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

Li Zhihua^a Zhou Xucheng^a Shi Jiyong^a Zou Xiaobo^{a,*} Huang Xiaowei^a Haroon
Elrasheid Tahir^a Mel Holmes^b

^a *College of Food and Biological Engineering, Jiangsu University, Zhenjiang 212013,
China*

^b *School of Food Science and Nutrition, the University of Leeds, Leeds LS2 9JT, United Kingdom*

** Corresponding author. Tel: +86 511 88780085; Fax: +86 511 88780201*

Email address: zou_xiaobo@ujs.edu.cn

1 **Abstract:** Porous thin film composites of PANI/NiTSPc were deposited across the gaps
2 of interdigitated Au electrodes (IAE) by an electrochemical polymerization method. The
3 PANI/NiTSPc films were characterized by scanning electron microscopy (SEM) images,
4 atomic force microscopy (AFM) images, energy dispersive spectra (EDS), Raman spectra
5 and Fourier transform infrared (FT-IR) spectra. Ammonia (NH₃) gas-sensing properties of
6 the films prepared at optimum conditions were examined at room temperature. The
7 observed response value (*S*) of the film to 100 ppm NH₃ was 2.75 with a response time as
8 short as 10 s. Furthermore, fast recovery rate, good reproducibility and acceptable long-
9 term stability were also observed over a concentration range from 5 to 2500 ppm. The
10 outstanding sensing performance may be attributed to the porous, ultra-thin film structure
11 and the “NH₃-capture” effect of the “flickering” NiTSPc molecules. Therefore, the
12 proposed PANI/NiTSPc nanocomposite thin film sensors are excellent potential
13 candidates for NH₃ detection.

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

15

16 **1. Introduction**

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

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

38 Furthermore, the important macrocyclic compounds, phthalocyanines (Pc) and its
39 derivatives, have been proved to be able to protonate the polyaniline base to form
40 conducting PANI-Pc composites by layer-by-layer assembly[3] or by
41 electropolymerization[10]. The composites obtained exhibited improved and attractive
42 optical and electrocatalytic properties. Besides, Pc and its derivatives have been
43 identified as promising candidates for gas sensors benefiting from the adjusted structure,
44 and good film forming, high sensitivity and selectivity. Zhou et al. reported the
45 preparation and NH₃-sensing properties of Lead(II) tetrakis(4-cumylphenoxy)
46 phthalocyanine spin-coating films, and the results indicated that the films displayed a
47 high and fast response and good reversibility to NH₃ at room temperature[11]; Rungnapa
48 Tongpool reported a Lead phthalocyanine (PbPc) films containing 93.0 wt.% PbPc
49 deposited by spin coating technique using polypyrrole (PPy) as a binder, which showed
50 good response to NO₂[12]. In terms of meta-phthalocyanine (MePc), the center metal ion
51 may provide the active site where coordination interactions occur and determine the
52 selectivity of the resulting sensor[13, 14]. Thus, if the MePc could be connected to the
53 thin film of PANI, the MePc may act as selective ‘tentacles’ to capture the NH₃ molecules
54 and then transfer them to PANI chains. According to the density functional theory study
55 on the interaction between Metalloporphyrins (a MePc analog) and NH₃[13], Ni-
56 porphyrin (NiP) showed some relative special properties when reacted with NH₃. On the
57 one hand, the distance between N and Ni atom was relatively long and the molecular
58 orientation of NH₃ would invert, suggesting that the N atom is exposed outside and may
59 be easier to interact with PANI; on the other hand; NiP showed the weakest binding
60 energy compared with other Metalloporphyrins, which may facilitate the desorption of

61 NH₃. This situation may also apply to MePc with Ni ion due to their similar structure.

62 Therefore, the thin films of polyaniline/Nickel phthalocyanine tetrasulfonic acid
63 (PANI/NiTSPc) composites were deposited on interdigitated Au electrodes (IAEs) with a
64 simple and low-cost electrochemical polymerization method. The fabricated films were
65 evaluated for their ability to detect NH₃ gas at room temperature.

66 **2. Materials and methods**

67 **2.1. Reagents**

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

72 **2.2. Fabrication of the PANI/NiTSPc thin film sensor**

73 The IAEs with silicon dioxide (SiO₂) substrate were purchased from Sinoraybo nano
74 science and technology co., LTD (Suzhou, China) to prepare NH₃ sensors. As shown in
75 Fig.1, the dimension of the IAE is 4 mm × 4.3 mm with electrode area of 2.4 mm ×
76 2.25 mm and a gap of 3 μm, the thickness of the Au interdigitated ‘fingers’ is 100 ± 10
77 nm. The IAEs were rinsed with alcohol and water successively before use.

78 Electrodeposition of PANI/NiTSPc composite films was performed with reference to
79 previous report[10]. Briefly, a solution of 0.05 M aniline in 0.5 M H₂SO₄ containing
80 different amounts of NiTSPc was used as the plating solution. The temperature of the
81 solution was controlled at 0 °C using ice-water bath, and both of the two bonding pad

82 of the IAE were connected to the working electrode of the electrochemical workstation.
83 Preferably, the potential of the working electrode was scanned between -0.2 and 0.9 V
84 at 20 mV/s for one full cycle to deposit a thin film of PANI/NiTSPc composites
85 between the interdigital ‘fingers’. When investigating the effects of NiTSPc
86 concentration, potential limit or scan rate, the other conditions remained the same.
87 After the modification procedure, the IAE was thoroughly rinsed with water and dried
88 under nitrogen.

89 **2.3. Characterization techniques**

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

100 **2.4. Measurement procedure**

101 The schematic diagram of the experimental setup[15] was illustrated in Fig.2.
102 Experiments were performed in a temperature-controlled room at 25 °C. Teflon tubing

103 was used as the connection pipeline. The gas chamber (250 mL in volume) was purged
104 with nitrogen (N₂) for 10 min before starting the tests. The standard NH₃ (5000 ppm) and
105 pure N₂ were purchased from Jiangsu SOPO (Group) Co., Ltd. (Jiangsu, China).
106 Concentration and humidity levels were controlled by mass flow controllers (MFC). The
107 flow rate of the gas through the test chamber was kept at 2 L/min. The resistance of the
108 sensor was measured by a multimeter (Agilent 34410A, USA) at two-second intervals.

109 The relative response of the sensor was defined as:

$$110 \quad S = (R - R_0) / R_0 \quad (1)$$

111 Where, R is the resistance when the sensor was exposed to NH₃ of different
112 concentrations, R_0 is the resistance when the sensor was exposed to N₂. The response
113 time was defined as the time taken by the sensor to attain 90% of the maximum increase
114 in resistance on exposure of target gas and recovery time as the time to restore 90% of the
115 maximum resistance when exposed to N₂ atmosphere[7].

116 **3. Results and discussion**

117 **3.1. Electrodeposition of PANI/NiTSPc composite thin films**

118 Fig.3 (a) shows the cyclic voltammogram (CV) recorded when the IAE was scanned
119 between -0.2 and 0.9 V at 20 mV/s for 1 full cycle with a NiTSPc concentration of 2 mM.
120 There are two groups of obvious redox peaks in the figure. For peak A, the diradical
121 dications may be generated, which is attributed to the further oxidation of PANI in the
122 form of quinoid (bipolaron state) as reported by literatures[10, 16]. For peak B, they
123 derive mainly from the redox reactions of dimers, oligomers, and the degradation
124 products such as p-benzoquinone, quinoneimines, p-aminodiphenylamine, hydroquinone,

125 and p-aminophenol[17, 18]. As a comparison, the CV of the IAE in the electrolyte
126 without NiTSPc is also shown. It can be observed that the peak currents are much larger
127 when scanned in electrolyte containing NiTSPc, which indicates that much more PANI
128 would be deposited on the surface of the IAE in the presence of NiTSPc. This may be
129 contributed to the significant effect of the catalytic action of NiTSPc on the PANI film
130 growth[10, 19]. The mechanism of this accelerated catalytic action may involve the
131 formation of ion-pair complexes between protonated aniline molecules or polyaniline
132 oligomers and peripheral sulfonic groups at the Pc ring[10]. During the electrodeposition
133 process, the salt bridges between the SO^{3-} groups from the phthalocyanine and the
134 protonated NH groups from PANI (see characterization in Section 3.2, explanation in
135 Section 3.3 and Scheme 1) would appear and act as binding forces between PANI and
136 the anionic sulfonated species[3, 20, 21].

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

145 **3.2. Characterization**

146 As mentioned above, the presence of NiTSPc in the plating solution results in the

147 catalyzed electrodeposition of PANI-NiTSPc film, which makes it possible to build a
148 'bridge' between the interdigital 'fingers' of the IAEs instead of only deposit on the Au
149 surface. To further evaluate this phenomenon, the SEM images are shown in Fig.4 to
150 reveal the different surface morphology of the IAEs after electrochemical polymerization
151 in the presence or absence of NiTSPc. For IAEs deposited in solution containing 2 mM
152 NiTSPc, it is clear that a porous thin film of PANI/NiTSPc composites is formed on the
153 surface of both the Au 'fingers' and the SiO₂ wafer between them (see Fig.4 (a), to reveal
154 the structure more clearly, a scratch was produced with a sharp blade). The details of the
155 porous film are shown in Fig.4 (b). The thickness of the PANI/NiTSPc film is only $100 \pm$
156 10 nm (see AFM images in Fig.4 (e)), and the resistance of the IAE is around 2.21 k Ω in
157 N₂ atmosphere at room temperature. This porous, ultra-thin film structure could provide
158 super large active surface areas for easy access of target gas and facilitate desorption of
159 the absorbed chemicals during the recovery process[2, 7, 15, 22]. After scanning of 5
160 cycles, the thickness increased to 1000 ± 150 nm (see Fig.4 (f)) and the resistance
161 decreased to only 2 Ω in N₂ atmosphere at room temperature. What's more, some large
162 agglomerates independent of the thin film as shown in Fig.4 (c) came into being, which
163 may be the reason for the unusual CV behavior mentioned in section 3.1. However, a
164 rather different morphology was observed for IAEs scanned for 5 cycles in the absence of
165 NiTSPc. As seen from Fig.4 (d), a more compact film of PANI formed on the surface of
166 the Au 'fingers', while, no PANI was found on the SiO₂ substrate between them. This
167 difference in polymerization behavior may be attributed to the attachment of NiTSPc to
168 the surface of SiO₂ substrate through the hydrogen bond between SiO₂ and the SO³⁻
169 group[23, 24]. Without NiTSPc as an active site and anchor point, it would be difficult

170 for PANI to form and adhere to the SiO₂ substrate. Thus, the resistance of the IAEs
171 deposited in the absence of NiTSPc remained extremely high (> 1.5 GΩ, out of the
172 measuring range), which renders them unsuitable for NH₃ sensing.

173 Additionally, EDS as shown in Fig.4 (g) was obtained to confirm the presence of
174 NiTSPc in the PANI/NiTSPc composites. The EDS spectrum manifests that the
175 composites are formed from C, N, O, Ni and S (Si comes from substrates), which
176 indicates the existence of -SO³⁻ and centre metal ions of NiTSPc.

177 Raman spectroscopy was further used to characterize the chemical composition of
178 the PANI/NiTSPc composites. As shown in Fig.4 (h), the characteristic bands found at
179 576, 1169, 1221, 1592 cm⁻¹ in the Raman spectrum agrees well with previous reports[25-
180 34]. The Raman bands of the PANI/NiTSPc film and their assignments are summarized in
181 Table 1. The peaks at 603 cm⁻¹ and 1406 cm⁻¹ exhibit the presence of pyrrole ring from
182 NiTSPc. The band at 1333.8 cm⁻¹ provides the information on the typical C~N⁺
183 vibrations of delocalized polaronic structures from PANI. All these results confirm the
184 formation of the PANI/NiTSPc composites.

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

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

Wavenumbers (cm^{-1})	Assignment	Reference
1592.2	$\nu(\text{C-C})_{\text{B}}$	[26]
1554.6	C-N-C	[27]
1485	$\nu(\text{C=N})_{\text{Q}}$	[26, 29]
1406	pyrrole ring	[33, 34]
1333.8	$\nu(\text{C}\sim\text{N}^{++})$	[28, 29, 31]
1258.6	$\nu(\text{C-N})_{\text{B}}$	[28, 29]
1221	$\nu(\text{C-N})_{\text{Q}}$	[28-30]
1169	$\delta(\text{C-H})$ 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]

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191 In addition, FT-IR spectra was obtained to confirm the appearance of the salt bridges
 192 between the SO_3^- groups and the protonated NH groups as mentioned in Section 3.1. The
 193 PANI/NiTSPc composites exhibited a similar spectrum compared with PANI as shown in
 194 Fig.4 (i). However, it should be noted that two additional peaks could be observed at
 195 1069 and 1224 cm^{-1} . The peak at 1069 cm^{-1} could be assigned to the SO_3^- stretch, which
 196 was shifted from 1061 cm^{-1} in NiTSPc since the formation of the salt bridges[35]. The
 197 peak at 1224 cm^{-1} also confirmed the appearance of the salt bridges, which was consist
 198 with previous literature[35].

199 3.3. Effects of NiTSPc concentration, potential limit, and scan rate

200 Attempts were made to optimize deposition parameters so that the composite film
 201 obtained exhibited increased sensing performance for NH_3 . Three variables were
 202 considered during the optimization, i.e. NiTSPc concentration, potential limit and scan

203 rate.

204 It was found that the NiTSPc concentration had a significant influence on the
205 sensing performance of the deposited films, which affected both the sensitivity and
206 response time. The dynamic resistance value of the sensor prepared in electrolyte
207 containing 0.5 mM, 2mM and 4 mM of NiTSPc toward NH₃ of 1000 ppm is shown in
208 Fig.5 (a), Fig.5 (b) and Fig.5 (c), respectively. Fig.5 (d) and Fig.5 (e) depict the
209 dependence of the resistance, response (*S*), response time and recovery time on the
210 concentration of NiTSPc. As can be seen, *R*₀ of the prepared IAE decreases dramatically
211 with increasing NiTSPc concentration from 0.5 to 4 mM. While, the maximum response to
212 1000 ppm NH₃ is observed when the NiTSPc concentration increases to 2 mM, and the
213 response decreases obviously with further increase of the NiTSPc concentration. These
214 results confirm the significant catalytic effect of NiTSPc on the PANI film growth.
215 Higher NiTSPc concentration would lead to more deposited PANI/NiTSPc composites
216 and a thicker film and hence lower resistance. However, an excessively thick film is
217 against the interaction between NH₃ and the composites in the inner side, thus the
218 sensitivity decreases.

219 Furthermore, it should be noted that both the response time and the recovery time
220 exhibited a downward trend with the increase in the concentration of NiTSPc, as shown
221 in Fig.5 (e). This may be attributed to the presence of NiTSPc in the composites and the
222 proposed mechanism is shown in Scheme 1. As mentioned in Section 3.1, the salt bridges
223 between the SO³⁻ groups from NiTSPc and the protonated NH groups from PANI would
224 appear and act as binding forces between PANI and NiTSPc during the deposition
225 process[3, 20, 21, 36]. When more than one PANI chain connects to the same NiTSPc

226 molecule, an accelerated film-forming process would be observed, explaining the
227 catalyzed electrodeposition well. While, for some of the NiTSPc molecules, only one or
228 two of the SO_3^- groups were occupied, and they would flicker on the surface of the PANI
229 chains as shown in Scheme 1 (left). It was expected that the flickering NiTSPc molecules
230 would be vulnerable to conformational change under the influence of NH_3 . **It is known**
231 **that the conductivity of PANI could be improved apparently by proton acids doping, and**
232 **the proton-exchange reactions play a central role in the conduction mechanism in**
233 **polyaniline[37].** When the PANI-NiTSPc composites were exposed to NH_3 atmosphere,
234 the flickering NiTSPc molecules could act as efficient “tentacles” to capture NH_3 by
235 interaction between NH_3 and Ni atom[13]. Attracted by the protonated NH groups from
236 the adjacent PANI chains, the captured NH_3 would be transferred to the protonated N
237 atom, and seize the proton finally[7]. Thus, the deprotonation process was completed
238 efficiently and rapidly with the help of the flickering “tentacles”, which resulted in the
239 significant increase of the resistance and decrease of the response time. Furthermore, it is
240 well known that the deprotonation process is reversible, the ammonium ion can be
241 decomposed to NH_3 gas and proton when NH_3 atmosphere is removed[7]. Considering
242 the opposing force of the Ni atom, the binding force between the ammonium ion and the
243 deprotonated N would be weakened facilitating easier desorption of the NH_3 from PANI.
244 Furthermore, the relative weak interaction between NH_3 and the Ni atom would also
245 allow the NH_3 to disconnect from the NiTSPc more easily[13]. Thus, the weakened
246 binding force and the weak NH_3 -Ni interaction may offer an explanation for the
247 downward trend of the recovery time.

248 In addition, both the potential limit and the scan rate influence the sensitivity of the

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

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

271 3.4. NH₃ gas sensing properties

272 The NH₃ sensing performance of the PANI/NiTSPc thin film sensor prepared with
 273 optimum conditions was measured at 25 °C. As shown in Fig.7 (a), the resistance of the
 274 sensor increased dramatically when exposed to different concentrations of NH₃ ranging
 275 from 5 to 2500 ppm, and then recovered toward the original value when NH₃ was
 276 replaced by N₂. The inset in Fig.7 (a) shows the details of the response-recovery property
 277 of the sensor in the range from 5 to 250 ppm. Moreover, Fig.7 (b) gives the changes in
 278 the response (*S*). The inset depicts the details at low NH₃ concentration. Results showed
 279 that the proposed PANI/NiTSPc thin film sensor exhibited an improved or comparable
 280 sensing performance to NH₃ compared with previous literatures[7, 15, 40-45] (see Table 2),
 281 especially for the significantly decreased response and recovery time. The outstanding
 282 sensing performance of the PANI/NiTSPc composites may be attributed to the porous,
 283 ultra-thin film structure[2, 7, 15, 22] and the “NH₃-capture” effect of the flickering
 284 NiTSPc molecules as explained previously.

285 **Table 2** Response (*S*), response time (*T*₁), recovery time (*T*₂), studied detection range (*D*_R),
 286 materials (*M*) and measured temperature (*T*_M) of the various NH₃ gas sensors.

Materials	<i>S</i>	<i>T</i> ₁ (s)	<i>T</i> ₂ (s)	<i>D</i> _R (ppm)	<i>T</i> _M (°C)	Authors
PANI/NiTSPc	0.60 (5 ppm), 2.75 (100 ppm)	10	46	5-2500	25	This paper
CSA doped PANI-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]
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289 3.5 Effects of humidity

290 To determine the effects of the relative humidity (RH), the response behavior of the
 291 PANI/NiTSPc thin film sensor exposed to 50 ppm NH₃ was tested at different RH levels
 292 at 25 °C. Fig.8 (a) shows the dependence of R , R_0 and response(S) of the sensor on RH
 293 levels. It was found that both R and R_0 of the sensor would decreased with increasing the
 294 RH levels, which may be attributed to dissolution of NH₃ into physisorbed water and
 295 “proton effect” of water[46]. Water molecules are ionisable, and dissociate into proton
 296 (H⁺) and hydroxyl ions (OH⁻). There are plenty of charged sites and H-bond
 297 accepting/donating sites (-NH-, -N=, =NH⁺-, -NH₂⁺- etc.) within the PANI emeraldine
 298 salt membrane. These charged or polar sites would help to shift the equilibrium towards
 299 the formation of proton through charge interactions and H-bonding. Consequently, the
 300 water molecules absorbed into the PANI matrix act as a source of proton which can either
 301 increase the doping level of the polymer and/or conduct charge themselves through the
 302 network of absorbed water molecules[46-48].

303 However, as defined in Section 2.4, the response (S) of the sensor was decided by
 304 both R and R_0 , hence S showed a different changing trend compared with R_0 . The
 305 response (S) decreased with increasing the RH level until it reached 50%, then increased
 306 with the further increase of the RH level. This sensing behavior agrees well with previous
 307 published literature[49, 50]. Between 0 and 50% of RH, the deprotonation effect of NH₃
 308 would be partially offset because of the “proton effect” of the adsorbed water, which

309 explains the decrease in the response (S) of the sensor. However, when the RH level is
310 higher than 50%, the PANI film would be solvated and allow the formation of a hydrated
311 surface layer on the PANI fibers[50]. Since the good solubility in water, the NH_3
312 molecules may concentrate in the hydrated surface layer, and hence promote the
313 deprotonation process leading to an increase in the response (S) of the sensor. To
314 eliminate the influence of humidity, sensor array technique or a RH controlled testing
315 environment may be employed in further work.

316 **3.6. Reproducibility and stability of PANI/NiTSPc thin film sensor**

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

325 **3.7. Sensing performance in air**

326 Since most of the application scenarios of NH_3 sensor would be in air, the sensing
327 performance of the sensor was tested with air as carrier gas to demonstrate its practical
328 applied foreground. Fig.9 presents the response behavior of the PANI/NiTSPc thin film
329 sensor exposed to (a)50 ppm and (b)500 ppm NH_3 in air or N_2 . Within experimental error,
330 it was found that the difference in carrier gas had no significant effect on the response of

331 the sensor, which was also observed in previous report[51]. It is well know that the
332 response of PANI sensor to NH_3 results from its reversible doping-dedoping property,
333 while, it is hard for CO_2 and O_2 to induce such process. Hence, it is supposed that the
334 sensor would also work in air.

335 **4. Conclusions**

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

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360 **Reference**

361 [1] Z. Pang, J. Fu, L. Luo, F. Huang, Q. Wei, Fabrication of PA6/TiO₂/PANI
362 composite nanofibers by electrospinning–electrospraying for ammonia sensor, *Colloids
363 and Surfaces A: Physicochemical and Engineering Aspects*, 461(2014) 113-8.

364 [2] J. Deng, R. Zhang, L. Wang, Z. Lou, T. Zhang, Enhanced sensing performance of
365 the Co₃O₄ hierarchical nanorods to NH₃ gas, *Sensors and Actuators B: Chemical*,
366 209(2015) 449-55.

367 [3] V. Zucolotto, M. Ferreira, M.R. Cordeiro, C.J.L. Constantino, W.C. Moreira, O.N.
368 Oliveira Jr, Nanoscale processing of polyaniline and phthalocyanines for sensing
369 applications, *Sensors and Actuators B: Chemical*, 113(2006) 809-15.

370 [4] U. Abaci, H.Y. Guney, U. Kadiroglu, Morphological and electrochemical
371 properties of PPy, PANi bilayer films and enhanced stability of their electrochromic
372 devices (PPy/PANi–PEDOT, PANi/PPy–PEDOT), *Electrochimica Acta*, 96(2013) 214-24.

373 [5] A.K. Sarker, J.-D. Hong, Electrochemical reduction of ultrathin graphene

374 oxide/polyaniline films for supercapacitor electrodes with a high specific capacitance,
375 Colloids and Surfaces A: Physicochemical and Engineering Aspects, 436(2013) 967-74.

376 [6] K.M. Zaidan, H.F. Hussein, R.A. Talib, A.K. Hassan, Synthesis and
377 characterization of (Pani/n-si)solar cell, Energy Procedia, 6(2011) 85-91.

378 [7] G.D. Khuspe, D.K. Bandgar, S. Sen, V.B. Patil, Fussy nanofibrous network of
379 polyaniline (PANi) for NH₃ detection, Synthetic Metals, 162(2012) 1822-7.

380 [8] H. Tai, Y. Jiang, G. Xie, J. Yu, X. Chen, Z. Ying, Influence of polymerization
381 temperature on NH₃ response of PANI/TiO₂ thin film gas sensor, Sensors and Actuators
382 B: Chemical, 129(2008) 319-26.

383 [9] M. Matsuguchi, T. Asahi, Properties and stability of polyaniline nanofiber
384 ammonia sensors fabricated by novel on-substrate method, Sensors and Actuators B:
385 Chemical, 160(2011) 999-1004.

386 [10] G. Milczarek, Self-doped polyaniline films prepared by electropolymerization
387 in the presence of sulfonated nickel phthalocyanine, Thin Solid Films, 517(2009) 6100-4.

388 [11] X. Zhou, B. Wang, Z. Han, Y. Wu, Z. Chen, C. He, Preparation and NH₃-
389 sensing properties of Lead(II) tetrakis(4-cumylphenoxy) phthalocyanine spin-coating
390 films, in: Y.H. Kim, P. Yarlagadda (Eds.), Sensors, Measurement and Intelligent Materials,
391 Pts 1-42013, pp. 45-8.

392 [12] R. Tongpool, S. Yoriya, Kinetics of nitrogen dioxide exposure in lead
393 phthalocyanine sensors, Thin Solid Films, 477(2005) 148-52.

394 [13] Z.F. Cao, Q.B. Chen, Y.X. Lu, H.L. Liu, Y. Hu, Density functional theory study
395 on the interaction between metalloporphyrins and NH₃, Int J Quantum Chem, 113(2013)
396 1137-46.

- 397 [14] C. Di Natale, R. Paolesse, A. D'Amico, I. Lundström, A. Lloyd-Spetz, Multi-
398 transduction of molecular recognition events in metalloporphyrin layers, *J Porphyr*
399 *Phthalocyanines*, 13(2009) 1123-8.
- 400 [15] Z. Wu, X. Chen, S. Zhu, Z. Zhou, Y. Yao, W. Quan, et al., Enhanced sensitivity
401 of ammonia sensor using graphene/polyaniline nanocomposite, *Sensors and Actuators B:*
402 *Chemical*, 178(2013) 485-93.
- 403 [16] Y. Cao, L. Guo, M. An, L. Zhu, X. Cui, Effects of Ethanol on Properties of
404 Polyaniline-modified Electrode Doped with Planar Binuclear Cobalt Phthalocyanine,
405 *Chin J Anal Chem*, 34(2006) 469-73.
- 406 [17] G. Milczarek, Electrochemical modification of poly-aniline films in the
407 presence of guaiacol–sulfonic acid, *Electrochem Commun*, 9(2007) 123-7.
- 408 [18] L.D. Arsov, W. Plieth, G. Koßmehl, Electrochemical and Raman spectroscopic
409 study of polyaniline; influence of the potential on the degradation of polyaniline, *J Solid*
410 *State Electrochem*, 2(1998) 355-61.
- 411 [19] I. Yilmaz, S. Arslan, S. Guney, I. Becerik, Synthesis, electro-
412 spectroelectrochemical characterization and electrocatalytic behavior towards dioxygen
413 reduction of a new water-soluble cobalt phthalocyanine containing naphthoxy-4-sulfonic
414 acid sodium salt, *Electrochimica Acta*, 52(2007) 6611-21.
- 415 [20] L.S. Li, R. Wang, M. Fitzsimmons, D.Q. Li, Surface electronic properties of
416 self-assembled, oppositely charged macrocycle and polymer multilayers on conductive
417 oxides, *J Phys Chem B*, 104(2000) 11195-201.
- 418 [21] L.S. Li, Q.X. Jia, A.D.Q. Li, Effects of organic self-assembled polymer and
419 metal phthalocyanine multilayers on the surface photovoltaic properties of indium tin

oxide and titanium oxide, *Chemistry of Materials*, 14(2002) 1159-65.

[22] S. Chen, G. Sun, High Sensitivity Ammonia Sensor Using a Hierarchical Polyaniline/Poly(ethylene-co-glycidyl methacrylate) Nanofibrous Composite Membrane, *ACS Applied Materials & Interfaces*, 5(2013) 6473-7.

[23] L.M. Jin, S.L. Yu, W.X. Shi, X.S. Yi, N. Sun, Y.L. Ge, et al., Synthesis of a novel composite nanofiltration membrane incorporated SiO₂ nanoparticles for oily wastewater desalination, *Polymer*, 53(2012) 5295-303.

[24] C.-C. Ke, X.-J. Li, Q. Shen, S.-G. Qu, Z.-G. Shao, B.-L. Yi, Investigation on sulfuric acid sulfonation of in-situ sol-gel derived Nafion/SiO₂ composite membrane, *International Journal of Hydrogen Energy*, 36(2011) 3606-13.

[25] K. De Wael, P. Westbroek, P. Bultinck, D. Depla, P. Vandenabeele, A. Adriaens, et al., Study of the deposition and Raman and XPS characterization of a metal ion tetrasulphonated phthalocyanine layer at gold surfaces: density functional theory calculations to model the vibrational spectra, *Electrochem Commun*, 7(2005) 87-96.

[26] M. Ferreira, C.J.L. Constantino, A. Riul Jr, K. Wohnrath, R.F. Aroca, J.A. Giacometti, et al., Preparation, characterization and taste sensing properties of Langmuir-Blodgett Films from mixtures of polyaniline and a ruthenium complex, *Polymer*, 44(2003) 4205-11.

[27] R.C. George, M. Durmuş, G.O. Egharevba, T. Nyokong, Electrostatic self-assembly of quaternized 2,(3)-tetra(oxo-pyridine) phthalocyaninato chloroindium(III) with a series of tetrasulfonated phthalocyanines, *Polyhedron*, 28(2009) 3621-7.

[28] M. Trchová, Z. Morávková, M. Bláha, J. Stejskal, Raman spectroscopy of polyaniline and oligoaniline thin films, *Electrochimica Acta*, 122(2014) 28-38.

- 443 [29] Z. Rozlívková, M. Trchová, I. Šeděnková, M. Špírková, J. Stejskal, Structure
444 and stability of thin polyaniline films deposited in situ on silicon and gold during
445 precipitation and dispersion polymerization of aniline hydrochloride, *Thin Solid Films*,
446 519(2011) 5933-41.
- 447 [30] G. Ciri-Marjanovic, M. Trchova, J. Stejskal, The chemical oxidative
448 polymerization of aniline in water: Raman spectroscopy, *J Raman Spectrosc*, 39(2008)
449 1375-87.
- 450 [31] Z. Liu, Z.-X. Chen, B. Jin, X. Zhang, Theoretical studies on the structures and
451 vibrational spectra of Ni, Pd, and Pt phthalocyanines, *Vibrational Spectroscopy*, 56(2011)
452 210-8.
- 453 [32] R. Tucceri, P.M. Arnal, A.N. Scian, Spectroscopic Characterization of
454 Poly(ortho-Aminophenol) Film Electrodes: A Review Article, *J Spectrosc*, (2013) 26.
- 455 [33] A. Toyama, Y. Takahashi, H. Takeuchi, Catalytic and Structural Role of a
456 Metal-Free Histidine Residue in Bovine Cu–Zn Superoxide Dismutase, *Biochemistry*,
457 43(2004) 4670-9.
- 458 [34] S. Luňák Jr, J. Vyňuchal, P. Horáčková, B. Frumarová, Z. Žák, J. Kučerík, et al.,
459 Structure and Raman spectra of pyridyl substituted diketo-pyrrolo-pyrrole isomers and
460 polymorphs, *Journal of Molecular Structure*, 983(2010) 39-47.
- 461 [35] V. Zucolotto, M. Ferreira, M.R. Cordeiro, C.J.L. Constantino, D.T. Balogh, A.R.
462 Zanatta, et al., Unusual Interactions Binding Iron Tetrasulfonated Phthalocyanine and
463 Poly(allylamine hydrochloride) in Layer-by-Layer Films, *The Journal of Physical*
464 *Chemistry B*, 107(2003) 3733-7.
- 465 [36] D.H. Huh, M. Chae, W.J. Bae, W.H. Jo, T.-W. Lee, A soluble self-doped

466 conducting polyaniline graft copolymer as a hole injection layer in polymer light-emitting
467 diodes, *Polymer*, 48(2007) 7236-40.

468 [37] W.W. Focke, G.E. Wnek, Y. Wei, Influence of oxidation state, pH, and
469 counterion on the conductivity of polyaniline, *Journal of Physical Chemistry*, 91(1987)
470 5813-8.

471 [38] M. Babaiee, M. Pakshir, B. Hashemi, Effects of potentiodynamic
472 electropolymerization parameters on electrochemical properties and morphology of
473 fabricated PANI nanofiber/graphite electrode, *Synthetic Metals*, 199(2015) 110-20.

474 [39] D.E. Stilwell, S.M. Park, *Electrochemistry of Conductive Polymers: V . In Situ*
475 *Spectroelectrochemical Studies of Polyaniline Films*, *Journal of The Electrochemical*
476 *Society*, 136(1989) 427-33.

477 [40] G.D. Khuspe, S.T. Navale, M.A. Chougule, V.B. Patil, Ammonia gas sensing
478 properties of CSA doped PANi-SnO₂ nanohybrid thin films, *Synthetic Metals*, 185–
479 186(2013) 1-8.

480 [41] H. Tai, X. Xu, Z. Ye, C. Liu, G. Xie, Y. Jiang, P–P heterojunction sensor of self-
481 assembled polyaniline nano-thin film/microstructure silicon array for NH₃ detection,
482 *Chemical Physics Letters*, 621(2015) 58-64.

483 [42] K.-P. Yoo, K.-H. Kwon, N.-K. Min, M.J. Lee, C.J. Lee, Effects of O₂ plasma
484 treatment on NH₃ sensing characteristics of multiwall carbon nanotube/polyaniline
485 composite films, *Sensors and Actuators B: Chemical*, 143(2009) 333-40.

486 [43] P.P. Sengupta, P. Kar, B. Adhikari, Influence of dopant in the synthesis,
487 characteristics and ammonia sensing behavior of processable polyaniline, *Thin Solid*
488 *Films*, 517(2009) 3770-5.

489 [44] C.-F. Li, C.-Y. Hsu, Y.-Y. Li, NH₃ sensing properties of ZnO thin films
490 prepared via sol-gel method, *Journal of Alloys and Compounds*, 606(2014) 27-31.

491 [45] S.-K. Lee, D. Chang, S.W. Kim, Gas sensors based on carbon nanoflake/tin
492 oxide composites for ammonia detection, *Journal of Hazardous Materials*, 268(2014)
493 110-4.

494 [46] F.-W. Zeng, X.-X. Liu, D. Diamond, K.T. Lau, Humidity sensors based on
495 polyaniline nanofibres, *Sensors and Actuators B: Chemical*, 143(2010) 530-4.

496 [47] P.K. Kahol, A.J. Dyakonov, B.J. McCormick, An electron-spin-resonance study
497 of polyaniline and its derivatives: polymer interactions with moisture, *Synthetic Metals*,
498 84(1997) 691-4.

499 [48] M. Matsuguchi, A. Okamoto, Y. Sakai, Effect of humidity on NH₃ gas
500 sensitivity of polyaniline blend films, *Sensors and Actuators B: Chemical*, 94(2003) 46-
501 52.

502 [49] M. Bouhadid, N. Redon, H. Plaisance, J. Desbrières, S. Reynaud, Effect of
503 Humidity on Ammonia Gas Sensitivity of Intrinsically Conducting Composite Films,
504 *Macromolecular Symposia*, 268(2008) 9-13.

505 [50] T. Mérian, N. Redon, Z. Zujovic, D. Stanisavljev, J.L. Wojkiewicz, M.
506 Gizdavic-Nikolaidis, Ultra sensitive ammonia sensors based on microwave synthesized
507 nanofibrillar polyanilines, *Sensors and Actuators B: Chemical*, 203(2014) 626-34.

508 [51] S. Virji, R.B. Kaner, B.H. Weiller, Hydrogen Sensors Based on Conductivity
509 Changes in Polyaniline Nanofibers†, *The Journal of Physical Chemistry B*, 110(2006)
510 22266-70.

511