiber was minished from 1000 to 200 μm . Moreover, the porous plastic probe with 200 μm in diameter exhibited better mechanical strength and flexibility.

3.3. Probe characteristics

The fluorescence spectroscopy of $[\text{Ru}(\text{dpp})_3]^{2+}$ is dominated by metal-to-ligand charge transfer (MLCT) process which involves the promotion of an electron from a metal d orbital to a ligand π^* orbital. The fluorescence spectra of $[\text{Ru}(\text{dpp})_3]^{2+}$

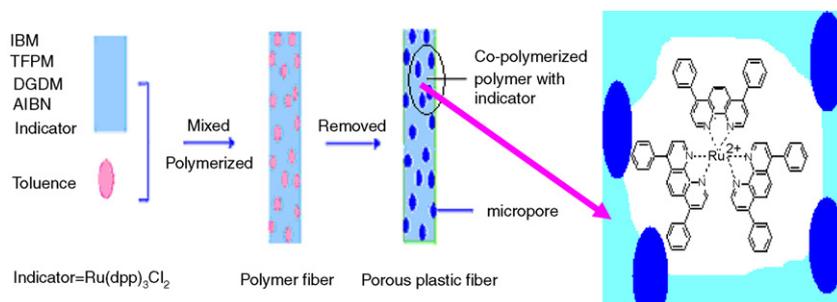


Fig. 2. The principle involved in preparation of the porous plastic optical fiber probe for dissolved oxygen.

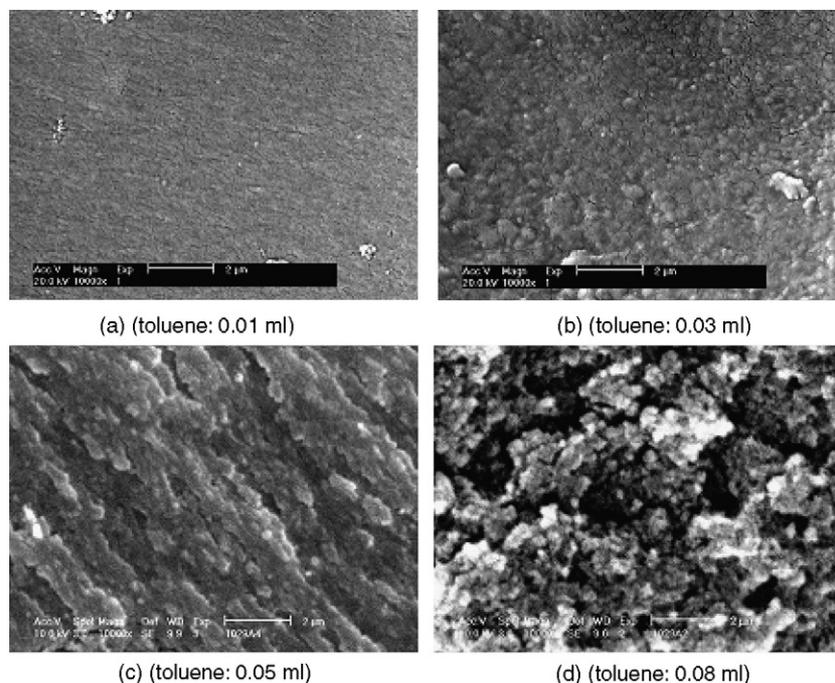


Fig. 3. SEM image of porous plastic optical fiber sample with different amount of the porogen. TFPM: 0.05 ml; IBM: 0.05 ml; DGDM: 0.05 ml; $[\text{Ru}(\text{dpp})_3]\text{Cl}_2$: 1.0×10^{-4} mmol. (a) Toluene: 0.01 ml, (b) toluene: 0.03 ml, (c) toluene: 0.05 ml, and (d) toluene: 0.08 ml

encapsulated in porous plastic probe is shown in Fig. 4. The $I_{\text{N}_2}/I_{\text{air}}$ value of the probe for dissolved oxygen was 4.00.

Fig. 5 showed the typical dynamic response of the probe on exposure to N_2 - and air-saturated water. The stable and reproducible signals could be obtained. T_{95} were about 1.5 min on going from N_2 - to air-saturated water and 3.0 min on going from air- to N_2 - saturated water. The obvious difference of such two equilibrium times would be explained by the faster diffusion rate of O_2 than that of N_2 in porous plastic fiber probe.

In the simplest hypothesis of a luminophore in a homogeneous micro- environment, luminophore quenching follows the Stern–Volmer relationship:

$$\frac{I_0}{I} = 1 + K_{\text{SV}} [\text{O}_2]$$

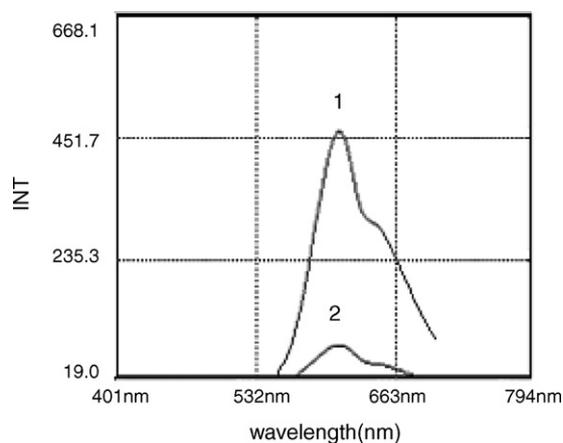


Fig. 4. Fluorescence spectra of porous plastic optical fiber probe in N_2 -saturated water and air-saturated water. (1) N_2 -saturated water and (2) air-saturated water.

where I_0 and I represent the steady-state luminescence intensities in the absence and presence of O_2 , respectively, K_{SV} is the Stern–Volmer quenching constant, and $[\text{O}_2]$ is the O_2 concentration. The fluorescence spectra obtained from the porous plastic probe at different dissolved oxygen concentrations are shown in Fig. 6. It can be seen that the fluorescence of $\text{Ru}(\text{dpp})_3\text{Cl}_2$ immobilized in porous plastic probe was quenched by dissolved oxygen. The intensity of fluorescence decreased with the increased oxygen concentration. Typical Stern–Volmer plot (Fig. 6) was fairly linear up to about 14 mg L^{-1} of dissolved oxygen and the approximate Stern–Volmer constant K_{SV} obtained from the linear part of the graph was 0.5523 L mg^{-1} . The limit of detection of the sensing probe was 0.1 mg L^{-1} , which was defined at a signal-to-noise ratio of $\text{S/N} = 3$.

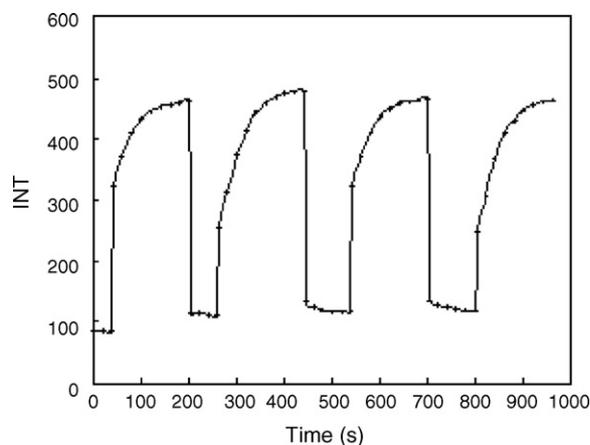


Fig. 5. Response time, reproducibility and relative intensity change of porous plastic fiber probe on exposure to N_2 - and air-saturated water.

Table 1
Determination of dissolved oxygen in seawater samples by the proposed and standard method

Sample no.	Proposed method ^a (mg L ⁻¹)	Iodimetry ^b (mg L ⁻¹)	Relative error (%)	Average error (%)
1	7.97 ± 0.28	7.61 ± 0.14	4.73	3.15
2	8.40 ± 0.20	8.22 ± 0.08	2.19	
3	8.35 ± 0.24	8.21 ± 0.10	1.70	
4	8.43 ± 0.25	8.50 ± 0.08	-0.07	
5	8.67 ± 0.21	8.30 ± 0.09	4.46	
6	8.43 ± 0.23	8.85 ± 0.11	-4.46	
7	8.58 ± 0.19	8.20 ± 0.12	4.63	

^a n = 6.

^b n = 3.

The leakage of [Ru(dpp)₃]²⁺ immobilized in the probe was also investigated. Because of the high hydrophobic property of the probe, the I_{N_2}/I_{air} value was constant after the probe was stored in water for a month. The porous plastic fiber probe was found independent of the salinity over the range from 5 to 40‰, this might also be attributed to the high hydrophobicity of the probe, which prevented the penetration of ions into the matrix and made it possible to on-line application in aggressive seawater.

3.4. Application for real seawater samples

The developed sensor system has been used for detection of dissolved oxygen in real seawater samples. The seawater samples were obtained from Xiamen area of Fujian, China. The salinity of the seawater sample in this area was measured and found to be 3.5043‰, which mainly consists of NaCl (3.0065‰) and MgSO₄ (0.4978‰). The samples were filtered through a 0.45 μm pore size membrane filter before being pumped into the flow cell. These seawater samples were also analyzed by the national standard method of China iodimetry for comparison with the proposed method. The results are shown in Table 1. It can be seen from Table 1 that there is no obvious difference between the proposed method and the standard method. The average error is lower than 4%.

4. Conclusion

A novel fiber-optical chemical sensor was developed for determination of dissolved oxygen in seawater based on the porous plastic probe, which serves as analyte-sensitive function as well as optical wave-guide. The porous plastic probe exhibited good response to dissolved oxygen except the relatively long response time. And the probe was prepared by cross-linking co-polymerization, which made the probe high hydrophobicity. This is very important for the sensor to resist the indicator leaching out and ion interference. The porous plastic probe shows promise as a relatively inexpensive, easily constructed sensor for the optical detection of dissolved oxygen in aqueous environment.

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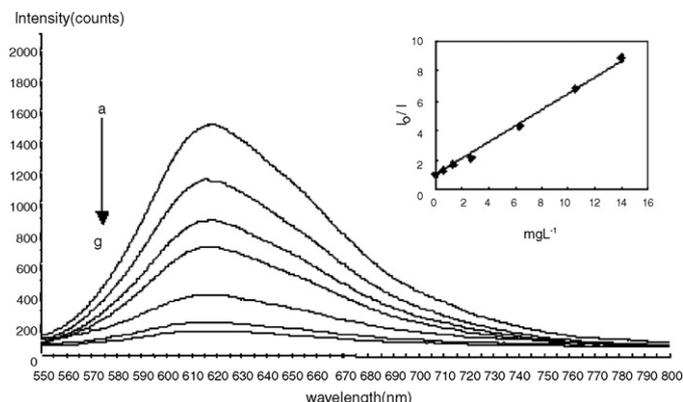


Fig. 6. Fluorescence spectrum of Ru(dpp)₃Cl₂ in porous plastic fiber under different concentration of dissolved oxygen. (a) 0 mg L⁻¹; (b) 0.56 mg L⁻¹; (c) 1.36 mg L⁻¹; (d) 2.71 mg L⁻¹; (e) 6.36 mg L⁻¹; (f) 10.0 mg L⁻¹; (g) 14.0 mg L⁻¹ dissolved oxygen. Conditions: λ_{ex} = 470 nm; λ_{em} = 610 nm; slit = 5 nm (ex), 10 nm (em) inset: Stern–Volmer plot.

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