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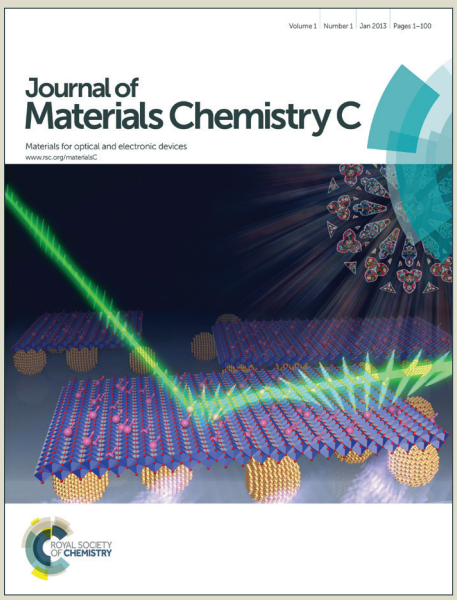

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ARTICLE TYPE

Simple and low-temperature polyaniline-based flexible ammonia sensor: A step towards laboratory synthesis to economical model design†

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Flexible and highly sensitive polyaniline-based (PAni) ammonia (NH_3) gas sensors were developed through an *in-situ* chemical oxidative polymerization process of aniline on a polyethylene terephthalate substrate at three different temperatures *viz.* 35°C, 0°C and -5°C. In the beginning stage, they were characterized with respect to their structural, morphological, and compositional analysis studies and in second stage, selectivity was tested for oxidizing (nitrogen dioxide, NO_2) and reducing (NH_3, ethanol, methanol and hydrogen sulphide, H_2S) gases. The sensor fabricated at 0°C showed optimum response of 26% to 100 ppm NH_3 gas which was superior to those obtained for sensors developed at 35°C (19%) and -5°C (23%). As-developed low-temperature flexible gas sensor has demonstrated fast response (19 s) as well as recovery times (36 s), 99 % reproducibility and good stability, enabling potential of commercial application, for example in industry where high temperature operation is prohibited. The impedance spectroscopy was used to investigate the plausible interaction mechanism of NH_3 gas molecules with flexible PAni film. Operation of NH_3 gas sensor, fabricated on a laboratory scale was tested and explored as a demo-video clip; available online as EIS.

1. Introduction

Nowadays, a new trend towards the manufacturing of sensor films on flexible substrate has become an interesting research topic, especially in modern electronics, where the fabrication of organic electronic devices on flexible substrates such as polyethylene terephthalate (PET) is essential for producing advanced portable consumer electronic items. Flexibility, shock resistance, low weight, and softness are few beneficial merits on the record of the PET substrate.[1] Flexible and low-cost sensors have a high potential of integration into smart electronics circuit used in fancy and life style items.[2,3] The main challenge in the field of gas sensor is not only the fabrication of the flexibility but also maintain other properties like sensitivity, stability, reproducibility, and mechanical and electrical strengths to a desired level. The detection of toxic gases in the environment appears to dominate recent sensor research. The gases released from natural and industrial processes can cause both long term and immediate human health problems. Particularly, ammonia gas released from agricultural industries during urea manufacturing process needs to be monitored. It has a sharp odor and if ammonia spills occur problems like coughing and irritation follow quickly. Therefore, the development of simple and low-cost ammonia sensors, for health and safety precaution is necessary.

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†*Video-clip of operation of designed flexible PAni sensor can be obtained from Electronic Supporting Information (EIS).*

Conducting polymers such as polyaniline (PAni), polypyrrole (PPy), and polythiophene (PTh) are being heavily studied currently, because of their remarkable electrical and mechanical properties, which frequently are used in sensors, actuators, and electronic devices.[4-6] Among the family of conducting polymers, PAni has attracted much attention due to its easy synthesis methods, good environmental stability and also its surface charge characteristics can be easily tailored by changing the dopant during synthesis process. In recent reports, PAni has been envisaged for the detection of various oxidizing and reducing gases. Crowley *et al.*[7] developed PAni sensor using piezoelectric inkjet and screen printing methods and applied for the detection of hydrogen sulphide (H_2S) where weak and slower response was detected. Sengupta *et al.*[8] prepared PAni by chemical oxidative polymerization method and used for NH_3 gas detection within 100–750 ppm range with as high as 480 s response time and 420 s recovery time at 100 ppm. Sutar *et al.*[9] prepared nanofibrous PAni films and used for NH_3 gas sensor with 60–100 s response time and 60-300 s recovery time within 0.5-20 ppm levels. Room temperature PAni nanofibers were synthesized using chemical oxidative polymerization method by Sadek *et al.*[10] and employed for detection of hydrogen (H_2) gas with 60 s recovery time. Recovery time of 150 s was reported for PANi films prepared from Langmuir-Blodgett method by Xie *et al.*[11] for 100 ppm of nitrogen dioxide (NO_2) gas.

To the best of our knowledge and experience in this field, synthesis of flexible PAni sensor on PET substrate by *in-situ* polymerization method operating for different temperatures has not been yet studied for detection of NH_3 gas. Following this idea, in the present work, flexible PAni sensors have been developed and operated at different temperatures where at 0°C, good response (26%), less response time (19 s) and excellent recovery time (36 s) towards 100 ppm of NH_3 gas were achieved. In addition, the sensors demonstrated a linear response in the range of 5-100 ppm as well as satisfying the conditions of stability and reproducibility too. NH_3 is an irritant with the Permissible Exposure Limit (PEL) of 25 ppm in air therefore the sensor is needed to design in such a way that it can easily sense the gas concentration well below PEL level. In present paper, we

report on the synthesis of flexible PAni sensor operating at 0°C in the range of 5-100 ppm of NH_3. Furthermore, we demonstrate the structural, morphological, and compositional analysis of as developed flexible sensor with Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and X-ray photoelectron spectroscopy (XPS) measurement techniques, respectively. The electrochemical impedance spectroscopy measurements were monitored in air and in NH_3 presence and the resistive and reactive components were computed. The circuit modeling study was carried out, for finding related electronic parameters, from the impedance data.[12] A laboratory scale model is also explored, demonstrating commercial importance of developed low-temperature NH_3 sensor. Based on operation, a video-clip demonstrating lamp ON when desired NH_3 level reached has been documented, which can been found in Electronic Supporting Information (EIS).

2. Experimental details

2.1 Materials

Aniline, ammonium persulphate (APS), and hydrochloric acid were purchased from sd-fine chemicals. Distilled water was used for solution preparation. All these solvents and reagents were used without further purification.

2.2 Fabrication of flexible PAni sensor

Flexible PAni sensor was designed by *in-situ* polymerization of monomer aniline with APS as an oxidant on PET substrate for three different temperatures *viz.* 35°C, 0°C and -5°C. The schematic formation of flexible PAni sensor is shown in fig. 1(a). The reaction mechanism of formation of PAni from aniline monomer is illustrated in fig. 1(b).

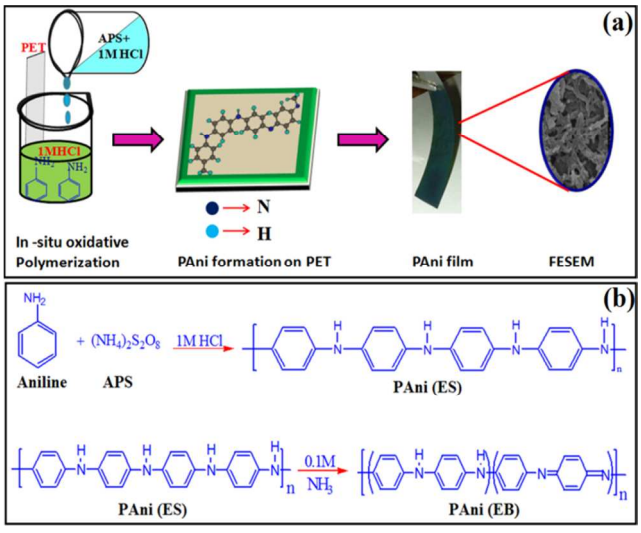

Fig.1: (a) Schematic formation of flexible PAni sensor film, (b) Reaction mechanism for the formation of PAni.

2.3 Characterizations of PANi sensor

The structural information of flexible PAni sensors fabricated by *in-situ* polymerization method on PET substrate for three constituent temperatures was obtained by X-ray diffraction (XRD) spectra by employing Cu-K_α radiation (Rigaku, Ultima IV, X-ray diffractometer). The chemical structure of polyaniline was obtained from the FTIR spectroscopy (Model: Perkin Elmer100), Raman spectra (Model: Horiba, 228 Lab Ram Hr 800) and XPS (VG, Multilab 2000, Thermo VG, Scientific UK). Morphologies of flexible sensors were examined by FESEM (MIRA3 TESCAN, USA) surface digital photoimages. The gas sensing capabilities were carried out by using custom fabricated gas sensing system presented in Fig. 2. Impedance spectroscopy measurement was carried out by Wayne Kerr precision impedance analyser (model: 6500 B) in the frequency range of 20 Hz–10 MHz.

3. Results and discussion

3.1 FTIR analysis

FTIR spectroscopy provides valuable information about the chemical structure of the compound chemistry. Fig.3 (a) shows the FTIR spectra of PAni flexible sensor prepared at 0°C. Table 1 depicts all the prominent FTIR peaks of flexible PAni prepared at 0°C with their assignments. All the observed characteristic FTIR peaks supported for the formation of PAni.

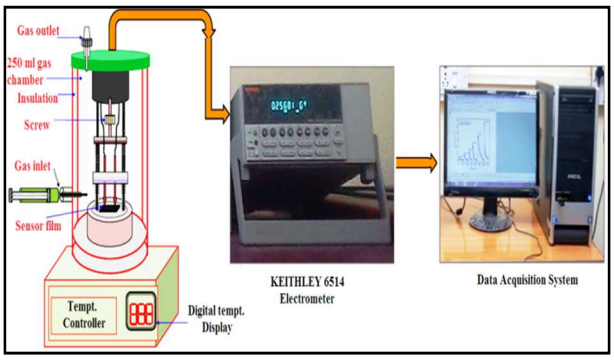

Fig.2: Schematic diagram showing experimental set-up used for gas sensing measurement.

3.2 RAMAN study

Raman spectroscopy is the important tool to study bonding between two components. Fig.3 (b) highlights the characteristic Raman spectrum of the flexible PAni sensor fabricated at 0°C (discussed later why it was only selected) where three prominent characteristic peaks at 1175 cm^{-1}, 1458 cm^{-1} and 1553 cm^{-1} were confirmed. The characteristic peak at 1175 cm^{-1} was assigned to the C-H in plane bending of quinoid ring.[18-19]

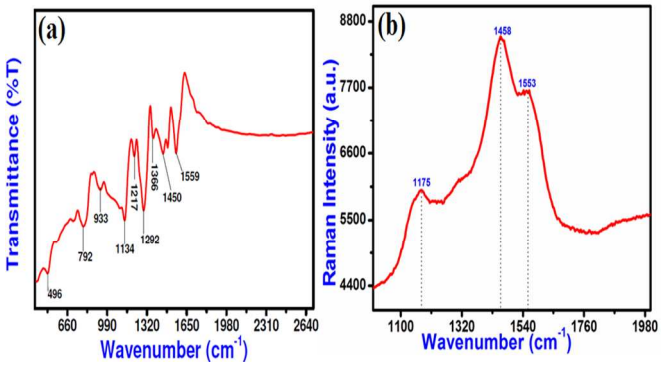

Fig.3: (a) FTIR and (b) Raman spectrums of flexible PAni (0°C).

The strong band seen at 1458 cm^{-1} supported for the C=N stretching of imine sites in emraldine form of PAni, which is the dedoped state of the PAni. The characteristic band observed at 1553 cm^{-1} was mainly due to N-H bending.[20] Thus, the Raman spectrum again confirmed the formation of PAni.

Table 1: Bonding-types and peak positions of FTIR spectra of flexible PAni sensors developed for three temperatures.

Assignment	Wavenumber (cm^{-1})	Ref.
C-H out of plane bending vibration, aromatic ring deformation	496	14
Out of plane deformation of C-H in para-disubstituted benzene ring	792	14,15
C-H in plane bending vibration	1134	16
C-H in plane bending	1217	14
C-N stretching vibration of PAni	1292	16
C-C stretching of benzenoid ring	1450	14
C=C stretching of quinoid ring	1559	17

3.3 Structural elucidation

Fig.4 (a-c) shows the XRD patterns of flexible PAni sensors developed at 35°C, 0°C and -5°C temperatures, respectively. Sensor of 35°C (Fig. 4 (b)) showed a single broad diffraction peak at 2θ = 15-35°, this is the characteristic of amorphous emeraldine form of PAni.[21] Figures 4(a) and (c) cover the XRD pattern of flexible PAni sensors prepared at 0°C and -5°C, respectively. Both XRD patterns revealed sharp and intense diffraction peaks at same diffraction angle i.e. at 2θ = 20-30°, indicating polycrystalline nature of PAni, in *juxta-pose* to its amorphous form. This could be associated with the presence of the planes of benzenoid and quinoid rings of PAni.[22] Also, at low-temperature, the polymer chains were more ordered.[23-25] From the XRD patterns of flexible PAni sensors it was corroborated that with decreasing synthesis temperature the intensity of diffraction peak increased, supporting for increase of the crystallinity; consistent to elsewhere reported observation.[26]

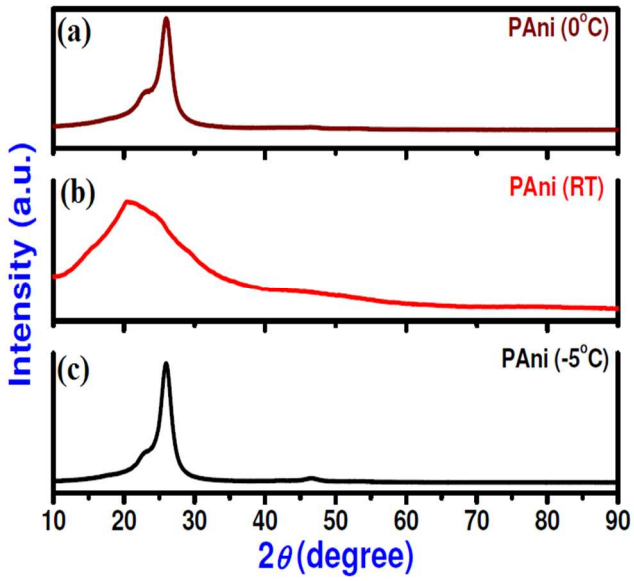

Fig.4: XRD patterns of flexible PAni sensors; (a) 35°C (room temperature), (b) 0°C, and (c) -5°C.

3.4 Morphological evolution

Surface morphologies of flexible PAni sensors developed at different processing temperatures were obtained using FESEM surface images. A close look of Fig. 5(a) shows broken PAni fibres dispersion in the sea of granular matrix of the PAni synthesized at 35°C. Fig. 5(b) shows surface image of flexible PAni sensor synthesized at 0°C. Continuous fibrous type morphology was evidenced. Several deep air voids of irregular dimensions were also noticed. This typical morphology can provide a high surface-to-volume ratio which will easily adsorb large quantity of gas molecules, and let them into and out of the PAni structure,[30-31] which is one of the essential conditions for efficient gas sensors.[27-29] The observed fibres were of 35-40 nm in diameters. Fig.5(c) shows discontinuous cluster of fibres. Thus, PAni fabricated at 0°C demonstrated more porous and fibrous structure than 35°C and 5°C. Also from the FESEM images, it was confirmed that the processing temperature was strongly influencing on the morphology of as-grown flexible PAni sensor.

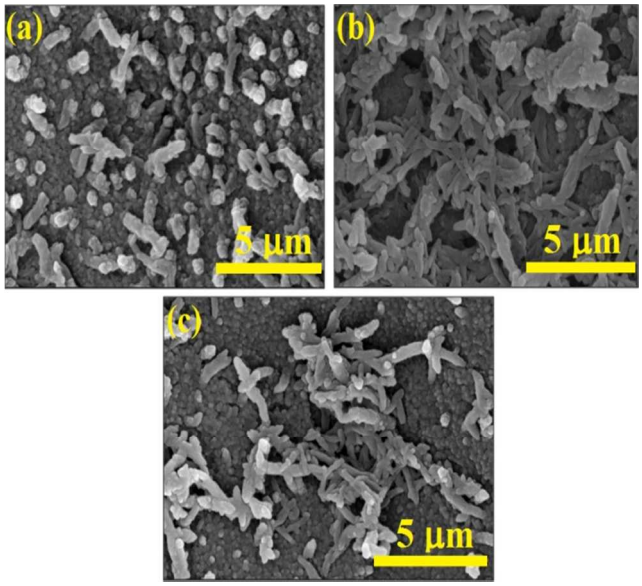

Fig.5: FESEM images of flexible PAni films; (a) 35°C (room temperature), (b) 0°C, and (c) -5°C.

3.5 XPS analysis

XPS measurement was carried out to examine the chemical structure of the flexible PAni sensor. Fig. 6 (a-c) shows the core level XPS spectra of C1s, N1s and O1s peaks of PAni sensors prepared at 0°C. In Fig.6 (a), high resolution C1s spectrum was deconvoluted with three other peaks centered at 284.65 eV (C-C), 286.35 eV (C-N, C=N, C-O)[32-34] and 288 eV ($C-N^+$, $C=N^+$, C=O).[34] N1s spectrum of PAni is shown in Fig.6 (b) was deconvoluted into single benzenoid amine (-NH-) species, located at 399.3 eV, similar to an earlier report by Li *et al.*[35] Fig.6 (c) shows XPS O1s analysis spectrum of PAni which was deconvoluted in to three other peaks at binding energies 530.4 eV, 531.8 eV and 533.3 eV respectively. Ideally there should not be oxygen peak as PANi demonstrates $(C_6H_5N)_n$ chemical formula; however it is there, which could due to unavoidable surface contamination of carbon hydrates[32] or substrate (i.e. PET) itself. The observed peak at 530.4 eV was due to the presence of C-O group. While the peaks situated at 531.8 eV and 533.3 eV were owing to the O-C=O oxalate group. All the observed core

levels and their binding energies matched well with those of reported in literature,[32-35] confirming the formation of PAni.

3.6 Gas sensing study

In order to compute the response for different gases, the changes in resistance of flexible PAni sensors were measured in the presence of air atmosphere and the test gas. To measure resistance, two silver contact electrodes separated by one centimeter apart were made onto a sensor using silver paste. Keithley electrometer (Model: 6514) was used to gauge the change in resistance. All the gas sensing study was carried out at room temperature using a home-built airtight stainless-steel chamber (of 250 cc capacity) containing sample holder geometry (Fig. 2). Different test gases such as NH_3, H_2S, methanol (CH_3OH), NO_2 and ethanol (C_2H_5OH) were procured from Space Cryo Gases Pvt. Ltd., India in the form of gas filled canisters (of 0.5 lit. capacity) with 1000 ppm concentration. A known concentration of gas in chamber was injecting by using syringe.

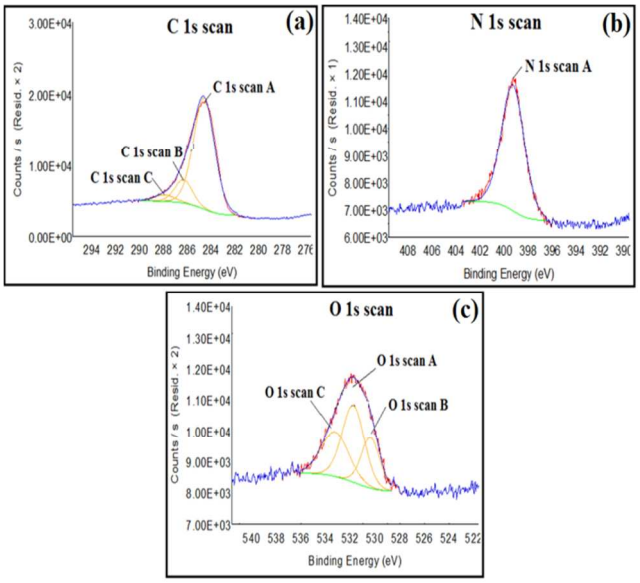

Fig.6: Core level; (a) C1s, (b) N1s and (c) O1s XPS spectrums of flexible PAni sensor prepared at 0ºC.

The recovery phase of the sensors was initiated by opening the lid of stainless-steel chamber. The change in resistance of flexible sensor was recorded as function of time *via* computer interfaced 6514 Keithley electrometer. The response of flexible PAni sensor was calculated using following relation;

$$\text{Response (\%)} = \frac{|R_a - R_g|}{R_a} \times 100 \qquad \ldots\ldots \quad (1)$$

3.7.1 Selectivity

Figure 7 (a) shows the histogram of selectivity study of prepared flexible PAni sensors (35ºC, 0ºC and -5ºC) against different toxic gases including NH_3, C_2H_5OH, H_2S, CH_3OH and NO_2 with each of 100 ppm concentration; operating at room temperature. As seen in Figure 7 (a), flexible PAni sensors prepared at 35ºC, 0ºC and -5ºC were highly selective and sensitive to NH_3 gas compared to other test gases, which confirmed the selectivity of flexible PAni sensors for NH_3 gas at room temperature. While, the flexible PAni sensor prepared at 0ºC demonstrated the maximum response to NH_3 (26%) when compared to flexible PAni sensors developed at 35ºC and -5ºC. Therefore, in the rest of the gas sensing studies the PAni flexible sensor developed at 0ºC was selected. The observed higher response was mainly ascribed to the typical morphology of flexible PAni (0ºC) sensor which might adsorb more gas molecules by offering more chemical reactions, resulting into increase in gas response.[36,37] Fig.7 (b) shows the plots of response as a function of time for flexible PAni sensor prepared at 35ºC, 0ºC and -5ºC towards 100 ppm exposure of NH_3 gas. The relation between the sensor response along with the response time and recovery time for all the prepared sensors to 100 ppm NH_3 gas is summarized in Table 2.

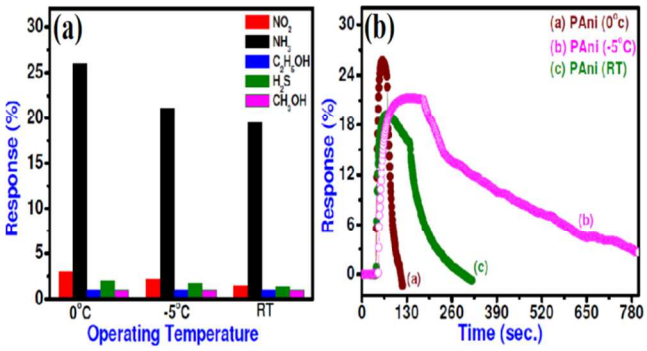

Fig.7: (a) Selectivity study of flexible PAni sensor at various processing temperatures, and (b) Response of PAni flexible sensors synthesized at 0ºC, -5ºC and 35ºC to 100 ppm NH_3.

Table 2: Sensing capabilities of flexible PAni sensors developed for different synthesis temperatures when 100ppm level of NH_3 gas concentration was fixed.

Process temperature	Response (%)	Response Time (s)	Recovery Time (s)	Selective Gas
35ºC	19.48	33	131	NH_3
0ºC	26	19	36	NH_3
-5ºC	21.22	87	1169	NH_3

3.7.2 Influence of NH_3 gas concentration

The flexible PAni sensor prepared at 0ºC was subjected to successive injections of NH_3 gas (5-200 ppm) and obtained results are displayed in Figure 8 (a). A stepwise increase in response was observed with increase in NH_3 gas concentration from 5 ppm to 200 ppm and during all recovery phases approached to its original baseline level as soon as sensor was exposed to air, indicating good reversibility of flexible PAni sensor. Plot of variation of sensor response as a function of NH_3 gas concentration is shown in Figure 8 (b). Linear variation in response was observed with increasing NH_3 gas concentration from the low 5 ppm to the high 200 ppm levels. It should be noted that the flexible sensor was capable to sense as low as 5 ppm concentration of NH_3 gas at room temperature. Plot of change in resistance of flexible PAni (0ºC) film as a function of time to 100 ppm exposure of NH_3 gas is shown in Figure 8 (c). The sudden increase in resistance value was observed upon interaction of gas molecules with very fast response (19 s) and recovery time (36 s) intervals.

3.7.3 Gas sensing mechanism

Increase in resistance with respect to time when the flexible PAni sensor was exposed to NH_3 gas is confirmed from Fig.8 (c). This increase in flexible PAni sensor resistance after exposure to NH_3 gas was attributed to the interaction between the reactive sites of PAni sensitive layer and NH_3 gas molecules. Here we used PAni emeraldine base (EB) which was half oxidized and half reduced state. Therefore, PAni (EB) experienced neutral state when PAni (EB) sensor was exposed to NH_3 gas due to the reducing nature of NH_3 (electron donating property), which supposed to accept H^+ ions from PAni (EB) by forming ammonium ion and decreasing the doping level of PAni[38,39] so as to convert into pernigraniline base (fully oxidized) form.[40] Due to the loss of H^+ ions, electron density increased and PAni was more negative, as a result the resistance of PAni sensor increased and the conductivity was decreased.[41-43] The pernigranilne base is basically unstable form of PAni because when PAni sensor is exposed to air, it will capture hydrogen from ammonium ion by restoring the initial doping level of PANi (EB),[41-46] which can add H^+ ion form N-H bond and thereby, there is decrease of the sensor resistance by attaining initial baseline resistance level.[47-50] The possible reaction mechanism is shown in Fig. 9.

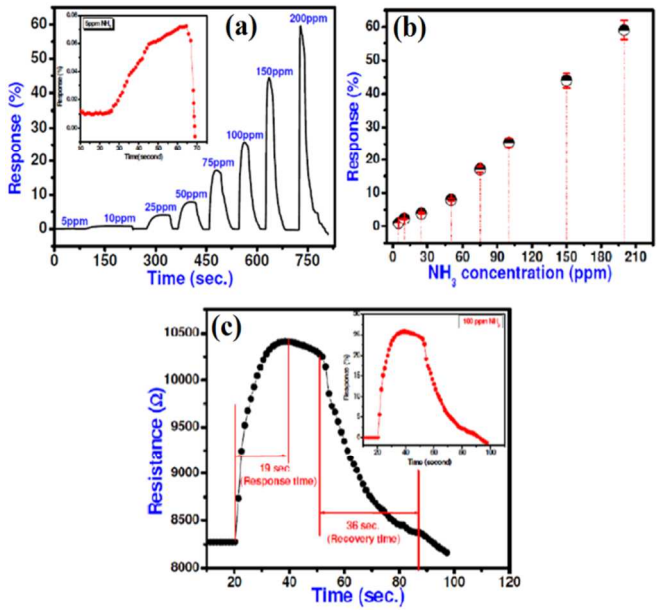

Fig.8: (a) Dynamic response of flexible PAni sensor (inset presents 5ppm NH_3 response), (b) sensor response as a function of NH_3 gas concentration. (c) change of resistance as a function of time for flexible PAni (0°C) sensor (inset shows the plot of response *vs.* time for the flexible PAni (0°C) sensor).

3.7.4 Response-recovery and stability studies

We also studied the other sensing properties such as response time, recovery time, reproducibility and stability with respect to NH_3 gas concentration for the developed flexible PAni sensor (Fig. 10). The response & recovery plots of PAni sensor for 5 to 200 ppm levels of NH_3 gas are shown in Fig.10 (a). The response and recovery times were calculated by using the dynamic response curve using a process reported elsewhere.[51-53] As the concentration of NH_3 was increased from 5 to 200 ppm both response and recovery times were found varied inversely i.e. response time was decreased from 80 s to 5 s while recovery time was increased from 5s to 73 s, evidencing good response and recovery capabilities of presented flexible PAni sensor.

In order to examine the reproducibility, the response of flexible PAni sensor was measured by exposing repeatedly to NH_3 gas and the equivalent outcome is displayed [Fig.10 (b)]. These observations revealed that the response of sensor was unchanged during three cycles of measurements, representing good repeatability of flexible sensor.

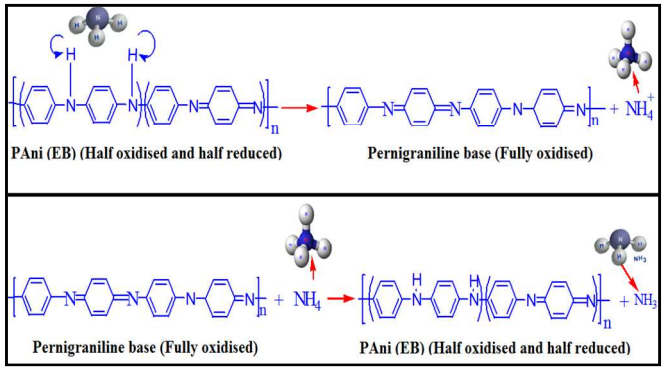

Fig.9: Proposed reaction mechanism of interaction of NH_3 with PAni.

Stability of flexible PAni sensor towards NH_3 gas for 60 days by the interval of 5 days was studied and highlighted in Fig. 10(c). Response value of PAni sensor was decreased with the number of days. Initially, sensor showed the response of 26%; which was decreased with time and stable response of 14% was attained after 40 days with 58% stability. Such a reduced response might be due to the humidity or aging induced effect.[51]

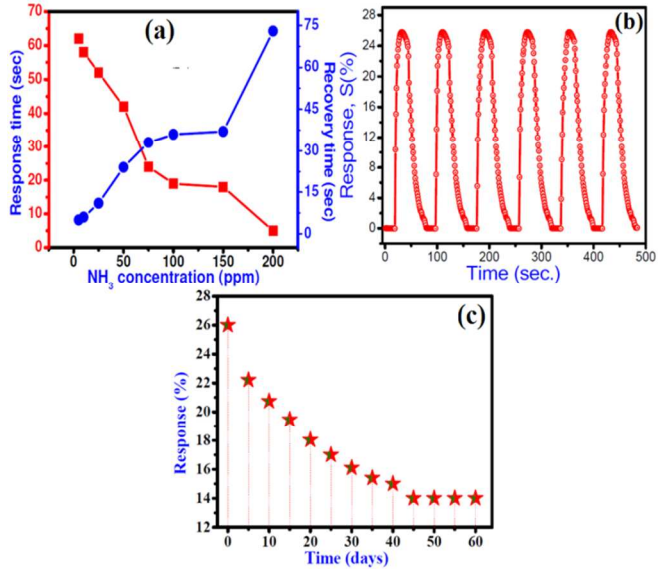

Fig.10: (a) Response and recovery time characteristics, (b) reproducibility, and (c) stability of flexible PAni sensor (0°C) at 100 ppm of NH_3 gas.

3.7.5 Impedance spectroscopy study

The interaction between flexible PAni sensor and NH_3 gas was also studied using impedance spectroscopy tool; providing information about various contributions of sensor response.[52] The

impedance study was carried out in presence of air and 100 ppm NH_3 gas by using WYNE KERR 6500B impedance analyzer in the 20Hz to 10MHz frequency range and observed results are displayed in Fig. 11. In this technique, the sensor is perturbed by AC signal of the form $V= V_0 \sin(\omega t)$. The impedance measured from the change of voltage and current is resolved into its real and imaginary parts (Cole-Cole plot).[53] Impedance study showed perfect semicircle from the low-frequency region to the high-frequency region.

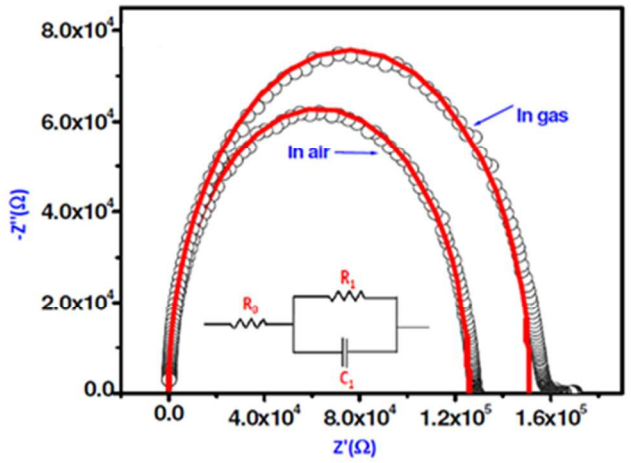

Fig.11: Impedance spectra of flexible PAni (0°C) sensor with and without NH_3 gas.

By using the equivalent circuit drawn as an inset of Fig.11 (R_o is the frequency independent resistance and R_1 & C_1 are parallel to each other), the experimental impedance data was fitted. There was a good agreement between the experimental data and simulated pattern. Table 3 illustrates the values of different physical parameters obtained from impedance spectra (before and after exposure to NH_3 gas). It was observed that the frequency independent parameter R_o was same for both air & gas but parameter R_1 was increased on exposure of NH_3, while C_1 was decreased marginally.

Table 3: Impedance parameter values for flexible PAni sensor used for fitting experimental data to that of the equivalent circuit.

Parameter / Values	R_0 (KΩ)	R_1 (MΩ)	C_1 (nF)
In air	1.6	0.126	1.96
In gas	1.6	0.151	1.25

3.7.6 Development of flexible PANi sensor laboratory scale model for detection of NH_3 gas

Fig. 12 (a) shows the block diagram of sensor circuit used for the detection of NH_3. For a practical demonstration, we deposited PAni sensor on PET substrate of 1 cm x 1.5 cm area. Fig. 12 (b) shows the actual photograph of flexible PANi sensor, we developed in our laboratory as a laboratory scale model. The flexible PANi sensor prepared at 0°C was used for the sensor fabrication. Fig.12(c) shows an example of the flexible PANi sensor which was used for detection of NH_3 gas at room temperature.

4. Conclusions

A novel low-temperature flexible polyaniline ammonia gas sensor was developed using *in-situ* chemical oxidative polymerization of aniline on polyethylene terephthalate substrate for three different temperatures *viz.* 35°C, 0°C and -5°C. The gas sensing observations confirmed that the sensor fabricated at 0°C demonstrated better response to ammonia gas than others. The gas sensing capabilities such as response, response and recovery times were surface morphology dependent i.e. synthesis temperature. The developed laboratory scale flexible PAni sensor evidenced industrial potential for dangerous spots dealing with hazardous gases due its easy synthesis methodology, low-cost, low-operation temperature, and flexibility etc., where high temperature operations are restricted.

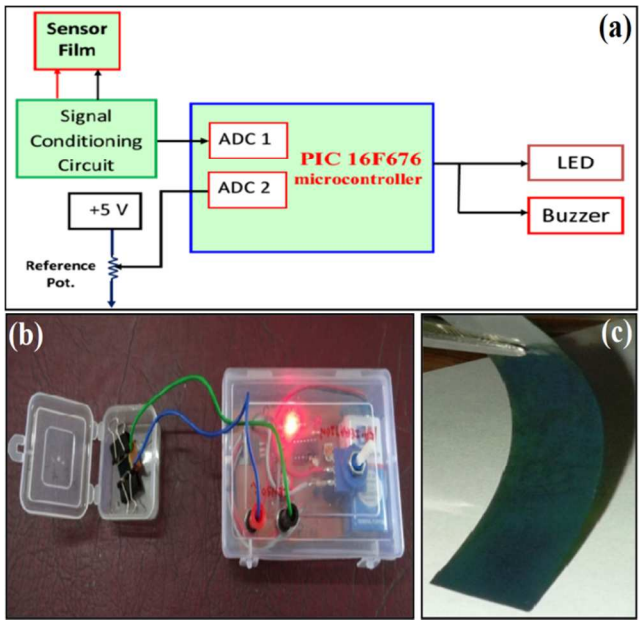

Fig.12: (a) Block diagram of flexible PANi sensor circuit, (b) photoimage of flexible PANi sensor, (c) flexible PANi sensor used for detecting ammonia.

Acknowledgements

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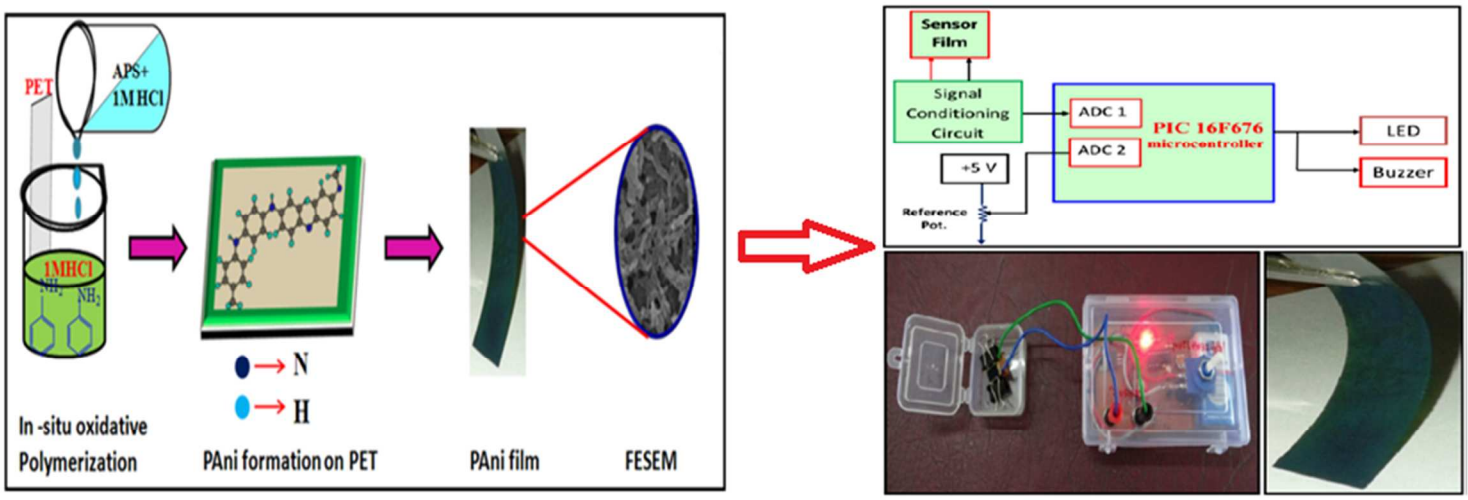
Low-temperature polyaniline-based flexible ammonia sensors: A step towards development of economical laboratory scale model†



Flexible PAni sensor not only exhibits high sensitivity, good selectivity and fast response but also has flexibility, cheap and wearable characteristics.