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Fast response ammonia sensor based on porous thin film of polyaniline/sulfonated nickel phthalocyanine composites

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Abstract: Porous thin film composites of PANI/NiTSPc were deposited across the gaps of interdigitated Au electrodes (IAE) by an electrochemical polymerization method. The PANI/NiTSPc films were characterized by scanning electron microscopy (SEM) images, atomic force microscopy (AFM) images, energy dispersive spectra (EDS), Raman spectra and Fourier transform infrared (FT-IR) spectra. Ammonia (NH_3) gas-sensing properties of the films prepared at optimum conditions were examined at room temperature. The observed response value (*S*) of the film to 100 ppm NH_3 was 2.75 with a response time as short as 10 s. Furthermore, fast recovery rate, good reproducibility and acceptable long-term stability were also observed over a concentration range from 5 to 2500 ppm. The outstanding sensing performance may be attributed to the porous, ultra-thin film structure and the "NH_3-capture" effect of the "flickering" NiTSPc molecules. Therefore, the proposed PANI/NiTSPc nanocomposite thin film sensors are excellent potential candidates for NH_3 detection.

Keywords: Polyaniline; Phthalocyanine; Ammonia; Sensor; Porous thin film

1. Introduction

As one of the most highly produced inorganic chemicals, ammonia (NH_3) is extensively used in many areas such as fertilizer production, clinical diagnosis and food processing[1]. However, even low concentration of NH_3 shows hazardous effects on the human respiratory system, skin and eyes. Furthermore, NH_3 is flammable at concentrations of ca. 15-28% by volume in air[2]. Therefore, the demand for a fast and sensitive NH_3 monitoring system is highly desirable across many industrial and commercial settings.

To date, there are many studies have been reported[3-11] which have evaluated materials for the purpose of NH_3 sensing. Among the employed materials, polyaniline (PANI) has been identified as one of the most important polymers, and has received much attention because of its potential applications in chemical and biological sensing[3], electronic devices[4], supercapacitor electrodes[5], as well as efficient and low cost solar cells [6]. Due to the remarkable mechanical and electrical properties e.g. low operating temperature, low cost, flexibility, and ease of manufacture, PANI also shows great potential in NH_3 detection. Fuzzy nanofibrous networks of polyaniline thin film, which showed good selectivity for NH_3 detection, was reported by G. D. khuspe and co-workers[7]; Huiling Tai et al. investigated the influence of polymerization temperature on the NH_3 sensing properties of PANI/TiO_2 thin films[8]; Masanobu Matsuguchi and Takuya Asahi reported that a DiOHP-doped PANI sensor fabricated by a novel on-substrate method showed sufficient detection sensitivity for NH_3 at concentrations of 25 ppm or less[9]. All the cited literature confirm the potential of PANI for NH_3 sensing.

Furthermore, the important macrocyclic compounds, phthalocyanines (Pc) and its derivatives, have been proved to be able to protonate the polyaniline base to form conducting PANI-Pc composites by layer-by-layer assembly[3] or by electropolymerization[10]. The composites obtained exhibited improved and attractive optical and electrocatalytic properties. Besides, Pc and its derivatives have been identified as promising candidates for gas sensors benefiting from the adjusted structure, and good film forming, high sensitivity and selectivity. Zhou et al. reported the preparation and NH_3-sensing properties of Lead(II) tetrakis(4-cumylphenoxy) phthalocyanine spin-coating films, and the results indicated that the films displayed a high and fast response and good reversibility to NH_3 at room temperature[11]; Rungnapa Tongpool reported a Lead phthalocyanine (PbPc) films containing 93.0 wt.% PbPc deposited by spin coating technique using polypyrrole (PPy) as a binder, which showed good response to NO_2[12]. In terms of meta-phthalocyanine (MePc), the center metal ion may provide the active site where coordination interactions occur and determine the selectivity of the resulting sensor[13, 14]. Thus, if the MePc could be connected to the thin film of PANI, the MePc may act as selective 'tentacles' to capture the NH_3 molecules and then transfer them to PANI chains. According to the density functional theory study on the interaction between Metalloporphyrins (a MePc analog) and NH_3[13], Ni-porphyrin (NiP) showed some relative special properties when reacted with NH_3. On the one hand, the distance between N and Ni atom was relatively long and the molecular orientation of NH_3 would invert, suggesting that the N atom is exposed outside and may be easier to interact with PANI; on the other hand; NiP showed the weakest binding energy compared with other Metalloporphyrins, which may facilitate the desorption of

NH_3. This situation may also apply to MePc with Ni ion due to their similar structure.

Therefore, the thin films of polyaniline/Nickel phthalocyanine tetrasulfonic acid (PANI/NiTsPc) composites were deposited on interdigitated Au electrodes (IAEs) with a simple and low-cost electrochemical polymerization method. The fabricated films were evaluated for their ability to detect NH_3 gas at room temperature.

2. Materials and methods

2.1. Reagents

Nickel phthalocyanine tetrasulfonic acid tetrasodium salt (NiTSPc) was obtained from Sigma-Aldrich, aniline from Sinopharm Chemical Reagent Co. Ltd (China). Aniline was distilled under reduced pressure before use. Doubly distilled water was used to prepare all solutions.

2.2. Fabrication of the PANI/NiTSPc thin film sensor

The IAEs with silicon dioxide (SiO_2) substrate were purchased from Sinoraybo nano science and technolory co., LTD (Suzhou, China) to prepare NH_3 sensors. As shown in Fig.1, the dimension of the IAE is 4 mm × 4.3 mm with electrode area of 2.4 mm × 2.25 mm and a gap of 3 μm, the thickness of the Au interdigitated 'fingers' is 100±10 nm. The IAEs were rinsed with alcohol and water successively before use.

Electrodeposition of PANI/NiTSPc composite films was performed with reference to previous report[10]. Briefly, a solution of 0.05 M aniline in 0.5 M H_2SO_4 containing different amounts of NiTSPc was used as the plating solution. The temperature of the solution was controlled at 0 ℃ using ice-water bath, and both of the two bonding pad of the IAE were connected to the working electrode of the electrochemical workstation. Preferably, the potential of the working electrode was scanned between − 0.2 and 0.9 V at 20 mV/s for one full cycle to deposit a thin film of PANI/NiTSPc composites between the interdigital ‘fingers’. When investigating the effects of NiTSPc concentration, potential limit or scan rate, the other conditions remained the same. After the modification procedure, the IAE was thoroughly rinsed with water and dried under nitrogen.

2.3. Characterization techniques

The cyclic voltammograms (CVs) were performed on a CHI660E electrochemical workstation (Chen Hua Instruments, Shanghai, China) with a three-electrode system, which employed a platinum wire as counter electrode, an Ag/AgCl (KCl (sat'd)) electrode as reference electrode. The scanning electron microscopy (SEM) images were taken on Hitachi S4800 (Hitachi, Ltd, Japan), and the energy dispersive spectra (EDS) was obtained from an X-max EDS spectrometer (Oxford, UK). The Raman spectra were obtained on a DXR Laser Raman Spectrometer (ThermoFisher, USA). Atomic force microscopy (AFM) images were obtained on a Bruker multimode-8 atomic force microscope system (Bruker, German). The FT-IR spectra were collected on a Thermo Scientific Nicolet iS50 FT-IR Spectrometer (ThermoFisher, USA).

2.4. Measurement procedure

The schematic diagram of the experimental setup[15] was illustrated in Fig.2. Experiments were performed in a temperature-controlled room at 25 ℃. Teflon tubing was used as the connection pipeline. The gas chamber (250 mL in volume) was purged with nitrogen (N_2) for 10 min before starting the tests. The standard NH_3 (5000 ppm) and pure N_2 were purchased from Jiangsu SOPO (Group) Co., Ltd. (Jiangsu, China). Concentration and humidity levels were controlled by mass flow controllers (MFC). The flow rate of the gas through the test chamber was kept at 2 L/min. The resistance of the sensor was measured by a multimeter (Agilent 34410A, USA) at two-second intervals.

The relative response of the sensor was defined as:

$$S = (R-R_0)/R_0 \qquad (1)$$

Where, R is the resistance when the sensor was exposed to NH_3 of different concentrations, R_0 is the resistance when the sensor was exposed to N_2. The response time was defined as the time taken by the sensor to attain 90% of the maximum increase in resistance on exposure of target gas and recovery time as the time to restore 90% of the maximum resistance when exposed to N_2 atmosphere[7].

3. Results and discussion

3.1. Electrodeposition of PANI/NiTSPc composite thin films

Fig.3 (a) shows the cyclic voltammogram (CV) recorded when the IAE was scanned between −0.2 and 0.9 V at 20 mV/s for 1 full cycle with a NiTSPc concentration of 2 mM. There are two groups of obvious redox peaks in the figure. For peak A, the diradical dications may be generated, which is attributed to the further oxidation of PANI in the form of quinoid (bipolaron state) as reported by literatures[10, 16]. For peak B, they derive mainly from the redox reactions of dimers, oligomers, and the degradation products such as p-benzoquinone, quinoneimines, p-aminodiphenylamine, hydroquinone, and p-aminophenol[17, 18]. As a comparison, the CV of the IAE in the electrolyte without NiTSPc is also shown. It can be observed that the peak currents are much larger when scanned in electrolyte containing NiTSPc, which indicates that much more PANI would be deposited on the surface of the IAE in the presence of NiTSPc. This may be contributed to the significant effect of the catalytic action of NiTSPc on the PANI film growth[10, 19]. The mechanism of this accelerated catalytic action may involve the formation of ion-pair complexes between protonated aniline molecules or polyaniline oligomers and peripheral sulfonic groups at the Pc ring[10]. During the electrodeposition process, the salt bridges between the SO^{3-} groups from the phthalocyanine and the protonated NH groups from PANI (see characterization in Section 3.2, explanation in Section 3.3 and Scheme 1) would appear and act as binding forces between PANI and the anionic sulfonated species[3, 20, 21].

CVs (Fig.3 (b)) for electrochemical polymerization of PANI/NiTSPc composites scanned for 5 cycles were performed to obtain further information on the electrochemical behavior. The currents of the peaks increased with the potential cycles increasing, which reflected the regular growth of the PANI films. It should be noted that the 5th cycle shows quite different behavior compared with the other cycles, which may be caused by the formation of large agglomerates as shown in the next section. Furthermore, weak oxidation peaks at around 0.16 V were observed since the 3rd cycle, which could be attributed to emeraldine/pernigraniline transformations[17].

3.2. Characterization

As mentioned above, the presence of NiTSPc in the plating solution results in the catalyzed electrodeposition of PANI-NiTSPc film, which makes it possible to build a 'bridge' between the interdigital 'fingers' of the IAEs instead of only deposit on the Au surface. To further evaluate this phenomenon, the SEM images are shown in Fig.4 to reveal the different surface morphology of the IAEs after electrochemical polymerization in the presence or absence of NiTSPc. For IAEs deposited in solution containing 2 mM NiTSPc, it is clear that a porous thin film of PANI/NiTSPc composites is formed on the surface of both the Au 'fingers' and the SiO_2 wafer between them (see Fig.4 (a), to reveal the structure more clearly, a scratch was produced with a sharp blade). The details of the porous film are shown in Fig.4 (b). The thickness of the PANI/NiTSPc film is only 100 ± 10 nm (see AFM images in Fig.4 (e)), and the resistance of the IAE is around 2.21 kΩ in N_2 atmosphere at room temperature. This porous, ultra-thin film structure could provide super large active surface areas for easy access of target gas and facilitate desorption of the absorbed chemicals during the recovery process[2, 7, 15, 22]. After scanning of 5 cycles, the thickness increased to 1000 ± 150 nm (see Fig.4 (f)) and the resistance decreased to only 2 Ω in N_2 atmosphere at room temperature. What's more, some large agglomerates independent of the thin film as shown in Fig.4 (c) came into being, which may be the reason for the unusual CV behavior mentioned in section 3.1. However, a rather different morphology was observed for IAEs scanned for 5 cycles in the absence of NiTSPc. As seen from Fig.4 (d), a more compact film of PANI formed on the surface of the Au 'fingers', while, no PANI was found on the SiO_2 substrate between them. This difference in polymerization behavior may be attributed to the attachment of NiTSPc to the surface of SiO_2 substrate through the hydrogen bond between SiO_2 and the SO^{3-} group[23, 24]. Without NiTSPc as an active site and anchor point, it would be difficult for PANI to form and adhere to the SiO_2 substrate. Thus, the resistance of the IAEs deposited in the absence of NiTSPc remained extremely high (> 1.5 GΩ, out of the measuring range), which renders them unsuitable for NH_3 sensing.

Additionally, EDS as shown in Fig.4 (g) was obtained to confirm the presence of NiTSPc in the PANI/NiTSPc composites. The EDS spectrum manifests that the composites are formed from C, N, O, Ni and S (Si comes from substrates), which indicates the existence of $-SO^{3-}$ and centre metal ions of NiTSPc.

Raman spectroscopy was further used to characterize the chemical composition of the PANI/NiTSPc composites. As shown in Fig.4 (h), the characteristic bands found at 576, 1169, 1221, 1592 cm^{-1} in the Raman spectrum agrees well with previous reports[25-34]. The Raman bands of the PANI/NiTSPc film and their assignments are summarized in Table 1. The peaks at 603 cm^{-1} and 1406 cm^{-1} exhibit the presence of pyrrole ring from NiTSPc. The band at 1333.8 cm^{-1} provides the information on the typical $C{\sim}N^{+\bullet}$ vibrations of delocalized polaronic structures from PANI. All these results confirm the formation of the PANI/NiTSPc composites.

Table 1 The Raman bands of the PANI/NiTSPc film and their assignments

Abbreviations: ν-stretching; δ-inplane bending; B-benzenoid ring; Q-quinonoid ring; SQ-semiquinonoid ring; ~-a bond intermediate between a single and a double bond; o.p.-out-of-plane.

Wavenumbers (cm^{-1})	**Assignment**	**Reference**
1592.2	ν(C–C)$_B$	[26]
1554.6	C–N–C	[27]
1485	ν(C=N)$_Q$	[26, 29]
1406	pyrrole ring	[33, 34]
1333.8	ν(C~N$^{+\bullet}$)	[28, 29, 31]
1258.6	ν(C–N)$_B$	[28, 29]
1221	ν(C–N)$_Q$	[28-30]
1169	δ(C–H) in SQ	[28, 30]
815	B ring deformation; substituted B ring deformation	[29-31]
603	pyrrole ring twisting	[27]
576	phenoxazine-type units	[28, 32]
521	ring deformation (o.p.) + silicon vibrations	[28]
415	ring deformation (o.p.)	[28]

In addition, FT-IR spectra was obtained to confirm the appearance of the salt bridges between the SO^{3-} groups and the protonated NH groups as mentioned in Section 3.1. The PANI/NiTSPc composites exhibited a similar spectrum compared with PANI as shown in Fig.4 (i). However, it should be noted that two additional peaks could be observed at 1069 and 1224 cm^{-1}. The peak at 1069 cm^{-1} could be assigned to the SO^3 stretch, which was shifted from 1061 cm^{-1} in NiTSPc since the formation of the salt bridges[35]. The peak at 1224 cm^{-1} also confirmed the appearance of the salt bridges, which was consist with previous literature[35].

3.3. Effects of NiTSPc concentration, potential limit, and scan rate

Attempts were made to optimize deposition parameters so that the composite film obtained exhibited increased sensing performance for NH$_3$. Three variables were considered during the optimization, i.e. NiTSPc concentration, potential limit and scan rate.

It was found that the NiTSPc concentration had a significant influence on the sensing performance of the deposited films, which affected both the sensitivity and response time. The dynamic resistance value of the sensor prepared in electrolyte containing 0.5 mM, 2mM and 4 mM of NiTSPc toward NH_3 of 1000 ppm is shown in Fig.5 (a), Fig.5 (b) and Fig.5 (c), respectively. Fig.5 (d) and Fig.5 (e) depict the dependence of the resistance, response (S), response time and recovery time on the concentration of NiTSPc. As can be seen, R_0 of the prepared IAE decreases dramatically with increasing NiTSPc concentration from 0.5 to 4 mM. While, the maximum reponse to 1000 ppm NH_3 is observed when the NiTSPc concentration increases to 2 mM, and the response decreases obviously with further increase of the NiTSPc concentration. These results confirm the significant catalytic effect of NiTSPc on the PANI film growth. Higher NiTSPc concentration would lead to more deposited PANI/NiTSPc composites and a thicker film and hence lower resistance. However, an excessively thick film is against the interaction between NH_3 and the composites in the inner side, thus the sensitivity decreases.

Furthermore, it should be noted that both the response time and the recovery time exhibited a downward trend with the increase in the concentration of NiTSPc, as shown in Fig.5 (e). This may be attributed to the presence of NiTSPc in the composites and the proposed mechanism is shown in Scheme 1. As mentioned in Section 3.1, the salt bridges between the SO^{3-} groups from NiTSPc and the protonated NH groups from PANI would appear and act as binding forces between PANI and NiTSPc during the deposition process[3, 20, 21, 36]. When more than one PANI chain connects to the same NiTSPc molecule, an accelerated film-forming process would be observed, explaining the catalyzed electrodeposition well. While, for some of the NiTSPc molecules, only one or two of the SO^{3-} groups were occupied, and they would flicker on the surface of the PANI chains as shown in Scheme 1 (left). It was expected that the flickering NiTSPc molecules would be vulnerable to conformational change under the influence of NH_3. It is known that the conductivity of PANI could be improved apparently by proton acids doping, and the proton-exchange reactions play a central role in the conduction mechanism in polyaniline[37]. When the PANI-NiTSPc composites were exposed to NH_3 atmosphere, the flickering NiTSPc molecules could act as efficient "tentacles" to capture NH_3 by interaction between NH_3 and Ni atom[13]. Attracted by the protonated NH groups from the adjacent PANI chains, the captured NH_3 would be transferred to the protonated N atom, and seize the proton finally[7]. Thus, the deprotonation process was completed efficiently and rapidly with the help of the flickering "tentacles", which resulted in the significant increase of the resistance and decrease of the response time. Furthermore, it is well known that the deprotonation process is reversible, the ammonium ion can be decomposed to NH_3 gas and proton when NH_3 atmosphere is removed[7]. Considering the opposing force of the Ni atom, the binding force between the ammonium ion and the deprotonated N would be weakened facilitating easier desorption of the NH_3 from PANI. Furthermore, the relative weak interaction between NH_3 and the Ni atom would also allow the NH_3 to disconnect from the NiTSPc more easily[13]. Thus, the weakened binding force and the weak NH_3-Ni interaction may offer an explanation for the downward trend of the recovery time.

In addition, both the potential limit and the scan rate influence the sensitivity of the film significantly. Fig.6 (a) shows the dependence of sensitivity and R_0 of the prepared sensors on the applied potential limit when the prepared sensors were exposed to 1000 ppm NH_3. It can be seen that the sensitivity of the prepared sensors increases in proportion with the potential limit until it reaches 0.9 V, then decreases with the further increase of the potential limit. As for potential limit less than 0.9 V, since the potential range for deposition is narrow, the rate of polymer growth is low inhibiting the likelihood that composites extend across the gap between the interdigital 'fingers'. However, when the potential limit is higher than 0.9 V, the amount of aniline deposited in each cycle becomes large and the thickness of the film would be excessively high which prevents the effective interaction between NH_3 and the composites in the inner side. Moreover, excessive oxidation of aniline reduced the activity of produced aniline[38]. A similar trend was observed when changing the scan rate from 5 to 80 mV/s as shown in Fig.6 (b), and the optimum sensing performance was observed at 20 mV/s. When the scan rate was very slow, the duration for aniline polymerization and the amount of PANI deposited become relatively increased leading to the formation of thick films. During potentiodynamic electropolymerization of aniline at very fast scan rates, the intermediates could be trapped within the PANI deposit because of fast and semi-continuing growth, this impurity may be the cause of the polymer's decreased sensitivity[38, 39].

Therefore, a NiTSPc concentration of 2 mM, potential limit of -0.2 to 0.9 V and scan rate of 20 mV/s were regarded as optimum conditions to prepare the PANI/NiTSPc thin films.

3.4. NH_3 gas sensing properties

The NH_3 sensing performance of the PANI/NiTSPc thin film sensor prepared with optimum conditions was measured at 25 °C. As shown in Fig.7 (a), the resistance of the sensor increased dramatically when exposed to different concentrations of NH_3 ranging from 5 to 2500 ppm, and then recovered toward the original value when NH_3 was replaced by N_2. The inset in Fig.7 (a) shows the details of the response-recovery property of the sensor in the range from 5 to 250 ppm. Moreover, Fig.7 (b) gives the changes in the response (*S*). The inset depicts the details at low NH_3 concentration. Results showed that the proposed PANI/NiTSPc thin film sensor exhibited an improved or comparable sensing performance to NH_3 compared with previous literatures[7, 15, 40-45] (see Table 2), especially for the significantly decreased response and recovery time. The outstanding sensing performance of the PANI/NiTSPc composites may be attributed to the porous, ultra-thin film structure[2, 7, 15, 22] and the “NH_3-capture” effect of the flickering NiTSPc molecules as explained previously.

Table 2 Response (S), response time (T_1), recovery time (T_2), studied detection range (D_R), materials (M) and measured temperature (T_M) of the various NH3 gas sensors.

Materials	S	T_1 (s)	T_2 (s)	D_R (ppm)	T_M (℃)	Authors
PANI/NiTSPc	0.60 (5 ppm), 2.75 (100 ppm)	10	46	5-2500	25	This paper
CSA doped $PANI\text{-}SnO_2$	0.91 (100 ppm)	46	3245	10-100	30	V.B. Patil[40]
Si/PANI	0.8 (20 ppm) 1.7 (90ppm)	25	360	10-90	25	Huiling Tai[41]
PANI	0.96 (100 ppm)	122	1245	10-100	25	V.B. Patil[7]
pf-MWCNT/PANI	0.015 (20 ppm), 0.075 (100 ppm)	100	700	0-100	25	Yoo et al.[42]
PANI	2.3 (100 ppm)	120	150	100	25	Basudam Adhikari[43]
Graphene/PANI	3.65 (20 ppm), 11.33 (100 ppm)	50	23	1-6400	25	Zuquan Wu[15]
ZnO film	0.27 (100 ppm)	160	660	50-600	150	Yuan-Yao Li[44]

CNFL/SnO_2	0.5 (100 ppm)	100	120	10-200	350	Sang Wook Kim[45]

3.5 Effects of humidity

To determine the effects of the relative humidity (RH), the response behavior of the PANI/NiTSPc thin film sensor exposed to 50 ppm NH_3 was tested at different RH levels at 25 ℃. Fig.8 (a) shows the dependence of R, R_0 and response(S) of the sensor on RH levels. It was found that both R and R_0 of the sensor would decreased with increasing the RH levels, which may be attributed to dissolution of NH_3 into physisorbed water and "proton effect" of water[46]. Water molecules are ionisable, and dissociate into proton (H^+) and hydroxyl ions (OH^-). There are plenty of charged sites and H-bond accepting/donating sites (–NH–, –N=, $=NH^+$–, $–NH_2^+$– etc.) within the PANI emeraldine salt membrane. These charged or polar sites would help to shift the equilibrium towards the formation of proton through charge interactions and H-bonding. Consequently, the water molecules absorbed into the PANI matrix act as a source of proton which can either increase the doping level of the polymer and/or conduct charge themselves through the network of absorbed water molecules[46-48].

However, as defined in Section 2.4, the response (S) of the sensor was decided by both R and R_0, hence S showed a different changing trend compared with R_0. The response (S) decreased with increasing the RH level until it reached 50%, then increased with the further increase of the RH level. This sensing behavior agrees well with previous published literature[49, 50]. Between 0 and 50% of RH, the deprotonation effect of NH_3 would be partially offset because of the "proton effect" of the adsorbed water, which explains the decrease in the response (*S*) of the sensor. However, when the RH level is higher than 50%, the PANI film would be solvated and allow the formation of a hydrated surface layer on the PANI fibers[50]. Since the good solubility in water, the NH_3 molecules may concentrate in the hydrated surface layer, and hence promote the deprotonation process leading to an increase in the response (*S*) of the sensor. To eliminate the influence of humidity, sensor array technique or a RH controlled testing environment may be employed in further work.

3.6. Reproducibility and stability of PANI/NiTSPc thin film sensor

The sensor reliability is strongly dependent on the reproducibility and stability exhibited by the sensor material. The reproducibility of the PANI/NiTSPc thin film sensor was measured by repeating the response measurement a number of times. Fig.8 (b) depicts the dynamic response transients of the sensor toward 1000 ppm NH_3 for 6 times. Results showed that the response of the material was almost constant confirming the reproducibility of sensor material. Furthermore, the response (*S*) of the PANI/NiTSPc thin film sensor remained 91.25% of the initial response after 60 days, which indicated an acceptable long-term stability.

3.7. Sensing performance in air

Since most of the application scenarios of NH_3 sensor would be in air, the sensing performance of the sensor was tested with air as carrier gas to demonstrate its practical applied foreground. Fig.9 presents the response behavior of the PANI/NiTSPc thin film sensor exposed to (a)50 ppm and (b)500 ppm NH_3 in air or N_2. Within experimental error, it was found that the difference in carrier gas had no significant effect on the response of the sensor, which was also observed in previous report[51]. It is well know that the response of PANI sensor to NH_3 results from its reversible doping-dedoping property, while, it is hard for CO_2 and O_2 to induce such process. Hence, it is supposed that the sensor would also work in air.

4. Conclusions

By utilizing the significant catalytic effect of NiTSPc on the PANI film growth, porous thin film of PANI/NiTSPc composites was deposited across the gaps of IAEs by electrochemical polymerization method. The SEM and AFM images revealed the morphology of the composites, and the hybridization between PANI and NiTSPc was confirmed by EDS, Raman spectra, and FT-IR spectra. The gas sensing property measurement showed that the PANI/NiTSPc nanocomposite thin film sensors exhibited fast response/recovery rate, high sensitivity, good reproducibility and acceptable long-term stability over a concentration range from 5 to 2500 ppm. This outstanding sensing performance may be attributed to the porous, ultra-thin film structure and the "NH_3-capture" effect of the flickering NiTSPc molecules. Therefore, the proposed PANI/NiTSPc nanocomposite thin film sensors are highly potential candidates for NH_3 detection.

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