

High-Performance Ammonia Sensing Electrode Based on a Graphene/Porphyrin–Polyaniline Nanocomposite Material

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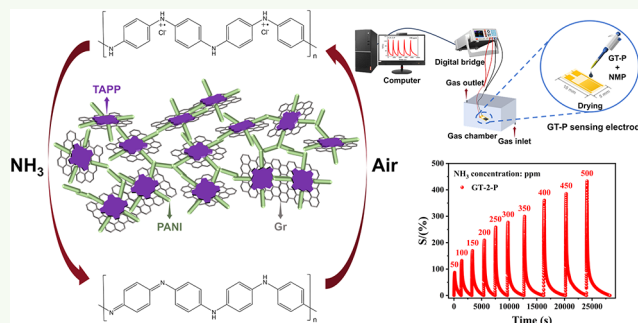
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ABSTRACT: In view of the hazards and special use value of ammonia (NH_3), the development of various types of sensors sensitive to NH_3 is one of the hot spots in today's research. Although the conductive polymer polyaniline (PANI) can detect NH_3 at room temperature, it suffers from a series of drawbacks such as low response value, poor selectivity, and long response time. In this study, a graphene/tetraaminophenylporphyrin-PANI (Gr/TAPP-PANI) nanocomposite (GT-P) was prepared by chemical synthesis, and a GT-P NH_3 sensing electrode was constructed by drop-casting deposition. The NH_3 sensing performance of the GT-P sensing electrode was significantly enhanced by optimizing the mass ratio of TAPP to Gr (2:1). At room temperature, the GT-P sensing electrode showed good response to NH_3 with a lower detection limit of 1.99 ppm, high selectivity, and excellent sensing stability. Gr accelerates the electron transfer while π – π stacking with TAPP exposes a larger active center area of TAPP, resulting in the excellent ammonia-sensitive performance of the GT-P sensing electrode. This study provides a strategy for the development of high-performance flexible NH_3 sensors, which has broad application prospects in the fields of environmental monitoring and wearable electronics.

KEYWORDS: ammonia sensing, porphyrin, graphene, polyaniline, sensing electrodes



1. INTRODUCTION

In recent years, industrial development has made great contributions to society, but accompanying air pollution has become one of the most serious environmental problems. Toxic gases, as the main cause of air pollution, pose a great threat to human life. Ammonia (NH_3), as an important industrial raw material and environmental pollution gas, is widely found in chemical production, agricultural farming, and the atmosphere.¹ Once the human body is exposed to high concentrations of NH_3 , it can cause a range of lung-related diseases. According to the United States Occupational Safety and Health Administration (OSHA), prolonged exposure to NH_3 at concentrations of 25 ppm or higher can lead to respiratory illness and even death.² High NH_3 concentration in livestock and poultry houses not only affects the growth of livestock and poultry but also reduces their resistance and induces various diseases. In the field of food packaging, due to the protein in the spoilage that will produce NH_3 , the freshness of high-protein meat in the bag can be used to monitor the NH_3 sensor in real time and can provide a more accurate and intuitive understanding of the freshness of meat food. Its high toxicity, corrosiveness, and potential threat to ecosystems make the development of efficient and sensitive NH_3 sensing

technologies an urgent need in the field of environmental monitoring, food safety, and industrial safety.

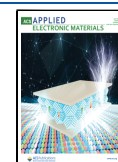
Conductive polymers are good alternative materials for room-temperature gas sensors, as the conductivity of the material changes when exposed to oxidizing or reducing gas molecules at room temperature. When interacting with gas molecules, the carrier concentration of the conductive polymer material changes, causing a change in conductivity and enabling the detection of the target gas. Currently, room-temperature gas sensors based on conducting polymers such as polyaniline (PANI),³ polypyrrole,^{4,5} and polythiophene^{6,7} have become a hot research topic. In recent years, PANI has attracted much attention due to its room temperature response, reversible protonation/deprotonation properties, and ease of modification. However, pure PANI still faces the problems of low conductivity, long recovery time, and low sensitivity, which limit its practical applications.

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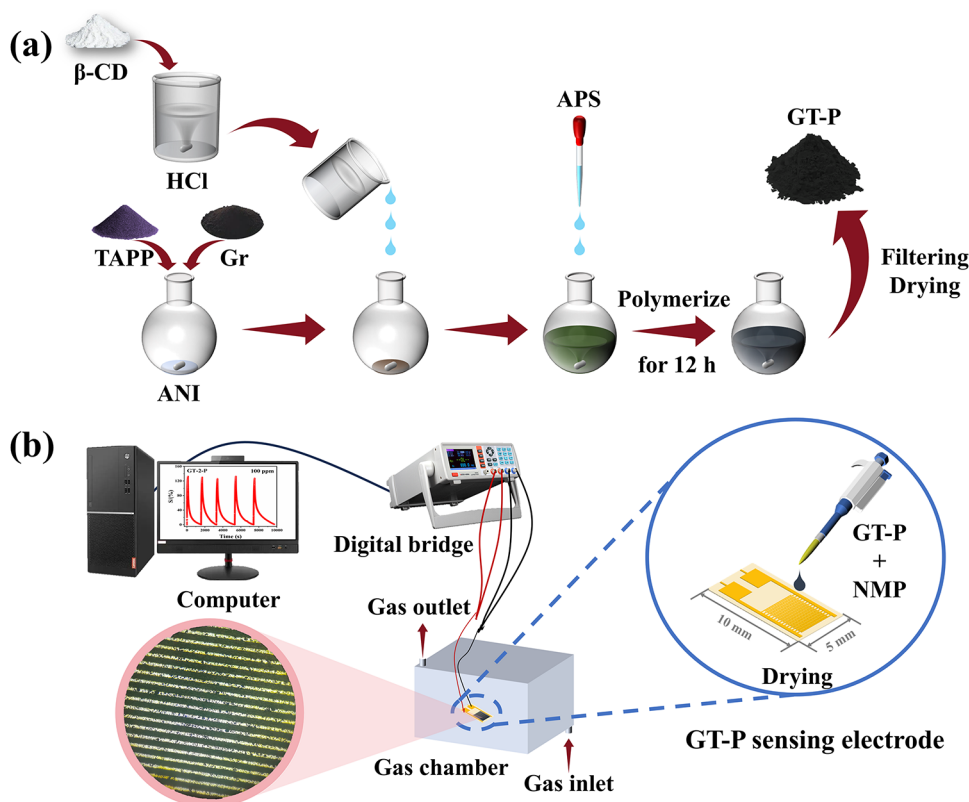


Figure 1. (a) Preparation process of GT-P composites. (b) Schematic diagram of the gas sensing test system.

Porphyrins are aromatic macrocyclic compounds that are obtained when the hydrogen atoms outside of the porphyrin ring are replaced by a different substituent group. Since the 20 carbon atoms in the porphyrin ring are basically in the same plane, they form a π - π conjugate structure. Such a rigid conjugated planar structure not only endows the porphyrin compounds with strong molecular recognition ability but also has outstanding photoelectric properties, which facilitates the rapid charge transfer between porphyrin and NH_3 molecules.⁸ Therefore, the introduction of porphyrin may enhance the NH_3 sensing performance of PANI. In recent years, graphene (Gr), as an emerging material, not only possesses a large specific surface area and high mechanical strength but also attracts the attention of researchers with its unique electronic structure, energy band structure, and excellent charge transport ability.^{9–11} For example, amine-functionalized¹² and N-doped^{13,14} Gr has been actively studied and applied in the field of gas sensing, especially for NH_3 . If Gr is combined with PANI, Gr provides a matrix for the growth of PANI and increases the specific surface area of the composite. Meanwhile, due to the π - π electronic interactions and the possible existence of overlapping π -electron clouds, a conjugated system is formed between Gr and PANI, which can significantly enhance the electron transfer rate.¹⁵

To overcome the bottleneck of pure PANI in NH_3 sensing, composite material design becomes a key strategy to enhance the sensing performance.^{16,17} In this work, a composite material, GT-P, was obtained by combining porphyrin, Gr, and PANI and prepared as a sensing electrode. The polymer GT-P was characterized and a series of tests were performed on the GT-P sensing electrode to assess its ammonia-sensitive properties. The NH_3 sensing mechanism of the GT-P sensing electrode is discussed in detail.

2. EXPERIMENTAL SECTION

2.1. Materials. Few-layer graphene (Gr) was purchased from Suzhou Tanfeng Technology Co. 5,10,15,20-Tetrakis (4-aminophenyl) porphyrin (TAPP) was synthesized following a literature procedure.¹⁸ Aniline (ANI) was purchased from Tianjin Damao Chemical Reagent Factory and distilled under reduced pressure at 80 °C before use. β -Cyclodextrin (β -CD) was supplied by Tianjin BASF Chemical Co. Hydrochloric acid (HCl) and ethanol were purchased from Beijing Chemical Reagents. Ammonium persulfate (APS) was supplied by Sinopharm Chemical Reagent Co. *N*-methylpyrrolidone (NMP) was supplied by Tianjin Opusheng Chemical Co. NH_3 standard gas cylinders were purchased from local chemical agents. All reagents were analytically pure.

2.2. Preparation of the Gr/TAPP-PANI Composite. Gr/TAPP-PANI (GT-P) was prepared by chemical synthesis. 0.05 g of TAPP and an amount of Gr were dissolved in 1 g of redistilled aniline. A homogeneous mixture was obtained after being continuously stirred for 10 min. The mixture was added dropwise to 100 mL of HCl (1 mol/L) containing 1 g of β -CD. After the mixture was stirred, an aqueous solution containing 2.448 g of APS was added dropwise to the mixture. It was polymerized for 12 h. The solid precipitate was filtered at the end of the reaction and washed with distilled water and ethanol, respectively. The filter cake was placed in a vacuum oven and dried at 60 °C under vacuum to obtain the composite GT-P. The mass of Gr was adjusted to 0.005, 0.025, 0.05, 0.1, and 0.5 g so that the mass ratio of TAPP to Gr was 10:1, 2:1, 1:1, 1:2, and 1:10, respectively. The samples obtained were named GT-1-P, GT-2-P, GT-3-P, GT-4-P, and GT-5-P. For comparison, pure PANI was also synthesized according to the same method without the addition of TAPP and Gr. The PANI with the addition of only TAPP or Gr was named T-P or G-P, respectively.

2.3. Preparation of the GT-P Sensing Electrode. The GT-P NH_3 sensing electrode was prepared by the drop cast deposition method. 5 mg of GT-P was dissolved in 1 mL of NMP and sonicated for 10 min to form a homogeneous mixture. 10 μL of GT-P dispersion droplets were sucked by a pipette and coated on a flexible interdigital

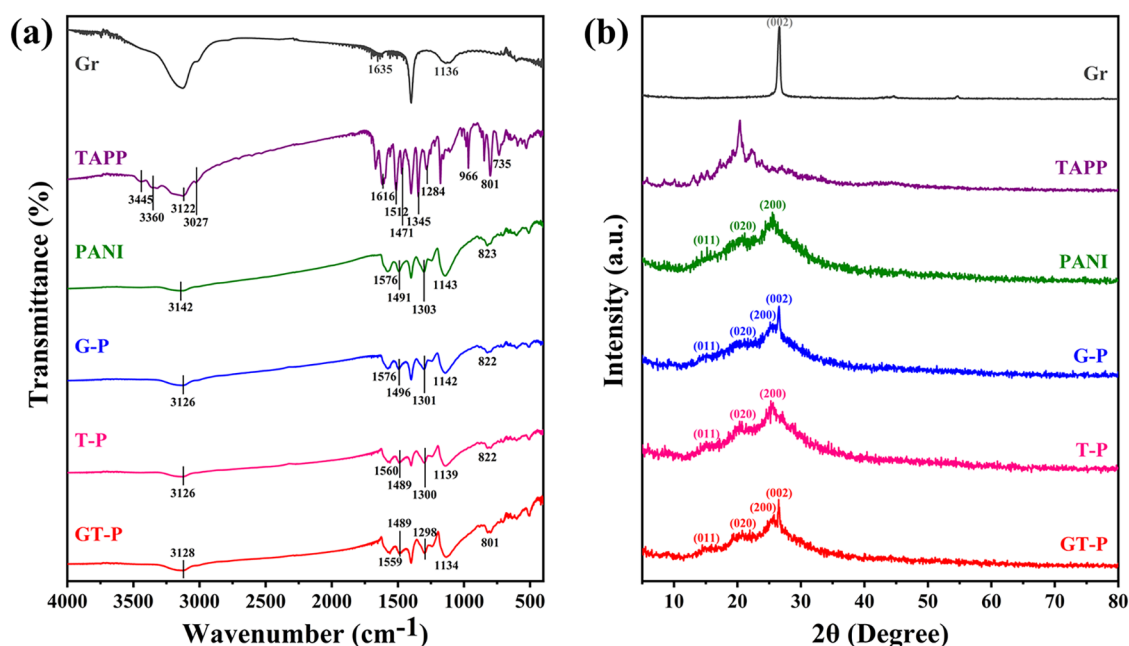


Figure 2. (a) FTIR spectra of Gr, TAPP, PANI, G-P, T-P, and GT-P composites. (b) XRD spectra of Gr, TAPP, PANI, G-P, T-P, and GT-P composites.

electrode on a PET substrate with the size of $10 \times 5 \times 0.5 \text{ mm}^3$ and dried at 60°C under vacuum to obtain the sensing electrode. The interdigital spacing of the electrodes is $50 \mu\text{m}$. The PANI sensing electrode, the T-P sensing electrode and the G-P sensing electrode were prepared by the same method. The interdigital electrodes were supplied by Suzhou Jutao Sensing Technology Co.

2.4. Characterization. The microstructure and morphology of the samples were characterized by a Nicolet iS10 Fourier transform infrared spectrometer (FTIR), TD-3700 X-ray diffractometer (XRD), an HT7700 transmission electron microscope (TEM), and a JSM-7500F scanning electron microscope (SEM). The FTIR test was performed by measuring the transmittance using the potassium bromide press method. XRD was performed using Cu K α radiation with a voltage of 30 kV, a current of 20 mA, and a step size of 0.05° . The accelerating voltage of TEM was 80 kV with a resolution of 0.2 nm. SEM was accelerated at 5.0 kV with a resolution of 1.0 (15 kV)/1.4 nm (1 kV). The chemical elemental composition of the samples was evaluated by energy-dispersive spectroscopy (EDS). The specific surface area and pore size distribution of the samples were determined using the N22–27E high-speed automated specific surface and a porosity analyzer (BET). The change in resistance of the sensing electrodes was detected by using a benchtop digital bridge (4091C, Victory Instruments).

2.5. Gas-Sensing Measurement. The gas-sensing performance of the sensing electrode was tested by placing it in a 17.5 L sealed chamber. Different concentrations of the target gas were introduced into the sealed chamber, and the resistance (R) of the sensing electrode was measured in real time by a benchtop digital bridge. The gases used for the test were made of pure target gas or target gas mixed with fresh air in a certain ratio. The relative humidity (RH) was adjusted in the range of 25 to 80%, and the effect of RH on the sensing performance of the sensing electrodes was investigated at room temperature (25°C). Meanwhile, the other tests of the gas sensitivity experiments were conducted at room temperature (25°C) and $25 \pm 3\%$ RH. The response value (S) is given by eq 1.¹

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

where R is the resistance of the sensing electrode in the target gas atmosphere and R_0 is the stable initial resistance of the sensing electrode after 12 h of placement in the air environment. The lower limit of detection (LOD) is given by eq 2.¹⁹

$$\text{LOD} = 3\sigma/s \quad (2)$$

where σ is the relative standard deviation of the detection digital bridge and s is the slope of the standard curve. In addition, the response time and recovery time were defined as 90% of the time required for the total resistance value to change when the sensing electrode was placed in the target gas and a fresh air atmosphere.

3. RESULTS AND DISCUSSION

In order to fabricate sensing electrodes with excellent sensing performance for NH_3 , a series of nanocomposite materials, GT-Ps, were designed and successfully prepared by chemical synthesis. Figure 1a shows a schematic of the synthesis route of the GT-P material. The GT-P composite material was prepared into a GT-P sensing electrode according to the experimental part of the method. As shown in Figure 1b, the resistance change of the GT-P sensing electrode in the gas chamber was detected in real time using a digital bridge by passing different concentrations of the target gas into the gas chamber. The sensing performance of the GT-P sensing electrode was detected by the response value reflected by the resistance change.

3.1. Characterization of Sensing Composites. Figure 2a shows the FTIR transmission spectra of Gr, TAPP, PANI, and GT-P composites. The characteristic bands of PANI are the stretching vibrations of two N atoms adjacent to the benzene ring (1491 cm^{-1}) and the stretching vibration of two N atoms adjacent to the quinone ring (1576 cm^{-1}).²⁰ The band at 1303 cm^{-1} corresponds to the C–N stretching vibration of the benzene ring.²¹ The bands at 1143 and 823 cm^{-1} are attributed to the bending vibration in the C–H plane and the bending vibration outside the C–H plane in the aromatic ring, respectively.²² For TAPP, the characteristic bands of the amino N–H stretching vibration appear at 3445 and 3360 cm^{-1} .²³ The characteristic bands of the benzene ring C–H stretching vibration appeared at 3122 and 3027 cm^{-1} . Characteristic bands of stretching vibrations of the aromatic ring carbon skeleton appear at 1616 , 1512 , and 1471 cm^{-1} .

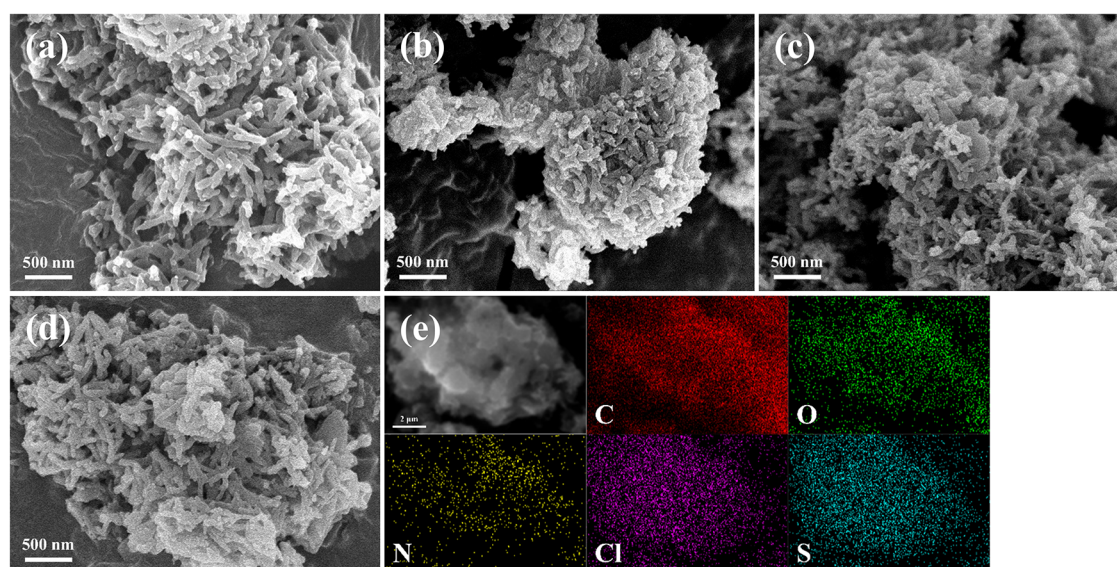


Figure 3. SEM images of (a) PANI, (b) T-P, (c) G-P, and (d) GT-P. (e) Elemental mapping of GT-P.

The characteristic band at 1345 cm^{-1} corresponds to the C–N stretching vibration on the porphyrin ring. The characteristic band of the C–N expansion vibration appeared at 1284 cm^{-1} . The characteristic band of N–H vibrational absorption in the pyrrole ring is represented at 966 cm^{-1} .²⁴ The characteristic bands of the C–H bending vibration on the benzene ring appeared at 801 and 735 cm^{-1} . In the infrared spectral spectrum of Gr, we can see an infrared absorption band at 1635 cm^{-1} , which is attributed to the C=C stretching vibration in the sp^2 structure. The bands at 1136 cm^{-1} are related to the C–C single bond stretching vibrations in Gr.²⁵ In GT-P composites, five vibrational bands belonging to PANI can be observed at 1559 , 1489 , 1298 , 1134 , and 801 cm^{-1} . These bands show a bathochromic shift under the influence of both TAPP and Gr compared to pure PANI. The red shift indicates the formation of stronger π – π conjugation between Gr and T-P, accelerating electron transfer from NH_3 to the conducting network. These may affect the strength of the gas molecule–material interaction, which in turn enhances the response value of GT-P composites. These shifts are also observed in the spectra of G-P and T-P composites. This phenomenon proves that GT-P composites have been successfully prepared.

The crystal structures of Gr, TAPP, PANI, and GT-P were characterized by X-ray diffraction (XRD), as shown in Figure 2b. For pure PANI, the three diffraction peaks at 15.1 , 20.8 , and 25.6° of the X-ray diffraction pattern correspond to the repeating units of the PANI chain, i.e., the periodic units perpendicular to the polymer backbone and the periodic units parallel to the polymer backbone.²⁶ These three diffraction peaks correspond to the (011), (020), and (200) planes of pure PANI, respectively.²⁷ The XRD spectra showed that the peak positions of TAPP were 20.4 , 22.3 , and 43.16° , respectively. This is consistent with the fact that porphyrins usually show amorphous peaks.²⁸ The diffraction spectrum of Gr has a very distinct diffraction peak at $2\theta = 26.6^\circ$, corresponding to the crystalline surface of the carbon material (002), and a weaker characteristic peak exists at $2\theta = 54.8^\circ$, indicating that the spatial structure of the Gr lamellae is very neatly arranged. This phenomenon is consistent with reports in the literature.²⁹ The XRD spectra of the GT-P composites

show that the characteristic diffraction peaks belonging to both PANI and Gr are present, and the diffraction peak belonging to TAPP is shifted from $2\theta = 43.16$ to 44.1° , which indicates that TAPP is not simply physically comingled with PANI and Gr, but rather, it interacts with them.³⁰ These phenomena were further confirmed in the G-P and T-P composites.

PANI, T-P, G-P, and GT-P were prepared by the experimental part of the method. The surface morphology of PANI, T-P, G-P, and GT-P were observed using SEM, as shown in Figure 3. In Figure 3a, we can see that pure PANI exhibits a nanorod-like structure, with nanorods having a diameter of about 50 – 100 nm and a length of about 300 – 500 nm . The nanorods are distributed as a disordered cross-linked network. The nanorods are stacked with each other without obvious agglomeration, and some pores exist. The introduction of TAPP led to a change in the surface morphology of PANI, as shown in Figure 3b. Due to J-aggregation of π -electrons, TAPP aggregates in T-P to form bulk particles.³¹ Compared with pure PANI, the nanorod structure of T-P was significantly coarsened, with lamellar coverings appearing on the surface, rod-like stacking forming in some regions, and significantly reduced porosity. As is known, Gr is a two-dimensional material with a lamellar structure. In Figure 3c, it can be clearly seen that PANI appears on the surface of the lamellar structure of the two-dimensional Gr through in situ polymerization. In the G-P composite, the lamellae of Gr are clearly visible, with PANI nanorods uniformly dispersed on the surface. The morphology of the GT-P composites is shown in Figure 3d. The composite has the advantages of T-P and G-P with significant morphology synergy. The lamellae of Gr are loaded with T-P nanoparticles to form a 3D porous network. This three-dimensional porous structure may provide a larger specific surface area and more gas adsorption sites, thus potentially enhancing the composite response value.³² Gr provides a 2D carrier to play a supportive role for the nanoparticles, which alleviates the aggregation of the particles of T-P into clumped particles. GT-P composites are looser than T-P composites, which facilitates the application of nanocomposites in gas sensors. In order to determine the elemental distribution on the surface of the GT-P composite, it was characterized using EDS, which is presented in Figure 3e.

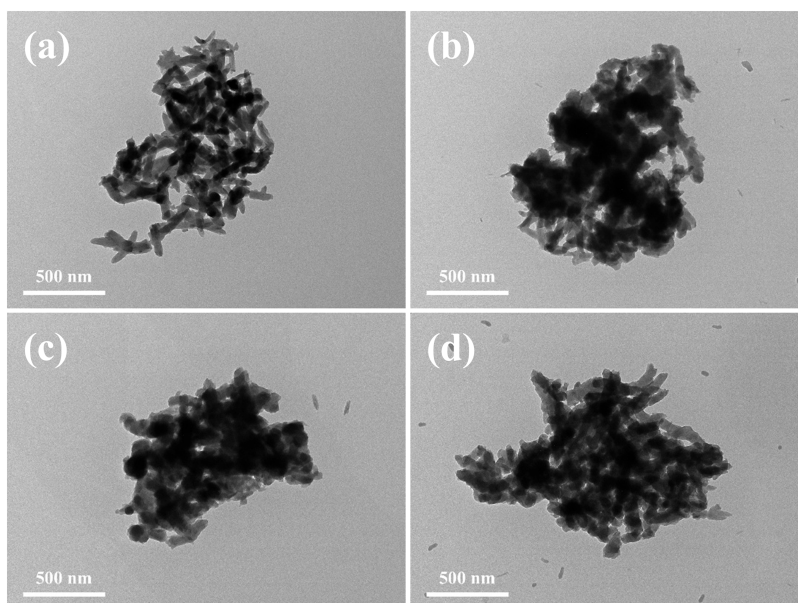


Figure 4. TEM images of (a) PANI, (b) T-P, (c) G-P, and (d) GT-P.

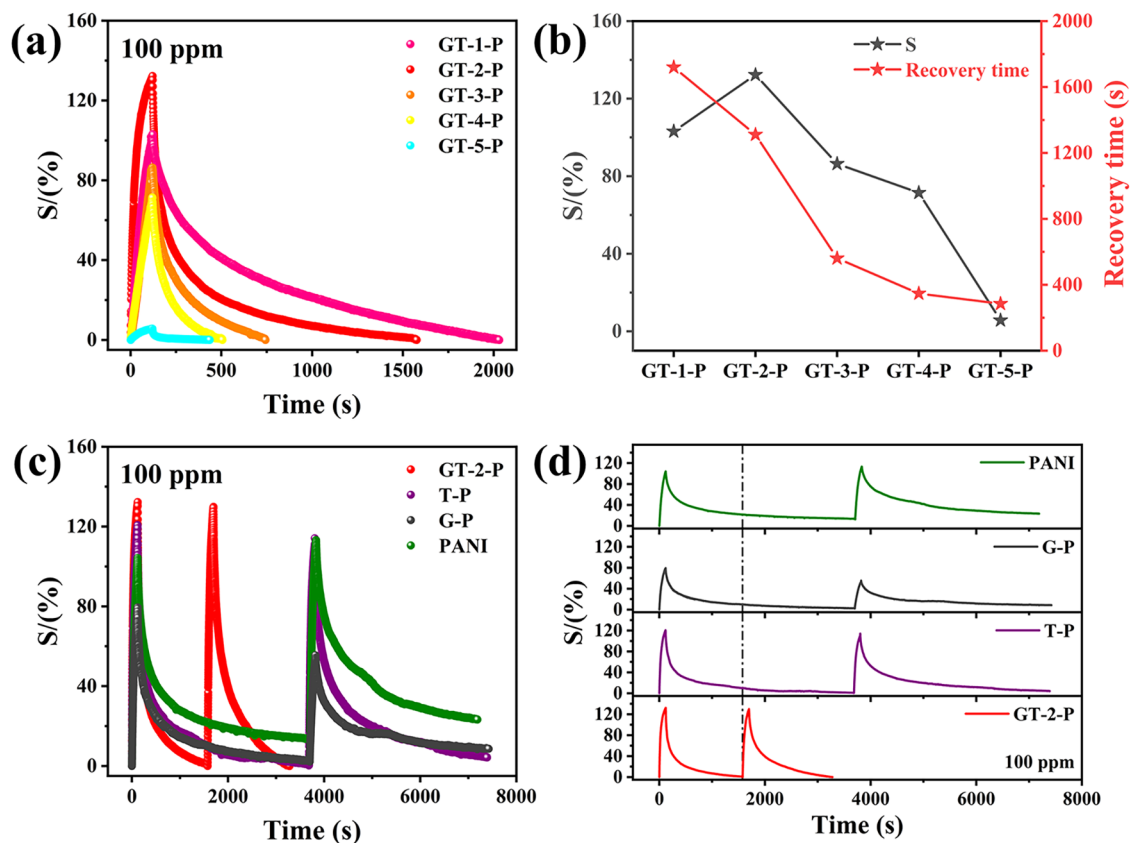


Figure 5. (a) Dynamic response–recovery curves of GT-1-P, GT-2-P, GT-3-P, GT-4-P, and GT-5-P sensing electrodes to 100 ppm of NH_3 . (b) Comparison of response values and recovery time of GT-1-P, GT-2-P, GT-3-P, GT-4-P, and GT-5-P sensing electrodes to 100 ppm of NH_3 . (c) Dynamic response–recovery curves of GT-2-P, T-P, G-P, and PANI sensing electrodes to 100 ppm of NH_3 . (d) Dynamic response–recovery curves of GT-2-P, T-P, G-P, and PANI sensing electrodes to 100 ppm of NH_3 .

The EDS image shows that the surface of the GT-P composite contains elements such as C, O, N, Cl, and S with uniform distribution.

The morphology of PANI, T-P, G-P, and GT-P was further observed by TEM, and the results are shown in Figure 4. In Figure 4a, pure PANI presents a typical nanorod-like structure,

forming a cross-linked network. The surface of the nanorods is relatively smooth without obvious impurities or coverings, and there are inhomogeneous pores between the nanorods. The T-P composites (Figure 4b) show an overall clustered state. Cluster-like structures were attached to the surface of the PANI nanorods, and the nanorod pores were filled but still

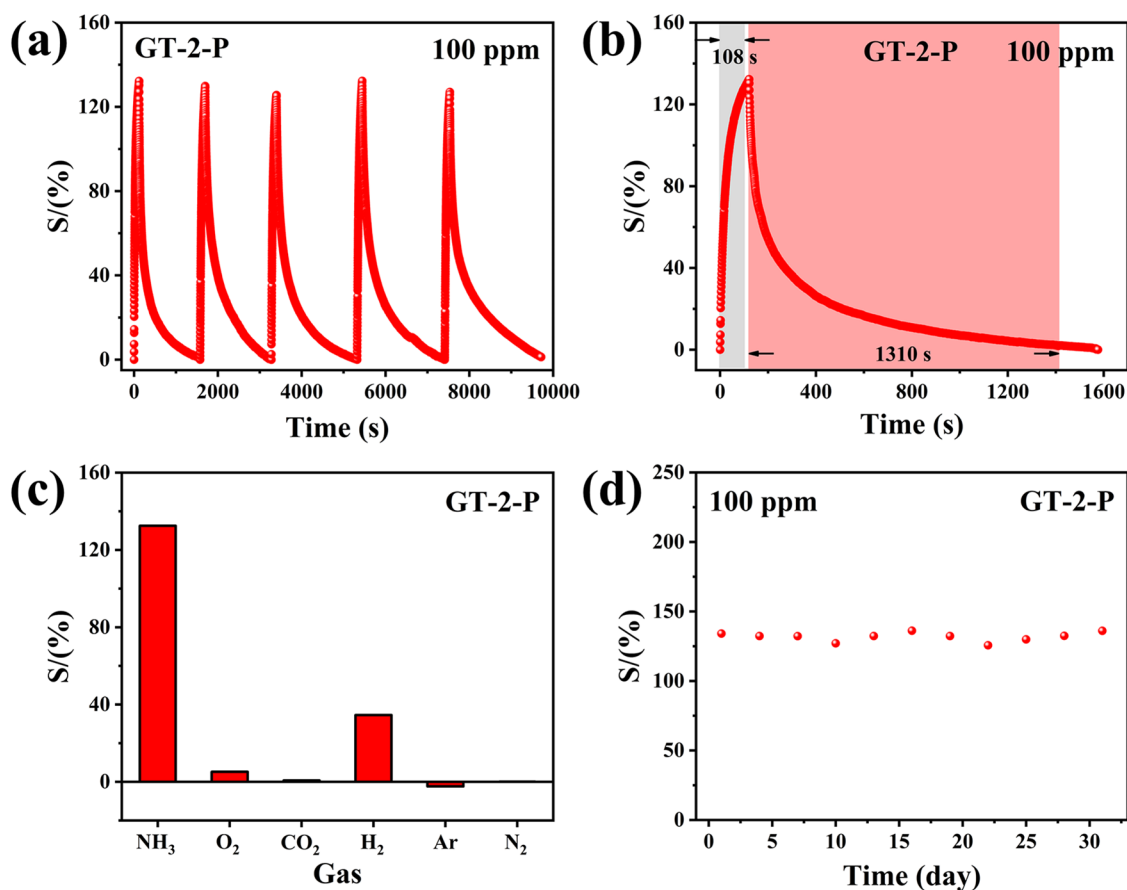


Figure 6. (a) Cyclic response–recovery curve of GT-2-P sensing electrode for 100 ppm of NH_3 . (b) Dynamic response–recovery curve of GT-2-P sensing electrode for 100 ppm of NH_3 . (c) Comparison of response values of the GT-2-P sensing electrode to different gases. (d) Long-term stability of the GT-2-P sensing electrode to 100 ppm of NH_3 .

retained a continuous network framework. As can be seen from Figure 4c, there is a Gr lamellar layer in the G-P complex without large agglomerations and tight interfacial bonding. The TEM images of the GT-P composites are shown in Figure 4d, where the agglomeration phenomenon is improved and the components are uniformly distributed to form a three-dimensional multistage pore structure.

3.2. Sensing Performance of the GT-P Sensing Electrode. In order to investigate the effect of different mass ratios between TAPP and Gr on the sensing performance, the prepared GT-1-P, GT-2-P, GT-3-P, GT-4-P, and GT-5-P sensing electrodes were placed in an environment of 100 ppm of NH_3 for 120 s, and then fresh air was passed in to detect the change of resistance of the sensing electrodes. The dynamic response–recovery curves for the five groups of sensing electrodes are shown in Figure 5a, and the response values versus recovery times are shown in Figure 5b. It can be seen that GT-2-P has the highest response value of 132.32%. However, with the continuing increase in the weight of Gr, the response value does not continue to increase but shows a continuous decrease. The increase in the ratio of Gr enhances the electrical conductivity, speeds up the recovery, and reduces the recovery time. GT-2-P (TAPP/Gr = 2:1) achieves an optimal balance between the response value and the recovery time with the best overall performance. GT-2-P was chosen to explore the gas-sensitive properties to NH_3 in the subsequent experiments.

The initial resistances of GT-2-P, T-P, G-P, and PANI sensing electrodes were 1.9, 11.0, 4.4, and 23.3 k Ω , respectively. Gr, as a highly conductive material, was added to significantly reduce the initial resistance of the composites. In particular, the GT-2-P composites, with Gr forming a continuous conductive path in the three-dimensional porous network, had the lowest initial resistance. All of the sensing electrodes were placed in an environment of 100 ppm of NH_3 for 120 s. Their dynamic response–recovery curves are shown in Figure 5c,d. Pure PANI sensing electrodes are difficult to restore to their original resistance value after removal from the NH_3 atmosphere. As the number of tests increases, the resistance becomes larger and less stable. The stability of the G-P sensing electrode was improved after the addition of Gr, but the response value was significantly reduced. Compared with the pure PANI sensing electrode, the response value of the T-P sensing electrode was significantly improved, but the recovery time was still long. When the time was 1576 s, the response values of PANI, G-P, and T-P recovered to 21.70, 10.03, and 9.96%, respectively. However, GT-2-P has completed a response–recovery cycle, where the resistance returns to its initial value and the response value decreases to zero. GT-2-P ensured the improvement of the response value while accelerating the recovery speed, and the recovery time was significantly reduced, which was significantly better than those of T-P and G-P. Pure PANI has poor electrical conductivity, limited active sites, and an underdeveloped pore structure, leading to low response values and long

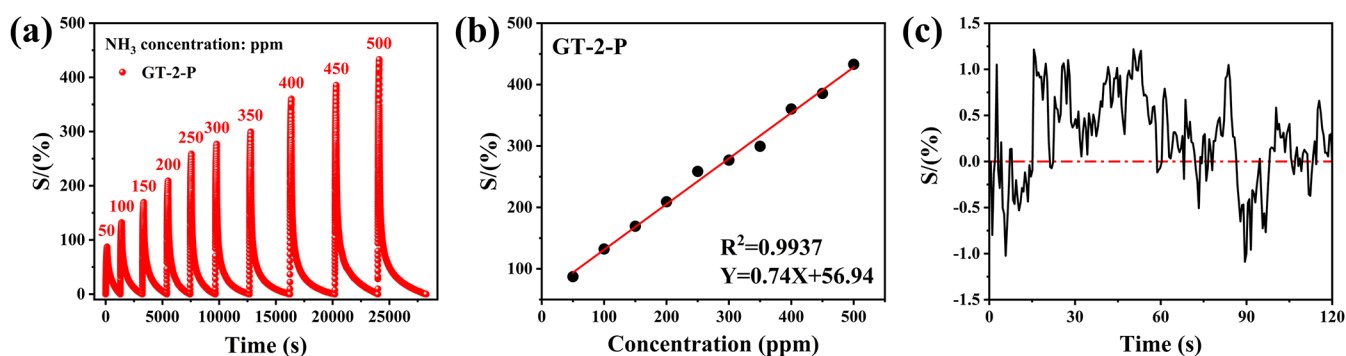


Figure 7. (a) Dynamic response–recovery curve of GT-2-P sensing electrode for 50–500 ppm of NH₃. (b) Linear relationship between response value and concentration of GT-2-P sensing electrode to 50–500 ppm of NH₃. (c) GT-2-P sensing electrode exposed to air atmosphere to test the electronic noise of digital bridge.

recovery times. For G-P composites, Gr improves the electrical conductivity and accelerates the electron transport, thus shortening the recovery time. However, the lack of TAPP active sites leads to insufficient adsorption capacity for NH₃ and low response values. The situation with T-P is exactly the opposite. TAPP provides more active sites, but due to the lack of Gr's conductive network, charge transport is slower, leading to prolonged recovery times. In the GT-2-P complex, TAPP provides the active center to enhance NH₃ adsorption, and Gr constructs a fast electron transport channel to provide conductive network support.³³ The two synergistically enhanced the response value and recovery speed of the PANI sensing electrode, which significantly improved the NH₃ sensing performance. In addition, the three-dimensional porous structure formed by the composite of TAPP, Gr, and PANI may have improved the gas diffusion efficiency.

In order to assess the value of the GT-2-P sensing electrode for practical applications, the sensing electrode was tested for reproducibility, response–recovery time, gas selectivity, and long-term stability. Figure 6a shows the dynamic response–recovery curve of the GT-2-P sensing electrode, which was exposed to 100 ppm of NH₃ for 120 s and then recovered by passing fresh air. The above process was repeated five times. The aim was to examine the recycling of the fabricated GT-2-P sensing electrode under the same concentration of NH₃. In Figure 6a, the GT-2-P sensing electrode shows a good response to 100 ppm of NH₃ with stable response values after five cycles. The response values corresponding to the five cycles were 132.3, 129.9, 125.6, 132.3, and 127.1%, respectively, with a relative standard deviation (RSD) of only 2.34%. Importantly, the resistance of the GT-2-P sensing electrode can be restored to the initial value when fresh air is passed in, indicating good recovery performance. The above test confirms that the GT-2-P sensing electrode has good reproducibility and can be recycled many times in the actual testing process.

Figure 6b shows the dynamic response–recovery curve of the GT-2-P sensing electrode to NH₃ (100 ppm) at room temperature. The response of the sensing electrode grows to 132.3% after 120 s of NH₃, with a response time of 108 s. When fresh air is introduced, the resistance decreases rapidly and then slows to return to the original level, corresponding to a recovery time of 1310 s.

Some gases, including O₂, CO₂, H₂, Ar, and N₂ with 99.99% purity, were chosen as interference gases to investigate the selectivity of the GT-2-P sensing electrode for NH₃ (100

ppm). The same GT-2-P sensing electrode was exposed to different types of gases for 120 s. The results of the response values are shown in Figure 6c. The GT-2-P sensing electrode showed poor response to O₂, CO₂, Ar, and N₂, with corresponding S-values of 5.21, 0.71, −2.32, and 0.13%, respectively. The GT-2-P sensing electrode showed a slightly higher response value of 34.59% for H₂. This is due to the supply of electrons by the H₂ molecule, which reduces the oxidation state of PANI and decreases the conductivity. In contrast, the GT-2-P sensing electrode was very responsive to NH₃ (100 ppm) with an S-value as high as 132.5%. The above results indicate that the GT-2-P sensing electrode has excellent selectivity for low concentrations of NH₃ at room temperature.

The prepared GT-2-P sensing electrode was stored at room temperature and tested for its response to 100 ppm of NH₃ every 2 days to assess the long-term stability of the sensing electrode. In Figure 6d, it can be seen that the sensing electrode maintains a stable response value within 30 days and has good storage stability. From the perspective of facilitating long-term storage, the sensing electrode has great potential for application.

The GT-2-P sensing electrode was exposed to different concentrations of NH₃ for 120 s, and then fresh air was introduced to recover the resistance. The dynamic response–recovery curves of the GT-2-P sensing electrode to 50–500 ppm of NH₃ at room temperature are shown in Figure 7a. The GT-2-P sensing electrode response values are different for different concentrations of NH₃, and the response values gradually increase as the NH₃ concentration grows. The response values of the GT-2-P sensing electrode were fitted to the NH₃ concentration (Figure 7b), and it was found that the response values show a good linear correlation with the NH₃ concentration in the range of 50–500 ppm. The GT-2-P sensing electrode's response value Y as a function of gas concentration X can be fitted as $Y = 0.74X + 56.94$. The correlation coefficient R^2 is 0.9937. The GT-2-P sensing electrode was placed in an air environment, and the dynamic response curve of the sensing electrode for 120 s was tested after its resistance was stabilized. The electronic noise of the digital bridge was tested, and the results are shown in Figure 7c. The relative deviation (σ) was calculated to be about 0.49, the slope of the standard curve was 0.74, and the lowest limit of detection (LOD) of the GT-2-P sensing electrode was calculated to be 1.99 ppm, according to eq 2. The GT-2-P sensing electrode was able to respond to the concentration of 1.99 ppm of NH₃ at room temperature.

The sensing performance of the prepared GT-2-P sensing electrode is compared to some recent reports on PANI-based NH_3 sensors in Table 1. Overall, the GT-2-P sensing electrode

Table 1. Comparison of the Sensing Performance of This Study and Other PANI-Based NH_3 Sensors

materials	detection range	response	detection limit	refs
PAWHs10	0.5–100 ppm	25% (100 ppm)	1.67 ppb	22
PANI/PVDF	0.1–5 ppm	100.7% (5 ppm)	0.1 ppm	34
PANI-SDS	0.1–40 ppm	5.4% (40 ppm)	0.1 ppm	21
PCT-3	50–500 ppm	114% (500 ppm)	0.83 ppm	35
rGO-PANI	0.05–80 ppm	33% (50 ppb)	50 ppb	36
P-rGO/PANI	20–200 ppm	773% (100 ppm)	1 ppm	37
PANI/BNF	10–200 ppm	28.2% (100 ppm)	10 ppm	38
GT-2-P	50–500 ppm	132.3% (100 ppm)	1.99 ppm	this work

shows obvious advantages in terms of higher response, wider detection range, and competitive LOD value, which meet the need for excellent ammonia-sensitive performance for future NH_3 sensors.

Ambient humidity has a large impact on the performance of conductive polymer-type sensor devices.^{39,40} In order to investigate the effect of RH on the sensing performance of the GT-2-P sensing electrode, the GT-2-P sensing electrodes were placed in NH_3 (100 ppm) environments with different RH values for 120 s, and the responses of the sensing electrodes were tested. As shown in Figure 8a, the response

value of the GT-2-P sensing electrode to NH_3 increases with increasing RH. The reason for this phenomenon may be that the PANI polymer structure contains a large number of iminos ($-\text{NH}-$), which can easily absorb water molecules in the environment (Figure 8b). The NH_3 has a large water solubility and easily combines to produce NH_4^+ and OH^- , and the presence of these ions hinders the transfer of π electrons between the molecular chains of the PANI, leading to an increase in the resistance of the material surface.^{41,42} Further, the response value of the sensing electrode increases with the increase of humidity.

3.3. Sensing Mechanism of the GT-2-P Sensing Electrode. The specific surface area and pore size distribution of PANI, G-P, T-P, and GT-P nanocomposites were determined by the N_2 adsorption–desorption method at 77 K. As shown in Figure 9a, the isotherms of all four samples show the characteristics of having type IV isotherms, which indicates that there are mesoporous structures in the four samples, which belong to mesoporous materials.⁴³ The BET specific surface areas of PANI, G-P, T-P, and GT-P were 238.882, 194.805, 193.958, and 221.971 m^2/g , respectively. Compared with pure PANI, the specific surface area of G-P and T-P was obviously reduced. This may be due to the conjugated interaction of Gr or TAPP, which leads to a tight packing of the material, and reduces the number of pores on PANI. The GT-P nanocomposites still maintained a high specific surface area, indicating that the components, Gr/TAPP-PANI, form a three-dimensional porous network structure for the π – π interaction of Gr and TAPP during the polymerization process. It effectively suppressed the Gr lamellae stacking and TAPP agglomeration and optimized the pore connectivity.

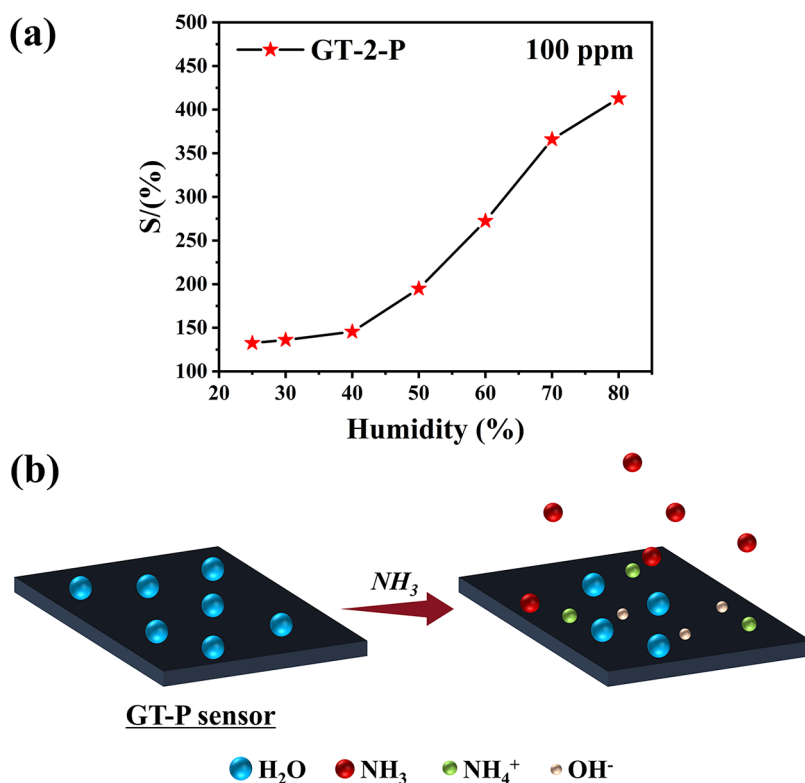


Figure 8. (a) Effect of RH on the gas response value of the GT-2-P sensing electrode. (b) Mechanism diagram of NH_3 sensing by the GT-2-P sensing electrode in a humid environment.

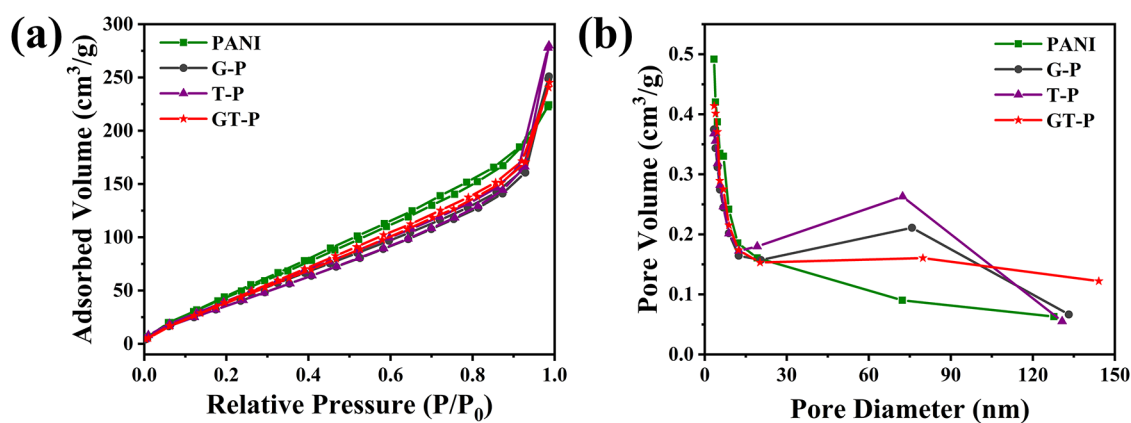


Figure 9. (a) Nitrogen adsorption–desorption isotherms of PANI, G-P, T-P, and GT-P. (b) Pore size distribution of PANI, G-P, T-P, and GT-P.

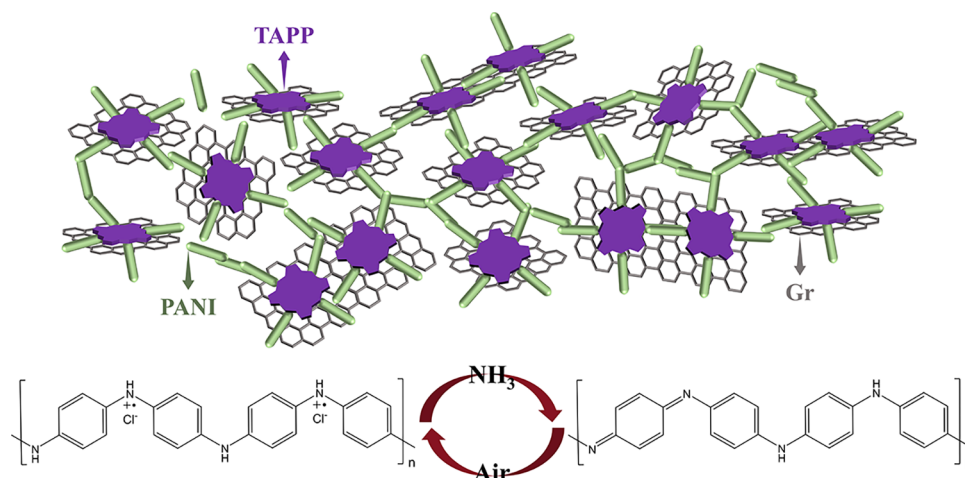


Figure 10. Schematic diagram of the NH₃ sensing mechanism of the GT-2-P sensing electrode.

The BJH pore size distribution curve is shown in Figure 9b, which confirms the mesoporous structure. The pore size distribution of PANI is mainly concentrated in the range of 3–20 nm. The pore size distribution of GT-P is relatively wide, mainly concentrated in the 3–20 nm mesopores, and there are also some narrow slit-shaped macropores formed by layered stacking, which is conducive to the diffusion of NH₃ molecules and the exposure of adsorption sites. Although G-P and T-P composite materials also contain some large pores, the stacking of Gr or TAPP flakes limits the gas diffusion rate. The multistage pore structure of GT-P composites with predominantly mesopores in combination with a small number of macropores synergistically enhances the specific surface area (high adsorption capacity) and the gas diffusion efficiency (fast response), which are the key factors for the superiority of its NH₃ sensing performance over other materials.⁴⁴

The sensing mechanism of the GT-2-P sensing electrode for NH₃ gas is shown in Figure 10, which mainly originates from the protonation/deprotonation process of PANI.⁴⁵ The intrinsic state of PANI exhibits insulating properties.⁴⁶ After doping with protonic acid (H⁺), the original quinone structure of PANI is destroyed, and a π – π conjugated structure is formed within the molecular chain; π electrons can be transferred within and between the molecular chains. When PANI is exposed to NH₃, NH₃ acts as an electron donor to capture the H⁺ in the PANI chain to form ammonium ions (NH₄⁺), resulting in an increase in resistance as PANI

transforms from the conducting emeraldine salt state (ES) to the insulating emeraldine base state (EB).^{47,48} This process is reversible. When NH₃ is desorbed, NH₄⁺ breaks down into NH₃ and H⁺, and proton regeneration restores the resistance.⁴⁹ However, the response–recovery time of the pure PANI sensing electrode is long, and the response value is not high. It may be due to the fact that PANI itself contains π -electrons, which makes the binding and detachment process of NH₃ molecules from the polymer molecules slow.

In the GT-2-P complex, TAPP is connected to PANI through chemical bonds, forming a conjugated network system.^{50,51} TAPP acts as an interaction center for PANI and NH₃, targeting the capture of NH₃ molecules through the coordination of the porphyrin ring. When NH₃ reaches the surface of the complex, this interactive central delivery is particularly efficient compared to direct contact between NH₃ and PANI. As a highly conductive two-dimensional material, Gr provides fast electron transport channels for PANI and shortens the carrier migration path.³⁴ Meanwhile, the p-type semiconductor properties of PANI and Gr are complementary, and a heterojunction-like structure is formed at the interface to enhance the carrier separation efficiency.⁵² Gr reduces the adsorption energy of NH₃ on the Gr surface through hydrogen bonding, which promotes the diffusion of gas molecules and further enhances the sensing performance.

Due to the relatively high electrical conductivity of Gr itself and the fact that Gr acts as a template, the TAPP molecules

form finer-grained microcrystals during the synthesis process. The interaction force between Gr and TAPP is the strongest in the composite system, which is significantly better than the van der Waals force of Gr-Gr and the π - π stacking of TAPP-TAPP. Therefore, Gr and TAPP are more inclined to bind to each other rather than stacking on themselves.⁵³ The formation of a tight π - π stacking between Gr and TAPP gives the complex a significantly improved electrical conductivity.⁵⁴ Due to the introduction of the competitive effect of Gr, the intermolecular force of TAPP decreases, and the molecular stacking decreases. This exposes a larger area of the active center, also known as the porphyrin ring, which accelerates the adsorption and desorption of NH_3 , speeding up the response and recovery and thus significantly reducing the response-recovery time.⁵⁵ This results in the superior sensing performance of GT-2-P compared with one-component PANI and two-component T-P and G-P.

TAPP acts as an anchor point connecting Gr and T-P in GT-P nanocomposites to form a supramolecular system. In addition, the interfacial electronic structure can be optimized between Gr and T-P through interfacial interactions such as π - π conjugation and hydrogen bonding, which promotes the efficient transfer of electrons between T-P and Gr and amplifies the resistance changes. Based on this, we can speculate that the high sensitivity of the GT-2-P sensing electrode may come from the synergistic trapping ability of the introduced TAPP and Gr for NH_3 .⁵⁵ The combination forms a 3D porous network, which provides abundant NH_3 adsorption sites and increases the gas diffusion path to enhance the response rate. This multicomponent synergy^{56,57} enables the GT-2-P sensing electrode to exhibit excellent sensing performance in NH_3 detection, which provides a new idea for the design of new gas sensors.

4. CONCLUSIONS

In this study, Gr/TAPP-PANI composites were prepared by chemical synthesis. The composite material was drop-coated onto an interdigital electrode of a PET substrate by the drop-casting deposition method to obtain a GT-P NH_3 sensing electrode. The results showed that among the composites with different mass ratios of TAPP to Gr, the sensing electrodes obtained from the GT-2-P composites were prepared with the highest response values to NH_3 . Compared to PANI, T-P, and G-P sensing electrodes, the GT-2-P sensing electrode has higher sensitivity and response-recovery speed to NH_3 in a room-temperature environment. The response value of the sensor electrode to 100 ppm of NH_3 is as high as 132.3%, the response time is 108 s, and the recovery time is 1310 s. The excellent ammonia-sensitive properties of GT-2-P are mainly attributed to the significant increase in the electrical conductivity of the complex through π - π stacking between Gr and TAPP, and the introduction of Gr exposes a larger area to the active center of TAPP, which accelerates the response-recovery rate. Meanwhile, the synergistic capture of NH_3 by TAPP and Gr improves the sensitivity of the sensing electrode. The synergistic effect of the three components makes the GT-2-P sensing electrode exhibit an excellent sensing performance in the detection of NH_3 . The GT-2-P sensing electrode showed good linear correlation at NH_3 concentrations of 50–500 ppm with a LOD of 1.99 ppm. The sensing sensitivity of the GT-2-P sensing electrode for NH_3 is relatively stable when the ambient RH is in the range of 25% to 40%. The GT-2-P sensing electrode demonstrated good cycling stability, excellent

selectivity, and long-term stability in NH_3 detection. In this study, Gr and conductive polymer PANI modified with TAPP were composited to obtain GT-P sensing materials with excellent performance, which showed great potential in NH_3 sensing, broke the inherent system of traditional NH_3 sensing materials, and provided a new idea for the preparation of NH_3 sensing materials.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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