Hydrothermal Synthesis of Polyaniline Nano-fibers as H$_2$S Gas Sensor

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Abstract. A simple hydrothermal method of synthesis of Polyaniline Nano-fibers was presented. Thin films from PANI have been deposited via spin-coating technique on silicon substrate. The structural, morphological, optical and sensitive properties were studied for prepared thin films. The XRD results exhibit that the prepared films show crystalline nature of polyaniline Nano-Fibers and that the crystallite size, evaluated by the Scherer formula, is about 30.1 nm. The FE-SEM image of Polyaniline proved that the film prepared have Nano fiber like structure. The optical measurements proved that the optical energy gap was found to be 2.88 eV. The H$_2$S sensing properties of thin films were measured for various operating temperatures. The best sensitivity of 7.32% was observed when operating at a working temperature of 150 °C, also the fast response time and recovery time behavior have been achieved.

Keywords: Polyaniline, Structural Properties, hydrothermal method, H$_2$S gas sensor, spin coating.

1. Introduction

Gas detection devices usually use metal oxide semiconductors, its principle of which is based on change in conductivity due to interacting with gas molecules and this attribute mainly depends on working temperature. Hence, metal oxide gas sensors need a high working temperature [1].

These gas sensors also generally have the disadvantage of little selectivity, and low sensitivity to extremely low concentrations of gases. As a result, many various approaches to solving these problems have been discussed. Newly, conducting polymers (CP) were used as an alternative materials to metal oxides for applications in gas sensors [2].

As compared to metal oxides, the CP like (polyaniline, polythiophene, and polypyrrole) possess attracted large interest because of its prominent advantages properties, such as low cost, easy synthesis, friendly operating condition and flexible modification [3]. In the conductive polymer family, Polyaniline (PANI) has gained a lot of attention due to its economic price, good environmental stability and high redox properties [4,5]. Many nanostructures of PANI have been used by as sensing materials for detecting many gases such as Acetone [6], NH$_3$ [7], CO [8], NO$_2$ [9], etc.

Gas sensors are very important for monitoring H$_2$S gas because of its a very toxic, corrosive and flammable explosive gas with the foul smell characteristic of rotten eggs, and also its widely used in...
different chemical industries and research laboratories [10-12]. However, Harmful effects of H₂S gas, need the development of sensitive and fast gas sensors.

In addition, the hydrothermal method has an advantage for forming high quality nanocrystals, low cost and simple procedure compared of other methods that need complex devices and tools with high production cost[13,14].

In this present work, PANI NFs was synthesized by hydrothermal method with relatively low cost. PANI in thin-film form have been deposited via utilizing spin-coating technique. Samples were characterized by means of XRD, FT-IR spectra, FE-SEM and UV-Vis spectroscopy. H₂S gas sensing properties of the samples at various operating temperatures were studied.

2. MATERIALS AND METHOD
Aniline (ANI), Ammonium Persulphate (APS) and Ethanol were obtained from Ltd, India. Hydrochloric acid (HCl) was acquired from CDH Ltd, India. and all the reagents were of analytical purity. Deionized water was used for the experiment.

In a typical procedure, (0.088 g) of ANI was first dissolved in 76 mL Deionized water solution at room temperature. After that, 4 mL of (0.219 g) APS and 1.4 ml of HCl were added sequentially into the above mixture under stirring for 20 min, then placed the mixture in a 100 mL Teflon-coated stainless steel for hydro-thermal reaction at 120 °C for 5 h, after that it cooled to room temperature quickly by placing into a water bath.

The obtained products were washed several times with distilled water, and ethanol. Finally, it is dried under vacuum at 70 °C for 4 h to obtain the PANI powder and re-dispersed into 50 mL of ethanol placed by in the ultrasonic for 2 h and this solution is deposited on a silicon substrate to prepare PANI thin film by spin coating technique at room temperature.

3. Results and Discussion
3.1 X-Ray Diffraction
The structural characteristics of PANI NFs film has been analyzed by X-ray diffraction pattern as shown in Fig1. XRD pattern of PANI has crystalline nature at 2θ=25° which is corresponds to (200) crystal planes of PANI NFs[15,16]. The crystalline nature for PANI is attributed to its nano fibrous structure and planer nature of the active groups banzenoid and quinoid[17].
The crystallite size ($D_{av}$) from a sharp peak at 25° for PANI was calculated by the Scherrer's formula [18]:

$$D_{av} = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

Where $\lambda$, $\theta$ and $\beta$ are X-ray wavelength (Cu Kα-1.54056 Å), the diffraction angle and full width at half-maxima in radians, respectively. The crystallite size was observed equal to 30.1 nm. The XRD analysis results of PANI NFs are illustrated in Table 1.

Table 1. X-ray analysis of PANI NFs.

| 2θ (Deg) | d (Å)    | $\beta$ (rad) | $D_{av}$ (nm) | hkl |
|---------|----------|---------------|--------------|-----|
| 25.0260 | 3.5553   | 0.0047        | 30.1         | (200) |

3.2 Field Emission-Scanning Electron Microscope (FE-SEM)
FE-SEM is a suitable technique to study surface morphology of nanostructured thin films. Figure 2 illustrates the FE-SEM image of PANI NFs film, and it can be observed the PANI possesses nano-fiber like structure with average particle size in the range about (25-40) nm. This image also observed that PANI have some voids or pores [19].

3.3 Fourier Transform-Infrared Spectroscopy (FTIR)
Figure 3 illustrates the FT-IR spectra of Pure PANI. The characteristic absorption of PANI at 1476 and 1575 cm$^{-1}$ referred to (C=C) and (C=N) stretching modes for benzenoid (B) and quinonoid (Q) rings, respectively [20,21]. Peak at 810 cm$^{-1}$ has been considered as the vibration of (C-H) and (C-C) in the benzenoid structures [22].
The N = Q = N stretching for quinoid ring, and (C–N) stretching for benzenoid ring can be observed at 1125 and 1295 cm\(^{-1}\), respectively[23]. The vibrational band around 3416 cm\(^{-1}\) has referred to the (N-H) stretching vibrations of polyaniline.

![FT-IR spectra of pure PANI NFs.]

**Figure 3.** FT-IR spectra of pure PANI NFs.

**3.4 UV-Vis Analysis**

UV–visible spectroscopy of PANI NFs solution in the spectral range of (190–1100) nm is illustrate in Fig. 4 and its observed that the PANI NFs strongly absorbs visible light and exhibits two distinctive peaks at about 314 and 605 nm, which are related to the benzenoid ring (\(\pi-\pi^*\)) and (\(\pi\)-polaron) transition exhibits the polaronic band that returns to the inter-ring charge transfer connected to the quinoid moieties by excitation from benzenoid[7].

![UV–visible spectra of PANI NFs.]

**Figure 4.** UV–visible spectra of PANI NFs.
The optical band gap value (Eg) can be calculated by using the Tauc formula[24]:

\[(\alpha h\nu) = A(h\nu - Eg)^r\]  \hspace{1cm} (2)

Where h\nu, \alpha, A and r are the photon energy, absorption coefficient, a constant, and a number that indicates the optical transition type, respectively. In this work, direct band gap value was obtained via plotting (\alpha h\nu)^2 versus the energy of photon (h\nu) in (eV) for PANI NFs as shown in Fig 5.

![Figure 5. (\alpha h\nu)^2 vs. photon energy for PANI NFs.](image)

3.5 Sensor measurements

The gas sensitivity measurement of PANI NFs was carried out at for various operating temperatures by injecting 25 ppm concentration of test gas H\textsubscript{2}S. Figure 6 shows The Variation of resistance with time to PANI NFs at four different operation temperature( RT, 50,100 and 150). The figures show that the resistance increases in opened the gas case when its exposed to H\textsubscript{2}S gas and decreases rapidly in closed gas. Being PANI is a p-type material[25,26], will lead to increase in the resistance of PANI film when interaction to H\textsubscript{2}S gas.

The sensitivity value of the PANI NFs gas sensors to H\textsubscript{2}S gas was calculated by equation[27]:

\[S = \left[\frac{R_g-R_a}{R_a}\right] \times 100\%\]  \hspace{1cm} (3)

Where, R\textsubscript{g} : the resistance of the sensor in target gas, R\textsubscript{a} :the resistance in air atmosphere. It was found that sensitivity increases quickly with the increase of the various operating temperatures as illustrated in Table 2.
Figure 6. The Variation of resistance with time to PANI NFs at different operation temperature.

Also Table 2 shows that the fast Response-Recovery time was achieved which was found to be < 1 sec. The fast response in this work indicates that the PANI NFs gas sensors to H₂S gas, has a good advantage, and it's may be used for monitoring and/or detecting dangerous gases that exist in low concentrations.

Table 2. Response time, Recovery time and Sensitivity %, of PANI NFs against H₂S gas

| TOC | Response Time (s) | Recovery Time (s) | S %   |
|-----|------------------|-------------------|-------|
| RT  | 0.8              | 0.58              | 4.13  |
| 50  | 0.77             | 0.87              | 5.57  |
| 100 | 0.79             | 0.82              | 6.32  |
| 150 | 0.81             | 0.79              | 7.32  |

4. Conclusions
Spin coating technique followed by hydrothermal method was used to fabricate PANI nanofibers based gas sensor. The formation of sample was confirmed from XRD, FE-SEM, UV-vis and FT-IR characterizations. The SEM image exhibited the formation of nanofibers with average particle size in nanoscale regime. The PANI nanofibers exhibited high sensitivity to H₂S gas at 25 ppm and as the operation temperature increases then sensitivity increases quickly and high sensitivity was observed at 150°C. Response-Recovery Time of H₂S gas was found to be < 1 sec. therefore, the prepared film as gas sensor has the ability to work for ecological monitoring.
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