Detection of Trimethylamine Based on a Manganese Tetraphenylporphyrin Optical Waveguide Sensing Element

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The sensitive detection of trimethylamine has been accomplished by using a homogeneous optical waveguide sensor system. Also the sensor can be easily fabricated by using tetraphenylporphyrin manganese (MnTPP) as sensitive materials to detect different volatile organic compounds (VOC). NMR (1H-NMR), field-emission scanning electron microscopy (FESEM), and X-ray photoelectron spectroscopy (XPS), infrared (IR), and ultraviolet-visible (UV-vis) instrumental means were used to characterize its structure. Gas-sensing measurements indicated that the sensing element has shown good selectivity, high sensitivity and a low detection limit level of 0.1 ppm to trimethylamine (TMA) with the presence of interference gases at room temperature. For a range of trimethylamine concentrations from 0.1 to 1000 ppm, the sensor has shown a short response time. Also the response time and recovery time are 1.5 and 50 s, respectively. Simulation experiments (dichloromethane, chloroform and carbon tetrachloride were selected as interference gases) showed little interference with its gas sensing. That may provide an ideal candidate for detecting the freshness of fish and seafood.

Keywords Tetraphenylporphyrin manganese, optical waveguide sensor, TMA, gas sensing

(Received November 9, 2017; Accepted December 23, 2017; Published May 10, 2018)

Introduction

Porphyrins and similar compounds have attracted tremendous interest due to their important roles in biological and chemical fields.1 Porphyrins have shown promise for use in high-sensitivity chemical sensors, typically with mass or optical-based transduction.2–6 The incorporation of metals into porphyrin structures change various properties of porphyrin, which provides a variety of information in detection of physical and chemical properties, such as the structure and optical behavior.7 Metalloporphyrins can be used as colorimetric sensors for the detection of metal-ligating vapors and organic molecules, due to various color changes in different metallation processes. Because with a high degree of conjugation of the π electronic system, metalloporphyrins possess open coordination sites for axial ligation, and show large spectral shifts upon binding when detected with a spectrophotometer.8,9 Their photoelectric properties such as strong absorption bands in the UV-vis region and a redox center, have opened a wide field of applications in photosensitive conductors, solar cells and chemical sensors.7,10–12

Trimethylamine (TMA) is usually generated from the microbial degradation of trimethylamine N-oxide during the deterioration of fish and seafood.13 Also the concentration of TMA will increase with the degree of decaying fish and seafood, which cause a great harm to a medical environment and human health, especially to endanger human life, causing headaches and stimulating the eyes and the respiratory system.14,15 Therefore, it is necessary to explore a kind of portable, sensitive sensing element to realize the detection of trimethylamine in real-time. Up to now, many analytical techniques, such as gas/ high-performance liquid chromatography,17 ion mobility spectrometry,18,19 and sensor technology,20,21 have been developed for the determination of TMA. However, these methods have their own advantages (high sensitivity and accuracy) and disadvantages. These methods are usually time consuming, non-portable, and involve expensive instruments with complicated preparation.22 Zhang et al.23 used an inexpensive colorimetric sensor array to detect trimethylamine with a detection limit of 0.1 ppm. Besides, most of the traditional gas-sensing materials were inorganic materials (metal oxides), and electrochemical testing requires a higher temperature,24 but the selectivity is not preferable at room temperature. Chen et al.13 used a cobalt imidazolate (im) framework material, [Co(im)₅]n, to detect trimethylamine, and achieved a low detection limit level of 2 ppm to TMA at 75°C. Many contributions that use porphyrins as gas-sensing materials have been reported in the field of sensor applications. Murakami et al.25 used 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin to detect organophosphorous pesticides. In addition, Paolesse et al.26 have studied the response of porphyrin derivatives to toxic and volatile gases by means of spectroscopic techniques. Among many sensors, the optical waveguide sensor has an advantage of high sensitivity,27–29 good response, being portable to carry and can be operated at room temperature.30–31 Meanwhile, because metalloporphyrins have strong absorption in the UV-vis region, we use a laser with a certain wavelength as the excitation light of an optical waveguide system. Given its advantages, we used porphyrins as sensitive materials, and applied them in the optical waveguide sensors, while achieving the detection of TMA.

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This work describes an optical waveguide sensor (OWG) based on a thin film of manganese tetr phenyl porphyrin (MnTPP) for the detection of trimethylamine. Furthermore, we simulated the influence of interfering gas on the sensing to trimethylamine. A MnTPP thin film/K⁺ exchanged glass waveguide sensing element was prepared by methods of spin-coating, using MnTPP as a sensitive reagent to detect a variety of gases. The gas-sensing mechanism of the optical waveguide was discussed. Compared with the detection of trimethylamine, the detection limit of trimethylamine and the operating temperature are lower than that reported in the literature. It was thus expected to apply in the detection of food quality, such as fish products. As far as we know, there have been no reports on the use of porphyrin thin films to detect mixed gases.

**Experimental**

**Chemical and materials**

Salicylic acid, benzene, formaldehyde and xylene were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China); N,N-dimethyl formamide and manganese acetate (CH₃COO)₂Mn were purchased from Shengao Chemical Reagent Co. Ltd of China. All reagents used were of analytical grade.

A powder of MnTPP was examined by an Ultraviolet visible spectrophotometer (UV-vis) (Shimadzu UV1780 spectrometer), and infrared (IR) (EQUI-NOX 55). X-ray photoelectron spectroscopy (XPS) measurements were obtained on an ESCALAB 25XI spectrometer equipped with an Al-Kα radiation source (1486.6 eV). The surface of thin film was directly observed through field-emission scanning electron microscopy (FESEM, JEOL JSM-7500F, operated at an accelerating voltage of 15 kV); the ambient humidity was obtained by a Humidity & Temperature Meter (Smart Sensor Co. Ltd of Hong Kong).

**Synthesis of MnTPP**

MnTPP was prepared by two steps. Firstly, according to reported literature we synthesized tetraphenyl porphyrin (H₂TPP) via the Alder method. Subsequently, MnTPP was synthesized following methods reported earlier, and but had minor modifications. Briefly, 1.5 g of pure tetraphenylporphyrin and 100 mL DMF were added to a 500-mL three-necked flask equipped with a reflux condenser and in a nitrogen atmosphere. The mixture was heated (120 °C) in a water bath, stirred and refluxed at the end of the reaction. Then, 0.6 g of (CH₃COO)₂Mn was added to 20 mL of methanol and the whole mixture was refluxed for 3 h, cooled overnight, and filtered with a suction filter. The solids were washed by dilute hydrochloric acid, water and ethanol, respectively. It was then dried in a vacuum for 24 h, and purified by column chromatography, while giving a yield of 77.50%.

**Fabrication of sensing element**

The sensing element was fabricated as follows. (1) A certain amount of MnTPP powder was dissolved in a chloroform solution. (2) The mixture was coated onto the surface of a K⁺ exchange glass OWG (n = 1.51 with the guiding layer being 1 and 2 mm deep) using a spin-coater over a period of 30 s at a rotation speed of 2100 rpm. (3) Wiping the glass components on both sides and leaving the middle width with about 1 cm of the film, the films were then placed in a vacuum desiccator at room temperature for 24 h.

**Gas sensing measurement**

The sensor element was placed in a small chamber using a self-assembled optical waveguide (OWG) gas testing system, shown in Fig. 1. The OWG gas testing system consisted of carrier gas (dry air), a laser source (532 nm), a prism, OWG-sensitive film, a photomultiplier tube, recorder and other components. The planar optical waveguide consisted of a substrate, waveguide layer and a cladding tube, and the index of the waveguide layer was higher than that of the substrate and cladding layer. The light entered into the propagating layer according the prism coupling method. In addition, part of the light would enter the sensitive film in the form of evanescent waves when the light propagates in the waveguide layer. And when the target gas would flow into the small chamber and be exposed with the sensitive layer, as a result the output light intensity would change. The photomultiplier converts the optical signal into an electrical signal and is recorded by computer. All processes are performed at room temperature.

Standard trimethylamine gas was obtained by vaporizing a given amount of trimethylamine solution (99.5%) inside a standard vessel (600 cm³). The concentration of the trimethylamine gas was confirmed using a commercial trimethylamine gas detection tube (Gastec, with a working range of 2 – 200 ppm, manufactured by Beijing Municipal Institute). Different amounts of the standard trimethylamine gas were diluted according to the stepwise dilution method in order to obtain the desired result, which was very low concentrations of trimethylamine (in the ppb range).

**Results and Discussion**

**Characterization of H₂TPP and MnTPP sample**

The synthesized sample was characterized by using ¹H-NMR, FT-IR and UV-vis (they are both shown in Supporting Information). H₂TPP: ¹H-NMR (CDCl₃, 400 MHz) δ: 7.734 – 7.791 (d, 12H, Ph–H), 8.221 – 8.243 (d, 8H, Ph–H), 8.86 (m, 8H, pyrrole–H), –2.756 (s, 2H, porphyrin N–H). ¹H-NMR analysis of MnTPP: the peak at chemical shift –2.756 disappeared, indicating that the metal manganese replaced the hydrogen of N-H bond to form a stable complex.

H₂TPP: IR (KBr) ν: 3417, 3031, 1464, 962, 700 cm⁻¹, MnTPP: IR (KBr) ν: 3050, 1527, 1008 cm⁻¹. The spectrum of H₂TPP showed the characteristic band at about 3417, 3031 cm⁻¹, this is ascribed to the C-H stretching vibration on the pyrrole ring and the benzene ring, band at 1464, 700 cm⁻¹ could be attributed to a benzene ring and a pyrrole ring skeleton vibration absorption peak. N-H stretching vibration and an in-plane bending vibration peak of the pyrrole ring occurred at 3417, 962 cm⁻¹, which is the characteristic peak of free base porphyrin structure.
With manganese ion entering the porphyrin rings, the two bands (3417, 962 cm\(^{-1}\)) would disappear and a new absorption characteristic peak would appear at the band of 1008 cm\(^{-1}\), due to the manganese ion entering the porphyrin ring, and a ring deformation vibration occurred. It is an important sign for the formation of manganese porphyrin, indicating that the manganese ion has been associated with the porphyrin ligand, forming a target complex.\(^{37}\)

H\(_2\)TPP: UV-vis (CHCl\(_3\)) \(\lambda_{\text{max}}\): 420, 515, 549, 580, 647 nm, MnTPP: UV-vis (CHCl\(_3\)) \(\lambda_{\text{max}}\): 420, 478, 584 nm. The H\(_2\)TPP shows that the strong absorption peak emerged at 420 nm of the Soret bond, and also shows four weaker absorption peaks (515, 549, 580, 647) for the Q band due to the \(\pi-\pi\) interaction between the molecules. The MnTPP shows the absorption peak of the Soret and Q bond at 478, 584, and 618 nm. There is a red shift (a shift in the absorption peak from 420 to 478 nm) of the Soret band of the manganese porphyrin; the splitting of the Soret band caused by Mn(III) gives rise to a band at 416.6 nm.\(^{38}\) Also the number of Q bands became obviously reduced, due to the four N atoms of the porphyrin ring being coordinated with the central metal; thus the symmetry increases, while decreasing the Q band absorption peak number. This is in agreement with literature data.\(^{39,40}\)

An XPS analysis was performed to examine the surface chemical composition and the valence state of the elements of MnTPP. The spectra of MnTPP are shown in Fig. 2. Figure 2(a) shows a survey scan of MnTPP, which it indicates that the composition of as-prepared materials should be C, N, Mn and O. Figs. 2(b) – 2(e) are results of its fitting analysis. Two fitting peaks with binding energy values of \(-654.0\) and \(-642.6\) eV, exhibited in the Mn 2p spectrum of Fig. 2(b), could be attributed to Mn 2p\(_{3/2}\) and Mn 2p\(_{1/2}\), respectively. The two peaks in the Mn

![Fig. 2 XPS spectra of MnTPP. (a) Survey spectrum, peak-fitting results of (b) Mn 2p level, (c) C 1s level, (d) N 1s level, (e) O 1s level.](image-url)
The 2p spectrum are in agreement with the +3 oxidant state of the manganese ion.\textsuperscript{41,42} The C 1s spectrum (Fig. 2c) of MnTPP exhibits two peaks centered at 284/285 eV, which correspond to C=C/C–C in the aromatic rings.\textsuperscript{43} As N 1s spectrum exhibited in Fig. 2(d) peak at around 398.9 eV confirms presence of nitrogen.\textsuperscript{44} The high-resolution spectrum of O 1s in Fig. 2(e) indicates the existence of two different oxygen species with a broad peak, which is fitted by two peaks at binding energies of ∼530 – 532 and ∼533.0 eV. The peak at ∼530.0 – 532 eV is characteristic for surface lattice oxygen that perhaps did not react completely during the synthesis process; ∼533.0 eV is for the surface-adsorbed oxygen species.\textsuperscript{45,46} Since the absorbed oxygen species are able to react with detected gases, they are absolutely instrumental in enhancing the gas performance.\textsuperscript{47}

Characterization of MnTPP thin film and the selection of an optical waveguide light source

The surface morphology of the sensing film was investigated by field-emission scanning electron microscopy (FESEM), as shown in Fig. 3(a). We can see from the FESEM images that the sample had a uniform distribution, which clearly shows that the surface of MnTPP was covered by a rough film of porphyrin.\textsuperscript{26} It can be seen from Fig. 3(b) that the surface of the sample had a granular distribution, which indicates that it is relatively smooth and increases its a specific surface area, and is conducive to the adsorption of gas on its surface.

In order to determine the optimal light source of the optical waveguide system, we analyzed the UV-vis spectroscopy of the sensitive film, which was done before and after exposure to trimethylamine gas (shown in Fig. 4). The absorbance changes greatly at wavelengths of 430 and 532 nm. Therefore, a semiconductor laser with 532 nm (the energy of 430 nm laser is too weak) was selected as the excitation light source of the optical waveguide system.

Optimization of preparation conditions for sensitive elements

We optimized the speed of preparing the sensitive film and the mass fraction of the solution as the reason why that the speed of the preparation of sensitive film and the mass fraction of the solution would affect the sensing element of the gas-sensitive properties directly. MnTPP thin films with different rotational speeds and different mass fractions were used as optical waveguide sensitive film, and many kinds of volatile organic compounds (VOCs) with the same concentration (1000 ppm) were used for gas sensing detection. The results show that the sensitive components have different responses to a certain extent to many kinds of VOCs at speeds of 1500, 1800, 2100 and 2400 rpm, and the mass fraction was 0.05, 0.07, 0.09 and 0.11%; but, the biggest response was to trimethylamine gas. The output light intensity shows the largest change when the rotation speed was 2100 rpm, and the mass fraction was 0.07%; therefore, the optimum conditions for preparing the sensitive films were determined.

Response mechanism and selective response of sensitive films

The output light intensity (transmitted light intensity) is related to the adsorption coefficient, refractive index, and thickness of the sensing film,\textsuperscript{48} given by the expression

\[ I = I_0(1 - aNde). \]  

(1)

Hence, \( I \) is the transmitted light intensity (output light), \( I_0 \) is the input light intensity, \( a \) is the absorption coefficient, \( N = d/2d_{tg}\theta \) is the reflectance number of the guided wave on the surface of the optical waveguide at a distance \( L \) and depth of the waveguide \( d, d_e = 2d/cos\theta \), is the length of the actual path of light in the sensing film of thickness \( d_e \). Here, the output light intensity decreased when the absorption coefficient, refractive index, and thickness of the sensing film were increased.

To discuss the surface sensitivity of the OWG sensor, we used “the relative sensitivity”,\textsuperscript{29} \( S_{\text{OWG}} \), which is expressed as follows:
\[ S_{\text{WG}} = \left( \frac{n_{\text{eff}}}{2N_{\text{eff}}} \right) \int_{-\infty}^{\infty} E_y(x)^2 \, dx. \]  

Hence, \( E_y(x) \) refers the electric field distribution of the guided light, \( E_y(0) \) is the electric field of the surface of the optical waveguide; \( N_{\text{eff}} \) is the effective refractive index, and \( n_{\text{surf}} \) is the average surface refractive index, defined by \((n_c^2 + n_j^2)^{1/2}\).

According to Eqs. (1) and (2) we can easily conclude that the surface refractive index of the sensitive layer is proportional to the surface sensitivity. After the sensitive layer contacts with the measured gas, the loss of scattering increases, and the transmittance decreases its attribute to changes of the guided wave in the sensitive layer, leading to the output light intensity being reduced.

The diverse gases with the same concentration were measured for gas-sensing performance. It can be seen from Fig. 5 that the output light intensity has a certain change when the sensitive film contacts with different target gases, but it showed the largest change after contacting with trimethylamine gas. It can be concluded that the sensing element has a better selective response to trimethylamine gas, and the response to other gases can be negligible regarding the trimethylamine gas response. Also the response time and the recovery time are 1.5 and 50 s, respectively. Therefore, we carried out a further study to test trimethylamine gas among a variety of gases.

Simulation experiment on sensitive components responding to trimethylamine gas

In order to eliminate the effects of interfering gases to sensing, we performed a simulation experiment. Dichloromethane, chloroform and carbon tetrachloride were selected as interference gases. Figure 6 shows the sensing results with the same concentration of interference gases; it can be seen that those three mixed gases have minor influence on the sensing of trimethylamine gas. Furthermore, we examined other three interfering gases (methylamine, ethanol and ammonia), and the results are similar to that of examined gases (dichloromethane, chloroform, carbon tetrachloride). Those can be explained by saying that porphyrin manganese has a good selective response to trimethylamine.

Based on the above experimental results, we measured the detection limit of sensitive components to trimethylamine with the presence of interference gases. The concentration of trimethylamine gas was reduced gradually, keeping the concentration of the interference gases as invariant; the results are given in Fig. 7(a). The output light intensity of the sensitive element is more obvious when the trimethylamine concentration is 0.1 ppm. It is shown that the detection limit is lower than 0.1 ppm where the signal-to-noise ratio (\(S/N\)) was 5. In order to determine the accuracy of the sensing element to TMA gas, we performed a parallel test, using the standard deviation as the Y-axis error; and made a Y-axis error bar graph; the results are shown in Fig. 7(b). It can be seen from Fig. 7(b) that there is a good linear relationship between the three parallel experiments, and the linear equation is \(y = (4.003 \pm 0.0628) + (0.3474 \pm 0.01453) \log c\), when \(R^2 = 0.9930\), \(n = 5\), there is no data uncertainty virtually in the concentration of 0.1 - 1000 ppm, which suggests the stability response of the sensitive element toward trimethylamine gas.

One of the most serious weaknesses in the current sensor technology is sensitivity to changes in humidity. To investigate the selective behavior of the sensing element and the behavior of MnTPP to TMA, we conducted an experiment to study the influence of the ambient humidity on the sensing element; the ambient humidity was measured for 30%RH, 50%RH, 70%RH, 90%RH, and the results are shown in Fig. 8. The error bar depicts that there was only a small influence of humidity on the sensing element. Furthermore, we tested the influence of the ambient humidity on the gas sensitivity to TMA (shown in Supporting Information). We detected the responses of...
trimethylamine and interfering gases by mixing water vapor under various RH conditions; the results indicated that the humidity has a minor influence on the gas sensitivity to TMA. However, when the ambient humidity was 90%RH, it showed a much bigger influence on the gas sensitivity to TMA than that of 30 - 70%RH. That may be attributed to the competition between TMA and H₂O.

Conclusions

In this paper, tetraphenylporphin manganese was synthesized via the Alder method, and was used as a sensitive reagent to detect a variety of gases. The experimental results show that the tetraphenylporphin manganese optical waveguide element has a good selective response to trimethylamine gas. This promising sensor element shows a fast response and high sensitivity, and can detect a volume ratio as low as 0.1 ppm with the presence of interference gases; the response time and the recovery time were 1.5 and 50 s, respectively. In the concentration range of 0.1 - 1000 ppm, there is a good linear relationship between the concentration and the output light intensity ($R^2 = 0.9930$). This method of preparing the sensing element is brief and it can realize the desire to detect low concentrated trimethylamine gas at room temperature. Further, the sensing element is insensitive to humidity. It is believed that the sensing element has a good application value in the detection of trimethylamine gas.

Acknowledgements

This study was financially supported by the National Natural Science Foundation of China (Grant Nos. 21765021).

Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/

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