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# Investigation of a flexible, room-temperature fiber-shaped NH<sub>3</sub> sensor based on PANI–Au–SnO<sub>2</sub>†

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A sensitive compound was successfully obtained by coating polyaniline (PANI) on the surface of composite nanoparticles consisting of Au-loaded tin dioxide, named as PANI–Au–SnO<sub>2</sub>, using an *in situ* polymerization method. NH<sub>3</sub> sensors in thin-film and fiber-shaped forms were prepared by inkjet printing and impregnation methods, respectively, based on PANI–Au–SnO<sub>2</sub>. The response characteristics of these NH<sub>3</sub> sensors developed from composite sensitive materials were investigated in detail. Results indicate an effective response of the sensors to NH<sub>3</sub> at room temperature. The thin-film sensor demonstrated a good linear relationship between the resistance change and NH<sub>3</sub> concentration within the range of 5–40 ppm, indicating its excellent repeatability and long-term stability. In comparison to the thin film sensor, the fiber-shaped sensor showed a consistently stable response to NH<sub>3</sub> even after 1000 cycles of repeated bending deformation. To demonstrate the practical application of the flexible fiber-shaped NH<sub>3</sub> sensor, a cap designed for NH<sub>3</sub> detection was fabricated by integrating the as-prepared sensor with a circuit board and an LED digital display. This assembly was incorporated into a commercially available ducktail cap, resulting in a wearable device capable of dynamically monitoring environmental NH<sub>3</sub> levels and displaying real-time values. This innovative application underscores the potential of these sensors in real-world scenarios, particularly in occupational safety, where workers might be exposed to harmful levels of NH<sub>3</sub>. The cap could serve as a personal safety device, alerting the wearer to hazardous concentrations of NH<sub>3</sub>, which is particularly relevant in industrial or agricultural settings.

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## 1. Introduction

Gas sensors are becoming essential in various fields, including medicine, industry, and defense. In particular, there is an urgent need to develop gas sensors that can operate at room temperature to monitor hazardous gas levels in the environment or indoor areas, especially in workplaces, to ensure human health and safety. Ammonia (NH<sub>3</sub>) is one of the critical hazardous substances with a strong irritating odor and is widely used in chemical industries and other fields,<sup>1</sup> with millions of tons released into the atmosphere every year.<sup>2,3</sup> The concentration of NH<sub>3</sub> in the atmosphere is typically very low (1–5 ppb).<sup>4</sup> In

indoor environments, the safety threshold for NH<sub>3</sub> concentration is considered to be below 0.2635 ppm, which is less than that in the industrial settings (39.53 ppm).<sup>5,6</sup> When inhaled at concentrations exceeding safe levels, NH<sub>3</sub> can be toxic and pose significant harm to humans due to its irritating and corrosive effects.<sup>7–10</sup> In addition, exhaled NH<sub>3</sub> serves as an important indicator of certain medical conditions.<sup>11,12</sup> Therefore, monitoring NH<sub>3</sub> is of great significance.

The development of room-temperature flexible NH<sub>3</sub> sensors is highly desired for wearable applications.<sup>13,14</sup> Developing NH<sub>3</sub> sensors with flexible and long-term stable operation remains a challenge. NH<sub>3</sub> sensors are widely used for dynamic monitoring of NH<sub>3</sub> concentration. In the field of smart wear, the performance of gas sensors has raised the bar for meeting practical application needs, which include room-temperature detection capability, lightweight nature, and flexibility.<sup>15–17</sup> Traditional rigid sensors, such as microelectromechanical systems (MEMS),<sup>18–21</sup> fail to meet these requirements, making the development of flexible NH<sub>3</sub> sensors essential. Metal oxide materials are often used in gas detection due to their resistance change when they encounter gas.<sup>22</sup> Metal oxides, such as zinc oxide (ZnO)<sup>23–25</sup> and tin oxide (SnO<sub>2</sub>),<sup>26,27</sup> were the earliest materials used for detecting NH<sub>3</sub>. Among these materials, SnO<sub>2</sub> is appealing due to its low cost, low toxicity, ease of

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manufacture, and excellent sensitivity. However, its gas detection requires high temperature, making it unsuitable for wearable applications.<sup>28</sup> For this reason, researchers have made numerous attempts to find alternatives, with organic–inorganic composites attracting much attention. Conductive polymers, which combine the mechanical properties of polymers with metal-like electrical properties, are important materials in the field of smart wearables.<sup>29–32</sup> Among the conductive polymers, polyaniline (PANI) is one of the most promising materials for detecting  $\text{NH}_3$  at room temperature. When PANI is used to sense  $\text{NH}_3$ , it offers the advantages of a rapid response and stable performance.<sup>33</sup> However, there are still issues with its sensitivity, processability, and so on.<sup>34–38</sup> Therefore, composites of metal oxides and conductive polymers have been investigated as they could offer significant advantages as  $\text{NH}_3$ -sensitive materials.<sup>39,40</sup> Indeed, many composites consisting of metal oxides and conducting polymers have been developed as  $\text{NH}_3$  sensors and have demonstrated excellent sensing performance. For example, Siqi Li<sup>41</sup> *et al.* prepared  $\text{SnO}_2$ -PANI nanocomposites with a well-defined microstructure and large specific surface area. The response speed of 20 mol%  $\text{SnO}_2$ -PANI to 100 ppm  $\text{NH}_3$  at room temperature was 6.2 times higher than that of the sensor based on PANI alone. Additionally, it could detect low concentrations with outstanding selectivity. In addition, doping precious metals, such as Au and platinum, as well as other nanoparticles, into metal oxides can effectively enhance the gas-sensing properties.<sup>42,43</sup> For example, Manish Deshwa<sup>44</sup> and others have prepared 3% v/v Au-doped ZnO thin films for use as acetone sensors. Compared to the undoped thin films, they found the response was significantly improved, exhibiting very high sensitivity, a rapid response and recovery time, and a lower optimal working temperature.

In the present study, we employed the wet impregnation method and *in situ* polymerization method to prepare sensitive materials of PANI-Au-SnO<sub>2</sub> and utilized these materials to fabricate sensor devices. It was found that fine-tuning the properties of the composites could directly affect the sensitivity, selectivity, response time, and recovery time of the  $\text{NH}_3$  sensors. These sensors were evaluated to assess not only their electrical response to  $\text{NH}_3$  exposure but also their mechanical durability, long-term stability under various environmental conditions, and the repeatability of the response. Smart sensor devices were developed that were highly sensitive and selective to  $\text{NH}_3$ , as well as durable enough to be utilized in flexible and wearable applications, which could help protect human health in potentially dangerous environments. The innovative approach used in this study reflects the increasing trend in sensor development to create multifunctional, reliable, and user-friendly devices for environmental monitoring and personal safety.

## 2. Experimental

### 2.1 Materials

Aniline, ethanol, and terpineol were purchased from Tianjin Damao Chemical Reagent Factory. Nano-SnO<sub>2</sub> was purchased from Hebei Yi Gui Welding Materials Co., Ltd. Chloroauric acid

( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) was purchased from Shanghai McLean Biochemical Technology Co., Ltd. Ammonium persulfate (APS) was purchased from Beijing Tong Guang Fine Chemical Co., Ltd. Concentrated  $\text{NH}_3$  water was purchased from Tianjin Guang Fu Technology Development Co., Ltd. Hydrochloric acid (HCl) was purchased from Saan Chemical Technology (Shanghai) Co., Ltd. Conductive silver ink was purchased from Shenzhen Saya Electronic Paste Co., Ltd. The e-PTFE waterproof breathable film was purchased from Polyfluorine New Material Technology Co., Ltd. Polydimethylsiloxane (PDMS) was purchased from Dow Corning, USA. The chemical reagents mentioned above were all analytically pure and were used as-received without further purification.

### 2.2 Preparation of the composite sensing materials

**2.2.1 Preparation of Au-SnO<sub>2</sub>.** First, 20 nm SnO<sub>2</sub> nanoparticles and  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  were added to 20 mL of ethanol and stirred magnetically. The mixture was then heated to 40 °C and allowed to evaporate completely. The mixture was then transferred to a crucible and calcined in a muffle furnace at 300 °C for 2 h to obtain Au-SnO<sub>2</sub> (Fig. 1(a)).

**2.2.2 Preparation of PANI-Au-SnO<sub>2</sub>.** Solution A was prepared by adding 1.14 g of APS to 15 mL of 1 M HCl and stirring continuously for 30 min, and was then placed in an ice water bath. A specific quantity of Au-SnO<sub>2</sub> was added to 15 mL of 1 M HCl and dispersed using ultrasonication. Subsequently, 10 mmol of aniline monomer was added and sonication was continued for 30 min, and then cooled to obtain solution B. Solution A was slowly added to solution B to obtain PANI-Au-SnO<sub>2</sub>. This was then left standing for 3 h resulting in a layered dark-green suspension, which was then vacuum filtered, and the obtained sample was washed with ethanol and deionized water. The collected material was placed in a drying oven at 80 °C and then ground into powder for use in sealed equipment (Fig. 1(b)).

The material was generally denoted as  $\text{PASn}_x\text{Ay}$ , where PA, Sn, and A represent PANI, SnO<sub>2</sub>, and Au, respectively,  $x$  represents the molar percentage of SnO<sub>2</sub> (mol%), and  $y$  represents

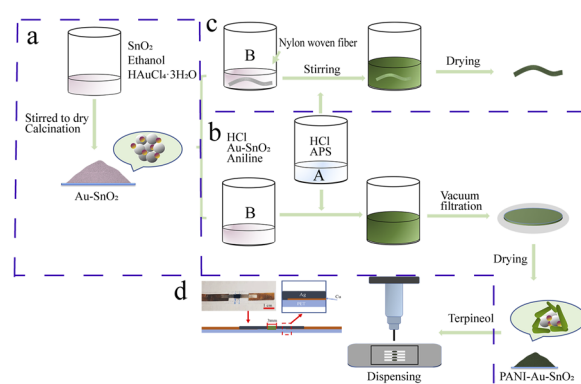


Fig. 1 Preparation of gas-sensitive materials and ammonia gas sensors. (a) Fabrication of Au-SnO<sub>2</sub> material. (b) Fabrication of PANI-Au-SnO<sub>2</sub> compound. (c) Preparation of the fiber-shaped sensor. (d) Fabrication of the thin film sensor.

that of Au (at%), respectively. For the different samples, the number before Sn represents the particle size of SnO<sub>2</sub>; for example, PA20Sn20A2, indicates 20 nm-sized SnO<sub>2</sub>, and 20 mol%, Au addition of 0.02 g.

### 2.3 Preparation of the flexible NH<sub>3</sub> sensor

The preparation process of the flexible sensor is shown in Fig. 1(c) and (d). First, 0.05 g of the sensitive material and an appropriate amount of terpineol were ground together evenly. This mixture was applied to a wide electrode (2 mm) printed by conductive silver ink and placed in an oven to dry at 80 °C for 2 h to obtain the thin film sensor (Fig. 1(d)). Meanwhile, a 3 cm nylon braid was added to solution B during the preparation of the PANI–Au–SnO<sub>2</sub> to obtain a fiber-shaped flexible NH<sub>3</sub> sensor. The other steps were the same as for the preparation of PANI–Au–SnO<sub>2</sub> (Fig. 1(c)).

### 2.4 Sample characterization

A drying oven (DZF-60030v, China), ultrasonic machine (DS2510DTH, China), muffle furnace (SX-B01123, China), and magnetic stirrer (DF-101S, China) were utilized in the preparation of the materials and sensors. The morphology, microstructure, and particle-size distribution of the NH<sub>3</sub>-sensitive materials were characterized by scanning electron microscopy (SEM, JSM7500F, JEOL, Japan). The elements of NH<sub>3</sub> sensitive materials were elucidated through transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan), X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi, Thermo Fisher Scientific, USA), and element analysis using energy dispersive spectroscopy (EDS, S-4800). The crystal structure was characterized by polycrystalline X-ray diffractometry (XRD, D8 Focus, Bruker, Germany). The chemical functional group information of the samples was characterized by Fourier transform infrared spectrometry (FTIR, IRPrestige-21, SHIMADZU, Japan). The sensor was tested for NH<sub>3</sub> sensing using a self-made gas test system (Fig. S1†). During NH<sub>3</sub> testing, the resistance of the gas sensors was measured using a data acquisition and recording multimeter system (DAQ6510, Keithley, USA). The cyclic bending performance of the sensor was tested at room temperature using a stepper motor with a lead of 2 cm and a module (Fig. S2†), and the resistance change was tested in real-time with a DAQ6510 system.

### 2.5 Gas-sensing measurements

The gas responses of the prepared sensors were tested by the device shown in Fig. S1.† The device consisted of a closed box, DAQ6510, and a notebook computer. The specific test method involved placing the sensor in the closed box and connecting the DAQ6510. When the resistance value displayed on the computer was stable, the closed box was filled with a pre-determined amount of gas to be tested, and the resistance value was measured until it became stable. Then, the closed box was opened, causing the stable resistance value to change, and this was again measured until it became stable, thus completing the test.

In this study, two concentration techniques for producing NH<sub>3</sub> were employed. Initially, the static testing method was utilized. Given that concentrated NH<sub>3</sub> water and NH<sub>3</sub> are corrosive, to protect the mass flowmeter from damage, we implemented the static testing method, where a specific concentration of NH<sub>3</sub> was generated through the evaporation of the concentrated NH<sub>3</sub> water. The detailed procedure involved connecting conductive tape at both ends of the flexible sensor to the DAQ instrument, and then recording the resistance value of the NH<sub>3</sub> gas sensor in real time. During the experiment, the heating stage was maintained at 80 °C to expedite NH<sub>3</sub> evaporation. Simultaneously, the slide was positioned on the heating stage, and 4 μL of concentrated NH<sub>3</sub> water was added dropwise. Subsequently, the flexible sensor and the slide with NH<sub>3</sub> water were enclosed in a transparent box with a volume of 3000 mL, creating a simple test environment of 600 ppm NH<sub>3</sub> concentration to initially evaluate the prepared sensitive materials. The formula for generating NH<sub>3</sub> gas is as follows:<sup>45</sup>

$$Q = (V \times C \times M) / (22.4 \times d \times \rho) \times 10^{-9} \times (273 + T_r) / (273 + T_B)$$

where  $Q$  is the volume of the liquid to be taken (mL),  $V$  is the volume of test container (mL),  $M$  is the molecular weight of the substance (g),  $\rho$  is the purity of the liquid,  $C$  is the concentration of the gas to be prepared (ppm),  $d$  is the liquid density (g cm<sup>-3</sup>), and  $T_r$  is the test environment temperature (°C).

The second methodology was the gas-distribution procedure, which involved diluting a defined concentration of standard NH<sub>3</sub> within a specified volume solvent bottle to establish the necessary test concentration. This technique evaluated the subsequent performance of the selected materials and devices, demonstrating optimal functionality. The experimental processing steps were the same as those in the static test method.

The sensitivity of a gas sensor is a measure of its ability to change its resistance in the presence of a target gas. It is defined by the ratio of the resistance of the sensor in a specific gas ( $R_g$ ) to the resistance of the sensor in air ( $R_a$ ). The sensitivity is generally expressed by  $S$ , where  $S = R_g/R_a$ . The response and recovery time are the intervals needed for the sensor to reach the total resistance change upon exposure to the target gas (response time), and then return to 90% of the baseline when the gas is removed (recovery time), respectively. Here, standard NH<sub>3</sub> was diluted to obtain the required concentration of NH<sub>3</sub> for testing, and the real-time resistance was measured using a digital multimeter system. The above tests were carried out at room temperature (25 °C) except for the test to determine the influence of temperature.

## 3. Results and discussion

### 3.1 Optimizing of the NH<sub>3</sub>-sensitive materials

To optimize the material ratio, the particle size and dosage of SnO<sub>2</sub>, and the Au doping amount were carefully selected. The size of SnO<sub>2</sub> particles has a significant impact on the doping efficiency of Au; therefore, sizes of 10, 20, and 50 nm were tested. The doping adjustment of Au was determined by the quantity of chloroauric acid, specifically 0.02, 0.04, and 0.08 g.



The PN junction formed by the P-type PANI and N-type SnO<sub>2</sub> is crucial for the NH<sub>3</sub> sensor to have good sensing performance. In the experiment, we compared three different SnO<sub>2</sub> contents, and the testing was carried out at room temperature, with a relative humidity of 44% and an NH<sub>3</sub> concentration of 600 ppm (Fig. S3†). The response value for each material combination was measured and documented using the testing system (Fig. S1†). Fig. S3† shows the gas-sensing results of the sensing materials prepared by changing the doping amounts of nanoparticles and the doping amount of gold with the doped SnO<sub>2</sub> nanoparticles of different diameters of 10, 20, and 50 nm, respectively. From Fig. S3a,† we can see that irrespective of the composite material, the response value was less than 2.5, which was worse than the sensing effect of pure PANI. It can be seen from Fig. S3b† that the sensing effect of PA20Sn20A2 was significantly higher than that of the other materials, and the response value was above 2.7. Fig. S3c† shows that the response value of the composite material of SnO<sub>2</sub> nanoparticles with a particle size of 50 nm was lower than 2.0, which was significantly lower than the others. Therefore, the doping amount of SnO<sub>2</sub> was fixed at 20 mol%, and then sensors were prepared by changing the particle size of SnO<sub>2</sub> nanoparticles and the doping amount of Au, and the response values were tested and compared (Fig. 2). The data in Fig. 2 suggest that the combination designated as PA20Sn20A2, which corresponded to PANI with 20 nm SnO<sub>2</sub> particles and Au doping amount with 0.02 g of chloroauric acid, exhibited the highest response at 600 ppm for NH<sub>3</sub>. The identification of PA20Sn20A2 as the material with the highest response indicates that this composite had the most suitable combination of particle size and doping level for the detection of NH<sub>3</sub> under the tested conditions.

### 3.2 Characterization of the NH<sub>3</sub>-sensitive material

The morphology of NH<sub>3</sub>-sensitive material was characterized using SEM, as shown in Fig. 3. The SEM of 20 nm SnO<sub>2</sub>

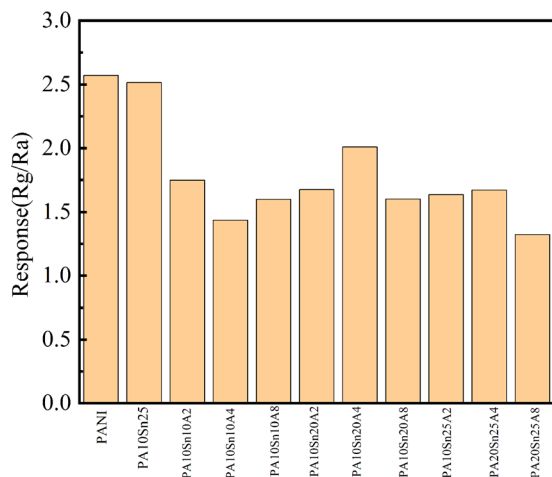


Fig. 2 Response values of different NH<sub>3</sub>-sensitive materials to 600 ppm NH<sub>3</sub> (from left to right is PANI, PA10Sn25, PA10Sn10A2, PA10Sn10A4, PA10Sn10A8, PA10Sn20A2, PA10Sn20A4, PA10Sn20A8, PA10Sn25A2, PA20Sn25A4, PA20Sn25A8).

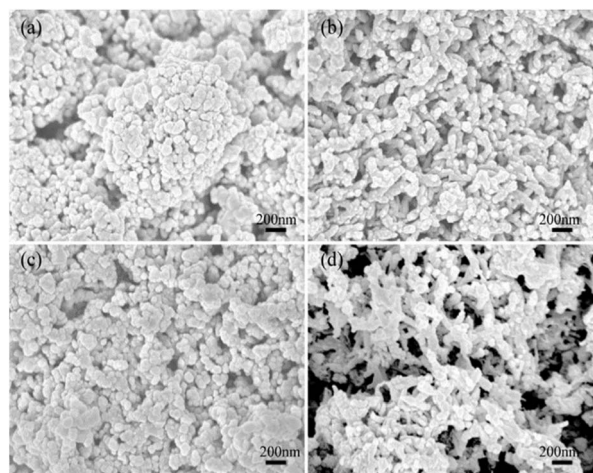


Fig. 3 SEM images of the NH<sub>3</sub> sensitive material. (a) 20 nm SnO<sub>2</sub>; (b) PA20Sn; (c) 20SnA2; (d) PA20Sn20A2.

(Fig. 3(a)) revealed spherical nanoparticles with a loosely arranged porous structure between them. This structure effectively increases the specific surface area, making it more conducive to the adsorption and diffusion of gas. Fig. 3(b) displays the 20 nm SnO<sub>2</sub>-PANI composite, where it can be seen that PANI was wrapped around the SnO<sub>2</sub>, forming a nanofibrous structure that was interconnected into a mesh structure with a diameter of about 100–200 nm. Fig. 3(c) shows the SEM image of 20 nm SnO<sub>2</sub> doped with a small amount of Au, and the microscopic morphology was similar to that of undoped SnO<sub>2</sub>. Fig. 3(d) presents the SEM of the PA20Sn20A2 composite material. It is evident from the figure that PA20Sn20A2 had a looser porous and three-dimensional network structure, which could improve the sensitivity of the NH<sub>3</sub> sensor.

XRD and EDS were used to characterize the composition of the material. The XRD pattern in Fig. 4(a) shows the phase and crystal structure of the material. The original PANI exhibited a diffuse diffraction peak between 20–35°, indicating an amorphous phase structure. However, there were also small diffraction peaks present at 50–60°, which could be attributed to impurities. These impurities were confirmed by comparing the XRD curve of pure SnO<sub>2</sub> with the standard card of rutile SnO<sub>2</sub> (JCPDS: 41-1445), which showed no other impurity peaks. The diffraction peaks of each component in the material exhibited noticeable changes in intensity. When comparing the Au-doped

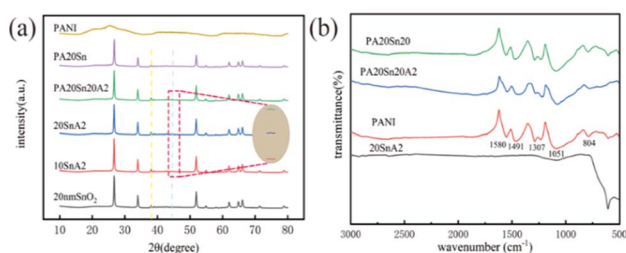


Fig. 4 (a) XRD curves of the NH<sub>3</sub>-sensitive materials. (b) Infrared spectra of the NH<sub>3</sub>-sensitive materials.



material with the undoped material, a small diffraction peak was observed at approximately  $45^\circ$ , but it was not prominent, indicating a low level of Au doping. Energy spectral analysis of PA20Sn20A2 and 20Sn20A2 (Fig. S4†) was conducted separately. However, due to the small amount of Au present, the corresponding peak may have been obscured by other peaks, making it difficult to detect the presence of Au. The specific element contents in the two materials can be found in Table 1 and Table S1.† Furthermore, From Fig. S5 and Table S2,† it can be seen that the XPS analysis of PA20Sn10Au2 verified the trace presence of Au.

The FTIR spectral characterization was conducted on four materials, namely the pure PANI, PA20Sn20, PA20Sn20A2, and 20SnA2. The wave number range of  $4000\text{--}500\text{ cm}^{-1}$  was used to discern the chemical bonding interactions present in the nanocomposites. Fig. 4(b) shows the main characteristic absorption peaks of PANI, which were located at 1580, 1491, 1307, 1051, and  $804\text{ cm}^{-1}$ . The absorption peaks at 1580 and  $1491\text{ cm}^{-1}$  corresponded to the C=C stretching vibration of the quinone ring (N=Q=N) and the benzene ring (N-B-N), respectively. The absorption peak at  $1307\text{ cm}^{-1}$  was attributed to the C-N stretching vibration. The peaks at 1051 and  $791\text{ cm}^{-1}$  represented the in-plane and out-of-plane bending vibrations of the benzene ring C-H, respectively. When comparing the IR spectra of PANI with PA20Sn20 and PA20Sn20A2, it could be observed that the characteristic absorption peaks of PA20Sn20 and PA20Sn20A2 were shifted to higher wave numbers. This shift was caused by the effect of  $\text{SnO}_2$  on PANI when it was compounded with  $\text{SnO}_2$ .

### 3.3 Characterization of the thin film sensor

Fig. 5(a) shows the real-time response curves of the thin film sensor based on the PA20Sn20A2 material at various concentrations of  $\text{NH}_3$  (5–40 ppm) at room temperature. The sensor displayed a rapid increase in resistance upon exposure to  $\text{NH}_3$ , stabilizing at 400–500 s. When fresh air was introduced, the resistance gradually decreased back to the initial value. However, it can be seen from the figure that the sensor resistance value did not fully recover after the gas concentration was greater than 30 ppm. This is because the test process was a continuous test, resulting in the sensor not being completely desorbed. At 20 ppm  $\text{NH}_3$ , the thin film sensor exhibited a response time of 93 s and recovery time of about 168 s (Fig. 5(b)). The resistance of the sensor increased with the  $\text{NH}_3$  concentration, showing a larger response at higher

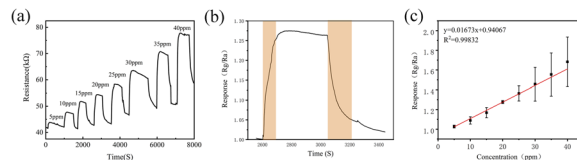


Fig. 5 Response properties of the thin film  $\text{NH}_3$  sensor based on the PA20Sn20A2 material at room temperature. (a) Dynamic response curve of the sensor to  $\text{NH}_3$  with a concentration of 5 to 40 ppm. (b) Response recovery curve of the sensor at 20 ppm  $\text{NH}_3$  concentration. (c) Response and linear fitting curves for various concentrations of  $\text{NH}_3$ . Error bars represent the standard deviations obtained from at least three independent measurements.

concentrations, with a maximum response of 1.68 at 40 ppm  $\text{NH}_3$ . Post 6000 s and exposure to 35 ppm, and 40 ppm  $\text{NH}_3$  concentration, the thin film sensor resistance could not return to its initial value. This may be due to the prolonged exposure causing  $\text{NH}_3$  molecules to spread and react with the sensitive material inside, which means they may not have completely desorbed, and instead reacted.

Fig. 5(c) is a linear fitting curve based on the response of the thin film sensor at different concentrations of PA20Sn20A2 at room temperature, and each concentration was tested three times. A linear relationship was found between the response and the correlation of the sensor. The correlation coefficient was 0.99832, indicating a highly accurate and reliable sensor performance.

### 3.4 Characterization of the fiber-shaped sensor

The flexibility of a sensor is crucial for a comfortable wearing experience. This can be measured by its ability to bend to a certain degree. We conducted bending experiments on two thin film  $\text{NH}_3$  sensors using a stepper motor with a lead of 2 cm and a module (Fig. S2†). The thin film displayed serious damage after only a few bends, as some of the  $\text{NH}_3$ -sensitive materials began to fall off from the PET substrate. To avoid this issue, we prepared a flexible fiber-shaped  $\text{NH}_3$  sensor using a nylon woven line as the substrate. Fig. S6† shows SEM photos of the fiber-shaped  $\text{NH}_3$  sensor with different magnifications. The nylon braided line was made up of multiple  $15\text{ }\mu\text{m}$  nylon fibers, coated with PA20Sn20A2. In Fig. 6(a), we can see the response of the fiber-shaped  $\text{NH}_3$  sensor at a concentration of 10–40 ppm. The illustration shows an optical image of the fiber-shaped flexible  $\text{NH}_3$  sensor, which measured  $30 \times 3 \times 2\text{ mm}$  and had

Table 1 Elemental analysis of PA20Sn20A2

Element	Concentration of element	Intensity correction	Percentage by weight	Percentage by weight sigma	Atomic percent ratio
C K	4.90	1.0015	43.61	0.83	68.16
O K	1.02	0.4374	20.84	0.74	24.45
S K	0.23	1.0642	1.91	0.08	1.12
Cl K	0.25	0.8770	2.55	0.10	1.35
Sn L	2.71	0.7799	31.08	0.58	4.92
Total			100.00		



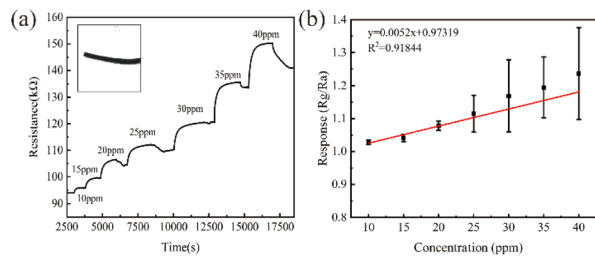


Fig. 6 (a) Dynamic response curve of the  $\text{NH}_3$  sensor to different concentrations (10–40 ppm) of  $\text{NH}_3$ , as illustrated by the optical image of the 30 mm fiber-shaped  $\text{NH}_3$  sensor. (b) Response and linear fitting curves for various concentrations of  $\text{NH}_3$ . Error bars represent the standard deviations obtained from at least three independent measurements.

a dark-green PANI coating. Despite its smaller size, the fiber-shaped  $\text{NH}_3$  sensor could still maintain a good response. In Fig. 6(b), we can see the response of the sensor at different  $\text{NH}_3$  concentrations and its linear fitting relationship with a correlation coefficient of 0.92. Due to the lower amount of  $\text{NH}_3$ -sensitive material on the fiber, its response was not as strong as the thin-film  $\text{NH}_3$  sensor.

We tested the response of the fiber-shaped sensor to various gases at room temperature, and the results are shown in Fig. 7(a). The responses to  $\text{CO}$ ,  $\text{H}_2\text{S}$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ , and  $\text{H}_2$  equaled 1.04, 1.05, 1.00, 1.12, 0.10, and 0.20, respectively. It can be seen from the figure that the response value of the sensor to  $\text{NH}_3$  was higher than that of other interfering gases, which proved that the sensor had good selectivity to  $\text{NH}_3$  at room temperature.

The continuous and stable response of the gas sensor to the target gas is also a very important performance. In Fig. 7(b), it can be seen that the fiber-shaped sensor was allowed to respond three times continuously to 40 ppm  $\text{NH}_3$  at room temperature to obtain a real-time resistance change curve. The analysis confirmed that the continuous response of the sensor to 40 ppm  $\text{NH}_3$  was relatively stable.

The stability of the fiber-shaped sensor was characterized by various factors, including temperature, curvature, humidity, and

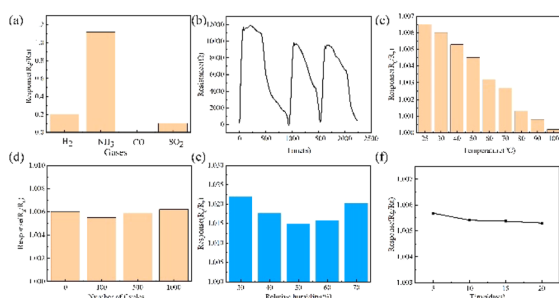


Fig. 7 (a) Response of fiber-shaped sensor towards different interference gases with a concentration of 40 ppm. (b) Cycling response toward 40 ppm  $\text{NH}_3$  at room temperature. (c) Response value of the  $\text{NH}_3$  sensor at different operating temperatures. (d) Response changes of  $\text{NH}_3$  sensors after different bending cycles. (e) Response values of the  $\text{NH}_3$  sensor at different relative humidities. (f) Temporal stability of the  $\text{NH}_3$  sensors.

time, at a concentration of 10 ppm  $\text{NH}_3$ . Fig. 7(c) shows the response of the sensor under different temperatures. As the ambient temperature increased, the sensor response value decreases from 1.0065 at 25 °C to 1.0002 at 100 °C. This indicates that the optimal operating temperature for this sensor was near room temperature. Fig. 7(d) shows the response of the sensor to  $\text{NH}_3$  after various bending cycles, and the results indicate that the response slightly improved and remained around 1.006, demonstrating excellent bending stability. This may be due to the increased porosity of the sensitive material during bending. Fig. 7(e) shows the effect of humidity on the sensor's response. From the results for the thin film sensor, it was obvious that the sensor response was affected by higher humidity. To combat this, an e-PTFE was covered on the sensor and sealed with PDMS on the end. When the humidity was as high as 70%, the response of the sensor was only 0.2% lower than that at 30% humidity. Even at 50% humidity, which was the most obvious decrease shown in the figure, the decrease was only 0.7% (Fig. 7(e)). This indicates that the e-PTFE helped the sensor resist the effects of humidity. Fig. 7(f) illustrates the change in sensor response value over time, indicating a decrease of 0.04% after 20 days of storage at room temperature. This result fell within the acceptable range and demonstrated good time stability. Table S3† presents a brief comparison of the performance of our  $\text{NH}_3$  sensor with other sensors. Compared with other room-temperature  $\text{NH}_3$  sensors, our PANI–Au– $\text{SnO}_2$  sensor showed faster response and recovery times for lower concentrations of  $\text{NH}_3$  at room temperature. In addition, the sensor based on PANI–Au– $\text{SnO}_2$  also had a higher response value than other sensors, indicating that this composite-based sensor could be applied for the potential monitoring of  $\text{NH}_3$  at room temperature.

### 3.5 Practical application

We fabricated a small PCB circuit board (Fig. S9(a)†) for data monitoring, which was connected to the fiber-shaped sensor and powered by a lithium battery. It could transmit real-time detected  $\text{NH}_3$  data to a mobile terminal or a computer terminal through Bluetooth. The sensing system depicted in Fig. S9(a)† was incorporated into the duck tongue cap *via* needle stitching, and the exposed circuit was refined with wool felt. Consequently, the  $\text{NH}_3$ -sensing duck tongue cap illustrated in Fig. S9(b)† was successfully fabricated. The cap was inserted into the testing apparatus and then  $\text{NH}_3$  was introduced. The LED display indicated the relative concentration of the  $\text{NH}_3$ . Fig. S9(c)† presents the circuit schematic of the whole system. The duck tongue cap could be expected to be used in the future to protect workers in  $\text{NH}_3$ -working environments all year round so that workers could timely understand whether the  $\text{NH}_3$  level in their environment is safe.

### 3.6 Gas-sensing mechanism

The conductive polymer PANI and its doped materials play a crucial role in the  $\text{NH}_3$  sensor. The sensitivity of the sensor was mainly attributed to the protonation and deprotonation process of PANI, which is reversible (Fig. 8(b)). This characteristic ensures that the sensitive material prepared using PANI



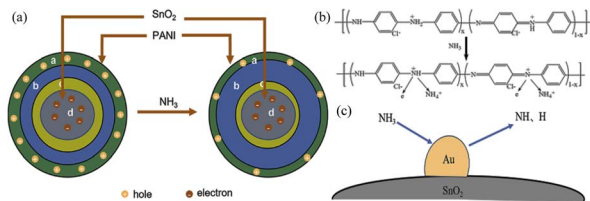


Fig. 8 (a) Mechanism diagram of the PANI–SnO<sub>2</sub> sensitive material. (b) Mechanism of the sensitivity of PANI to NH<sub>3</sub>. (c) Facilitating effect of Au to the NH<sub>3</sub> response.

can repeatedly offer NH<sub>3</sub> detection. Initially, PANI is non-conductive, but when it is doped with acid, it becomes polarized and has a dual-polarized structure, making it conductive. When the sensor is exposed to NH<sub>3</sub>, the proton acid doped in PANI reacts with NH<sub>3</sub>, resulting in the formation of NH<sub>4</sub><sup>+</sup>. This reaction causes PANI to change from a doped conductive aniline salt state to a non-conductive aniline alkali state, leading to a significant increase in resistance. However, when the NH<sub>3</sub> atmosphere is removed and the sensor is placed in fresh air, NH<sub>4</sub><sup>+</sup> decomposes into NH<sub>3</sub> and H<sup>+</sup>. The H<sup>+</sup> then participates in PANI again, transforming it into an aniline salt state and reducing the resistance, thereby restoring the conductivity.<sup>45,46</sup> The gas-sensing properties of the Au-doped SnO<sub>2</sub> composite PANI material were significantly improved. This improvement could be attributed to the formation of a p–n heterojunction between the p-type PANI and n-type SnO<sub>2</sub>, as well as the catalytic properties of the noble metal Au. The presence of a p–n heterojunction has been shown to greatly enhance the sensitivity of sensitive materials to NH<sub>3</sub>.<sup>47–49</sup> When PANI is composited with SnO<sub>2</sub> during the acidification process, it forms a core-shell structure on the surface of SnO<sub>2</sub> nanospheres, as described in Fig. 8(a). In the presence of air, the holes of PANIH<sup>+</sup> and the electrons of SnO<sub>2</sub> nanospheres diffuse toward the middle, creating a depletion layer at the interface between the two materials (regions b and c in Fig. 8). This depletion layer leads to an increase in resistance. However, in the presence of air, the depletion layer is relatively narrow, resulting in a high conductivity and low resistance of the sensitive material. When the sensor is exposed to NH<sub>3</sub>, the NH<sub>3</sub> captures H<sup>+</sup> ions in PANIH<sup>+</sup>, causing PANI to convert from an emerald salt to emerald alkali. This reduces the number of holes, resulting in a wider depletion layer (region b), which significantly increases the resistance.<sup>50,51</sup> The enhancement of performance by precious metals is mainly due to the spillover mechanism of these metals, which possess catalytic properties.<sup>52–54</sup> On the one hand, the presence of Au increases the contact between the material and the reducing gas, increasing the specific surface area of the sensitive material and improving the performance of the NH<sub>3</sub> sensor. Additionally, Au acts as a catalyst for surface catalytic activity. NH<sub>3</sub> molecules diffuse on the surface of Au and adsorb onto it. The p orbital of NH<sub>3</sub> interacts with the d orbital of the Au atom, producing a highly reducible hydrogen atom. This promotes the reaction of PANI.<sup>55–57</sup> The process is illustrated in Fig. 8(c). Therefore, Au can effectively improve the performance of the material.<sup>58–60</sup>

## 4. Conclusions

In summary, a new flexible NH<sub>3</sub> sensor based on PANI–Au–SnO<sub>2</sub> was successfully developed. We prepared a sensitive material of a PANI composite loaded with Au–SnO<sub>2</sub> through *in situ* polymerization. Thin-film and fiber-shaped NH<sub>3</sub> sensors were then prepared using a printing, coating, and impregnation method, respectively. The p–n heterojunction formed between PANI and SnO<sub>2</sub> along with the catalytic effect of Au significantly improved the gas-sensing performance of the NH<sub>3</sub> sensor. Both sensors showed good responses in the range of 5–40 ppm of NH<sub>3</sub> at room temperature. The compactness, flexibility, lightweight, and good stability of the fiber-shaped NH<sub>3</sub> sensor make it suitable for wearable NH<sub>3</sub>-sensing applications. Additionally, the NH<sub>3</sub>-monitoring system addressed the issues faced by traditional electrical signal monitoring methods and provides a solution for the entire process from preparation to application. We integrated the fiber-shaped NH<sub>3</sub> sensor on a duck tongue cap and linked this to a display screen to display the NH<sub>3</sub> content in the environment in real-time, providing a certain safety guarantee for workers working in the NH<sub>3</sub> environment, which is expected to become an important part of the application of wearable devices. However, the high error rates of the fiber-shaped NH<sub>3</sub> sensor necessitate some subsequent operations to enhance the sensor precision. Future advancements in fiber preparation and post-processing methods could be anticipated to enhance the sensor performance.

## Data availability

The data supporting this article are included in the ESI.†

## Author contributions

Qiuning Wang: conceptualization, data curation, investigation, methodology, writing—original draft. Yuan Peng: conceptualization, data curation, investigation, methodology, writing—original draft. Bin Guo: electrical guidance. Jianhai Sun: performance characterization of the sensor. Yaxia Liu: textile design guidance. Yanjun Wang: textile production. Hongyan Zhang: overall planning and guidance.

## Conflicts of interest

There are no conflicts to declare.

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