

Electrospun Poly(methyl Methacrylate)/Polyaniline Blend Nanofibres with Enhanced Toxic Gas Sensing at Room Temperature

Rajashree Anwane and Subhash Kondawar*

Department of Physics, Rashtrasant Tukadoji Maharaj Nagpur University,
Amravati Road, Nagpur, Maharashtra 440033, India

*Corresponding author: sbkondawar@yahoo.co.in

Published online: 25 April 2018

To cite this article: Anwane, R. & Kondawar, S. (2018). Electrospun poly(methyl methacrylate)/polyaniline blend nanofibres with enhanced toxic gas sensing at room temperature. *J. Phys. Sci.*, 29(1), 101–119, <https://doi.org/10.21315/jps2018.29.1.7>

To link to this article: <https://doi.org/10.21315/jps2018.29.1.7>

ABSTRACT: *Continuous progress in the methods of preparation of new materials for sensing of toxic gases has attracted considerable interest due to environmental problems. In the present investigation, poly(methylmethacrylate)/polyaniline (PMMA/PANI) blend nanofibres were prepared by electrospinning and dip-coating polymerisation techniques. The semiconducting behaviour of PMMA/PANI blend was found to be highly sensitive for toxic gases like NH₃ and HCl at room temperature suggesting the PMMA/PANI blends as a potential material for effective gas sensing in the environmental monitoring safety systems, chemical industry, automotive industry and medical application areas. Fourier transform infrared (FTIR) spectra clearly show the characteristic peaks indicating the presence of quinoid and benzenoid rings of PANI confirming the formation of PMMA/PANI blend. Clusters of PANI on the uniform fibres of PMMA can be seen in the SEM images. Good thermal stability of PMMA/PANI nanofibres showed to be highly sensitive with fast response and recovery on exposure to NH₃ and HCl gases. The phenomenon of increase in sensitivity with the increase in concentration of NH₃ and HCl gases was found to be adsorption dominated indicating that the PMMA/PANI blend nanofibres are more sensitive to the surrounding due to their increased porosity and high aspect ratio. The sensing mechanism of PMMA/PANI blend nanofibres on account of more protonation and de-protonation due to exposing towards HCl and NH₃ gases respectively is systematically explained in the present investigation.*

Keywords: Polyaniline, poly(methyl methacrylate), nanofibres, electrospinning, gas sensing

1. INTRODUCTION

Toxic gases are a major concern for the environmentalists due to the possibility of accidental leakage of gases in chemical storage. Due to increased human safety concerns and environmental monitoring requirements, there is a considerable attention in recent years on sensors based on advanced materials for toxic gases.^{1,2} NH₃ and HCl gases are not only hazardous to humans but also harm the aquatic life on a large scale since both gases are soluble in water. The widespread use of ammonia in farms and industrial locations makes humans vulnerable to its exposure. Ammonia gas forms the very caustic ammonium hydroxide in contact with the available moisture in skin, eyes, oral cavity and respiratory tract. Similarly, the colourless, with a pungent odour of HCl gas forms hydrochloric acid on contact with the moisture. Exposure to HCl gas may occur by inhalation, ingestion, or eye or skin contact. Skin contact causes burns and ulcers in case of exposure to higher concentrations of HCl gas.

In order to save human and aquatic life from the unwanted harmful effects of these toxic gases, it is necessary to detect them at possible sites of more than warranted exposure at room temperature. Higher levels of HCl and ammonia gases are easily detected since both gases have pungent and penetrating odour. However, it may be extremely necessary to detect and quantify the low concentrations of these gases in specific application areas since the human nose fails at such lower concentrations. For example, in a chemical industry where several processes may be carried out at temperatures as high as 500°C, leakage alarms are required to be installed to detect ammonia leakages in the range of 20 ppm to less than 1000 ppm within minutes of leakage. At present, much of the research work has been carried out for the detection of ammonia gases.^{3,4} Several gas sensors have been developed in the past suitable for the specific application purpose.⁵ A gas sensor is a chemical sensor that transforms chemical information such as the concentration of a specific gas component into a useful analytical signal. As compared to the commercially available gas sensors mostly based on metal oxides and operated at high temperatures, the sensors fabricated from conducting polymers have added advantages.⁶⁻⁸ They have relatively high sensitivity and short response time, which makes them attractive commercially, especially when these features are ensured at or near room temperature. Since the nanostructure materials prepared in the form of thin films have large surface area to volume ratio, a porous surface morphology which allows for larger adsorption of gas molecules, nanoscale conducting polymers may be the right candidates for sensing application with high sensitivity, less response time at room temperature. The nanofibres (1D) of conducting polymers have superior mechanical characteristics such as higher stiffness and tensile strength as well as flexibility in surface functionalities.⁹ Therefore these materials are most suitable for gas as well as bio-chemical

sensing as compared to thin films made of nanoparticle (0D) or nanofilm (2D) or nanocrystal (3D) materials.

In recent years, a number of processing techniques has been used to prepare conducting polymer nanofibres such as hard templates, soft templates, phase separation, self-assembly, seeding, interfacial polymerisation, rapidly mixing and electrospinning.^{10,11} Although there are various methods to fabricate nanofibres of the conducting polymers, electrospinning is the most simple, cost effective, convenient, and versatile process to produce fibres with a very large aspect ratio in mass scale.¹² Polyaniline is one of the most extensively studied conducting polymers because it can be easily synthesised and exhibits moderately high conductivity on doping. Moreover, electronic structure and electrical properties of polyaniline can be reversibly controlled by oxidation as well as protonation.

The polymer chains of conducting polyaniline are short to be electrospun into long fine fibres. Therefore, another polymer with sufficiently long chain length is required to blend with polyaniline for electrospinning. Polymers such as polyethylene (PEO), polymethyl methacrylate (PMMA), polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), polyacrylonitrile (PAN), polystyrene (PS), etc., can be used not only as carrier polymer for electrospinning to get sufficient viscosity of the polymer solution. Blends of conducting and nonconducting polymers are prepared to extract the desirable properties of the individual constituents which may be otherwise absent in them. The sensing materials used in sensors largely influence the performance parameters such as stability, response time, reliability, sensitivity, performance temperature, lifetime, accuracy, etc. Many kinds of materials such as metal oxides, semiconductors, polymers, carbon, graphite and organic/inorganic composites and blends have been used as sensing materials to detect the targeted gases using several sensing principles and techniques.^{13,14}

It would be noteworthy here that the sensitivity of chemical gas sensors is strongly determined by the specific surface area of sensing material exposed to the gases. A higher specific surface of the sensing material will lead to higher sensitivity of the sensor. The nanofibres not only offer higher surface area to volume ratio but also inherent large aspect ratio which makes it a quick sensor as compared to the thin films. A very low concentration of chemical vapours is sufficient to change the electrical properties of the sensing elements made of nanofibres.

In the present study, PMMA/PANI blend nanofibres have been synthesised through electrospinning and dip-coating polymerisation. The novelties of this work are the blend nanofibre preparation and its application for toxic gases. The coating of conducting PANI on PMMA nanofibres ensures a change in the conductivity on exposure to HCl as well as ammonia gas thus enabling the use of prepared blend

as a chemical gas sensor. A decrease in the conduction (or increase in resistance) confirms the presence of NH_3 whereas an increase in the conduction (or decrease in the resistance) confirms the presence of HCl . Keeping in view the fact that exposure to high HCl and NH_3 concentration is dangerous for human beings, PMMA/PANI blend nanofibres were explored for the sensing of HCl and NH_3 gas at room temperature.

2. EXPERIMENTAL

2.1 Materials

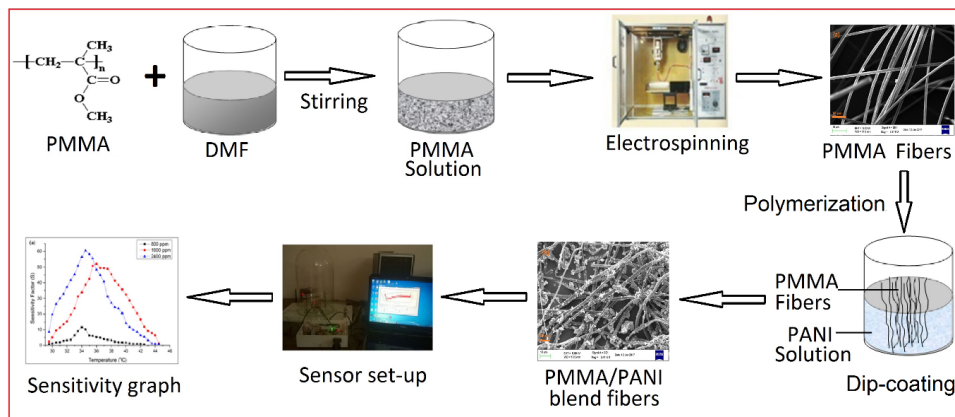
Aniline ($\text{C}_6\text{H}_5\text{NH}_2$, mol.wt. 93.13 g mol^{-1} , purity 99%) was obtained from Fisher Scientific. Ammonium peroxydisulphate (APS (NH_4)₂ S_2O_8 , mol.wt. $228.19 \text{ g mol}^{-1}$, purity 99%) and poly (methyl methacrylate) (PMMA ($\text{C}_5\text{O}_2\text{H}_8$)_n, mol.wt. 350,000) were procured from Sigma Aldrich. Hydrochloric acid (HCl , mol.wt. 36.46 g mol^{-1}) and N, N-Dimethyl Formamide (DMF, $\text{C}_3\text{H}_7\text{ON}$, mol.wt. 73.09 g mol^{-1} , purity 99.5%) were procured from Hi-media. All chemicals were of analytical grade and used as received except aniline which was purified and kept below 5°C before being used. Deionised water was used in all syntheses.

2.2 Synthesis of PMMA/PANI Blend Nanofibres

Firstly, 2.2 g PMMA was dissolved in 15 ml DMF and magnetically stirred for 1 h to get homogeneous solution. PMMA solution was then loaded into a 5 ml disposable plastic syringe with the metallic needle of 0.5 mm diameter for electrospinning. During the electrospinning process at room temperature in air, the solution was fed to the tip using a computer-controlled syringe pump at a flow rate of 0.2 ml h^{-1} . A positive voltage of 20 kV was applied to the needle of the syringe containing solution and the metallic plate wrapped with aluminium foil was grounded and kept at a distance of 15 cm from the needle of the syringe. The electrospun nanofibres were collected on the conducting foil (aluminium). After electrospinning, the nonwoven membrane of PMMA nanofibres was dried at 60°C .¹⁵ Further, as-prepared PMMA nanofibres were used for coating polyaniline to form PMMA/PANI blend nanofibres by using dip-coating in-situ chemical oxidative polymerisation process.^{16,17}

In the typical process of polymerisation, 0.4 M aniline solution was prepared with 50 ml of 1 M HCl in double distilled water. A solution of 0.45 M ammonium peroxydisulphate (APS) was prepared with 50 ml of 1 M HCl in double distilled water and mixed to aniline solution drop wise at 5°C while stirring for 5 h. As-prepared PMMA nanofibres were inserted into the solution during polymerisation

using dip-coating technique. PANI grew on PMMA nanofibres due to chemical oxidation of aniline and the solution turned dark green. PMMA/PANI nanofibres were clearly washed with double distilled water and dried at 80°C in vacuum oven. The schematic of preparation and application of PMMA/PANI blend nanofibres is shown in Scheme 1.



Scheme 1: Schematic of preparation and sensing application of nanofibrous PMMA/PANI blend nanofibres.

2.3 Instrumental Analysis

Pure PMMA and PMMA/PANI blend fibres were characterised by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and thermal gravimetric-differential thermo-gravimetric analysis (TGA-DTG) techniques. SEM images of were recorded on Carl Zeiss EVO-18 scanning electron microscope. FTIR spectra were recorded on Bruker Alpha Spectrophotometer in the 4000–500 cm^{-1} range. TGA-DTG was done on Hitachi STA7200 Thermal Analysis System.

3. RESULTS AND DISCUSSION

3.1 SEM

SEM images of pure PMMA and PMMA/PANI blend nanofibres are shown in Figure 1. Pure PMMA exhibits long and uniformly thin nanofibres compared to that of PMMA/PANI blend nanofibres. White coloured clusters of PANI can be seen coated on the PMMA nanofibres confirming the formation of PMMA/PANI with increased in diameter compared to that of pure PMMA.

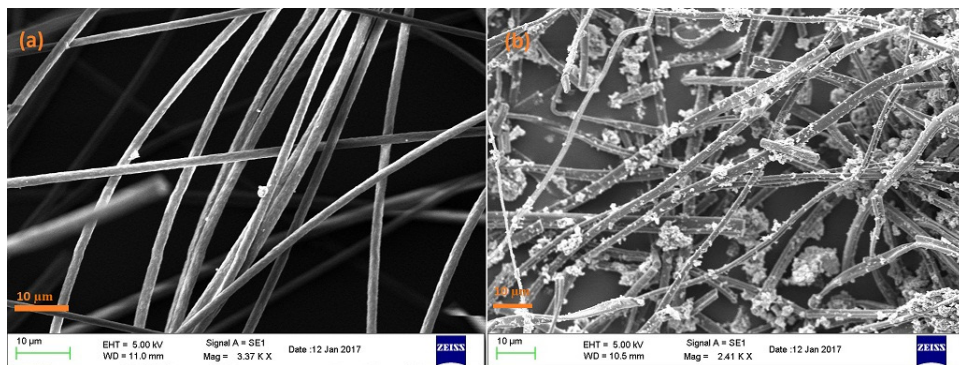


Figure 1: SEM images of PMMA nanofibres and PMMA/PANI blend nanofibres.

3.2 FTIR Spectroscopy

FTIR spectra for PMMA and PMMA/PANI blend nanofibres are shown in Figure 2. The peak at 2977.29 cm^{-1} corresponds to the C-H stretching vibrations.^{18,19} The intense peak at 1725.90 cm^{-1} is attributed to the C=O stretching vibrations. The asymmetrical bending vibrations of C-O-C are located at 1241.11 cm^{-1} and 1146.46 cm^{-1} .^{20,21} In the FTIR of the blend, a peak at 1699.87 cm^{-1} is attributed to the COO stretching vibrations confirming the presence of carboxyl group.²² The peaks due to the C=C stretching of the quinoid ring and the benzenoid ring can be seen located at 1615 cm^{-1} and 1458.43 cm^{-1} respectively, confirming the existence of PANI in the blend.²³ The peak due to the bending of C-H of aromatic ring is observed at 1136.95 cm^{-1} .²⁴ Increase in the intensity of the peaks in the FTIR of PMMA/PANI blend can be seen at 751 cm^{-1} , 3738 cm^{-1} and 3860 cm^{-1} which are obtained due to the vibrations of polymer chains.

3.3 TGA-DTG Analysis

TGA and DTG curves of pure PMMA and PMMA/PANI blend nanofibres are shown in Figure 3. The three stages of weight loss in PMMA can be seen at 140°C – 250°C , 270°C – 325°C and 325°C – 410°C .²⁵ The lower weight loss in the first two degradation steps may be attributed to the evaporation of the residual solvent and the splitting of small molecules. The higher loss in weight in the third degradation step indicates the structural decomposition of bonds due to heat at higher temperature. The high intensity peak in the DTG of pure PMMA may be attributed to the corresponding higher weight loss in the third degradation step.²⁶ The degradation of the PMMA-PANI also takes place in three steps. Increased thermal stability of PMMA-PANI blend can be attributed to the shift in the third degradation step of PMMA-PANI towards higher temperature.²⁷

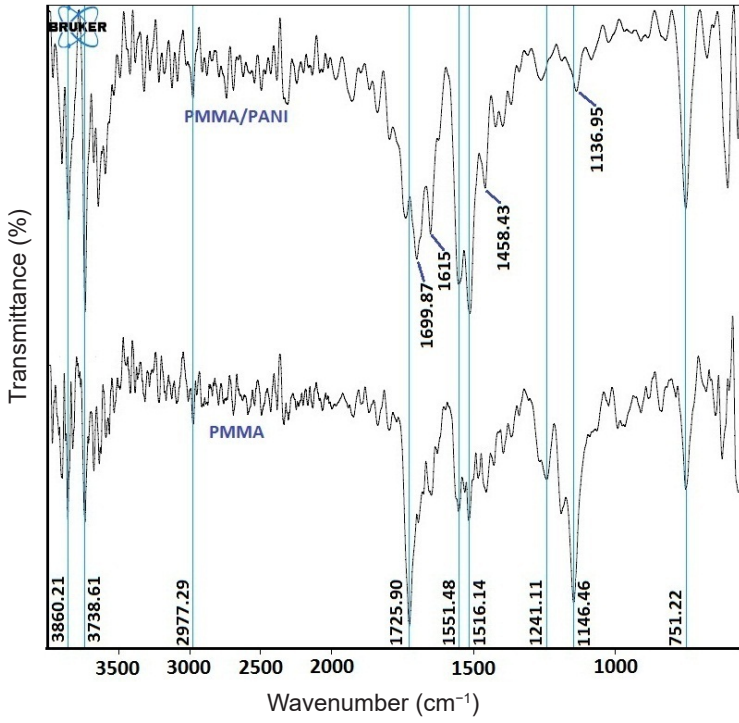


Figure 2: FTIR spectra of PMMA and PMMA/PANI blend nanofibres.

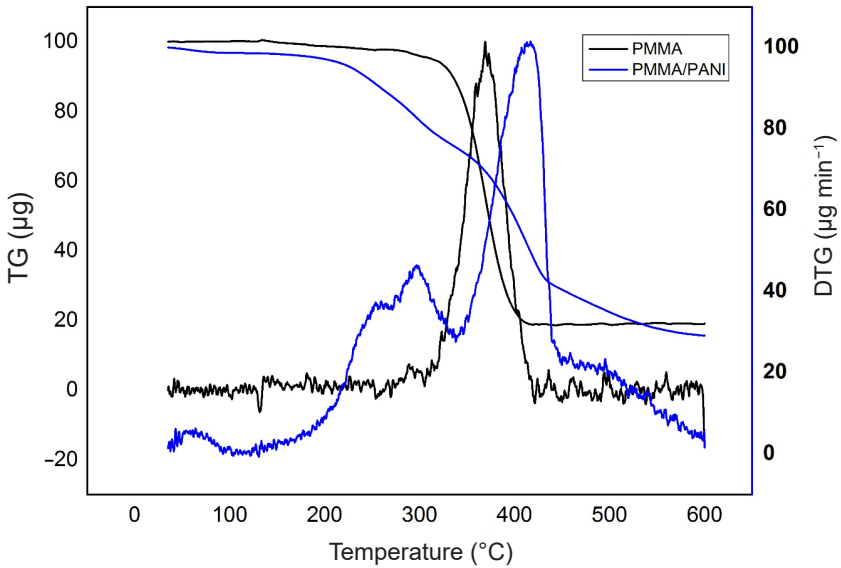


Figure 3: TGA-DTG curves of PMMA and PMMA/PANI blend nanofibres.

3.4 HCl and NH₃ Gas Sensing

Gas sensors are the detectors which sense or detect a particular gas (analyte) and convert the information into a useful analytical signal, mostly electrical.^{28–30} Although an ideal gas sensor must have all ideal characteristics such as high sensitivity, good selectivity, low detection limit, good linearity, small hysteresis and response time, and long life cycle, efforts can be made to approach only some of these ideal characteristics and disregarding the others since the real applications usually do not require all perfect characteristics at once. There are several papers which report the use of different organic polymers as well as metal oxide-based polymer nanocomposites as efficient gas sensors for ammonia as well as HCl gases.^{31–34} The synthesised PMMA/PANI blend nanofibres were used as the receptor for analyte gas molecules. Exposure of the fabricated PMMA/PANI sensor to HCl gas showed decrease in the resistance with increasing temperature whereas an increase in the resistance with increasing temperature was observed for ammonia gas.

The PANI layer in the blend acts as the active sensing layer and shows changes in the resistivity on adsorption of the analyte gas molecules. The sensitivity of PMMA/PANI sensor calculated for both HCl and NH₃ gas for different concentrations are shown in Figures 4 and 5, respectively. It was observed that the sensitivity of the sensor increases for higher concentration of HCl gas. It is worth mentioning that the sensitivity is highest at near room temperature although the working temperature slightly differs with concentrations.

Also, the sensitivity of the sensor increases with increasing concentration of ammonia gas, though the highest sensitivity here is lower than the sensitivity for the corresponding HCl concentration. The sensing mechanism is found to be governed by protonation and deprotonation phenomena. The resistivity of the blend increases in the presence of ammonia gas due to the reduction or undoping of charge carriers by adsorption of ammonia molecules on the surface of blend. The sensitivity factor was found to be 11.53, 52.10 and 60.47 for 800 ppm, 1600 ppm and 2400 ppm of HCl at temperatures of 34°C, 36°C and 34.5°C, respectively. For ammonia gas, the sensitivity factor was obtained as 11.29, 19.38 and 27.84 for 800 ppm, 1600 ppm and 2400 ppm at temperatures of 36.5°C, 39°C and 42°C respectively. A plot of response (R_g/R_a) and recovery of the sensor for the analyte gases HCl and NH₃ with respect to time is shown in Figures 6 and 7, respectively. It can be seen that the response of the sensor increases for increasing concentration of HCl as well as NH₃ gas with the highest response for 2400 ppm of ammonia gas. Figure 8 depicts the plot of sensitivity versus concentration for the values of factor S for different concentrations obtained from the Figures 4

and 5 at room temperature. A plot of response versus concentration of the two gases is shown in Figure 9.

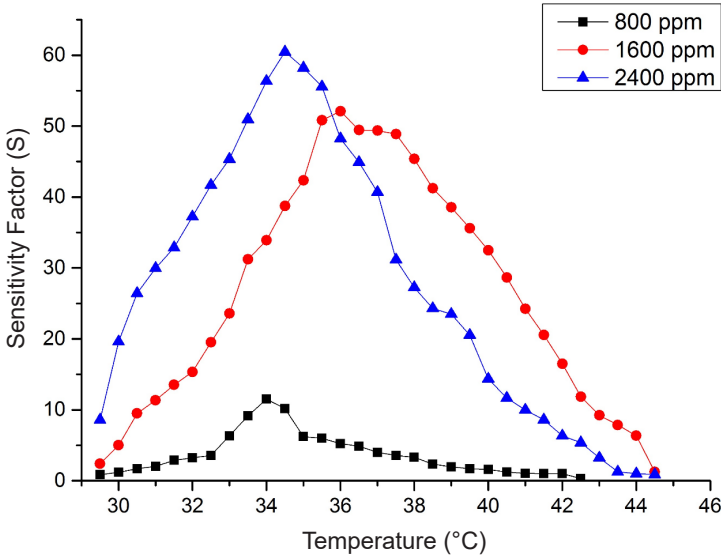


Figure 4: Sensitivity of the PMMA/PANI blend sensor for HCl gas at different concentrations.

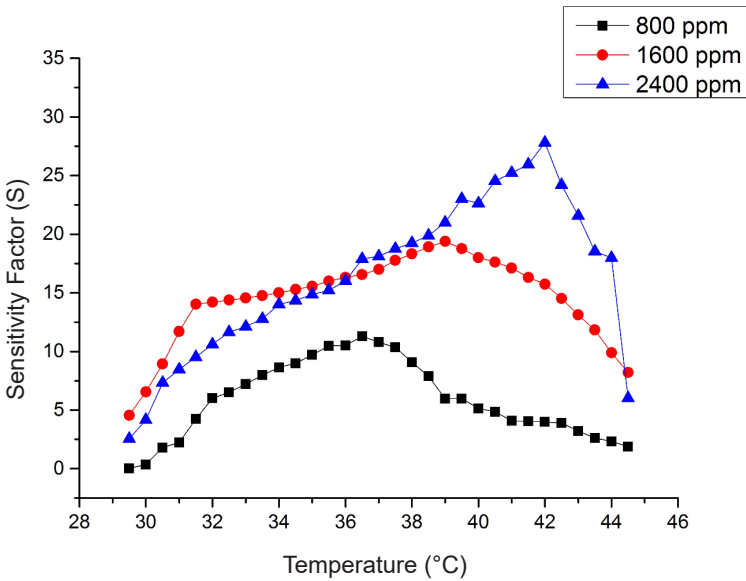


Figure 5: Sensitivity of the PMMA/PANI blend sensor for NH₃ gas at different concentrations.

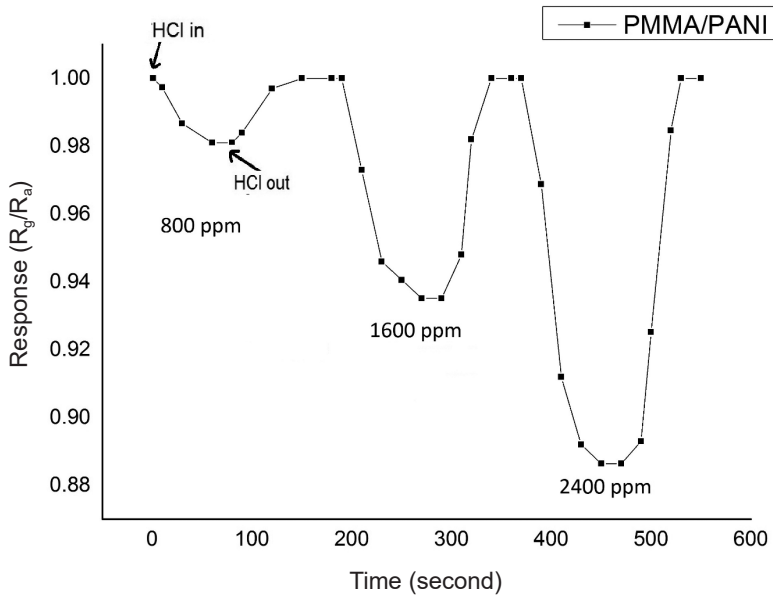


Figure 6: Response and recovery of PMMA/PANI blend sensor for HCl gas at different concentrations.

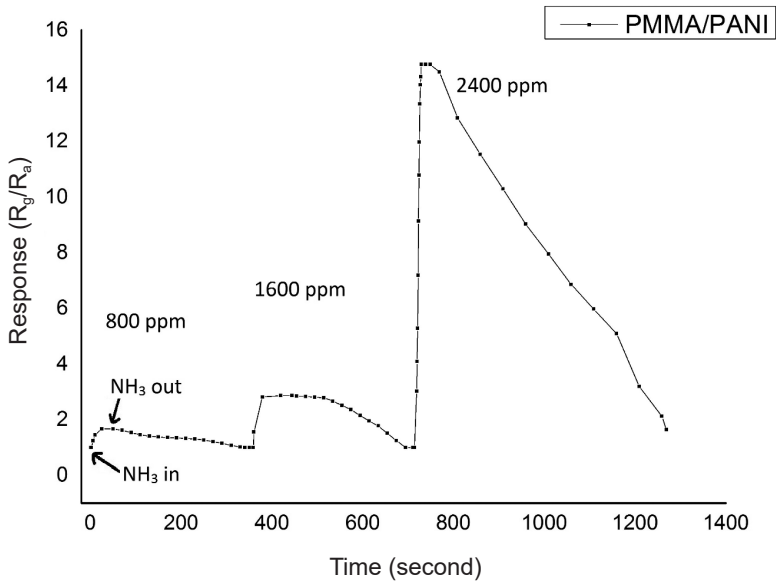


Figure 7: Response and recovery of PMMA/PANI blend sensor for NH₃ gas at different concentrations.

The nanofibrous gas sensor fabricated from the PMMA/PANI blend in the present work is a good sensor since it is highly sensitive for HCl as well as NH₃ gases and has operating temperature below 37°C for HCl gas and 42°C for ammonia gas, much closer to room temperature. The nanofibrous morphology of the sensor allows for the quick diffusion of the gas molecules enabling the sensor to show quick response. Tables 1 and 2 show the comparison of the sensitivity, response time, recovery time and operating temperature of as-synthesised PMMA/PANI blend nanofibres for NH₃ and HCl gases respectively with that of the work for other materials such as camphor sulfonic acid doped PANI/SnO₂, polyaniline/titania (PANI/TiO₂), polyaniline particles/reduced graphene oxide-polyaniline fibres (PPANI/rGO-FPANI), polyaniline-single walled carbon nanotubes (PANI-SWNTs), polyaniline/zinc oxide (PANI/ZnO), tetracationic porphyrin/titania (TMPyP/TiO₂), meso-tetramesitylporphyrin (MTMP), when used for gas sensing reported in literature.^{35–41} There are many composite materials used for NH₃ gas sensing, but very few materials are used for HCl gas sensing. Thus, PMMA/PANI blend nanofibres proves to be a good sensor for HCl as well as NH₃ gases closed to room temperature compared to other materials reported not used for both the gases sensing.

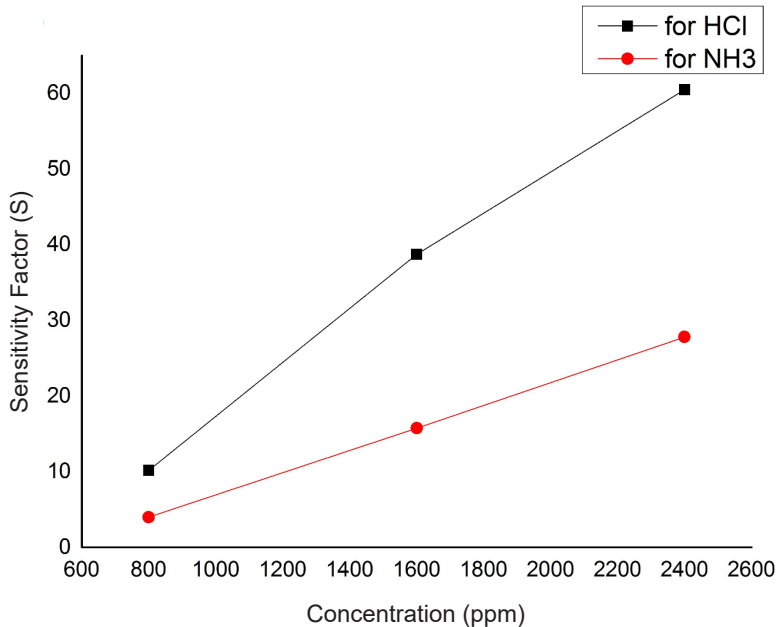


Figure 8: A plot of sensitivity versus concentration of PMMA/PANI blend sensor for HCl and NH₃ gas.

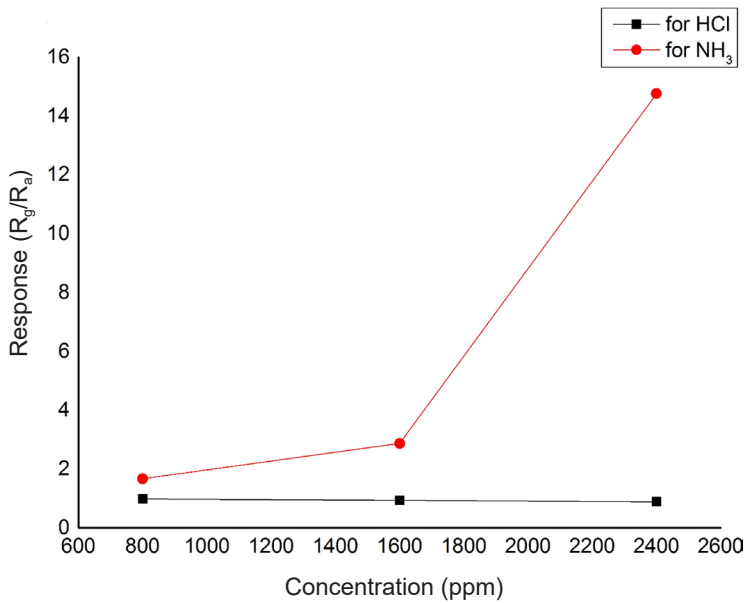


Figure 9: A plot of response versus concentration of PMMA/PANI blend sensor for HCl and NH_3 gas.

Table 1: Comparison of the sensitivity, response time, recovery time and operating temperature of as-synthesised PMMA/PANI blend nanofibres for NH_3 .

Sensing materials	Operating temperature ($^{\circ}C$)	Sensitivity (S%)	Response time (s)	Recovery time (s)	Reference
PMMA/PANI	42	27.8	22	400	Present work
CSA doped PANI/ SnO_2	30	0.91	46	3245	Khusp et al. ³⁵
PANI/ TiO_2	RT	12	72	–	Pawar et al. ³⁶
PPANI/rGO-FPANI	40	5	36	18	Gua et al. ³⁷
PANI-SWNT	RT	5.8	450	–	Lim et al. ³⁸
PANI-ZnO	45	4.6	153	135	Patil et al. ³⁹

Table 2: Comparison of the sensitivity, response time, recovery time and operating temperature of as-synthesised PMMA/PANI blend nanofibres for HCl.

Sensing materials	Operating temperature ($^{\circ}C$)	Sensitivity (S%)	Response time (s)	Recovery time (s)	Reference
PMMA/PANI	34.5	60.4	60	90	Present work
(TMPyP)/ TiO_2	80	0.91	50	300	Kaushik et al. ⁴⁰
MTMP	557	12	600	900	Kalimuthu et al. ⁴¹

3.5 Sensing Mechanism

The sensing mechanism that takes place on the molecular level due to the adsorption of HCl and NH₃ gas on the PANI layer is depicted in Figures 10 and 11, respectively. Since HCl is used as a dopant during polymerisation in this work, PANI is obtained in the form of emeraldine salt. When exposed to HCl gas during sensing, the HCl molecule donates H⁺ ions to the PANI chain, thus increasing the number of positively charged carriers in the material. The process is termed as protonation and gives bipolarons due to excess doping of PANI and results in decrease in the electrical resistivity of the sensor. With the increasing concentration of the analyte HCl gas, the sensitivity is increased which is attributed to the diffusion of more HCl molecules into the fibre at higher concentration. On the other hand, when the sensor is exposed to the ammonia gas, deprotonation takes place. NH₃ molecules of gas take up the hydrogen atom from the PANI chain and form NH₄⁺ ammonium ions. The emeraldine salt form of the PANI thus changes into the emeraldine base form with decrease in the number of carriers. This leads to the decrease in the number of polarons and the electrical resistivity of the sensor increases. Here too the sensitivity is found to increase with the increasing concentration of the NH₃ gas which indicates that more NH₃ molecules diffuse into the fibre at higher concentration.

The response and recovery time are defined as the time to reach 90% of the resistance change during exposure and on removal of gas respectively. The response and recovery time of the PMMA/PANI blend nanofibres based sensor on exposure to different HCl concentrations was found to be almost the same indicating adsorption and desorption of HCl molecules in the blend takes almost same time on exposure to the gas and removal of gas respectively. The lower response time of the PMMA/PANI blend for NH₃ gas indicates the faster diffusion of the gas molecules into the fibre immediately upon exposure to the gas. On the other hand, the recovery time (reversibility) of the sensor was found to be poor. This may be attributed to the difficulty of the adsorbed NH₃ molecules to desorb from the fibre. The response and recovery rate may be improved by fabricating a nanofibrous sheet of aligned nanofibres of PMMA which will further increase the available surface area for PANI coating during dip-coating polymerisation, thereby increasing the possibility of quick response and recovery. Attempts can be made to spin the PMMA nanofibres of reduced diameters by optimising the affecting parameters. This will again result in increased specific surface area leading to quicker gas response and reversibility.

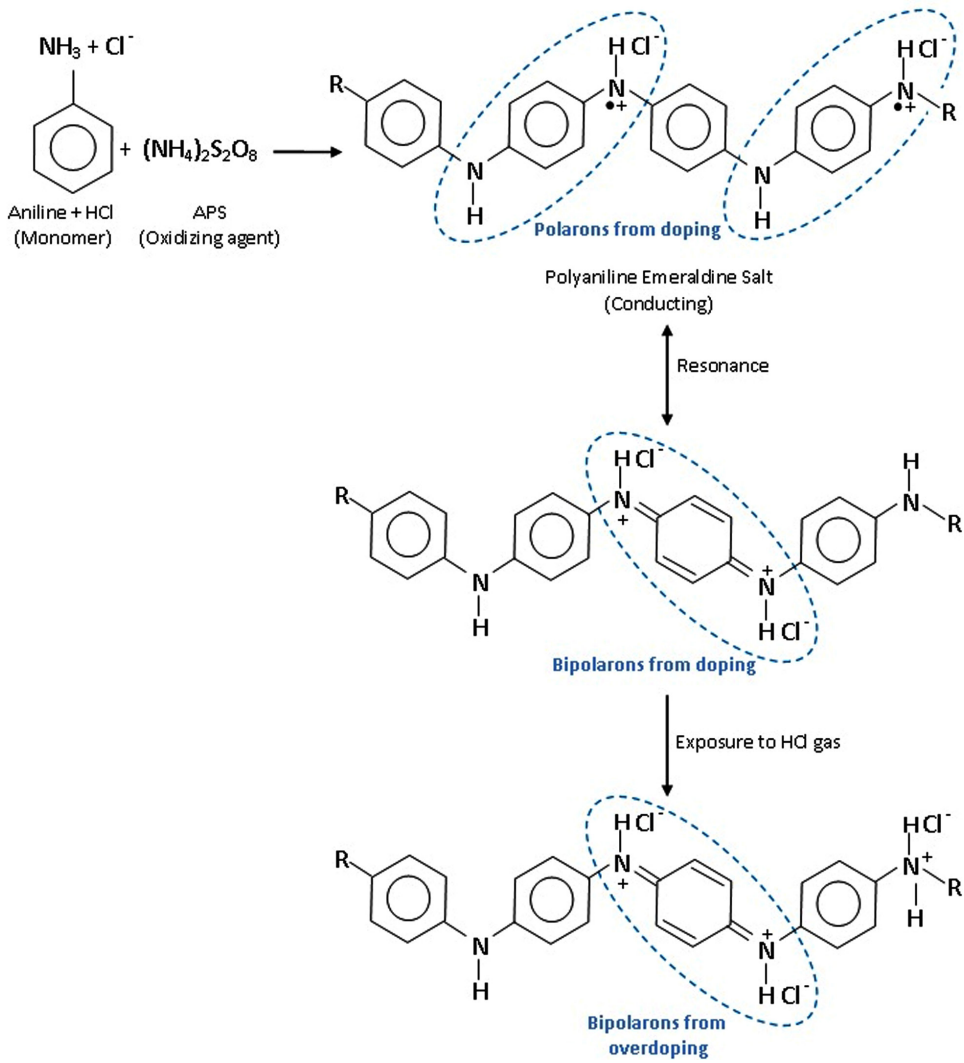


Figure 10: Sensing mechanism of the PMMA/PANI blend on exposure to HCl gas.

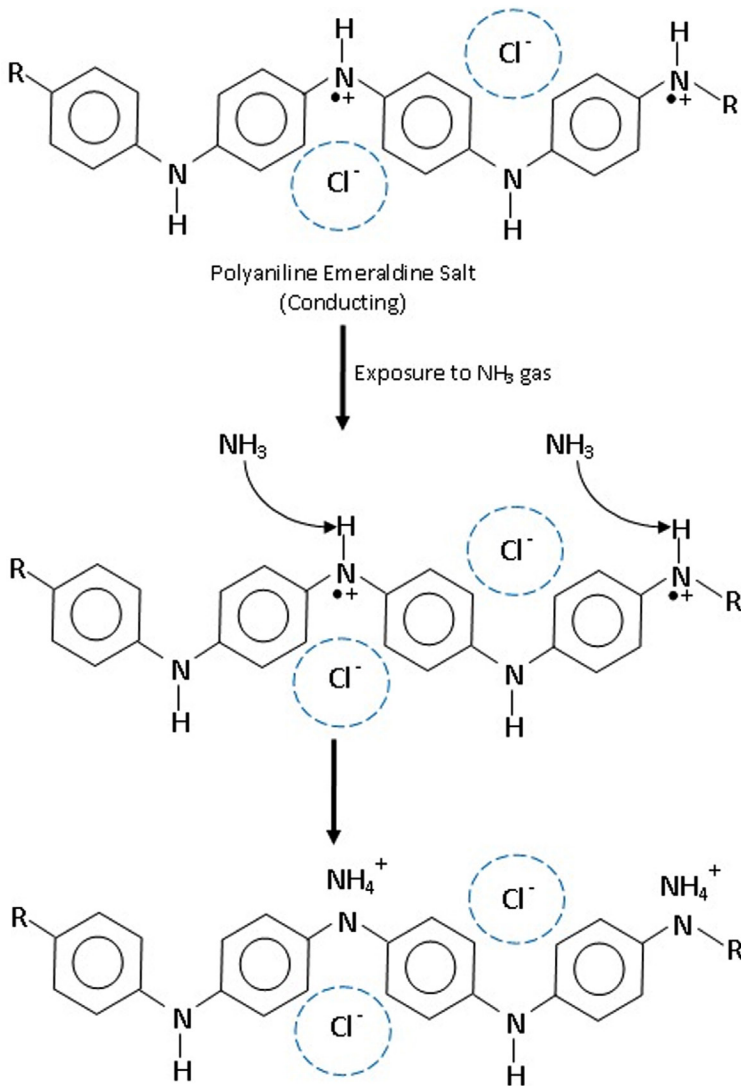


Figure 11: Sensing mechanism of the PMMA/PANI blend on exposure to NH₃ gas.

4. CONCLUSION

PMMA/PANI blend nanofibres have been synthesised successfully by electrospinning and dip-coating polymerisation. The formation of PMMA/PANI blend is confirmed by SEM, FTIR and TGA-DTG analysis. The studies of PMMA/PANI blend as a sensor for HCl and NH₃ gas show sensitivity which increases with the increasing concentration of both the gases. The operating temperature of PMMA/PANI blend for HCl as well as NH₃ gas sensor was found to be near room temperature. These results, along with low response time, confirmed the possible use of the prepared material as a potential candidate for the sensing of HCl and NH₃ gas in the environmental monitoring safety systems, chemical industry, automotive industry and medical application areas.

5. ACKNOWLEDGEMENTS

Authors gratefully acknowledge the University Grants Commission (UGC), India for financial assistance provided under the Research Project (39-540/2010-SR) and Department of Science and Technology (DST), India under the DST-FIST Program (SR/FST/PSI-178/2012-C).

6. REFERENCES

1. Wang, Y. et al. (2009). Ammonia gas sensor using polypyrrole-coated TiO₂/ZnO nanofibers. *Electroanal.*, 21(12), 1432–1438, <http://dx.doi.org/10.1002/elan.200904584>.
2. Chen, S. & Sun, G. (2013). High sensitivity ammonia sensor using a hierarchical polyaniline/poly(ethylene-co-glycidyl methacrylate) nanofibrous composite membrane. *ACS Appl. Mater. Interf.*, 5(14), 6473–6477, <http://dx.doi.org/10.1021/am402217s>
3. Kondawar, S. B. et al. (2012). Conductive polyaniline–tin oxide nanocomposites for ammonia sensor. *Adv. Mat. Lett.*, 3(5), 393–398, <http://dx.doi.org/10.5185/amlett.2012.6361>.
4. Lakard, B. et al. (2015). Review – Gas sensors based on electrodeposited polymers. *Metals*, 5(3), 1371–1386, <http://dx.doi.org/10.3390/met5031371>.
5. Bjorn, T. et al. (2005). Ammonia sensors and their applications – A review. *Sens. Actuat. B*, 107(2), 666–677, <http://dx.doi.org/10.1016/j.snb.2004.11.054>.
6. Kondawar, S. B. et al. (2014). Chemical vapor sensing properties of electrospun nanofibers of polyaniline/ZnO nanocomposites. *Adv. Mat. Lett.*, 5(7), 389–395, <http://dx.doi.org/10.5185/amlett.2014.amwc.1037>.

7. Chen, J. et al. (2010). NH₃ and HCl sensing characteristics of polyaniline nanofibers deposited on commercial ceramic substrates using interfacial polymerization. *Synth. Met.*, 160(23), 2452–2458, <http://dx.doi.org/10.1016/j.synthmet.2010.09.026>.
8. Sharma, H. J. et al. (2015). Electrospun SnO₂/polyaniline composite nanofibers based low temperature hydrogen gas sensor. *Fib. Polym.*, 16(7), 1527–1532, <http://dx.doi.org/10.1007/s12221-015-5222-0>.
9. Huang, Z. M. et al. (2003). A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Compos. Sci. Technol.*, 63(15), 2223–2253, [http://dx.doi.org/10.1016/S0266-3538\(03\)00178-7](http://dx.doi.org/10.1016/S0266-3538(03)00178-7).
10. Pethe, S. M. & Kondawar, S. B. (2014). Optical and electrical properties of conducting polyaniline nanofibers synthesized by interfacial and rapid mixing polymerization. *Adv. Mat. Lett.*, 5(12), 728–733, <http://dx.doi.org/10.5185/amlett.2014.amwc550>.
11. Talwar, V. et al. (2014). ZnO assisted polyaniline nanofibers and its application as ammonia gas sensor. *Sens. Actuat. B Chem.*, 191, 276–282, <http://dx.doi.org/10.1016/j.snb.2013.09.106>.
12. Frenot, A. & Chronakis, I. S. (2003). Polymer nanofibers assembled by electrospinning. *Curr. Opin. Coll. Inter. Sci.*, 8(1), 64–75, [http://dx.doi.org/10.1016/S1359-0294\(03\)00004-9](http://dx.doi.org/10.1016/S1359-0294(03)00004-9).
13. Huang, J. & Wan, Q. (2009). Gas sensors based on semiconducting metal oxide one-dimensional nanostructures. *Sens.*, 9(12), 9903–9924, <http://doi.org/10.3390/s91209903>.
14. Nicolas, D. D. & Poncin, E. F. (2003). Polyaniline as a new sensitive layer for gas sensors. *Anal. Chim. Acta*, 475, 1–15, [http://doi.org/10.1016/S0003-2670\(02\)01229-1](http://doi.org/10.1016/S0003-2670(02)01229-1).
15. Wang X. et al. (2002). Electrospinning technology: A novel approach to sensor application. *J. Macromol. Sci. A*, 39(10), 1251–1258, <http://doi.org/doi/abs/10.1081/MA-120014850>.
16. Tang, C. C. et al. (2012). Synthesis, structural and gas sensing properties of nanobranched coaxial polyaniline fibers by electrospinning. *Adv. Mater. Res.*, 562, 308–311, <http://doi.org/10.4028/www.scientific.net/AMR.562-564.308>.
17. Zhang, H. D. et al. (2014). High-sensitivity gas sensors based on arranged Polyaniline/PMMA composite fibers. *Sens. Actuat. A Phys.*, 219, 123–127, <http://dx.doi.org/10.1016/j.sna.2014.09.005>.
18. Mbese, J. Z. & Ajibade, P. A. (2014). Preparation and characterisation of ZnS, CdS and HgS/Poly(methyl methacrylate) nanocomposites. *Polym.*, 6(9), 2332–2344, <http://doi.org/10.3390/polym6092332>.

19. Garcia, O. P. et al. (2015). Use of lead(II) sulphide nanoparticles as stabilizer for PMMA exposed to gamma irradiation. *Mater. Res.*, 18(2), 365–372, <http://dx.doi.org/10.1590/1516-1439.330214>.
20. Meneghetti, P. et al. (2004). Synthesis of polymer gel electrolyte with high molecular weight poly(methyl methacrylate)–clay nanocomposite. *Electrochim. Acta*, 49, 4923–4931, <http://dx.doi.org/10.1016/j.electacta.2004.06.023>
21. Buga, M. R. et al. (2015). Surface modification of silk fibroin fibres with poly (methyl methacrylate) and poly(tributylsilyl methacrylate) via RAFT polymerisation for marine antifouling applications. *Mater. Sci. Eng. C*, 51, 233–241, <http://dx.doi.org/10.1016/j.msec.2015.03.006>.
22. Nguyen, L. H. et al. (2012). Portable cholesterol detection with polyaniline-carbon nanotube film based interdigitated electrodes. *Adv. Nat. Sci. Nanosci. Nanotechnol.*, 3(1), 015004, <http://dx.doi.org/10.1088/2043-6262/3/1/015004>.
23. Asha, et al. (2014). Synthesis and characterisation of polyaniline/TiO₂ composites. *Ind. J. Pure Appl. Phys.*, 52, 341–347.
24. Liu, D. et al. (2015). Crosslinked carbon nanotubes/polyaniline composites as a pseudocapacitive material with high cycling stability. *Nanomater.*, 5(2), 1034–1047, <http://dx.doi.org/10.3390/nano5021034>.
25. Korobeinyk, A. V. et al. (2012). High temperature oxidative resistance of polyacrylonitrile–methylmethacrylate copolymer powder converting to a carbonised monolith. *Eur. Polym. J.*, 48, 97–104, <http://dx.doi.org/10.1016/j.cur.polymj.2011.10.006>.
26. Valandro, S. R. et al. (2013). Thermal properties of poly(methyl methacrylate)/organomodified montmorillonite nanocomposites obtained by *in situ* photopolymerization. *Mater. Res.*, 17(1), 265–270. <http://dx.doi.org/10.1590/S1516-14392013005000173>.
27. Tomar, A. K. et al. (2011). Thermal properties of PMMA doped with polyaniline. *AIP Conf. Proc.*, 1393(1), 145, <http://dx.doi.org/10.1063/1.3653651>.
28. Wang, C. et al. (2010). Metal oxide gas sensors: Sensitivity and influencing factors. *Sens.*, 10(3), 2088–2106, <http://dx.doi.org/10.3390/s100302088>.
29. Gupta, N. et al. (2006). Advances in sensors based on conducting polymers. *J. Sci. Ind. Res.*, 65, 549–557, <http://hdl.handle.net/123456789/4862>.
30. Ji, S. et al. (2008). Gas sensing properties of a composite composed of electrospun poly(methyl methacrylate) nanofibers and *in situ* polymerised polyaniline. *Sens. Actuat. B Chem.*, 133(2), 644–649, <http://doi.org/10.1016/j.snb.2008.03.040>.

31. Li, Y. et al. (2016). Highly sensitive NH₃ gas sensors based on novel polypyrrole-coated SnO₂ nanosheet nanocomposites. *Sens. Actuat. B Chem.*, 224, 449–457. <http://doi.org/10.1016/j.snb.2015.10.078>.
32. Hong, K. H. et al. (2004). Polyaniline-nylon 6 composite fabric for ammonia gas sensor. *J. Appl. Polym. Sci.*, 92(1), 37–42, <http://dx.doi.org/10.1002/app.13633>.
33. Bai, H. & Shi, G. (2007). Gas sensors based on conducting polymers. *Sens.*, 7(3), 267–307, <http://dx.doi.org/10.3390/s7030267>.
34. Virji, S. et al. (2004). Polyaniline nanofiber gas sensors: Examination of response mechanisms. *Nano Lett.*, 4(3), 491–496, <http://dx.doi.org/10.1021/nl035122e>.
35. Khusp, G. D. et al. (2013). Ammonia gas sensing properties of CSA doped PANi-SnO₂ nanohybrid thin films. *Synth. Met.*, 185, 1–8, <https://doi.org/10.1016/j.synthmet.2013.09.032>.
36. Pawar, S. G. et al. (2011) Fabrication of polyaniline/TiO₂ nanocomposite ammonia vapor sensor. *J. Nanoelectr. Phys.*, 3, 1056–1063.
37. Guo, Y. et al. (2016) Hierarchical graphene-polyaniline nanocomposite films for high-performance flexible electronic gas sensors, *Nanosci.*, 8, 12073–12080, <http://dx.doi.org/10.1039/C6NR02540D>.
38. Lim, J. H. et al. (2010) Electrical and gas sensing properties of polyaniline functionalized single-walled carbon nanotubes. *Nanotechnol.*, 21(7), 075502–075509. <https://doi.org/10.1088/0957-4484/21/7/075502>.
39. Patil, S. L. et al. (2011) Fabrication of polyaniline-ZnO nanocomposite gas sensor, *Sens. Trans.*, 134(11), 120–131.
40. Kaushik, A. et al. (2015) Organic–inorganic hybrid nanocomposite-based gas sensors for environmental monitoring. *Chem. Rev.*, 115(11), 4571–4606, <https://doi.org/10.1021/cr400659h>
41. Kalimuthu, P., Sivanesan, A. & Abraham John, S. (2012). Fabrication of optochemical and electrochemical sensors using thin films of porphyrin and phthalocyanine derivatives. *J. Chem. Sci.*, 124(6), 1315–1325.