Sensing Characteristics of Nanostructured PANI/Ag Thin Films as H₂S Gas Sensor

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Abstract: Nanocomposites of polyaniline (PANI) and Silver (Ag) nanoparticles (NPs) have been successfully synthesis using hydrothermal and chemical method respectively. The nanocomposite films were deposited by spin coating technique on Si substrates and examined using XRD, FE-SEM, EDX, FT-IR techniques as well as their sensing properties were studied towards H₂S gas. The XRD pattern showed a presence of crystalline nature of PANI NFs film and cubic structure of PANI/Ag films. FE-SEM images revealed that PANI film has nanofibers structure, whereas the PANI/Ag films composite revealed that Ag NPs caped with PANI nanofiber. The sensing analysis indicated that on exposure to H₂S gas at low concentration 25 ppm, it was observed that the PANI/Ag films sensor composite showed high sensitivity compared with pure PANI NFs, and the maximum sensitivity (73.35%) was obtained at 200 °C with faster response/recovery times < 1 sec.

Keywords: Polyaniline NFs, PANI/Ag composite, hydrothermal method, H₂S gas sensor spin coating.

1. Introduction
In our environment, gases with various concentrations, origins and properties are available. Part of those gases are important for indicators of safety or life, while others are very toxic and dangerous. Therefore, gas detection and monitoring sensors are needed to in different fields, including environmental conservation, vehicle emission control, industrial process monitoring, safety and agricultural, etc[1,2].

Hydrogen sulfide (H₂S) is one of the toxic and harmful gases, which effects on human that and could cause death due to concentration and exposure time and often produced in sewage plants, oil mines and coal or natural gas industries [3-5] Therefore, it is necessary to have small, fast, portable and sensitive sensors which can detect/monitor H₂S gas with low concentration is highly important to protect human lives.

The recent developments of conducting polymers (CP) such as polyaniline(PANI) polypyrrole and polythiophene promise future advances in some fields of modern technology, including in sensors, microelectronics, biochemical engineering and biosensors as well as solar cells, due to their prominent
properties such as easy process ability, low cost, facile synthesis, friendly operating condition, etc [6,7]. Polyaniline is one of the most important semiconducting polymer because of its good advantages such as low price, easy preparation, good redox, high chemical stability, high conductivity [8,9].

In recent reports, PANI and PANI/metal nanoparticle composite have been investigated for improve electrical and optical properties [10-13]. Many of researches displayed that The PANI/Ag composite having enhanced sensing properties for detect different gases, like Ethanol [14], Formaldehyde [15] and Ammonia [16].

The H2S gas sensing properties of spin-coated PANI/Ag composites have not been registered, to the best of our knowledge. In this work, PANI and its composites were prepared on Si substrate via using spin-coating technique. The nano-composites were investigated by XRD, FESEM, EDX, FT-IR technique. The gas-sensing properties of the samples to H2S at different working temperature were studied.

2. Experiment
2.1 Preparation of Polyaniline NFs
Polyaniline NFs was synthesized by hydrothermal method. To do this, 0.088 g of Aniline (CDH Ltd, India) was dispersed in 76 ml deionised water. Then, 4 ml of Ammonium persulfate solution and 1.4 ml of HCL (CDH Ltd, India) were dropped into the above solution and stirred at room temperature for 10 min. After that, This mixture was moved into a Teflon-lined autoclave with 100 ml capacity and heated at 120 °C for 5 h.

The autoclave was then allowed cooled to room temperature by putting into a water bath and the product was collected and rinsed twice with water and distilled absolute ethanol and then dried at 70 °C for 4 h in vacuum, a fine PANI powder was obtained. Finally, The obtained powder was dispersed in 15 ml ethanol by used the ultrasonic treatment for 2 h and its deposited by spin-coating technique on cleaned silicon substrate at RT to prepare thin films.

2.2 Preparation of PANI/Ag Nanostructures
The solutions of Silver nitrate, AgNO3 (BDH, England) and polyvinyl pyrrolidone, PVP (M.w. > 180000 - BDH, England) were prepared separately by dissolving appropriate amounts of (0.1M) AgNO3 and (0.1mM) PVP in distilled water and in two- beakers at room temperature. After that, two solutions were mixed together and then stirred for 45 min at room temperature.

This mixture was putted in oven and keep at 70 °C for 3 h. Finally, the obtained solution was used to prepare PANI/Ag composites and its deposited by spin-coating technique on cleaned silicon substrate.

Polyaniline NFs were mixed with different concentrations of Ag. PANI/Ag composites were prepared by adding solution Ag to solution PANI with different volume ratios as listed in Table 1. Then, the mixed solutions were moved into the ultrasonic for 2 h. Finally, this mixture were deposited on cleaned silicon substrates by spin-coating.

| Sample       | Volume Ratios (mL) |
|--------------|--------------------|
| Pure PANI    | 10 : 0             |
| PANI / Ag    | 9 : 1              |
| PANI / Ag    | 5 : 5              |

Table 1. different volume ratios of pure PANI and PANI/Ag composites.
3. Results and Discussion

3.1 X-ray diffraction analysis:
The XRD patterns of PANI and PANI/Ag composites films are shown in Figure 1(A-C). Figure 1(A) shows the XRD pattern of PANI NFs has crystalline nature at $2\theta \approx 25^\circ$ corresponding to the (200) crystal plane of PANI NFs\cite{17,18}. The crystalline PANI is due to its nano-fiber shape and Planar nature of the functional groups Banzenoid and Quinoid, this consistent with Bhagwat et al.\cite{19}. Compared with Figure 1(A), new peaks at $2\theta \approx 38^\circ$, $44^\circ$, $64^\circ$ and $77^\circ$ showed in Figure 2(B,C), which corresponded to (100), (200), (220) and (311) diffractions pattern of cubic structure Ag nanoparticles (JCPDS: 04-0783)\cite{15,16}. In addition, the other peak occurs at $2\theta \approx 28^\circ$, which is refer to Si substrate\cite{20}.

![XRD pattern of PANI and PANI/Ag composites films](image)

The crystallite size of PANI and its composites, can be obtained by using Scherrer’s equation\cite{21}:

$$D_{av} = \frac{0.9\lambda}{\beta \cos \theta}$$

where $D_{av}$ is crystallite size, $\theta$ is diffraction peak position, $\lambda$ is XRD wavelength (Cu Kα-1.54056 Å). It was noticed that the crystallite size for the PANI film equals 30.1 nm, and it increases for PANI/Ag composite films with the content of Ag increases to become 36.1nm.

3.2 FE-SEM analysis
The surface morphology of PANI and its composites were examined by Field Emission Scanning Electron Microscope (FE-SEM) with two various magnification. Figure 2(A) image illustrate the images for PANI
film, The FESEM image of polymer clearly indicates that the PANI have nanofiber like structure with diameter in the range 25-40 nm and contains some voids or pores.

Figure 2(B,C) illustrates the images of PANI/Ag composites films, The surface morphology of this composite has fiber like shape where the Ag nanoparticles are homogenously dispersed in the PANI matrix, The average diameter of PANI/Ag composite was 35 ±5 nm.

![Figure 2. FESEM images of (A) Pure PANI, (B) PANI/Ag (9:1) and (C) PANI/Ag (5:5).](image)

### 3.3 EDX analysis

Dispersive X-Ray Spectroscopy (EDX) has been used to examine the PANI, and the spectra are shown in Figure 3. EDX images confirmed that the samples contain C, N and Ag in the PANI/Ag. In composite, The H signal is not present because of its lower energy[22]. The characteristics of the samples obtained from the fibers are particularly useful features for gas sensing applications where the surface plays an important part in the detection process.

![Figure 3. EDX images of (A) Pure PANI, (B) PANI/Ag (9:1) and (C) PANI/Ag (5:5).](image)
3.4 FTIR analysis

Figure 4 presents the molecular structure of PANI and its composites as obtained from FT-IR spectra analysis. The characteristic bands observed for pure PANI (Figure 4A) at 1476 and 1575 cm\(^{-1}\), referred to benzenoid (B) and quinonoid (Q) ring-stretching vibrations, this agreement with Li et al. [23]. The absorption band at 1295 cm\(^{-1}\) was attributed to C–N stretching for benzenoid ring. Peak at 1125 cm\(^{-1}\) was considered as bending vibration of N = Q = N stretching for quinoid ring[24]. Absorption bands at 810 cm\(^{-1}\) was attributed to C-H, C-C stretching modes for benzenoid structures[25]. The N-H stretching vibrations of PANI may be observed at 3416 cm\(^{-1}\).

Figure 4(B,C) illustrate spectrum of PANI/Ag composites. The molecular structure of this composite was comparable to that of pure PANI, although some peaks were not entirely identical. Vibrations of B and Q were shifted from 1476 and 1575 cm\(^{-1}\) to 1496 and 1653 cm\(^{-1}\), respectively. This phenomenon is described as: due to the electrostatic interaction between electrons and aniline cation, a large number of electrons around silver atoms tend to conjugate the Q and B structure. As a result, leading to a shift in the absorption of infrared[26].

![Figure 4. FTIR spectra of (A) Pure PANI, (B) PANI/Ag (9:1) and (C) PANI/Ag (5:5).](image)

3.5 Gas Sensing properties

The sensing properties of PANI and its composites were studied for H\(_2\)S gas with 25ppm concentration by measuring the variation in resistance with the time at different working temperature (RT, 100, 150 and 200 °C) are shown in Figure 5. The figures show The resistance increases in exposed films to H\(_2\)S gas, then the resistance decreases when the closure of the gas.
Gas sensor operating temperature defined as the temperature when the sensor resistance is approximate to a constant value. This mechanism of samples is attributed to the ion sorption upon the material surface when the exposure to reducing (electron-donating) gases, which leading to relocate charge between gas and surface molecules and therefore cause an decrease in the conductivity and increase in the value of resistance [27,28,14,16].

Figure 5. Change in resistance of (A) Pure PANI, (B) PANI/Ag (9:1) and (C) PANI/Ag (5:5) with respect to time on the exposure of H2S gas at RT, 100, 150 and 200 °C.

The sensitivity($S$) of the sensor films is calculated using the relation [29]:

$$ S = \left| \frac{R_g - R_a}{R_a} \right| \times 100\% $$

Where $R_g$ and $R_a$ are electrical resistance in existence of gas and in air, respectively. Figure 6 shows the sensitivity of PANI and its composites at different operating temperature which were deposited on Si substrate. Result observed that the sensitivity increases with the increasing temperature. Moreover the sensitivity increases as the Ag concentration increases. The PANI/Ag (5:5) composite film shows best sensitivity of 73.35% at 200°C.
Figure 6. The sensitivity of pure PANI to H₂S (25 ppm) at different operating temperature.

Table 2 shows response and recovery time of PANI NFs and their composites against H₂S gas with different working temperatures. The table shows that all films have a quickly response speed and low recovery time less than 1 s.

Table 2. Recovery / Response time of PANI NFs and their composites against H₂S gas.

| Sample         | Response Time (s) | Recovery Time (s) |
|----------------|-------------------|-------------------|
|                | RT 25°C | 100°C | 150°C | 200°C | RT 25°C | 100°C | 150°C | 200°C |
| PANI           | 0.8     | 0.79   | 0.81   | 0.82  | 0.58     | 0.82   | 0.79   | 0.78  |
| 9 mL PANI–1 mL Ag | 0.86   | 0.81   | 0.79   | 0.78  | 0.78     | 0.78   | 0.83   | 0.86  |
| 5 mL PANI–5 mL Ag | 0.76   | 0.82   | 0.79   | 0.82  | 0.74     | 0.81   | 0.8    | 0.81  |

The fast response sensor toward H₂S gas may be due to quickly gas oxidation[30]. In the real situations a quick response time is usually required in sensing measurement, but recovery time is the least influenced, although they are important in order for the sample to return to its original state.

4. Conclusions
PANI NFs has been successfully synthesized with hydrothermal method. PANI and PANI/Ag nano-composite films has been successfully prepared by spin-coating technique. The structure and morphology of the samples are confirmed via using XRD, FE-SEM, EDX and FTIR techniques. Gas sensing properties were carried out of H₂S at different working temperature. It is noticed that, The PANI/Ag (5:5) composite film display a better sensitivity of 73.35%. Moreover, the as-prepared thin films show rapid response/recovery time and which suggest the promising application in gas-sensor field.

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