

Room Temperature Ammonia Gas Sensing Using Polyaniline Nanoparticles Based Sensor

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Abstract

In the present research effort, we account for the acquisition of room temperature ammonia gas sensor based on polyaniline (PANI) nanoparticles. The polyaniline thin film was deposited on porous silicon substrate using the spin coating method. PANI nanofilms were characterized for their structural as well as surface morphologies. The XRD analysis showed partially crystalline nature polyaniline thin film. The Ammonia gas sensing response of PANI was obtained for different concentration of ammonia (50, 100, 200, 300, 400, 500 and 600 ppm). The sensitivity of PANI was observed to increase with the increase in the concentration of ammonia.

Keywords: Ammonia, Sensitivity, Nanocomposite, Morphology

INTRODUCTION

Ammonia (NH₃) is a natural gas present throughout the atmosphere. It is extensively used as a synthesis material in various chemical industries. It is also widely used in fertilizer industry, refrigeration, food processing, medical diagnosis and fire power plant etc [1]. It is a colourless gas with special order and is very harmful to human being [2, 3]. Its leakage to the surroundings can lead to health hazard like irritating to respiratory system, skin and eyes. Exposure to high concentration of ammonia can cause pulmonary oedema, accumulation of liquid in lungs etc [4, 5]. Though, in

comparison to other odorous gasses, human nose is very sensitive to ammonia but when quantification and detection at lower concentration is needed, human nose fails. Therefore, there is a need to have some informative system that can detect and warn for the concentration of ammonia in the surroundings.

There are many techniques for sensing ammonia described in literature [6, 7, 8, 9, 10]. A different sensor is used in the exhaust pipe of automobiles than for measuring ultra-low concentrations of ambient ammonia for environmental surveillance. The most frequently used techniques in commercial ammonia detectors are, metal-oxide gas sensors, conducting polymer ammonia analyzers and optical ammonia detection techniques. Conducting polymer proved to be a much more stable for sensing ammonia. The polymer is believed to be deprotonated by ammonia, which results in the change in conduction [6]. Conducting polymers have been extensively studied for gas sensing applications. Sensor characteristics of diverse conducting polymers such as polypyrrole, polyhexylthiophene, polymethylthiophene, polyethylene and polyaniline in the sensing of gases like Nitrogen dioxide, Carbon monoxide, Ammonia, Hydrogen, Moisture and number of organic volatile compounds have been studied [7, 8, 9, 10]. Polyaniline is one of the most prominent polymers among the variety of conducting polymers due to its exclusive electrical characteristics, environmental stability, easy fabrication process and intrinsic redox reactions [11, 12, 13].

In the present work, an effort has been made to synthesis polyaniline by the oxidative polymerization of aniline monomers. Further 'as synthesized' polyaniline was deposited on porous silicon substrate using spin coating technique. The developed coating was characterized for structural and morphological analysis using XRD and FESEM respectively. Further, the developed coatings have been explored for the sensing of ammonia at room temperature.

EXPERIMENTAL

Synthesis of PANI

PANI was synthesized by the oxidative polymerization of aniline monomers. Aniline (0.9104 ml) was dissolved in 100 mL (1 M) HCl. Ammonium Per Sulphate, APS (2.2820 g), which acted as an oxidant, was dissolved in 100 mL DI (Deionize water). APS was added drop-wise in the aniline solution. Temperature of the reaction was controlled below 5 °C by using an ice bath. As the time of reaction goes by, the colour of the mixture had transformed from milky white to dark green. PANI was obtained by centrifuging the green mixture at 8000 rpm for 15 min, then washed with DI-water and acetone 3 times, and dried at 90 °C for 3 h.

Substrate Preparation

Porous Silicon substrate were prepared on an n type, <100> oriented silicon wafer, resistivity of 10 Ω cm by anodisation in the electrochemical cell with platinum as cathode and silicon wafer as anode immersed in electrolyte solution of HF (48%) and ethanol (99%) in a ratio of 1:1 by volume. Constant DC current was provided in the cell to ensure the formation of homogeneous porous layer.

Characterization

Phase identification of PANI was done by X-Ray Diffraction(XRD) using bruker AXSD8 differactometer with Cu- α radiation. Morphological study of etched and polyaniline coated silicon substrates were carried out by field emission scanning electron microscopy (FESEM; Philips, EM 400; TECHNAI 20G2-S-TWIN). The Fourier Transform Infrared Spectroscopy was obtained in the range 400 to 4000 cm^{-1} was recoded using Thermo Scientific Smart Omni-Transmission Nicolet Is10 spectrometer. PANI, coating on porous silicon is made using spin coating technique. The thin film of $\sim 3 \mu\text{m}$ was deposited on porous silicon substrate. Silver paste is used for making the contacts. The gas sensing characteristics were studied in a custom made testing chamber. The sensitivity of the film was determined by measuring the change in resistance of the sensing surface when exposed to ammonia. The resistance measurements of the samples were carried out by two Platinum probes using two-point probe method with a digital multimeter. The experimental set up used for gas sensing analysis is reported elsewhere [14].

RESULTS & DISCUSSION

The XRD Pattern of PANI is shown in the Figure 1. For PANI, the characteristic peaks appeared at 15.00, 20.4 and 25.48, corresponding to (011), (020) and (200) crystal planes (Figure 1) are similar to those observed by other researchers [15, 16]. XRD pattern of polyaniline indicates that the material is partially crystalline. The pattern of PANI includes three prominent broad peaks and few smaller peaks riding over a broad hump, indicating that chain ordering is primarily restricted to short range. The average particle size is determined by Scherrer method. The crystallite size of the nano particles is given by the Scherre's formula, $D = 0.9 \lambda / \beta \cos\theta$, where λ (1.5406 \AA) is the used X - ray radiation wavelength, β is the full width at half-maximum (FWHM) and 2θ is the diffraction angle. Assessments of the particle size of the sample at different peaks were repeated and the average crystallite size is found to be 80 nm for nano structured polyaniline.

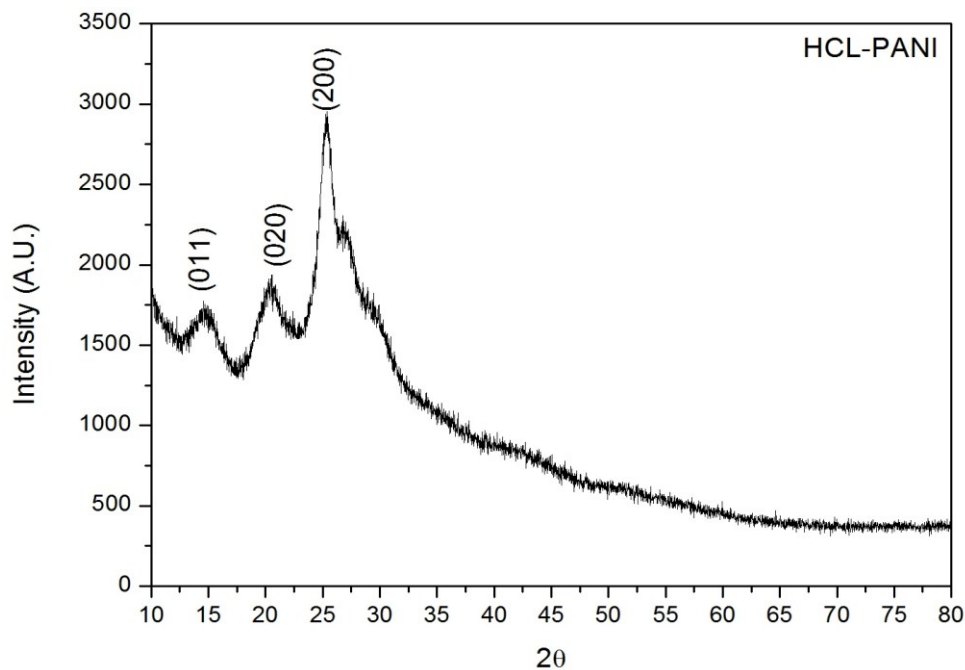


Fig. 1 XRD pattern of nanostructured polyaniline prepared at reaction time 6h

The chemical structures of polyaniline were characterized by Fourier Transform Infrared (FTIR) spectroscopy (Figure 2).

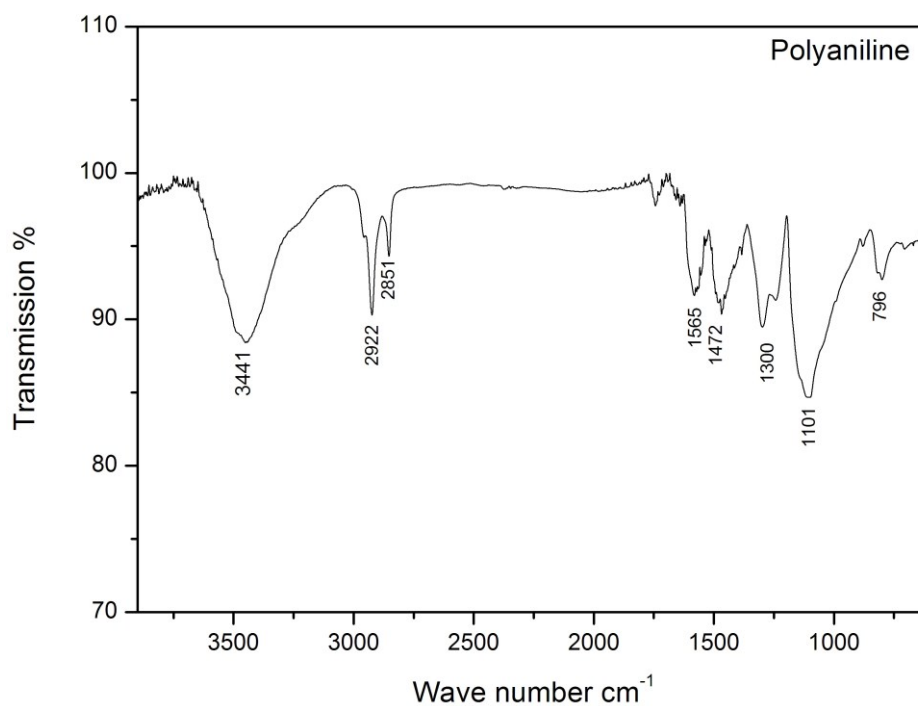


Fig. 2 FT-IR spectra of polyaniline nanostructure.

The characteristic peaks at 3441 cm^{-1} , 2922 cm^{-1} , 1566 cm^{-1} correspond to absorption of N-H stretching vibration, C-H stretching and C=C stretching vibration of quinoid ring respectively. The characteristic absorption peaks at 1472 cm^{-1} , 1302 cm^{-1} , 796 cm^{-1} attributed to stretching vibrations of benzenoid ring, stretching of C-N bonds of secondary aromatic amine and N-H out of plane bending in rocking mode respectively. This is a typical PANI spectrum, in accordance with work reported in the literature [17]. The FESEM micrographs of the porous Si substrate, and polyaniline nanoparticles are shown in Figure 3. Figure 3a showed the formation of pores on the silicon substrate. The pore average size obtained was lying in the range of 150-160nm. Figure 3c shows the formation of needle shaped polyaniline nanoparticles with length lying in the range of 80-90 nm and breadth from 20-30 nm. The image of polyaniline nanoparticles shows that there is no agglomeration.

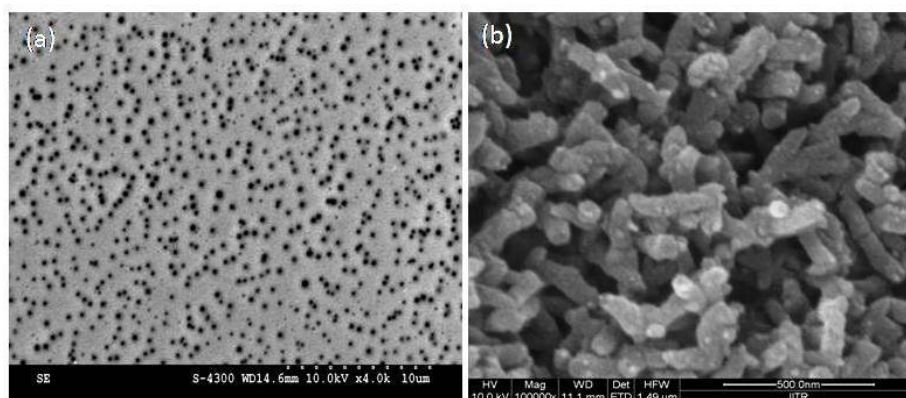


Fig. 3 FESEM micrograph of a) porous silicon substrate, b) polyaniline nanoparticles.

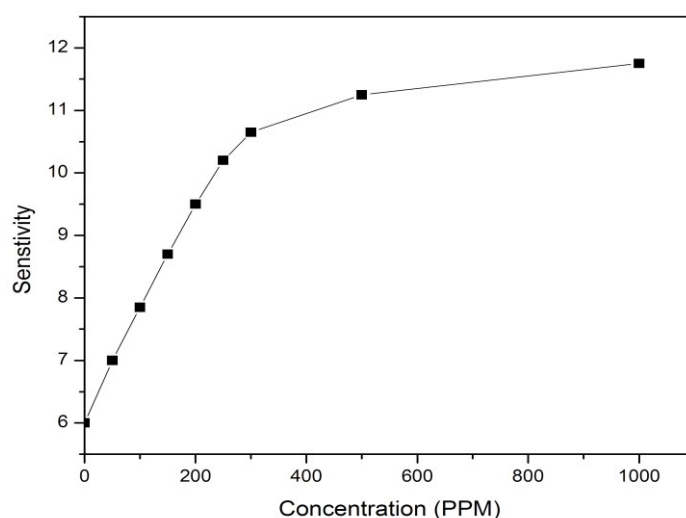


Fig. 4 Showing the correlation between gas concentration and sensitivity of polyaniline nanoparticles at room temperature.

Gas response (S) is defined as the ratio of the change in resistance of the sensor on exposure to the target gas to the original resistance in air. The relation for S is as: $S = \frac{R_g - R_a}{R_a}$, where R_a and R_g are the resistance of sensing materials in air and in a target gas medium (ammonia) respectively. Figure 4 shows the variation of sensitivity of polyaniline nanoparticles for various concentration of ammonia gas (50, 100, 150, 200, 250, 300, 500 and 1000 ppm). It is known that during synthesis of polyaniline with HCl acid, the protonation reaction take place as follows:



Where, PA and PAH^+ are undoped and doped repeated block of polyaniline, respectively. As a result of above reaction, neutral polyaniline molecule takes proton and result in forming energetically favourable $N^+ - H$ chemical bonds. So positively charged local centres placed at nitrogen atom are formed which in turn allow the hopping of valence electron from one such center to another, giving rise to P type conduction [18]. When Polyaniline react with ammonia, the following reversible reaction take place.



In the presence of ammonia, the above reaction goes predominantly toward right side: ammonia molecule gain proton from PANI thus forming energetically more favorable ammonium (PANI dedoping reaction). In air (with no ammonia), the reaction (2) begins to go towards the left. Ammonium decomposes into ammonia and protons which being added to PANI molecule restore the initial level of doping [19]. It can be seen that sensitivity tends to saturate with increase in concentration of ammonia gas. For small concentrations of gas, there is a lower surface reaction took place due to lower coverage of gas molecules on the grain surface. An increase in gas concentration, the number of the surface reactions and sensitivity also increase. At higher concentrations, saturation is reached due to full surface coverage with test gas molecules. Figure 5 shows the typical response characteristics at room temperature for polyaniline nanoparticles for 200 ppm of ammonia. The time taken to reach 90% of the maximum sensitivity is 2-4min. Recovery time for tested samples to attain 90% from maximum sensitivity is 2 min.

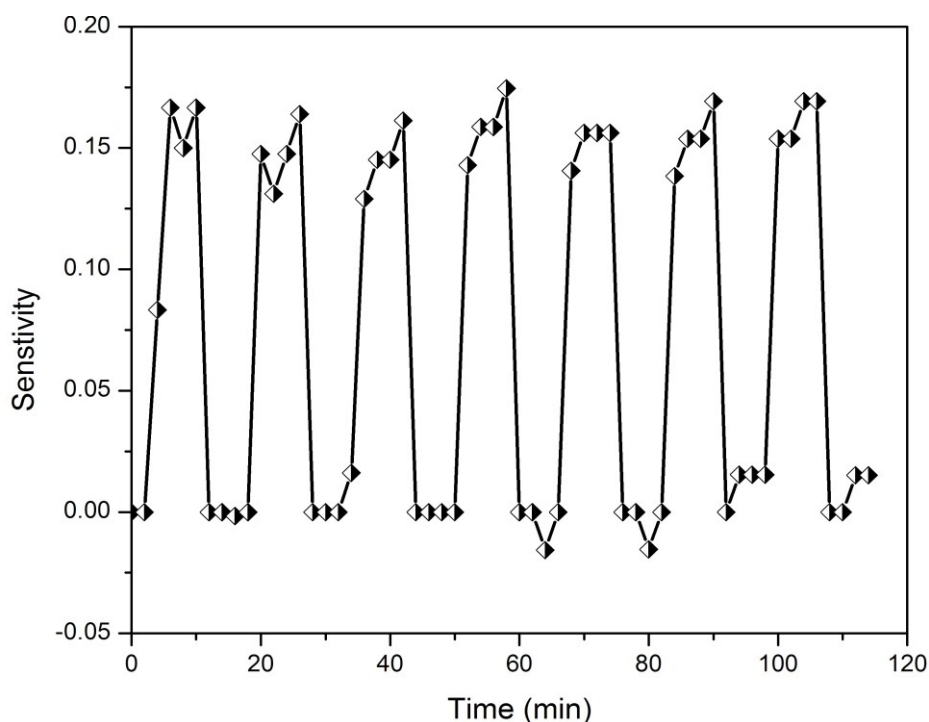


Fig. 5 The response-recovery characteristic of polyaniline nanoparticles to 200ppm ammonia at room temperature.

CONCLUSIONS

Polyaniline nanoparticles having crystallite size of about 80 nm were synthesized by oxidative polymerization of aniline monomers. From FESEM study, polyaniline nanoparticles are observed to have needle shaped morphology with average particle size in the range of 80-90nm. The chemical structures of PANI nanostructure were characterized by Fourier Transform Infrared (FTIR) spectroscopy. From the sensitivity data of PANI, sensitivity was observed to increase with increase in ammonia concentration. The minimum concentration of 50 ppm is detected successfully at room temperature.

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