

QUARTZ CRYSTAL MICROBALANCE GAS SENSOR FOR DETECTION OF VOLATILE ORGANIC COMPOUNDS USING TITANIUM DIOXIDE COATED WITH DYE-PORPHYRIN

Syariena Arshad¹, Muhammad Mat Salleh¹, and Muhammad Yahaya²

¹Institute of Microengineering and Nanoelectronics (IMEN)
Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, MALAYSIA

²School of Applied Physics, Faculty of Science and Technology
Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, MALAYSIA

ABSTRACT

A bulk acoustic sensor system was fabricated and used to detect some volatile organic compounds namely ethanol, acetone, cyclohexane, toluene, o-xylene and 2-propanol. The sensing sensitivity was based on the changes of the quartz crystal microbalance (QCM) frequency upon exposure towards the vapors. In order to improve the sensing sensitivity and selectivity properties, the QCM was deposited with thin films using sol-gel dip coating method. The thin films were titanium dioxide (TiO₂), porphyrin and TiO₂ coated with dye porphyrin with the variation of TiO₂ and porphyrin ratio, i.e. 1:2, 1:4, 1:6 and 1:8 by volume. The porphyrin used was 5, 10, 15, 20-tetraphenyl-21H, 23H-manganese (III) chloride. It was found that all the thin films were sensitive towards all type of vapors and showed different degree of sensitivity for different type of vapors.

INTRODUCTION

Gas sensor with high sensitivity and selectivity has been a great demand in recent years as the environmental pollution has getting worse, cause by combustion in automobile engines, various industrial process and environmental activities. Gas sensor is use to monitor pollutant in environment and can provides early diagnostics in human healthcare. Humans are easily exposed to these chemicals by breathing and through skin. Exposure to volatile organic compounds (VOCs) even at low concentration can cause bad health impact to human. Thus, Quartz Crystal Microbalance (QCM) sensor is a possible option for the gas sensor requirement since it is highly sensitive to small mass change. When expose to the vapor, the frequency of quartz crystal is decreased by the adsorption of VOCs molecules by the surface of QCM. The decreasing of frequency is proportional to the mass of foreign molecules deposited on the crystal surface, according to the Sauerbrey law:

$$\Delta f = -k S_m \Delta m \quad (1)$$

where k is geometric factor for the fraction of the active device area being perturbed, S_m is the device specific constant and Δm is the change in mass/area on the device surface.

A QCM sensor can be made selective by coating the surface of quartz crystal with thin film of a particular material. Much research has been done to improve the sensitivity and selectivity of the gas sensor by using different method to develop thin film and different sensing material [1-3]. In this research, titanium dioxide (TiO₂) and porphyrin were studied as sensing materials. Nanostructured TiO₂ thin film have attracted much interest because nanostructure thin films give larger surface area and provides high sensitivity at low gas concentrations [4]. TiO₂ has been extensively studied for sensing purposes such as to detect organic vapors [5], oxygen [6], ammonia [7], water vapor [8] and nitric acid [9], while organic compound has become a good candidate for sensing element because of its high sensitivity, good recoverability and selectivity. Porphyrin is a very interesting material since a simple modification on the structure of the central molecule and the structure of the ring through substitution of atoms or ligands can change the characteristic of this compound [10]. These two materials show promising gas sensing properties but TiO₂ is less selective and is affected by humidity [11] while organic compound has poor reliability[12]. Nanoparticles TiO₂ coated with dye-porphyrin thin film has been developed to improve the response properties of a sensing element to the presence of VOCs. The incorporation of nanostructure TiO₂ and porphyrin is expected to achieve high sensitivity and good stability.

In this work, we study the sensing performance of TiO₂, porphyrin and TiO₂ coated dye-porphyrins thin films with the variation of TiO₂ and porphyrin ratio, i.e. 1:2, 1:4, 1:6 and 1:8 by volume towards VOCs. The metalloporphyrin compound used was 5,10,15,20-tetraphenyl-21H,23H-porphine manganese (III) chloride (MnTPPCL). The sol gel dip coating method was used to prepare the thin films. The sensing sensitivity was based on the change in the fundamental frequency of the QCM upon exposure towards six vapor samples, namely ethanol, acetone, cyclohexane, toluene, o-xylene and 2-propanol.

EXPERIMENT DETAILS

Preparation of solutions.

The TiO₂ sol was prepared by using titanium (IV) ethoxide (TEOT), potassium chloride (KCl) and ethanol. Firstly, KCl powder was dissolved in deionized water and added into ethanol with stirring. Then TEOT was dropped wisely into the solution under nitrogen in a glove box. Acetylacetone as stabilizer was added into the solution and was stirred for 2 hours at room temperature. Nanoparticles TiO₂ sol were successfully prepared.

0.2 mg/ml metalloporphyrin solution was prepared by dissolving the metalloporphyrin powder in toluene.

To prepare the TiO₂ coated porphyrin solution, Poly-L-Lysine (PLL) was added drop-wise into the TiO₂ sol and keeps stirring to charge the TiO₂ nanoparticles into positive charge. Then metalloporphyrin solution was added drop-wise into the TiO₂ solution. Both solutions were stirred for several hours to obtain a complete mixture of porphyrin and TiO₂ nanoparticles. The variation of TiO₂ and porphyrin mixture by volume was

1:2, 1:4, 1:6 and 1:8.

Deposition of thin films.

The QCM substrate used was 10 MHz AT-cut quartz crystal (13.5mm in diameter) with gold electrodes (5 mm in diameter) on each side. The thin film was deposited onto QCM substrate using sol-gel dip coating method. The substrate was dipped in solution for 30 minutes and pulled out with slow and uniform pulling rate of 40 mm/min. A thin uniform film was formed on the substrate and dried with nitrogen at room temperature. Surface analysis was conducted with scanning electron microscopy (SEM).

Gas sensing measurement.

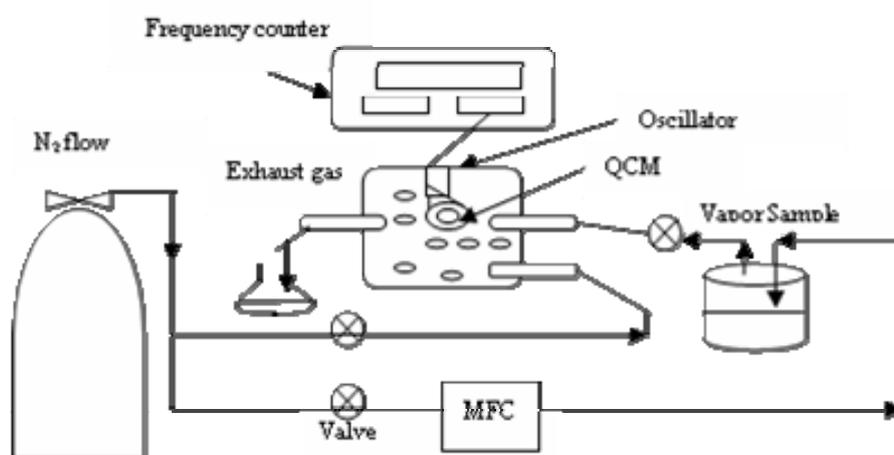
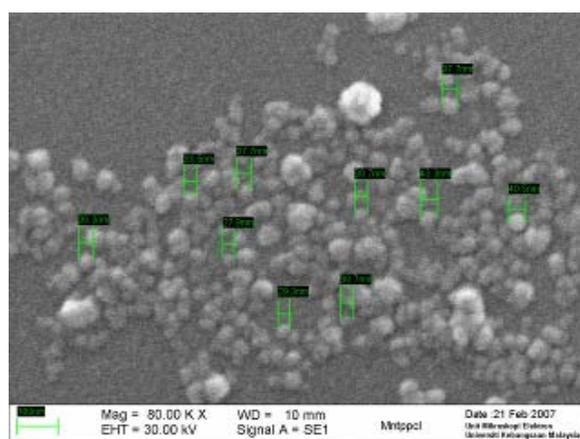


Figure 1: The bulk acoustic system set-up.

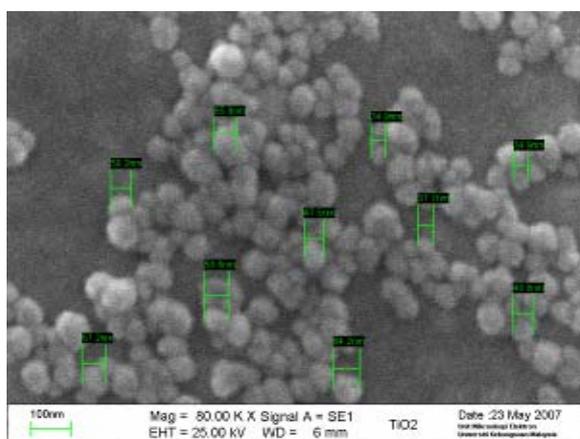
Figure 1 shows an experimental set-up for the bulk acoustic sensor system. The QCM coated with thin film was positioned in the sensor chamber. A power voltage of 4.5 V was supplied to the oscillator circuit. Nitrogen gas was purged into the sensor chamber for 30 minutes to remove the air out of the chamber. The detection of VOCs; ethanol, acetone, cyclohexane, toluene, o-xylene and 2-propanol were started by exposing the thin films to the vapor with the flow rate of 10 ml/min. The gas flow rate was controlled by mass flow controller (MFC). The sensitivity of the thin films to the VOCs were studied by measuring the QCM frequency changes using FC-7015U universal frequency counter and the data were transferred to the computer. The recovery time was recorded starting from when the VOC vapor is cut off and pure nitrogen is purged into the system.

RESULTS AND DISCUSSION

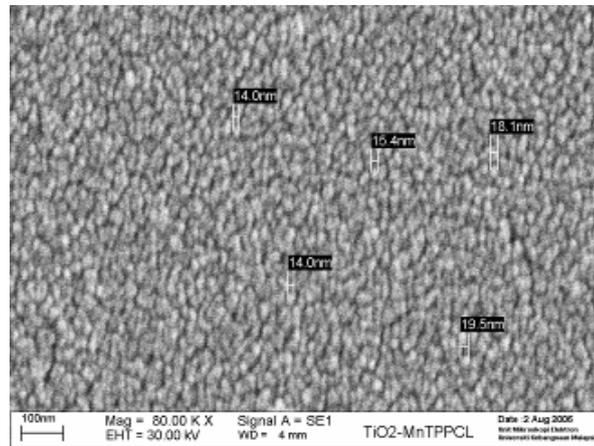
Figure 2 shows the SEM images of all thin films. From table 1, we can see that the particles of single material thin films are larger than coated thin films. It is because of cohesive force between the same molecules that tend to stick together. For the coated thin film, the presence of porphyrin molecules that coated the TiO_2 molecules prevent the TiO_2 molecules from sticking together. The thin film particles with the ratio of 1:2 are small and uniformly distributed throughout the whole sample with the size of 14.0 nm to 19.5 nm (Figure 2c). When the porphyrin volume increased, the small particles start to agglomerate to form larger particles (Figure 2d). The particles size of TiO_2 coated MnTPPCl with the ratio of 1:4 are in the range of 18.1 nm to 33.5 nm. With the increasing of porphyrin volume up to six times of TiO_2 volume, the solution turned into gel and deposited film contains large grain and holes (Figure 2e). When the volume of porphyrin was increased further, the additional molecules of porphyrin were deposited as thin film at the bottom and some of TiO_2 coated particles were deposited on the top of it (Figure 2f).



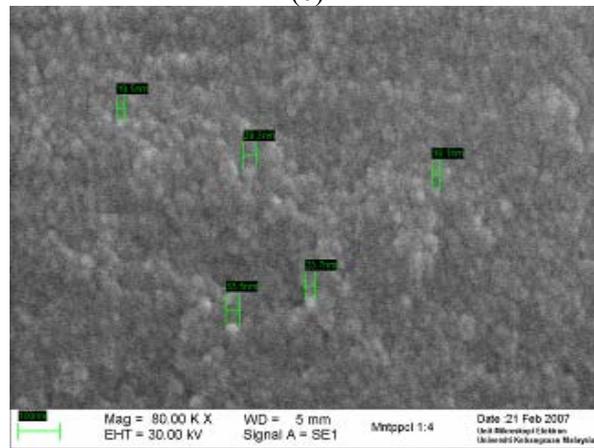
(a)



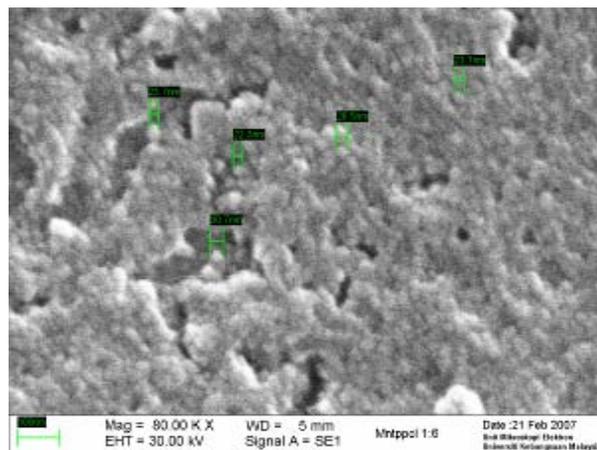
(b)



(c)



(d)



(e)

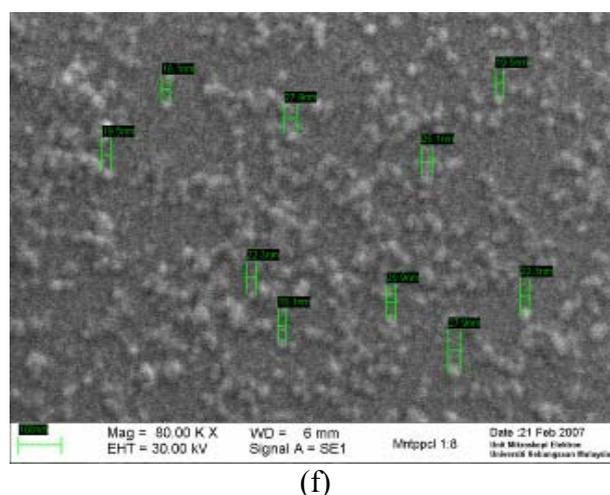


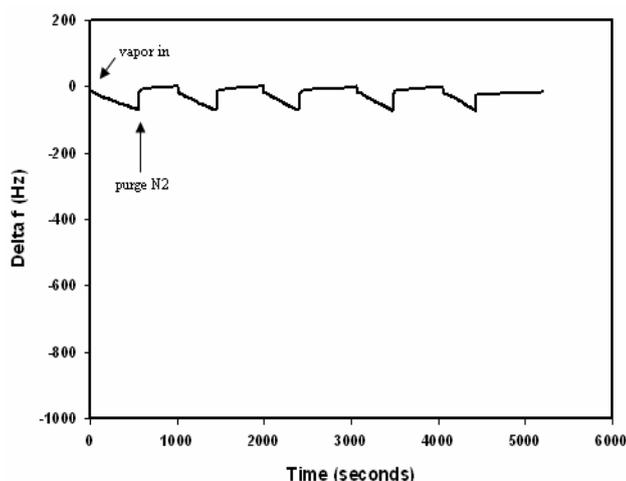
Figure 2: SEM image of (a) MnTPPCL, (b) TiO₂, TiO₂ coated MnTPPCL with the ratio of (c) 1:2, (d) 1:4, (e) 1:6 and (f) 1:8 thin films.

Table 1: Summary of the grains size of all the thin films.

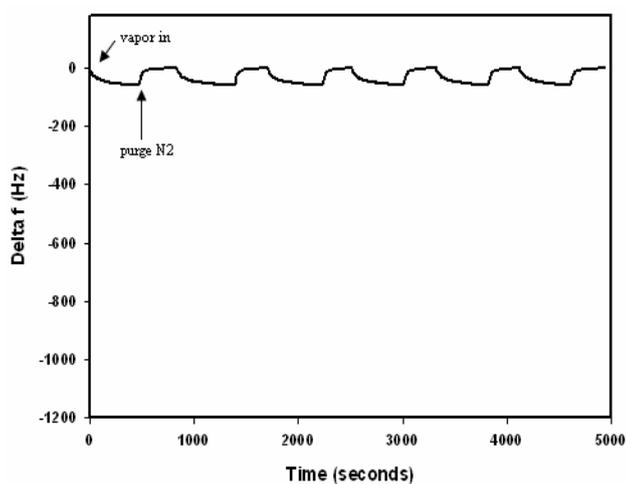
Thin films	Grains size (nm)
TiO ₂	27.9 - 43.3
MnTPPCL	34.9 - 64.2
TiO ₂ coated MnTPPCL ratio 1:2	14.0 - 19.5
TiO ₂ coated MnTPPCL ratio 1:4	18.1 - 33.5
TiO ₂ coated MnTPPCL ratio 1:6	22.3 - 30.7
TiO ₂ coated MnTPPCL ratio 1:8	18.1 - 27.9

Figure 3 shows the response of thin films towards cyclohexane vapor. When the thin films were exposed to the vapor, the frequency of QCM was decreased to a certain values depending on the thin film sample. After the vapor was removed from the system, the frequency response was recovered back to the original frequency and the sensing experiment was repeated for six cycles. All thin films show good recoverability except for TiO₂ coated MnTPPCL ratio 1:8 thin film. It was observed that the TiO₂ coated MnTPPCL thin films exhibited better sensing performance than the single material thin films i.e. TiO₂ and MnTPPCL. From Figure 2, we can see that the size of thin film grain size is reduced with the incorporation of porphyrin to TiO₂. The smaller grain size of coated thin films provides larger surface area for the VOCs molecules to adsorb and enhance the sensing properties. TiO₂ coated MnTPPCL with the ratio of 1:6 thin film shows the highest response but the response time are slower as the cycle number increases. This may be due to the surface of this film that is very rough and contains pores where the vapor is able to penetrate deep into the film and hence

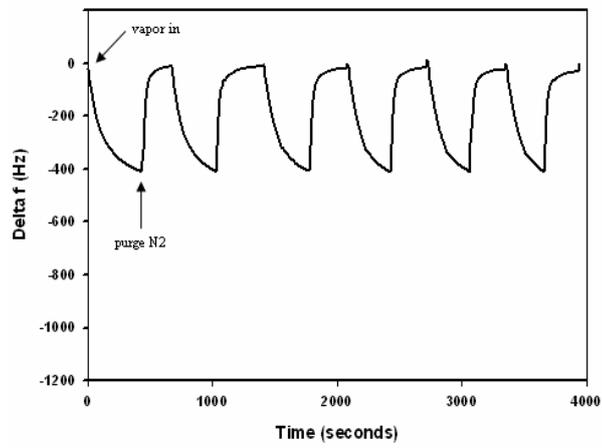
increases the mass of the film, and the frequency response decreases further. However, it takes longer time for the nitrogen gas to purge the vapor out of the film. The responses of TiO₂ coated MnTPPCl with the ratio of 1:4 thin film is lower than that of TiO₂ coated MnTPPCl with the ratio of 1:2 thin film. TiO₂ coated MnTPPCl with the ratio of 1:2 thin film is the best film as it showed good reversibility and recoverability up to six cycles of sensing experiment and good stability as it had almost similar response time and recovery time for each cycle.



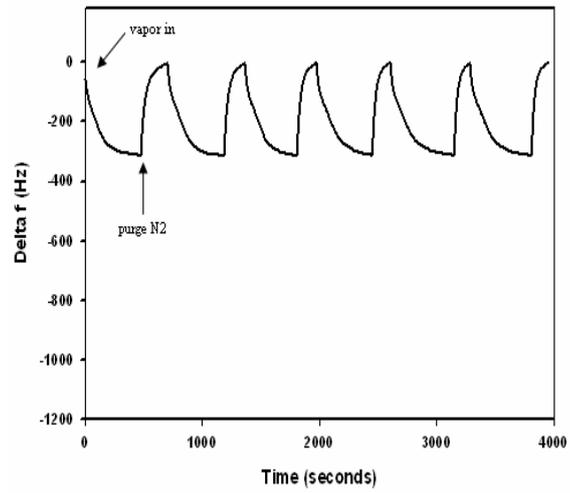
(a)



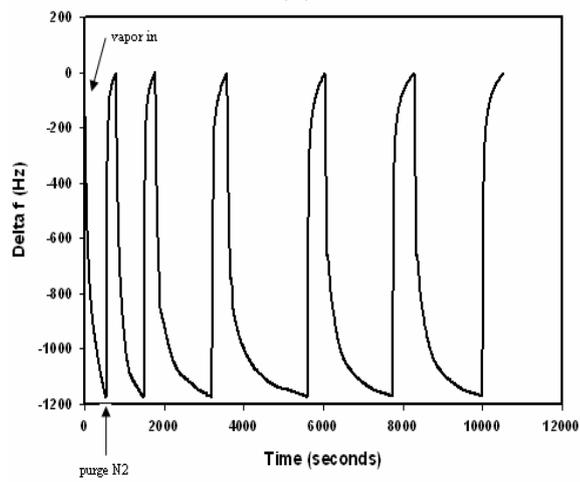
(b)



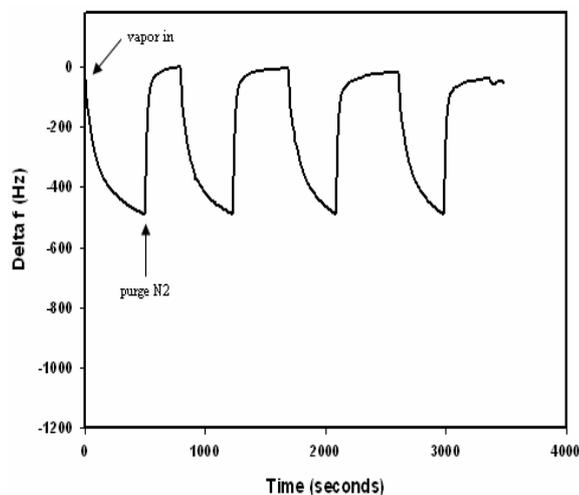
(c)



(d)



(e)



(f)

Figure 3: Response of (a) MnTPPCL, (b) TiO₂, TiO₂ coated MnTPPCL with the ratio of (c) 1:2, (d) 1:4, (e) 1:6 and (f) 1:8 thin films towards cyclohexane vapor.

Figure 4 shows the variation of response for ethanol, acetone, 2-propanol, cyclohexane, toluene and o-xylene vapors towards all thin films. It was observed that MnTPPCL thin film and all TiO₂ coated MnTPPCL thin films have good selectivity properties towards these gases, while TiO₂ thin film has poor selectivity. The difference of response towards each vapor may be due to the different strength of interaction between different types of vapors with the film.

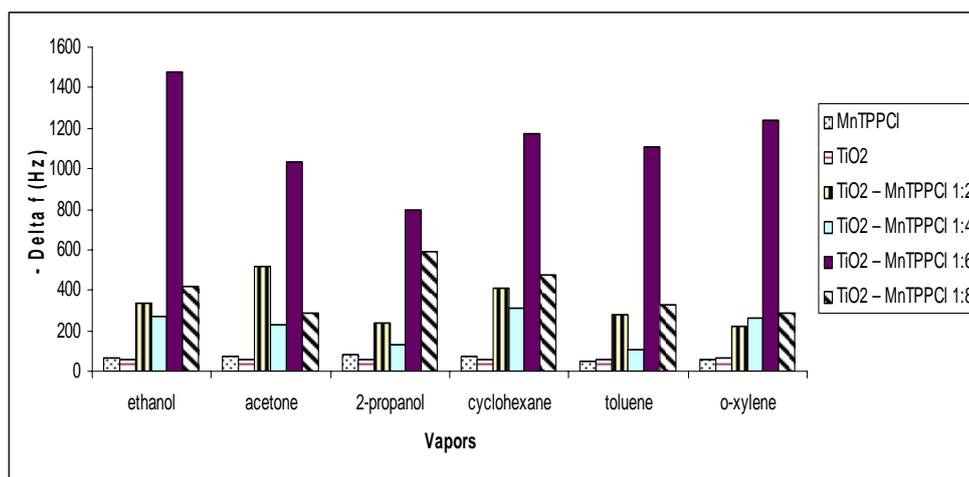


Figure 4: The variation response for all thin films towards various vapors.

CONCLUSION

It was found that all thin films have good recoverability except for TiO₂ coated porphyrin with ratio 1:8. The incorporation of nanostructure TiO₂ and porphyrin had achieved high sensitivity and selectivity towards VOCs. All coated thin films showed higher frequency response towards VOCs compared with single material thin film. TiO₂ coated MnTPPCL with the ratio of 1:6 thin film shows the highest response but the response time is slower as the cycle number increase. TiO₂ coated MnTPPCL ratio 1:2 thin film showed the best performance because it showed good reversibility, recoverability and stability.

ACKNOWLEDGEMENT

This work was supported by the Malaysian Ministry of Higher Education under Research University grant UKM-OUP-BTT-26/2007.

REFERENCES

- [1]. W. G. Shim, H. Moon, J. W. Lee, (Sept. 2006); *Microporous and Mesoporous Materials*, **94**, 15–28.
- [2]. J. M. Kim, S. Y. Yoo, H. K. Shin, Y. S. Kwon, (March 1997) *Synthetic metal*, **85**, 1423-1424.
- [3]. M. Kikuchi, S. Shiratori, (July 2005); *Sensors and Actuators B*, **108**, 564–571.
- [4]. M.C. Carotta, M. Ferroni, D. Gnani, V. Guidi, M. Merli, G. Martinelli, M.C. Casale, M. Notaro, (Sept. 1999); *Sensor Actuators B*, **58**, 310-317.
- [5]. A. Teleki, S.E. Pratsinis, K. Kalyanasundaram, P.I. Gouma, (Dec. 2006); *Sensors and Actuators B*, **119**, 683-690.
- [6]. B. Karunakaran, P. Uthirakumar, S.J. Chung, S. Velumani, E.-K. Suh, (Sept. 2006); *Materials Characterization*, **58**, 680-684.
- [7]. N. Bonini, M. C. Carotta, A. Chiorino, V. Guidi, C. Malagù, G. Martinelli, L. Paglialonga and M. Sacerdoti, (Aug. 2000), *Sensors and Actuators B*, **68** 274-280.
- [8]. P. M. Faia, C. S. Furtado and A. J. Ferreira, (June 2004); *Sensors and Actuators B*, **101**, 183-190.
- [9]. L. Gao, Q. Li, Z. Song, J. Wang, (Dec. 2000); *Sensors and Actuators B*, **71** 179-183.
- [10]. M. Akrajas, M. M. Salleh, M. Yahaya, (July 2002); *Sensors and Actuators B*, Vol. **85**, 191-196.
- [11]. T. Tesfamichael, N. Motta, T. Bostrom and J. M. Bell, (March 2007); *Applied Surface Science*, **253**, 4853-4859.
- [12]. T. Toccoli, S. Capone, L. Guerini, M. Anderle, A. Boschetti, E. Iacob, V. Micheli, P. Siciliano and S. Iannota, (April 2003); *IEEE Sensors Journal*, **3**, pp. 199-205.