Synthesis of organic semiconductor hexadecachloro zinc phthalocyanine and its gas sensitivity*

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Abstract: Due to the difficulty in synthesizing perhalogenated metallophthalocyanine, the method of ammonium molybdate solid phase catalysis was introduced, and by using tetrachlorophthalic anhydride and urea as the raw materials, hexadecachloro zinc phthalocyanine ($ZnPcCl_{16}$) was synthesized. Components of the composite were analyzed by energy spectrum, and its functional group structures and absorption peaks were characterized by IR and UV-vis spectroscopy. The thin films of gas sensors were prepared in a vacuum evaporation system and evaporated onto SiO_2 substrates, where sensing electrodes were made by MEMS micromachining. The optimal conditions for the films are: substrate temperature of 150 °C evaporation current of 95 A and film thickness of 50 nm. The result showed that the sensors were ideally sensitive to Cl_2 gas and could detect the minimum concentration of 0.3 ppm.

Key words: hexadecachloro zinc phthalocyanine; organic semiconductor; gas sensitivity
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1. Introduction

Phthalocyanine (Pc) is a prominent class of organic molecular material, which consists of macrocyclic tetraazaporphyrin structure[1]. It is characterized by novel electrical and optical properties, and chemical and thermal stability, and these properties can be changed by peripheral or axial replacement, or by altering the central metal atom[2]. The applications can be found in a wide range of high technical fields such as nonlinear optics, liquid crystals, Langmuire Blodgett films, photovoltaic cells, chemical sensors, laser recording materials, organic field effect transistors, and even biomedical applications[3−5].

Metal phthalocyanines (MPcs) are p-type organic semiconductors which exhibit high sensitivity to both electron acceptor gases such as Cl_2 and hole donor gases such as NH_3 in low concentration (ppm or even ppb level). It is well established that gas adsorption on the surface of crystals or films of MPcs is followed by charge transfer reactions which induce the generation of charge carriers and enhance the conductivity. In most cases, atmospheric oxygen has always been considered as being the doping agent mainly responsible for the increase in electrical conductance of the MPcs, but de Haan *et al.* demonstrated that the main effect of conductance change must rather be attributed to traces (ppm) of strongly oxidizing gases present in air[6]. Recently, with the frequent occurrence of explosion and toxication, MPcs were made gas sensing materials to detect the toxic gases such as Cl_2, NO_2, NH_3 etc[7]. So far, the synthesis methods of $ZnPcCl_{16}$ available are very few, let alone reports made on $ZnPcCl_{16}$ using as sensing materials. Nevertheless, we believe that $ZnPcCl_{16}$ should be a good sensing material for detecting toxic gases. That is why we carried out this experiment.

Tetrachlorophthalic anhydride and urea were used as raw materials in this experiment, and after imidization, amination and dehydrolyzation, molecular fragments were obtained. Then, $ZnPcCl_{16}$ was synthesized by introducing ammonium molybdate solid phase catalysis and characterized by the spectroscopic analysis. In addition, its gas sensitivity was also studied in this work.

2. Experiment

2.1. Synthesis of molecular fragments

After imidization, amination and dehydrolyzation, tetrachlorophthalic anhydride was transformed to tetrachlorophthalimide (i), tetrachlorophthalic diamide (ii) and tetrachlorophthalonitrile (iii), respectively; then $ZnPcCl_{16}$ (iv) was synthesized by catalyzing intermediate product (iii), as shown in Fig. 1.

2.1.1. Tetrachlorophthalimide

Tetrachlorophthalic anhydride (5.72 g, 20 mmol), urea (3 g, 50 mmol) were mixed, homogenized in a flask, and heated
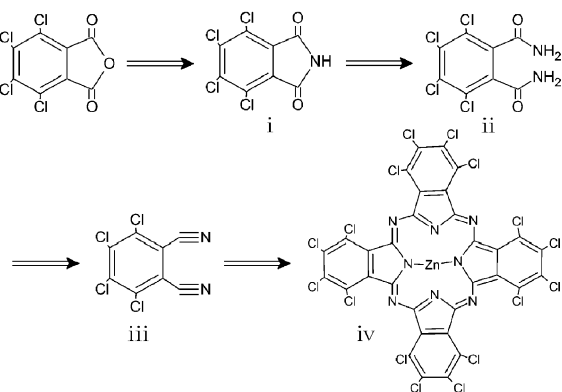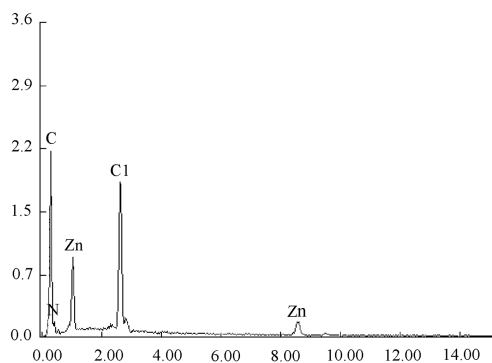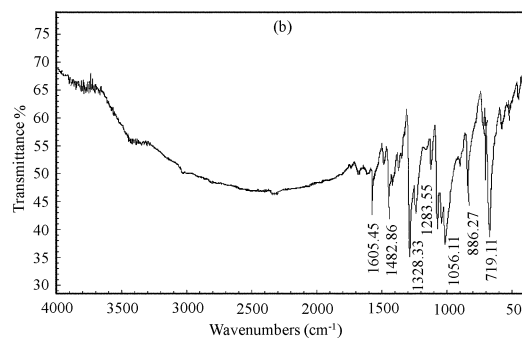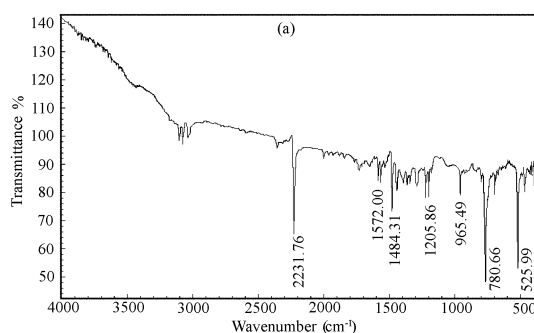
Fig. 1. Synthesis route of the target compounds.

Fig. 2. Energy spectrum of ZnPcCl$_{16}$.

Fig. 3. IR spectra of compounds iii and iv: (a) Tetrachlorophthalonitrile; (b) ZnPcCl$_{16}$.

in an oil bath. When reaching 230–240 °C, the mixture began melting, and then was slowly brought to 260 °C until it completely turned into liquid. Immediately, a mass of yellow acicular crystals appeared and swelled to as 3–4 times as the initial. The crystals were cooled and dispersed by adding water (250 mL), recrystallized with water repeatedly, filtered, and dried to get yellowy flake crystals.

2.1.2. Tetrachlorophthalic diamide

Under magnetic stirring, tetrahydrofuran (100 mL) was added to tetrachlorophthalimide (7.2 g, 25 mmol) in the flask. The suspended gradually dissolved after heating, and absolutely disappeared at 50 °C. Then ammonia (72 mL) was poured into the solution, and the block precipitates instantly appeared in large amount. Meanwhile, the precipitates were kept under the ammonia atmosphere for 2 h, then cooled to 0 °C, filtered, washed and dried, so white product was obtained.

2.1.3. Tetrachlorophthalonitrile

Thionyl chloride (25 mL) was slowly added to dried N-Ndimethyl formamide (250 mL) in a 500 mL three necked round-bottom flask fitted with a magnetic stirrer, a thermometer and a dry pipe of CaCl$_2$. After 10 min, tetrachlorophthalic diamide was poured into the flask in batches for a couple of times. 45 min later, it was stirred at room temperature for 2 h, then poured into 700 g ice blocks, washed with water and sodium bicarbonate, filtered, and dried to give white product.

2.2. Synthesis of final product

Tetrachlorophthalonitrile (3.99 g, 15 mmol), urea (4.5 g, 75 mmol) and zinc acetate dihydrate (0.825 g, 3.75 mmol)

were mixed, then heated with ammonium molybdate (0.03 g) used as catalyst. The mixture was brought to 180 °C in an hour. The heating was carried on for 5 h. The mixture was alternatively washed with 1 M HCl and 1 M NaOH solution in a hot bath under ultrasonic waves until the washes were colorless. The product was then rinsed with hot water and dried. The blue black powder was purified by soxhlet extraction with methanol, and after vacuum dried the blue ZnPcCl$_{16}$ was obtained.

2.3. Device preparation

ZnPcCl$_{16}$ powder was purified by recrystallizing in concentrated H$_2$SO$_4$ and made into thin films of gas sensors by a conventional vacuum evaporation method. The ZnPcCl$_{16}$ thin films were evaporated onto SiO$_2$ substrates in a vacuum evaporation system operating at a base pressure of 8×10^{-4} Pa. The substrates whose size is 3.5×3.5 mm^2, provide gold interdigital electrodes whose total length is 20 mm and the distance between them is 25 μm. The electrodes made in this way mainly include the following processing routes: templates design, substrates cleaning, vacuum drying, photoresist coating, soft-baking, exposuring, developing, hardening, magnetron sputtering，residual surface removing, heat treating, and laser cutting. The substrate temperature was varied from 100 to 170 °C. The evaporation current of ZnPcCl$_{16}$ powder was varied from 60 to 100 A. The ZnPcCl$_{16}$ thin film thickness produced in this manner ranged from 50 to 300 nm.

The ZnPcCl$_{16}$ thin film gas sensors were set on a heater in a glass bell jar. The current flowing through the electrodes of the sensors in the atmosphere was under the limit of detection at an applied voltage of 3 V. The sensitivity of ZnPcCl$_{16}$
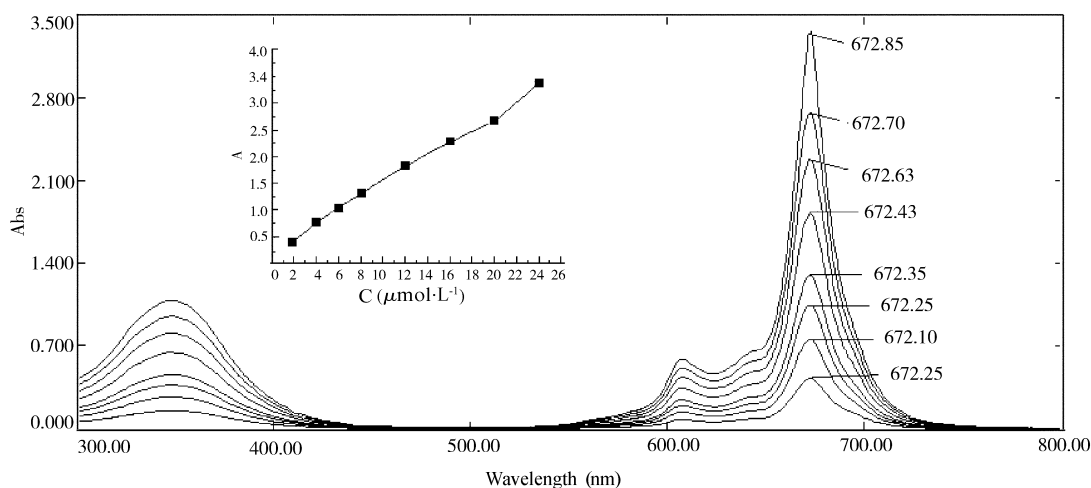
Fig. 4. UV spectra of ZnPcCl$_{16}$ in DMSO in different concentrations. (Concentration is: 2, 4, 6, 8, 12, 16, 20, 24 μmol/L)
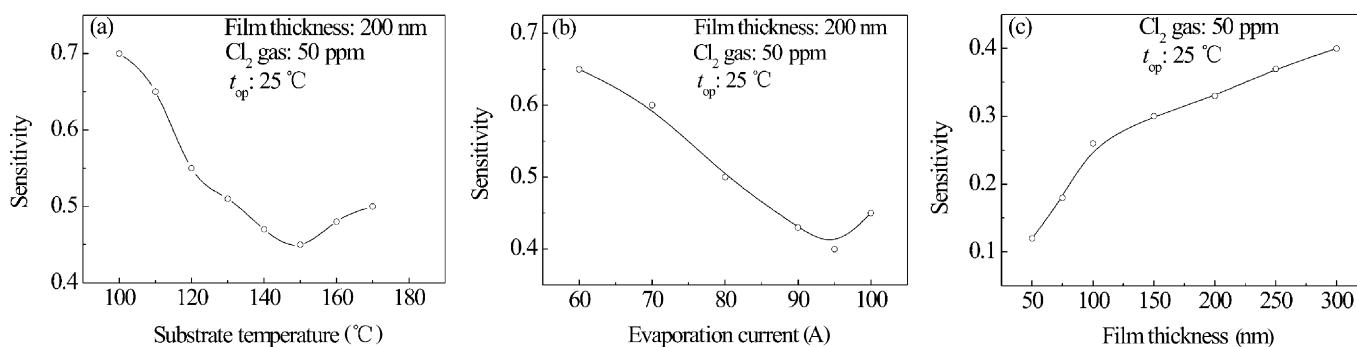

Fig. 5. Influence of different factors on sensitivity of ZnPcCl$_{16}$ thin film gas sensors: (a) Substrate temperature; (b) Evaporation current; (c) Film thickness.

thin film gas sensors at various operating temperatures was estimated by measuring the resistivity during the repeated introduction and removal of Cl$_2$ gas from the ambient air. The Cl$_2$ gas was introduced by injector into the glass bell jar.

3. Results and discussion

3.1. Characterization

As can be clearly seen from Fig. 2, the presence of elements (C, N, Cl, Zn) and their components in the composite can preliminarily predict that the desired product (ZnPcCl$_{16}$) has been synthesized.

Comparing the IR spectra of tetrachlorophthalonitrile and ZnPcCl$_{16}$ in Fig. 3, we can observe that the distinctions between them are as follows: (1) the absorption peak of the nitrile C≡N bonds appears at 2231.76 cm^{-1} in tetrachlorophthalonitrile but disappears in ZnPcCl$_{16}$, which indicates the formation of ZnPcCl$_{16}$; (2) generally speaking, the stretching frequency of the C=N bonds is close to 1300–400 cm^{-1}, and the absorption in Fig. 3(b) is 1328.33 cm^{-1}, which is peculiar to ZnPcCl$_{16}$ in these compounds; (3) ZnPcCl$_{16}$ also displays a N–Zn–N vibration, whose absorption is at 886.27 cm^{-1}. It should be noted that the bands of aromatic C=C bonds and C–Cl bond are shifted at a certain range as a result of the impact of ligand on Zn central metal. For example, the aromatic C=C bonds change from 1572 to 1605.45 cm^{-1}.

Owing to insolubility of ZnPcCl$_{16}$ in usual organic sol-

vents, its spectra were obtained in DMSO and in concentrated H$_2$SO$_4$ (Table 1). Two absorption bands appear in the UV spectra as shown in Fig. 4. These bands are the intense "Q" band which peaks at near 672 nm and the less intense "B" band which peaks at about 350 nm. In addition, a weak band is observed near at 610 nm. As the concentration increases, both the absorption bands display red shifts in a small range. Compared with the unsubstituted ZnPc, the perchlorinated substituent ZnPcCl$_{16}$ shows a red shift from 661 to 672 nm in the Q band, and from 326 to 347 nm in the B band.

It is well known that MPcs have a high stability in an acidic or alkalic condition[8]. The spectroscopic data of ZnPcCl$_{16}$ dissolved in DMSO and in concentrated H$_2$SO$_4$ were listed in Table 1. Regardless of neutral, acidic or alkalic in DMSO, ZnPcCl$_{16}$ shows the Q band almost the same and the B band with a small shift. In a way, it really reflects its chemical stability. Obviously, there is nearly 100 nm red shift in both Q band and B band in concentrated H$_2$SO$_4$. To understand the reason for the extraordinary red shift seen with ZnPcCl$_{16}$ requires further experiments.

3.2. Gas sensitivity

As mentioned above, Cl$_2$ gas is an electron acceptor gas and ZnPcCl$_{16}$ is a p-type organic semiconductor. Therefore, the conductivity of ZnPcCl$_{16}$ thin film gas sensors will increase when exposed to Cl$_2$ gas. Here, gas sensitivity is defined as the ratio R_g/R_0, where R_g and R_0 are the resistance of
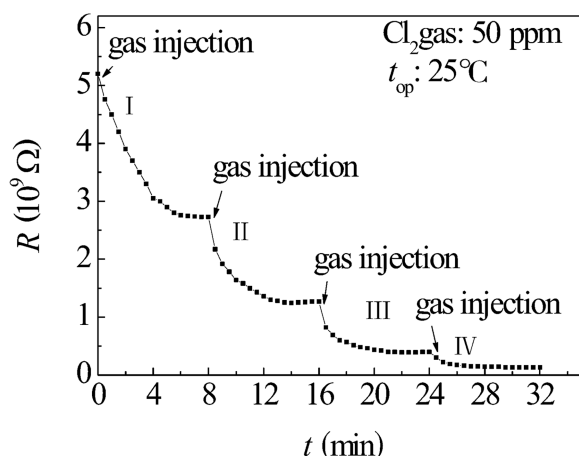
Fig. 6. Response curve in different concentrations.

Table 1. Spectroscopic data of ZnPcCl₁₆ dissolved in DMSO and in concentrated H₂SO₄.

Absorption solvent		B-band peak (nm)	Q-band peak (nm)	
DMSO	Neutral	347	607	672
	Acidic	341	608	673
	Alkalic	335	608	673
Concentrated H₂SO₄		438	700	786

sensors after and before Cl_2 gas introduction, respectively. As a result, the sensitivity is less than one, the smaller the ratio the better the sensitivity. Although $ZnPcCl_{16}$ thin film gas sensors exhibited high sensitivity to Cl_2 gas, the sensitivity was dependent on a variety of factors, such as substrate temperature, evaporation current, film thickness and so on.

In order to demonstrate the influencing factors possible, some of them were investigated in the experiment. Figure 5 shows the sensitivity of $ZnPcCl_{16}$ thin film gas sensors operated at 25 °C and exposed to Cl_2 gas with a concentration of 50 ppm under different preparation conditions. The optimal substrate temperature should be at 150 °C as shown in Fig. 5(a). However, if substrate temperatures are above 180 °C, $ZnPcCl_{16}$ thin films could not be deposited very well. As for the evaporation current, we can clearly see from Fig. 5(b) that as the current increases from 60 to 95 A, the sensitivity would be improved considerably; and at the same time, it should be noted that the films would be carbonized if the current increased further. The current of 95 A should be thought the best in this experiment. It was also found that the sensitivity was strongly dependent on the film thickness. Figure 5(c) shows that the sensitivity was degraded when the film thickness increased from 50 to 300 nm. It is too thick films that restrain the gas diffusion, which can be attributed to the compact accumulation of the molecules. It was also found that $ZnPcCl_{16}$ thin films deposited with a thickness of below approximately 50 nm were unstable under long term operation. Therefore, thickness of about 50 nm was the best for $ZnPcCl_{16}$ thin film in the experiment.

$ZnPcCl_{16}$ thin film gas sensors were prepared under the optimized preparation conditions and operated at 25 °C.
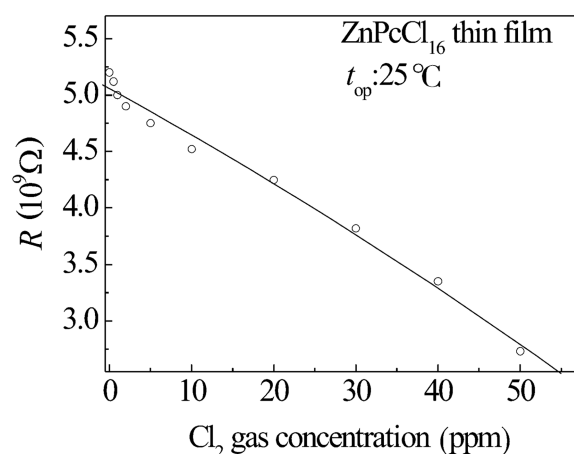

Fig. 7. Relation curve between Cl_2 gas concentration and output resistance of the sensor.

200 ppm Cl_2 gas was injected periodically for four stages (I, II, III, IV) as shown in Fig. 6. From the response curve, we can discover that the resistance decreased immediately at the beginning and then gradually went steady in each stage. Figure 6 also shows the response time shortened when Cl_2 gas concentration increased. However, it needed a long period to return to the original state, which may be caused by its poor desorption. Figure 7 shows the relation curve between Cl_2 gas concentration and output resistance of $ZnPcCl_{16}$ thin film gas sensors prepared under the optimized preparation conditions. The $ZnPcCl_{16}$ thin film gas sensors operated at 25 °C. As can be seen in Fig. 7, the resistance of the $ZnPcCl_{16}$ thin film as a sensor decreased approximately linearly with the Cl_2 gas at a concentration in the range of 0.3–50 ppm. In addition, the $ZnPcCl_{16}$ thin film gas sensor was very stable in the high concentration Cl_2 gas atmosphere. Theoretically, they can be explained by introducing sensing mechanism of gas sensors. But sensing mechanisms of $ZnPcCl_{16}$ thin film gas sensors are complicated and we are not able to sufficiently explain them in detail here.

4. Conclusion

The IR and UV spectra of newly synthesized $ZnPcCl_{16}$ have been presented in this work. It turned out that $ZnPcCl_{16}$ thin film gas sensors exhibited good sensitivity to Cl_2 gas. The sensitivity of $ZnPcCl_{16}$ thin film gas sensors was strongly dependent on the $ZnPcCl_{16}$ thin film preparation conditions. The optimal conditions for the films are: substrate temperature of 150 °C, evaporation current of 95 A and film thickness of 50 nm. The $ZnPcCl_{16}$ thin film gas sensor was very stable in the high concentration Cl_2 gas atmosphere. Thus, the further study on the gas sensitivity of $ZnPcCl_{16}$ is of great importance in exploiting organic gas sensing material.

References

[1] Obirai J, Nyokong T. Synthesis, spectral and electrochemical characterization of mercaptopyrimidine-substituted cobalt, manganese and Zn (II) phthalocyanine complexes. Elec-

trochimica Acta, 2005, 50: 3296

[2] Derkowska B, Wojdyla M, Bala W, et al. Influence of different peripheral substituents on the nonlinear optical properties of cobalt phthalocyanine core. J Appl Phys, 2007, 101(8): 83112

[3] Yu S, Ma C, Cheng C, et al. Synthesis and 0.88 mm near-infrared electroluminescence properties of a soluble chloroindium phthalocyanine. Dyes and Pigments, 2006, 76: 492

[4] Senthilarasu S, Velumani S, Sathyamoorthy R, et al. Characterization of zinc phthalocyanine (ZnPc) for photovoltaic applications. Appl Phys A: Materials Science and Processing, 2003, 77(3/4): 383

[5] Tret'yakova I N, Chernij V Ya, Tomachinskaya L A, et al. Applications of phthalocyanine complexes. Ukrainskij Khimicheskij Zhurnal, 2005, 71(11/12): 85

[6] de Haan A, Debliquy M, Decroly A. Influence of atmospheric pollutants on the conductance of phthalocyanine films. Sensors and Actuators B, 1999, 57: 69

[7] Shi Yunfen, Shi Yunbo, Sun Mojie, et al. A PdPc-PANI modified SAW sensor and phosphorous-containing toxic gas detection. Journal of Semiconductors, 2008, 29(5): 998 (in Chinese)

[8] Shen Yongjia. The syntheses and applications of phthalocyanines. Beijing: Chemical Industry Press, 2001 (in Chinese)