

# Preparation of meso-tetra(4-pyridyl)porphyrin film for optical gas sensor

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## Abstract

The work presented a simple way to prepare a meso-tetra(4-pyridyl)porphyrin (MTPyP) film for optical gas sensor. The dip-dry coating method that was developed by our research shows a strong absorption band at 418 nm. We also proposed a simple method, peak ratio, to do the semi-quantitative analysis of hydrochloric acid (HCl) and ammonia (NH<sub>3</sub>) molecules adsorbed on the dip-dry coating MTPyP film by their absorption bands. The MTPyP film was prepared on glass substrate and spectrometer was used to obtain the spectra as sensing the vapor molecules. The ratio of peaks values at 418 nm and 450 nm was used to identify the vapor types and to determine the concentrations. The results show that the peak ratio of HCl is approaching less than one and the peak ratio of NH<sub>3</sub> is always larger than one for two-hour measurement.

**Key words:** MTPyP film optical gas sensor, hydrogen chloride/ammonia detection, dip-dry coating, peak ratio

## 1. Introduction

In recent years, porphyrin complexes have become one of hot research topics for developing gas sensors and optical sensors because of its advantages of light sensitivity, chemical and thermal stability, and easy modification. The optical properties of porphyrins would change as specific gases combined with porphyrin molecules, like NO<sub>2</sub>, NO, CO, HCl, which are based on a rich  $\pi$ -electron system. Hence, some optical methods, such as the ultraviolet, infrared, fluorescence, phosphorescence and Raman spectroscopy, could be used to detect the changes of optical properties of porphyrins [1]. Therefore, porphyrin complexes becomes an ideal sensing model to study the porphyrin-based sensors. Various techniques have been proposed to prepare the porphyrin films, such as self-assembled monolayer [2], Langmuir-Blodgett Technique [3], and vacuum deposition [4], but these techniques are so complicated for practical application since it takes a lot of time. At same time, these techniques require expensive equipment, which lead to higher costs. Additionally, the optical gas sensors also suffer the problem of drifting baselines, which is also the problems for most optical sensors.

To solve the above problems, a simple method for preparing the Meso-tetra(4-pyridyl)porphyrin(MTPyP) thin film which called dip-dry method was proposed. Then the UV-VIS

spectrometer was used to obtain their characteristics of absorption spectra of the MTPyP dip-coating film as sensing NH<sub>3</sub> and HCl molecules. In addition, we also proposed a simple method, peak ratio, to do the semi-quantitative analysis of HCl and NH<sub>3</sub> molecules adsorbed on the dip-dry coating porphyrin film.

## 2. Materials and Methods

### 2.1 Fabrication of MTPyP thin film

1.25 mM and 1 mM MTPyP (Frontier Scientific) solutions were prepared individually in 1% and 10% toluene (TEDIA) solutions that were a mixture of ethanol (Anhydrous) and toluene with a volume ratio of 99 to 1 and of 9 to 1, respectively. In spin-coating, a 50  $\mu$ l drop of 1.25mM MTPyP was spread out by the spin-coater (Laurell) to form a thin film on glass surface at a speed of 800 rpm for the first 10 s and then 2000 rpm for 40s. In the dip coating methods, 1.25 mM MTPyP with a volume of 12ml was deposited directly on glass surface to form a thick film. Finally, in the method of dip-dry coating, a 50  $\mu$ l drop of 1 mM MTPyP was dropped on glass surface, and then the specimen was treated by nitrogen gas to remove the residual MTPyP solution.

### 2.2 Instrumentation

The absorption spectra of MTPyP film and gaseous detection were carried out by a UV-VIS spectrometer (Varian) at the room temperature. Two handmade acrylics cell with

volume of 22.5 and 30 cm<sup>3</sup> are for static gas sensing. Glass slide is the substrate.

### 2.3 Sensing procedure of MTPyP thin film

At first, the 25% NH<sub>3</sub> and 37% HCl liquid without dilution was individually put into the handmade acrylics cell with a volume of 30 cm<sup>3</sup> and then sealed the cell in the measurement process. The optical absorption of the MTPyP thin film ranged from 370 to 500 nm was continuously measured until the vapour pressure of the cell reached to dynamic equilibrium state at room temperature.

The absorption spectra of MTPyP thin films were also investigated by static measurement after adding 5ul drops of HCl, and NH<sub>3</sub> with the lower concentration of 3M to a cell with volume of 22.5 cm<sup>3</sup> individually. The detection time was over 20 minutes.

## 3. Result and discussion

### 3.1 The characterization of MTPyP films produced by different methods

The absorption spectra of MTPyP films prepared by spin-coating, dip-coating and dip-dry coating are shown in Fig. 1 and the absorption bands, Soret bands, are 425, 419, 418 nm, respectively. The film prepared by spin-coating presents a weaker intensity than the other two methods. The spin-coated film is not uniform, because solvent with high evaporation rate contributed to the non-uniform films. The highly volatile characteristic of MTPyP in ethanol-toluene mixture, which prone to completely vaporized during spin-coating process, may dry up too fast to form a film. The dip-dry coated film presents a stronger intensity than the other two methods, because less volume and rarer concentration of MTPyP solution for dip-dry coating could obtain a uniform film after removing the residual solution by N<sub>2</sub> gas.

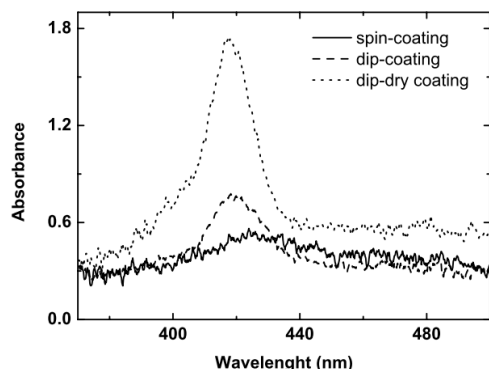


Fig. 1. Absorption spectra of MTPyP thin films prepared by spin-coating, dip-coating and dip-dry coating, and concentrations of MTPyP are 1.25, 1.25 and 1 mM, respectively.

### 3.2 Sensing of NH<sub>3</sub> and HCl gas using MTPyP dip-dry coating film

In the experiment of NH<sub>3</sub> detection, Fig. 2(a)

shows the absorption spectra of the MTPyP film exposed to NH<sub>3</sub> vapor. The solid black line with an absorption peak of 418 nm is the original spectrum without exposing to NH<sub>3</sub> vapor. Then, 10ml of ammonia solution with a concentration of 25% was added into a transparent cell with a volume of 30 cm<sup>3</sup> where a MTPyP film had been placed in advance. The intensity of absorption spectra at 418 nm decreased during 0 s to 1418 s. Decreasing intensity of absorption peak at 418 nm induced by NH<sub>3</sub> gaseous molecules might cause by the electrostatic force between the ammonia molecules and porphyrin, since the porphyrin we adopted here without central metal ion. Moreover, only the intensity of Soret band decreased as more ammonia was evaporating to the air and no Soret red-shifting occurred in this result, which indicates that no electron transfer occurred between ammonia and porphyrin molecules.

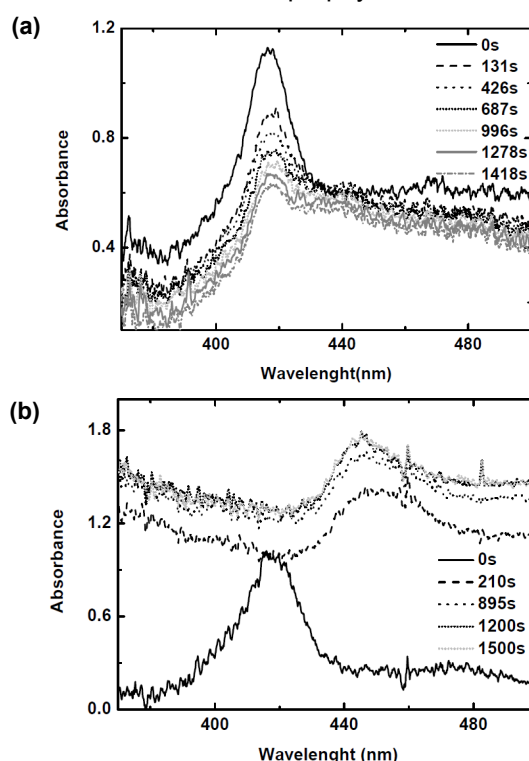


Fig.2. (a) Absorption spectral changes of MTPyP film by exposing to NH<sub>3</sub> gas (b) Absorption spectral changes of MTPyP film by exposing to HCl gas

In Fig. 2(b), the solid black line is the spectrum of MTPyP film before exposing to any HCl gas. The absorption bands, Soret band, is 418 nm. Then, 1.7 µl drop of hydrochloric acid with a concentration of 37 % without dilution was put into a small transparent cell with a volume of 30 cm<sup>3</sup> where a MTPyP film had been placed in advance, and the spectra ranged from of 350 nm to 500 nm were obtained with time series. During this period, the hydrochloric acid molecules evaporated and attached onto this solid state sensor of MTPyP film.

After approximately 200 s, the results of this experiment were observed. The intensity of Soret band decreased due to more and more hydrochloric acid molecule absorbed, and the Soret band shifted from 418 nm to 450 nm. However, at the time of 15 minutes, 900 seconds, the absorption band had a blue shift to 445 nm, which might be caused by the interference of water vapor that continued evaporating before reaching the state of vapor pressure. Finally, the position of the Soret band at 445 nm were not shifted after approximately 20 minutes, when hydrochloric acid solution and vapor reach to dynamic equilibrium of vapor-liquid phase. Therefore, the response time for the Soret band shifting toward 445 nm highly depends on the concentration of hydrochloric acid solution. Moreover, the red shift of Soret band was caused by the attachment of proton on the peripheral pyridyl groups of porphyrin and the inner nitrogen atoms of pyrrole ring [6]. The relative intensity of Soret band at 418 nm become smaller than the Soret band before exposing to hydrochloric acid molecules, and the absorption of spectra also became higher as more proton evaporated into air.

### 3.3 The semi-quantitative analysis of $\text{NH}_3$ and HCl gas using MTPyP films

In Fig. 2 (b), the absorption unit of 418 nm at 210 s is overlap with the original spectrum, but its Soret band had shifted to 450 nm. Hence, the quantitative analysis is not enough to determine the variance of absorption intensity and the shifting of Soret band. Furthermore, the determination of the precise response time of MTPyP film to HCl molecule should carry out by removing the interference of water vapor in the future. Although the experiment demonstrated here is simple, it could reflect the practical circumstance as the acid vapor leaks in a closed space. Although the intensity and the position of Soret band of porphyrin would change as HCl and  $\text{NH}_3$  absorbed, the baseline of every spectrum did not vary regularly with increasing the concentration of vapor molecules. In Fig. 2, we could observe that the first two spectra exposed to the HCl molecules were higher than the original spectrum (the solid black line), but the other spectra were lower than the black line. However, the quantitative method to locate the variance of Soret band and then to compare with the original spectrum is not enough for the purpose of detecting proton in real time. For the detection of  $\text{NH}_3$  molecules, the variance of spectra was not complicated, but the baselines were also drifting as more molecules attached. Therefore, we proposed to utilize the ratios of peaks values at 418 nm and 450 nm for every

spectrum to identify the types and to roughly determine the concentrations of vapor molecule. The peak ratio ( $A_{418}/A_{450}$ ) is defined as the ratio of the absorbance bands at 418 nm and 450 nm in the same spectrum.

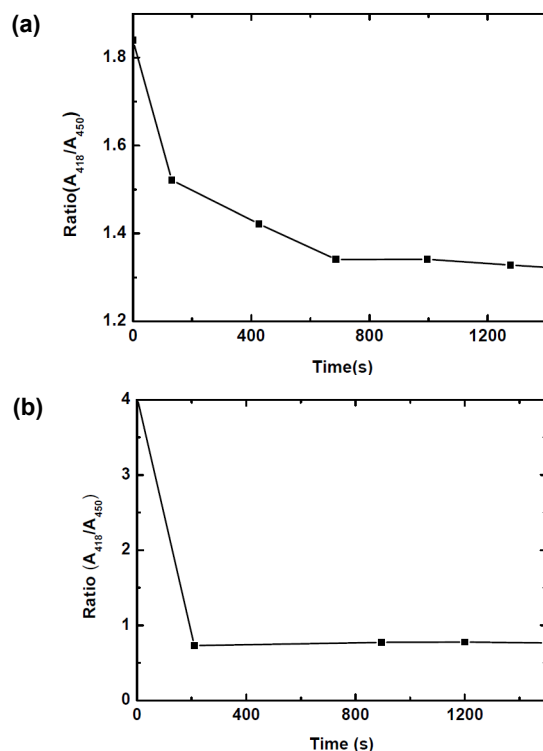


Fig.3. (a) Peak ratio of 418 nm and 450 nm changed with time obtained from Fig.2.(a); (b) Peak ratio of 418 nm and 450 nm changed with time obtained from Fig.2.(b).

The value of peak ratio was small than 1, after exposing to HCl gas (Fig. 3(a)). Due to the red shift of Soret band to 450 nm, the value approached steady as more molecules attached on the MTPyP film. The value of peak ratio closed to 1, after exposing to  $\text{NH}_3$  gas (Fig. 3(b)). After two hours, the value of peak ratio approached 1.3. Hence, the differences values of peak ratio of 418 nm and 450 nm in the spectra of sensing HCl and  $\text{NH}_3$  were obvious. We could obtain the value of peak ratio for HCl was less than 1, and the value of peak ratio for  $\text{NH}_3$  was always larger than 1. This result indicated that the potential of porphyrin-based optical gas sensor provided a simple method to identify HCl and  $\text{NH}_3$  gas.

### 3.4 Sensing of $\text{NH}_3$ and HCl gas at lower concentration

In fig.4 (a) and (b), we could found that the lower concentration of  $\text{NH}_3$  and HCl solutions were difficult be evaporated into air, so the variance of the spectra changed with time were not as apparent as those in high concentration. According to the results, the related intensity of absorption spectra for  $\text{NH}_3$  almost didn't change. However, only the  $\text{H}^+$  from the HCl gas caused

an obvious red shift, from 418 nm to 450 nm. The MTPyP film showed the better sensitivity to HCl gas compared with that of  $\text{NH}_3$  gas.

In fig.5 (a), the value of peak ratio was approaching to 2, due to the relative intensity of the Soret band at 418nm was almost constant (fig.4 (a)). The spectra after 90 s were almost unchanged during by exposing to less  $\text{NH}_3$  gas. However, in fig.5 (b), the value of peak ratio was also smaller than 1, as the Soret band exposed to HCl gas. This results showed that the slope of the peak ratio before 400 seconds did not change dramatically.

These results indicated that the use of MTPyP dip-dry coating films for the development of optical gas sensor had the advantages for detection of HCl, whether the porphyrin thin films in high concentration or low concentration, moreover, they showed the poor sensitivity in lower ammonia concentration.

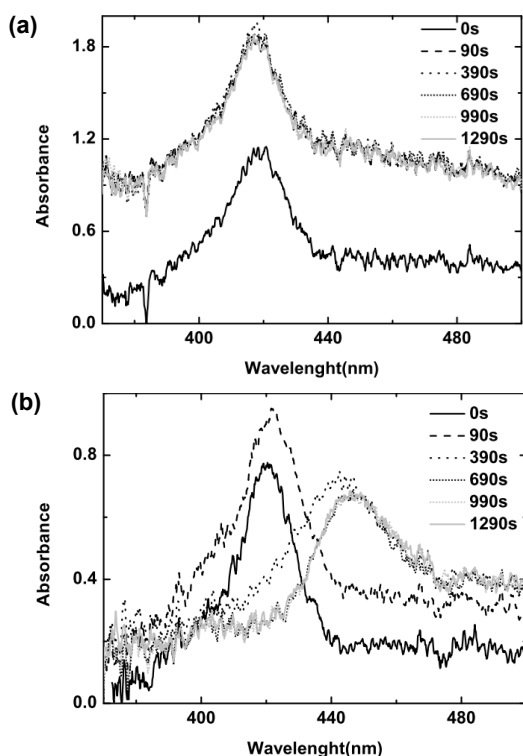


Fig.4. The spectra for sensing various acid/basic vapor, (a)  $\text{NH}_3$ ; (b) HCl. The concentrations of solutions were all 3 M.

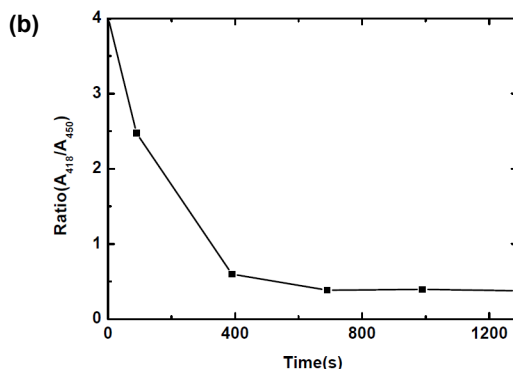
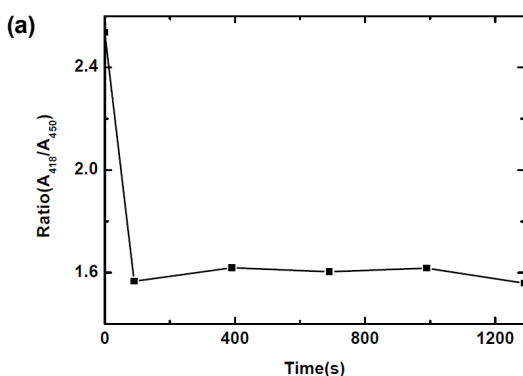


Fig.5. (a) Peak ratio of 418 nm and 450 nm changed with time obtained from Fig.4.(a); (b) Peak ratio of 418 nm and 450 nm changed with time obtained from Fig.4.(b).

#### 4. Conclusions

This work demonstrated a simple way to prepare MTPyP films for  $\text{NH}_3$  and HCl gas sensor, and we also presented a semi-quantitative analysis of  $\text{NH}_3$  and HCl gas using MTPyP films. The results demonstrated that this MTPyP film shows a good potential to identify the HCl and  $\text{NH}_3$  gas at room temperature.

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