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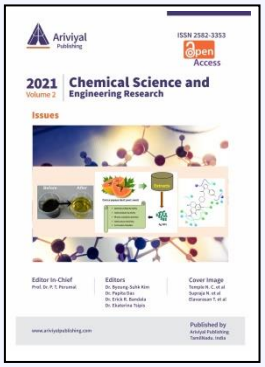

Polyaniline Based Nano composite Sensor for Sensing of Ammonia Gas

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Abstract: In this work, the synthesis of polyaniline nanocomposite based sensing materials using different processes and methods has been presented and discussed. The obtained materials were characterized by using advanced techniques like XRD and FT-IR. In order to check the sensing properties, the synthesized sensor was fabricated and was exposed to different concentrations of ammonia gas. The minimum concentration of ammonia gas at which the sensor responded was found 5 ppm.

Keywords: Polyaniline; Sensing; XRD; FT-IR; Ammonia

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1. Introduction

A sensor is a device that has the ability to measure a physical quantity, and convert it into a signal which can be detected by an observer or by an instrument.[1-2] Sensors are classified into two types: one is physical sensors and another is chemical sensors. Gas sensors are chemical sensors which are able to convert the chemical properties of volatile and toxic gases into detectable electrical signals.[3-4] The new gas sensors with specified properties and applications are of great attention to scientific community from recent decades. They are used for monitoring toxic gases, to maintain the system safe and avoid any unexpected threats. There are number of gas sensors used for detection of different gases like oxygen (O_2), carbon dioxide (CO_2), nitrogen (N_2), methane (CH_4), hydrogen cyanide (HCN) and carbon monoxide (CO). The gas detectors can be used to detect the leakage of the harmful gases and hence monitoring of the air quality in industries and offices could be made. The modernization and industrialization have tremendously increased environmental pollution. Due to this growing industrialization, constant environmental monitoring and pollution control becomes very essential.[8] Hence, the detection of harmful gases such as CO, nitrogen dioxide (NO_2), ammonia (NH_3), Sulphur dioxide (SO_2), CO_2 and HCN for domestic and industrial safety becomes very important in order to protect environment and human lives. Furthermore, these gas sensors can be used to detect warfare agents like phosgene chlorine and sarin for national security and defense.[9-10]

A standard fabricated sensor should have features like operation at room temperature, no requirement of external stimulus, should detect harmful gases at low concentrations, should have high sensitivity and reproducibility, quick response, low cost, low power consumption, long durability and most importantly environmental friendly.[5-7] Among various types of gas sensors, polyaniline (PANI) based sensors are extensively employed for sensing applications due to its easy synthesis, exceptional doping/de-doping chemical reaction, high conductivity, outstanding environmental stability, and excellent responsively to NH_3. Examples of different polyanilines and their structure have been shown below (Fig 1).

In this work, we describe the fabrication of a nanocomposite based on the conducting polymer PANI-rGO-CNT composite. Accordingly, the fabricated material is expected to display improved gas-sensing properties and excellent repeatability. The synthesis, structure elucidation and gas-sensing properties of the synthesized composites are classified in the following discussion.

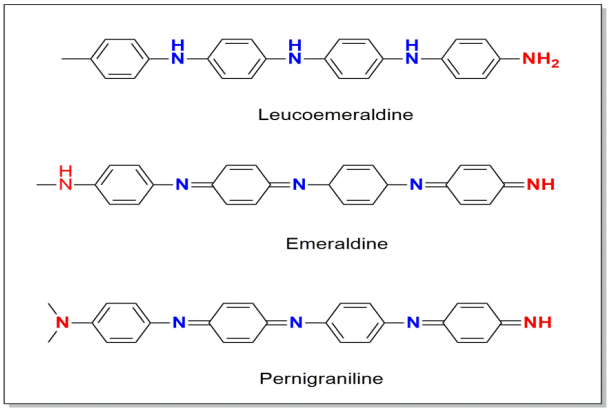

Fig. 1. Structure of different ployanilines based gas sensing materials

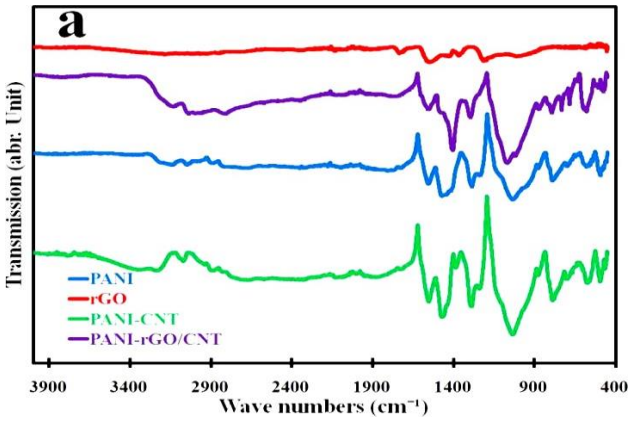

Fig. 2. FT-IR results of PANI, rGO, PANI/CNT, PANI-rGO-CNT

2. Experimental Method

This portion includes the methods and processes for the preparation of the various gas sensing materials. The various materials synthesized include:

2.1. Synthesis of Polyaniline (PANI)

The 0.5 M of aniline is added to the 30 ml of distilled water and stirred for 30 minutes with the help of magnetic stirrer. This is followed by addition of 0.5 M of Sulphuric Acid (H_2SO_4). In another set up, 0.5 M of Ammonium per sulphate $(NH_4)_2S_2O_8$ (APS) is added to 30 ml of deionized (DI) water, and stirred for 30 minutes on magnetic stirrer. This is added to the above solution. The assembly is left for 8 hours to complete the polymerization reaction while maintaining the temperature below 100°C. After which the polymer is separated by filtration using Whatman filter paper. The polymer is washed several times to remove the unreactive chemicals. Finally, polymer is dried at 65°C.

2.2. Preparation of Polyaniline/Carbon Nanotubes (PANI-CNT)

The 0.07 grams of multi-walled carbon nanotubes (MWCNT) is added to the 30 ml of double distilled water and stirred for 15 minutes on a magnetic stirrer, and the aniline is added to the solution. This stirred again with magnetic stirrer and then 0.5 M of H_2SO_4 is added to the above solution. In the second step 0.5 M of $(NH_4)_2S_2O_8$ is added to 30 ml of DI water and stirred for 30 minutes on magnetic stirrer and is added to the above solution. The polymer obtained is filtered using Whatman filter paper. The polymer is washed several times to remove unreactive chemicals. Finally, it is dried at 65°C.

2.3. Preparation of Reduced Graphene Oxide (rGO)

For preparation of reduced Graphene Oxide (rGO), 0.5 ml of hydrazine hydrate is added to 5 ml of double distilled water, and then added to the graphene oxide obtained from Hummers method. The solution is centrifuged again and then kept in oven for heating resulting in the formation of reduced graphene oxide.

2.4. Preparation of PANI-rGO-CNT Composites

The preparation of the RGO/CNT/PANI is carried out in different proportions. For first sample preparation, we take 20 ml of double distilled water, and added to it the mixture of 0.025 grams of CNT, 0.05 grams of rGO and 0.04 grams of Citric acid. The solution is kept for constant stirring for 2 hours. After 2 hours, the solution is transferred to Teflon line steal outer clip and kept at the temperature of 175°C in the oven for 5 hours. After that the material obtained is polymerized with aniline and Ammonium per sulphate (APS) solution both taken as 0.5 M.

3. Characterization

3.1. FT-IR Studies

The FT-IR studies of PANI, PANI-CNT were done to confirm and identify chemical bonds in our sample. FT-IR spectra of PANI, rGO, PANI-CNT and PANI-rGO-CNT composites are shown in (Fig 2). The typical FT-IR spectrum of PANI, rGO, PANI-CNT and PANI-rGO-CNT is an agreement with previous work.[10] The bands at 3202 cm^{-1}, 1580 cm^{-1}, 1490 cm^{-1}, and 1300 cm^{-1} correspond to N-H amine group, CN in imine group, C-C in aliphatic hydrocarbon, C- N to benzenoid functional groups respectively. However, in case of normal graphene oxide the peak appears at 3400 cm^{-1} but as soon as we reduce the graphene oxide, the peak disappears. For PANI-CNT the peak shifts and appears at 3300 cm^{-1} which corresponds to the N-H amine group. The peak shifting arises due to the increase in bond strength between OH and NH group.[11] For PANI-CNT-rGO, there is a less stretching frequency which may be due to the higher molecular mass (there exists inverse relation between stretching frequency and molecular mass). These are characteristics absorption bands of PANI, confirming the successful synthesis of PANI. The FTIR spectrum of rGO–PANI is almost the same as PANI which confirms the successful coating of PANI nanorods. It is worth mentioning here that the peaks related to the PANI matrix in the rGO–PANI composites shift to higher wavenumbers. These shifts may arise from π–π interaction and hydrogen bonding between rGO sheets and the polymer backbone.[12]

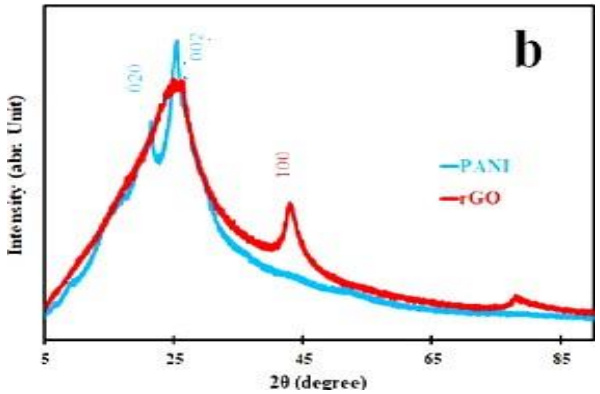

Fig. 3. XRD pattern of PANI and rGO

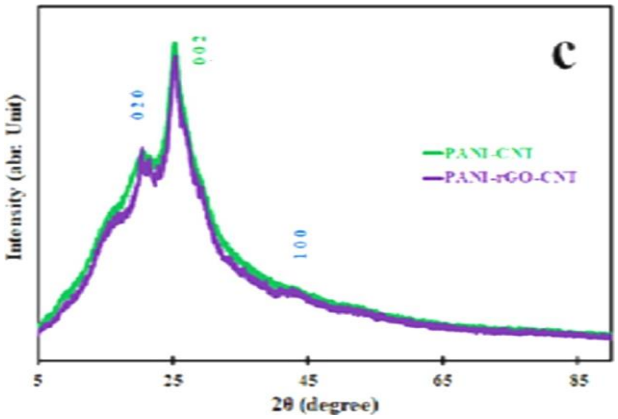

Fig. 4. XRD pattern of PANI-CNT and PANI-rGO-CNT

3.2. XRD Analysis

The XRD analysis of our PANI sample is shown in Fig 3. The sharp peak at 26.40 (002) suggests the crystalline nature of the conducting polymer. However, the peak 45.50 (100) suggests the presence of rGO. For PANI-CNT composite, the characteristic peaks are almost same for PANI-CNT composite as that of pure PANI.[13] The XRD result of PANI, rGO and PANI-CNT, PANI-rGO-CNT are shown in Fig 4.

As we know that the polymers have the amorphous/non crystalline nature. However, the crystalline nature of the polymer lies between the amorphous and semiconductor substances. Hence we can study the structural nature of the polymer by XRD analysis. The sharp peak at 22.66 (020) suggests the fact that the conducting polymer is crystalline in nature.[14] The d- spacing of PANI, rGO, PANI-CNT, rGO-PANI-CNT can be calculated by using Bragg's law

$$n\lambda = 2d\ sin\theta$$

From above equation the d-spacing value for PANI is 0.35 nm, for PANI-CNT value sis 0.35 nm, for rGO the value is 0.21 nm and for PANI-CNT-rGO the value came out 0.35 nm. The **crystallite size** of the polymer is calculated by using the Debye Scherer's formula

$$\tau = \kappa\lambda\beta Cos\theta$$

Here the different parameters are as below

τ = mean size of the ordered (crystalline) domains,

K = dimensionless shape factor with a value close to unity,

Fig. 5. Gas Sensor fabricated for sensing of NH_3 gas

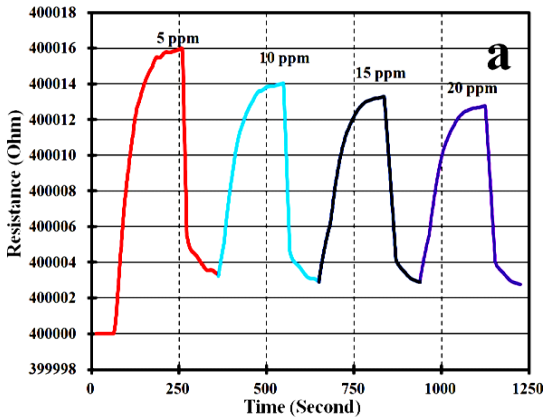

Fig. 6. Sensor response graph of PANI-CNT-rGO for NH_3

λ = wavelength

β = line broadening at half the maximum intensity (FWHM).

From above equation the crystallite size is calculated for PANI, rGO, PANI-CNT, PANI-CNT- rGO. It is found that the value for PANI is 394.86 nm, for PANI-CNT value is 3.16 nm, for rGO value is 3.43 nm and for PANI-CNT-rGO the crystallite size is 2.10 nm.

4. Results and Discussions (Gas Sensing Studies)

The synthesized material (PANI-CNT-rGO) is drop casted on the prepared electrode (Fig. 5). The fabricated sensor is placed inside the home made (1 liter) gas chamber for testing. Different concentration of ammonia gas is introduced inside the gas chamber. Before and after every exposure, the chamber is flashed with the air. The sensor was exposed to detect ammonia (NH_3) at different concentrations of 5 ppm, 10 ppm, 15 ppm and 20 ppm. From the graph, it is observed that the sensor is able to detect minimum concentration of 5 ppm ammonia gas. It is observed that the sensor does not recover back to the base line, which may be due the physical binding of the ammonia molecules with the sensing material (Fig. 6).

5. Conclusions

We have synthesized PANI, PANI-CNT and PANI-CNT-rGO based nanocomposite materials. The characterization is carried out by using XRD and FT-IR techniques. The synthesis of nanocomposite was followed by fabrication of gas sensor which is suitable to detect a minimum of 5 ppm for NH_3 gas. We believe synthesis of such materials is cost-effective and obtained materials demonstrate potential promise for real-time applications after further modifications.

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Conflicts of Interest

The authors declare no conflict of interest.

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