



High-performance ammonia sensor based on cobalt porphyrin-polyaniline polymer

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ABSTRACT

Aiming at the problems of low sensitivity, poor selectivity and poor stability of traditional ammonia (NH₃) sensors, a novel preparation strategy for NH₃ sensors was proposed in this study. The polymer material cobalt porphyrin-polyaniline (TAPPCo-PANI, TC-P) was prepared by adding TAPPCo during the polymerisation of aniline, and the TC-P NH₃ sensor was constructed by drop-coating the TC-P on the PET-based interdigital electrode. The TC-P sensor was tested for NH₃ sensing, and the results showed that it had a fast response time (108 s) to NH₃, and the TC-P sensor response values showed a linear correlation in the range of NH₃ concentrations between 50 and 500 ppm. In addition, the TC-P sensor has high sensitivity, strong selectivity and good stability. The addition of TAPPCo accelerates the electron transfer rate, which gives the sensor excellent gas-sensitive performance. Therefore, TC-P is expected to be a reliable NH₃ sensor material.

1. Introduction

Ammonia (NH₃) is considered to be a toxic and harmful substance that mainly originates from agricultural production, chemical plants and animal husbandry. NH₃ is produced when proteins deteriorate, and NH₃ sensors can be used to monitor the freshness of high-protein meats. It has been reported that if a person breathes in NH₃ concentrations as high as 0.82 to 14.7 ppm, this can be considered an indication of kidney disease [1]. Thus, it is important to develop NH₃ sensors with good sensing performance.

Polyaniline (PANI) has reversible doping/de-doping properties and good electrical conductivity and environmental stability make PANI a potential candidate for room temperature NH₃ sensing. However, issues such as poor NH₃ selectivity and low responsiveness have hindered the widespread use of pure-phase PANI sensors. In the current report, the sensing performance of PANI can be enhanced by increasing the specific surface area [2], compounding with metal oxides [3] and compounding with carbon materials [4]. Metalloporphyrins are obtained by coordination between porphyrins and metal ions, and have a special rigid conjugated planar structure. This structure enables rapid charge transfer between the metalloporphyrin and the NH₃ molecule [5]. Thus, improving the electronic motion by introducing metalloporphyrin is expected to enhance the NH₃ sensing performance of PANI.

In this work, a polymer was obtained by combining PANI and cobalt

porphyrin (TAPPCo) and prepared as a sensor. The prepared polymer and its sensor were characterized and tested for NH₃ sensing. The results show that the sensor has excellent sensing properties for NH₃, such as high sensitivity, stability and selectivity for NH₃.

2. Experimental methods

The chemical reagents used in this experiment are all analytical grade. A substitution approach was used to prepare 5,10,15,20-Tetrakis (4-aminophenyl) cobalt porphyrin (TAPPCo). 5,10,15,20-Tetrakis (4-aminophenyl) porphyrin (TAPP) was synthesized following previous literature [6]. Firstly, 0.15 mmol of TAPP and 0.6 mmol of Co (CH₃COO)₂·4H₂O were added into 50 mL of N,N-Dimethylformamide. The obtained solution was condensed and re-fluxed at 110 °C for 12 h under argon atmosphere and subsequently poured into deionized water for settling. The precipitate was filter-dried to obtain TAPPCo.

TAPPCo-PANI (TC-P) was prepared by chemical synthesis [7]. An amount of TAPPCo powder was dissolved in 1 g of re-distilled aniline and added drop-wise into 100 mL of HCl (1 mol/L) containing 1 g of β-cyclodextrin. After mixing well, an aqueous solution containing 2.448 g of ammonium persulfate (APS) was added drop-wise for 12 h of polymerization. The precipitate was washed and filtered, then dried under vacuum at 60 °C. TC-P was prepared by adjusting the mass of TAPPCo at 0 % (pure PANI), 0.5 %, 1 %, 2 %, 5 % and 10 %, respectively.

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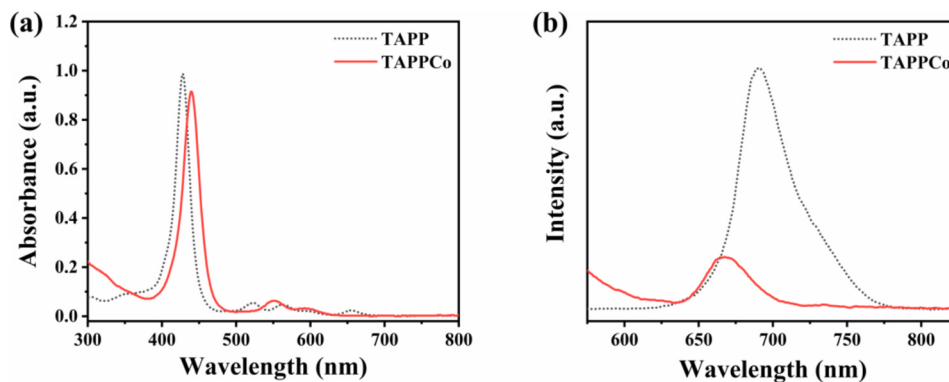


Fig. 1. UV-Vis absorption spectra (a) and fluorescence emission spectra (b) of TAPP and TAPPCo.

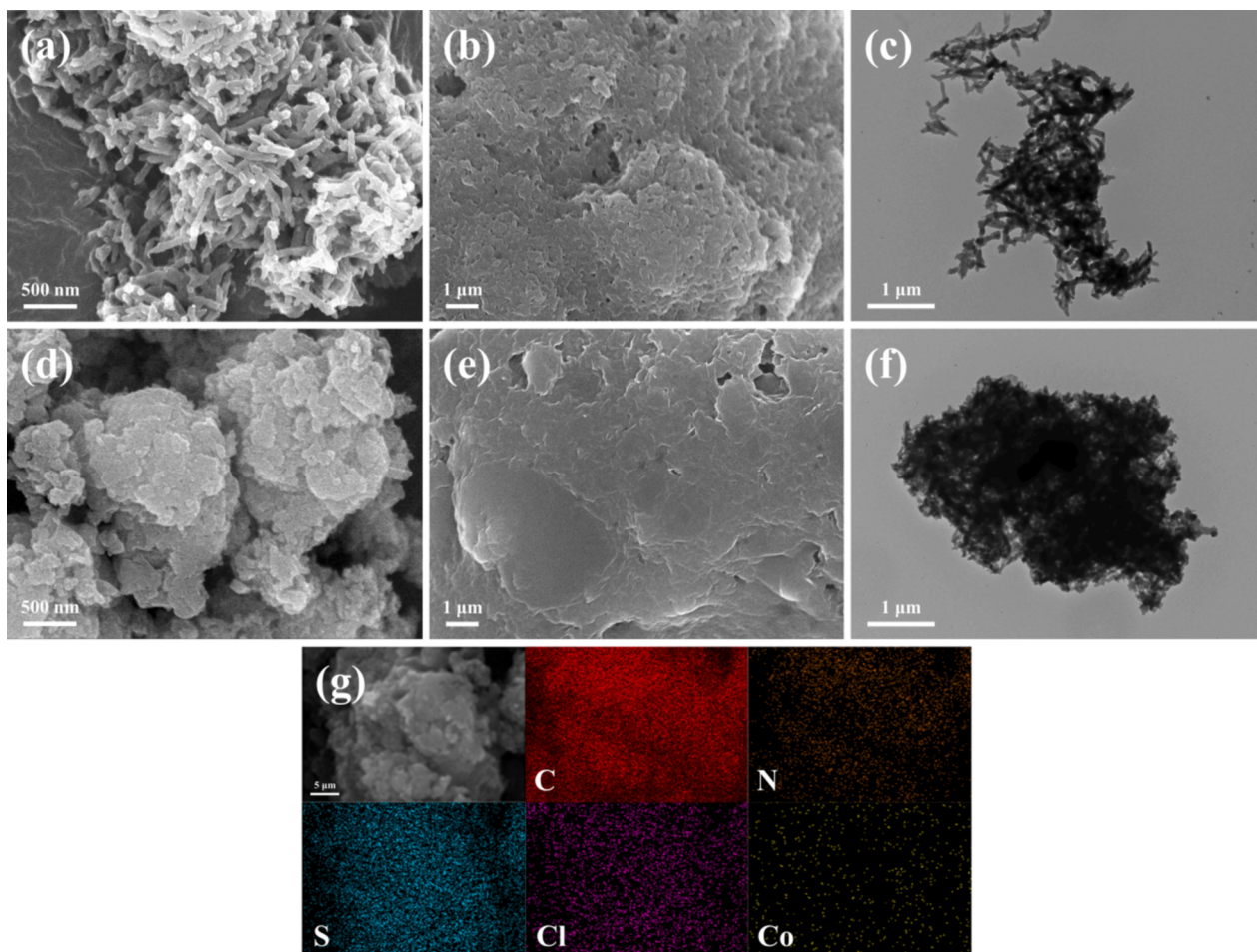


Fig. 2. SEM images of PANI (a) and PANI sensor (b), TEM images of PANI (c). SEM image of TC-P (d) and TC-P sensor (e), TEM (f) and EDS-mapping (g) images of TC-P.

The NH_3 sensor was prepared by drop-casting deposition method. 1 mg of TC-P with different contents of TAPPCo were taken and dissolved in 1 mL of N-Methylpyrrolidone respectively. Then the mixture was drop-coated onto the PET-based interdigital electrode and dried under vacuum at 60 °C. The sensing performance of the sensor was carried out in a homemade sealed chamber and tested by a benchtop digital bridge (4091C, Victory Instruments). The gases used for the tests are obtained by mixing the corresponding pure gases and fresh air in the appropriate proportions. All experiments were conducted at room temperature (25 °C) under 50 % RH. The response value (S) is obtained by Eq. (1).

$$S = (R - R_0)/R_0 \times 100 \% \quad (1)$$

where R and R_0 are the resistance of the sensor in the target gas and air, respectively. In addition, the response and recovery time is defined as 90 % of the time required for a change in the total resistance value of the sensor.

3. Results and discussion

The curves in Fig. 1a show the UV-vis spectra of TAPP and TAPPCo.

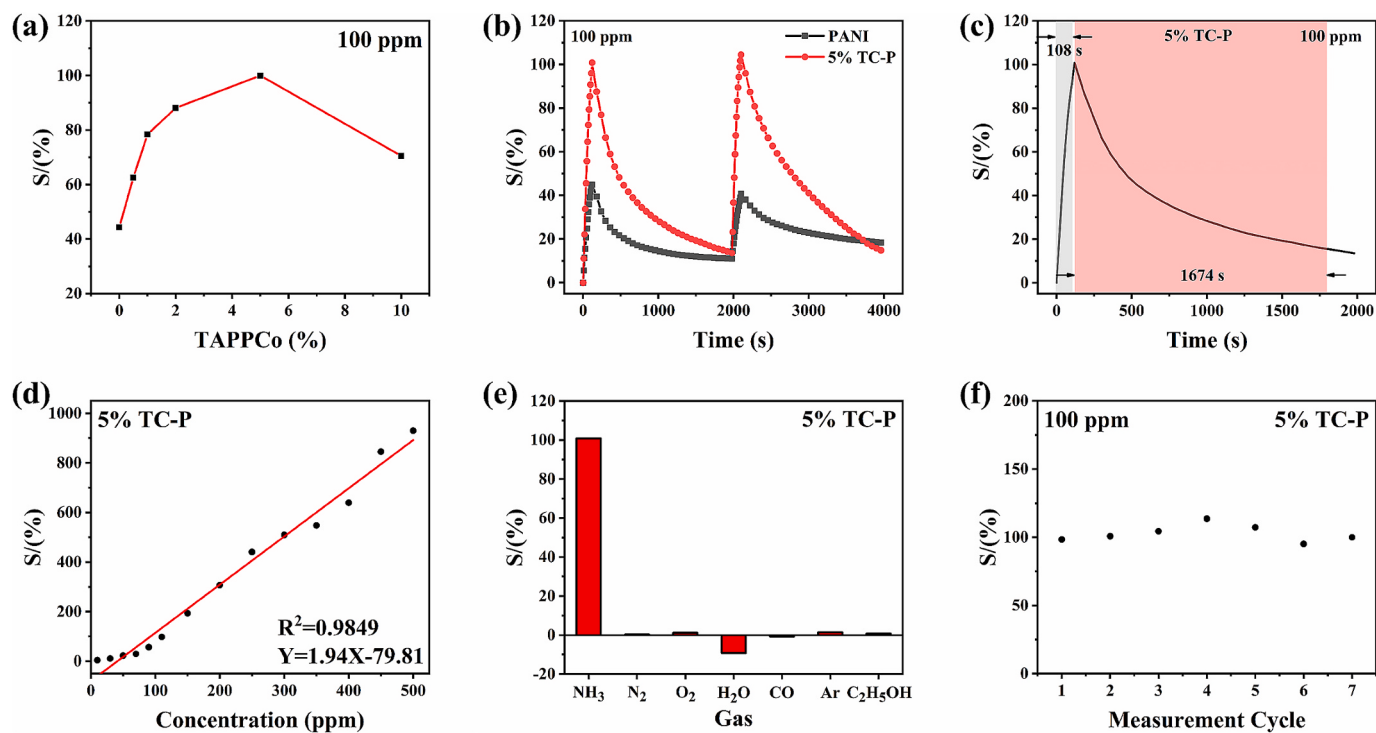


Fig. 3. The NH_3 sensitivity of sensors prepared with different contents of TAPPCo (a); cyclic response-recovery curves for PANI and TC-5-P sensors (b); the TC-5-P sensor: dynamic response-recovery curve for 100 ppm NH_3 (c); linear-relationship between NH_3 concentrations and responses (d); selectivity (e); reproducibility (f).

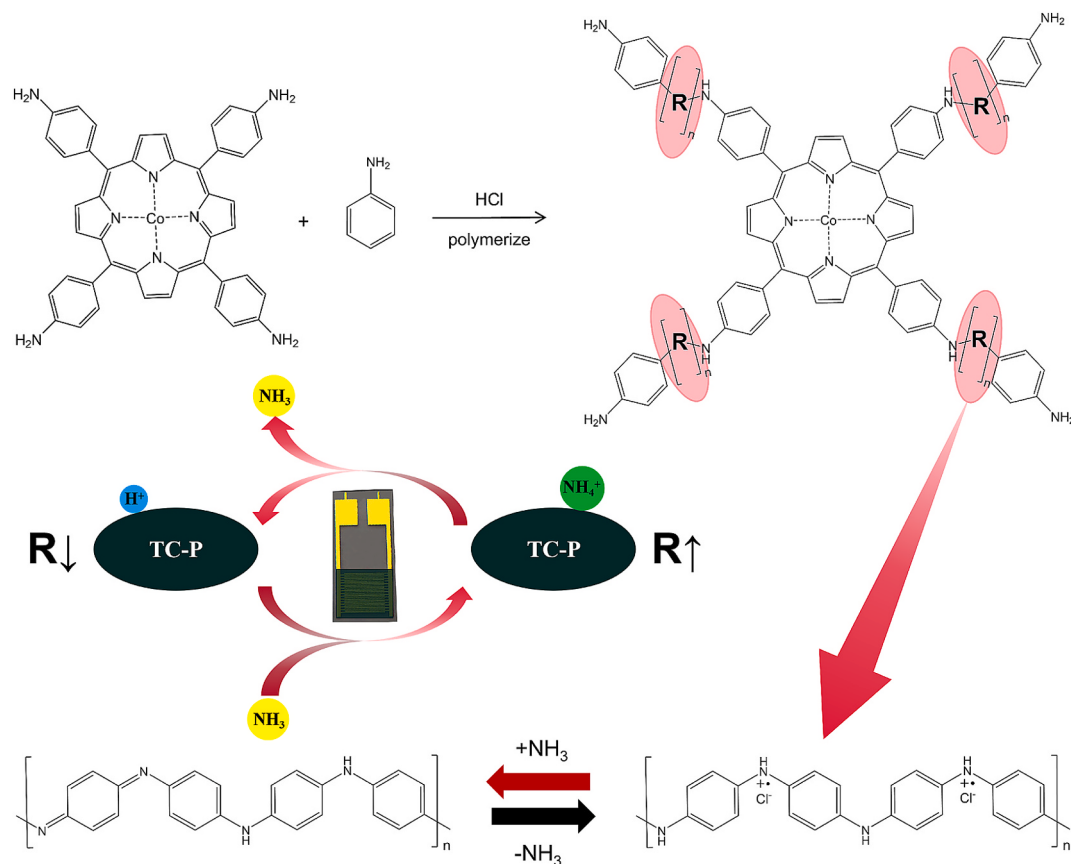


Fig. 4. Sensing Mechanisms of TC-P Sensors.

Compared with the metal-uncoordinated TAPP, the Soret band of TAPPCo was red-shifted from 428 nm to 440 nm, and the absorption peaks of the Q band of TAPPCo were changed from four to two [8]. It was demonstrated that the H at the -NH position in the porphyrin ring was replaced by the metal Co to synthesize TAPPCo. Fig. 1b shows the fluorescence changes of TAPP after the addition of Co^{2+} . The fluorescence emission peak of TAPP complexed with Co^{2+} is blue-shifted from 690 nm to 665 nm. This is mainly due to the introduction of metal ions, which are caused by the interactions with π -electrons on the ring [9], and the fluorescence intensity is weakened, and bursting occurs. This indicates that cobalt porphyrin compounds have been synthesized.

The surface morphology of PANI, TC-P and their corresponding sensors were observed by scanning electron microscopy (SEM). In Fig. 2a, PANI exhibits a nanorod structure, while TC-P aggregated into many lumpy particles (Fig. 2d). It may be due to J-aggregation occurring in TAPPCo [10]. However, compared with the PANI sensor (Fig. 2b), the TC-P sensor (Fig. 2e) has a smoother and flatter surface morphology. Further observation was made by transmission electron microscopy (TEM) as shown in Fig. 2c and 2f. In TC-P, it was found to aggregate into clumps, which were composited with nanorod PANI. This is because the π - π interaction of TAPPCo leads to the aggregation of TC-P polymers [10]. In addition, a relatively uniform distribution of C, N, S, Cl and Co elements was observed on the TC-P surface by EDS (Fig. 2g), indicating that TAPPCo was well composited with PANI.

Fig. 3a shows the sensing performance of the sensors prepared with different contents of TAPPCo for 100 ppm NH_3 . The results show that the gas response value grows gradually with the increase of TAPPCo content. The response value started to decrease at 10 % TAPPCo content, which may be due to the aggregation of TAPPCo affecting the NH_3 sensing effect of PANI. In the subsequent experiments, 5 % content of TC-P was chosen to investigate the sensitivity to NH_3 , named TC-5-P. The PANI and TC-5-P sensors were subjected to 100 ppm NH_3 for 120 s, then air was introduced for recovery and the two cycles were repeated. In Fig. 3b, the TC-5-P sensor has a significantly higher and more stable response value with good recovery performance compared to the PANI sensor. In Fig. 3c, the TC-5-P sensor has a response time of 108 s and a recovery time of 1674 s for 100 ppm NH_3 , which is consistent with previous reports [11]. At the NH_3 concentration of 10–500 ppm, the function fitting between the response value Y of TC-5-P sensor and the gas concentration X is $Y = 1.94X - 79.81$, and the correlation coefficient R^2 is 0.9849, showing a good correlation coefficient (Fig. 3d). The TC-5-P sensor was placed in NH_3 (100 ppm), N_2 (pure), O_2 (pure), H_2O (60 % RH), CO (100 ppm), Ar (pure) and $\text{C}_2\text{H}_5\text{OH}$ (100 ppm) to investigate the sensor selectivity. The results showed that the selectivity of the TC-5-P sensor for NH_3 was superior to the other interfering gases (Fig. 3e). Fig. 3f shows that the relative standard deviation (RSD) of the TC-5-P sensor was only 6.03 % for seven repetitions, indicating good reproducibility of the sensor.

The NH_3 sensing mechanism originates from the deprotonation process of acid-doped PANI. In Fig. 4, when PANI is exposed to NH_3 , the NH_3 traps protons in PANI to form NH_4^+ , leading to deprotonation of the PANI chain. This causes the PANI doping concentration to decrease and the resistance to increase [12]. When the PANI is placed in air, the NH_4^+ can be broken down into NH_3 and protons, protonating the PANI again and restoring its resistance. In TC-P material, TC-P molecules are combined through interactions such as strong electrostatic attraction to form a larger π - π conjugated system [13]. When NH_3 reaches the polymer surface, TAPPCo acts as an interaction centre between PANI and NH_3 , transferring electrons into the PANI molecular chain through the conjugation system [5]. This interaction centre transfer is more efficient compared to the direct contact between NH_3 and PANI. Thus the TC-P

sensor demonstrates superior performance in all aspects.

4. Conclusions

In summary, the TC-P NH_3 sensor was prepared by drop-coating deposition method on the PET-based interdigital electrode. The TC-P sensor's fast and efficient detection of NH_3 is due to the fact that TAPPCo transfers electrons to the PANI molecular chain through the conjugated system and accelerates their movement. The results showed that the TC-5-P sensor showed the highest response to NH_3 with a response time of 108 s and a recovery time of 1674 s. In addition, the TC-5-P sensor was approximately linear at NH_3 concentrations of 50–500 ppm, with good cyclic stability, excellent selectivity and reproducibility. Therefore, TC-P can be used as an effective and stable NH_3 sensing material.

CRediT authorship contribution statement

Tong Lin: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Huimin Liang:** Supervision, Methodology. **Jianzhong Li:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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