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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

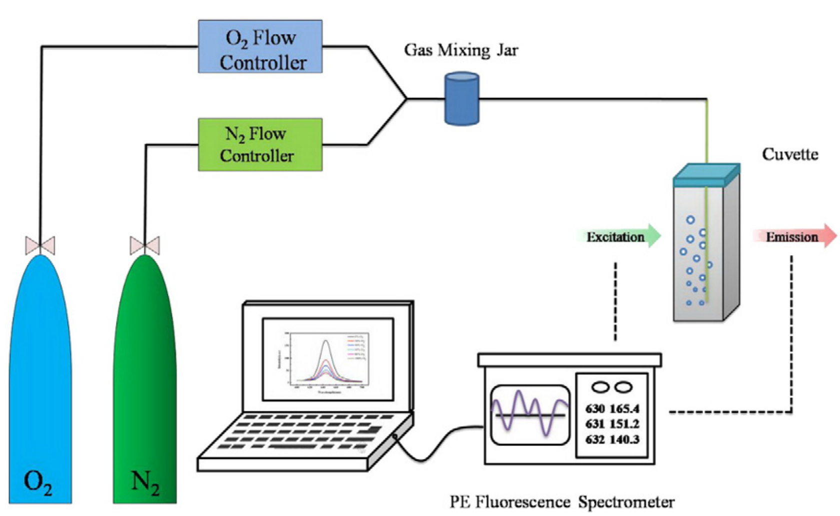

Fig. 1. Self-regulating gas (nitrogen/oxygen) mixture device.