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## FABRICATION OF POLYANILINE/TiO<sub>2</sub> NANOCOMPOSITE AMMONIA VAPOR SENSOR

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*Polyaniline/Titanium dioxide (PANi/TiO<sub>2</sub>) nanocomposite was fabricated from PANi, prepared by oxidative chemical polymerization and TiO<sub>2</sub>, synthesized by sol gel method. The PANi/TiO<sub>2</sub> thin film sensors were prepared by spin coating technique. PANi/TiO<sub>2</sub> nanocomposites were characterized by XRD and SEM. The cross sensitivity of thin film sensor indicate that the sensor exhibit selectivity to ammonia (NH<sub>3</sub>). The gas sensing measurements were carried out for different concentrations of NH<sub>3</sub>. The gas sensing study revealed that the response value increases with increasing concentration of NH<sub>3</sub>. Moreover, as concentration of NH<sub>3</sub> increases, the response time decreases while recovery time increases, which can be attributed to the varying adsorption and desorption rates of an ambient gas with increasing concentration.*

**Keywords:** PANi/TiO<sub>2</sub> NANOCOMPOSITE, RESPONSE, SELECTIVITY, RESPONSE TIME, RECOVERY TIME.

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### 1. INTRODUCTION

In recent years, the demand for gas sensors for safety control requirements and environmental monitoring has expanded enormously. Choice of suitable sensing material along with efficient microelectronics for the detection system is the key step in such efforts [1]. The use of conducting polymers as sensing elements in chemical sensors is attracting attention due to their high sensitivity in change of the electrical and optical properties when exposed to different types of gases or liquids. The ease in synthesis of these polymers and sensitivity at room temperature add to the sensor's advantages. This can be of importance particularly as ammonia sensors that are used in different applications such as industrial process, fertilizers, food technology, clinical diagnosis, farms and environmental pollution monitoring [2]. Polyaniline is one of the most attractive materials among the variety of conducting polymers due to its unique electrical properties, environmental stability, easy fabrication process and intrinsic redox reaction [3-5]. Polyaniline has also been used in different applications such as light emitting diodes [6], rechargeable batteries [7] and photovoltaic cells [8]. However, the problems with these conducting polymers are their low processing ability, poor chemical stability and mechanical strength [9]. There is a tremendous approach for the enhancement of the mechanical strength and characteristics of sensors by combining the organic materials with inorganic counterparts to form composites [10, 11]. Accordingly, organic inorganic nanocomposite sensors have been developed by several research groups. Dhawale et al. [12] fabricated polyaniline titanium dioxide heterostructure gas sensor for LPG

sensing, Tai et al. [13] fabricated a polyaniline titanium dioxide nanocomposite for NH<sub>3</sub> and CO sensors and reported that the resistance of the composite increased with increasing concentration of the gases. The PANi/SnO<sub>2</sub> hybrid material was prepared by a hydrothermal method and studied for gas sensing of ethanol and acetone by L. Geng et al. [14]. Parvatikar et al. [15] fabricated polyaniline/WO<sub>3</sub> composite based sensor and reported that the film conductivity increased with increasing humidity. Among the inorganic materials, nanocrystalline TiO<sub>2</sub> is one of the most attractive and extensively used materials for detection of H<sub>2</sub>, LPG, NO<sub>2</sub> and NH<sub>3</sub> gases [12].

In the present paper, we report fabrication of polyaniline/TiO<sub>2</sub> nanocomposite thin film gas sensors working at room temperature. The cross sensitivity of the sensor to various gases indicate the selectivity of the sensor to ammonia. The nanocomposites were characterized by X-ray diffraction (XRD) in  $2\theta$  range of 10-70° using X-ray Diffractometer (Model: Philips PW3710). Morphological study of PANi/TiO<sub>2</sub> (0-50 weight %) composite films was carried out using scanning electron microscopy (SEM Model: JEOL JSM 6360) operating at 20 kV. The gas sensing measurements were made using gas sensor set up at room temperature.

## 2. EXPERIMENTAL

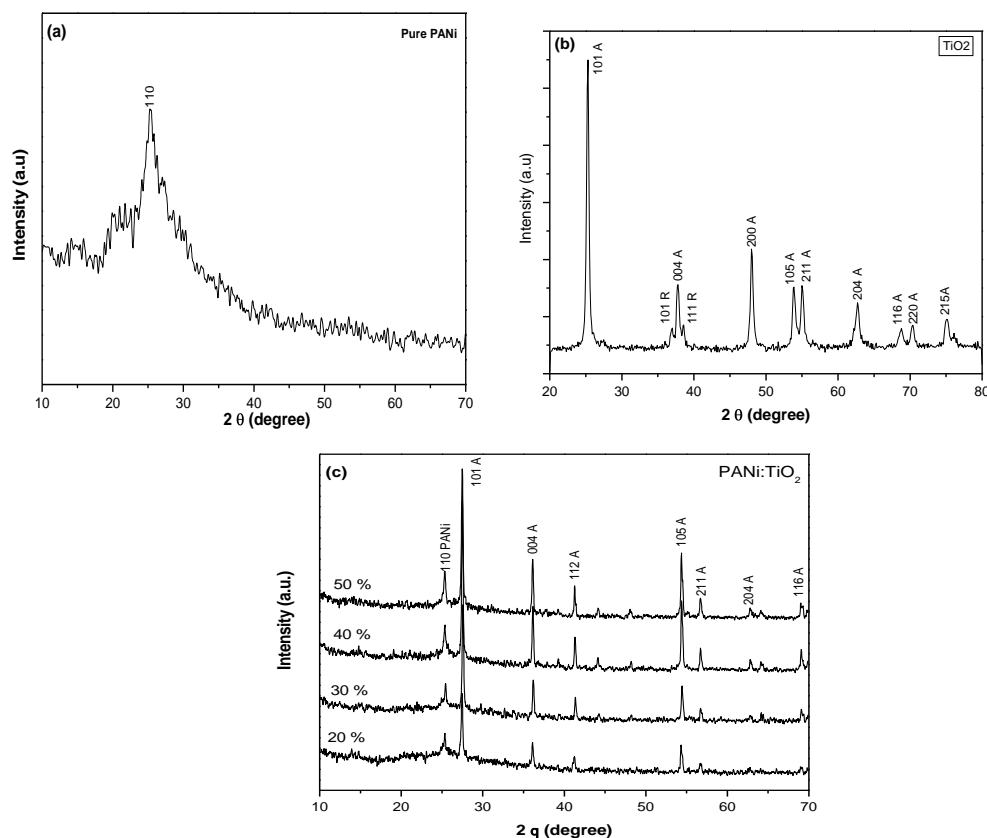
### 2.1 Fabrication of PANi/TiO<sub>2</sub> nanocomposite sensor films

The TiO<sub>2</sub> nanocomposites with PANi were prepared by adding TiO<sub>2</sub> in different weight percentage (0 – 50 weight %) in smooth agate mortar and pestle. The nanocomposite powder was put in m-cresol and stirred for 11 hrs to get casting solution. Thin films were prepared on glass substrates by spin coating method at 3000 rpm for 40 s and dried on hot plate at 100°C for 10 min [16]. The silver paste strips of 1 mm wide and 1 cm apart from each other were made on films for contacts.

## 3. RESULTS AND DISCUSSION

### 3.1 X-ray diffraction studies

Fig. 1 denotes X-ray diffraction patterns of the PANi, TiO<sub>2</sub> and PANi/TiO<sub>2</sub> nanocomposites (20-50 wt %) materials. The XRD pattern of PANi (Fig. 1 a) shows a broad peak at  $2\theta = 25.30^\circ$  which corresponds to (110) plane of PANi [17]. The diffraction pattern of TiO<sub>2</sub> (Fig. 1 b) show sharp and well defined peaks, indicate the crystallinity of synthesized material. The intensities of diffraction peaks for PANi/TiO<sub>2</sub> nanocomposites (Fig. 1 c) are lower than that for TiO<sub>2</sub>. The presence of amorphous PANi reduces the mass volume percentage of TiO<sub>2</sub> and sequentially weakens diffraction peaks of TiO<sub>2</sub>. It has also been observed that the crystallinity of PANi is improved by the addition of TiO<sub>2</sub> nanoparticles. XRD diffractograms of PANi/TiO<sub>2</sub> nanocomposites have shown that all major diffraction peaks of nanocrystalline TiO<sub>2</sub> and are in the same peak angle positions. The observed  $2\theta$  values are consistent with the standard JCPDS values (JCPDS No. 78-1285 & 86) which enumerate the mixed anatase and rutile tetragonal structure of TiO<sub>2</sub>.

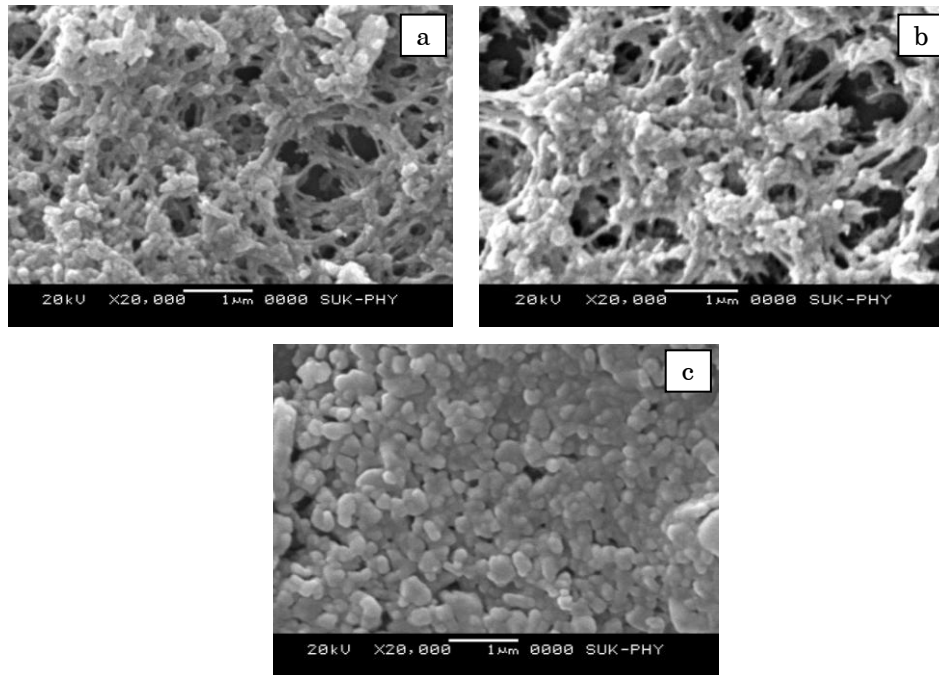


**Fig. 1** – X-ray diffraction patterns of Pure PANi (a),  $\text{TiO}_2$  (b) and PANi/ $\text{TiO}_2$  (0-50 wt %) (c).

### 3.2 Scanning electron microscopy

Fig. 2 a, b and c shows the scanning electron micrographs of PANi,  $\text{TiO}_2$  and PANi/ $\text{TiO}_2$  (50 wt %) films at  $\times 20,000$  magnification, respectively. The SEM image of the polyaniline film (Fig. 2 a) exhibits a fibrous structure with many pores and gaps among the fibers. Fig. 2 b shows the surface morphology of the  $\text{TiO}_2$  nanoparticles film, annealed at  $700^\circ\text{C}$  for 1 h. The image shows that the nanoparticles are fine with an average grain size of about 60 nm. The image of the nanocomposite (Fig. 2 c) shows that there is no agglomeration and uniform distribution of the  $\text{TiO}_2$  particles in the PANi matrix. It was considered that the nanostructured  $\text{TiO}_2$  particles embedded within the netlike structure built by PANi chains.

The morphology plays an important role in sensitivity of the gas sensing films. The grain sizes, structural formation, surface to volume ratio and film thickness are important parameters for gas sensing films. It can be seen that the PANi and PANi /  $\text{TiO}_2$  films have a very porous structure, interconnected network of fibers and high surface area. It has also been pointed out that such structure contributes to a rapid diffusion of dopants into the film.

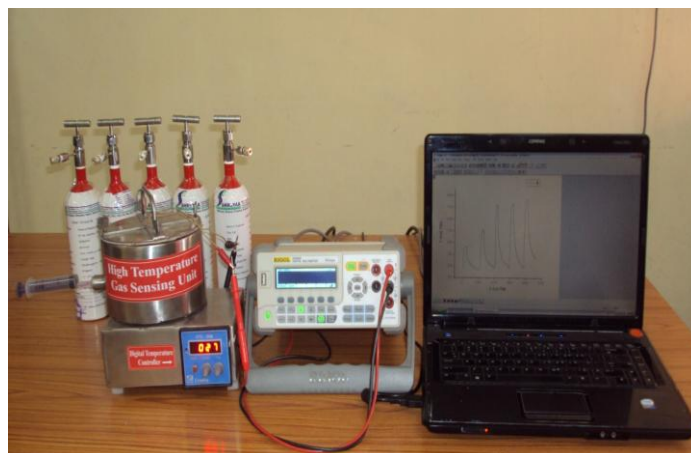


**Fig. 2** – Scanning electron micrographs of a) PANi, b) TiO<sub>2</sub> and c) PANi/TiO<sub>2</sub> (50 wt %) films

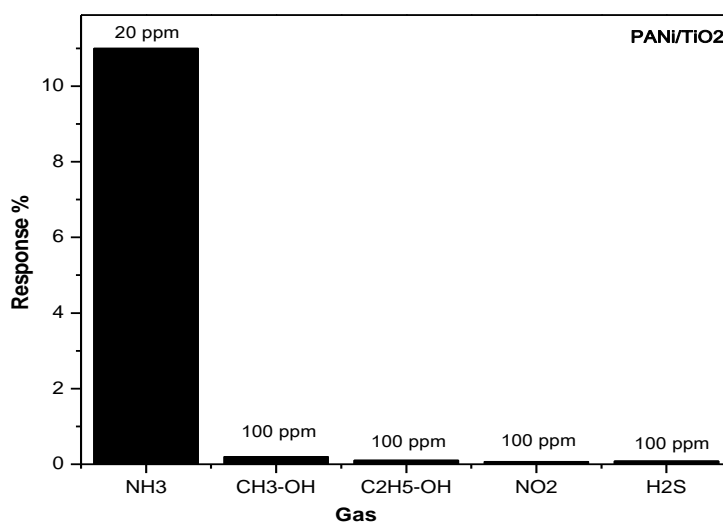
### 3.3 Gas sensing measurements

In order to record response to different gases, contacts were made on the silver paste strips, 1 mm wide and 1 cm apart from each other. The films deposited on the glass substrates were mounted in an airtight SS housing of 250 cc and measured quantity of desired gas (from a standard canister of 1000 ppm concentration) was injected through syringe so as to yield desired gas concentration in the housing. The room temperature gas response to various concentrations of different oxidizing and reducing (ammonia, ethanol, methanol, nitrogen dioxide and hydrogen sulfide) gases were measured by recording the resistance of the film in air and in presence of any particular ambient. A Rigol 3062 (6 S digit) DMM was used to measure the resistance variation of the sensor films. The sensor response ( $S$ ) was defined as  $S = (R_g - R_a)/R_a$ , where  $R_g$  and  $R_a$  are the resistance of sensor film in a measuring gas and in clean air respectively [13]. The gas sensing measurement set up used is as shown in Fig. 3.

An attempt was made to study selectivity of PANi/TiO<sub>2</sub> films for lower concentration of NH<sub>3</sub> (20 ppm) as compared to the sensitivities for higher concentration of CH<sub>3</sub>-OH, C<sub>2</sub>H<sub>5</sub>-OH, NO<sub>2</sub> and H<sub>2</sub>S (100 ppm). The bar chart for selectivity is as shown in Fig. 4. It is observed that PANi/TiO<sub>2</sub> thin films can sense lower concentration of NH<sub>3</sub> with higher sensitivity value as compared to large concentration of other gases. The plausible mechanism of selectivity for NH<sub>3</sub> may be traced to the characteristics of vapor adsorbed over the surface of PANi/TiO<sub>2</sub> nanocomposite.



**Fig. 3** – Gas sensing measurement set up

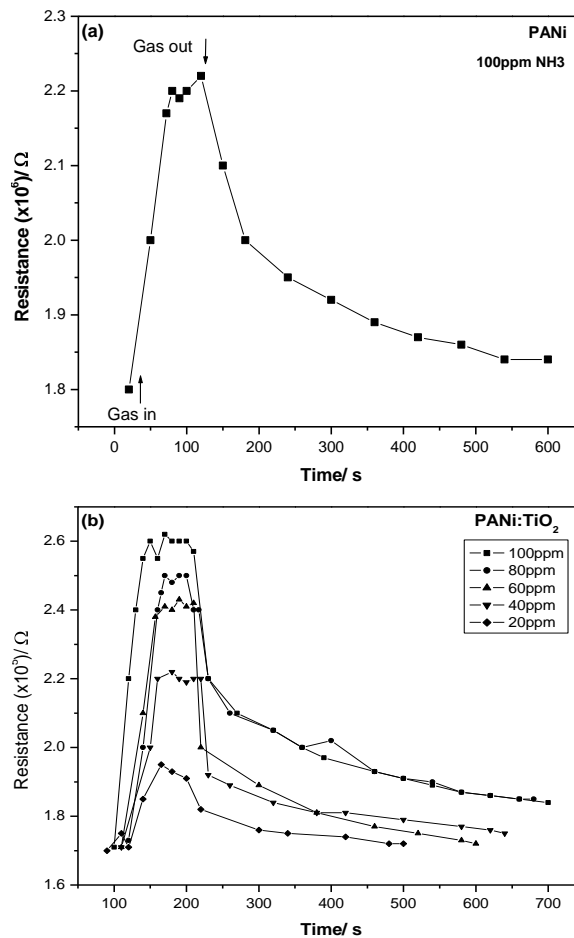


**Fig. 4** – Gas responses of PANi/TiO<sub>2</sub> sensor film to 20 ppm of NH<sub>3</sub> and 100 ppm of CH<sub>3</sub>-OH, C<sub>2</sub>H<sub>5</sub>-OH, NO<sub>2</sub> and H<sub>2</sub>S

Therefore the sensing capability of PANi / TiO<sub>2</sub> (50 wt %) nanocomposite sensor towards different concentrations (20-100 ppm) of ammonia vapour has been explored and compared with the results obtained for PANi sensor film. Fig. 5 (a) shows electrical response of PANi to 100 ppm of NH<sub>3</sub> and Fig. 5 (b) of PANi / TiO<sub>2</sub> to 20, 40, 60, 80 and 100 ppm of NH<sub>3</sub>. As seen for both the sensor films, the resistance increases dramatically upon exposure to ammonia vapor, attains stable value and decreases gradually after being transferred to clean air.

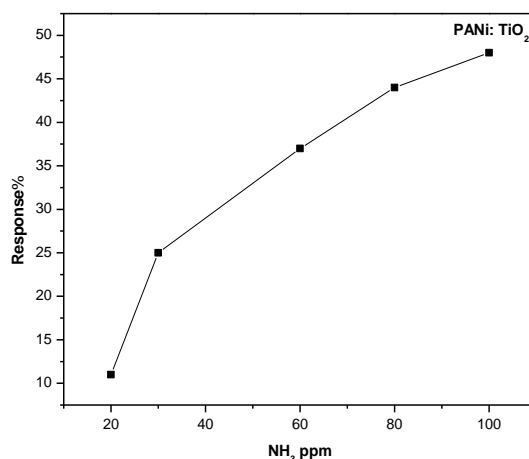
Moreover, the nanocomposite sensor exhibit high response to ammonia than pure PANi sensor. The increase in resistance after exposure to NH<sub>3</sub> may be because of porous structure of PANi/TiO<sub>2</sub> films leads to the predominance

of surface phenomena over bulk material phenomena, which may again be due to surface adsorption effect, and chemisorptions leads to the formation of ammonium. The resistance attains stable value when dynamic equilibrium is attained [19]. In order to explain the higher response and gas sensing mechanism of PANi/TiO<sub>2</sub> nanocomposite H. Tai et al. [13] postulated that PANi and TiO<sub>2</sub> may form a p-n junction and the observed increased response of the nanocomposite material may be due to the creation of positively charged depletion layer on the surface of TiO<sub>2</sub> which could be formed owing to inter-particle electron migration from TiO<sub>2</sub> to PANi at the heterojunction. This would cause the reduction of the activation energy and enthalpy of physisorption for NH<sub>3</sub> gas.



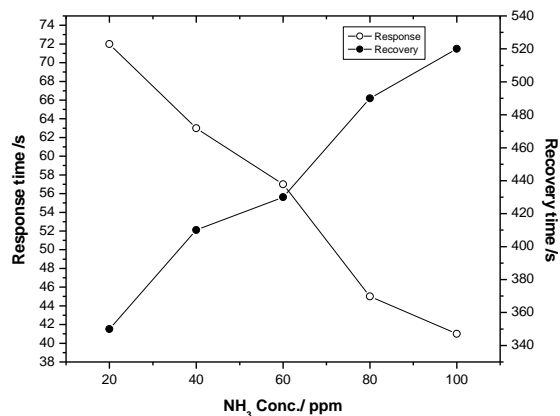
**Fig. 5** – Gas responses of PANi/TiO<sub>2</sub> sensor film to 20 ppm of NH<sub>3</sub> and 100 ppm of CH<sub>3</sub>-OH, C<sub>2</sub>H<sub>5</sub>-OH, NO<sub>2</sub>, and H<sub>2</sub>S

The response values of PANi/TiO<sub>2</sub> sensor film is plotted as a function of NH<sub>3</sub> concentration in Fig. 6. It is observed that the response slows down at higher concentration; this may be due to less availability of surface area with possible reaction sites on surface of the film.



**Fig. 6** – Response of PANi/TiO<sub>2</sub> thin film sensor to NH<sub>3</sub> (20-100 ppm)

The response/recovery time is an important parameter use for characterizing a sensor. The response time and recovery time are defined as the times of 90 % total resistance change [12]. Fig. 7 shows the response and recovery times of PANi / TiO<sub>2</sub> for different concentrations of NH<sub>3</sub>. It is revealed that the response time decreases from 72 s to 41 s, when NH<sub>3</sub> concentration increased from 20 ppm to 100 ppm, this may be because of high surface area due to porous structure of exposed film which facilitates rapid diffusion of gas molecules into the film. From the same graph, it is found that for higher concentration of NH<sub>3</sub>, the recovery time was long. This may probably due to lower desorption rate and reaction products are not leaving from the interface immediately after the reaction.



**Fig. 7** – Variation of response and recovery time of the PANi / TiO<sub>2</sub> thin film sensor with NH<sub>3</sub> concentration

#### 4. CONCLUSIONS

The PANi/TiO<sub>2</sub> thin film sensor was fabricated by spin coating technique. The composites have poorer crystallinity than TiO<sub>2</sub>, because of amorphous structure of PANi. But crystallinity of nanocomposites has been improved with increasing percentage of TiO<sub>2</sub> nanoparticles. It can be seen that PANi/TiO<sub>2</sub> film has a very porous structure, interconnected network of fibers and high surface area which contributes to a rapid diffusion of dopants into the film. The cross sensitivity of thin film sensor indicate that the sensor exhibit selectivity to ammonia (NH<sub>3</sub>). The gas sensing measurements were carried out for different concentrations of NH<sub>3</sub> at room temperature. It is observed that the response slows down at higher concentration; this may be due less availability of surface area with possible reaction sites on surface of the film. Moreover, as concentration of NH<sub>3</sub> increases, the response time decreases while recovery time increases, which can be attributed to the varying adsorption and desorption rates of an ambient gas with increasing concentration.

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