

Enhancement in Ammonia Sensitivity with Fast Response by Doping Al_2O_3 in Polyaniline

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ABSTRACT: Al_2O_3 mixed polyaniline composite with different dopant concentrations have been synthesized successfully by chemical oxidation method. X-ray diffraction, Fourier transform infrared spectroscopy, and UV–visible spectroscopy confirm the synthesis of the polyaniline and Al_2O_3 mixed polyaniline composite. Scanning electron microscopy shows the weak crystalline quality of the samples. The samples are found sensitive to ammonia gas. The sensing properties have been studied at different temperatures i.e. 25°C, 50°C, and 100°C by varying the ammonia concentration over a range of 100–1500 ppm. The sensitivity increases with increasing Al_2O_3 concentration, increasing ammonia concentration, and also with increasing the sensing temperature. Sensitivity of these samples to ammonia gas is good with fast response. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1941–1948, 2013

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INTRODUCTION

Polymer–metal composites are attracting considerable attention of the researchers because of their striking advantageous properties such as easy processing flexibility and light weight.^{1–5} All conducting polymers exhibit reversible redox behavior with a distinguished chemical memory and hence have been considered as a most important class of new materials for the fabrication of biological and chemical sensors. The adsorption and desorption of volatile species cause a measurable change in the resistance of conducting polymers. Conducting polymeric sensors have advantages over metal oxide sensors. First a wide variety of polymers are available. Secondly, they are easily grown by chemical polymerization of monomer and also sense at room temperature.^{6–8} Among the conducting polymers, polyaniline (PAni) is advantageous because of comparatively high conductivity that can be achieved by doping.^{8–11} Fabrication of PAni with different nanostructures without using any foreign material is difficult. The use of inorganic component such as Al_2O_3 can assist the process. It can serve as a catalyst, absorbent, fire retardant, as well as a filler for structural materials. In addition, Al_2O_3 is stable in both acidic and oxidative environments during polymerization of aniline. Thus Al_2O_3 is a good candidate as seed to fabricate different PAni/ Al_2O_3 nanostructures. Several device applications of PAni include electrodes of rechargeable batteries, sensors, electrochromic displays, and photovoltaic devices.¹¹ In fact the metal cations of the inorganic salts form complexes with PAni and the material

exhibits different properties depending on the dopant polymeric–solvent interactions. The studies on the interaction of the metal ions with PAni suggest that the metal ions oxidize benzoid group in PAni and the reduced metal ion forms a co-ordination complex with the PAni molecules.¹² One of the disadvantages of PAni is its comparatively low mechanical strength, which limits its applications to some extent. However, still there are several reports on improving sensitivity and selectivity of PAni by making use of new methods, such as its synthesis in nano-structured forms or by addition of metalcatalysts and by combination with other polymers.¹³

PAni is a good choice for gas sensing and to our knowledge sensitivity of Al_2O_3 mixed PAni composite towards ammonia with varying sensing temperature is reported for the first time in this article. The prepared samples have been characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), UV–Vis spectra, and electrical resistance measurement.

EXPERIMENTAL

Pellet Preparation

Aniline hydrochloride (2.59 g) was dissolved in distilled water in a volumetric flask to make 50 mL solution. Ammonium peroxydisulfate (5.71 g) was dissolved in water also to make 50 mL of solution. Both the solutions were kept for 1 hour at room temperature. They were then mixed with a brief stirring and left

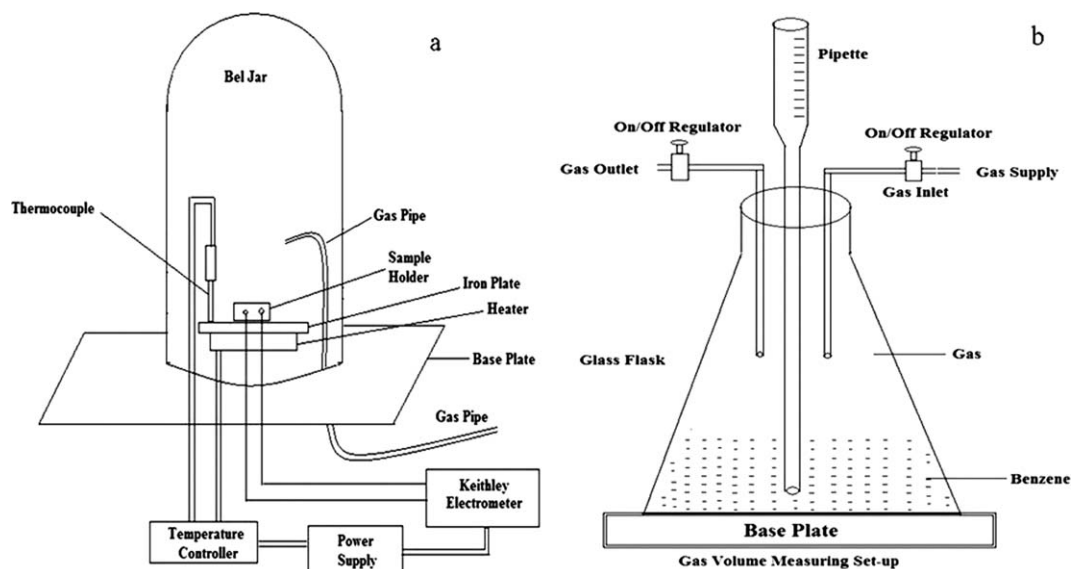


Figure 1. An experimental setup to monitor ammonia sensing. (a) Ammonia sensing chamber. (b) Gas volume measuring setup.

at rest to polymerize. The solution turned to dark green within few minutes. Next day PANi precipitate was collected on a filter paper, washed three times with 100 mL portions of 0.2M HCl to remove the unreacted aniline and its oligomers from the precipitate. After this process, precipitate was washed three times with 100 mL portions of acetone to absorb the water molecules and for the removal of any residual organic impurities. PANi, synthesized by this method, is formed in its protonated state. The precipitate was firstly dried in air for 30 min and then in oven for 3 hours at 60°C. The synthesized PANi has been mixed by Al₂O₃ in ratio of 2, 4, 6 and 8 wt %. The pure and Al₂O₃ mixed PANi composite was ground in form of fine powder.

Pellets were prepared by compressing the powder under a pressure of 10 tons with the help of a hydraulic press machine. All the pellets were annealed at 100°C for one hour. The thickness of the pellets of composite samples was found to be 0.65 mm. The diameter of the pellets was also found to be 13 mm. The 0, 2, 4, 6, and 8 wt % Al₂O₃ mixed PANi composite are denoted as samples a, b, c, d, and e, respectively.

Characterizations

The XRD spectra of all the samples recorded by Phillips X'pert PW3020 diffractometer using CuK α radiation ($\lambda = 1.54056 \text{ \AA}$) were presented for structural analysis of the samples. The SEM images of all the sample pellets were taken by scanning electron microscope (Model-430, LEO Cambridge, England). FTIR spectra of all the samples in the form of powder were recorded on the Bruker Alpha spectrometer to determine the formation of polyaniline. To record absorbance spectra, 0.01 g of each sample is dissolved in 5 mL of dimethyl formamide. Then the absorption spectra of the solutions thus formed were recorded with UV-Vis spectrophotometer (Model No.V-670 Jasco).

Setup for Gas Sensing

An experimental setup to monitor the ammonia sensing by PANi/Al₂O₃ pellets at room temperature and at higher temperatures is

developed in our laboratory [Figure 1(a)]. It consists of designed chamber with a provision of heater, thermocouple, substrate holder, connecting electrodes, a fan, gas inlet and outlet valves, and a gas volume measuring setup with conical flask of 1 L capacity. Gas sensing chamber is made of air tight glass bell jar with a rubber seal on the base kept on an iron plate.

A setup to measure and deliver known amount of gas to the sensing chamber has been developed as shown in Figure 1(b). It consists of a conical flask neck of which is sealed by a cork that has three holes on top. In one of these holes a graduated pipette is inserted. Benzene is dropped in the flask through the pipette such that end of this graduated pipette gets dipped in it. Benzene is used here because ammonia does not get dissolved in benzene. In other two holes small copper tubes are mounted, which are further connected to rubber tubes via two on/off teflon-coated ball regulators. These tubes are for inlet and outlet of gas and are connected to ammonia supply and gas sensing chamber, respectively. When the inlet regulator is turned on (keeping outlet off) the NH₃ from the cylinder is filled in the flask and an equivalent amount of benzene is displaced in the measurement pipette. Thus the NH₃ occupies a volume equivalent to the benzene that has risen in the pipette. Now the outlet regulator is turned on (keeping inlet off), which makes the NH₃ to flow in the sensing chamber where the undoped or Al₂O₃-doped polyaniline pellet is kept. The level of benzene in the pipette then falls. This fall is equivalent to the gas inserted into the chamber. Thus a known volume of gas can be easily introduced in the chamber.

A heater with a chromel-alumel thermocouple kept inside the gas sensing chamber for monitoring the temperature of the sample is attached to a digital temperature controller (Thermotech TIC-4000) to adjust the temperature. The fan fitted inside the sensing chamber spreads the ammonia gas homogeneously. Pressure contacts of copper of diameter equal to that of pellets

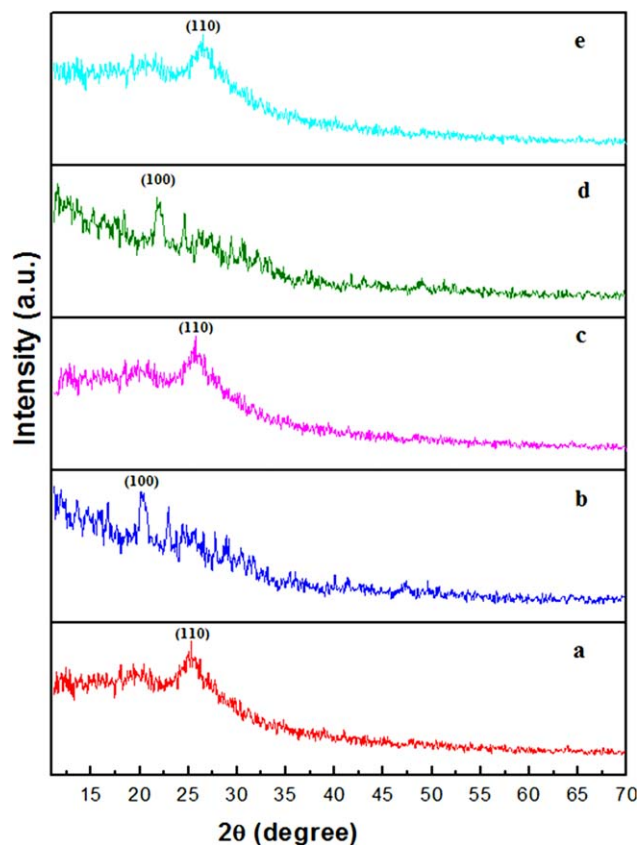


Figure 2. XRD spectra for the samples a, b, c, d, and e. Curves a, b, c, d, and e correspond to 0, 2, 4, 6, and 8 wt % Al_2O_3 mixed PANi composite, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are used as electrodes. Two fine copper wires insulated by ceramic beads are taken out from the electrodes to measure the resistance of the samples using Keithley electrometer.

Sample is kept inside the chamber and its resistance is measured in air, which is denoted by R_0 . A known volume of the ammonia gas was then introduced and the resistance R_x was measured. The resistance varies initially and after some time it becomes stable. These observations facilitate the determination of response time. Similarly, observations were taken for the other samples. After this, the variation in the resistance of the pellets was studied by introducing different concentrations of NH_3 within the range of 100–1500 ppm in the closed chamber at room temperature. Similarly, observations at other temperatures i.e. 50°C and 100°C were also taken.

Response and recovery times are determined for 100 ppm for all the samples. For determining the response time, 100 ppm of NH_3 gas was introduced in the sensing chamber. And the change in resistance is noted, which increases initially and after some time it becomes stable. The response time is defined as the time required for a pellet resistance to reach 90% of its saturation value from the initial value on gas exposure.¹³ The sensor element was then removed from the closed chamber and kept in ammonia-free atmosphere to monitor the recovery time. Resistance decreases gradually and then becomes stable.

The recovery time is defined as the time required for a pellet resistance to drop 90% of initial value on removal of the gas.¹³ This process was repeated five times and the response time was found to be stable.

RESULTS AND DISCUSSION

X-ray Diffraction

XRD spectra of the pure and the Al_2O_3 mixed PANi composite samples a, b, c, d, and e (Figure 2) show the weak crystalline quality of all the samples. There is a main peak around $2\theta = 25^\circ$ in sample a, c, e and around 20° in samples b and d, which correspond to (110) and (100) planes, respectively. Both the peaks of PANi are earlier reported by Zhu et al. and Krishna et al.^{1,12} There is no peak for the aluminium oxide in the composite sample, which indicates that the low percentage of Al_2O_3 does not affect the lattice structure of PANi. Thus the XRD spectra suggest that during the doping of metal oxides in PANi, PANi undergoes interfacial interactions with metal crystallites and loses its own morphology. The particle size for all the samples is estimated from Debye–Scherrer's (DS) formula¹⁴:

$$t_{\text{DS}} = \frac{k \lambda}{\beta \cos \theta}$$

The estimated particle size for all the samples lies between 20 and 40 nm.

Scanning Electron Microscopy

SEM is used here to study the surface morphology of the samples. SEM images of the samples show the formation of spongy structures (Figure 3), which are almost the same for all the pure and PANi/ Al_2O_3 composite samples. Figure 2(a–e) corresponds to 0, 2, 4, 6, and 8 wt % Al_2O_3 mixed PANi composites, respectively. The spongy structure formation in the polyaniline takes place by heterogeneous nucleation. As a result, granular coral like structures are formed. As a characteristic of polyaniline, secondary nucleation also takes place because of which the granular coral like particles come together to form aggregates. We noticed that as the amount of Al_2O_3 was increased, the number of pores and the size of pores were also increased, which is very important for gas sensing. The change in morphology can be explained by the adsorption and intercalation of PANi on the surface of Al_2O_3 . There is another possibility that the Al_2O_3 is sandwiched between the PANi layers or Al_2O_3 uniformly mixed into the PANi matrix. The aniline monomer is likely to be absorbed onto the surface of Al_2O_3 through electrostatic attraction and by the formation of weak charge-transfer complexes between aniline monomer and the structure of Al_2O_3 . As a result of this absorption process, Al_2O_3 are finely coated by PANi particles by the polymerization of aniline monomer. Thus, it is aptly believed that adsorption probability of aniline monomer on the whole surface of Al_2O_3 is equipotent, resulting in the formation of continuous PANi coating on the surface of Al_2O_3 . Therefore, because of the change in surface morphology, porosity of the PANi increases with the addition of the Al_2O_3 .

Fourier Transform Infrared Spectroscopy

FTIR spectra of all the samples were obtained in the transmission range 700–4000 cm^{-1} and are shown in Figure 4. FTIR

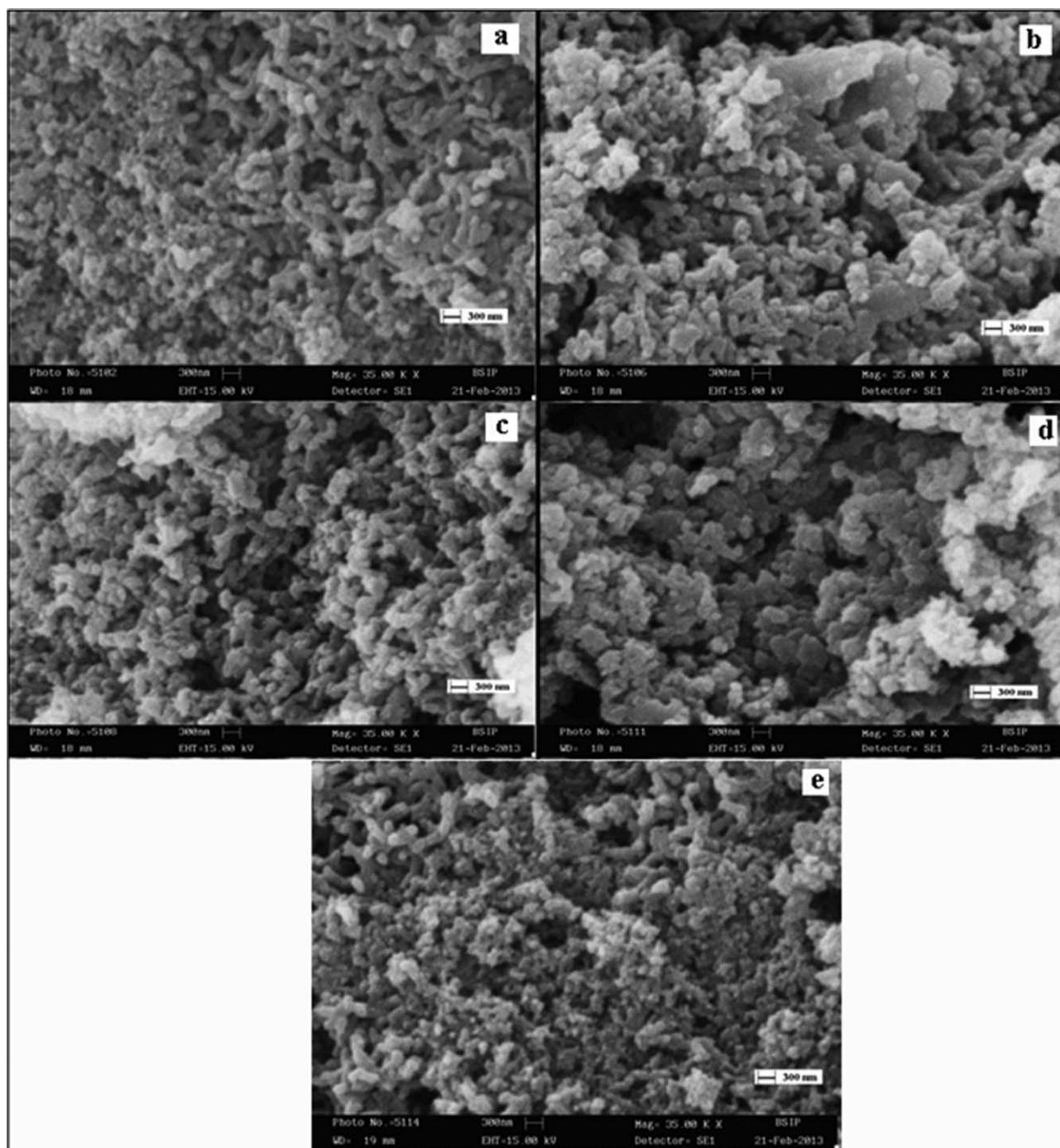


Figure 3. SEM images of samples a, b, c, d, and e. Images a, b, c, d, and e correspond to 0, 2, 4, 6, and 8 wt % Al_2O_3 mixed PANi composite, respectively.

spectra of all the samples show strong absorption bands, in the region $750\text{--}1500\text{ cm}^{-1}$, which correspond to the characteristics of polyaniline.

The peak at frequency 928 cm^{-1} is observed in all samples that is because of N–H out-of-plane bending.¹⁵ The C–N stretching vibrations mode in the polymer chain gives rise to peak at 1152 cm^{-1} . Similar peak at 1155 cm^{-1} is earlier reported by Bairi et al.¹⁶ The peak at 1288 cm^{-1} may be attributed to the C–N

aromatic stretching vibrations.^{13,17} The broad peaks in FTIR spectra present at 2315 , 1523 , and 1483 cm^{-1} are associated with $(\text{N-H})^+$ unsaturated amine, aromatic C–C stretching, and C–N stretching, respectively.^{9,18} The peak at 2983 cm^{-1} is because of the C–H stretching vibrations¹⁸ and its intensity increases with dopant concentration up to 2 wt % and then decreases for further increase in dopant concentration. Additionally the reason behind the peaks at 1152 and 1288 cm^{-1}

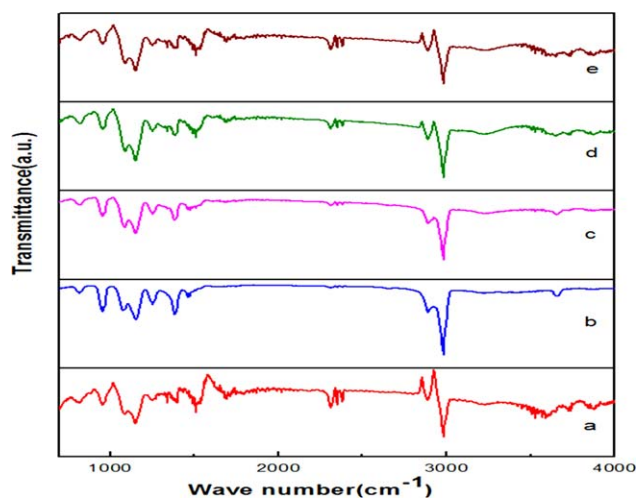


Figure 4. FTIR spectra for the samples a, b, c, d, and e. Curves a, b, c, d, and e correspond to 0, 2, 4, 6, and 8 wt % Al_2O_3 mixed PANi composite, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

may be the interaction between nitrogen lone pair of electrons and metal oxides.^{19,20} The absorption peaks are present in all the samples from a to e and no significant shift is observed in any of the samples.

UV–Visible Absorption

The UV–vis absorption spectra of the polyaniline and the metal composites are recorded at room temperature by using a spectrophotometer between the wavelength range 200–900 nm and are shown in Figure 5. The UV absorption spectra have been recorded with base line correction. The UV absorption can significantly determine the interaction between the Al_2O_3 and

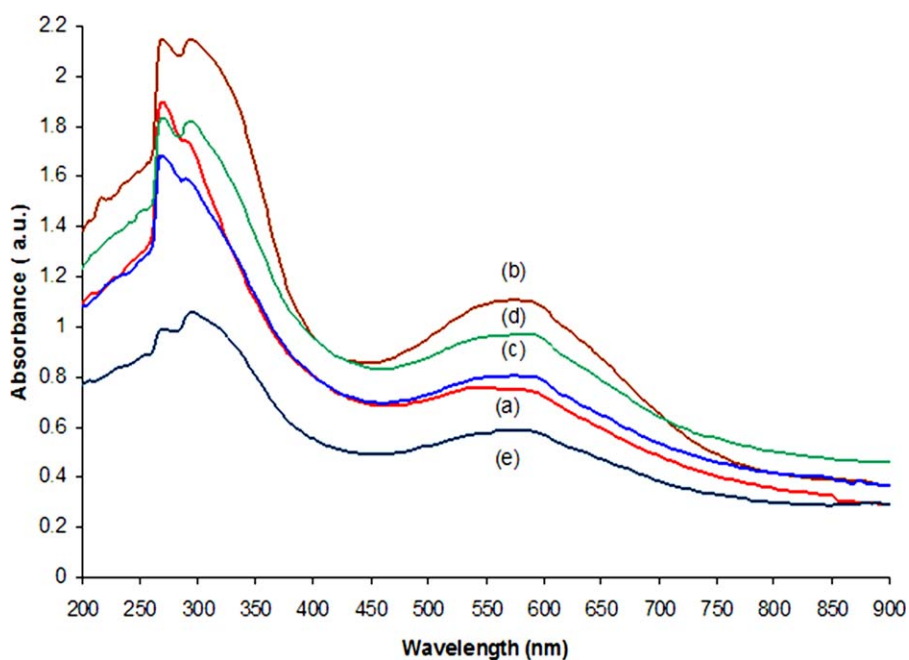


Figure 5. UV–Vis absorption spectra for the samples a, b, c, d, and e at room temperature. Curves a, b, c, d, and e correspond to 0, 2, 4, 6, and 8 wt % Al_2O_3 mixed PANi composite, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PAni.¹⁶ Solutions of all the samples show three peaks at 273, 300, and 590 nm. The peaks at 273 and 300 nm are associated with the exciton transition of π – π^* and the peak at 590 nm is because of the transition between benzenoid to quinoid ring.²¹ Normally, the change in first and second peaks is because of the degree of oxidization and the change in third peak is because of the change in polymerization.^{8,21} Intensity of the peak is randomly varied as the dopant concentration increases and there is no shift in the peaks at 273, 300, and at 590 nm. Peak at 300 nm was already reported by Ameen et al.²² for pure PANi and mixed with $\text{ZrO}_2/\text{PbI}_2$. The other peaks at 230 and 630 nm are reported by Moon and Park.²¹

Effect of NH_3 Concentration

Sensing experiment has been carried out to observe the changes in the resistance of the samples on exposing them to different concentrations of ammonia, varying from 100 to 1500 ppm at room temperature and two other temperatures, i.e. 50°C and 100°C.

The resistance for PANi sample in air decreases as the temperature is increased as can be seen from curve a, Figure 6. Similar variation is seen for the doped samples also. Here curves b, c, d, and e correspond to 2, 4, 6, and 8 wt % Al_2O_3 mixed polyaniline composites, respectively. It is also seen that, at a given temperature, resistance decreases as the dopant concentration increases. The decrease in resistance with increasing temperature, indicates negative temperature coefficient of resistance and hence the semiconducting behavior of all the samples.

This decrease in resistance with temperature is the characteristic of “thermal activated behavior”. The decrease in resistance could be because of the increase in the efficiency of charge transfer between the polymer chains and the dopant with increase in temperature. It is also possible that the thermal curing affects

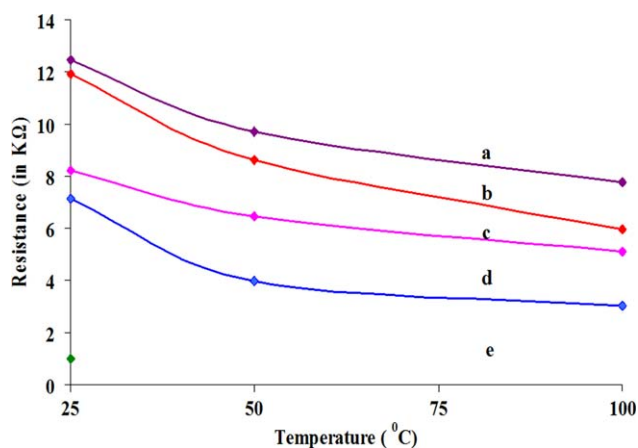


Figure 6. Changes of resistance with variations in temperature for samples a, b, c, d, and e. Curves a, b, c, d, and e are corresponds to 0, 2, 4, 6, and 8 wt % Al_2O_3 mixed PANi composite, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the chain alignment of polymer, which leads to the increase of conjugation length and that, brings about increase in conductivity. This decrease in resistance could possibly be explained on the basis of percolation theory. Which predicts that at a certain amount of concentration of filler material, a continuous full conducting path is formed for the flow of current give rise more conductivity than that of the pure PANi.^{23,24}

The resistance value increases as the ammonia concentration increases for all the samples at each temperature i.e. 25°C, 50°C, and 100°C. The sensitivity, R_g/R_0 , of the samples for different concentrations of NH_3 gas is determined and the variation of sensitivity with ammonia concentration for all the samples at room temperature 25°C is shown in Figure 7(a). Such variation at 50°C and 100°C are shown in Figure 7(b,c), respectively. Curves a, b, c, d, and e correspond to 0, 2, 4, 6, and 8 wt % Al_2O_3 mixed PANi composite in all the three Figure 7(a–c). It is seen that the sensitivity is higher for higher ammonia concentration for all the samples. The curves do not show any particular trend with dopant concentration at 25°C. However, for higher analyte gas concentration, i.e. more than 600 ppm, sensitivity is highest for sample e, which is having the highest dopant concentration.

For higher pellet temperature, i.e. 50°C the variation in sensitivity with variation in NH_3 concentration as well as with variation in dopant concentration shows a clear trend. Sensitivity increases almost linearly with increasing ammonia concentration and has widely different values at higher concentration, i.e. more than 150 ppm. For sample b, sensitivity is almost same as that for pure PANi sample up to 1000 ppm and some change in sensitivity has been observed for samples c and d. But a large change in the sensitivity for sample e has been noticed. At 1100 ppm sensitivity changes from 2.78 to 9.92 as dopant concentration changes from 0 to 8 wt %. The plot in the inset of Figure 7(b) shows that for given ammonia concentrations, e.g. 300, 600, and 1200 ppm, sensitivity increases with the increasing dopant concentration. Similar behavior of sensitivity occurs for

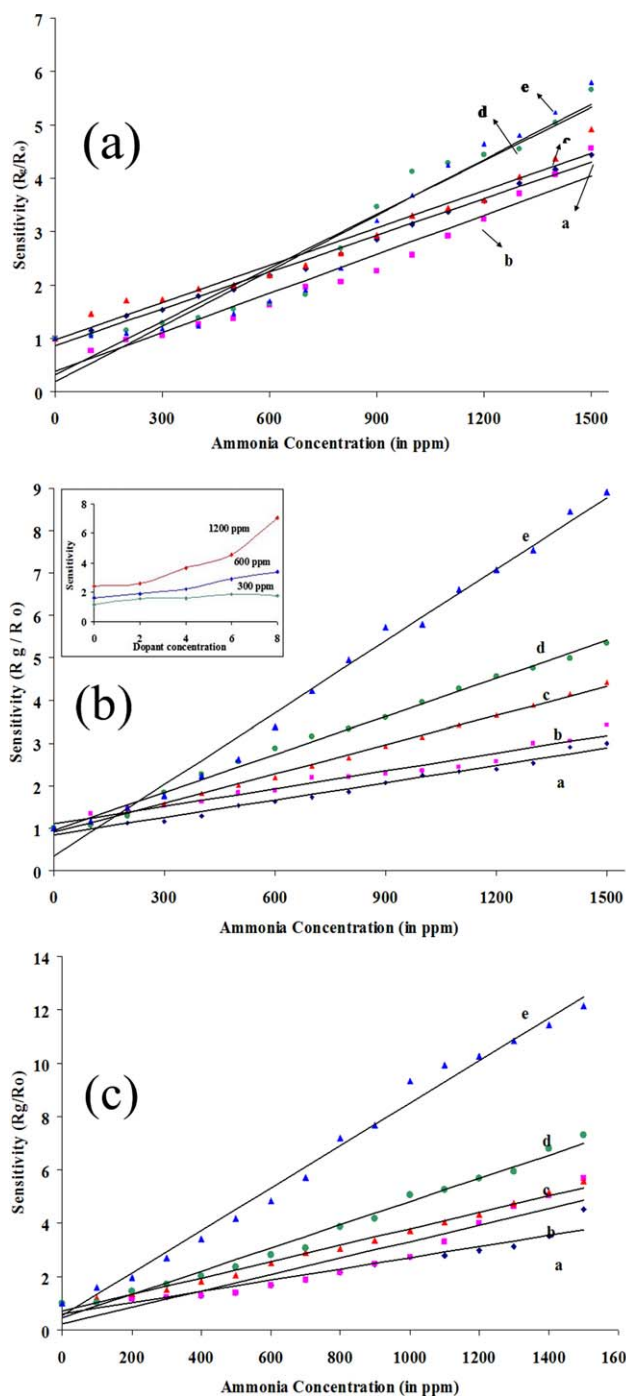


Figure 7. Change in sensitivity with variation in ammonia concentration at (a) 25°C, (b) 50°C, and (c) 100°C. Curves a, b, c, d and e correspond to 0, 2, 4, 6, and 8 wt % Al_2O_3 mixed PANi composite, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

further higher temperature, i.e. 100°C as can be seen from Figure 7(c). It is important to note that at 100°C sensitivity is highest for sample e for all the concentrations, i.e. 0–1500 ppm of ammonia. Sensitivity is higher for 8 wt % Al_2O_3 mixed polyaniline composite because the number of pores is more than

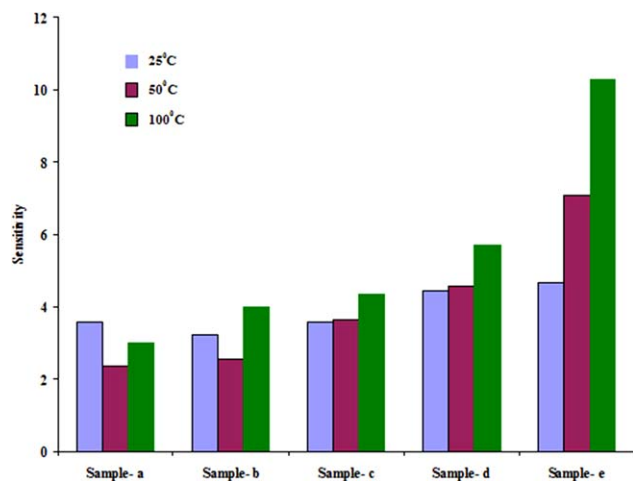


Figure 8. Change in sensitivity towards ammonia for 1200 ppm at 25°C, 50°C, and 100°C. Samples a–e correspond to 0, 2, 4, 6, and 8 wt % Al₂O₃ doped in PANi respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pure polyaniline. The size of pores is also larger compare to pure PANi that is clear from SEM images.

Above 1100 ppm of ammonia, sensitivity significantly increases as dopant concentration increases for the samples c, d, and e as can be seen from Figure 7(b,c). Using the data of Figure 7(a–c), variation of sensitivity with temperature is plotted and is shown in Figure 8. For given ammonia concentration say 1200 ppm, sensitivity is higher for higher sensing temperature.

It is found that the sensitivity increases with: (i) increase in temperature, (ii) increase in dopant concentration as well as (iii) increase in analyte gas, i.e. ammonia concentration. The mechanism of ammonia gas sensing of PANi is explained by compensation effect. When the protonic-acid-doped conductive emeraldine salt is exposed to ammonia gas, the dopant is

partially dedoped by forming ammonium salts, which leads to the increment of resistance. But out of sensing chamber because of N₂, ammonium will decompose into ammonia gas and protons restore the initial level of doping. So the sensor recovers to its original state again.

On the other hand, the sensing mechanism of the composite for detection of NH₃ may be ascribed as follows. When the composite sample is exposed to the analyte gas NH₃, the hole conducting composite surface will interact with the electron-donating analyte. The PANi accept electrons from the adsorbed gas molecules, and thus the delocalization degree of conjugated π electrons along the PANi backbones increases with the density drop of charge carriers that transfer along the polymer chains as well as Al₂O₃. The yield of the neutral PANi backbones and decrease of charge carriers, induce a conductivity drop of the samples. So the resistance of all the samples increases as ammonia concentration increases. Conversely, the absorbed gas molecules will be separated from the samples out of sensing chamber. The desorption of the analyte molecules will induce the electron depletion in the Pani chains, leading to the increase of the charge carriers (holes) in the polymer matrix. Therefore, the resistance of the samples will recover towards its initial value. Similar behavior of Sn mixed PANi composite towards carbon dioxide gas sensing at room temperature has been reported by Nemade et al.⁹ The increment in ammonia concentration enhances the rate of diffusion of ammonia molecules into the pellets. Therefore the number of molecules which are able to interact with the sensing area of the sample in a given time increases which results in increased sensitivity.

Response and Recovery time

The response and the recovery times for all the samples for 100 ppm ammonia concentration has been studied at three different temperatures i.e. 25°C, 50°C, and 100°C. We have recorded response for five cycles and we got the same response. It means that the responses were reproducible up to ~5 cycles. The errors are estimated to be ~1.3%. The results are shown in Table I.

An inspection of response times across Table I shows that response time of each sample reduces with increase in sensing temperature. Down the table it is seen that for each temperature response time again reduces with increase in dopant concentration.

The response time for sample e is less at all temperatures as compared to the samples a, b, c and d. The response time decreases as the dopant concentration as well as the temperature increases. Response time for sample e as compared to sample a at 25, 50 and 100°C is 10%, 9%, and 13% less, respectively. Recovery time also decreases with increase in dopant concentration as well as increase in temperature.

CONCLUSION

In brief, we have synthesized pure and Al₂O₃ mixed PANi composite by the chemical oxidation method. The prepared samples have been characterized by XRD, SEM, and FTIR. XRD spectra show the weak crystalline quality of all the samples. The study of FTIR spectra confirms the formation of PANi and also

Table I. Response and Recovery Time of Samples a–e for 100 ppm Ammonia at 25°C, 50°C, and 100°C

Samples	Response time (sec) (error in time ±1 sec)		100°C	Recovery time (sec) (error in time ±1 sec)		
	25°C	50°C		25°C	50°C	100°C
a (PANi + 0 wt %Al ₂ O ₃)	78	76	75	495	475	415
b (PANi + 2 wt %Al ₂ O ₃)	77	76	75	492	471	413
c (PANi + 4 wt %Al ₂ O ₃)	78	75	73	487	465	465
d (PANi + 6 wt %Al ₂ O ₃)	76	72	71	480	460	395
e (PANi + 8 wt %Al ₂ O ₃)	70	69	65	465	445	360

suggests that mixing of Al₂O₃ in PANi does not affect its structure. The UV–Vis absorption spectra of the solutions of all the samples contain three peaks at 273, 300, and 590 nm out of which the peaks at 273 and 300 nm are associated with the excitation transition of π – π^* and the peak at 590 nm is because of the transition between benzenoid and quinoid ring. The SEM images of all the samples show coral like structure. The ammonia sensing properties of all the samples have also been studied.

The sensing properties of pure and Al₂O₃ mixed polyaniline composite have been observed at room temperature (25°C) and two other higher temperatures, i.e. 50°C and 100°C. It is found that the sensitivity increases with: (i) increase in temperature, (ii) increase in dopant concentration as well as (iii) increase in analyte gas, i.e. ammonia concentration. Response and recovery times for pure PANi and lower concentration 2–4 wt % of Al₂O₃ in PANi is not different significantly but as the concentration of Al₂O₃ in PANi is increased to 8 wt %, the response and recovery times reduce by almost 13%. Ammonia, being harmful for environment and human being because of its toxicity, needs monitoring and this article suggests that Al₂O₃ mixed PANi composite pellets with proper Al₂O₃ concentration can be used as sensing material for ammonia.

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REFERENCES

- Zhu, J.; Wei S.; Zhang L.; Mao Y.; Ryu, J.; Haldolaarachige, N.; Young, D. P.; Guo, Z.; *J. Mater. Chem.* **2011**, *21*, 3952.
- Rodrigues, P. C.; Cantao, M. P.; Janissek, P.; Scarpa, P. C. N.; Mathias, A. L.; Ramos, L.P.; Gomes, M. A. B.; *Eur. Polym. J.* **2002**, *38*, 2213.
- Rimbu, G. A.; Stamatini, I.; Jackson, C. L.; Scott, K.; *J. Optoelectron. Adv. Mater.* **2006**, *8*, 670.
- Lim, J. H.; Phibolsirichit, N.; Mubeen, S.; Deshusses, M. A.; Mulchandani, A.; Myung, N. V.; *Nanotechnology* **2010**, *21*, 075502.
- Arenas, M. C.; Sancez, G.; Nicho, M. E.; Torres, J. E.; Castano, V. M. DOI 10.1002/s00339.011-6704-6.
- Prasad, G. K.; Radhakrishnan, T. P.; Kumar, D. S.; Krishna, M. G. *Sens. Actuators B*, **2005**, *106*, 626.
- Matsuguchi, M.; Asahi, T. *Sens. Actuators B*, **2011**, *160*, 999.
- Koul, S.; Chandra, R.; Dhawan, S. K. *Sens. Actuators B*, **2001**, *75*, 151.
- Nemade, K. R. *J. Sens. Transducers* **2011**, *135*, 110.
- Ameen, S.; Ali, V.; Zulfequar, M.; Haq, M. M.; Husain, M. J. *Appl. Polym. Sci.* **2009**, *112*, 2315.
- Matsuguchi, M.; Io, J.; Sugiyama, G.; Sakai, Y. *Synth. Met.* **2002**, *128*, 15.
- Krishna, J. B. M.; Saha, A.; Okram, G. S.; Soni, A.; Purakayastha S.; Ghosh, B. *J. Phys. D: Appl. Phys.* **2009**, *42*, 095404.
- Deshpande, N. G.; Gudage, Y. G.; Sharma, R.; Vyas, J. C.; Kim, J. B.; Lee, Y. P. *Sens. Actuators B* **2009**, *138*, 76.
- Misra, K. P.; Shukla, R. K.; Srivastava, A.; Srivastava, A. *Appl. Phys. Lett.* **2009**, *95*, 031901.
- Hieu, N. V.; Dung, N. Q.; Tam, P. D.; Trung, T.; Chien, N. D. *Sens. Actuators B* **2009**, *140*, 500.
- Bairi, V. G.; Warford, B. A.; Bourdo, S. E.; Biris, A. S.; Viswanathan, T. *J. Appl. Polym. Sci.* **2012**, *124*, 3320.
- Nabid, Golbabaee, M. R.; Moghaddam, M.; Dinarvand, A. B. R.; Sedghi, R. *Int. J. Electrochem. Sci.* **2008**, *3*, 1117.
- Singh, V.; Mohan, S.; Singh, G.; Pandey, P. C.; Prakash, R. *Sens. Actuators B* **2008**, *132*, 99.
- Arora, M.; Gupta, S. K. *AIP Conf. Proc.* **2008**, *1075*, 118.
- Lee, S. H.; Lee, D. H.; Lee, K.; Lee, C. W. *Adv. Funct. Mater.* **2005**, *15*, 1495.
- Moon, H. S.; and Park, J. K. *Macromolecules* **1998**, *31*, 6461.
- Ameen, S.; Lakshmi, G. B. V. S.; Husain, M. J. *Phys. D: Appl. Phys.* **2009**, *42*, 105104.
- Kobyashi, A.; Ishikawa, H.; Amano, K.; Satoh, M. *J. Appl. Phys.* **1993**, *74*, 296.
- Suri, K.; Annapoorni, S.; Tandop, R. P. *Bull. Mater. Sci.* **2001**, *24*, 563.