Sains Malaysiana 40(3)(2011): 203–208

Influence of PANI Additions on Methanol Sensing Properties of ZnO Thin Films

(Pengaruh Penambahan PANI ke atas Sifat Pengesanan Wap Metanol oleh Filem Nipis ZnO)

MOHAMMAD HAFIZUDDIN HAJI JUMALI*, NORHASHIMAH RAMLI,
IZURA IZZUDDIN, MUHAMAD MAT SALLEH & MUHAMMAD YAHAYA

ABSTRACT

The influence of PANI additions on methanol sensing properties of ZnO thin films at room temperature had been investigated. Commercial polyaniline powder (PANI) was mixed into 3 mL ZnO solution in five different weight percentages namely 1.25, 2.50, 3.75, 5.00 and 6.25% to obtain ZnO/PANI composite solutions. These solutions were spin coated onto glass substrate to form thin films. Microstructural studies by FESEM indicated that ZnO/PANI films showed porous structures with nanosize grains. The thickness of the film increased from 55 to 256 nm, proportionate to increment of PANI. The presence of 2 adsorption peaks at ~310 nm and ~610 nm in UV-Vis spectrum proved that addition of PANI has modified the adsorption peak of ZnO film. Methanol vapour detection showed that addition of PANI into ZnO dramatically improved the sensing properties of the sensor. The sensors also exhibited good repeatability and reversibility. Sensor with the amount of PANI of 3.75 wt% exhibited the highest sensitivity with response and recovery time was about 10 and 80 s, respectively. The possible sensing mechanism of the sensor was also discussed in this article.

Keywords: Gas sensor; methanol vapour; microstructure; UV-Vis analysis; ZnO/PANI thin film

ABSTRAK

Pengaruh penambahan PANI ke atas sifat pengesanan wap metanol oleh filem nipis ZnO telah dikaji pada suhu bilik. Lima amaun serbuk polianilina (PANI) dengan peratusan berat 1.25, 2.50, 3.75, 5.00 dan 6.25% dicampurkan ke dalam 3 mL larutan ZnO untuk menghasilkan larutan komposit ZnO/PANI. Larutan ini kemudiannya dimendapkan ke atas substrat kaca menggunakan teknik salutan berputar untuk membentuk filem nipis. Analisis mikrostruktur melalui FESEM menunjukkan filem nipis komposit ZnO/PANI adalah poros dengan saiz butiran yang terhasil berskala nanometer. Nilai ketebalan filem yang diperolehi meningkat daripada 55 sehingga 256 nm setara dengan penambahan amaun PANI. Analisis UV-Vis mengesahkan kehadiran PANI yang mengubah puncak penyerapan filem ZnO dengan penghasilan 2 puncak penyerapan pada panjang gelombang ~310 nm dan ~610 nm. Ujian pengesanan sensor terhadap wap metanol menunjukkan kehadiran PANI telah meningkat sifat pengesanan sensor secara mendadak dengan menonjolkan sifat kebolehulangan dan kebolehbalikan yang baik. Diperoleh, sensor dengan amaun PANI sebanyak 3.75 wt% mempamerkan kepekaan tertinggi dengan masa tindak balas dan pemulihan masing-masing adalah 10 dan 80 s. Andaian mekanisme pengesanan sensor dibincangkan dalam artikel ini.

Kata kunci: Analisis UV-Vis; filem nipis ZnO/PANI; mikrostruktur; sensor gas; wap metanol

INTRODUCTION

Gas sensor devices commonly employ metal oxide semiconductors like ZnO, TiO_2 and SnO_2 as sensing materials because of their excellent properties in electrical conductivity (Hooker 2002). Nevertheless, the high operating temperatures of the sensors generally impaired the sensor's performance while increase the power consumption (Geng et al. 2006). Therefore several different approaches have been explored in order to overcome these issues such as doping with other elements (Sahay & Nath 2008; Shukla et al. 2005), surface modification (Han et al. 2006) and hybridization with inorganic material (Nardis et al. 2004; Hosono et al. 2005). Previous reports revealed that conducting polymers such as polyaniline, polypyrrole and polyacetylene have great advantages of higher sensitivity toward VOC's gases, lower detectable limit and great potential to operate at room temperature. Among various conducting polymers, polyaniline (PANI) is found to be an attractive candidate as a gas sensor due to its good environmental and chemical stability, inexpensive monomer and easy to synthesis (Tai et al. 2008). The enhancement in gas sensitivity of PANI has been reported for the thin films (Agbor et al. 1995). However, the long response time as well as recovery period due to the orderly structure limits their usage and suitability as commercial gas sensor.

Recent studies showed that gas sensors based on various metal oxides composite with PANI have attracted a lot of attention and considerable interest. Few reports on application of the composites such as SnO_2/PANI (Geng et al. 2007), TiO_2/PANI (Haji Jumali et al. 2009; Tai et al. 2007) and WO_3/PANI (Kaushik et al. 2009) recommended that these materials are good for gas sensors. It has been proven that the composites could synergize or complement the sensitive properties of pure metal oxides or conducting polymers. Therefore, in this work the improvement in methanol sensing properties of ZnO thin film has been investigated by additions of PANI. The morphological and optical properties characterizations of the ZnO/PANI thin films are discussed.

EXPERIMENTAL PROCEDURES

ZnO solution was prepared by the sol gel method. As a starting material, zinc acetate dihydrate (purity ≥ 99.5%) was used. Ethanol (purity ≥ 99.8%) and diethanolamine (purity ≥ 99.8%) were used as a solvent and stabilizer, respectively. 0.6585g of zinc acetate dihydrate was first dissolved in 10 mL of ethanol. Then, an equimolar amount of diethanolamine was added into the mixture. The solution was stirred for 30 min at 60°C to yield a clear and homogeneous solution. The ZnO/PANI composite solution was made 1 day after the ZnO solution was prepared, in which five amounts of polyaniline emeraldine base powder (from Sigma Aldrich) namely 1.25 wt%, 2.5 wt%, 3.75 wt%, 5.0 wt% and 6.25 wt% were added into 3 mL ZnO solution. The mixture was stirred for about 18 h to ensure homogeneous solution of both materials. Then, thin films were fabricated by spin coating the composite solution at 2000 rpm for 30 s onto glass substrate and kept in air for 1 h at room temperature. The procedure was repeated twice to get multi-layers.

The Au comb-type electrode was deposited onto the film by the sputtering technique for fabrication of the sensor. Then, a small amount of silver paste was applied to the films and followed by copper wires to act as an electrical lead. The sensor was put in an airtight chamber and electrically connected to a power supply with constant voltage of 5 V. The methanol vapour was then introduced into the chamber alternately with N_2 for 180 s at constant rate of 3 L/min. The measurement was carried out at room temperature and the electrical response of the sensor was measured and collected automatically in 1s using a data acquisition (DAQ) and Advantech AdamView Runtime software (Figure 1).

The microstructure and cross-section of the films were assessed by Zeiss (Gemini) FESEM. The UV-Vis absorption spectra of ZnO and ZnO/PANI were recorded on Shimadzu UV-Vis-Spectrophotometer model no. 160A using uncoated glass as the reference.

RESULTS AND DISCUSSION

FESEM micrographs for all samples are shown in Figure 2. The micrographs revealed that the composite films showed porous structure with nanosize grains as compared to the film with 0 wt% of PANI. Excellent response of the sensor was expected because small grain sizes, relatively large specific area and pore microstructures have noticeable effect the sensing behavior. This is due to the fact that the gas diffusion occurs more easily in porous structure and hence increases the reaction between gas molecules and the films (Tai et al. 2007). Cross-sectional images (inset) revealed the film thickness was significantly increased from 55 nm (0 wt%) to 256 nm (6.25 wt%), proportionate to the increment of PANi amount. Figure 3 showed the UV-visible spectrum of ZnO and ZnO/PANI thin films. It was found that addition of PANI has modified the adsorption peak of ZnO, with the presence of 2 adsorption peaks at about 300 – 400 nm and 550 – 650 nm.

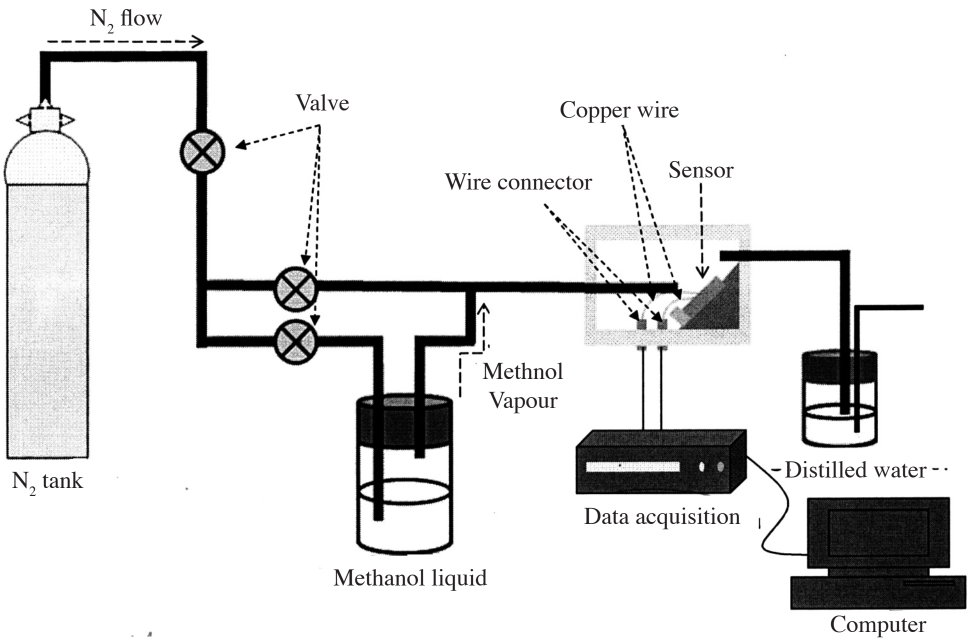

FIGURE 1. The sensing measurement setup

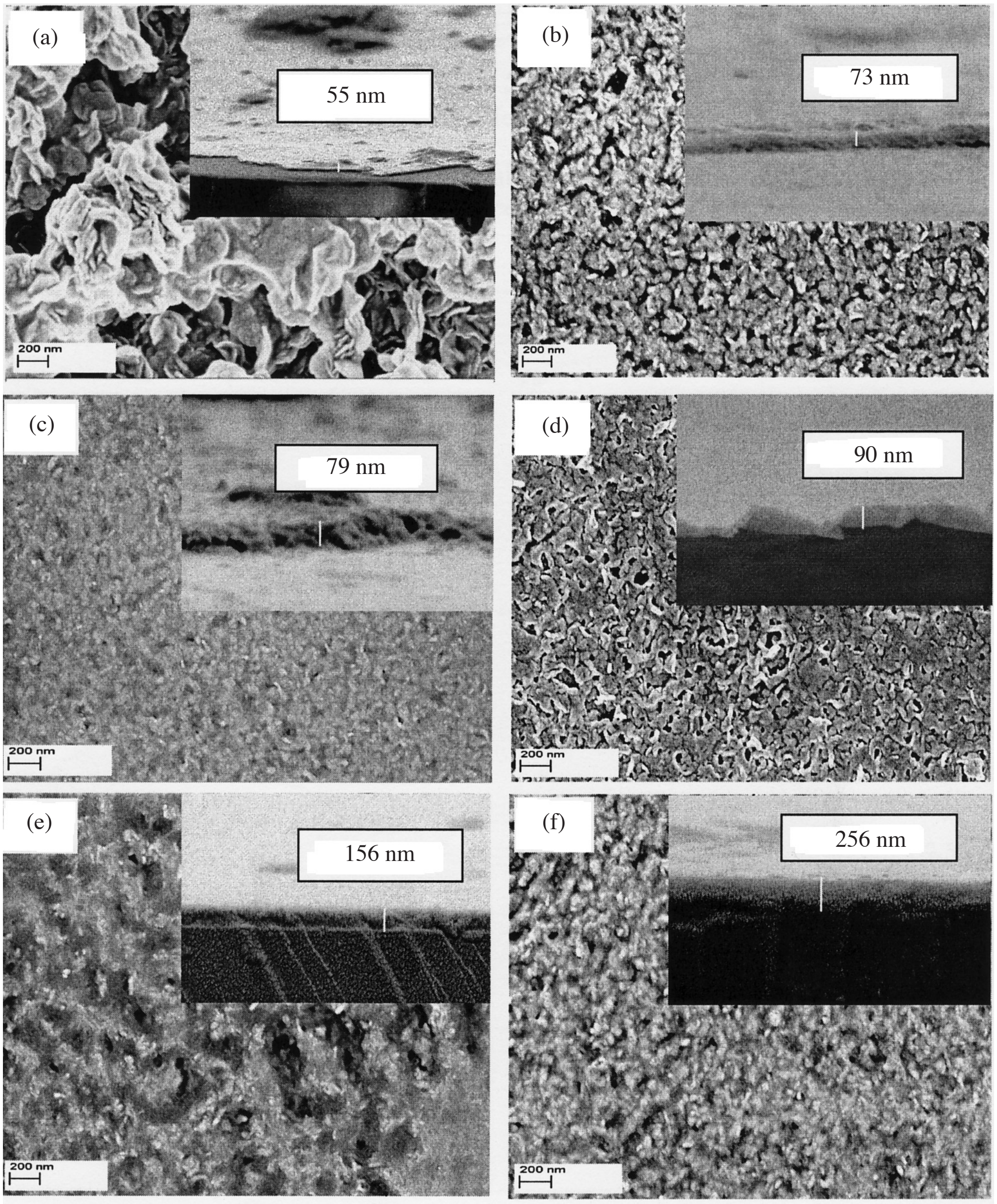

FIGURE 2. FESEM micrographs of ZnO thin film of (a) 0 wt% PNI (b) 1.25 wt% PANI (c) 2.50 wt% PANI (d) 3.75 wt% PANI (e) 5.00 wt% PANI (f) 6.25 wt% PANI and inset (upper right) shows the cross-sectional view of the films

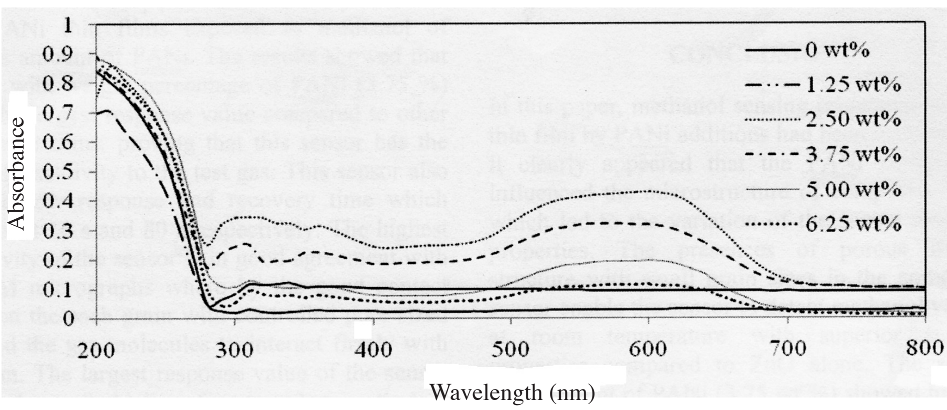

FIGURE 3. Variation of the UV-Visible absorption spectrum of ZnO as a function of weight percentage of PANI

Ram & Malhotra (1996) reported that the existence of both peaks at these 2 ranges is attributed to the π- π* transition centred on benzenoid ring and the n- π* polaron transition of PANI, respectively.

The sensor's response of all samples was depicted in Figure 4. A distinct pattern and voltage response of the sensors were observed. ZnO thin film (0 wt%) PANI was also tested for comparison.

The dramatic reduction in magnitude voltage response over four cycles was observed in this sensor proved that this sensor has poor response and reversibility toward methanol vapour. The lack of reversibility seems attributed to the difficulty of desorption of the adsorbed methanol gas molecules in the sensor (Matsuguchi et al. 2002). In addition, smaller size of pores exhibited by FESEM images probably reduced the diffusion and penetration depth of the gas molecules in the film.

In contrast, all composite sensors exhibited good response towards methanol vapour with superior sensing properties under similar testing conditions. These sensors also showed excellent reversibility and repeatability, indicating the importance of PANI in the detection of methanol vapour at room temperature. Interestingly, addition of PANI into ZnO dramatically affects the sensor's response, wherein the voltage of the sensor increased dramatically when exposed to methanol vapour and then gradually decreased when vapour was replaced by N_2 gas. This response confirmed that PANI is a suitable composite material for ZnO film among the considered conducting polymers. However, a slight shift of the response voltage observed in sensor with 2.5 wt% of PANI amount, which indicated the sensor was not stable and failed to return to their baseline value (initial voltage) after being transferred to N_2 gas.

Table 1 shows the detailed description of response value, response and recovery time of ZnO/PANI thin films exposed to methanol of various amount of PANI. The results showed that sensor with weight percentage of PANI (3.75%) have the largest response value compared to other composite films, proving that this sensor has the highest sensitivity to the test gas. This sensor also showed low response and recovery time which was about 10 s and 80 s, respectively. The highest sensitivity of the sensor is in good agreement with FESEM micrographs where by the good contact between the each grain with controlled pore sized allowed the gas molecules to interact firmly with the film. The largest response value of the sensor is also due to its high surface-to-volume ratio to a degree. Besides,

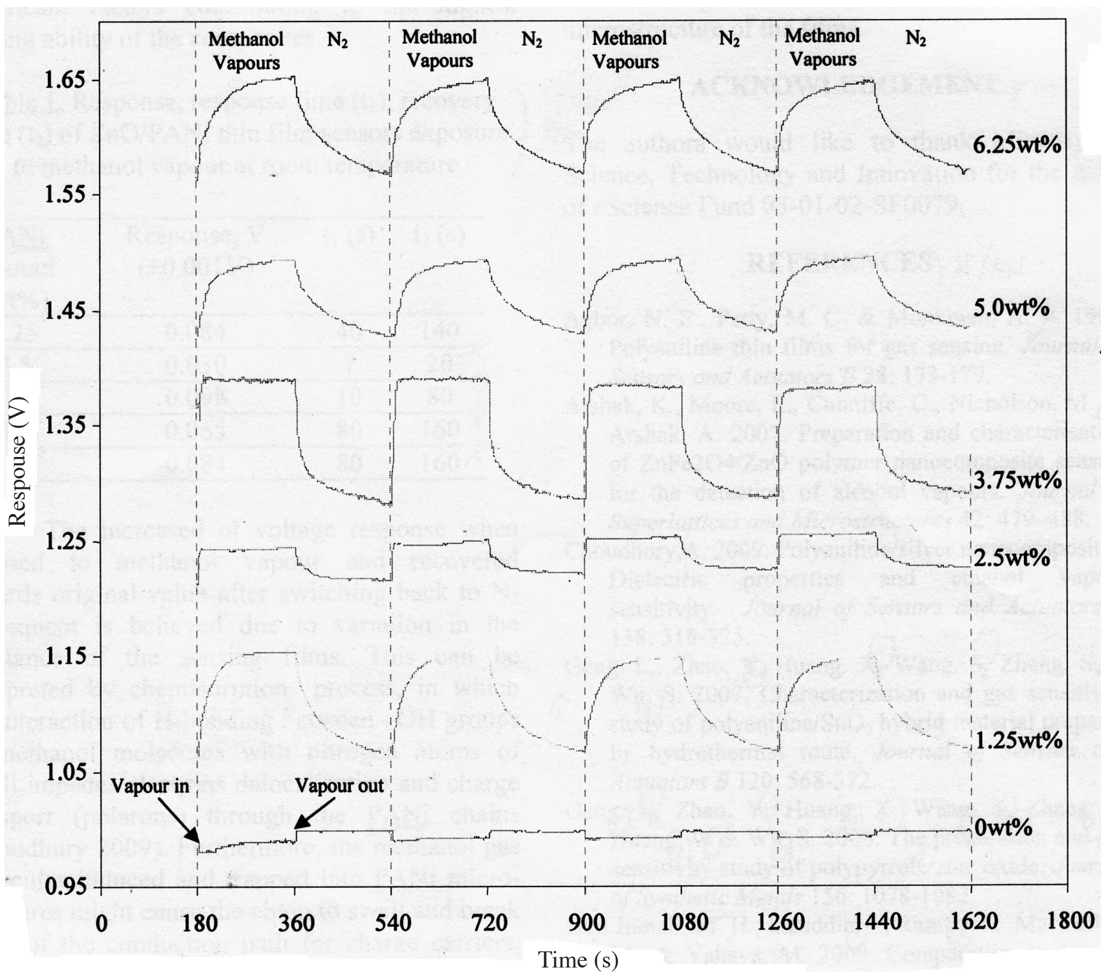

FIGURE 4. Sensor response of ZnO thin film with different weight percentage of PANI

TABLE 1. Response, response time (t_1), recovery time (t_2) of ZnO/PANI thin film sensors exposure to methanol vapour at room temperature

PANI amount (wt%)	Response, V (±0.001V)	t_1 (s)	t_2 (s)
1.25	0.084	40	140
2.5	0.030	7	20
3.75	0.098	10	80
5.0	0.065	80	160
6.25	0.084	80	160

the mixture also exhibited the best homogeneity among the ZnO/PANI composites which is believed to be one of the significant factors contributing to the highest sensing ability of the composites.

The increase of voltage response when exposed to methanol vapour and recovered towards original value after switching back to N_2 consequent is believed due to variation in the resistance of the sensing films. This can be interpreted by chemisorptions process, in which the interaction of H-bonding between –OH groups of methanol molecules with nitrogen atoms of PANI impedes electrons delocalization and charge transport (polarons) through the PANI chains (Choudhury 2009). Furthermore, the methanol gas molecules induced and trapped into PANI micro-structures might cause the chain to swell and break some of the conduction path for charge carriers, hence resulted in higher resistance. The factor that increase the amount of the gas molecules permeates is high levels of free volume and good segmental chain mobility of the microstructures (Arshak et al. 2007).

CONCLUSION

In this paper, methanol sensing properties of ZnO thin film by PANI additions had been investigated. It clearly shows that the PANI components influenced the microstructure of composite films, which led to the variation of the sensor response properties. The presences of porous fibrous structure with small grain sizes in the composite sensor enable the sensor to detect methanol vapour at room temperature with superior sensing properties compared to ZnO alone. The sensor with amount of PANI 3.75 wt% showed highest response voltage with low response and recovery time. Thus the sensor response is determined not only by the character of the sensing materials but also by the microstructure of the films.

ACKNOWLEDGEMENTS

The authors would like to thank Ministry of Science, Technology and Innovation for the grant of eScience Fund 03-01-02-SF0079.

REFERENCES

Agbor, N.E., Petty, M.C. & Monkman, A.P. 1995. Polyaniline thin films for gas sensing. *Journal of Sensors and Actuators B* 28: 173-179.

Arshak, K., Moore, E., Cunniffe, C., Nicholson, M. & Arshak, A. 2007. Preparation and characterisation of ZnFe2O4/ZnO polymer nanocomposite sensors for the detection of alcohol vapours. *Journal of Superlattices and Microstructures* 42: 479-488.

Choudhury, A. 2009. Polyaniline/silver nanocomposites: Dielectric properties and ethanol vapour sensitivity. *Journal of Sensors and Actuators B* 138: 318-325.

Geng, L., Zhao, Y., Huang, X., Wang, S., Zhang, S. & Wu. S. 2007. Characterization and gas sensitivity study of polyaniline/SnO_2 hybrid material prepared by hydrothermal route. *Journal of Sensors and Actuators B* 120: 568-572.

Geng, L., Zhao, Y., Huang, X., Wang, S., Zhang, S., Huang, W. & Wu, S. 2006. The preparation and gas sensitivity study of polypyrrole/zinc oxide. *Journal of Synthetic Metals* 156: 1078-1082.

Haji Jumali, M.H., Izzuddin, I., Ramli, N., Mat Salleh, M. & Yahaya, M. 2009. Comparative studies on microstructural and gas sensing performance of TiO_2 and TiO_2-PANI nanocomposite thin films. *Solid State Science and Technology* 17: 126-131.

Han, C.H., Han, S.D. & Khatkar, S.P. 2006. Enhancement of H_2-sensing properties of F-doped SnO_2 sensor by surface modification with SiO_2. *Journal of Sensors* 6: 492-502.

Hooker, S.A. 2002. Nanotechnology advantages applied to gas sensor development. *Proceedings of the 2002 Nanoparticles Conference*.

Hosono, K., Matsubara, I., Murayama, N., Woosuck, S. & Izu, N. 2005. Synthesis of Polypyrrole/MoO_3 hybrid thin films and their volatile organic compound gas sensing properties. *Journal of Chemistry Material* 17: 349-354.

Kaushik, A., Khan, R., Gupta, V., Malhotra, B.D., Ahmad, S. & Singh, S.P. 2009. Hybrid cross-linked polyaniline-WO_3 nanocomposite thin film for NO_x gas sensing. *Journal of Nanoscience and Nanotechnology* 9: 1792-1796.

Matsuguchi, M., Io, J., Sugiyama, G. & Sakai, Y. 2002. Effect of NH_3 gas on the electrical conductivity of polyaniline blend films. *Journal of Synthetic Metals* 128: 15-19.

Nardis, S., Monti, D., Natable, C.D., Amico, A.D., Siciliano, P., Forleo, A., Epifani, M., Taurino, A., Rella, R. & Paolesse, R. 2004. Preparation and Characterization of Cobalt Porphyrin modified tin dioxide thin films for sensor application. *Journal of Sensors and Actuator B* 103: 339-343.

Ram, M.K. & Malhotra, B.D. 1996. Preparation and characterization of Langmuir-Blodgett films of polyemeraldine base. *Journal of Polymer* 37: 4809-4813.

Sahay, P.P. & Nath, R.K. 2008. Al-doped ZnO thin films as methanol sensors. *Journal of Sensors and Actuators B: Chemical* 134: 654-659.

Shukla, S., Agarwal, R., Cho, H.J., Seal, S., Ludwig, L. & Parish, C. 2005. Effect of ultraviolet radiation exposure on room-temperature hydrogen sensitivity of nanocrystalline doped tin oxide sensor incorporated into microelectromechanical system device. *Journal of Applied Physics* 97: 1-13.

Tai, H., Jiang, Y., Xie, G., Yu, J. & Chen, X. 2007. Fabrication and gas sensitivity of polyaniline-titanium dioxide nanocomposite thin film. *Journal of Sensors and Actuators B* 125: 644-650.

Tai, H., Jiang, Y., Xie, G., Yu, J., Chen, X. & Ying, Z. 2008. Influence of polymerization temperature on NH_3 response of PANI/TiO_2 thin film gas sensor. *Journal of Sensors and Actuators B*129: 319-326.

Mohammad Hafizuddin Haji Jumali*, Norhashimah Ramli, Izura Izzuddin & Muhammad Yahaya
School of Applied Physics
Faculty of Science & Technology
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor D.E.
Malaysia

Muhamad Mat Salleh
Institute of Microengineering and Nanoelectronic (IMEN)
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor D.E.
Malaysia

*Corresponding author; e-mail: hafizhj@ukm.my

Received: 15 May 2010
Accepted: 3 September 2010