

Article

Room-Temperature NH₃ Gas Surface Acoustic Wave (SAW) Sensors Based on Graphene/PPy Composite Films Decorated by Au Nanoparticles with ppb Detection Ability

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Abstract: Exhaled human breath analysis has great potential for the diagnosis of diseases in non-invasive way. The ¹³C-Urea breath test for the diagnosis of *Helicobacter pylori* infection indicates the ammonia concentration of 50–400 ppb in the breath. This work successfully developed a surface acoustic wave (SAW) resonator based on graphene/polypyrrole composite films decorated by gold nanoparticles (AuNPs-G/PPy) with sensitivity and selectivity to detect ammonia in parts-per-billion concentrations, which is promising for the accurate diagnosis of *H. pylori* infection. XRD, EDS, and SEM characterized the AuNPs-G/PPy nanocomposites, providing comprehensive insights into their structural, compositional, and morphological properties. The gas-sensing capabilities of the fabricated SAW sensors were extensively investigated, focusing on their response to NH₃ gas at ambient temperature. The concentration of ammonia gas was effectively quantified by monitoring the frequency shift of the SAW device. Notably, our developed SAW sensor demonstrated outstanding sensitivity, selectivity, repeatability, and reproducibility for 50–1000 ppb NH₃ in dry air. The excellent sensing performance of the AuNPs-G/PPy hybrid composite film can be attributed to the synergistic effects of graphene's superior conductivity, the catalytic properties of gold nanoparticles, and the conductivity sensitization facilitated by electron-hole recombination on the polypyrrole surface.

Keywords: surface acoustic wave; ammonia; AuNPs-G/PPy; sensitivity; selectivity



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1. Introduction

Ammonia is a toxic and corrosive gas, capable of causing varying degrees of harm to humans and industrial settings. Ammonia corrodes pipelines within factories, thereby compromising both workplace safety and product quality. The Occupational Safety and Health Administration (OSHA) in the United States has set the permissible exposure limit for ammonia at 25 ppm for an 8 h period and 35 ppm for a 15 min duration. Inhalation of gas exceeding 500 ppm for 30 continuous minutes adversely affects the central nervous system [1]. The maximum allowable concentration of ammonia gas in both occupational and living environments, as defined by OSHA, is 35 ppm [2]. Prolonged exposure to concentrations of ammonia gas exceeding 50 ppm can result in respiratory and ocular damage, while exposure to concentrations exceeding 5000 ppm can cause sudden fainting or death. Consequently, the presence of gas sensors capable of monitoring low concentrations of ammonia [3] is paramount for ensuring a safe working and living environment, as well as saving lives.

Among various available sensing techniques, such as potential, current, chemical resistance, calorimetry, and optics, the utilization of surface acoustic waves (SAWs) for gas

detection presents distinct advantages due to its rapid response, recovery speed, and the ability to perform wireless sensing in hard-to-reach areas. The origin of SAW technology traces back to 1885, when Lord Rayleigh analyzed the propagation patterns of elastic waves in isotropic materials, which are referred to as Rayleigh waves. However, the primary application of Rayleigh waves was limited to seismic studies until the 1960s due to the lack of suitable and efficient transducers. In 1965, the excitation and reception of SAWs using metal electrodes became feasible after R.M. White and F.W. Voltmer published their findings on the excitation of oscillating electric fields through paired metal electrodes. This led to the creation of interdigital transducers (IDT) and the effective excitation of SAWs by fabricating IDTs on piezoelectric substrates, marking the advancement of SAW research. In the past decade, with the advancements in micro-electromechanical systems (MEMS) technology, SAWs have found widespread application due to their high sensitivity to analytes' physical and chemical changes. The fundamental principle of SAW sensors lies in analyte adsorption on the sensing film, which causes changes to the surface acoustic wave propagation characteristics. With the increasing breadth of sensing applications, SAW sensor design expanded to detect both gases and liquids, such as acoustic plate-mode (APM), Love wave, and surface transverse wave (STW) devices [4–8].

The commonly used sensing materials exhibiting good response to ammonia gas include conductive polymers [9,10], metal oxide semiconductors [11], and composite materials [12,13]. Sensors utilizing semiconductor metal oxide materials typically require higher operating temperatures to exhibit a significant response to the target gas, and they have poorer recovery abilities. In contrast, sensors using conductive polymers operate at room temperature but only exhibit a noticeable response at high analyte concentrations, with longer recovery times. Due to the limitations of individual sensing materials, developing new composite materials as sensing materials has become a trend in recent years. These include composite materials of conductive polymer/metal oxide [14,15], conductive polymer/metal oxide/graphene oxide (GO) [16,17], conductive polymer/graphene (G) [18,19], and conductive polymer/metal oxide/reduced graphene oxide (rGO) [20]. In particular, composites of graphene and traditional sensing materials such as noble metals, metal oxides, and conductive polymers not only retain individual characteristics but also exhibit additional new properties.

Previous findings have shown PPy-conducting polymer films exhibit high sensitivity to NH_3 and excellent signal recovery [12,21]. Graphene is used as a sensing material due to its high specific surface area and unique electrical properties such as high mobility and low noise [22]. Gold nanoparticles have been utilized to modify electrochemical electrodes made from GO or rGO/metal oxide nanocomposites, further enhancing their sensitivity and selectivity towards the target gas [23,24]. Combining PPy, graphene, and gold nanoparticles effectively leverages the unique attributes of each material while mitigating their respective limitations. PPy offers selectivity, graphene provides high surface area and conductivity, and gold nanoparticles contribute to catalytic activity. The synergy of these three materials results in a sensor with improved sensitivity, selectivity, and response speed for NH_3 detection. Their distinct properties also enable a more comprehensive analysis of the NH_3 concentration and reduce the risk of false readings due to interfering gases. Hence, this study focuses on the preparation of AuNPs-G/PPy hybrid nanocomposite sensing films through in situ chemical oxidation polymerization of AuNPs, graphene, and pyrrole, along with the incorporation of low-loss surface acoustic wave devices. The combination of these elements results in a highly sensitive SAW sensor capable of detecting NH_3 at ppb-level concentrations at room temperature. The sensors thus show promising potential in detecting parts per billion-level NH_3 , which may open up new applications for the accurate diagnosis of *H. pylori* infection.

2. Materials and Methods

2.1. Materials and Reagents

Graphene and AuNPs (core size: $20\text{ nm} \pm 2\text{ nm}$) were purchased from Acros (Bergen County, NJ, USA). The pyrrole monomer was obtained from Acros and purified through distillation at reduced pressure before use. Other reagents, including PSSA (ALFA) and ammonium peroxydisulfate (APS; Showa, Gyoda, Japan), were used without further purification. All chemicals used here were of analytical reagent grade. NH_3 gas (50 and 1000 ppb) was obtained from Jing-De Gas Co. (Kaohsiung, Taiwan).

2.2. Preparation of AuNPs-G/PPy Hybrid Nanocomposite Film

Figure 1 illustrates the process of AuNPs-G/PPy hybrid nanocomposite preparation. The AuNPs-G/PPy hybrid nanocomposite was synthesized through in situ chemical oxidative polymerization. First, 13.3 mL of PSSA and 2.0 g of AuNPs in 16.7 mL of distilled water were added to a reaction vessel containing a stirrer. Then, 0.3 g of graphene was mixed with the 0.1 g of surfactant solution (SDS) and ultrasonicated for 3 h to form a soft template in solution. Freshly distilled pyrrole monomer (0.5 g) was slowly added dropwise into the aforementioned solution, with continuous stirring for 30 min in an ice bath. Next, 2.0 g of APS in 10 mL of distilled water was slowly added into this solution. The polymerization process lasted 3 h at about 5°C with constant mechanical stirring. The synthesized AuNPs-G/PPy hybrid nanocomposite was filtered and rinsed several times with distilled water and methanol. The obtained powder was vacuum dried at 60°C for 24 h. The obtained powder of AuNPs-G/PPy hybrid nanocomposite was mixed with appropriate amounts of distilled water to prepare AuNPs-G/PPy hybrid nanocomposite sensitive films using spin coating. The surface morphology and composition of these nanocomposite powder and films were characterized on an environmental scanning electron microscope (ESEM, Quanta 200, FEI, Hillsboro, OR, USA) equipped with an energy dispersive X-ray spectroscopy (EDS). The crystalline structure and resistivity of these nanocomposite films were characterized and measured on an X-ray diffraction (XRD, Siemens D5000, Bruker, Mannheim, Germany) and a Hall effect measurement system (HMS-3000, Ecopia, Anyang-si, Republic of Korea), respectively.

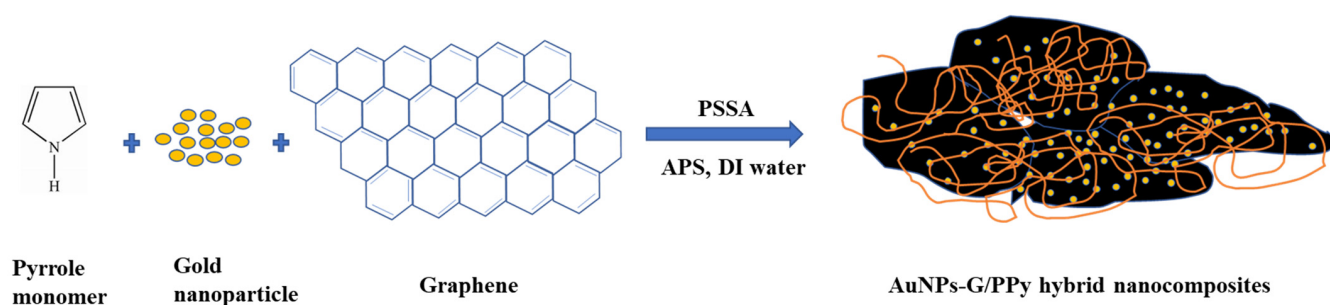


Figure 1. Schematic illustration for the preparation of AuNPs-G/PPy hybrid nanocomposite.

2.3. SAW Sensor Fabrication

Two-port SAW resonators fabricated on a ST-cut quartz substrate were used to detect NH_3 gas. A dual-track configuration was used to reduce interference from the environment. The input/output IDTs in each channel adopted the electrode-width-controlled single-phase unidirectional transducer (EWC/SPUDT) structure and were combined with the reflection grating on both sides of the channel to form a two-port resonator. Figure 2 presents a top view of the EWC/SPUDT IDT and a dual-track configuration of SAW resonators employed in this study, which are the same as in our previous study [13]. A sensing track was produced by spin-coating a $1.5 \times 0.5\text{ mm}^2$ sensitive area of the AuNPs-G/PPy hybrid nanocomposite layer in between two IDTs, such that the reference track surface was free. The thickness of the AuNPs-G/PPy hybrid nanocomposite film was

measured using an optical thin-film measurement instrument (TF-166, New Span Opto-Technology Inc., Miami, FL, USA), and the thickness of the sensing film was approximately 130 nm.

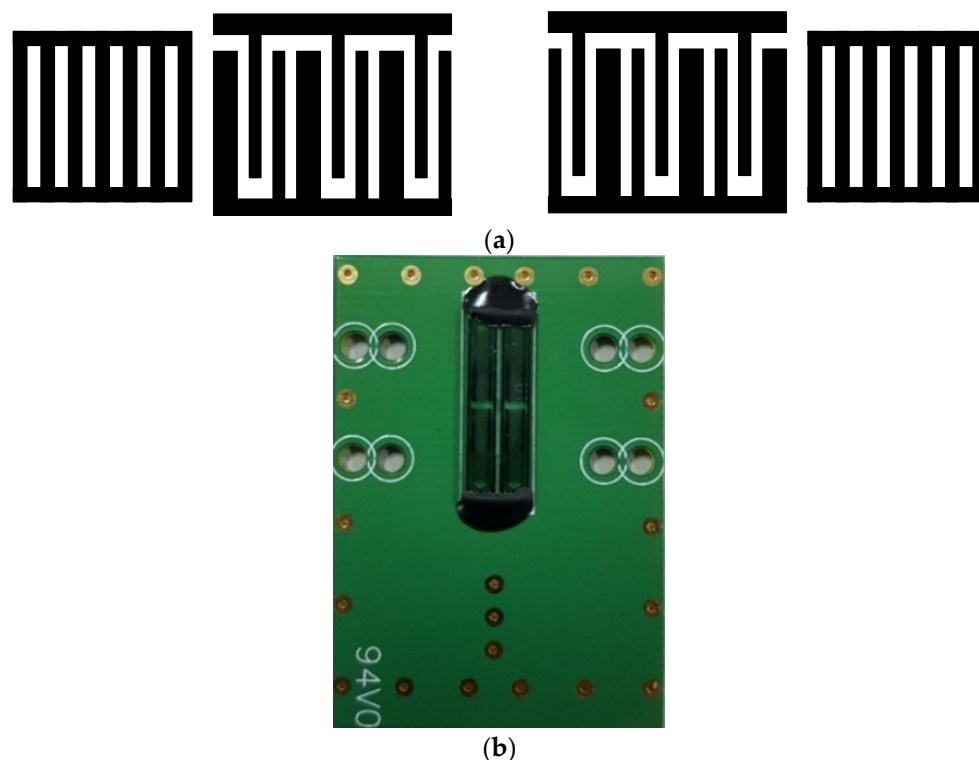


Figure 2. Schematic illustration of (a) two-port resonators consisting of EWC/SPUDT IDT and (b) SAW device.

2.4. Gas Sensing Measurements

The sensing properties of the fabricated sensors were measured within an enclosure containing various concentrations of NH_3 gas. Mass flow controllers (MFC, Sierra, Kyoto, Japan) were used to produce the required gas dilutions using certified 2 ppm NH_3 and dry air cylinders (Jing-De Gas, Kaohsiung, Taiwan). The NH_3 and dry air were transported using an MFC to change the NH_3 gas-to-dry ratio. A NH_3 sensor (FENO, Bedford, UK) was used to independently confirm NH_3 gas concentration for gases generated using the aforementioned dilution method. The outflow was maintained at a constant rate of 110 mL/min during the measurements. The dual-track sensor was placed in a temperature-stabilized, sealed 5 cm³ sensing chamber integrated with the oscillation circuit. A temperature controller kept experiments at a constant temperature of 24 °C. Figure 3 illustrates the experimental system under dry conditions.

The frequency changes of the SAW sensor were measured using a frequency counter (53132A, Agilent, Santa Clara, CA, USA). Firstly, dry air was introduced into the sensing chamber for 30 min, to stabilize the experimental environment and electrical signals. NH_3 , as the sensing gas, was mixed with dry air (carrier gas), and the desired concentration was controlled using an MFC. The gas mixture was allowed to blend for at least 30 min to ensure homogeneous mixing of gases. The gas valve was then switched to introduce the desired concentration of NH_3 gas into the sensing chamber, and the sensing time was set to 3 min. After 3 min, the valve was switched back, and dry air was continuously supplied to the sensing chamber for 30 min to complete one cycle (approximately 1 h). After the experiments, the sensor was stored in a sealed container filled with nitrogen gas to prevent contamination or moisture absorption by the sensing film.

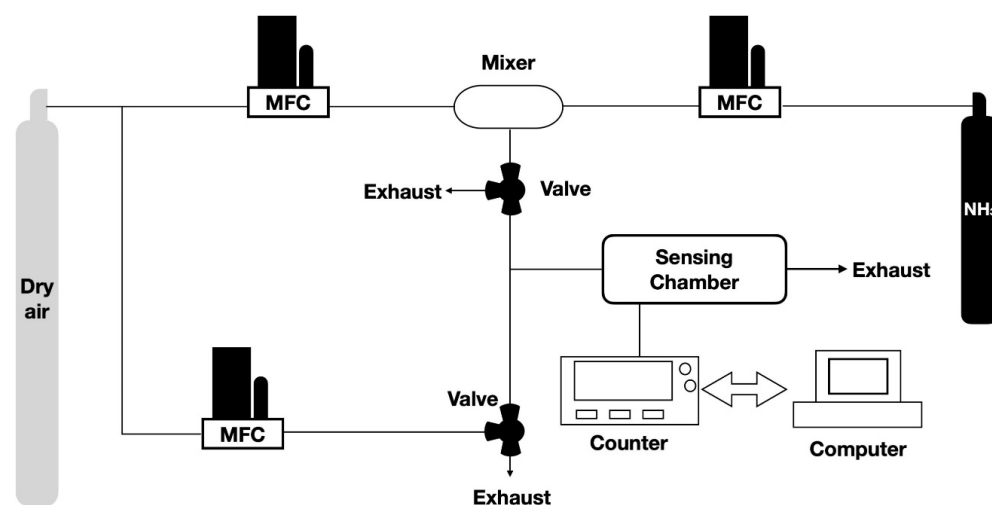


Figure 3. Experimental setup for ammonia gas sensing measurement.

3. Results and Discussion

3.1. Material Analysis of the AuNPs-G/PPy Hybrid Nanocomposite

Figure 4 shows the XRD patterns of the AuNPs-G/PPy hybrid nanocomposite. As can be seen, one broad peak at $2\theta = 10^\circ \sim 30^\circ$ may be ascribed to the doped PPy chains [25]. The broad peak is due to the scattering of the PPy chains at the interplanar spacing. The graphene samples showed a main reflection peak at 26.5° , which could be indexed to the characteristic peak reflections of graphite from the graphene (JCPDS No. 01-0646) [26]. The additional four sharp diffraction peaks centered at $2\theta = 38.2^\circ$, 44.3° , 65.2° , and 78.5° were due to Bragg's reflections from the (111), (200), (220), and (311) planes of the face-centered cubic Au, respectively (JCPDS card No. 004-0784) [27].

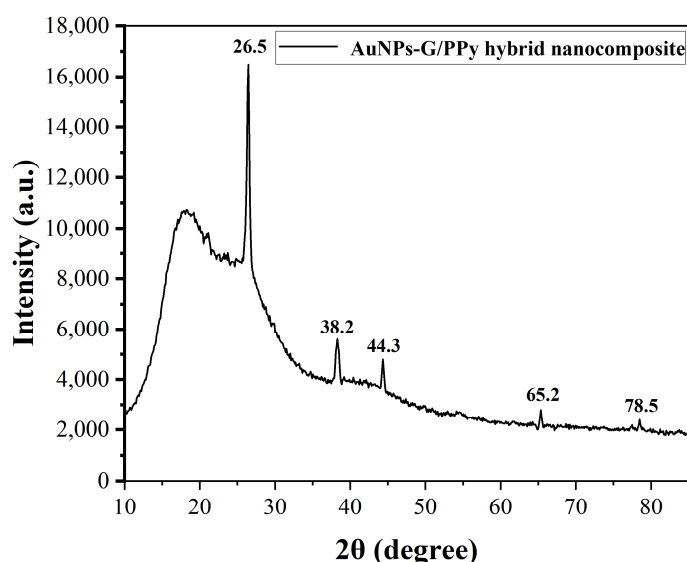


Figure 4. XRD pattern of the AuNPs-G/PPy hybrid nanocomposite on glass substrate.

The SEM image of the AuNPs-G/PPy hybrid nanocomposite in Figure 5 shows the uniformly dispersed spherical AuNPs decorating the large graphene sheets. It can be clearly seen that well-dispersed small gold nanoparticles were in a strong interaction with graphene/PPy, and the average diameters of the gold nanoparticles were about 20 nm. All these results strongly confirm the successful preparation of AuNPs-G/PPy hybrid nanocomposites using an in situ chemical method. Figure 5 also shows various wrinkle patterns on the film surface, which increased the overall adsorption surface area, enabling

effective ammonia adsorption. Figure 6 displays the EDS analysis of the AuNPs-G/PPy nanocomposite film, confirming the distribution of elements such as C, N, S, and Au, consistent with the expected material characteristics.

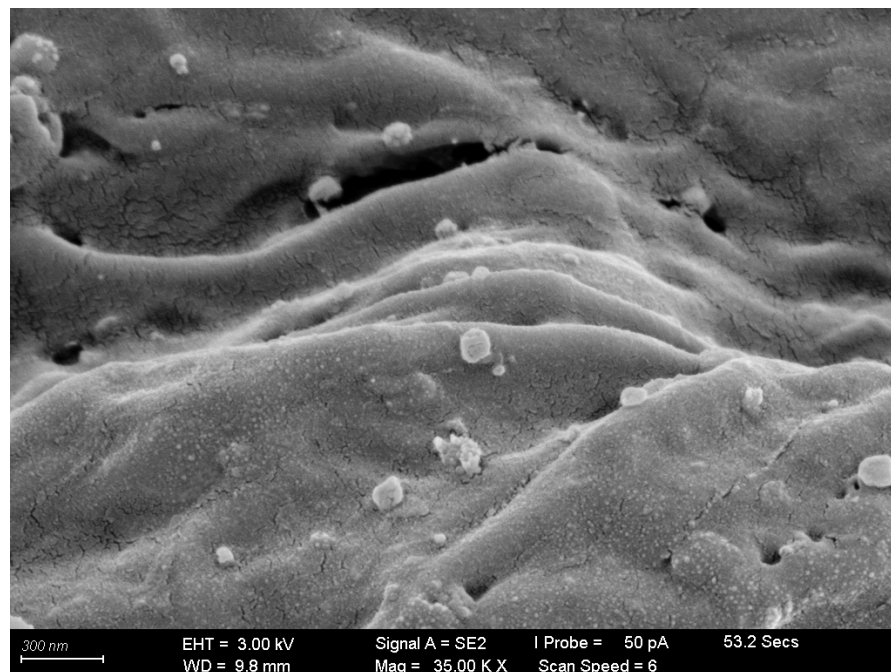


Figure 5. Top view SEM images of the AuNPs-G/PPy hybrid nanocomposite film (35,000 $\times$).

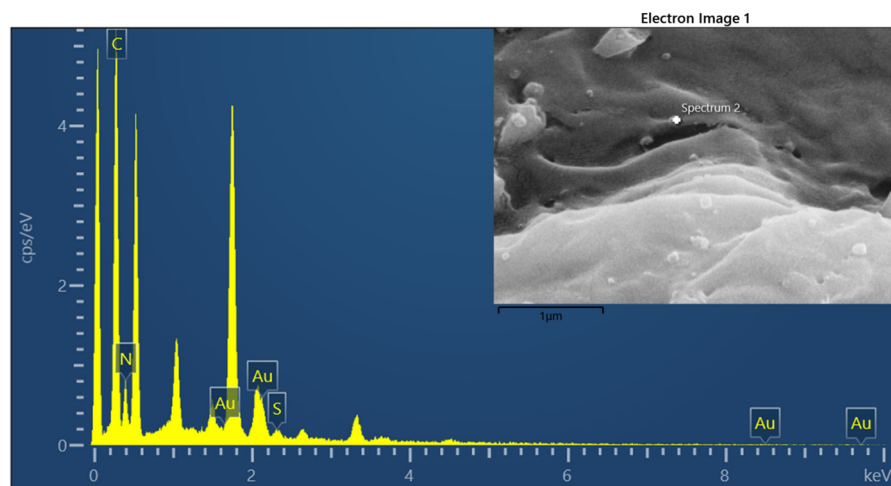


Figure 6. EDS mapping of the AuNPs-G/PPy hybrid nanocomposite film.

The Hall measurement analysis instrument was utilized to measure the resistivity of the AuNPs-G/PPy hybrid nanocomposite film. It was observed that the original resistivity of the AuNPs-G/PPy nanocomposite film was $8.706 \times 10^{-3} \Omega/\text{cm}$. However, after the sensing film adsorbed 800 ppb NH_3 gas, the resistivity increased to $1.329 \times 10^{-1} \Omega/\text{cm}$. The increased resistivity of AuNPs-G/PPy nanocomposite film upon NH_3 exposure indicates P-type semiconductor characteristics. The SEM images in Figure 5, magnified at 45,000 $\times$, reveal the wrinkled multilayer structure of PPy, which resulted from its polymerization between the large graphene sheets, facilitating charge carrier conduction between the graphene and PPy [28]. The presence of spherical AuNPs attached to the graphene surface can also be observed in Figure 5.

3.2. Gas Sensing Properties

The SAW sensors were coated with a sensing layer for chemical sensing. Any changes in the mass, mechanical, or electrical properties of this sensing layer upon exposure to the foreign molecules can perturb the surface acoustic waves, enabling the devices to be used as sensors [29]. The perturbation from the wave propagation characteristics after gas adsorption can be written as

$$\frac{\Delta f}{f_0} \cong \frac{\Delta v}{v_0} = -c_m f_0 \Delta \left(\frac{m}{A} \right) + 4c_e f_0 (\Delta h G') - \frac{K^2}{2} \Delta \frac{1}{(v_0 C_s / \sigma_s)^2 + 1} \quad (1)$$

where c_m and c_e are the coefficients of mass sensitivity and elasticity, respectively; m/A is the change in mass per unit area; h is the thickness of the sensitive layer; G' is the shear modulus; K^2 is the electromechanical coupling coefficient; and σ_s is the sheet conductivity of the sensitive layer. The first term on the right-hand side of Equation (1) represents the mass-loading effect that results in negative frequency shifts and is a function of the NH_3 gas concentration. The second and the third term are the contribution of the elastic properties and the acoustoelectric effect of the sensitive layer, respectively, and produce a positive frequency shift because NH_3 is a reducing gas [30].

The sensing performance of the SAW sensors was evaluated in terms of analytical validations such as sensitivity, limit of detection (LOD), repeatability, stability, and selectivity. These analytical parameters are essential to demonstrate the quality and reliability of the sensor. Figure 7 shows the frequency transient response of the SAW sensor with AuNPs-G/PPy sensing film to 1 ppm NH_3 in a dry air environment. Since NH_3 gas is a reducing gas, the acoustoelectric effect and elastic effect exhibit a positive frequency change, while the mass loading induces a negative frequency change. Figure 7 shows that the SAW sensor with AuNPs-G/PPy sensing film generated a positive frequency change when detecting NH_3 , indicating that the sum of the acoustoelectric effect and elastic effect was greater than the mass loading. It indicates that the AuNPs-G/PPy hybrid nanocomposite film exhibited an increase in electrical resistance when detecting NH_3 gas. This led to a positive response in the third term on the right side of Equation (1), which, when combined with the second term of the elastic effect, was greater than the negative change caused by the first term of the mass loading. Consequently, the SAW sensor demonstrated a positive frequency response, as Figure 7 confirms.

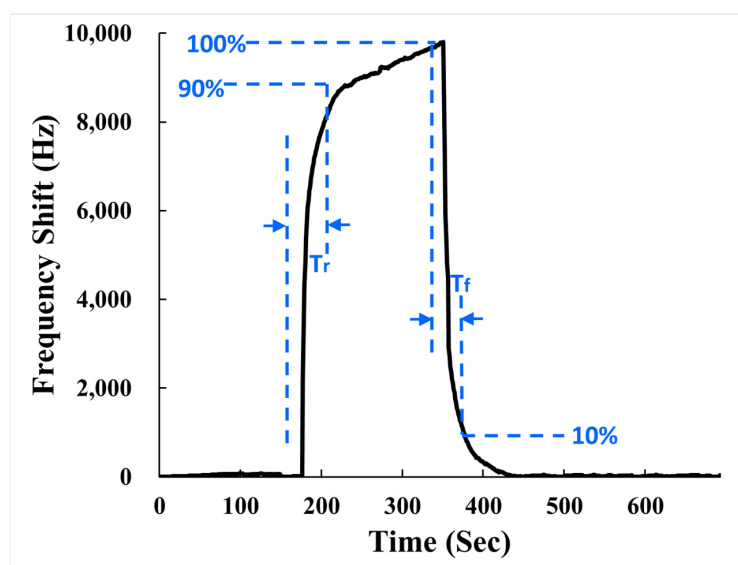


Figure 7. Frequency transient response of the SAW sensor with AuNPs-G/PPy sensing film to 1 ppm NH_3 in dry air at room temperature.

Figure 8 illustrates the frequency shift of the SAW sensor coated with AuNPs–G/PPy sensing film when detecting NH_3 concentrations ranging from 50 to 1000 ppb in a dry air environment. The data presented for each concentration represents the results of three experimental measurements. As the SAW sensor detected NH_3 , the frequency shift increased with the increasing NH_3 concentration. Figure 8 shows a linear relationship between the response of the proposed SAW sensor and NH_3 concentration in the concentration range of 50 to 1000 ppb. The sensitivity of the SAW sensor in detecting 50 to 1000 ppb NH_3 was 8 Hz/ppb, demonstrating excellent sensitivity for NH_3 detection. The concentration of ammonia in the exhaled breath of healthy individuals ranges from approximately 425 ppb to 1800 ppb [31], whereas individuals with *Helicobacter pylori* infection typically exhibit ammonia concentrations ranging from 50 ppb to 400 ppb after undergoing the carbon-13 urea breath test [32]. Since this study aims to develop a sensor for detecting *Helicobacter pylori* infection, experiments involving NH_3 concentrations higher than 1000 ppb were not conducted.

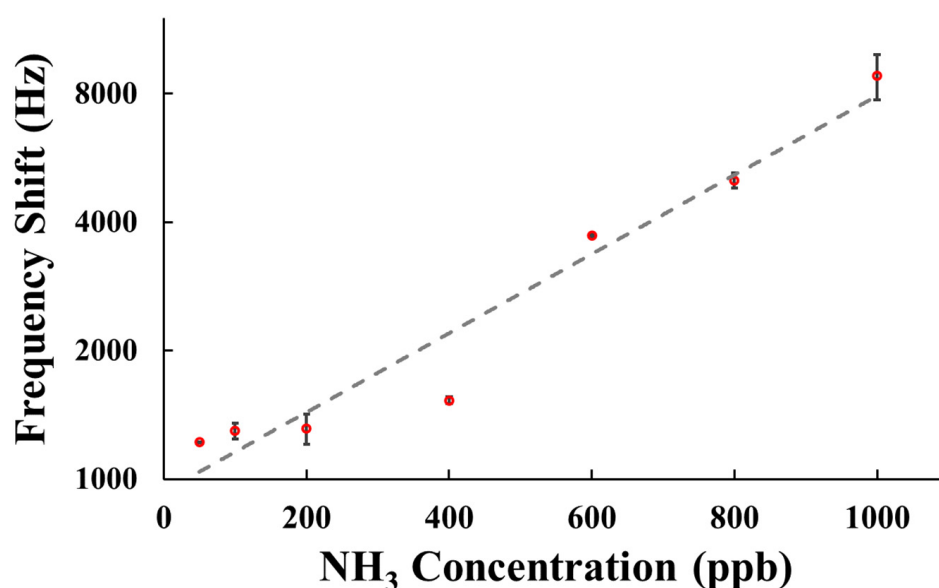


Figure 8. Frequency shifts of a SAW sensor coated with AuNPs–G/PPy sensing film to various concentrations of NH_3 gas in dry air at room temperature.

The minimum detectable limit (limit of detection, LOD) of a sensor is typically defined as the signal-to-noise ratio (S/N) of 3. In the case of the SAW sensor developed in this study, the frequency change for detecting 50 ppb NH_3 was 1222 Hz, with noise of 17 Hz, resulting in an S/N ratio of 72. Therefore, the estimated LOD of this sensor is 3 ppb.

A sensor with good repeatability demonstrates high reliability during the sensing process and yields consistent results under repeated operations. Figure 9 illustrates the repeatability experiment results of the AuNPs–G/PPy-coated SAW sensor for detecting 600 ppb NH_3 in dry air. The calculation formula for repeatability is as follows:

$$\text{Repeatability} = \frac{\Delta f_5}{\Delta f_1} \times 100\% \quad (2)$$

where Δf_1 represents the frequency response obtained in the first experiment, and Δf_5 represents the frequency response obtained in the second experiment. Based on the Equation (2) calculation, for the AuNPs–G/PPy-coated SAW sensor in the repeatability experiment with 600 ppb NH_3 , the frequency shifts for the first and fifth experiments were 3679 Hz and 3559 Hz, respectively. This yields a repeatability of 97%, demonstrating the excellent repeatability of the AuNPs–G/PPy-coated SAW sensor. In this work, the reproducibility of the identical sensor was also tested by having two independent investigators measure the

sensor response to 600 ppb NH₃ in dry air. The frequency shifts measured were 3679 Hz and 3700 Hz for each investigator. The close alignment of results between investigators further confirms the high reproducibility of the proposed sensor.

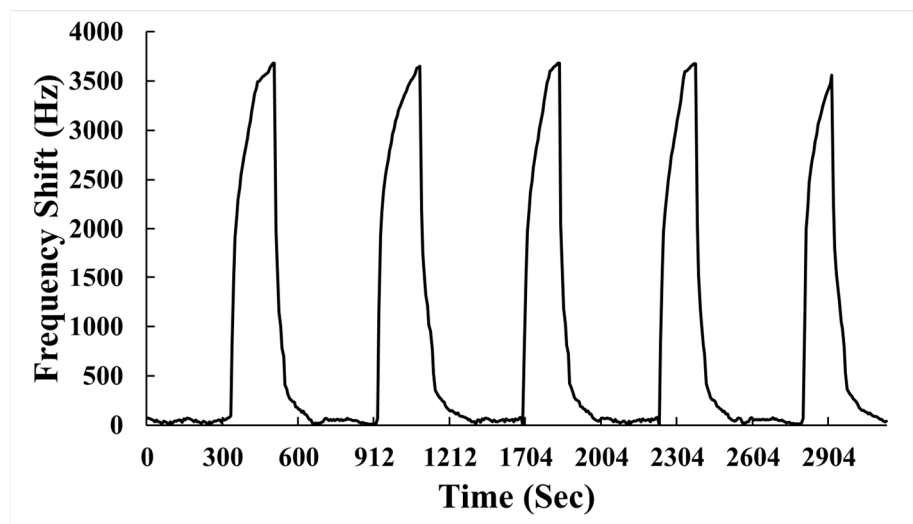


Figure 9. Repeatability of a SAW sensor coated with AuNPs–G/PPy sensing film exposed to 600 ppb NH₃ gas.

Table 1 shows the frequency shift, response time, and recovery time of the AuNPs–G/PPy-coated SAW sensor for different concentrations of NH₃ gas in a dry air environment. The response time (T_r) is defined as the time required for the response frequency to increase to 90% of the maximum response after introducing NH₃ gas (as illustrated in Figure 7). The recovery time (T_f) is defined as the time required for the response frequency to return to 90% of the baseline after removing NH₃ gas. It is clearly seen from Table 1 that the SAW sensor coated with AuNPs–G/PPy exhibited response and recovery times within 2.5 min in a dry air environment.

Table 1. Sensing response of the SAW sensor coated with AuNPs–G/PPy sensing film toward various concentrations of NH₃ gas in dry air.

NH ₃ Concentration (ppb)	50	100	200	400	600	800	1000
Frequency shift (Hz)	1222	1353	1208	1559	3692	4808	9867
Response time (s)	128	125	120	118	98	76	61
Recovery time (s)	140	120	122	120	87	77	56

Table 2 presents the long-term response characteristics of the SAW sensor coated with AuNPs–G/PPy to 50 ppb NH₃ in a dry air environment at room temperature. On day 1, the frequency change was 1273 Hz. By day 20, it had decreased to 1219 Hz, and by day 30, it had further reduced to 563 Hz. This indicates that the frequency change of the SAW sensor decays over time during NH₃ detection. The long-term stability can be calculated using the following formula:

$$\text{Long-term stability (\%)} = \frac{\Delta f_n}{\Delta f_1} \times 100\% \quad (3)$$

where Δf_n represents the frequency shift on the n th day. For this calculation, Δf_1 is the frequency shift on the first day (1273 Hz), and Δf_{30} is the frequency shift on the 30th day (563 Hz). Using the formula, the 20-day long-term stability of the AuNPs–G/PPy-coated

SAW sensor is calculated as 96%, while the 30-day stability is 44%. The sensor exhibited stable long-term response within the first 20 days but experienced a rapid decline after 20 days.

Table 2. Stability of a SAW sensor coated with AuNPs–G/PPy sensing film to 50 ppb NH₃ gas for 30 days.

Time (Day)	1	10	20	30
Frequency shift (Hz)	1273	1222	1219	563

Selective analysis of gas sensors is crucial to demonstrate whether the SAW sensor responds to specific gases without being affected by other gases. In this study, 1 ppm H₂, 1 ppm CO, and 1 ppm CO₂ were tested as interfering gases. Figure 10 illustrates the frequency shift for various gases. The selectivity can be calculated using the following formula:

$$\text{Selectivity} = \frac{\Delta f_{\text{NH}_3}}{\Delta f_{\text{int}}} \times 100\% \quad (4)$$

where Δf_{NH_3} and Δf_{int} represent the frequency shift of the sensor to NH₃ and the interfering gases, respectively. It is clearly seen from Figure 10 that the frequency shift for 1 ppm NH₃ gas was over 1.5 times higher than for 1 ppm H₂, 1 ppm CO, and 1 ppm CO₂. Accordingly, the SAW sensor coated with AuNPs–G/PPy hybrid nanocomposite film can selectively detect ammonia at ppm levels in dry air at room temperature despite the presence of common interfering gases.

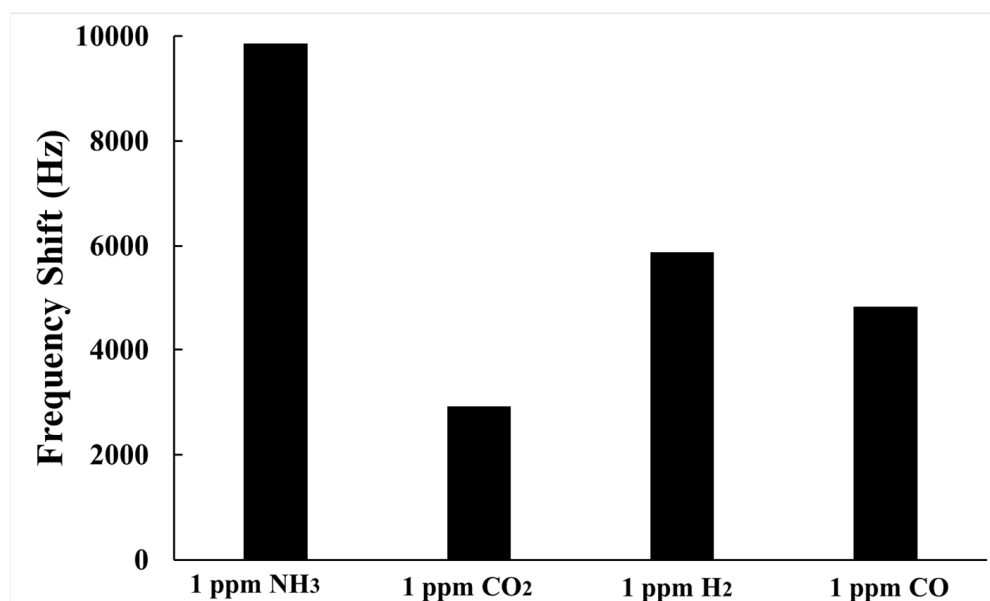


Figure 10. Frequency shifts of a SAW sensor coated with AuNPs–G/PPy sensing film towards 1.0 ppm NH₃ gas, 1.0 ppm CO₂ gas, 1.0 ppm H₂ gas, and 1.0 ppm CO gas.

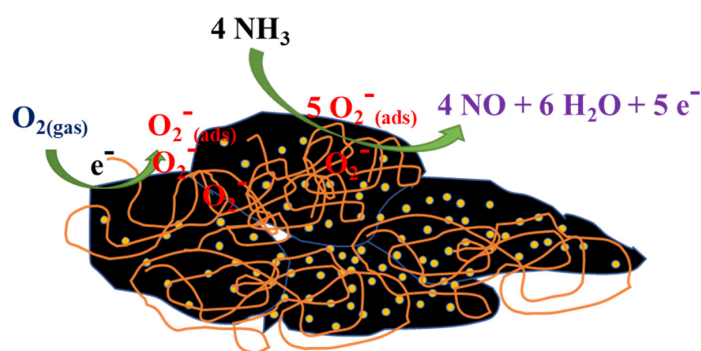
Table 3 shows some of the NH₃ sensors operating at room temperature that are reported in the literature [11,14,15,18,21,33–35]. Compared to other ammonia sensors, the apparent frequency response in the present work is rapidly towards ppb-level NH₃. Hence, the present EWC/SPUDT SAW sensor coated with AuNPs–G/PPy hybrid nanocomposite film is able to sensitively detect NH₃ concentrations of the order of parts per-billion at room temperature.

Table 3. Comparison of different NH₃ sensors operating at room temperature reported in the literature.

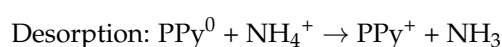
Sensing Film	Sensitivity	Detection Limit (LOD)	Response Time	Recovery Time	Reference
SnO ₂ /Co ₃ O ₄	3.33 Hz/ppm	9 ppm	100–120 s	30–50 s	[11]
PANI/WO ₃	121% to 100 ppm	1 ppm	32 s	388 s	[14]
PANI/SnO ₂	29 to 100 ppm	≥1.8 ppm	31 s	-	[15]
PANI/HNTs	257.14% (50 ppm)	10 ppb	158 s	162 s	[33]
PANI-rGO	13% (15 ppm)	0.3 ppm	96 s	22.1 min	[34]
Yttrium Stabilized Zirconium (YSZ)	3.53×10^{-14} F/ μ M	2.5 ppb	-	-	[35]
PPy/G	1.7% to 1 ppm	1 ppm	2 min	5 min	[18]
PPy	12% to 20 ppm	5 ppm	20 s	20 min	[21]
AuNPs-G/PPy	8 Hz/ppb	3 ppb	128 s	140 s	This work

3.3. Mechanism of Gas Sensing

The P-type semiconductor nature of the AuNPs-G/PPy hybrid nanocomposite film, enhanced by graphene's high electron mobility at room temperature, facilitates rapid carrier transport within the film, resulting in improved sensing characteristics. Furthermore, graphene's large surface area and wrinkled multilayer structure provide favorable conditions for ammonia molecule adsorption on the sensing film surface [36]. In dry air, oxygen molecules spontaneously adsorb on the gold nanoparticles, graphene, and PPy surface, capturing electrons to form reactive electrophilic oxygen ions, O₂[−]. Upon exposure to NH₃, two simultaneous processes occur in the AuNPs-G/PPy hybrid nanocomposite film. On one hand, NH₃ molecules react with O₂[−] to generate a large number of electrons, as shown in the following equation: $4 \text{NH}_3(\text{g}) + 5 \text{O}_2^-(\text{ads}) \rightarrow 4 \text{NO}(\text{g}) + 6 \text{H}_2\text{O}(\text{g}) + 5 \text{e}^-$ [37]. Figure 11 illustrates the schematic representation of the sensing mechanism.

**Figure 11.** The sensing mechanism illustration of the AuNPs-G/PPy hybrid nanocomposite film.

On the other hand, an oxidation–reduction reaction takes place between PPy and NH₃, as illustrated by the following equations:



When NH₃ molecules encounter PPy, ammonia molecules lose electrons, transferring them to PPy forming ammonium ions, leading to an increase in PPy's resistivity. Upon the removal of NH₃ gas and renewal with air, the conductivity of the AuNPs-G/PPy nanocomposite film can be restored. Additionally, as suggested in the literature [38], there may be π – π stacking between the graphene and PPy layers, allowing for electron transfer

between them. The electrons generated from the reaction between NH_3 and O_2^- enter the PPy layer, further promoting the redox reaction between PPy and NH_3 . This results in the deprotonation of P-type PPy and a reduction in charge carriers in the PPy main chain. Finally, the electrons rapidly transfer to the AuNPs-G/PPy nanocomposite film and recombine with the holes in the P-type semiconductor. These simultaneous processes of electron and hole recombination in the PPy and graphene contribute to a decrease in hole density and an increase in resistance, particularly pronounced at higher concentrations of NH_3 . Compared to the response process, the AuNPs-G/PPy nanocomposite film quickly loses electrons by reacting with adsorbed oxygen molecules, thereby returning to the baseline position rapidly. The presence of AuNPs allows for more NH_3 gas molecules to adsorb onto the surface of the graphene, as NH_3 gas molecules can strongly bind to the surface. This indirectly enhances the adsorption capacity of graphene for NH_3 gas molecules, consequently improving the sensitivity of NH_3 detection [39].

3.4. Humidity Effect

Considering that environmental humidity fluctuations can be significant in practical sensor applications, we investigated the influence of humidity (0–80% RH) on the sensing characteristics of our SAW sensor. Figure 12 illustrates the dynamic response of the SAW sensor with AuNPs-G/PPy composite film when exposed to 100 ppb NH_3 at various relative humidities (RH). At 0% RH, the sensor exhibited a positive frequency response. However, in humid environments (>20% RH), the frequency response became negative due to the NH_3 molecules' pronounced affinity for H_2O molecules. This negative shift increased with higher humidity levels. Within the range of 20–80% RH, the sensor demonstrated a more pronounced negative frequency change, indicating that ambient H_2O assisted the AuNPs-G/PPy nanocomposite film in capturing more NH_3 molecules, thereby increasing the mass loading. Furthermore, we conducted tests on the SAW sensor with AuNPs-G/PPy composite film to assess the frequency shift at different humidity levels, as depicted in Figure 13. The negative frequency response increased with rising humidity, exhibiting a similar phenomenon to that in Figure 12, albeit with a lesser response magnitude at the same humidity level. Figures 12 and 13 collectively illustrate that the SAW sensor with AuNPs-G/PPy composite film exhibits a negative frequency response in humid conditions, which intensifies with rising humidity. This implies the negative mass-loading change outweighs the positive elastic and acoustoelectric effects in humid environments. Moreover, at humidity increases, the AuNPs-G/PPy nanocomposite film captures a greater quantity of NH_3 molecules, resulting in a more substantial mass loading, a phenomenon validated by the results in Figure 12.

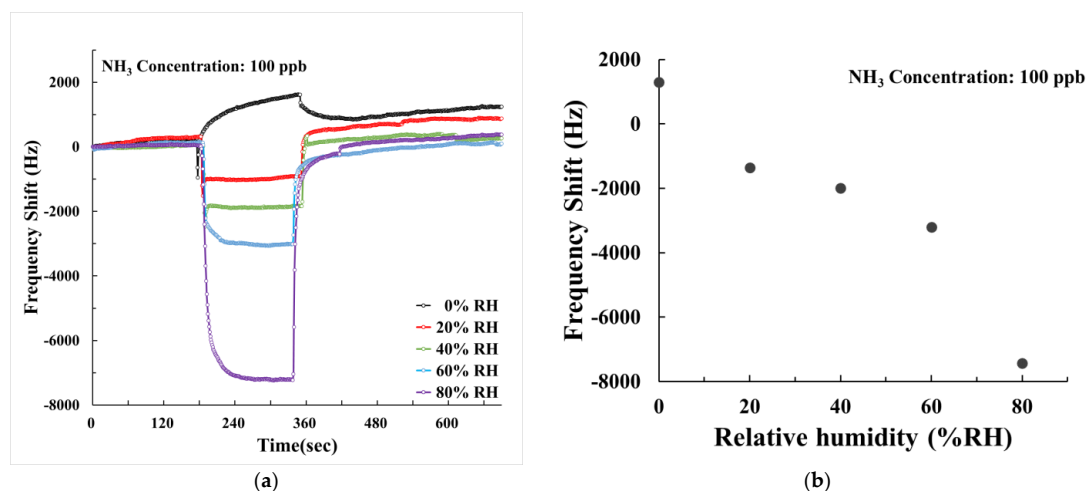


Figure 12. (a) Frequency transient responses and (b) frequency shifts of the AuNPs-G/PPy SAW sensor at different humidity towards 100 ppb NH_3 .

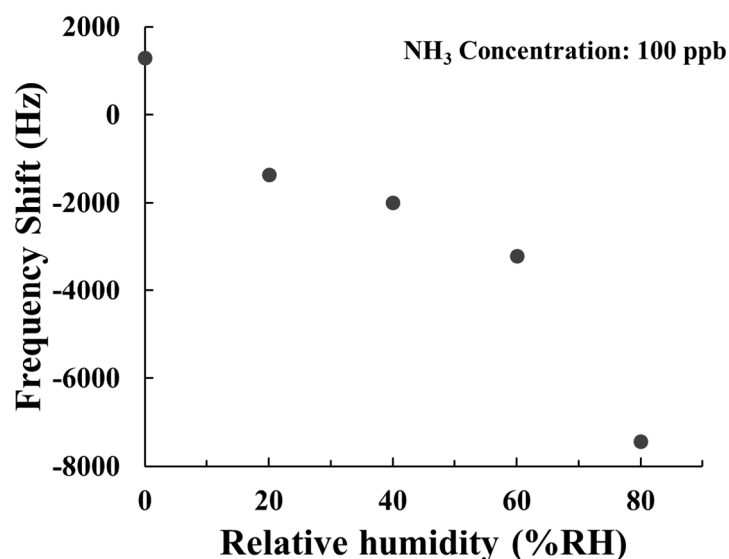


Figure 13. The frequency shift of the AuNPs-G/PPy SAW sensor in various humidity environments.

4. Conclusions

This study presents a SAW sensor based on AuNPs-G/PPy hybrid nanocomposite film for highly sensitive and rapid detection of ammonia gas at ppb levels at room temperature. The AuNPs-G/PPy sensing film was characterized by XRD, EDS, and SEM techniques. The film exhibited a wrinkled and multilayered structure, which increased the gas adsorption surface area. The interaction between graphene and PPy promoted electron conduction. Experimental results showed that the SAW sensor coated with AuNPs-G/PPy exhibited a positive frequency shift when detecting 50–1000 ppb NH_3 in dry air, indicating that the combined elastic and acoustoelectric effects exceeded mass loading. The frequency response increased stably and linearly with rising ammonia concentration. The sensitivity of the SAW sensor in detecting 50–1000 ppb NH_3 was 8 Hz/ppb, demonstrating the excellent NH_3 detection. Furthermore, the SAW sensor coated with AuNPs-G/PPy showed fast response, reproducibility, and selectivity, remaining stable for 20 days. Based on these findings, the SAW sensor coated with AuNPs-G/PPy hybrid nanocomposite film developed in this study effectively detected 50–1000 ppb NH_3 in dry air, exhibiting potential for medical diagnosis through human breath analysis. While fluctuations in environmental humidity do influence the outcomes of sensor detection, a practical approach is to dehydrate the exhaled human breath gases before undertaking subsequent ammonia concentration measurements.

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