Dissolved oxygen sensor by using Ru-fluorescence indicator and a U-shaped plastic optical fiber

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A dissolved oxygen (DO) sensor based on U-shape plastic optical fiber (POF) and dichlorotris (1, 10-phenanthroline) ruthenium ($[\mathrm{Ru(dpp)}^3]^{2+}$) as an oxygen indicator was described. Fluorescence intensity and lifetime were measured when the sensor was soaked into a water bath blasted with air with varied O_2/N_2 ratios. The influence of Ru concentration, annealing time and U-shaped POF curve radius on the system sensitivity was also studied. A two-layer model was proposed to analyze the deviation from linear relation described by Stern-Volmer equation, and to explain the deviation and the dependence of the fluorescence on curvature of U-shape POF. By fitting the experimentally measured sub-linear relation of τ_0/τ ratio versus oxygen concentration, the proportion of effectively sensitive layer and the Stern-Volmer coefficient can be evaluated to be $f = 0.59$ and $K_{SV} = 0.61$ typically.

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Measurement of oxygen concentration dissolved in water is of major importance, especially in medical sensing, environmental monitoring, and agriculture, for determining the oxygen content of blood and assessing the quality of water supplies. Considerable efforts have been devoted to developing optical and electrochemical methods for the quantitative analysis of dissolved oxygen (DO). Compared with other kinds of DO sensors, optical sensors show some basic advantages, such as immunity to exterior electromagnetic field interference, inertness against sample flow rate or stirring speed, no requirement for a reference electrode, and no O_2 consumption in the measurement. Ruthenium bonded with phenanthroline group is characterized by strong absorption in the blue-green region, large Stokes shift (emitting in the orange/red spectral region), high quantum yield, long unquenched fluorescence lifetime (on the order of ms), and higher stability. It has been suggested by many authors[1−3] as a particularly promising DO sensor for practical applications. In addition the Ru-incorporated organics are very soluble in typical sol-gel precursors[4]. In this paper, we used dichlorotris (1,10-phenanthroline) ruthenium ($[\mathrm{Ru(dpp)}^3]^{2+}$) as an oxygen indicator, and plastic optical fiber for delivering the excitation light and picking up the longer wavelength fluorescence radiation. To enhance exciting efficiency, the POF sensor head was bent in U-shape. It is found experimentally that the obtained characteristics show deviation from linear relation described by commonly used Stern-Volmer equation. A two-layer model was proposed to explain the phenomena. The effect of oxygen indictor concentration, sol-gel film annealing time and U-shape POF curve radius on the sensitivity was also studied.

Oxygen as a triplet molecule is able to efficiently quench fluorescence of certain fluorophores. The quenching degree relates to the frequency of collisions between oxygen and fluorophore molecules, and therefore to the concentration, pressure and temperature of the media containing oxygen. The oxygen quenching decreases not only the fluorescence intensity, but also the fluorescence lifetime. It is shown that the ratio of the fluorescence intensities to lifetimes in absence (I_0/τ_0) and presence (I/τ) of oxygen can be described by Stern-Volmer equation:

$$I_0/I = \tau_0/\tau = 1 + K_{SV}[\mathrm{O}], \qquad (1)$$

where K_{SV} is Stern-Volmer constant, and [O] is the concentration of oxygen, in other words, it is the proportion of oxygen in the mixed gas.

The lifetime can be measured by the phase-fluorometry method, which has a merit of immunity to fluctuation of the light source and is more reliable than intensity measuring alone. In the method, the exciting source is modulated sinusoidal and the phase shift between excitation and fluorescence is measured in absence (ϕ_0) and presence (ϕ) of oxygen. The fluorescence lifetime can be obtained with the relation of $\tan \phi = 2\pi f \tau$[5], where f is the modulation frequency. Then the relation between ϕ and [O] can be obtained:

$$\tan \phi_0 / \tan \phi = 1 + K_{SV}[\mathrm{O}]. \qquad (2)$$

In the experimental setup, the phase shift is calculated by the correlation method[6]. Signals of the modulated exciting light and generated fluorescence are measured respectively as

$$x(t) = A\sin(2\pi f t + \varphi_1) + N_x(t), \qquad (3\mathrm{a})$$

$$y(t) = B\sin(2\pi f t + \varphi_2) + N_y(t), \qquad (3\mathrm{b})$$

where $x(t)$ and $y(t)$ stand for the two signals, A and B are the amplitudes, $N_x(t)$ and $N_y(t)$ are respective noises, which must be taken into consideration in a practical measuring system. Correlation $R_{xy}(\Delta t)$ between them can be expressed as

$$R_{xy}(\Delta t) = \frac{1}{T} \int_0^T [A\sin(2\pi f t + \varphi_1) + N_x(t)]$$

$$\times [B\sin(2\pi f(t + \Delta t) + \varphi_2) + N_y(t + \Delta t)]\mathrm{d}t. \quad (4)$$

Generally, correlations between noises and between the noise and signal can be considered to be zero due to the broadband property of noise spectrum. Then we have the relation when condition of $\Delta t = 0$ is satisfied:

$$R_{xy}(0) = \frac{AB}{2}\cos(\varphi_1 - \varphi_2). \tag{5}$$

The amplitudes can be obtained by autocorrelations: $A = \sqrt{2R_{xx}(0)}$ and $B = \sqrt{2R_{yy}(0)}$. The required phase shift can then be obtained:

$$\phi = \varphi_1 - \varphi_2 = \arccos\left[\frac{R_{xy}(0)}{\sqrt{R_{xx}(0)R_{yy}(0)}}\right]. \tag{6}$$

To excite the fluorescence of Ru-incorporated DO sensor, a short wavelength light source must be used, and the generated longer wavelength fluorescence must be detected. An optical fiber can not only deliver the exciting light, but also transport the fluorescence. Plastic optical fiber (POF) has an aperture much larger than the silica fiber used in optical communications, making it easier to couple with source and to connect with each other, and suitable for delivering both the exciting light and fluorescence with low losses. In addition, POF shows advantages of low cost and high mechanical stability. Hecht reported a sensor array aided with POF as light guide to detect weathering process[7]. In this paper, the sensing material of Ru-incorporated sol-gel is coated onto the surface of POF. The excitation of fluorescence relies mostly on the evanescent field along the fiber of boundary of the exciting light propagating in the POF. It has been shown in Ref. [8] that fiber bending will couple guided modes to radiation mode, low order modes to high order modes, and will also change spreading of the evanescent field, namely, it will expand at the outer side of the bending and shrink at the inner side. In this paper, we make the POF into a U-shape head to enhance its sensitivity.

Sol-gel materials are used very often in sensors for its advantages of low-cost, easy-processing, and variety of material composition. Sol-gel films can provide a microporous support matrix, in which analyte-sensitive fluorophore may be entrapped and smaller analyte species may diffuse and interact with the fluorophore. It has been reported that the oxygen quenching process in organic modified silicate (ormosil) is stronger than that in inorganic sol-gel materials[9]. In this letter, tetraethoxysilane (TEOS) was used as precursors, methyl-triethoxysilane (MTEOS) as an organic modifier. The sol-gel process was the same as Refs. [10,11]. 3.6-ml ethanol, 2-ml TEOS, and 6-ml MTEOS were mixed in an open vial, and 1.1 ml of 0.02 mol/L hydrochloric acid and $[Ru\,(dpp)_3]^{2+}$ were added into the vial. The solution was then stirred for 6 hours in a 50 °C water bath.

POF made of poly methyl methacrylate (PMMA) with core diameter of 1 mm was used to be the substrate of DO sensor, which plays also as a passage of both exciting light and fluorescence. The jacket of a section of POF about 3-cm long was stripped, and bent into a U-shaped sensor head. The prepared sol-gel was dip-coated on the section. Figure 1(a) shows a photo of sensor head, and Fig. 1(b) is a microscopic photo of the coated POF cross-section, from which the thickness of sol-gel coating can
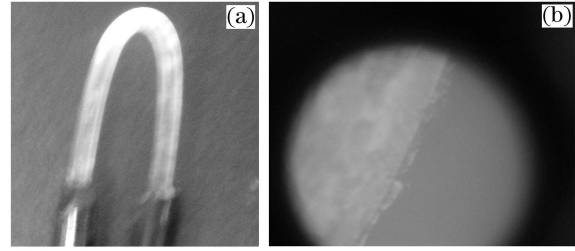

Fig. 1. (a) Photo of sensor head; (b) microscopic photo of fiber cross-section.
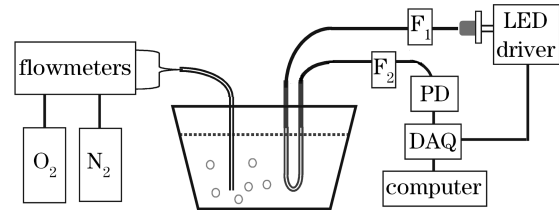

Fig. 2. Schematic diagram of experimental setup.

be estimated to be about 10 μm, with some variation in fiber length and around the circle. The prepared organic and inorganic mixed sol-gel was sticker than pure inorganic sol-gel that makes the coating easier and thicker.

Figure 2 shows a photo of sensor head being excited and a schematic of the experimental setup. A high brightness blue light emitting diode (LED) was used as the excitation source with spectrum centered at 470 nm. The output power of the LED was set at around 0.55 mW. A photodiode was used to detect the fluorescence. In order to separate the exciting light and the fluorescence in spectrum, two filters were used to block unwanted signal: F_1 was a narrow band filter to cut off long wavelength tail of the LED, and F_2 was a low frequency pass filter to weaken the exciting light. The LED emission was sinusoidally modulated at 20 kHz, and its current signal was fed to the data acquisition card(DAQ) of the computer to correlate with fluorescence signal and calculate the phase difference. A water bath was used as samples with various oxygen concentrations, which were changed by an air muzzle connecting to an oxygen tank and a nitrogen tank through their respective flowmeters, just as Ref. [12].

The lifetime varied with oxygen concentration was measured firstly, as shown typically in Fig. 3. It is worth to notice that the curve is not a straight line as expressed by Stern-Volmer equation.
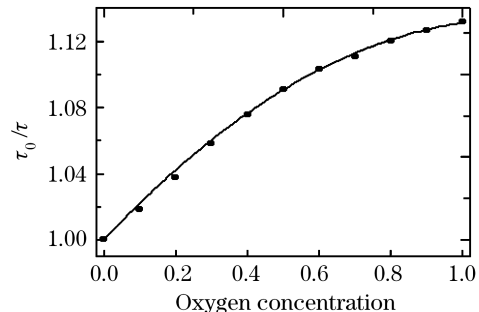

Fig. 3. Ratio of fluorescence lifetimes varied with DO concentration.

Secondly, effect of Ru concentration on the sensitivity was investigated by adding 2, 4, 6, and 8-mg/ml $[Ru(dpp)^3]^{2+}$ solutions in the sol-gel coating. The experiment result is shown in Fig. 4. We can see that τ_0/τ will increase with the increase of $[Ru(dpp)^3]^{2+}$ concentration from 2 to 4 mg/ml, but decrease from 4 to 8 mg/ml. This phenomenon may be caused by self-quenching[13].

As described in Ref. [8], the curvature of U-shape POF will change the evanescent field around the POF. It was verified by experiment results. Figure 5 is the measured ratio of τ_0/τ for two U-shaped POF heads with curvature radii of 6 and 10 mm, showing the sensitivity increasing with the curvature.

To explain the sub-linear characteristics of I_0/I and τ_0/τ varied with oxygen concentration, Refs. [2,14] proposed a two site luminophore model with a revised Stern-Volmer relation instead of linear Stern-Volmer relation as

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = \left[\frac{f_1}{1 + K_{SV1}[O]} + \frac{f_2}{1 + K_{SV2}[O]}\right]^{-1}, \quad (7)$$

where f_1 and f_2 are the fractional contributions of the two site luminophores, $f_1 + f_2 = 1$, but detailed descriptions of the different luminophores were not given.

Since the diffused oxygen concentration will decrease rapidly with the depth and may not pass through the whole sol-gel layer thickness, and the excitation intensity usually decreases from the interface between the POF and coating to surface, the behaviors of I_0/I and τ_0/τ may differ from those in the uniform case. The evanescent field of excitation and the oxygen concentration diffused into the sol-gel layer are depicted schematically
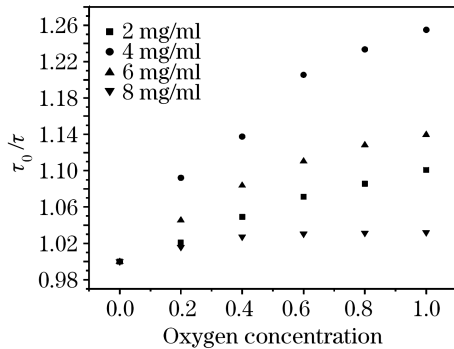

Fig. 4. Experimental curve with different $[Ru(dpp)^3]^{2+}$ concentrations.
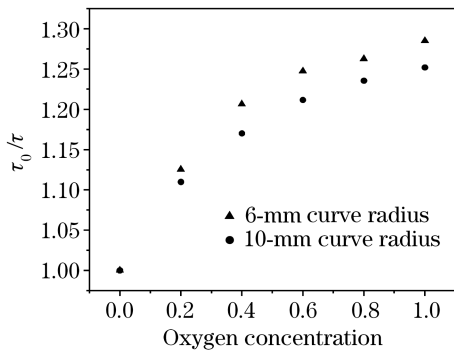

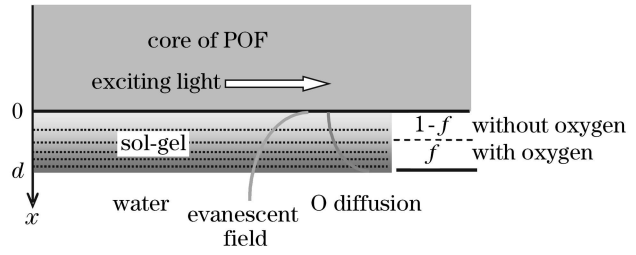Fig. 5. Experimental curve with different curve radii.

Fig. 6. A two-layer model to explain sub-linear quenching behavior.

in Fig. 6. Taking the distribution of excitation light intensity $A(x)$ and oxygen concentration $[O](x)$ in the sol-gel layer thickness into account, the fluorescence intensity can be written as

$$I = \int \frac{A(x)}{1 + K_{SV}[O](x)}dx = \int \frac{A(0)e^{-\gamma x}}{1 + K_{SV}[O](d)e^{\beta(x-d)}}dx, \quad (8)$$

where the intensity of micro volume is supposed to be satisfied with Stern-Volmer law, γ, β are the attenuation coefficients of excitation light and oxygen concentration in the sol-gel layer, $A(0)$ is the excitation light intensity in the layer $x = 0$, $[O](d)$ is the oxygen concentration at the position $x = d$. In the second integral of Eq. (8), the excitation and oxygen concentration distributions are expressed in exponential functions, which are usually considered satisfactory approximations to the real situation. In case of no oxygen,

$$I_0 = \int A(0)e^{-\gamma x}dx = A(0)(1 - e^{-\gamma d})/\gamma. \quad (9)$$

Thus their ratio can be written as

$$\frac{I}{I_0} = \frac{\gamma}{1 - e^{-\gamma d}} \int \frac{e^{-\gamma x}dx}{1 + K_{SV}[O](d)e^{\beta(x-d)}}$$

$$\approx \frac{\gamma}{1 - e^{-\gamma d}} \int e^{-\gamma x}[1 - K_{SV}[O](d)e^{\beta(x-d)}]dx$$

$$= 1 - K_{SV}[O](d)e^{-\beta d}\frac{\gamma}{\gamma - \beta}\frac{e^{-\beta d} - e^{-\gamma d}}{1 - e^{-\gamma d}}. \quad (10)$$

In the above, deducting an approximation is taken for the usual case of $K_{SV}[O](d) \ll 1$.

To take into account of this mechanism, referring to Refs. [2] and [14], the varied sensitive sol-gel coating can be equivalently considered as a two layer composite: the outer layer contacts surrounding medium and senses the dissolved oxygen directly, while the fluorescence of inner layer will not be quenched by the oxygen as a part of the whole fluorescence. The total fluorescence intensity can be considered as that emitted by the two layers: $I = fI_1 + (1 - f)I_2$, and the measured lifetime can be regarded as an average lifetime of the two layers: $\tau = f\tau_1 + (1 - f)\tau_2$, where f is the effective portion of sensitive layer, and subscripts 1 and 2 are for the amount of outer and inner layers, respectively. Thus we get a new

relation as

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = [1 - f + \frac{f}{1 + K_{SV}[O]}]^{-1}$$

$$= 1 + \frac{fK_{SV}[O]}{1 + (1 - f)K_{SV}[O]}$$

$$\approx 1 + fK_{SV}[O] - f(1 - f)K_{SV}^2[O]^2. \qquad (11)$$

It is just the sub-linear characteristics observed experimentally. The fractional factor can be attributed to the non-uniform distribution of excitation and diffused oxygen concentration. Combining Eqs. (11) and (12), the factor f can then be expressed as

$$f = [1 + K_{SV}[O]]\frac{\gamma}{\gamma - \beta}\frac{e^{-\beta d} - e^{-\gamma d}}{1 - e^{-\gamma d}}$$

$$\approx \frac{\gamma}{\gamma - \beta}\frac{e^{-\beta d} - e^{-\gamma d}}{1 - e^{-\gamma d}}. \qquad (12)$$

The approximation holds in the usual case of $K_{SV}[O] \ll 1$. By fitting the experimentally measured data shown typically in Fig. 2 with Eq. (11), the parameters can be obtained to be $f = 0.59$ and $K_{SV} = 0.61$.

It can be deduced from Eqs. (11) and (12) that the sensitivity of DO sensor increases with the portion factor f, and f will increase with the decrease of both coefficients γ and β. Since most DO sensors are made of sol-gel coated on some transparent substrates, the two-layer model may be helpful to understand the mechanism. By the model, the dependence of sensitivity on U-shape curvature can also be explained. As the radius of the bending POF increases, the evanescent field will expand to the sol-gel layer, which will cause the decrease of γ_x and the increase of f. On the other hand, the increase of the sol-gel layer's refractive index will also help to expand the evanescent field. This needs further research on the sol-gel material design and fabrication.

In conclusion, a novel dissolved oxygen sensor is proposed. The measured ratios of fluorescence intensity and lifetime in absence of and in presence of oxygen are shown to be sub-linear. The dependences of sensitivity on Ru concentration and on curvature radius of the U-shape are investigated. A two layer model is proposed and used to explain the experimental results. These results will be useful for developing a kind of practical optical oxygen sensor.

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