

Controlled Fabrication of Highly Monodispersed, Gold Nanoparticles Grafted Polyaniline (Au@PANI) Nanospheres and their Efficient Ammonia Gas Sensing Properties

Abdulla S, Dhakshanamoorthi J, Dinesh VP and Pullithadathil B*

Nanosensor Laboratory, PSG Institute of Advanced Studies, Coimbatore, India

Abstract

In the present study, highly monodispersed polyaniline (PANI) and gold nanoparticles grafted PANI nanospheres (Au@PANI) have been fabricated through a facile wet-chemical synthesis process by *in-situ* polymerization of aniline. The structural characterization of the PANI and Au@PANI nanospheres were carried out by UV-Vis spectroscopy, FT-IR spectroscopy, and High Resolution Transmission Electron Microscopy (HR-TEM). Stable uniform sized nanospheres of PANI and Au@PANI obtained were found to exhibit superior gas sensor performance towards trace-level concentration of ammonia (NH₃) gas in the range of 1-5 ppm. A comparative analysis of the sensor properties of PANI and Au@PANI nanospheres were performed under ambient conditions. Au@PANI nanospheres exhibited enhanced gas sensing performance with high sensitivity (58.2%), rapid response (48 s) and recovery (58 s) characteristics (1 ppm of NH₃). The results indicate the potential use of Au@PANI nanospheres for fabrication of efficient NH₃ sensors for varied applications.

Keywords: PANI nanospheres; Nanocomposites; Chemiresistors; Gas sensors; NH₃ gas monitoring

Introduction

Polyaniline (PANI), one of the widely used conducting polymers gained its potential place in sensors, photocatalyst, electrochemical industries owing to its unique electrical and redox properties [1]. The existence of polymorphic forms of polyaniline viz., reduced leucoemeraldine form and the fully oxidized pernigraniline form makes them as an interesting class of redox materials for various sensors based application exclusively [2]. Several synthetic strategies have been widely used by researchers and various morphological structures have been developed using template-free, template-based and electrochemical methods [3]. In addition, nanocomposites based on PANI having metal-polymer or metal oxide-polymer hybrid structures also have been shown superior properties and used for fabrication of sensor devices [4,5]. The combination of conducting π -conjugated polymer network with metal/metal oxide interfaces favour the surface adsorption process of target gas molecules. The localized electronic states in conducting polymers generally make them to behave as *p*-type semiconductors. Due to their redox behaviour of these polymers, the conductivity could be easily altered by doping and de-doping the material [6].

Ammonia is one of the harmful environmental pollutants as-well recognized as a biomarker related to in kidney and liver dysfunctions in the exhaled human breath [7]. Hence, developing room temperature ammonia sensors with enhanced sensitivity and selectivity for device fabrication is highly significant in the current sensor development. So far, there are many reports on PANI based gas sensors exist in literature [8]. But, the sensors based on these materials usually suffer from degradation due to environmental effects and are highly unstable. Issues on the reliability of the polymer based chemosensors are mainly attributed to their polydispersity as well as irregular morphology. In metal nanoparticles integrated PANI nanocomposites, the electron rich polymer matrix acts as a scaffold for the secondary component with high electron density [9]. Introducing metal nanoparticles enhances the selectivity of the sensors and such hybrid materials can be achieved by altering the redox behaviour of polyaniline. These hybrid

nanocomposites possess several advantages as high surface area, more active sites, higher stability and selectivity [10,11]. In this paper we have synthesized highly monodispersed PANI and hybrid Au@PANI nanocomposites by a facile *in-situ* polymerization method to study their gas sensor performance towards NH₃ gas. Highly enhanced room temperature ammonia sensing properties of PANI and Au@PANI nanospheres are reported for the detection of trace level (1-5 ppm) NH₃ gas. The superior gas sensor performance of hybrid Au@PANI nanospheres and gas/material interaction mechanism due to the presence of hybrid interfaces are reported.

Materials and Methods

Aniline (C₆H₅NH₂, 99.9%, Merck) was used as the monomer for synthesis of PANI which was distilled under reduced pressure before use. Tetrachloroauric acid trihydrate (HAuCl₄·3H₂O, 99.999% Sigma Aldrich) HCl (35.4%, Merck) and NaOH (98% Merck) were used for synthesis and used without any further purification. Ultrapure water ((Merck-Millipore, resistivity: 18.2 M Ω .cm) was used throughout the experiments.

Synthesis of PANI and Au@PANI nanospheres

For the synthesis [12] of uniform sized PANI nanospheres 1.0 mmol of aniline was dissolved in 100 mL of deionized water and then the acidity of the solution was adjusted to a certain pH (3) value as the initial pH value by the addition of trace amounts of HCl or NaOH.

***Corresponding author:** Pullithadathil B, Assistant Professor (Sr. Gr.) in Nanotechnology, Nanosensor Laboratory, PSG Institute of Advanced Studies, Coimbatore - 641 004, India, Tel: +91 422 4344000, Extn (4193); E-mail: bijuja123@yahoo.co.in

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Similarly, 0.3 mmol of HAuCl_4 was dissolved in 100 mL of deionized water and the acidity of the solution was adjusted to the corresponding pH (3) value. Subsequently, these two solutions were mixed rapidly at room temperature and the reaction was allowed to proceed without any disturbance for 24 h. The product was centrifuged at 2500 rpm to remove the gold agglomerates formed as a by-product. The upper liquid phase was centrifuged at 7000 rpm to obtain the PANI precipitate. Finally, the resulting PANI was washed with deionized water and ethanol several times to remove residual reactant and dried under vacuum at 50°C for 24 h. For the synthesis of Au@PANI, the reaction mixture (aniline + HAuCl_4) was continuously stirred for additional 24 h which led to the formation of Au nanoparticles adhered on the surface of PANI nanospheres due to the surface nucleation of Au under vigorous continuous stirring condition.

Characterization techniques

The purified PANI and Au@PANI nanospheres were characterized using various spectroscopic and microscopic techniques. UV-Vis absorption spectra were acquired using T90+ UV-Visible spectrophotometer (PG Instruments, UK). FT-IR spectra of the samples were recorded using Nicolet Impact 400 FT-IR spectrophotometer using KBr. The structure and morphology of the nanocomposite were examined using High-Resolution Transmission Electron Microscopy (JEOL JEM-2010, HRTEM, Japan) in-built with energy-dispersive X-ray spectrometer (Oxford INCA, Instruments, UK).

Gas sensor fabrication and testing

For testing and calibration of NH_3 gas sensor, gold sputtered interdigitated array electrode (IDA) was used. The PANI and Au@PANI nanospheres were then dispersed in ethanol and sonicated for 15 min prior to coating on to the IDA electrode. The material was further spincoated (1500 rpm for 60 s) onto the IDA electrodes and dried at 60°C for 30 min. The gas sensing experiments of PANI and Au@PANI nanospheres were performed by monitoring the changes in resistance (ΔR) of the sensor upon exposure of NH_3 gas. Nitrogen (N_2) was used as the carrier gas for all experiments. The schematic illustration of the experimental setup used is shown in Figure 1. The sensor was placed inside a double-walled stainless steel sensing chamber and the resistance change was monitored as a function of adsorbed gas at room temperature using an Agilent 34401A digital multimeter which is connected to a computer by USB interface for data acquisition.

Results and Discussion

For the enhancement in the gas sensing property analysis, the morphology of nanostructured PANI plays an active role compared to its bulk counterparts. In the present work, monodispersed nanospheres of PANI and Au@PANI were prepared in order to enhance the effective surface area of PANI. The PANI and Au@PANI nanospheres were synthesized using HAuCl_4 as an oxidant for polymerization. Ammonium peroxydisulfate (APS) was used as an oxidant in the chemical synthesis of PANI. In contrast, when HAuCl_4 was used as an oxidant the morphological evolution was observed in the PANI under various pH conditions. It is well known that the standard oxidation/reduction potential of HAuCl_4 (0.994 V) is lower than that of APS (2.0 V) which allows the controlled growth of PANI nanostructures [13-16]. Hence, reaction time was kept for longer period in the presence of HAuCl_4 which might be helpful in hindering the process of elongation of nanospheres into nanotubes or nanofibers and will only lead to the formation of monodispersed, uniform PANI nanospheres [13]. The formation of PANI and Au@PANI nanospheres could be explained

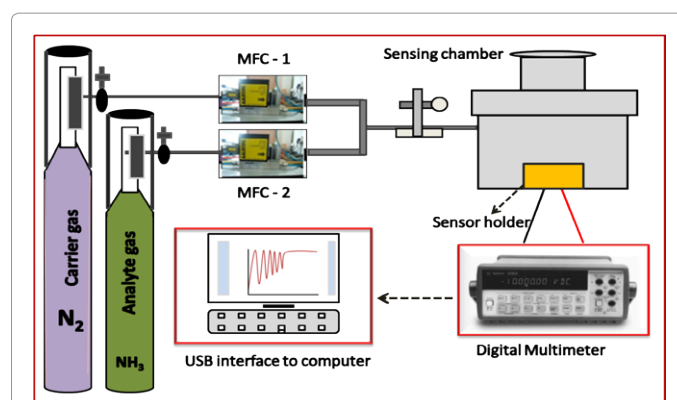


Figure 1: Schematic diagram of the experimental setup used for gas sensor performance analysis.

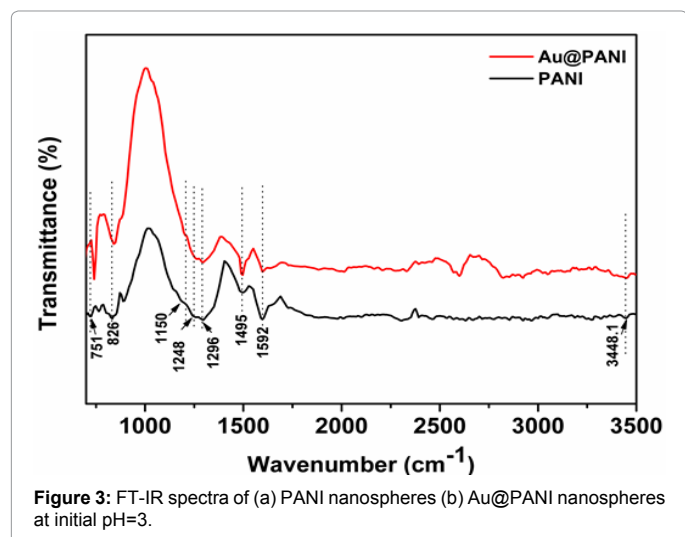
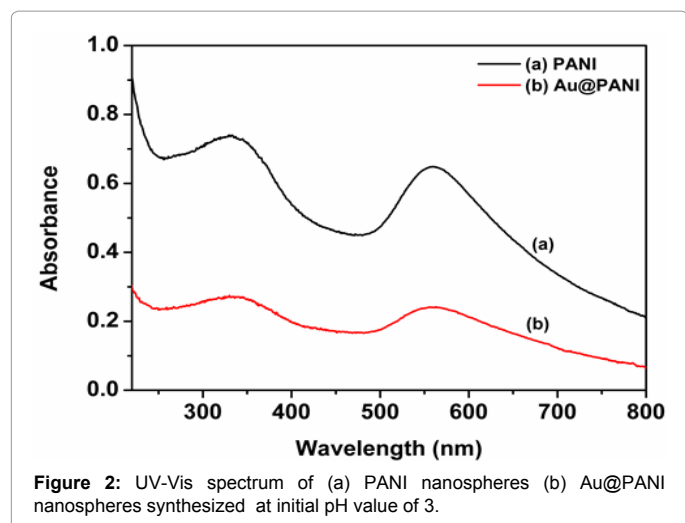
on the basis of nucleation theory reported by Jiahua Shi, Aniline is an organic base with $\text{pK}_a = 4.6$ at 25°C . At different pH-initial aqueous solutions, the anilinium ions and neutral aniline molecules coexist in different proportions, leading to different PANI nanostructures. In the present work initial pH value was set to 3. At pH initial = 3, anilinium ions and neutral aniline molecules coexist in different proportions. The anilinium ion shows good solubility, while neutral aniline molecules will form nanodroplets due to the limited miscibility in water and these aniline molecules are easier to oxidize since the electron pair on nitrogen is delocalized in neutral aniline molecules rather than localized in the anilinium ion [10,13,17]. When HAuCl_4 is added to the aniline solution, the heterogeneous nucleation will first take place at the interface of water/aniline nanodroplets which would act as a template guiding the formation of PANI nanospheres and then anilinium ions in the bulk solution would subsequently participate in the PANI growth at the surface of these nanospheres to form solid PANI nanospheres [18]. In the case of Au@PANI, due to the vigorous stirring, nucleation of Au(0) happens on the surface of PANI nanospheres and gradually grow into nanoclusters constituting the Au@PANI nanospheres.

UV-Vis spectroscopic analysis

UV-Vis spectrum of PANI shows characteristics peaks at 329 nm, 435 nm which are associated with $\pi-\pi^*$ and π -polaron transitions respectively [11,12]. Here, to the π -polaron transitions are disappeared and n- π^* absorbance was observed at 560 nm which is associated with a benzenoid to quinoid excitonic transitions [13] (Figure 2a). UV-Vis spectra of Au@PANI nanospheres shows characteristics peaks at 338 nm, 554 nm which is blue shifted in comparison with the PANI nanospheres (Figure 2b). The shift in the $\pi-\pi^*$ and π -polaron transitions clearly indicates the interaction between PANI and Au. The characteristic peak of Au NPs appears generally at 510 nm which is caused by the surface plasmon resonance. But the plasmon band of Au was not observed in the composite which might be due to the reduction of absorption intensity by the surrounding PANI. This result further suggests that, Au NPs has been adsorbed in to the PANI structure efficiently [4].

FT-IR spectroscopic analysis

The chemical structure of the as prepared PANI and Au@PANI nanospheres were identified using FT-IR analysis. Figure 3 depicts the FT-IR spectra of PANI and Au@PANI nanospheres synthesized at initial pH value of 3. In the spectra of PANI nanospheres, peaks at 1592 and 1495 cm^{-1} were identified which are the characteristics peaks of



PANI corresponding to the C=C stretching of quinoid and benzenoid rings respectively. The peaks at 1296 and 1248 cm^{-1} are attributed to the C-N (of the secondary aromatic amines) and C=N stretching modes. The peak appeared at 1150 cm^{-1} is assigned to the in-plane bending of aromatic C-H which is also considered as a measure of the degree of delocalization of electrons in PANI and it is directly related to the degree of doping and electrical conductivity of PANI [11,12-15].

The characteristic N-H stretching mode was found to be present at 3448, 3317 cm^{-1} . The peaks observed at 826 cm^{-1} , 751 cm^{-1} was attributed to the out-of-plane bending of C-H in the 1,4-disubstituted benzene ring) and vibrations of the monosubstituted benzene ring respectively [13]. The peaks observed for PANI nanospheres are in good agreement with the reported value for PANI. In the FT-IR spectra of Au@PANI nanospheres the similar peaks were observed confirming the presence of PANI in the composites.

Transmission electron microscopic analysis

The morphological studies of PANI and Au@PANI nanospheres were carried out using High resolution Transmission Electron Microscopy (HRTEM). Figure 4 depicted the TEM analysis of the PANI and Au@PANI nanospheres. The formation of nanospheres of

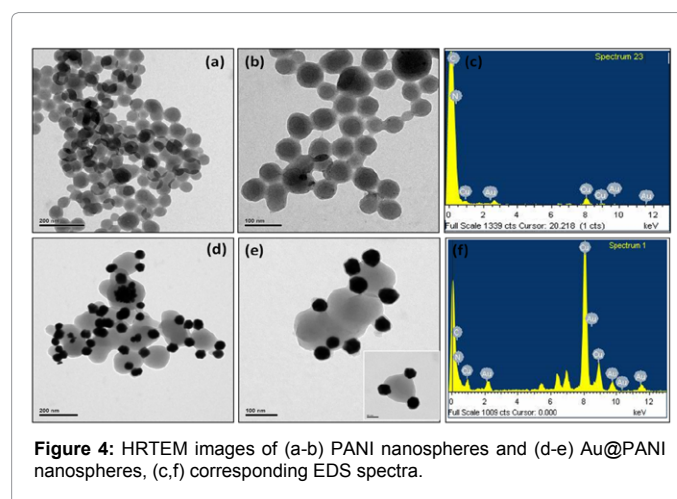
PANI is well evident from the Figure 4a and 4b. The PANI nanospheres were observed to be highly uniform and monodispersed. The diameter of the spheres was found to be ~ 63-64 nm.

The EDS spectrum of PANI nanospheres is depicted in Figure 4c. The spectrum strongly revealed the presence of pure PANI containing C, N and traces of Au signatures. The formation of Au@PANI composites were well cleared from the TEM analysis. Figure 4d and e shows the TEM images of Au@PANI nanospheres. The average diameter of the Au nanoparticles was found to be ~25 nm. EDS spectrum in Figure 4f shows strong signatures of Au compared to that of PANI indicating the nanocomposite formation. It is observed that, during the growth of the PANI spheres, Au nanoparticles are well dispersed in the PANI. In the initial stage of the synthesis, the seed-mediated growth of Au was attained followed by the reduction to the Au nanoparticles. Hence, simultaneous growth of Au and PANI spheres were observed in the composites and each PANI spheres were found to have bond with Au nanoparticles suggesting the fact that, partial oxidation and reduction was happened during the composite formation. .

Gas sensing performance analysis

The gassensing performance of the PANI and Au@PANI nanospheres towards trace-level NH_3 gas under ambient conditions have been studied. Initially, PANI and Au@PANI nanospheres were spin coated on sputtered gold IDA electrodes and the electrical resistance of both the sensors were measured initially at room temperature under atmospheric pressure conditions. The enhancement in the electrical properties of PANI and Au@PANI nanospheres was studied by performing the current-voltage (*I-V*) characteristics using two-probe technique. Figure 5 represents *I-V* curves of the PANI and Au@PANI nanospheres recorded at room temperature. Both the PANI and Au@PANI based sensor exhibited ohmic behaviour within the range of -1 to +1 V.

In chemiresistive based sensors, the response and recovery characteristics depend on the rate of diffusion of the analyte gas molecules and the subsequent reaction between the sensing materials. The gas sensing response of the PANI and Au@PANI nanospheres based sensors was analyzed for various concentrations analyte molecules. The change in the resistance was measured upon exposure to NH_3 gas molecules. The dynamic responses of the sensor materials, their reversibility, and detection limits towards NH_3 (3 ppm) were studied at room temperature. Figure 6a and b) shows the response and



recovery characteristics of the PANI and Au@PANI nanospheres based sensor towards the exposure of 3 ppm of NH_3 .

As presented in Figure 6 the response time (T_{90}) of the PANI nanospheres sensor was calculated to be 36 s whereas, for Ag@PANI nanospheres based sensor it was found to be 61 s for 3 ppm of NH_3 . The sensitivity of the Ag@PANI nanospheres based sensor were found to be enhanced compared to PANI nanospheres (Scheme 1).

Figure 7a and b represents the dynamic sensor response graph of PANI and Au@PANI nanospheres towards the trace-level concentrations of ammonia gas (2-10 ppm) under ambient conditions. From the results, it is evident that, the sensor resistance of both the sensors increased immediately upon exposure to target gas. The sensor was found to be completely recoverable at room temperature suggesting the physisorption of gas molecules with the sensing materials. Significant improvement in the sensitivity of the Au@PANI nanospheres was observed upon exposure to different concentrations of NH_3 gas compared to PANI nanospheres. For example, the sensitivity of the PANI nanospheres was found to be 20.2%. Whereas, Au@PANI nanospheres based sensor exhibited higher sensitivity of 50.2% (Figure 7c). The sensor was tested under various oxidizing and reducing gases such as NO_2 , H_2S , $\text{C}_2\text{H}_5\text{OH}$, C_5H_8 . Figure 7d depicts the selectivity result of the Au@PANI nanospheres at concentration of 2 ppm of each analyte gas. It was observed that, Au@PANI nanospheres based sensor was highly selective towards ammonia (62.3%) compared to the other interfering gases. The observed enhancement in the gas sensing performance of the Au@PANI nanospheres could be attributed to the

Concentration (ppm)	Sensitivity ($\Delta R/R_A$ %)		Response Time (s)		Recovery Time (s)	
	PANI	Au@PANI	PANI	Au@PANI	PANI	Au@PANI
1	20	50.2	21	48	46	58
2	30.6	62.3	26	55	55	71
3	39.2	79.4	36	61	61	75
4	56.9	98.5	50	75	66	90
5	76.1	108.7	66	83	101	114

Table 1: Comparison of sensitivity, response time, recovery time of PANI and Au@PANI nanospheres.

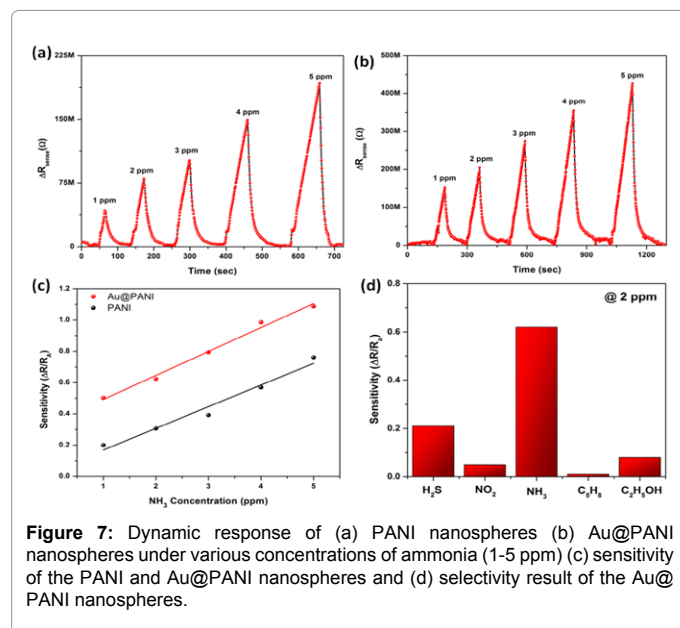


Figure 7: Dynamic response of (a) PANI nanospheres (b) Au@PANI nanospheres under various concentrations of ammonia (1-5 ppm) (c) sensitivity of the PANI and Au@PANI nanospheres and (d) selectivity result of the Au@PANI nanospheres.

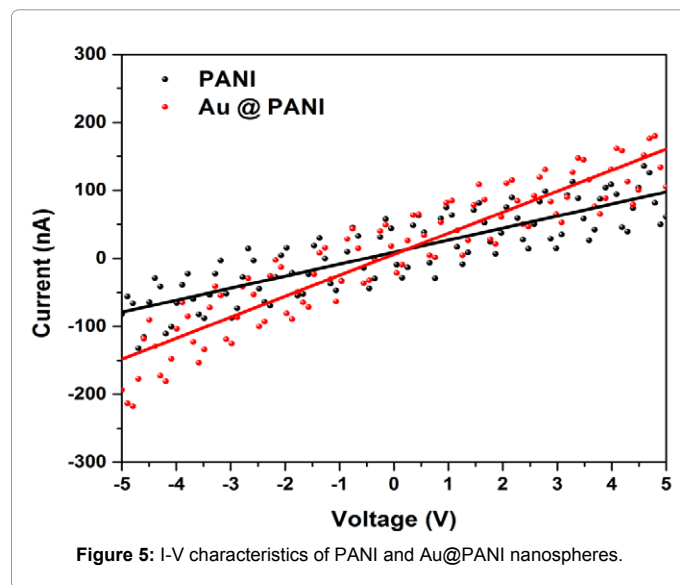


Figure 5: I-V characteristics of PANI and Au@PANI nanospheres.

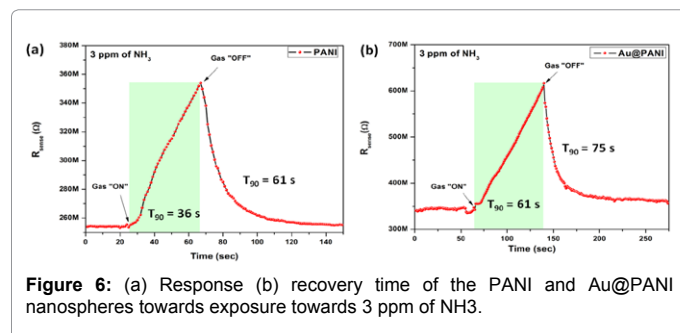
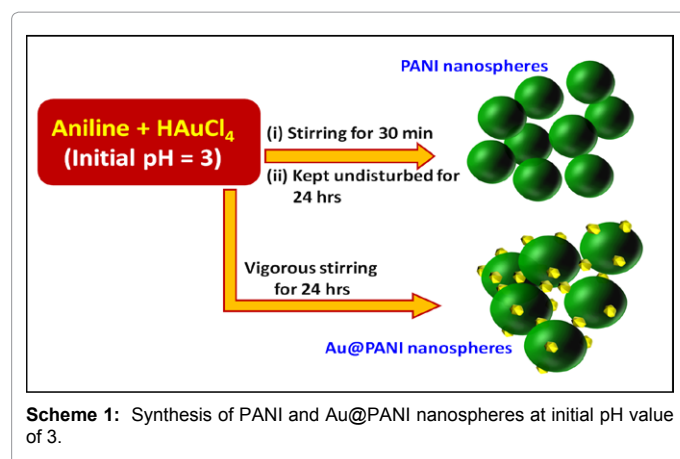


Figure 6: (a) Response (b) recovery time of the PANI and Au@PANI nanospheres towards exposure towards 3 ppm of NH_3 .



Scheme 1: Synthesis of PANI and Au@PANI nanospheres at initial pH value of 3.

following reason. (i) increased surface area of the nanospheres, which provided large number of active sites for ammonia adsorption. (ii) controlled doping of Au nanoparticles in the PANI nanospheres which created an easy pathway for charge transfer. The sensing mechanism of PANI with NH_3 is well understood [19]. It is mainly governed by the combination of protonation/deprotonation reaction in PANI. PANI is a *p*-type semiconductor. On exposure to the electron donating ammonia gas molecules, the proton on the N^+-H groups of PANI and forms NH_4^+ ions and lead to the localization of polarons of conducting PANI as represented in equation (1). This causes protonation in PANI

and increases its electrical resistance. When the sensor is exposed to the fresh air again, the NH_4^+ ions decompose into NH_3 molecules and protons. This reversible transformation results in restoring the initial degree of doping and the resistance of the sensor material [19]. In the presence of Au nanoparticles, on the surface of the PANI, due to surface doping Au could interact with NH_3 and transfer electrons to the PANI. The Au doping has also could increase the surface area of the polymer and will provide large number of active sites for ammonia adsorption. It is plausible to conclude that, the synergetic effect between the metal nanoparticles and conducting polymer had resulted in better performance compared to its individual component. The sensors were observed to be completely recoverable after each exposure towards ammonia at room temperature. Consolidated results of the response and recovery time of both sensors are summarized in Table 1.

Conclusion

A novel facile template free (*in-situ* polymerization of aniline) chemical approach method was adopted for the synthesis of PANI and hybrid Au@PANI nanospheres. Monodispersed polyaniline with an average diameter of 64 ± 0.5 nm was observed from TEM studies, and its characteristic π -polaron transition in UV-visible spectrum suggesting the as-synthesised polyaniline exist in emeraldine base form. FT-IR studies of polyaniline supports it strongly for the existence of emeraldine form with its characteristic C=C, C-N and C=N stretchings. The peak appearing at 1150 cm^{-1} assigned to the in-plane bending of aromatic C-H considered as a measure of the degree of delocalization of electrons in PANI and was directly related to the degree of doping and electrical conductivity of PANI. Similarly Hybrid Au@PANI nanospheres prepared by *in-situ* polymerization shows the characteristic π -polaron in UV-visible studies along with the surface plasmon peak of Au nanospheres thus proving the formation of hybrid Au@PANI nanospheres with electron transfer process. TEM observation clearly suggests the decoration of Au nanospheres ($25 \pm .5$ nm) over the PANI spheres thereby increasing the conjugation and formation of interfaces between Au and PANI nanospheres. Comparative NH_3 gas sensing evaluation of PANI and Au@PANI nanospheres exhibit an enhanced sensing for hybrid Au@PANI nanospheres for trace level analyte molecules in the range of 1-5 ppm under ambient conditions. The superior sensing behaviour of Au@PANI nanospheres with high sensitivity (58.2%), rapid response (48 s) and recovery (58 s) characteristics are due to the synergetic effect of Au and PANI nanospheres at the interface, thus proves to a potential NH_3 sensor device fabrications in near future.

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