



# Polyaniline/TiO<sub>2</sub> Nanocomposite Thin Film Based Carbon Dioxide Gas Sensor

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## Abstract

Polyaniline (PANI) and Titanium dioxide (TiO<sub>2</sub>) nanocomposite thin film based chemiresistor type gas sensors synthesized by solution route technique helps to monitor carbon dioxide (CO<sub>2</sub>) gas present in atmosphere with high concentration at low temperature. Thin films of titanium dioxide-intercalated polyaniline nanocomposites have been deposited, through solution route technique on simple glass using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and ammonium persulphate (APS) in acidic medium at 0-5° C. The thin film was studied for some of the useful physicochemical properties, making use of XRD, FTIR, SEM, UV-Vis spectra and DC conductivity etc. Morphological and structural studies were done with SEM and XRD respectively which confirm the formation of nanocomposites. PANI/TiO<sub>2</sub> nanocomposites images showed that the growing of PANI on TiO<sub>2</sub> nanoparticle surfaces. FTIR and UV-Vis spectra reveal that the PANI component undergoes an electronic structure modification as a result of the TiO<sub>2</sub> and PANI interaction. On exposure to fixed concentration of carbon dioxide gas (1000 ppm in air) at room temperature, it was found that the nanocomposites (PANI /TiO<sub>2</sub>) thin film resistance increases from the respective unexposed value.

**Keywords:** Conducting polymer, Polyaniline, Titanium dioxide, nanocomposites, thin film, CO<sub>2</sub> gas sensor.

## Introduction

Variety of carbon dioxide sensors have been proposed for measuring carbon dioxide concentration. Usually, the change in the electrical response upon exposure of different carbon dioxide concentrations is used as the technique for carbon dioxide detection. The electrical responses, such as electronic current or capacitance measurement in a resistivity-type and capacitance-type sensor play a key role in sensing CO<sub>2</sub> [1]. Therefore, research on sensing materials has been focused to design a high performance and elevated efficiency gas sensing elements with suitable sensing materials which can sense high concentration of carbon dioxide (CO<sub>2</sub>) gas in atmosphere. Generally, gas sensor can be classified mainly into two main categories i.e. organic and inorganic materials. ZnO, TiO<sub>2</sub>, SnO<sub>2</sub> etc. have been well studied for gases detection and considered attractive for their low cost and simple sensing method. However, the high temperature operation of the sensor make the lifetime of the sensor become shorter, increasing resistance and thus required more electricity for operation. Other problems related to metal oxide thin films are their poor performance regarding the sensitivity, stability and selectivity at certain low concentration of the gas [2]. For organic materials category, conducting polymers such as polyaniline, polypyrrole, polythiophene etc. have been widely investigated as effective materials for chemical sensors. Among the conducting polymers polyaniline (PANI) is frequently used because of its ease of synthesis, environmental stability, intrinsic redox reaction,





high electrical conductivity and response to acid/base doping, it was thoroughly studied for its application as an active material for gas sensors. However, the problem with these conducting polymers is their low processing ability, poor mechanical strength and chemical stability [3]. 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. Accordingly, organic-inorganic nanocomposite sensors have been developed by several research groups. Pawar et al [4] fabricated PANI/TiO<sub>2</sub> nanocomposite ammonia vapor sensor, Deshpande et al [5] discovered good sensitivity; reproducibility and faster response to NH<sub>3</sub> at room temperature achieved by using SnO<sub>2</sub>/PANI nanocomposites films while under the same conditions pure SnO<sub>2</sub> films remain inert. They found that resistance of the nanocomposite (SnO<sub>2</sub>-PANI) films decreases while pure PANI film resistance increases when exposed to NH<sub>3</sub> indicating SnO<sub>2</sub> doping totally changed the electrical property of PANI. Srivastava et al [6] fabricated TiO<sub>2</sub> doped polyaniline composites for hydrogen gas sensing, Huyen et al [7] studied effect of TiO<sub>2</sub> on the gas sensing features of TiO<sub>2</sub>/PANI nanocomposites. Tai et al [8] showed comparative studies of Polyaniline (PANI), polyaniline/titanium dioxide (PANI/TiO<sub>2</sub>), polyaniline/tin oxide (PANI/SnO<sub>2</sub>) and polyaniline/indium oxide (PANI/In<sub>2</sub>O<sub>3</sub>) thin films developed by using an in-situ self-assembly method at 10<sup>0</sup>C for NH<sub>3</sub> gas sensor. Su et al [9] fabricated a humidity sensor based on TiO<sub>2</sub> nanoparticles / polypyrrole composite thin films on alumina substrate and was investigated the humidity sensing mechanism of TiO<sub>2</sub> nanoparticles / PPy composite thin films via the results of activation energy and impedance spectroscopy. Meena et al [10] fabricated LPG gas sensor using PANI/TiO<sub>2</sub> nanocomposites at 400 ppm. Among the inorganic materials, Titanium dioxide (TiO<sub>2</sub>) was chosen due to its unique physical and chemical properties such as large energy gap, dielectric constant, and environmental-friendliness and easy to synthesis [11]. TiO<sub>2</sub> belongs to the family of transition metal oxides. There are four commonly known polymorphs of TiO<sub>2</sub> found in nature: anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal). Besides these polymorphs, two additional high-pressure forms have been synthesized from the rutile phase. In particular, TiO<sub>2</sub> films have been investigated as sensors for the reducing gas like H<sub>2</sub>, LPG, NO<sub>2</sub>, CO and NH<sub>3</sub> gases which are reacts with the negatively charged oxygen adsorbed on the surface of TiO<sub>2</sub> nanoparticles and supplies electrons to the conduction band, leading to a decrease in electric resistance [12].

In the present paper, we report fabrication of Polyaniline/TiO<sub>2</sub> nanocomposite thin film CO<sub>2</sub> gas sensor synthesized by solution route technique at low temperature. The as-grown film of PANI/TiO<sub>2</sub> composites was tested for CO<sub>2</sub> gas at varying temperature from 30-60 °C. For this film having metallic contacts were kept in the test chamber of known volume with electrical leads taken out for electrical parameter measurements. A fixed amount (corresponding to 1000 ppm) of CO<sub>2</sub> gas was injected into the test chamber, and film resistance measured with respect to temperature (for 10 interval). The as-grown PANI/TiO<sub>2</sub> composite film was characterized using X-ray





diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Ultra violet visible (UV-VIS) spectroscopy, Scanning electron microscopy (SEM).

## Experimental

Solution-route technique [5] was used to synthesize titanium oxide/polyaniline nanocomposites. In this technique, formation of nanocomposites proceeds through an inorganic/organic interface reaction. Aniline monomer was distilled under reduced pressure. Initially, 0.1 M of  $\text{TiCl}_3$ , was hydrolyzed, in 50 ml of double distilled water (DDW) with constant stirring for half an hour, and its pH was maintained at  $\leq 4$ , using 3-4 drops of concentrated HCl. 10 ml of Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was added in the above solution, which oxidizes titanium ions to tin oxide, and the solution turns into brown colored due to presence of  $\text{TiO}_2$  into that solution mixture. From this reaction mixture, 40 ml volume was taken and treated 0.2 M of aniline, and keep for constant stirring for 15 minutes the color of solution was gradually changed from brown to dark viscous brown and that reaction mixture kept on ice bath for 30 minutes. After that the reaction mixture was kept at normal temperature for 20 minutes then add APS ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) solution in the above mixture to make reaction bath mixture and simultaneously inserted pre-cleaned glass substrates were inserted vertically. It was found that after few minutes the solution color changed dark brown, blue and dark green color indicating the polymerization of PANI as occurring in the solution also mark the growth of film on the substrate. The precipitate produced in the reaction was removed by filtration, washed repeatedly with 1 M HCl and dried under vacuum for 24 hours. The composite powder was conductive emeraldine salt (ES) form of PANI/ $\text{TiO}_2$  nanocomposite.

## Results and discussion

Fig. 1 shows the XRD pattern of PANI/ $\text{TiO}_2$  nanocomposites. The XRD pattern showed diffraction peaks along (1 1 0), (1 0 1), (1 1 1), (2 0 0), (2 1 0) centered at  $2\theta = 23.68^\circ$ ,  $26.28^\circ$ ,  $30.62^\circ$ ,  $32.92^\circ$  and  $38^\circ$  respectively. On comparing the observed XRD peaks and corresponding planes with the standard (h k l) planes of the  $\text{TiO}_2$  reported elsewhere [2-5], good matching was observed, confirming that the nanocomposites consist of  $\text{TiO}_2$  having tetragonal rutile phase. The peaks related to the  $\text{TiO}_2$  nanoparticles became more sharp and crystalline in composites. These peaks are slightly shifted from their respective standard positions, may be due to presence of PANI matrix. This confirmed that PANI/ $\text{TiO}_2$  nanocomposites become more crystalline as the concentration of  $\text{TiO}_2$  is increased and PANI deposited on the surface of  $\text{TiO}_2$  particles has no effect on the crystallization behavior of  $\text{TiO}_2$  particles in the nanocomposites [13-15].



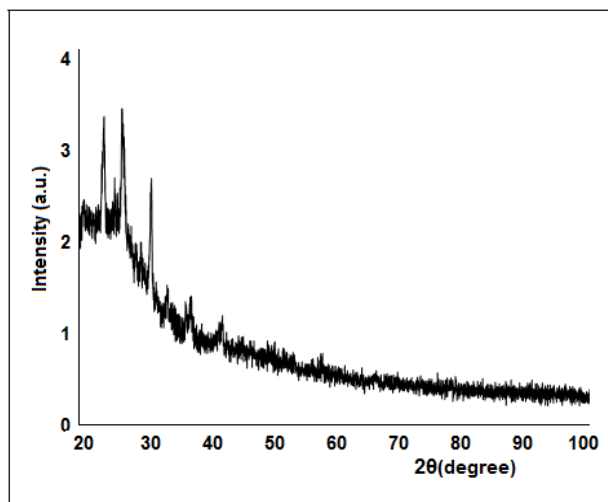


Fig. 1: XRD pattern of PANI/ TiO<sub>2</sub> nanocomposite

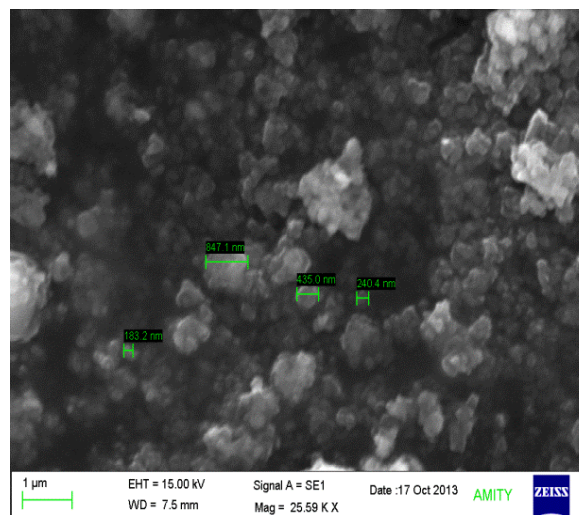


Fig. 2: SEM image of PANI/TiO<sub>2</sub> nanocomposite

The surface morphology of PANI/TiO<sub>2</sub> nanocomposite thin films was determined by scanning electron microscopy (SEM). In case of PANI/TiO<sub>2</sub> composite, the SEM micrograph revealed that the composite particles are highly dispersed with agglomeration with an interlocking arrangement of granular particles (Fig. 2). This suggests that the most of TiO<sub>2</sub> nanoparticles were coated with PANI during polymerization process. A close investigation of the surface of thin film revealed that PANI/TiO<sub>2</sub> composite exhibited a porous open structure and high surface area, which is suitable for gas sensing applications. It has been pointed out that such porous structure significantly enhanced the rapid diffusion of gas molecules due to its larger exposure area. Therefore the reaction between gas molecules and thin film occurs easily and resulted in alteration of resistance of thin films. This observation is in good agreement with other reported findings [14, 15].

Fig. 3 shows FTIR spectra of PANI/TiO<sub>2</sub> nanocomposites. The characteristic peaks at 1543 cm<sup>-1</sup> (C=C stretching mode of the quinoid rings), 1512 cm<sup>-1</sup> (C=C stretching mode of benzenoid rings), 1313 cm<sup>-1</sup> (C-N stretching mode) and 1158 cm<sup>-1</sup> (N-Q-N, where Q represents the quinoid ring) and 3861 cm<sup>-1</sup> corresponds to N-H stretching [16]. The FTIR spectra reveal the presence of Ti-O-Ti vibrational peak and characteristic vibrational peaks of PANI indicating the interaction of TiO<sub>2</sub> particles in PANI matrix. The 1590-1650 cm<sup>-1</sup> vibration band is due to the C=N stretching vibration of quinoid rings whereas 1498-1501 cm<sup>-1</sup> vibration band arises due to the C=C stretching vibration associated with the benzenoid ring [17]. The 1439- 1440 cm<sup>-1</sup> vibration band is attributed to C-C aromatic ring stretching of the benzenoid diamine unit. In the region close to 1390 cm<sup>-1</sup> the peaks are attributed to the presence of aromatic amines present in polyaniline. The band at 1251-1254 cm<sup>-1</sup> linked with various stretching and bending vibrations associated with C-N single bond. The vibration band at 1158-1100 cm<sup>-1</sup> range is the characteristic band of PANI corresponding to charge delocalization proving the protonation which is shifted towards higher wavelength side due to the interaction of

TiO<sub>2</sub> in PANI matrix. . It is also observed that the peaks at around 800-850 cm<sup>-1</sup> corresponds to the C-H bending out of the plane for 1, 4 substituted aromatic ring indicating the linear structure which is slightly deviated due to the presence of TiO<sub>2</sub> particles. There are strong peak at 761.23 and 686 cm<sup>-1</sup> which are due to the antisymmetric Ti-O-Ti mode in TiO<sub>2</sub>.The vibrational modes are shows shifting in the peaks towards higher wavelength side as the concentration of titanium dioxide increases [18].

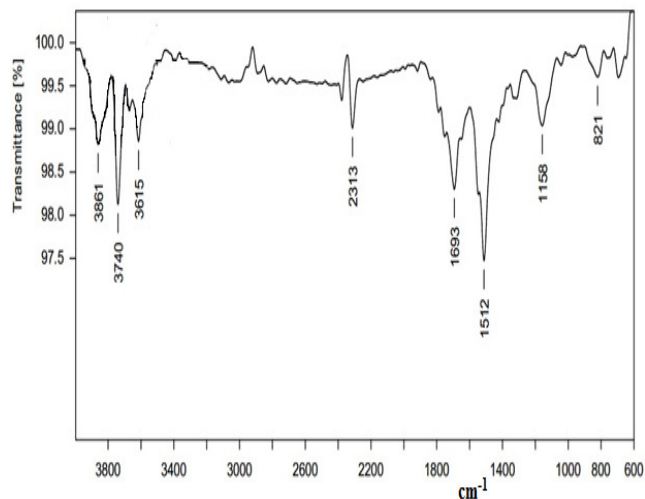


Fig. 3: FTIR spectra of PANI/TiO<sub>2</sub> nanocomposite

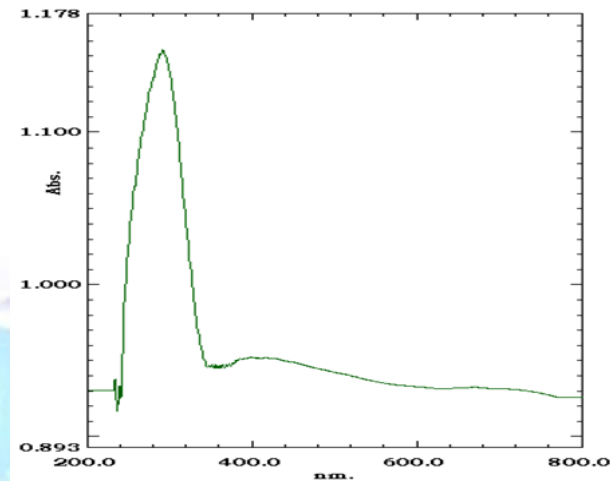


Fig. 4: UV-Vis spectra of PANI/TiO<sub>2</sub> nanocomposite

Fig. 4 shows the UV-Vis absorption spectra of PANI/TiO<sub>2</sub> composite thin films exhibit three absorption bands at 291, 428 and 700-800 nm. The bands at 291 nm and 428 nm are attributed to the  $\pi$ - $\pi^*$  and polaron- $\pi^*$  transition in the conducting PANI. The localized polaron band around 700-800 nm indicates a compact coiled conformation of PANI. It can be noted that there are some shifts in the peaks for PANI /TiO<sub>2</sub> composites thin films as compared to the pure PANI thin film. It may be due to that the encapsulation of TiO<sub>2</sub> nanoparticles has the effect on the doping of conducting PANI or coordinate complex formation between TiO<sub>2</sub> nanoparticles and PANI chains [19, 20].

For gas sensing test, the sensor device called as chemiresistor and measurement system were designed using the concept of resistance variation in the sensing materials after CO<sub>2</sub> gas exposure. The gas sensing behavior of chemiresistor sensors was studied by calculating change in the surface resistance of sensing film with temperature in the range of 30-60 °C towards pure air and CO<sub>2</sub> gas exposure. The resistance variation was measured by Keithley 2000 multimeter and temperature was controlled by 'Temperature Controlled VI Characterization System'. The increase in resistance for the composite film after exposure to CO<sub>2</sub> was observed. This may be due to 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. The resistance attains stable value when dynamic equilibrium is attained [21]. The

response/recovery time is an important parameter use for characterizing a sensor. It is revealed that the response time was found to be 70 to 80 s, if CO<sub>2</sub> concentration increased from 1000 ppm. It is found that for higher concentration of CO<sub>2</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 [22, 23]. The sensor response results from the change of electrical resistance due to the test gases. The sensitivity of PANI/TiO<sub>2</sub> nanocomposite for CO<sub>2</sub> with increasing temperature is shown in fig. 5. This graph shows that sensitivity of nanocomposite is higher at normal temperature and it goes on decreasing with increasing temperature. Therefore it is concluding that PANI/TiO<sub>2</sub> nanocomposite is good chemiresistor sensor for CO<sub>2</sub> gas at normal temperature only. The sensitivity of PANI/TiO<sub>2</sub> nanocomposite was recorded repeatedly for same concentration of gas and it was always nearly same.

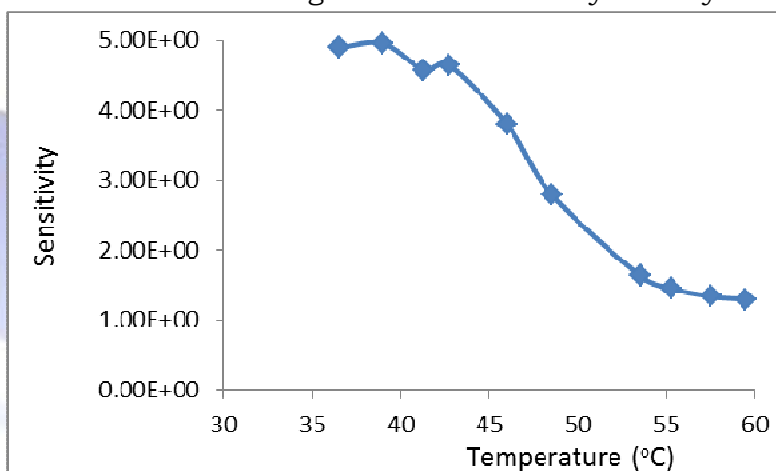


Fig. 5: Sensitivity Vs Temperature graph of PANI/TiO<sub>2</sub> nanocomposites

## Conclusions

The PANI/TiO<sub>2</sub> thin film sensor was fabricated by solution route technique. The composites have poorer crystallinity than TiO<sub>2</sub>, because of amorphous structure of PANI. PANI/TiO<sub>2</sub> film has a very porous structure, highly dispersed with agglomeration interlocking arrangement of granular particles and high surface area, which contributes to a rapid diffusion of dopants into the film. The sensitivity of thin film sensor indicate that the sensor exhibit high sensitivity for CO<sub>2</sub> gas. PANI/TiO<sub>2</sub> nanocomposite was found to be good chemiresistor sensor for CO<sub>2</sub> gas at normal temperature.

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