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Ultra-sensitive polyaniline-iron oxide nanocomposite room temperature flexible ammonia sensor


A novel flexible, ultra-sensitive, selective, and room temperature operable polyaniline/iron-oxide (PAni/α-Fe₂O₃) nanocomposite ammonia (NH₃) gas sensor was developed onto a flexible polyethylene terephthalate (PET) substrate by in-situ polymerization process. The observations were recorded to 100ppm fixed level for various gases including NO₂, CH₃OH, C₂H₅OH, NH₃, and H₂S through monitoring the change in resistance of the developed sensor. The flexible PAni/α-Fe₂O₃ nanocomposite sensor demonstrated better selectivity towards NH₃ (response = 39% and stability = 74%). The synergistic response of the flexible PAni/α-Fe₂O₃-sensor was remarkable than that of the PAni and α-Fe₂O₃ alone; indicating the effective improvement in the performance of PAni flexible sensor on nanocomposite process. Moreover, the flexible sensor detected NH₃ at low concentration (5ppm) with a fast response (27s) and very short recovery time (46s). Further, PAni/α-Fe₂O₃ flexible sensor films were characterized by X-ray diffraction, field-emission scanning electron microscopy, UV-visible and Raman spectroscopy, Fourier transform infrared and X-ray photoelectron for structural analysis, morphological evolution, optical and surface related studies.

1. Introduction

Detecting ammonia (NH₃) gas at its low level has attracted considerable attention due to its toxicity and its impact on living organisms. According to the US Environmental Protection Agency, a concentration of NH₃ above 25 ppm creates health issues. Therefore, it is essential to develop an NH₃ sensor which is reliable and inexpensive for detecting below the toxic limit. Recently, flexible substrate sensor has been attracting considerable attention due to its interesting characteristics, such as softness, lightness, flexibility and shock resistivity. In general, gas sensors require high temperature to operate effectively and efficiently (>200°C). This is above the continuous operating temperature of most of the polymers, thus, limiting their direct application. So fabricating a sensor, operating at low-temperature i.e. room (≤45°C), not only avoids the heating assembly but also makes the sensor setup simple, portable, and cheaper. Most of the conducting polymers (e.g. polyaniline (PAni), polypyrrole, polythiophene etc.) demonstrate potential gas sensing properties. Their advantages include low cost, flexibility in design, tunability, low power consumption and excellent performance at room temperature. PAni is one of the scientifically potential polymers with versatile applications including gas sensors and emerged as a star material in the field electrochemical sciences because of its intriguing properties such as high conductivity, good environmental stability, ease of preparation methods etc. Furthermore, PAni can be facilely oxidised and reduced; making it suitable for gas sensing application.

The presence of -NH- group in PAni favours the oxidation, reduction and various physical and chemical properties. Besides the sensing capabilities, it can also be used in rechargeable batteries, supercapacitors, light emitting diodes, corrosion protection systems, and electrochromic display devices. But, PAni suffers from a major disadvantage of poor chemical solubility in organic solvents and also hinders while operating at higher temperatures, limiting its applications. Most semiconducting metal oxide-based gas sensors (tin oxide, zinc oxide, nickel oxide, tungsten oxide and iron oxide etc.) are widely used as a chemiresistive type gas sensors, alternative to conducting polymers due to their ability to detect various gases, high sensitivity, fast response, recovery time and low cost. Most of the metal oxides are n-type semiconductors, because electrons are naturally produced due to adsorption of O⁺ during oxide formation. The major disadvantage of metal oxide gas sensors is the need of high temperature. For example, iron oxide (Fe₂O₃) used for nitrogen dioxide (NO₂) sensing required >250°C for a better selectivity, a CdO-Fe₂O₃ ethanol sensor activated at 300°C. This demands a low-temperature controlled heating system to operate the sensor, as sensor operation at elevated temperature causes gradual changes in the physical and chemical properties of sensor, which promotes deviation in gas sensing properties of sensor with respect to time.

To overcome this difficulty, new prospects can be opened by designing the flexible sensor based on organic-inorganic composite nanostructures. The inorganic materials are thermally more stable as compared to organic i.e. polymer matrices and can improve the sensing characteristics such as sensitivity, selectivity, stability of polymer. The most important advantage of organic-inorganic composite nanostructures is that, by combining individual materials different property profiles leads to produce desirable properties in composites. The physicochemical properties of organic-inorganic hybrid nanocomposites depend on the distribution of filler particles into polymer matrix as well as on interfacial bonding between the inorganic filler and polymer matrix. Khuspe et al. reported that the incorporation of metal oxides into polymer matrix greatly modify the microstructure and...
the mechanical properties of original polymer\textsuperscript{26} and improves the sensing performance of sensor.\textsuperscript{27}

In the present study, PANi was functionalized with $\alpha$-Fe$_2$O$_3$ to acclimatize its structural properties and to boost its gas sensing performance in order to induce stronger and faster chemical reactions between PANi sensor and target gas. It is worth noticing that the properties of $\alpha$-Fe$_2$O$_3$ not only make them a new class of composites, but also make them capable for reinforcement of fillers within a host PANi matrix.\textsuperscript{28} The effect of $\alpha$-Fe$_2$O$_3$ filler particles on gas sensing properties of PANi was studied in terms of change in sensor resistance, sensor response, response/recovery time and stability etc. We believe, the unique physical and chemical properties of PANi/$\alpha$-Fe$_2$O$_3$ nanocomposite enabling sensing activity at lower concentration of NH$_3$ gas.

PANI/$\alpha$-Fe$_2$O$_3$ composite flexible sensor was fabricated by in-situ polymerization process using aniline as monomer. In-situ polymerization is an excellent approach to form homogenous mixture of two materials. This is simple, low-cost and time saving process and a fine clad of different materials with conducting polymers can be designed on flexible substrates.\textsuperscript{29}

2. Experimental details

2.1 Chemicals used

Ferric chloride hexahydrate (FeCl$_3$).6H$_2$O purchased from Aldrich was used for preparation of iron oxide, methanol was purchased from s-d fine chemicals, aniline as monomer and ammonium persulphate as an oxidant, all are AR grade purchased and were used as received. Polyethylene terephthalate (PET) thickness were purchased and used as it is without any physical and chemical processing.

2.2 Fabrication of flexible PANi/$\alpha$-Fe$_2$O$_3$ sensor films

Chemically adapted PANi/$\alpha$-Fe$_2$O$_3$ nanocomposite flexible sensors were prepared on flexible PET by in-situ polymerization process using aniline as monomer and ammonium persulphate as an oxidant in HCl solution; resulting procedure is as follows; 0.1 M APS (Ammonium Per Sulphate) $\left[ \left( \text{NH}_3 \right) _2 \text{S}_2 \text{O}_8 \right]$ was added in 0.2 M aniline ($\text{C}_6 \text{H}_5 \text{NH}_2$) and 0.2 M HCl (Hydrochloric Acid) mixture. The resulting mixture was kept at room temperature for 3 h followed by continuous stirring. After polymerization, green precipitate was occurred and is nothing but the emeraldine salt form of PANi. To get emeraldine base form of PANi; de-doping of PANi from 10 to 50 Wt.\% (1-5 mass \%). After 3 h, blue thin layer of PANi deposited on the PET substrate. The resulting film was washed in distilled water to eliminate the low molecular weight organic intermediates and dried at the ambient temperature and used for further studies. The synthesis process for the development of PANi/$\alpha$-Fe$_2$O$_3$ nanocomposite on PET substrate is illustrated through Scheme 1.\textsuperscript{26, 29}

2.3 Characterizations and gas sensing measurements

X-ray diffraction (XRD) pattern was recorded on Rikagu Altima-IV diffractometer using Cu-K$_\alpha$ radiation with a wavelength 1.5406Å in continuous scan mode at an acceleration voltage of 40kV and current of 40mA. The composite formation and bonding characteristics were investigated by a Nicolet IS-10 (Thermo Fischer Scientific Instruments) Fourier transform infrared spectroscopy (FTIR) spectra. The surface morphology of flexible nanocomposite sensor film was analysed by field-emission scanning electron microscopy digital photographs (Model: MIRA3 TESCAN, USA). The interaction of $\alpha$-Fe$_2$O$_3$ with PANi was confirmed by UV-visible spectroscopy. The effect of addition of $\alpha$-Fe$_2$O$_3$ on polyaniline was investigated by Raman spectroscopy (Model: Horiba, 228 Lab Ram Hr 800). The electrochemical impedance spectroscopy (Precision Impedance Analyzer 6500B) measurement was used to quantify the sensor response to the gases tested. X-ray photoelectron spectroscopy (XPS, VG, Multilab 2000, Thermo VG, Scientific UK) spectra was carried out to investigate the structure of core-level electron and to resolve binding energies of PANi/$\alpha$-Fe$_2$O$_3$ nanocomposite.

Gas sensing properties were studied using a home-made gas sensor unit equipped with computer-attached KEITHLEY 6514 Electrometer. The NH$_3$ nitrogen dioxide (NO$_2$), methanol (CH$_3$OH), ethanol (C$_2$H$_5$OH) and liquefied petroleum gases (LPG) etc., have been purchased from space cryo gases Pvt. Ltd., Mumbai. The resultant sensitivity of composite flexible sensor was expressed according to following equation defining the response.

\[
\text{Response (\%)} = \left| \frac{R_a - R_g}{R_a} \right| \times 100 \quad \ldots \ldots (1)
\]

where $R_a$ and $R_g$ are resistances of film sensor in air and target gas, respectively.

\textbf{Scheme1:} Schematic representation of synthesis route of PANi/$\alpha$-Fe$_2$O$_3$ nanocomposite on PET substrate by in-situ oxidative polymerization.

3. Results and discussion

3.1 Structural identification

Fig.1 shows the XRD patterns of as-synthesized PANi, $\alpha$-Fe$_2$O$_3$ and PANi/$\alpha$-Fe$_2$O$_3$ nanocomposite flexible films. From the XRD pattern of pure PANi, single broad peak (Fig.1(a)) in the range of 20-30°(2θ) was evidenced which was higher in enclosed area and intensity, but in the case of composite i.e. PANi/$\alpha$-Fe$_2$O$_3$, several new planes were evidenced. The broad nature of XRD pattern clearly indicated amorphous behavior of synthesized PANi. XRD pattern of $\alpha$-Fe$_2$O$_3$ is shown in Fig.1(b). It is noteworthy that high intense XRD peak of PANi at 25.82° is disappeared for composite structure. Shift in XRD peak of PANi in composite structure is eccentric. However, there are few reported wherein
shift of PANi XRD peak position is evidenced when compositeis formed\cite{30}, but in present case we believe it could be due to a change of its structure when composite is formed and obtained small intense PANi XRD peak might be a shoulder of previously found broad intense peak. The other peaks of PANi/α-Fe$_2$O$_3$ composite were similar to the peaks observed in XRD pattern of α-Fe$_2$O$_3$\cite{27}, confirming the type of α-Fe$_2$O$_3$ crystal structure which was well-maintained after preparing composite in base media. The XRD result showed the presence of two different phases i.e. PANi and α-Fe$_2$O$_3$, supporting for the formation of PANi/α-Fe$_2$O$_3$ nanocomposite.

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{fig1.png}
\caption{XRD patterns of (a) PANi, (b) α-Fe$_2$O$_3$, and (c) PANi/α-Fe$_2$O$_3$ nanocomposite films.}
\end{figure}

\subsection*{3.2 Surface analysis}

To identify the presence of α-Fe$_2$O$_3$ in the composite and to observe the association between the PANi and the α-Fe$_2$O$_3$, FTIR spectra of flexible PANi and PANi/α-Fe$_2$O$_3$ nanocomposite films were recorded. The peak at 569 cm$^{-1}$, characteristic of the Fe-O stretching vibration, clearly supported for the presence of α-Fe$_2$O$_3$ in PANi matrix and shift of peak suggested the interaction of α-Fe$_2$O$_3$ with polyaniline\cite{31-33}. The peak observed (fig.2 (a)) at wave numbers $672$ cm$^{-1}$ and $736$ cm$^{-1}$ was attributed to C-H out of plane bending vibrations\cite{34}. The peak at $856$ cm$^{-1}$ was the characteristic of C-C and C-H for benzenoid ring occurred from C-H out of plane bending vibration of benzene ring\cite{35-38}. The absorption peak at 1061 cm$^{-1}$ was due to C-H bending\cite{38}. Also the peak observed at $1283$ cm$^{-1}$ was on account of C-N stretching of primary aromatic amine ring and the peak observed at $1490$ cm$^{-1}$ was assigned to C=N stretching in aromatic ring\cite{39}. The peak at $1442$ cm$^{-1}$ was in favour of C=C stretching mode of benzenoid ring which was shifted to $1450$ cm$^{-1}$ on addition of α-Fe$_2$O$_3$\cite{40, 41}. The absorption peak at $1591$ cm$^{-1}$ was due to C=C stretching vibration\cite{42} and peak at $1723$ cm$^{-1}$ was due to C=O bond stretching vibration. Comparing the FTIR spectra of PANi and PANi/α-Fe$_2$O$_3$ composite, it was concluded that the most of the peaks of PANi were shifted towards higher wavenumber side i.e.PAni/α-Fe$_2$O$_3$ composite (fig.2 (b)) which could be due to an interaction between PANi and α-Fe$_2$O$_3$\cite{43}. As when nanoparticles of metal oxide are incorporated into a polymer matrix so as to obtain chemically, environmentally and thermally stable composite material, the constituents demonstrate strong intermolecular interactions, resulting in change of electron density distribution followed FTIR shift\cite{27}.

\subsection*{3.3 Raman shift analysis}

Chemical structures of PANi and PANi/α-Fe$_2$O$_3$ nanocomposite flexible films were studied by Raman spectroscopy. Raman spectra of pure PANi (fig.2 (c)) showed the characteristic band at $1175$ cm$^{-1}$ due to C-H stretching\cite{44, 45}, $1458$ cm$^{-1}$ due to C-N vibration of quinoid ring\cite{46} and band at $1553$ cm$^{-1}$ was lined to N-H bending.\cite{47} Raman spectra of PANi/α-Fe$_2$O$_3$ (fig.2 (d)) composite noted a characteristic band of α-Fe$_2$O$_3$ at $283$ cm$^{-1}$. Bands of pure PANi at $1458$ cm$^{-1}$ and $1553$ cm$^{-1}$ shifted in the vicinity of $1304$ cm$^{-1}$ and $1578$ cm$^{-1}$ when α-Fe$_2$O$_3$ was introduced. The shifting of the band was due to a strong mutual interaction of hydrogen bonding between Fe-O of α-Fe$_2$O$_3$ and −NH- group of PANi.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig2.png}
\caption{(a, b) FTIR, and (c, d) Raman spectrums of PANi, and PANi/α-Fe$_2$O$_3$ nanocomposite film surfaces.}
\end{figure}

\subsection*{3.4 Surface morphological studies}

Figure 3 shows the FE-SEM digital micrographs of PANi, α-Fe$_2$O$_3$, and PANi/α-Fe$_2$O$_3$ nanocomposite flexible films prepared by in-situ polymerization process. FE-SEM micrograph of PANi (Fig.3 (a)) presents well-grown interconnected fibres of nearly identical diameter, covered uniformly the surface of flexible film. All fibres were porous in surface morphology. Fig.3 (b) shows the FE-SEM micrograph of Fe$_2$O$_3$ film prepared from a powder annealed at 700$^\circ$C. The particles were elongated-type with few remissence of the hexagonal corundum structure of α-Fe$_2$O$_3$. α-Fe$_2$O$_3$ nanoparticles were embedded within the net like structure consisting of PANi fibres in the case of PANi/α-Fe$_2$O$_3$ composite, suggesting a significant change in the original individual morphologies. As a consequence, PANi/α-Fe$_2$O$_3$ composite film (Fig.3 (d)) possessed both well-defined forms i.e.PAni and α-Fe$_2$O$_3$, implying a highly micro-porous structure and providing a path for insertion and extraction of gas molecules and ensuring high rate of reaction.
3.5 Surface analysis

An XPS spectrum was employed to analyse the effect $\alpha$-Fe$_2$O$_3$ and to understand the different electronic structures and chemical bonding information of PAni/$\alpha$-Fe$_2$O$_3$ composite. XPS core level spectrum of PAni/$\alpha$-Fe$_2$O$_3$ nanocomposite demonstrated C1s, O1s, N1s and Fe 2p peaks, which were related to the binding energies of C, O, N, and Fe, respectively. Fig. 4(a) presents the C1s core-level spectrum of PAni/$\alpha$-Fe$_2$O$_3$ composite; deconvoluted into three components at binding energies 283.8eV, 285.85eV and 287.7eV, respectively. Peak assigned at binding energy 283.8eV was due to C-H band. The peaks observed at binding energy 285.85eV and 287.7eV were attributed to C-N and C=O band, respectively. Core-level O 1s in XPS spectrum of PAni/$\alpha$-Fe$_2$O$_3$nanocomposite highlighted in Fig. 4(b). The spectrum deconvoluted into three components; peak observed at lower binding energy (530eV) was the characteristic peak of $\alpha$-Fe$_2$O$_3$, which was attributed to O-H band. The peak observed at 531.9eV was assigned to surface oxygen due to chemisorbed water and the peak evidenced at higher binding energy (533eV) was due to oxygen within the Fe-O-H bond because the estimated binding energy of O 1s electron for adsorbed water is 533eV. N1s core-level spectrum of PAni/$\alpha$-Fe$_2$O$_3$ nanocomposite is shown in Fig. 4(c). The N1s core-level spectrum situated around a binding energy of 399.4eV, indicating the existence of benzenoid ring in the PAni/$\alpha$-Fe$_2$O$_3$ nanocomposite as well as the prepared PAni could be in the neutral media with emeraldine form. Fig. 4(d) shows the core-level spectrum of Fe with two peaks located at binding energies of 710.85 eV (Fe$^{2+}$ state) and 724.35 eV, respectively, and were well-matched with values reported in literature. These observed bands indicated the presence of inorganic phase of $\alpha$-Fe$_2$O$_3$ in the composite.

![Image](image_url)

**Fig.3:** FESEM micrographs of; (a) PAni, (b) $\alpha$-Fe$_2$O$_3$, and (c) PAni/$\alpha$-Fe$_2$O$_3$ composite films.

3.6 Gas sensing studies

3.6.1 Selectivity

High selectivity is an important parameter for excellent working of sensor. To confirm the selectivity of the sensor to a particular gas, chemo-resistive properties were studied for PAni and PAni/$\alpha$-Fe$_2$O$_3$ nanocomposite sensors by exposing sequentially for different gases. Selectivity study of PAni/$\alpha$-Fe$_2$O$_3$nanocomposite sensor was performed for NH$_3$, H$_2$S, C$_2$H$_5$OH, CH$_3$OH, and NO$_2$ at 100 ppm concentration of each gas and given in Fig. 5(a). Resistance of PAni film sensor was not changed to C$_2$H$_5$OH and CH$_3$OH gases, hence, the response was considered to be zero, confirming that these gases are not interacting with the PAni sensor. But when PAni sensor was exposed to NO$_2$ and H$_2$S gases, responses were increased by 1% and 0.5%, respectively; considerably lower as compared to NH$_3$ (26%) gas. Selectivity study clearly supported that PAni/$\alpha$-Fe$_2$O$_3$ sensor was more selective to NH$_3$ than other test gases and exhibited higher selectivity to NH$_3$ when compared to pure PAni. After addition of $\alpha$-Fe$_2$O$_3$ nanoparticles in PANI matrix, quinoid structure (higher conjugation) of PAni was transformed into benzoid structure (lower conjugation) and made it more selective to target gas (herein NH$_3$).

![Image](image_url)

**Fig.4:** (a) C 1s, (b) O 1s, (c) N 1s, and (d) Fe2p of PAni/$\alpha$-Fe$_2$O$_3$ composite.

3.6.2 NH$_3$ dependent response of PAni/$\alpha$-Fe$_2$O$_3$ flexible sensor

NH$_3$ gas sensing behaviour of PAni/$\alpha$-Fe$_2$O$_3$nanocomposite flexible sensor was determined by monitoring the electrical resistance. At first PAni/$\alpha$-Fe$_2$O$_3$ sensor was exposed to air to measure the sensor resistance in air ($R_a$). Fig.5(b) shows the response of flexible PAni/$\alpha$-Fe$_2$O$_3$nanocomposite sensor to NH$_3$ gas at room temperature. From the response graph, it was observed that the sensor resistance was increased immediately with time when sensor exposed to NH$_3$ gas. At the beginning when NH$_3$ gas was injected into the chamber, the measured resistance of sensor increased rapidly, reached to its maximum value and became stable, which was used to define the resistance of sensor in gas ($R_g$). Recovery of sensor was achieved by opening the lead of chamber, leading to a strong gradual decrease of the measured resistance of PAni/$\alpha$-Fe$_2$O$_3$nanocomposite sensor until reaching to its initial value $R_a$. Decrease in resistance of sensor after exposure to air was due to a decrease of NH$_3$ concentration. According to equation (1), the response obtained
for PAni/α-Fe₂O₃ nanocomposite flexible sensor was 39% for 100ppm level of NH₃ gas with short response (27s) and (46s) recovery times, defined as the time from exposure to NH₃ to the peak in resistance and the time from exposure to pure air till the previous resistance, respectively.

During the process NH₃, as a deprotonating agent, might interact with H⁺ ion on the PAni backbone, withdrawing protons from N-H sites followed transferring them to ammonium (NH₄⁺) ions as shown in Scheme 2. After attaining optimum we found there was decrease in resistance before switching gas to its off level within 50-75 s, which was unusual, and might arise from an interaction of NH₃ gas molecules with host material i.e. as NH₃ is electron donating moiety thereby when it interacts with composite thin film which is p-type in nature; shift in its Fermi energy level towards conduction band position side with reduced resistivity is anticipated. The increase in electrical resistance was attributed to proton charge transfer from PAni to NH₃ gas.⁵ Due to loss of H⁺ ion, surface depletion region was increased, thereby; the conductivity of PAni was decreased. When sensor film was exposed to air; could capture hydrogen from NH₄⁺ and renovate the initial doping level of PAni.⁹,10,13 This added H⁺, form N-H bond and thus the resistance of sensor was decreased. However, the mechanism for NH₃ gas molecules and α-Fe₂O₃ interactions in composite form was unprecedented. Our previous results showed that, the resistance of α-Fe₂O₃ remained unchanged upon exposure to NH₃ gas⁵⁷, suggesting NH₃ can be an inert gas for α-Fe₂O₃.

3.6.4 Influence of NH₃ concentration

The performance of PAni/α-Fe₂O₃ flexible sensor was determined by measuring the sensor response for different ammonia gas concentrations at room temperature (30°C) (Fig.5(c)), revealing to be sensitive as low as 5ppm of NH₃. From Fig. 5 (c) it is revealed that, the response of PAni/α-Fe₂O₃ sensor was increased with rising NH₃ gas concentration. At higher concentration of ammonia (100 ppm) it showed not only the maximum response (39%) but also very short response time (27 s), with increase of concentration the number of gas molecules interacting with sensor surface increases as well.

3.6.5 Reproducibility, response-recovery, stability and impedance studies

Reproducibility study of PAni/α-Fe₂O₃ nanocomposite flexible sensor revealed that the sensor maintained its initial amplitude with short response and recovery times for three cycles of NH₃ gas exposure, indicating good stability of sensor [Fig. 6(a)]. Complete recovery of sensor resistance to its initial baseline value after exposition to air, evidencing favourable industrial and market quality of developed sensor. This was due to protonation and deprotonation of polyaniline. Fig.6 (b) shows response vs. recovery time graph of PAni/α-Fe₂O₃ flexible sensor to different NH₃ gas concentrations. Very short response time (27 s) and recovery time (46 s) were noted at 100ppm of NH₃ gas concentration. Whereas, at the lowest concentration of NH₃ gas (5 ppm), 76 s response time and 5 s recovery time were recorded, giving an indicator for the speed of the adsorption-desorption of NH₃ gas on the sensor. From the response-recovery observations, it was evident that with increase of the NH₃ gas concentration, response time was decreased drastically and recovery time was increased intensively; faster than previously reported literature values.⁵⁵,⁵⁸ The stability of the sensor was determined by measuring the response of the sensor for every five days for one month [Fig. 6 (c)] by fixing the constant concentration (100ppm) of NH₃ gas, showing a decrease of response for the first few days until reach to an equilibrium level i.e. response after 15 days. Hence, PAni/α-Fe₂O₃ flexible sensor showed good (74%) long-term stability. The impedance spectra of PAni/α-Fe₂O₃ flexible sensor was measured in air and gas at room temperature and

Fig.5: (a) Selectivity study of PAni and PAni/α-Fe₂O₃ sensor films, (b) Change in resistance as a function of time of PAni/α-Fe₂O₃ sensor film upon 100 ppm exposure of NH₃ gas, and (c) Response of flexible composite sensor to different NH₃ concentrations.

Scheme 2: Possible sensing mechanism of NH₃ gas with PAni/α-Fe₂O₃ film sensor.
covers in Fig. 6 (d). Impedance was measured in the frequency range of 20Hz to 10 MHz; the plot of imaginary component (Z") against the real component (Z') exhibited a perfect semicircle. The series resistance R_s was found by the value of real impedance at the highest frequency intercept. R_t and R_c1 component in the equivalent circuit correspond to the bulk properties while R_t and C_c2 component correspond to the grain boundary properties of the PANi/α-Fe_2O_3. Table 1 summarizes the values of impedance parameter in air and gas. When the gas was injected into the chamber resistance R_s was increased and capacitance C_c1 was decreased.

Fig. 6: (a) Reproducibility, (b) Response vs. recovery variation, (c) Stability of PANi/α-Fe_2O_3 nanocomposite sensor, and (d) Impedance spectra (Z' vs. Z") of PANi/α-Fe_2O_3 in presence of air and NH_3 gas. Inset shows an equivalent circuit.

Table 1: Impedance parameters for PANi/α-Fe_2O_3 flexible nanocomposite sensor.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>R_0 (KΩ)</th>
<th>R_1 (KΩ)</th>
<th>R_2 (KF)</th>
<th>C_1 (nF)</th>
<th>C_2 (nF)</th>
</tr>
</thead>
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<tr>
<td>Air</td>
<td>3</td>
<td>109.80</td>
<td>216.66</td>
<td>1.23</td>
<td>0.21</td>
</tr>
<tr>
<td>Gas</td>
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<td>199.13</td>
<td>254.930</td>
<td>1.15</td>
<td>2.02</td>
</tr>
</tbody>
</table>

4. Conclusions

PANi/α-Fe_2O_3 composite ammonia sensor was successfully developed on PET substrate by in-situ polymerization method. The resulting composite sensor was a mixture of fibers PANi and crysalitlles of α-Fe_2O_3. There was strong coupling between PANi and α-Fe_2O_3 as well as the formation of composite of PANi and α-Fe_2O_3. PANi/α-Fe_2O_3 nanocomposite flexible sensors was highly selective to NH_3 gas at room temperature compared to other test gases. The sensor response was measured with the change of resistance which was linearly increased with an increase of NH_3 concentration from 5ppm to 100ppm. The NH_3 sensor showed highest response of 39% with a fast 27s response time and 47s recovery time at 100ppm of NH_3 gas. Impedance spectra measured in air and gas and was well-fitted by with two time constants in series. Due to the room temperature operation and low development cost, flexible substrate, developed composite sensor can find numerous applications in domestic and industrial market areas from the points of safety, ecology and economy.

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Ultra-sensitive polyaniline-iron oxide nanocomposite room temperature flexible ammonia sensor

We report for the first time a room temperature smart NH$_3$ sensor based on PAni-Fe$_2$O$_3$ nanocomposite loading on flexible PET substrate by in-situ chemical oxidative polymerization method. The sensor not only exhibits high sensitivity, good selectivity and fast response but also has flexibility, cheap and wearable features.