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High sensitivity and accuracy dissolved oxygen (DO) detection by using PtOEP/poly(MMA-*co*-TFEMA) sensing film

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ABSTRACT

Fluorinated acrylate polymer has received great interest in recent years due to its extraordinary characteristics such as high oxygen permeability, good stability, low surface energy and refractive index. In this work, platinum octaethylporphyrin/poly(methylmethacrylate-*co*-trifluoroethyl methacrylate) (PtOEP/poly(MMA-*co*-TFEMA)) oxygen sensing film was prepared by the immobilizing of PtOEP in a poly(MMA-*co*-TFEMA) matrix and the technological readiness of optical properties was established based on the principle of luminescence quenching. It was found that the oxygen-sensing performance could be improved by optimizing the monomer ratio (MMA/TFEMA = 1:1), tributylphosphate(TBP, 0.05 mL) and PtOEP (5 μg) content. Under this condition, the maximum quenching ratio I_0/I_{100} of the oxygen sensing film is obtained to be about 8.16, Stern-Volmer equation is $I_0/I = 1.003 + 2.663[O_2]$ ($R^2 = 0.999$), exhibiting a linear relationship, good photo-stability, high sensitivity and accuracy. Finally, the synthesized PtOEP/poly(MMA-*co*-TFEMA) sensing film was used for DO detection in different water samples.

1. Introduction

The concentration of dissolved oxygen (DO) is the key indicator in water quality monitoring, sewage treatment, food, fermentation, aquaculture, and clinical diagnosis [1]. Generally, DO concentration in drinking water is not lower than 6 mg/L. When lower than 4 mg/L in ecosystems, fish suffocate from hypoxia [2]. In the field of food and fermentation, the control of DO concentration is an important consideration in ensuring the growth of microorganisms and the formation of products [3]. In life science, disease diagnosis can be obtained by mastering the content of DO in living cells to understand the metabolic status of cells and tissues [4].

Recently, optical oxygen sensors have been developed for monitoring the concentration of DO based on the principle of dynamic fluorescence quenching [5], which affords excellent characteristics such as long-term stability, high sensitivity, and good anti-electromagnetic interference capabilities as well as no oxygen consumption [6,7]. The optical oxygen sensor consists of fluorescence indicator molecules and appropriate matrix materials. The organic complexes of transition metals such as Tris (2,2′-bipyridine)ruthenium dichloride ($Ru(bpy)_3Cl_2$) [8] and metalloporphyrin complexes like (5,10,15,20)-tetrakis (pentafluorophenyl) porphyrin (PtTFPP) [9], palladium octa ethyl porphine (PdOEP) [10] and platinum octa ethyl porphine (PtOEP) [11] have been widely used as fluorescence indicator because of their uniquely of high sensitivity to oxygen, no oxygen-consumption, good stability, long excited-state lifetime and great stokes shift. Furthermore, polystyrene (PS) [12], poly (methylmethacrylate) (PMMA) [13] and polycarbonate (PC) [14] were usually used as matrix materials for the immobilization of the fluorescence indicator. Nevertheless, there has been increasing attention towards fluorinated polymers in recent time owing to the fact that they demonstrate good diffusion and permeability to oxygen, good thermal stability and photostability, and can disperse the fluorescent indicator uniformly. Note that the C—F bond length (1.32 nm) is short as compared with a C—H bond [15], and the bonding energy of the C—F bond (485 kJ/mol) is larger than that of a C—H bond (416 kJ/mol), which results in better stability. On the other hand, the lower surface energy of fluorinated polymer and stronger electronegativity of the fluorine atom can enhance affinity and induction forces towards oxygen molecules [16]. Therefore, fluorinated polymer is suitable for use as a matrix material for the oxygen sensor.

Most available optical oxygen sensors employ immobilized fluorescence indicator embedded within a matrix material via a physical embedding method to prepare the corresponding sensing films. Yutaka et al. [17] prepared two different optical oxygen sensors by immobilized PtOEP and PdOEP in a poly (styrene-*co*-pentafluorostyrene) film, and both have high sensitivity and accuracy when the concentration of oxygen is between 0 and 100% and 0–20%, respectively. In addition, the DO sensors were prepared by the encapsulation of PtOEP [18] and tris (2-phenylpyridine anion) iridium (III) complex ($Ir(ppy)_3$) [19]

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into poly (vinylidene-*co*-tetrafluoroethylene-co-propylene) [18] and poly(styrene-*co*-2,2,2-trifluoroethyl methacrylate) (poly(styrene-*co*-TFEMA)) films [19], respectively, which exhibit good photostability, and fast response times. In this work, we synthesized PtOEP/poly(MMA-*co*-TFEMA) film by varying monomer ratios, plasticizer and indicator loadings so as to investigate the effect of various parameters on oxygen sensing performance and obtain the optimal synthesis condition for a high-performance oxygen sensing film. Finally, the prepared oxygen sensor was applied in detecting the DO concentrations of Harbin beer, local tap water and Wahaha enriched oxygen water, respectively.

2. Experimental

2.1. Materials

Platinum octaethylporphyrin (PtOEP), trifluoroethyl methacrylate (TFEMA) and tributylphosphate (TBP) were purchased from J&K Chemical Company Limited. Methyl methacrylate (MMA) and 2, 2-azobisisobutyronitrile (AIBN) were supplied by Aladdin Industrial Corporation. Methyl alcohol (CH_3OH), methylbenzene, anhydrous $MgSO_4$ and anhydrous ethyl alcohol were obtained from Tianjin Kermel and Tianli Chemical Reagent Company Limited, respectively. HNO_3 and NaOH were purchased from Xilong Chemical Reagent Company Limited. Before use, MMA and TFEMA were washed with 5% NaOH to eliminate the inhibitor, then subsequently washed with distilled water until a neutral pH was obtained, and dried with anhydrous $MgSO_4$. AIBN as an initiator was used after recrystallization from ethanol.

The oxygen sensitivity of PtOEP/poly(MMA-*co*-TFEMA) was measured by a fluorescence spectrometer (LS55, Perkin Elmer, America) equipped with a self-regulating gas mixture device (Fig.1).

2.2. Preparation of PtOEP/poly(MMA-co-TFEMA) oxygen sensing film

2.2.1. Synthesis of poly(MMA-co-TFEMA) copolymer

Firstly, MMA and TFEMA were mixed in different monomer ratios (1:2, 2:3, 1:1, 2:1, 3:1, and 4:1), then 0.1 mL toluene solution of AIBN (0.001 g/mL) was added into the mixture dispersed by a vortex shaker. Subsequently, the reaction was carried out at 60 °C for 5 h in the argon atmosphere to obtain the colorless and transparent copolymer. Finally, the copolymer was washed with ethanol to remove the non-reactive monomer and stored at room temperature.

2.2.2. Preparation of the oxygen sensing film

0.1 g Poly (MMA-*co*-TFEMA) copolymer was dissolved in 1 mL of methylbenzene, followed by the addition of PtOEP and Tributylphosphate (TBP) in forming a well-mixed solution. A certain amount of the above mixture solution was evenly spread on a slide (12.5 × 40 mm), then the transparent film was obtained after evaporation of the solvent at room temperature. The oxygen sensing film was stored in a dark environment after soaking in ultra-pure water for 3 h. Finally, the high-performance oxygen sensing film was obtained.

3. Results and discussion

3.1. Effect of monomer ratios on the sensitivity of oxygen sensing film

Fig. 2 shows the quenching ratio (I_0/I_{100}) changing with the ratio of monomers. Here, I_0 and I_{100} are the intensities of PtOEP/poly(MMA-*co*-TFEMA) sensing film in 100% nitrogen (N_2) and 100% oxygen (O_2) [6], respectively. The ratio (I_0/I_{100}) represents the sensitivity of the film to DO. It is noted that there is a significant improvement in response to O_2 in PtOEP/poly(MMA-*co*-TFEMA) sensing film when compared with that of PMMA film ($I_0/I_{100} = 2.42$). The maximum value of I_0/I_{100} is resolved to be 4.05 when the ratio of MMA/TFEMA is 1:1. The C—F bond with its high bond energy can play a part in the protection of non-fluorinated segments [20], and it's beneficial in enhancing the permeability of oxygen in the matrix [15]. However, when the ratio of MMA/TFEMA is greater than 1, excessive amounts of TFEMA will be enriched over the surface and have a negative effect on oxygen sensing performance [21]. Therefore, we determined the best monomer ratio of MMA/TFEMA is 1:1 for the preparation of an oxygen sensing film.

3.2. Effect of the content of plasticizer on the sensitivity of oxygen sensing film

As the strong intermolecular force in the poly (MMA-*co*-TFEMA) easily weakens the flexibility and mechanical stability of the sensing film, it has a negative influence on the sensitivity of DO detection [22, 23]. To solve this problem, a plasticizer, TBP was added into poly (MMA-*co*-TFEMA), which could improve the activity of polymer chains, reduce the viscosity of the system, and enhance stability, flexibility and oxygen permeability [24–26]. Fig. 3 indicates the quenching ratio (I_0/I_{100}) against fluctuations in TBP. With the increase of TBP, I_0/I_{100} demonstrates a gradual improvement and reaches a maximum of 5.32, while it declines dramatically and is stable at around 3.8 when the amount of TBP exceeds 0.05 mL. This results from the fact that an excessive

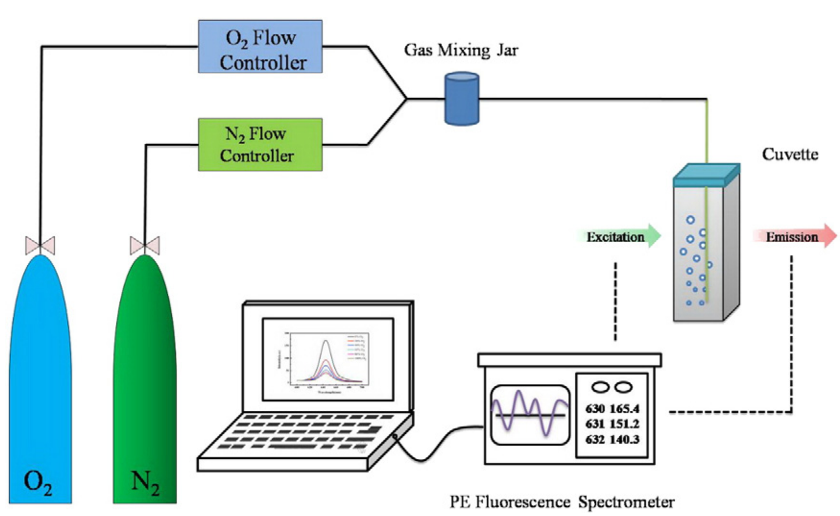

Fig. 1. Self-regulating gas (nitrogen/oxygen) mixture device.

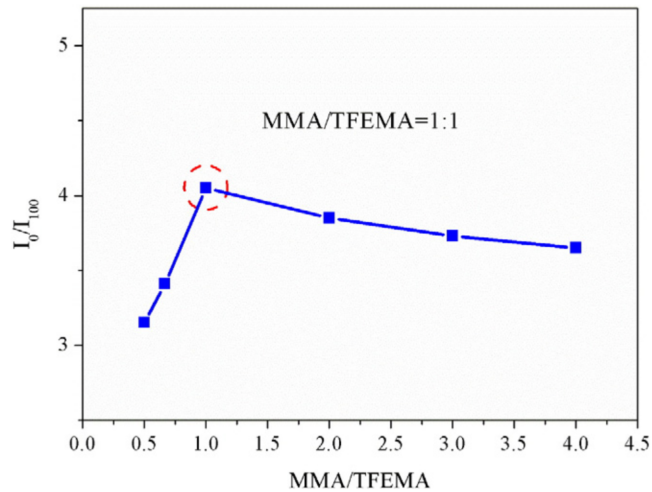

Fig. 2. Quenching ratio (I_0/I_{100}) versus monomer ratios (MMA/TFEMA).

quantity of TBP makes the polymer overplasticized and disperses its physical crosslinking points, depressing its stability, resulting in variations of the film's sensibility [27].

3.3. Effect of the concentration of indicator on the sensitivity of oxygen sensing film

The fluorescence intensity of poly (MMA-*co*-TFEMA) oxygen sensing film depends not only on the ratio of monomers [28], and the amount of plasticizer [29], but is also strongly influenced by the concentration of indicator [30]. In order to investigate the influence of the indicator on oxygen sensing performance,poly (MMA-*co*-TFEMA) was prepared with a monomer ratio of MMA/TFEMA (1:1) and 0.05 mL of TBP under different indicator loadings. Fig. 4 shows the quenching ratio against the amount of PtOEP, which reveals that I_0/I_{100} increases with an increase of PtOEP in the range of 0.5-5 μg, and then begin to decreases beyond 5 μg. The aggregation of an excessive amount of indicator molecules lead to the strong fluorescence quenching effect [31] and the deviation from the linear relationship between the quenching ratio and the concentration of DO [32].

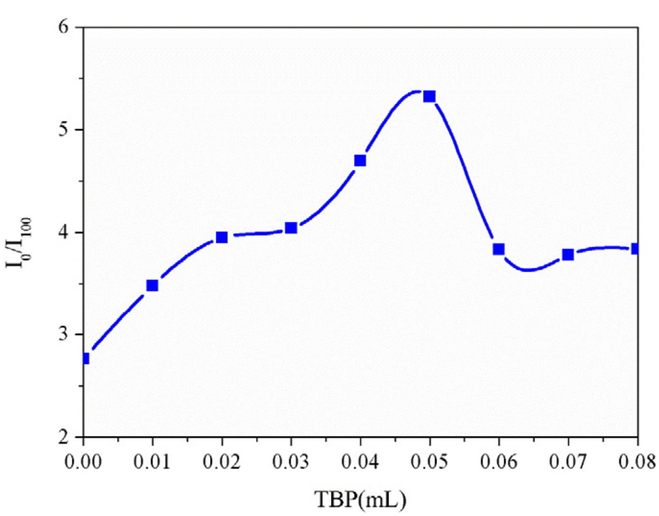

Fig. 3. Quenching ratio (I_0/I_{100}) versus the amount of TBP.

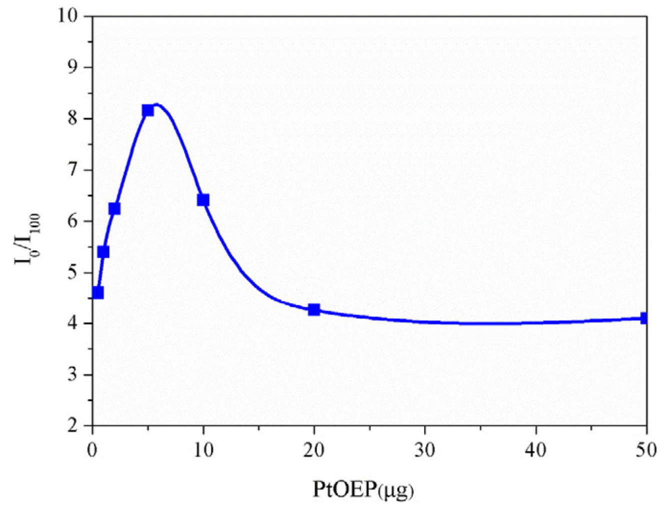

Fig. 4. Quenching ratio (I_0/I_{100}) versus the amount of PtOEP.

3.4. Stern-Volmer equation for the oxygen sensing film

The Stern-Volmer equation is a common tool for viewing and analyzing luminescence lifetimes and intensity quenching data [33]. It is given as:

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

here, I_0 and I are the fluorescence intensities in the deoxygenated and oxygenated conditions [6], respectively, which are controlled by the self-regulating gas mixture device. Both I and I_0 are steady-state luminescence signals obtained at 650 nm. I_0/I is the quenching ratio, and K_{sv} is the quenching constant which is a function of the lifetime of the probe and the solvent, $V[O_2]\%$ is the volume fraction of oxygen in the sample [34]. Fig. 5 shows the S—V equation of the oxygen sensing film, finding that the quenching ratio has a better linear relationship with the concentration of DO, and the maximum quenching ratio is 3.66. It indicates that a Poly (MMA-*co*-TFEMA) copolymer matrix provides a homogeneous microenvironment for the indicator [9] and sensing film yielding a good sensitivity. However, when the fluorescent indicator molecules are not well dispersed in the polymer matrix,

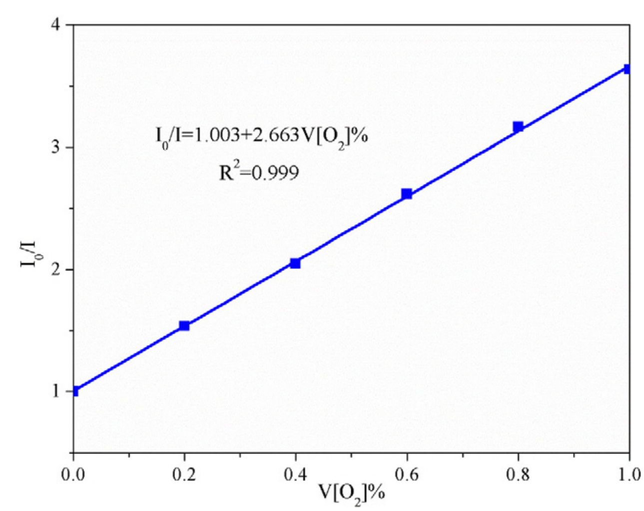

Fig. 5. Stern-Volmer equation of PtOEP/poly(MMA-*co*-TFEMA) oxygen sensing film.

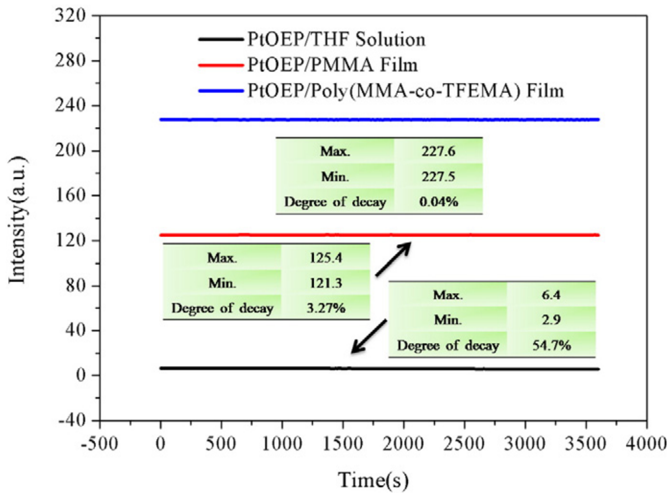

Fig. 6. Photostability of the PtOEP/poly(MMA-*co*-TFEMA) film, PtOEP/PMMA film, and PtOEP in THF solution.

which has a different response to the quenching of fluorescence by oxygen, resulting in a nonlinear Stern-Volmer equation [18].

3.5. Photostability of PtOEP/poly(MMA-co-TFEMA) oxygen sensing film

The light quenching phenomenon has a direct influence on long-term real-time monitoring [35–37]. The film was placed into the ultra-pure water and the photostability (the variation of the fluorescence intensity) with time was recorded as shown in Fig. 6. The experimental result shows that the fluorescence intensity of PtOEP/poly(MMA-*co*-TFEMA) film changes from 227.6 to 227.5 under continuous irradiation for 1 h, with the decay degree being below 0.04%. In comparison, when PtOEP is dispersed in THF solution or just embedded in a PMMA matrix, decay degrees are about 54.7% and 3.27%, respectively. It indicates that poly (MMA-*co*-TFEMA) copolymer matrix can efficiently prevent the leakage of PtOEP by introducing fluoride components, suggesting a good photostability.

Table 1
Values of DO in different water samples.

Sample	The concentration of DO(mg/L)	Standard(mg/L)
Ultra-pure water	0	0
Harbin beer	0.18	0.2[38]
Tap water	6.98	7[2]
Wahaha enriched oxygen water	32.58	30–40

3.6. Measurement of the content of DO in different water samples using oxygen sensing film

An aqueous solution with different concentration of DO is formulated in accordance with the following formula:

$$S_{O_2} = M_{O_2} \cdot P \cdot V[O_2]\% / V_{H_2O} \cdot K_{O_2 \cdot H_2O} (2.)$$

In this formula, S_{O_2} is the concentration of DO and its unit is mg/L, M_{O_2} is the relative molecular weight of oxygen which value is 32.00 g/mol, V_{H_2O} is molar volume of aqueous solution and its value is approximately 1.8×10^{-5} m^3/mol for dilute solution, P is the standard atmosphere which is 101.325 kPa, $K_{O_2 \cdot H_2O}$ is the Henry constant and its value is 4.40×10^6 kPa at the temperature of 298 K and standard atmosphere. Substituting (2) into (1), the new Stern-Volmer equation is used to measure the concentration of DO in different samples. Selecting ultra-pure water under the condition of nitrogen saturation as the standard, whose value of DO content is 0 mg/L, other samples are Harbin beer, local tap water (Harbin Water Supply Group Co., Ltd) from the laboratory and Wahaha enriched oxygen water purchased from a supermarket (Carrefour Supermarket, No.80, Xidazhi street, Nangang District, Harbin), respectively. Fig. 7a is the S—V plot of the sensing film, Fig. 7b shows the fluorescence intensity in different water samples and values of DO are given in Table 1. For tap water and Harbin beer, the results of the concentration of DO exhibit small deviation from the standard values. For Wahaha enriched oxygen water, standard values of the concentration of DO are derived from its supplied packaging, and the experimental result is of the standard level. The test results of the concentration of DO in different water samples indicate that PtOEP/poly(MMA-*co*-TFEMA) oxygen sensing film can measure the content of DO accurately.

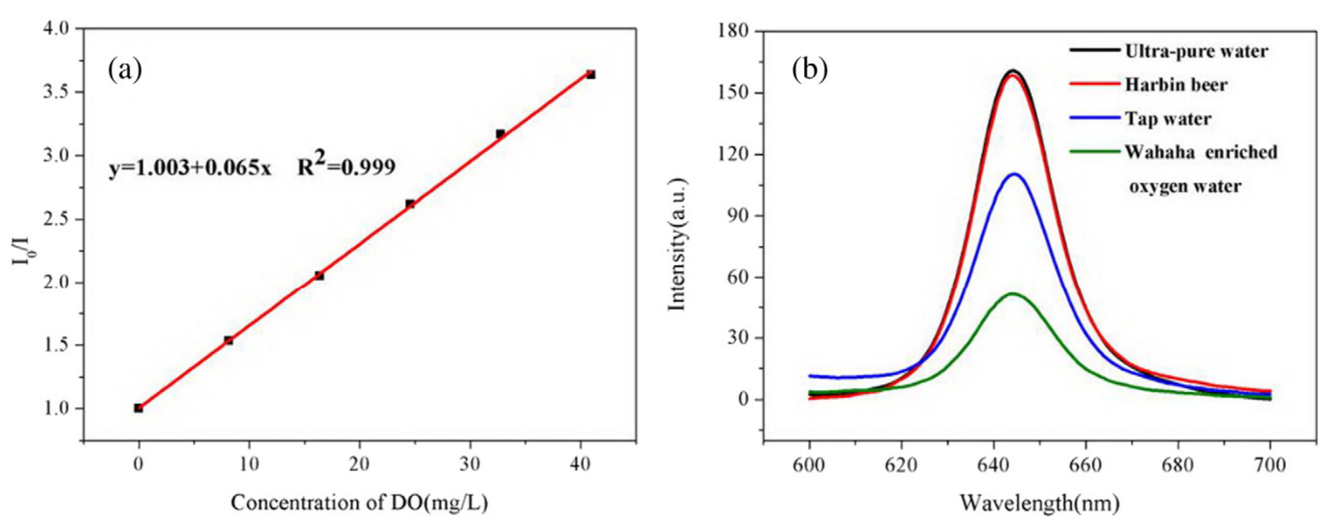

Fig. 7. (a) S-V plot of the sensing film (b) Fluorescence intensity in different water samples.

4. Conclusion

In summary, we prepared a series of PtOEP/poly(MMA-*co*-TFEMA) oxygen sensing films via a solvent evaporation technology. By varying monomer ratios, plasticizer and indicator loadings, the best technological condition for the preparation of a high-performance oxygen sensing film was optimized, which resolved as the 1:1 ratio of MMA/TFEMA, 0.05 mL of TBP and 5 μg of PtOEP. In addition, the Stern-Volmer equation with a good linear correlation was obtained as ($I_0/I = 1.003 + 2.663 [O_2]$, $R^2 = 0.999$), suggesting that the poly (MMA-*co*-TFEMA) matrix provided a homogeneous microenvironment for PtOEP and demonstrated a potent permeability to oxygen. Moreover, the decay degree of the fluorescence intensity is below 0.04% under continuous irradiation for 1 h. The PtOEP/poly(MMA-*co*-TFEMA) film can effectively prevent the leakage of indicator molecules and improve the stability of system. Finally, the PtOEP/poly(MMA-*co*-TFEMA) oxygen sensing film was applied to monitor the DO content in different samples such as Harbin beer, local tap water and Wahaha enriched oxygen water purchased from a supermarket, finding that the test results are within the reference range. Therefore, PtOEP/poly(MMA-*co*-TFEMA) oxygen sensing film as an effective oxygen sensor can be used in other different fields for DO monitoring.

Acknowledgements

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