



in situ Chemical Synthesis of PANI by Using Aromatic Carboxylic Acid as Dopant for Detection of Ammonia at Room Temperature

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In this work, polyaniline (PANI) film was successfully synthesized by *in situ* chemical polymerization technique by using aromatic carboxylic acids like benzoic acid, *p*-methoxybenzoic acid and *p*-nitrobenzoic acid, doped in presence of ammonium persulphate as an oxidant. Electric conductivity study of doped polyaniline has been studied concerning temperature. Surface composition morphology and structure of synthesized carboxylic acid doped polyaniline were characterized *via* different methods such as the electrical conductivity by two probes, UV-vis spectroscopy, FTIR spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The PANI based ammonia gas sensor was synthesized by using, benzoic acid, *p*-methoxybenzoic acid and *p*-nitrobenzoic acid as dopant which has excellent selectivity towards NH₃ and 28, 426 and 327% response of ammonia gas at 100 ppm concentration, respectively at room temperature.

Keywords: Gas sensing, Polyaniline, Conductivity, *in situ* Chemical polymerization, Ammonia.

INTRODUCTION

In earlier days, optical procedure for gas recognition has become striking due to their insensitivity to magnetic interference, quick reply instant and potential use in a hazardous surrounding [1]. Electrical conducting polymers, like polythiophene (PTh), polypyrrole (PPy), polyaniline (PANI), are used as the active films of gas sensors. The commercially accessible sensors, base typically on inorganic metal containing oxides and worked at above normal temperature. The electrically conducting polymers area short response time and high sensitivities [2]. The electrically conducting polymer materials have so many applications for new technologies, like storage of energy, electronic devices, electromagnetic interference and gas sensors. By advantage of their electrical conduction and chemical structural characteristics, organic conducting polymers have enlarged significance as current resources [3]. At current, polyaniline doped with several acid protons is the large amount capable key electrically conducting polymers due to their comparatively large thermal and environmental steadiness and cost-effective manufacturing ways [4]. In the synthesis of PANI, many inorganic acids are used like phosphoric acid and sulfuric acid, but they are rarely used for the enhanced conductivity of

PANI. while mostly PANI is synthesized in dilute HCl [5]. Polyaniline can be reduced and reversibly oxidized between three different forms, pernigraniline, emeraldine and leuco-emeraldine [6]. PANI occurs in two diverse natures of emeraldine salt as a conductive form and emeraldine base as an insulating form. These two kinds of PANI retain their particular chemical and physical properties [7]. The type of dopant ions have an effect on the electrical conductivity of PANI [8]. The development of extremely conjugated π -bond arrangements in the electrically conducting polymers indication significant optical, electric and physico-chemical properties in massive areas such as electrochemical actuators, light-emitting diodes, sensors, redox capacitors, drug delivery systems, field-effect transistor fabrications [9].

The living atmosphere exposes humans to a diversity of poisonous vapours and gases such as NO₂, NH₃, SO₂, this has intended the event of sensitive and species individual observance sensors, that area unit able of police investigation such virulent gas [10]. Ammonia gas, one in every one of the harmful gases, free by the majority agricultural production and chemical industries, has toxic nauseating odour and harsh to eyes and metastasis body part [11,12]. By the national standard of workplace hazardous occupational exposure limits, the

majority acceptable concentration of ammonia in the area of the workplace is 40 ppm, hence, improvement of NH₃ gas sensing element with large gas sensing concert together with little recognition edge and high sensitivity [13].

Herein, the synthesis of PANI using benzoic acid, *p*-methoxybenzoic acid and *p*-nitrobenzoic acid as a dopant for ammonia gas sensing is reported. Also, the effects of these carboxylic acids on the structure and morphological changes in PANI by FTIR, UV-vis, X-ray diffraction, scanning electron microscopy (SEM) were also investigated. The doped PANI was used for the recognition of NH₃ gas at room temperature. The results indicate that the doped PANI sensor shows enhanced NH₃ sensing properties compared to the pure PANI sensors. Easy, strong sensitivity, selectivity along longstanding constancy at low ammonia concentration are attractive features of the synthesized PANI sensor.

EXPERIMENTAL

As obtained, ammonium persulphate (Merck) was used. By vacuum distillation, aniline (Merck) was purified for earlier use. As ordered, benzoic acid, *p*-methoxybenzoic acid and *p*-nitrobenzoic acid (Thomas-Baker) were used. Throughout the experiments, double-distilled deionized water was used. From Sigma-Aldrich, ammonia (NH₃) and dried out air were purchased and used as obtained.

Synthesis of polyaniline (PANI): To a magnetically stirred of 1 M HCl in distilled water (40 mL) at 0 °C (ice bath) added aniline (1 g) dropwise. A solution of ammonium persulphate (3 g) was prepared by adding in 40 mL distilled water which was then added gradually more than 10-15 min at 0-5 °C. The formed solution was kept under constant stirring for 24 h. The green colour precipitate was washed with distilled water and then finally with absolute ethanol to eliminate additional HCl. The solid was then dried in a vacuum oven at 60 °C at 24 h and ground to a fine powder using mortar and pestle.

***in situ* Synthesis of PANI composite:** The polyaniline was synthesized by using the *in situ* polymerization technique. The mixture of 1 g of aniline in 40 mL of distilled water and 0.75 g of benzoic acid, *p*-methoxybenzoic acid and *p*-nitrobenzoic acid was kept under constant stirring between 0-5 °C, respectively. This solution containing 3 g of ammonium persulphate in 40 mL of distilled water was slowly added in dropwise 15-20 min intervals. The reaction mixture was kept under constant stirring for 24 h. At room temperature precipitated polymer was washed with distilled water and finally with ethanol to remove excess acid. The green colour precipitate was then dehydrated in a vacuum oven at 60 °C for 24 h. The dehydrated mass was ground to a fine powder using mortar and pestle.

Characterization and ammonia gas sensing measurements: The UV-vis spectroscopy, the surface morphology of polyaniline film was studied through scanning electron microscopy (MIRA3TESCAN) and the structure of PANI films was investigated *via* X-ray diffractometer (Rigaku, UltimanIV diffractometer). FTIR spectroscopy (Perkin-Elmer 100) explores the chemical structure and bonding features. The gas sensing activities of the PANI film sensor were specifically studied using a custom-development room temperature gas sensing

setup attached with a programmable electrometer (Keithley 6514 System). The sensing dimension was permeable out at 40% absolute moisture. In air (R_a) and test gas (R_g), the electrical resistance of the sensor film was reported and the resulting responses were calculated by following eqn. 1:

$$\text{Responses (\%)} = \frac{R_a - R_g}{R_a} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

UV-vis analysis: The UV-vis signal was observed near 440 nm and is assigned to the transition π - π^* that corresponds to the degree of conjugation in the polymer chain between neighbouring benzene rings. The peak of absorption at about 600-640 nm, which is known to excite the transition from the benzenoid to the quinoid segment triggered by the transmission of interchain charge [14-16]. Hydrogen-bonding has identified a wide-ranging band at 440-450 nm owing to polaron/bipolaron transition [17]. The UV-vis spectra were observed for PANI-*p*-methoxybenzoic acid doped PANI signals at 454 and 603 nm. While the peak was observed at 441 and 610 nm in Fig. 1c of PANI-*p*-methoxybenzoic acid and 448 and 636 nm was observed in Fig. 1d of PANI-*p*-nitro methoxybenzoic acid. These findings show that the polymers are in the emeraldine state, which can be converted to a conductive emeraldine salt by acid treatment. Generally, organic acid doped polyaniline increases their mobility in a chain of the polymer without the fall on the pH of a polymer solution.

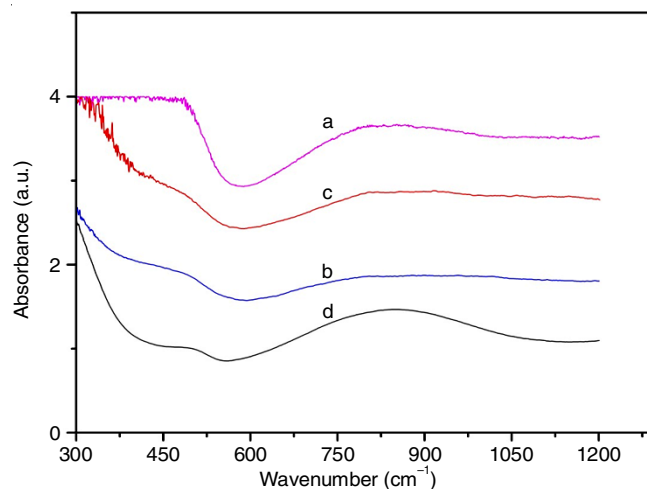


Fig. 1. UV-vis spectra of solutions in DMSO of (a) PANI, (b) benzoic acid PANI, (c) PANI-*p*-methoxybenzoic acid, (d) PANI-*p*-nitrobenzoic acid

Fourier transform infrared spectroscopy analysis: The FTIR spectra of PANI and PANI-benzoic acid PANI, PANI-*p*-methoxybenzoic acid, PANI-*p*-nitrobenzoic acid is shown in Fig. 2. The occurrence of quinoid C=C and benzenoid C=C stretching vibrations was observed at 1534, 1542, 1570 and 1578 cm⁻¹, correspondingly, confirmed the formation of Emeraldine salt of PANI. The band at 3400-3220 cm⁻¹ due to the -NH stretching of aromatic amines, at 2987-2980 cm⁻¹ due to aromatic CH-stretching and 545-520 cm⁻¹ due to CH

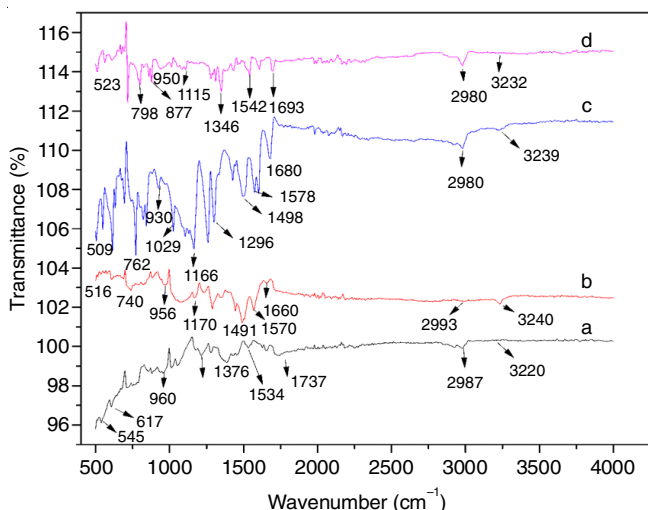


Fig. 2. FTIR assignments of (a) PANI, (b) PANI-benzoic acid, (c) PANI-*p*-methoxybenzoic acid, (d) PANI-*p*-nitrobenzoic acid

out-of-plane bending vibration [18]. The shift of bands to higher wavelengths such as 1570-1534 and 1578-1542 cm^{-1} , respectively to doped PANI is the major maybe due to the quinoid rings change into benzenoid rings [19]. The bands at 1693, 1680 and 1660 cm^{-1} correspond to carboxyl groups (benzoic acid, *p*-methoxybenzoic acid and *p*-nitrobenzoic acid) of the dopant. The bands observed at 956, 950 and 930 cm^{-1} respectively to the doped PANI. The charge delocalization upon the polymer ring is described by PANI, which are the characteristic conduction bands. PANI shows a characteristic conduction band corresponding to the charge delocalization upon the polymer ring [20]. In-plane bending vibration of the C-H mode causes the bands in the 1170-1115 cm^{-1} range.

X-ray diffraction studies: The XRD spectra of benzoic acid, PANI-*p*-methoxybenzoic acid and PANI-*p*-nitrobenzoic acid doped electrical conducting PANI thin films were recorded at 2θ from 10° to 80° range is shown in Fig. 3. The sharp intense peaks and some weak peaks with short intensity were detected and these peaks suggested that the carboxylic acids doped PANI films have microcrystalline nature [21-23].

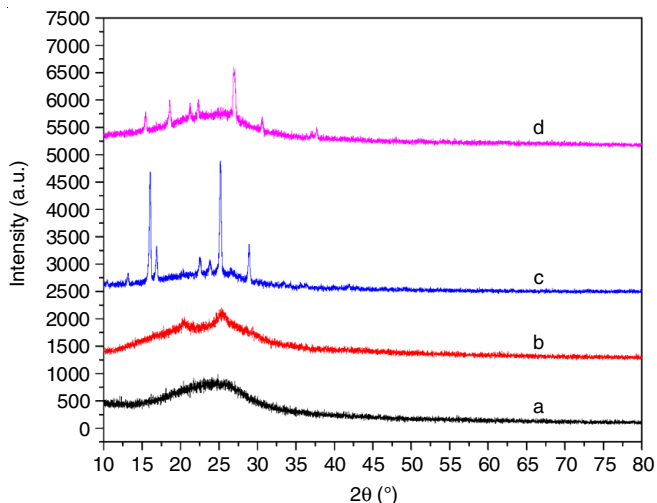


Fig. 3. X-ray diffractogram of (a) PANI, (b) PANI-benzoic acid, (c) PANI-*p*-methoxybenzoic acid, (d) PANI-*p*-nitrobenzoic acid

The organic acid doped PANI show well distinct sharp peaks (2θ) with high-intensity were detected at 20.52° and 25.24° for PANI-benzoic acid, 13.53° , 15.91° , 16.96° , 22.50° , 23.66° , 25.11° and 29.00° for *p*-methoxybenzoic acid 15.53° , 18.67° , 18.67° , 22.35° , 26.96° , 30.63° and 37.72° for PANI-*p*-nitro methoxybenzoic acid correspondingly which expressed the steady monomeric unit polymer existing in the sample with a planar phenyl ring which is closely packed [24,25].

SEM studies: The two-dimensional surface morphology image of PANI and doped PANI thin films have been studied by using the scanning electron microscopy technique. Fig. 4 shows the SEM images of PANI thin film exhibits a small aggregated granular structure. The grain size of pure PANI (Fig. 4a) film was found $2 \mu\text{m}$ with low porosity. While the SEM images of PANI-benzoic acid (Fig. 4b) show regular granules whose grain size was found $1.66 \mu\text{m}$ and its porosity is small that will produce a high conducting compound [26]. The PANI-*p*-methoxybenzoic acid shows that the film has a highly porous nature with grain size $1.42 \mu\text{m}$ (Fig. 4c). The SEM image of PANI-*p*-nitrobenzoic acid (Fig. 4d) shows that the film has porous nature with a grain size of $2.5 \mu\text{m}$. The SEM image indicated that benzoic acid and substituted benzoic acids doping has a strong impact on PANI morphology, as PANI has different structures such as nanofibers, granular, etc. [27].

Conductivity measurement: The DC electrical conductivity of doped PANI film was conducted using custom fabricated two probe method at the 35-140 K temperature range and their temperature dependence can be integral to a usual Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{KT}\right)$$

where E_a is the conductivity activation energy.

The DC electrical conductivity dependent is shown in Fig. 5. The PANI structure shows the chain of a regular arrangement of PANI monomer units given that conjugations of π -electron clouds on the aromatic ring and the electron pair on the nitrogen atoms are unshared pair, which overlap below and above the polymer chain plane.

The effect of substituents on PANI's electronic physical phenomenon is determined by their composition. The electron-withdrawing group in the macromolecule causes a decrease or increase in electrical conductivity, which is caused by completely different factors. The conductivity of PANI-*p*-nitrobenzoic acid film showed the highest conductivity than PANI-benzoic acid and *p*-methoxybenzoic acid PANI film. The PANI-*p*-nitrobenzoic acid gives high electrical conductivity (Table-1) showed various temperature-dependent DC conductivity values.

Gas sensing study: The change in resistance of the doped PANI sensors in the presence of air and ammonia atmosphere was deliberately arranged to analyze the response. The PANI sensor electrical resistance change was calculated as a function of time through the 6514 Keithley CPU interface electrometer. PANI sensor response was calculated by eqn. 3:

$$\text{Responses (\%)} = \frac{R_a - R_g}{R_a} \times 100 \quad (3)$$

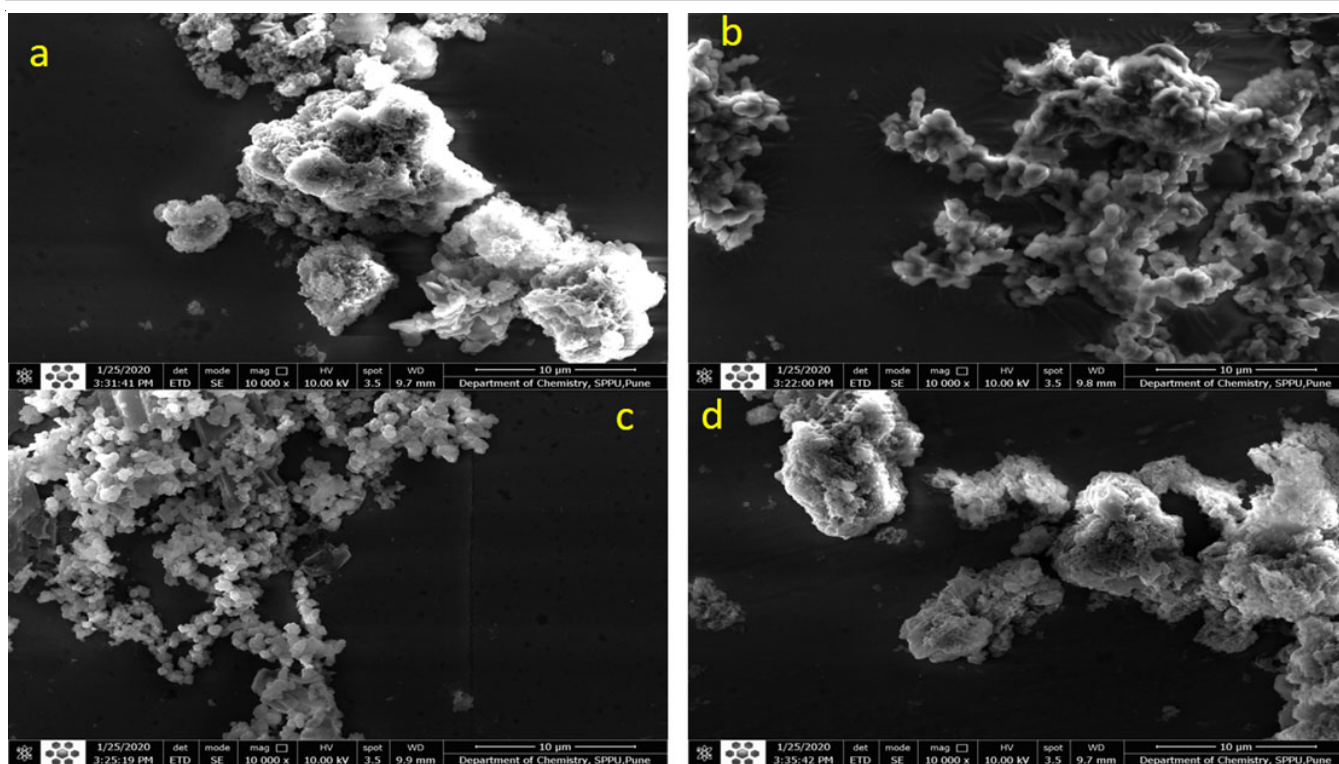


Fig. 4. SEM micrograph of (a) PANI, (b) PANI-benzoic acid, (c) PANI-*p*-methoxy benzoic acid, (d) PANI-*p*-nitrobenzoic acid

TABLE-1
DC ELECTRICAL CONDUCTIVITY ($S\text{ cm}^{-1}$) OF DOPANT

	35 °C	50 °C	100 °C	135 °C
PANI-benzoic acid	3.25×10^{-4}	3.56×10^{-4}	3.97×10^{-4}	4.35×10^{-4}
PANI- <i>p</i> -methoxybenzoic acid	1.05×10^{-4}	2.17×10^{-4}	3.43×10^{-4}	4.75×10^{-4}
PANI- <i>p</i> -nitrobenzoic acid	2.06×10^{-3}	2.74×10^{-3}	3.06×10^{-3}	4.65×10^{-3}

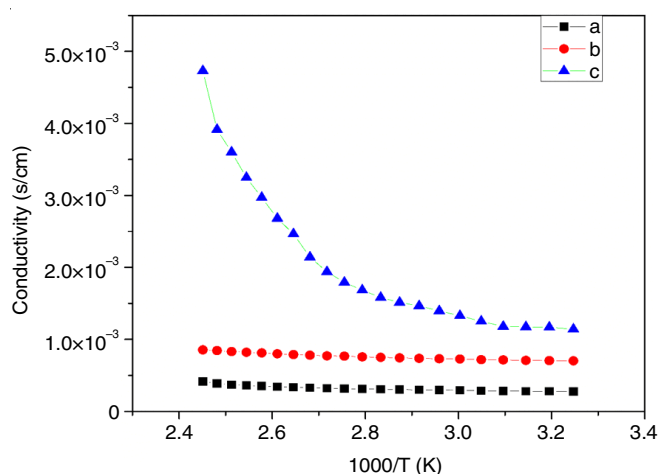


Fig. 5. Conductivity of (a) PANI-benzoic acid, (b) PANI-*p*-methoxybenzoic acid, (c) PANI-*p*-nitrobenzoic acid

where R_a and R_g are the doped PANI sensor film resistance values in the occurrence of ambient air and the ammonia gas, correspondingly.

Response study: In terms of percentage response characteristics, the sensing efficiency of PANI films was evaluated by exposing them to various ammonia (1-100 ppm) concentra-

tions (Fig. 6). The relative plot shows doped PANI shifts in time sensing response at room temperature to 100 ppm ammonia concentrations. The results of the gas response obtained in the existent study are associated with the accessible information on polyaniline-centered sensors. The PANI shows a 30% response at 100 ppm ammonia gas [28,29]. The PANI-*p*-methoxybenzoic acid shows an ammonia gas sensor reveals a good response of

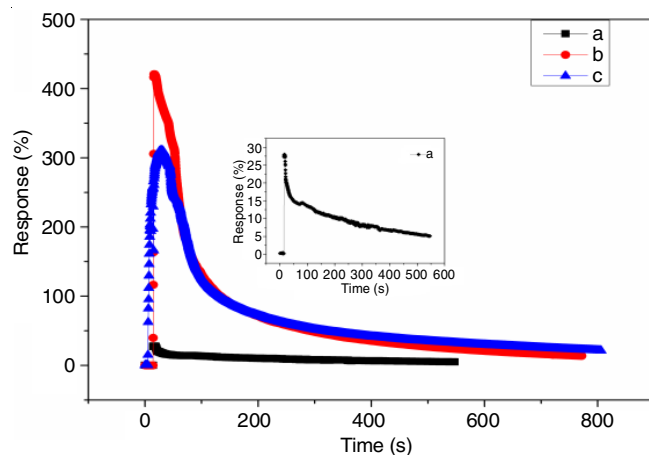


Fig. 6. Response study of (a) PANI-benzoic acid, (b) PANI-*p*-methoxybenzoic acid, (c) PANI-*p*-nitrobenzoic acid 100 ppm NH_3

426% with a response time of 13 s while PANI-*p*-nitrobenzoic acid shows 317% with a response time of 28 s and PANI-benzoic acid shows 28.18% with a response time of 17 s. The shift in response is primarily related to the NH₃ gas concentration. A great response at greater attention suggests that the extreme quantity of dynamic interface locations obtainable for NH₃ gas adsorption on the doped PANI film surface exists.

Gas sensing mechanism: It is recognized that polyaniline film sensor gas retort mostly regulated by the doping reaction, *i.e.* the method of protonation and deprotonation [10,12,13,30,31]. In this study, a rise in resistance of polyaniline film sensor upon the interface of ammonia gas fragments was observed. Ammonia is a reducing gas and retains an electron-donating nature. Neutral polyaniline gain proton which causes the doping reaction and encouraged the N⁺-H bonds, foremost to the enlargement of positive charge local center situated at N-atoms. This enables valence electrons to transport from one center to another compound chain or the adjacent molecules, resulting an increase in the electrical conductivity. When the polyaniline thin-film sensing element is exposed to ammonia gas particles, it receives proton to form the emeraldine base of polyaniline in the form of NH₄⁺ particle and reducing the PANI doping level, so turning it into an oxidized form. Thus, due to the loss of a proton, the electron's compactness will increase and therefore, the physical phenomenon reductions, increasing the resistance of the PANI system [10,30]. In comparison, after it has been exposed to contemporary air, the reaction path has been reversed and the system resistance decreases. If exposed to sunlight, the PANI film system collects chemical elements from NH₄⁺ particles and reestablishes early PANI doping stage, which can be attached to the H⁺ particle to produce an N-H bond and thus doped PANI film resistance improves to the starting point stage. The sensing results show that for NH₃ molecules, the desorption and adsorption process for doped PANI film remained extremely reversible. In previous studies [10,12,13,30,31], the same form of interface among the square measure of PANI and gas molecules accounted for.

The method among fragments of polyaniline and ammonia gas is shown below:



In presence of NH₃ gas molecules, the reaction (eqn. 3) stability goes mostly in the way of the righthand portions. Whereas, in the existence of air, the reaction balance is reconditioned.

Conclusion

In this work, PANI was synthesized by *in situ* chemical oxidation polymerization using benzoic acid and substituted benzoic acids as a dopant. Since, the polaron rate in PANI-*p*-nitrobenzoic acid is higher than in PANI-*p*-methoxybenzoic acid and PANI-benzoic acid, the conductivity clearly showed that PANI-*p*-nitrobenzoic acid has a higher conductive property than PANI-*p*-methoxybenzoic acid and PANI-benzoic acid. The gas sensing results showed that PANI-*p*-methoxybenzoic acid film is extremely sensitive to NH₃ gas, with a maximum ammonia sensing response of 426% and a response time of 15 s at room temperature. While the PANI-benzoic acid and

PANI-*p*-nitrobenzoic acid sensors show 28.18% with a rapid response time of 17 s and 317% with a slow response time of 28 s, respectively. Gas sensing results showed that the doped PANI films are found to be an extremely eye-catching ammonia gas sensing material and has a high-quality potential in domestic and industrial areas for gas sensing applications.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- A. Airoudj, D. Debarnot, B. Bêche and F. Poncin-Epaillard, *Anal. Chem.*, **80**, 9188 (2008); <https://doi.org/10.1021/ac801320g>
- H. Bai and G. Shi, *Sensors*, **7**, 267 (2007); <https://doi.org/10.3390/s7030267>
- P.P. Sengupta, S. Barik and B. Adhikari, *Mater. Manuf. Process.*, **21**, 263 (2006); <https://doi.org/10.1080/10426910500464602>
- X. Lu, H.Y. Ng, J. Xu and C. He, *Synth. Met.*, **128**, 167 (2002); [https://doi.org/10.1016/S0379-6779\(01\)00668-3](https://doi.org/10.1016/S0379-6779(01)00668-3)
- J. Stejskal, D. Hlavatá, P. Holler, M. Trchová, J. Prokeš and I. Sapurina, *Polym. Int.*, **53**, 294 (2004); <https://doi.org/10.1002/pi.1406>
- G.M. Spinks, A.J. Dominis and G.G. Wallace, *Corrosion*, **59**, 22 (2003); <https://doi.org/10.5006/1.3277532>
- A.G. MacDiarmid, *Curr. Appl. Phys.*, **1**, 269 (2001); [https://doi.org/10.1016/S1567-1739\(01\)00051-7](https://doi.org/10.1016/S1567-1739(01)00051-7)
- A. Mostafaei and A. Zolriasatein, *Prog. Nat. Sci. Mater. Int.*, **22**, 273 (2012); <https://doi.org/10.1016/j.pnsc.2012.07.002>
- M.R. Devi, A. Saranya, J. Pandiarajan, N. Prithivikumar, J. Dharmaraja and N. Jeyakumar, *J. King Saud Univ. Sci.*, **31**, 1290 (2019); <https://doi.org/10.1016/j.jksus.2018.02.008>
- D. Xie, Y. Jiang, W. Pan, D. Li, Z. Wu and Y. Li, *Sens. Actuators B Chem.*, **81**, 158 (2002); [https://doi.org/10.1016/S0925-4005\(01\)00946-7](https://doi.org/10.1016/S0925-4005(01)00946-7)
- Y. Hou and A.H. Jayatissa, *Appl. Surf. Sci.*, **309**, 46 (2014); <https://doi.org/10.1016/j.apsusc.2014.04.158>
- S. Bai, Y. Tian, M. Cui, J. Sun, Y. Tian, R. Luo, A. Chen and D. Li, *Sens. Actuators B Chem.*, **226**, 540 (2016); <https://doi.org/10.1016/j.snb.2015.12.007>
- S.P. Li, L. Lin, L. Zhao, C. Wang, D. Liu, F. Liu, P. Sun, X. Liang, F. Liu, X. Yan, Y. Gao and G. Lu, *Sens. Actuators B Chem.*, **259**, 505 (2018); <https://doi.org/10.1016/j.snb.2017.11.081>
- J. Stejskal, M. Omastova, S. Fedorova, J. Prokes and M. Trchova, *Polymer*, **44**, 1353 (2003); [https://doi.org/10.1016/S0032-3861\(02\)00906-0](https://doi.org/10.1016/S0032-3861(02)00906-0)
- M.M. Ayad, N.A. Salahuddin, A.K. Abou-Seif and M.O. Alghaysh, *Eur. Polym. J.*, **44**, 426 (2008); <https://doi.org/10.1016/j.eurpolymj.2007.11.025>
- E.T. Kang, K.G. Neoh and K.L. Tan, *Prog. Polym. Sci.*, **23**, 277 (1998); [https://doi.org/10.1016/S0079-6700\(97\)00030-0](https://doi.org/10.1016/S0079-6700(97)00030-0)
- R. Gangopadhyay, A. De and G. Ghosh, *Synth. Met.*, **123**, 21 (2001); [https://doi.org/10.1016/S0379-6779\(00\)00573-7](https://doi.org/10.1016/S0379-6779(00)00573-7)
- D.C. Trivedi and S.K. Dhawan, *Synth. Met.*, **58**, 309 (1993); [https://doi.org/10.1016/0379-6779\(93\)91140-W](https://doi.org/10.1016/0379-6779(93)91140-W)
- H. Yan and N. Toshima, *Synth. Met.*, **69**, 151 (1995); [https://doi.org/10.1016/0379-6779\(94\)02398-1](https://doi.org/10.1016/0379-6779(94)02398-1)
- S. Stafström, B. Sjögren, O. Wennerström and T. Hjertberg, *Synth. Met.*, **16**, 31 (1986); [https://doi.org/10.1016/0379-6779\(86\)90151-7](https://doi.org/10.1016/0379-6779(86)90151-7)
- M.A. Estermann, W.I.F. David, K. Shankland, L.B. McCusker and C. Baerlocher, *Structure Determination from Powder Diffraction Data*, Oxford Science Publications: New York (2002).
- H.P. Klug and L. E. Alexander, *X-Ray Diffraction Procedures: for Polycrystalline and Amorphous Materials*, p. 992 (1974).

23. A.M. Goldstein, *Handbook of Psychology: Forensic Psychology*, John Wiley & Sons Inc., Vol. 11 (2003).
24. H.K. Chaudhari and D.S. Kelkar, *Polym. Int.*, **42**, 380 (1997); [https://doi.org/10.1002/\(SICI\)1097-0126\(199704\)42:4<380::AID-PI727>3.0.CO;2-F](https://doi.org/10.1002/(SICI)1097-0126(199704)42:4<380::AID-PI727>3.0.CO;2-F)
25. S. Singh, M. Chawla, P.F. Siril and G. Singh, *Thermochim. Acta*, **597**, 85 (2014); <https://doi.org/10.1016/j.tca.2014.10.016>
26. J. Stejskal and R.G. Gilbert, *Pure Appl. Chem.*, **74**, 857 (2002); <https://doi.org/10.1351/pac200274050857>
27. P.S. Shewale, V.B. Patil, S.W. Shin, J.H. Kim and M.D. Uplane, *Sens. Actuators B Chem.*, **186**, 226 (2013); <https://doi.org/10.1016/j.snb.2013.05.073>
28. A.N. Andriianova, Y.N. Biglova and A.G. Mustafin, *RSC Adv.*, **10**, 7468 (2020); <https://doi.org/10.1039/C9RA08644G>
29. D.K. Bandgar, S.T. Navale, A.T. Mane, S.K. Gupta, D.K. Aswal and V.B. Patil, *Synth. Met.*, **204**, 1 (2015); <https://doi.org/10.1016/j.synthmet.2015.02.032>
30. P. Barta, T. Kugler, W.R. Salaneck, A.P. Monkman, J. Libert, R. Lazzaroni and J.L. Brédas, *Synth. Met.*, **93**, 83 (1998); [https://doi.org/10.1016/S0379-6779\(97\)03947-7](https://doi.org/10.1016/S0379-6779(97)03947-7)
31. G. Li, M. Josowicz, J. Janata and S. Semancik, *Appl. Phys. Lett.*, **85**, 1187 (2004); <https://doi.org/10.1063/1.1779948>