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A Fiber Optic Sensor for 2,4-dichlorophenol Analysis based on Optical Composite Oxygen-sensitive Film

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Abstract: A novel fiber optic sensor based on optical composite oxygen-sensitive film was developed for determination of 2,4-dichlorophenol (DCP). The optical composite oxygen-sensitive film consists of tris(2,2'-bipyridyl) dichloro ruthenium(II) hexahydrate ($\text{Ru}(\text{bpy})_3\text{Cl}_2$) as the fluorescence indicator and iron(III) tetrasulfophthalocyanine ($\text{Fe}(\text{III})\text{PcTs}$) as bionic enzyme. A lock-in amplifier was used for detecting the lifetime of the composite oxygen-sensitive film by measuring the phase delay of the sensor head. The different variables affecting the sensor performance were evaluated and optimized. Under the optimal conditions (*i.e.*, pH 6.0, 25 °C, $\text{Fe}(\text{III})\text{PcTs}$ concentration of 5.0×10^{-5} mol/L), the linear detection range, detection limit and response time of the fiber optic sensor are 3.0×10^{-7} - 9.0×10^{-5} mol/L, 4.8×10^{-8} mol/L (S/N=3), and 220 s, respectively. The sensor displays high selectivity, good repeatability and stability, which have good potentials in analyzing DCP concentration in practical water samples.

Key words: 2, 4-dichlorophenol; optical composite oxygen-sensitive film; fiber optic sensor; phase delay

1 Introduction

Chlorinated phenols are widely used in the manufacturing of pharmaceuticals, resins and plastics, coal refineries, painting, pulp and paper, pesticides, herbicide and even from food processing industries^[1-3]. They have become primary pollutants of various industries. 2,4-dichlorophenol(DCP) is of particular interest since it is a precursor for the synthesis of carcinogenic endocrine, 2,4-dichlorophenoxyacetic acid, which is the active ingredient of more than 1500 herbicides. The toxicity linked to DCP exposure has been evidenced to cause endocrine related cancers and chronic conditions such as chloracne and porphyria in humans^[4,5]. Due to the toxic properties, the detection of DCP in water or soil have an important significance to human health and natural environment^[6-8]. Several methods have been used for the determination of DCP including the gas chromatography^[9,10], flow injection analysis^[11], HPLC^[12], photocatalysis^[13], electrode^[14],

and electrochemical sensor^[15,16]. However, these methods have many deficiencies, such as high cost, complicated sample preparation, difficult operation and impossibility of online detection^[17,18]. The fiber optic sensor have many advantages, such as resist disturbance, high selectivity, long distance sensing and low cost, especially can be used for on-line and real time detection^[19,20]. Therefore, the fiber optic sensors based on DCP oxidation catalyzed by enzyme supply the preferred way for DCP detection^[21].

The determinant of high performance fiber optic biosensor is high performance sensing materials, which have both catalytic and photosensitive properties. Most of sensing materials based on enzymatic catalysis consist of separate two parts, photosensitive film and enzyme film. They have been limited by slow response speed, low accuracy, poor stability and repeatability. Moreover, the separate films increase the volume of sensor probe, which is adverse to the development of fiber optic micro-biosensor. The optical composite oxygen-sensitive films consist of both bionic enzyme and fluorescence indicator, and the catalytic effect of the bionic enzyme directly reach the fluorescence indicator. Meanwhile, the usability of the optical composite films reduces the cost of fiber optic sensor, which is beneficial to practical application of the composite films. Therefore, the composite films can overcome the defects of traditional sensing materials, and they have been studied as an effective alternative

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to the traditional ones.

In our previous work, we studied the oxidation of DCP catalyzed by Fe(III)PcTs^[22]. In this work, Fe(III)PcTs was chosen as biomimetic enzyme by significant catalytic property to DCP, Ru(II)(bpy)₃Cl₂ was used as the fluorescence indicator to sense consumption of oxygen. A optical composite oxygen-sensitive film consisting both Fe(III)PcTs and Ru(II)(bpy)₃Cl₂ has been prepared and characterized. A novel fiber optic sensor based on the DCP oxidation by optical composite oxygen-sensitive film has been designed and fabricated, and the effects of different conditions, such as pH, temperature and catalyst concentration on the sensor performance were investigated. The linear detection range, detection limit and response time of this sensor are 3.0×10^{-7} - 9.0×10^{-5} mol/L, 4.8×10^{-8} mol/L, 220 s, respectively. The fiber optic sensor shows good repeatability, selectivity and stability, and the detection results of real samples by using this sensor indicate a promising application prospect.

2 Experimental

2.1 Reagents and apparatus

Fe(III)PcTs was synthesized and purified according to the methods reported in the Ref.[23]. Fluorescence indicator Ru(bpy)₃Cl₂ was purchased from Sigma-Aldrich. DCP, dimethyl diethoxy silane(DDS), ethyl orthosilicate(TEOS), 36.5% HCl, polyethylene glycol (PEG 400), 98% H₂SO₄, 30% H₂O₂, 25% NH₃·H₂O, and 4-Aminoantipyrine(4-AAP) were obtained from Shanghai Chemical Reagent Company. All the reagents were of analytical grade and used without further purification.

The absorption spectra were recorded on a UV-2450 spectrophotometer (Shimadzu, Japan). A lock-in amplifier (SR830, Stanford Research Systems, USA) was used for measuring the phase delay of the sensor head. The IR spectrum was taken onto a FT-IR spectrometer(60SXB, USA). The morphological characterization were evaluated by JSM-5600 FESEM and DI Nanoscope IV AFM. The Raman spectrum was determined using a microscopic confocal laser raman spectrometer(RENISHAW Co., UK).

2.2 Preparation of optical composite oxygen-sensitive film

The activated glass substrates were prepared according to our previously work^[24]. DDS as modified agent, TEOS, hydrochloric acid solution and PEG 400 were mixed and stirred. 8mg/mL Ru(bpy)₃Cl₂ was added and hermetically stirred at room temperature for 2 h. A certain amount of Fe(III)PcTs water solution was

added in the mixture and stirred at room temperature for 4h to form uniform organic-inorganic hybrid solution. The solution was partially hermetically aged for 3-5 days at room temperature, and spun onto the activated glass substrates to form a certain thickness of composite film. The composite film was placed in a glass dish and partially hermetically aged for 2 days at room temperature. The sol-gel optical composite sensitive film could be obtained.

2.3 Preparation and principle of fiber optic sensor

The detecting system consists of a lock-in amplifier, a LED with the excitation wavelength of 416 nm as the light source, a sensor head with a film and a computer for data processing as shown in Fig.1(a). The optical composite oxygen-sensitive film was placed at the bottom of the sensor head, and a multimode optical fiber bundle directly above the film is used for exciting light incidence and reflected fluorescence collection(in Fig.1(b)).

The principle of the sensor is based on the fluorescence quenching and consumption of oxygen^[25]. Fe(III)PcTs in optical composite oxygen-sensitive film catalyzed DCP oxidation, consuming oxygen in solution. The change of oxygen concentration is detected by measuring fluorescence of Ru(bpy)₃Cl₂ quenched by oxygen. Since a lock-in amplifier is used, the quenching can be described as:

$$\frac{\tan\varphi_0}{\tan\varphi} = 1 + K_{sv}[Q] \quad (1)$$

where, φ_0 and φ are the phase delay change of the sensor in the absence and presence of the oxygen quencher, respectively, K_{sv} is the Stern-Volmer constant, and $[Q]$ is the oxygen concentration. Since φ is very small ($i.e., <5^\circ$) in the experiment, $\tan\varphi \approx \varphi$. By collecting the data of phase delay φ the quantification of DCP is achieved.

2.4 Measurements

For the detection of DCP concentration, measurements were performed with the setup shown schematically in Fig.1. The sensor head embedding the optical composite oxygen-sensitive film was placed into a 80 mL glass beaker which was available for a small quantity of sample. The reaction cell contained 40 mL of deionized water, 5 mL of 4-AAP aqueous solution (1.0×10^{-3} mol/L) and 5 mL of DCP were dissolved in it. In order to eliminate the interference of oxygen from the open air, an entire airtight reaction cell was introduced. All the measurements were carried out under continuous and constant stirring. The fluorescence signal was collected by PIN and guided

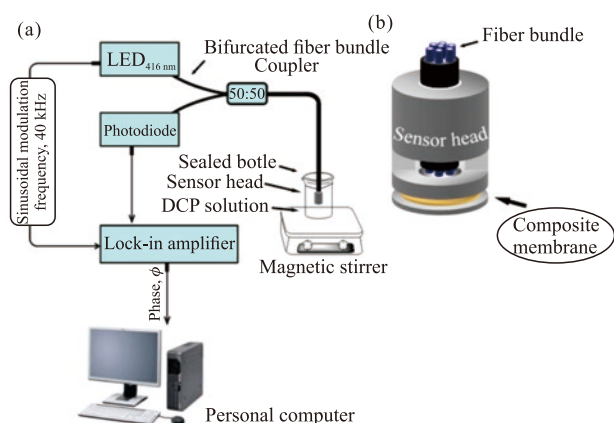


Fig.1 (a)Schematic representation of the fiber optic sensor for DCP detection; (b)The model of sensor head containing a composite film in its testing region

to the lock-in amplifier through the output bundle, and then transferred to phase-delay collected by the computer. The reaction was performed in different conditions to investigate the performance of fiber optic sensor.

3 Results and discussion

3.1 Preparation of optical composite oxygen-sensitive film

We investigated and obtained the optimal preparation conditions which are shown in Table 1.

3.2 Structure of optical composite oxygen-sensitive film

The typical transmission IR spectra of composite film is shown in Fig.2. The characteristic peak at 3428 cm^{-1} is attributed to oxhydryl stretching vibration, which is indicated that film contained crystal water. Absorption peak at 1700 cm^{-1} shows the existence of frame vibration octave band of benzene ring. Absorption peaks at 1629 cm^{-1} and 1362 cm^{-1} are attributed to phthalocyanine ring of C=C and C=N stretching vibration, respectively, indicating the existence of phthalocyanine ring. Absorption peak at 1229 cm^{-1} shows substitute benzene ring bending vibration. The characteristic peak at 953 cm^{-1} is metal-ligand vibration absorption peak formed by central metal Fe and four nitrogen atoms bonding on the the luo ring. Absorption peak at 1095 cm^{-1} is multiple vibration absorption peak of sulfonic group, and absorption peak at 796 cm^{-1} is telescopic vibration

absorption peak of C-S, that indicates the existence of sulfonic group substituent^[23]. These peaks proved that Fe (III) PcTs has been synthesized in composite film, however the characteristic absorption peaks of indicator $\text{Ru}(\text{bpy})_3\text{Cl}_2$ could not be observed clearly.

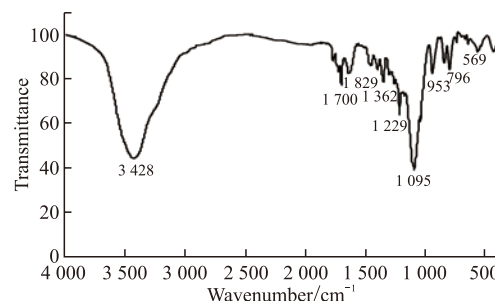


Fig.2 IR spectrum of optical composite oxygen-sensitive film

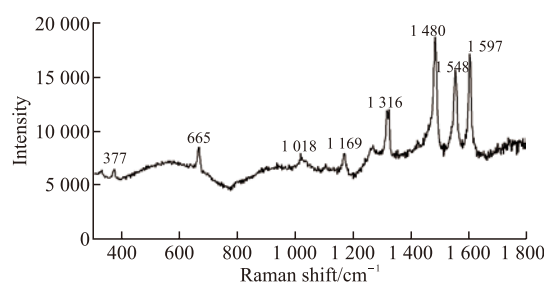


Fig.3 Raman spectrum of optical composite oxygen-sensitive film

Fig.3 shows Raman spectrum of composite film. The characteristic Raman peaks located at 1480 , 1548 , and 1597 cm^{-1} in range of $1400\text{--}1600\text{ cm}^{-1}$ are attributed to the ligand structure of indicator $\text{Ru}(\text{bpy})_3\text{Cl}_2$. Raman peaks at 377 and 665 cm^{-1} are caused by the deformation vibration of conjugate large ring and benzene ring, respectively. Raman peaks at 1018 , 1169 , and 1316 cm^{-1} are C-H contraction vibration peaks of benzene ring^[26]. The above results indicate that fluorescence indicator $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and Fe(III)PcTs were synthesized in optical composite sensitive film.

In order to observe the surface structure of the sensitive film, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were employed. The SEM image in Fig.4 presents that the surface of the composite film is smooth and uniform. Due to $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and Fe(III)PcTs have good water solubility, they evenly dispersed in the three-dimensional network structure of the composite film. The structure of film was dense, which could avoid the leak of indicator.

Table 1 The optimal preparation conditions of composite film

TEOS/DDS	HCl concentration (/mg/mL)	PEG volume (/mL)	$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ concentration(/mg/mL)	Spin coater speed/(r/min)	Spin time (/s)	Drying temperature (/°C)	Drying time (/day)
1:1	5.48	0.2	8	2000	30	25	10

The AFM image also indicated that average thickness of the film is 2 μm , and roughness of the sensitive film was found to 106.87 nm. Fe(III)PcTs and Ru(bpy)₃Cl₂ molecules were well distributed in composite film (in Fig.5). When the sensor head embedding this film was put into the reaction system, DCP could easily catalyzed by Fe(III)PcTs, and Ru(bpy)₃Cl₂ could easily fluorescence quenched by oxygen molecules.

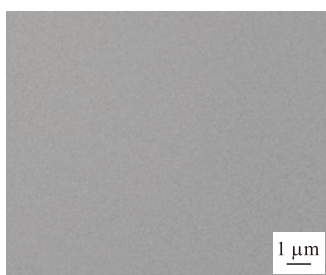


Fig.4 SEM morphology of optical composite oxygen-sensitive film

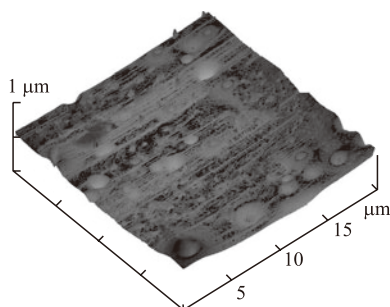


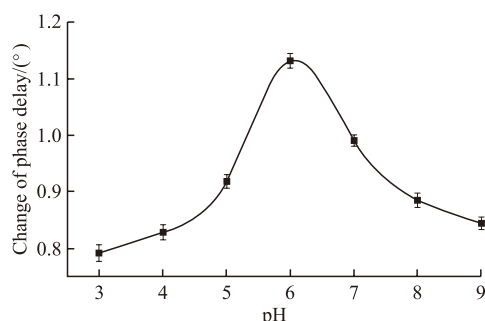
Fig.5 AFM morphology of optical composite oxygen-sensitive film

3.3 Effect of different variables on fiber optic sensor

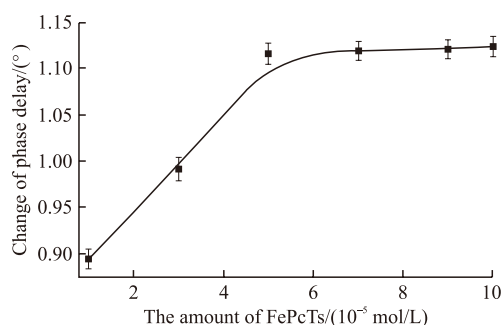
Our previous work documented that the different variables affect the sensor performance^[27]. The catalytic oxidation of DCP is closely related to pH because the relative contents of undissociated chlorophenol and corresponding chlorophenols vary with pH of aqueous solution^[28]. Therefore, pH influence on the phase delay change of fiber optic sensor was investigated in the range of pH 3.0-9.0 by using different buffer (the concentration of DCP was 5.0×10^{-5} mol/L). As it could be noticed in Fig.6(a), a maximal value of phase delay change was observed at pH 6.0. This pH was selected for our subsequent investigations.

A series of optical composite oxygen-sensitive films with different concentrations of catalyst Fe(III)PcTs in the same area were obtained, and the effect of catalyst concentration on the phase delay change of fiber optic sensor embedding different films was investigated (Fig.6(b)). The change of phase delay increased with the increasing concentrations of Fe(III)PcTs added from 1.0×10^{-5} to 5.0×10^{-5}

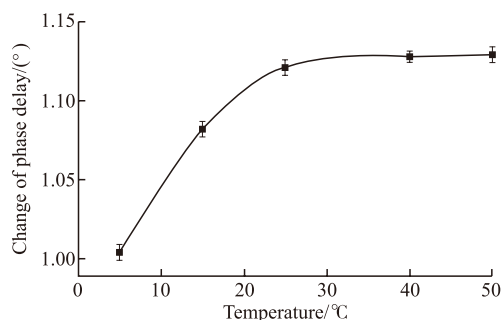
mol/L during the time for experiments carried out with a DCP concentration of 5.0×10^{-5} mol/L. The further increasing in the Fe(III)PcTs amount could not obviously enhance change of phase delay. Therefore, 5.0×10^{-5} mol/L of the catalyst was recommended for the sensor detection.



(a) Effect of pH on the fiber optic DCP sensor. Conditions: $T=25$ °C, Fe(III)PcTs concentration was 5.0×10^{-5} mol/L, [DCP]= 5.0×10^{-5} mol/L



(b) Effect of Fe(III)PcTs concentration on the fiber optic DCP sensor. Conditions: $T=25$ °C, pH=6.0, [DCP]= 5.0×10^{-5} mol/L



(c) Effect of temperature on the fiber optic DCP sensor. Conditions: Fe(III)PcTs concentration was 5.0×10^{-5} mol/L, pH=6.0, [DCP]= 5.0×10^{-5} mol/L

Fig.6

The enzyme catalyzed reaction will be significantly influenced by temperature. Therefore, the effect of temperature on the phase delay change of fiber optic sensor was investigated as shown in Fig.6(c). As the temperature increased from 5 to 25 °C, the phase delay change of fiber optic sensor significantly increased. When the temperature further increased to 50 °C, change of phase delay could not obviously enhance. Since the evaporation of DCP intensified at higher temperature, and the oxygen sensing film will be destroyed when the temperature was higher than 40 °C^[25]. In order to prolong the lifetime of the sensor,

Table 2 Analysis results of the fiber optic DCP sensor

Rang of concentration (mol/L)	Equation	R^2	Standard deviation
$1.0 \times 10^{-5} - 9.0 \times 10^{-5}$	$Y=0.875+0.075X$	0.974	5.2%
$1.0 \times 10^{-6} - 9.0 \times 10^{-6}$	$Y=0.502+0.055X$	0.976	5.6%
$3.0 \times 10^{-7} - 9.0 \times 10^{-7}$	$Y=0.192+0.016X$	0.987	6.2%

25 °C (room temperature) was recommended for our subsequent investigations.

3.4 Dynamic response of fiber optic sensor

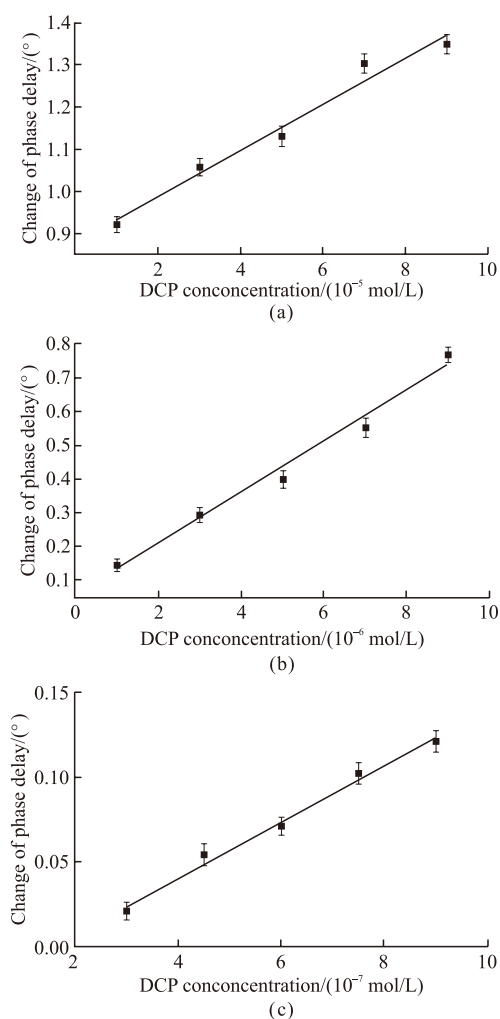


Fig.7 (a)Typical calibration curve of the fiber optic DCP sensor at various concentration of DCP in the range of $1.0 \times 10^{-5} - 9.0 \times 10^{-5}$ mol/L; (b)Typical calibration curve of the fiber optic DCP sensor at various concentration of DCP in the range of $1.0 \times 10^{-6} - 9.0 \times 10^{-6}$ mol/L; (c)Typical calibration curve of the fiber optic DCP sensor at various concentration of DCP in the range of $3.0 \times 10^{-7} - 9.0 \times 10^{-7}$ mol/L (Conditions: $T = 25$ °C, Fe(III)PcTs concentration was 5.0×10^{-5} mol/L, pH =6.0, $n=3$)

By detecting the change of phase delay of the sensor we can detect the DCP concentration, which is based on the fluorescence quenching and consumption of oxygen. Fig.7 depicts the relationship between the

change of phase delay ϕ and DCP concentration in the concentration range from 3.0×10^{-7} mol/L to 9.0×10^{-5} mol/L (The integrated waste water discharge standard of China for DCP is 3.68×10^{-6} mol/L). Three sensing calibration curves were observed and the corresponding equations are presented in Table 2. In the higher concentration of DCP, the phase delay of sensitive film increased fast, and in the lower concentration of DCP, the change rate of phase delay decreased. It can be explained that there is enough dissolved oxygen in the solution to react with the DCP in the process of DCP detection of high concentration. Although there were three linear relationships of different slopes between the phase delay ϕ and DCP concentrations, a good linear relationship and small standard deviation could be obtained in each detection range of DCP concentration. The response time of the sensor was taken as 220s because most of the DCP was oxidized in this time. The detection limit was 4.8×10^{-8} mol/L (S/N=3). As the catalytic effect of catalyst Fe (III) PcTs could be directly to the fluorescence indicator $\text{Ru}(\text{bpy})_3\text{Cl}_2$, the response speed and detection precision of the sensor effectively improved, the detection limit of the sensor effectively reduced.

3.5 Properties of fiber optic sensor

3.5.1 Repeatability and reversibility

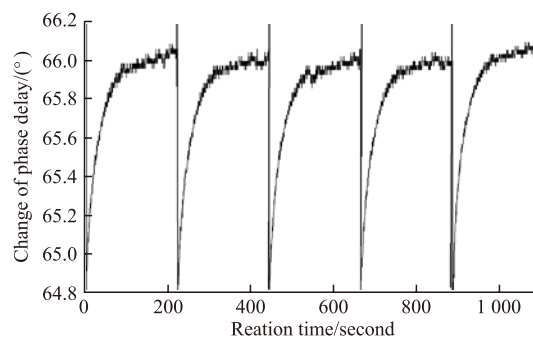


Fig.8 Repeatability and reversibility test on the sensor by exposing the sensor to five cycles of buffer, 5.0×10^{-5} mol/L DCP, respectively; Conditions: $T = 25$ °C, Fe(III)PcTs concentration was 5.0×10^{-5} mol/L, pH =6.0

The reversibility of the sensor embedding the same film was assessed by exposing the sensor to five cycles of buffer, 5.0×10^{-5} mol/L DCP, respectively. The results in Fig.8 show that it has a highly

reproducible and reversible response to DCP solution with RSD=4.6%, indicating the good reversibility of the sensor. The repeatability of the response of the sensor was also investigated by subjecting the sensor to a 3.0×10^{-5} mol/L DCP solution. The relative standard deviation (RSD.) was 4.81% for 10 successive measurements, also indicating the good repeatability of the sensor.

3.5.2 Long-term stability

To investigate the lifetime of the sensor, the response values of the oxygen sensing film in contact with 5.0×10^{-5} mol/L of DCP were recorded after keeping the film in water for 0, 1, 3, 5, and 7 days. The results shown in Table 3 that the change of phase delay of the sensor under optimal conditions only decreased by 1.2%, 2.3%, 3.3%, and 4.9%, respectively, indicating the good long-term stability of the sensor. The indicator leaking from the film might be responsible for the loss of sensitivity.

Table 3 Long-term stability of the optical complex sensing film

Days of keeping in water	Change of the phase delay
0	1.138
1	1.125
3	1.112
5	1.101
7	1.082

3.5.3 Selectivity against interference

5.0×10^{-5} mol/L was selected as the actual concentration of DCP, and the interference rate in the presence of potential interferents with different concentrations were used as indicators for the sensor selectivity. The results are summarized in Table 4. We can see that all the interferents did not cause significant interference on the response of the sensor, demonstrating a good selectivity for this sensor.

3.5.4 Detecting in real water samples

The fiber optic DCP sensor was validated by

applying it to the determination of DCP in samples from water of East Lake and Yangtse River in Wuhan, China. The DCP concentrations in two samples were determined, in triplicate, using the proposed sensor. The results are shown in Table 5. It can be concluded that this sensor is suitable for the determination of DCP in practical samples.

Table 4 Interference test of the fiber optic DCP sensor on exposure to various interferents

Interferents	Concentration / (mmol/L)	Interference rate $((C-C_0)/C_0 \times 100\%)$
K ⁺	15.0	-4.8
Na ⁺	15.0	-3.2
Cl ⁻	15.0	4.1
SO ₄ ²⁻	15.0	4.3
Br ⁻	5.0	-5.1
Al ³⁺	5.0	-5.6
Mn ²⁺	5.0	3.2
NH ₄ ⁺	5.0	-2.1
Zn ²⁺	5.0	2.8
CO ₃ ²⁻	5.0	3.4
PO ₄ ³⁻	5.0	-4.9
CH ₃ COO ⁻	5.0	5.6
Ca ²⁺	5.0	3.5
Mg ²⁺	5.0	-4.8

We determined the DCP concentrations in two samples, in triplicate, using the HPLC and electrochemical sensor. The results are shown in Table 6. The sample preparation for HPLC is much more complicated and the detection is a time-consuming process. The cost of HPLC is rather high, and it can not be used for real-time and on-line detection. Compared with the proposed sensor, the detection limit of electrochemical sensor is 5.6×10^{-6} mol/L (S/N=3), which is two orders higher than that of our sensor. And the response time of electrochemical sensor is 14 min, the response rate is much slow.

Table 5 Detection of practical samples using fiber optic DCP sensor based on optical complex sensing film

Samples	DCP added (10^{-5} mol/L)	DCP added/ $(10^{-5}$ mol/L)(n=3)	Recovery/100%
Water in Yangtse River	5.00	5.19 ± 0.06	103.8
Water in East Lake	5.00	4.88 ± 0.08	97.6

Table 6 Detection of practical samples using HPLC and electrochemical sensor

Method	Samples	DCP added / (10^{-5} mol/L)	DCP added / (10^{-5} mol/L)(n=3)	Recovery / 100%
HPLC	Water in Yangtse River	5.00	5.14 ± 0.12	102.8
	Water in East Lake	5.00	4.84 ± 0.06	96.8
Electro-chemical sensor	Water in Yangtse River	5.00	5.22 ± 0.10	104.4
	Water in East Lake	5.00	4.86 ± 0.08	97.2

4 Conclusions

In summary, we developed a fiber optic sensor based on the optical composite oxygen-sensitive film. The results indicated that the composite film is smooth and uniform. Moreover, bionic enzyme Fe(III)PcTs and fluorescence indicator Ru(bpy)₃Cl₂ molecules were well distributed in the film. The fiber optic sensor based on the oxidation by oxygen with Fe(III)PcTs catalysis and the fluorescence quenching of Ru(II)(byp)₃Cl₂ is a precise, low cost, easily prepared, sensitive and highly selective device for the determination of DCP. The optimal determination conditions were pH 6.0, 25 °C, Fe(III)PcTs concentration of 5.0×10^{-5} mol/L. The sensor offered good linear dynamic in DCP concentrations by means of the measured phase delay φ on the fluorescence lifetime-based sensing. Three sensing calibration curves between φ and DCP concentrations were obtained in the detection range of 1.0×10^{-5} - 9.0×10^{-5} mol/L, 1.0×10^{-6} - 9.0×10^{-6} , and 3.0×10^{-7} - 9.0×10^{-7} mol/L. The detection limit of this sensor was 4.8×10^{-8} mol/L (S/N=3) and the response time was 220 s. Since the integrated waste water discharge standard of China for DCP is 3.68×10^{-6} mol/L, the proposed sensor can meet the need of practical application. The sensor showed good repeatability, selectivity and stability. Finally, the sensor could be successfully applied to detect DCP in real water sample, demonstrating a great application prospect for fast and accurate measurement of phenolic pollutants.

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