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FABRICATION OF POLYANILINE/TIO₂ NANOCOMPOSITE AMMONIA VAPOR SENSOR

**S.G. Pawar, S.L. Patil, M.A. Chougule, P.R. Godse,
D.K. Bandgar, V.B. Patil**

Materials Research Laboratory, School of Physical Sciences,
Solapur University, Solapur-413255, M.S., India
E-mail: drvbpatal@gmail.com

Polyaniline/Titanium dioxide (PANI/TiO₂) nanocomposite was fabricated from PANi, prepared by oxidative chemical polymerization and TiO₂, synthesized by sol gel method. The PANi/TiO₂ thin film sensors were prepared by spin coating technique. PANi/TiO₂ nanocomposites were characterized by XRD and SEM. The cross sensitivity of thin film sensor indicate that the sensor exhibit selectivity to ammonia (NH₃). The gas sensing measurements were carried out for different concentrations of NH₃. The gas sensing study revealed that the response value increases with increasing concentration of NH₃. Moreover, as concentration of NH₃ 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/TiO₂ 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_3 and CO sensors and reported that the resistance of the composite increased with increasing concentration of the gases. The PANi / SnO_2 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_3 composite based sensor and reported that the film conductivity increased with increasing humidity. Among the inorganic materials, nanocrystalline TiO_2 is one of the most attractive and extensively used materials for detection of H_2 , LPG, NO_2 and NH_3 gases [12].

In the present paper, we report fabrication of polyaniline / TiO_2 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 2θ range of $10\text{--}70^\circ$ using X-ray Diffractometer (Model: Philips PW3710). Morphological study of PANi / TiO_2 (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_2 nanocomposite sensor films

The TiO_2 nanocomposites with PANi were prepared by adding TiO_2 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 1000°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_2 and PANi/ TiO_2 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_2 (Fig. 1 b) show sharp and well defined peaks, indicate the crystallinity of synthesized material. The intensities of diffraction peaks for PANi/ TiO_2 nanocomposites (Fig. 1 c) are lower than that for TiO_2 . The presence of amorphous PANi reduces the mass volume percentage of TiO_2 and sequentially weakens diffraction peaks of TiO_2 . It has also been observed that the crystallinity of PANi is improved by the addition of TiO_2 nanoparticles. XRD diffractograms of PANi/ TiO_2 nanocomposites have shown that all major diffraction peaks of nanocrystalline TiO_2 and are in the same peak angle positions. The observed 2θ values are consistent with the standard JCPDS values (JCPDS No. 78-1285 & 86) which enumerate the mixed anatase and rutile tetragonal structure of TiO_2 .

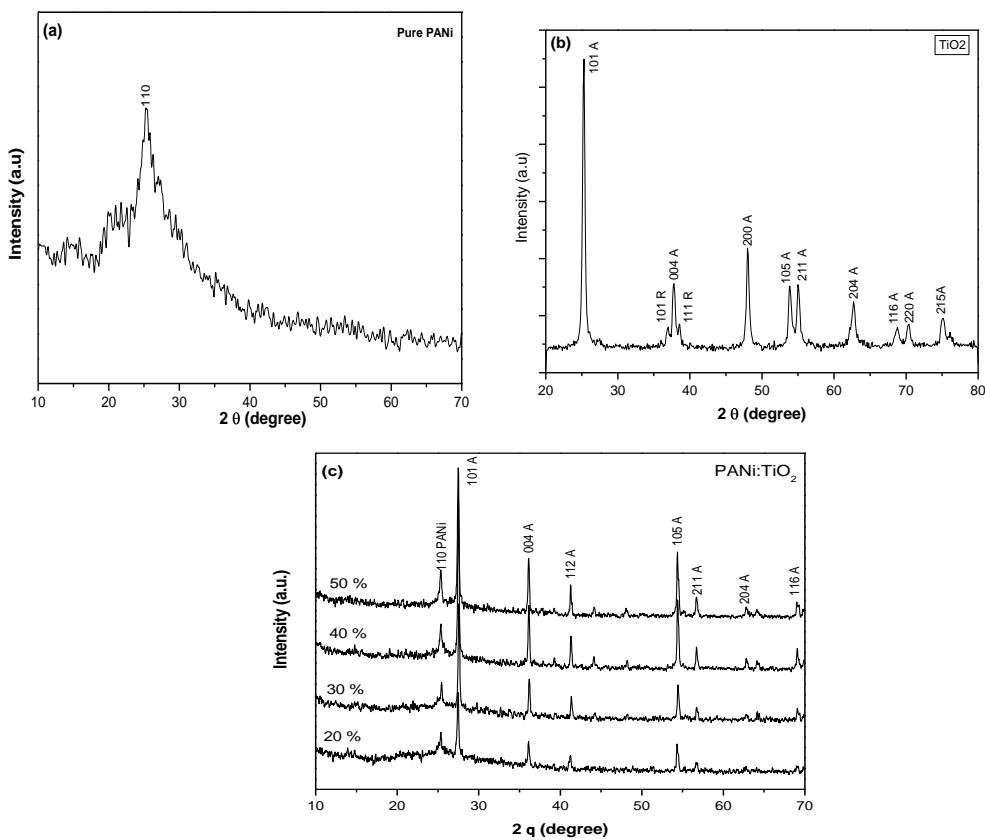


Fig. 1 – X-ray diffraction patterns of Pure PANi (a), TiO₂ (b) and PANi/TiO₂ (0-50 wt %) (c).

3.2 Scanning electron microscopy

Fig. 2 a, b and c shows the scanning electron micrographs of PANi, TiO₂ and PANi/TiO₂ (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 TiO₂ nanoparticles film, annealed at 700°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 TiO₂ particles in the PANi matrix. It was considered that the nanostructured TiO₂ 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 / TiO₂ 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.

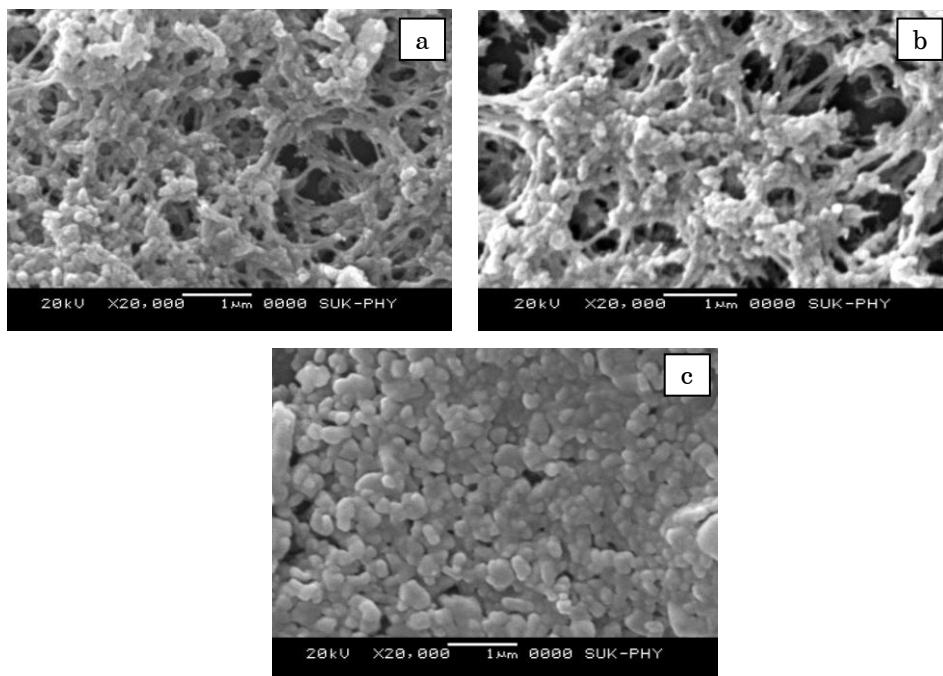


Fig. 2 – Scanning electron micrographs of a) PANi, b) TiO₂ and c) PANi/TiO₂ (50 wt %) films

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/TiO₂ films for lower concentration of NH₃ (20 ppm) as compared to the sensitivities for higher concentration of CH₃-OH, C₂H₅-OH, NO₂ and H₂S (100 ppm). The bar chart for selectivity is as shown in Fig. 4. It is observed that PANi/TiO₂ thin films can sense lower concentration of NH₃ with higher sensitivity value as compared to large concentration of other gases. The plausible mechanism of selectivity for NH₃ may be traced to the characteristics of vapor adsorbed over the surface of PANi/TiO₂ nanocomposite.

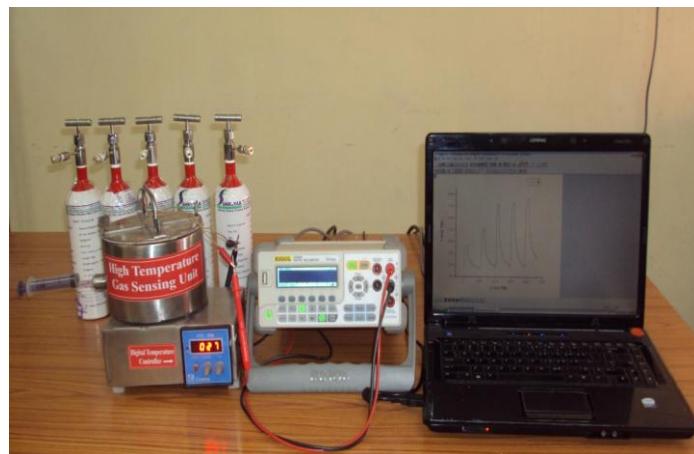


Fig. 3 – Gas sensing measurement set up

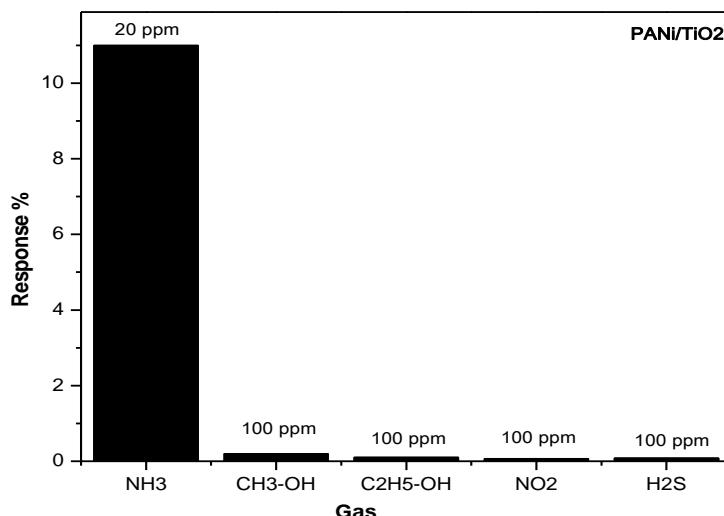


Fig. 4 – Gas responses of PANi/TiO₂ sensor film to 20 ppm of NH₃ and 100 ppm of CH₃-OH, C₂H₅-OH, NO₂ and H₂S

Therefore the sensing capability of PANi / TiO₂ (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 NH₃ and Fig. 5 (b) of PANi / TiO₂ to 20, 40, 60, 80 and 100 ppm of NH₃. 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 NH₃ may be because of porous structure of PANi/TiO₂ 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_2 nanocomposite H. Tai et al. [13] postulated that PANi and TiO_2 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_2 which could be formed owing to inter-particle electron migration from TiO_2 to PANi at the heterojunction. This would cause the reduction of the activation energy and enthalpy of physisorption for NH_3 gas.

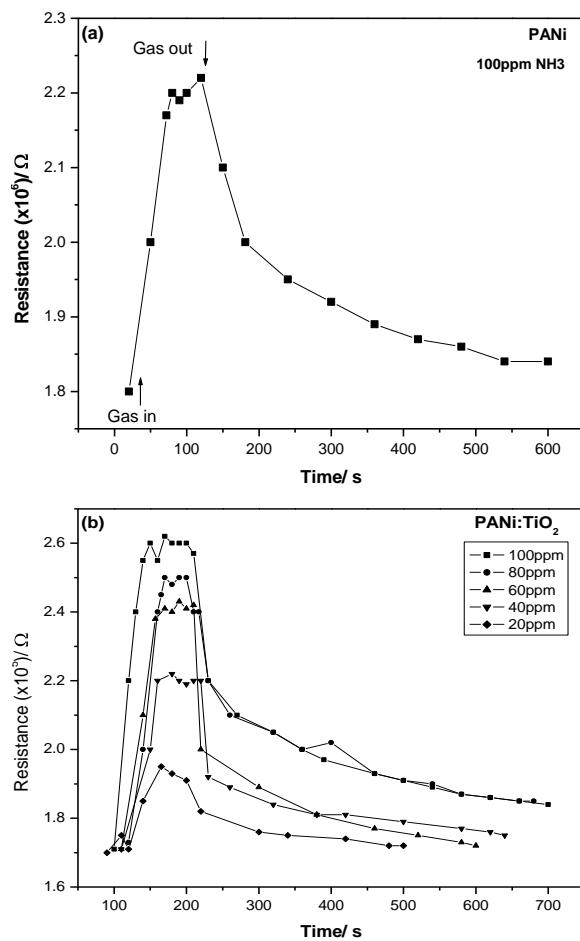


Fig. 5 – Gas responses of PANi/ TiO_2 sensor film to 20 ppm of NH_3 and 100 ppm of $\text{CH}_3\text{-OH}$, $\text{C}_2\text{H}_5\text{-OH}$, NO_2 , and H_2S

The response values of PANi/ TiO_2 sensor film is plotted as a function of NH_3 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.

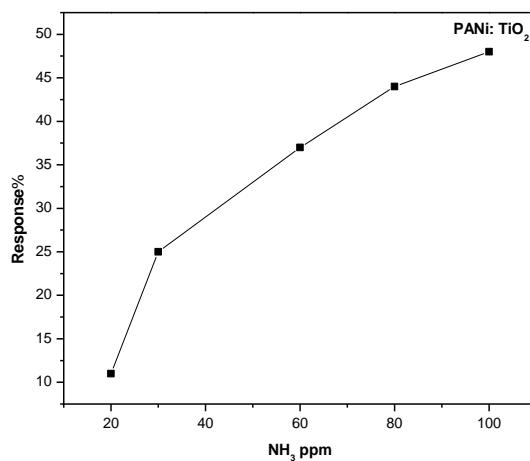


Fig. 6 – Response of PANi/TiO₂ thin film sensor to NH₃ (20-100 ppm)

The response/recovery time is an important parameter used 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 / TiO₂ for different concentrations of NH₃. It is revealed that the response time decreases from 72 s to 41 s, when NH₃ 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 NH₃, 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.

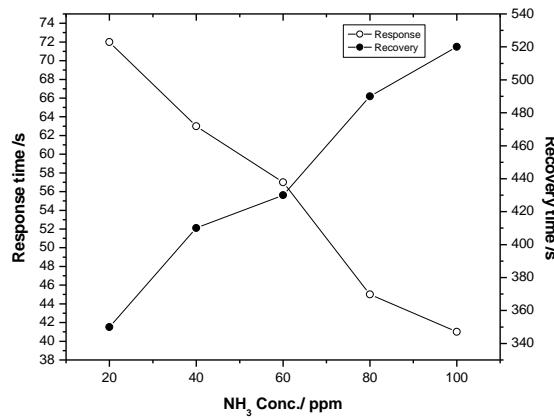


Fig. 7 – Variation of response and recovery time of the PANi / TiO₂ thin film sensor with NH₃ concentration

4. CONCLUSIONS

The PANi/TiO₂ thin film sensor was fabricated by spin coating technique. The composites have poorer crystallinity than TiO₂, because of amorphous structure of PANi. But crystallinity of nanocomposites has been improved with increasing percentage of TiO₂ nanoparticles. It can be seen that PANi/TiO₂ 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 (NH₃). The gas sensing measurements were carried out for different concentrations of NH₃ 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 NH₃ 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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REFERENCES

1. G.K. Prasad, T.P. Radhakrishnan, D.S. Kumar, M.G. Krishna, *Sens. Actuat. B-Chem.* **106**, 626 (2005).
2. C. Wrenn, *Occup. Health Saf.* **69b**, 64 (2000).
3. R.L.N. Chandrakanthi, M.A. Careem, *Thin Solid Films* **417**, 51 (2002).
4. P.R. Soman, R. Marimuthu, U.P. Mulik, S.R. Mulik, S.R. Sanikar, D.P. Amalnerkar, *Synth. Met.* **106**, 45 (1999).
5. Y. He, *Mater. Chem. Phys.* **92**, 134 (2005).
6. S.A. Chen, K.R. Chuang, C.I. Chao, H.T. Lee, *Synth. Met.* **82**, 207 (1996).
7. A.G. MacDiarmid, L.S. Yang, W.S. Huang, B.D. Humphrey, *Synth. Met.* **18**, 393 (1987).
8. D. Verma, V. Dutta, *Sens. Actuat. B-Chem.* **134**, 373 (2008).
9. M. Mastuguchi, A. Okamoto, Y. Sakai, *Sens. Actuat. B-Chem.* **94**, 46 (2003).
10. F.Y. Chaung, S.M. Yang, *Synth. Met.* **152**, 361 (2005).
11. A.Z. Sadek, W. Włodarski, K. Shin, R. Bkaner, K. Kalantazadeh, *Nanotechnology* **17**, 4488 (2006).
12. D.S. Dhawale, R.R. Salunkhe, U.M. Patil, K.V. Gurav, A.M. More, C.D. Lokhande, *Sens. Actuat. B-Chem.* **134**, 988 (2008).
13. R. Zeggari, B. Wacogne, C. Pieralli, C. Roux, T. Gharbi, *Sens. Actuat. B-Chem.* **125**, 664 (2007).
14. L. Geng, Y. Zhao, X. Huang, S. Wang, S. Zhang, S. Wu, *Sens. Actuat. B-Chem.* **120**, 568 (2007).
15. J. Wang, I. Matsubara, N. Murayama, S. Woosuck, N. Izu, *Thin Solid Films* **514**, 329 (2006).
16. S.G. Pawar, S.L. Patil, M.A. Chougule, A.T. Mane, D.M. Jundale, V.B. Patil, *Int. J. Polym. Mater.* **59**, 777 (2010).
17. S.G. Pawar, S.L. Patil, A.T. Mane, B.T. Raut, V.B. Patil, *Archives of Applied Science Research* **1(2)**, 109 (2009).
18. S.G. Pawar, S.L. Patil, M.A. Chougule, D.M. Jundale, V.B. Patil, *J. Mater. Sci: Mater. Electron.* **22**, 260 (2011).
19. H. Tai, Y. Juang, G. Xie, J. Yu, X. Chen, Z. Ying, *Sens. Actuat. B-Chem* **129**, 319 (2008).