Solid State Science and Technology, Vol. 16, No 1 (2008) 63-74
ISSN 0128-7389

FLUORESCENCE GAS SENSOR USING TiO_2 NANOPARTICLES COATED WITH PORPHYRIN DYE THIN FILMS

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ABSTRACT

This paper explores the possibility of using fluorescence technique to detect the presence of volatile organic compounds based on TiO_2 nanoparticles coated with porphyrin dye thin films. Porphyrin dye used was Iron (III) meso-tetraphenylporphine chloride. The thin films were prepared with the variation of TiO_2 and porphyrin ratio, i.e. 1:2, 1:3, 1:4 and 1:5 by volume. The purpose of this study is to search the most suitable variation of TiO_2 and porphyrin ratio in the fabrication of the thin film in order to optimize the sensitivity of the fluorescence gas sensor. All the thin films were deposited on quartz substrate using self-assembly through dip coating technique. The sensing properties of the thin films toward volatile organic compounds; ethanol, acetone and 2-propanol were studied using luminescence spectrometer. In the presence of air and volatile organic compounds, thin films produced different emission spectra and ease for chemical identification process except for ratio 1:5. The thin film of TiO_2 nanoparticles coated porphyrin with ratio of 1:2 produced more intensive interaction and exhibit good sensitivity than other thin films. The thin film has smallest size; it will give the larger surface area and increase the interaction with VOCs. Hence, it is potentially be used as fluorescence gas sensor.

INTRODUCTION

Volatile Organic Compounds (VOCs) are organic chemicals that easily vaporize at room temperature. VOCs are emitted as gases by a wide array of products such in paints, cleaning supplies, pesticides and building materials. Long exposure time to the VOCs cause bad health effect and cancer for human. Hence, it is very important to have a sensor for identification of the hazardous VOCs. Recently, sensor base on optical sensing technique has received growing interest as an alternative to sensors based on electrical resistance which operates at high temperature. Various techniques have been employed, which include fluorescence [1], UV-VIS absorption [2], refractive index [3] and surface plasmon resonance (SPR) [4].

In this paper, we explore the possibility of using fluorescence technique in developing gas sensor to detect the presence of volatile organic compound (VOCs). This technique offers several advantages over other methods such as sensitivity, high efficiency and

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specificity. Fluorescence technique has been sought for huge potential applications in food quality control [5], medical [6] and environmental [7]. The technique also has been used for measuring various gaseous levels, including sulfur dioxide [8], chlorine [9-10] and nitrogen dioxide [11].

The sensing materials that we used for fabrication thin film were TiO_2 nanoparticles coated with porphyrin dye. Porphyrin is considerable interest for development of gas sensor system. Porphyrin has shown a high sensitivity and selectivity toward a wide spectrum of organic gases [12]. Their interesting features in the interactions with the gaseous molecules have been widely described elsewhere [12-13]. The used of porphyrin will modify TiO_2 nanoparticles structure and enrich its properties as gas sensor.

The thin films were prepared using self-assembly layer through dip coating technique. In order to increase the sensitivity of the thin film, we study effect of variation ratio for porphyrin dye and TiO_2 nanoparticles. The volume ratio of porphyrin to TiO_2 was 2, 3, 4 and 5 to 1. The effect of variation ratio for porphyrin dye and TiO_2 nanoparticles were characterized using SEM, AFM and luminescence spectrometer. We also study the performance of thin films towards VOCs; ethanol, acetone and 2-propanol. The sensing sensitivity was based on the changes of thin films in presence of volatile organic compounds. The thin films will produce different photoluminescence spectra. The peak position of these spectra was used to identify the type of VOCs.

EXPERIMENT DETAILS

Materials used for synthesis TiO_2 nanoparticles in the experiment were titanium (IV) ethoxide (TEOT), kalium chloride (KCl) and ethanol. Poly-L-Lysine (PLL) with m_w = 70,000 was used to charge substrate surface into positive charge. These chemicals were purchase from Aldrich Corporation. Porphyrin dye used for sensing material was Iron (III) meso-tetraphenylporphine chloride was purchase from Stream Chemical.

TiO_2 nanoparticles colloid was synthesized from titanium (IV) ethoxide in ethanol with addition of kalium chloride (KCl) as stabilizer [14] with some modifications. Firstly, ethanol was mixed with KCl and stirred for one hour to get a complete mixture. Then, titanium ethoxide was dropped wisely to the admixture solution in glove box under nitrogen atmosphere and humidity at 15%. Acetylaceton was dropped into the solution at room temperature and stirred for two hours to form a clear, transparent yellowish solution.

TiO_2 nanoparticles coated with porphyrin dye colloid were prepared as follow: firstly, porphyrin dye; Iron (III) meso-tetraphenylporphine chloride dissolved in toluene at a concentration of 0.2 mg/ml. Then, porphyrin solution was added drop wisely into the TiO_2 solution and stirred for one hour to obtain a complete mixture of porphyrin and TiO_2 nanoparticles. The volume ratio of porphyrin to TiO_2 was 2, 3, 4 and 5 to 1.

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TiO_2 nanoparticles coated with porphyrin dye were self-assembled prepared on quartz substrate. The clean quartz substrate was immersed in polycation solution for 30 minutes to charge the surface into positive charge. Then, the substrate was rinse with deionized water. Using KSV Dip coating system, the substrate was dipped into the TiO_2 nanoparticles coated with porphyrin dye colloid. The substrate was kept in the colloid for 30 minutes and lifted up at a constant speed of 15 mm/min. At the first stage, one bilayer of TiO_2 nanoparticles coated with dye thin film was formed on the substrate surface. The procedure was repeated for preparation of all thin films.

The prepared thin films were characterized using scanning electron microscopy (SEM) to study the formation of nanoparticles and measure the size of nanoparticles. The surface morphology of thin film was recorded using atomic force microscopy (AFM). Luminescence spectrophotometer was used to measure emission spectra of the thin films.

The sensing properties of the thin films toward volatile organic compounds; ethanol, acetone and 2-propanol were studied using Perkin Elmer luminescence spectrophotometer. The experimental set-up depicted in Figure 1 was used to evaluate the fluorescence gas sensing capabilities of the thin films. Nitrogen flow is used to carrier gas bubbling through a glass balloon flask containing 10 ml of VOCs in airflow at rate of 16 ml/min which was control by Brook's mass flow meter controller. Then, the gases enter the analysis chamber and reach to the thin films surface, where each thin film will produce photoluminescence spectra with a distinct emission peaks.

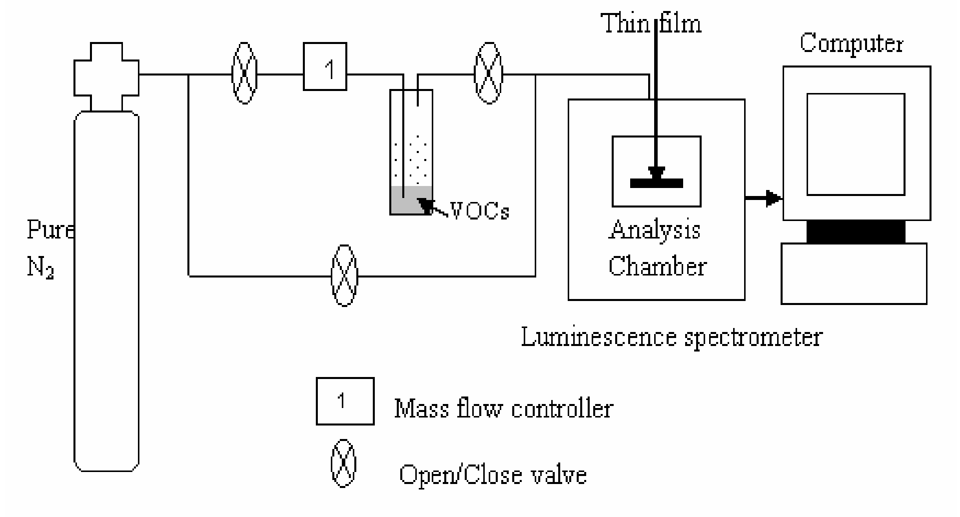

Figure 1: Fluorescence gas sensing system setup.

RESULT AND DISCUSSION

The thin films of TiO_2 nanoparticles coated with porphyrin with variation of 1:2, 1:3, 1:4 & 1:5 were deposited onto quartz substrate using self assembly technique. Figures 2 and 3 show the SEM and AFM images of all the thin films. The averages diameters of

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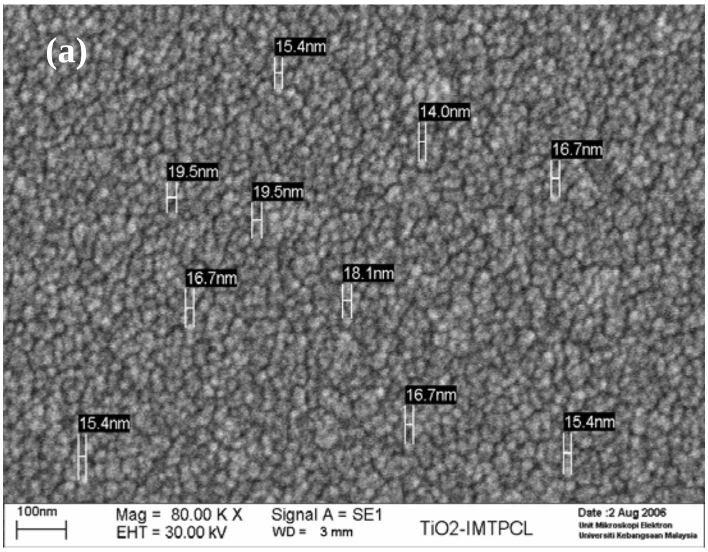
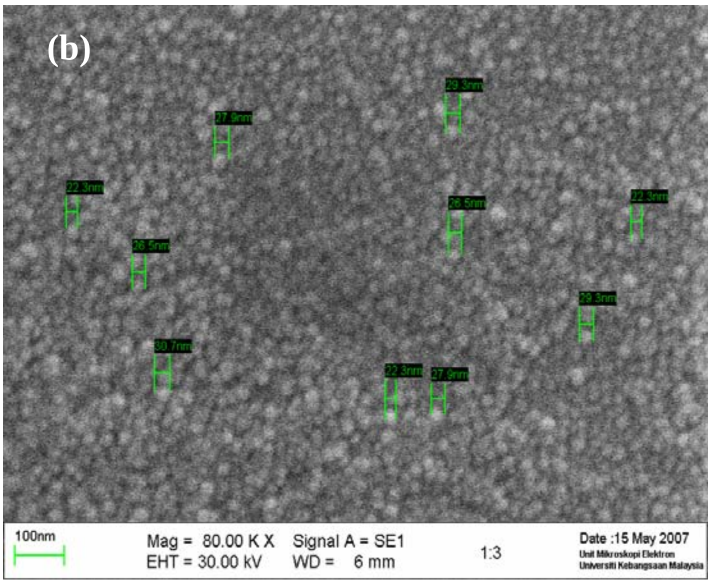
nanoparticles that have been synthesized and surface roughnesses deduce in table 1. It was found that, higher TiO_2 and porphyrin ratio produce larger grain size and surface roughness. This grain size and surface roughness is important to determine the sensitivity of the thin film for detection of volatile organic compounds in sensing experiment.





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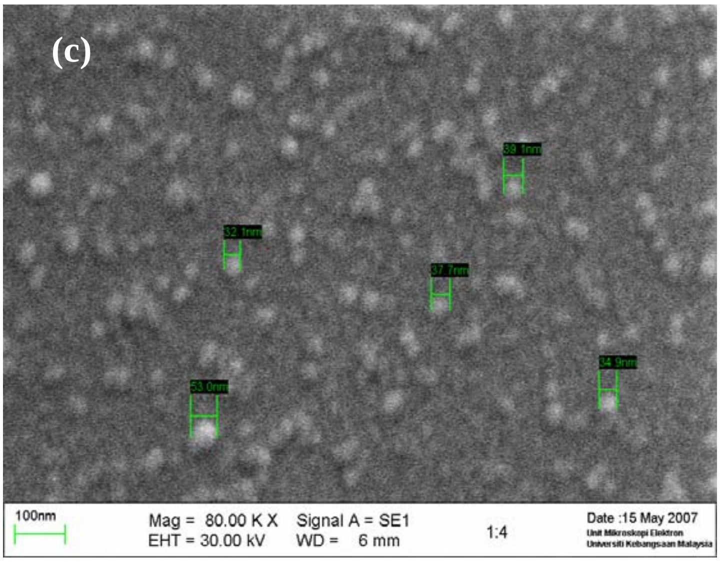

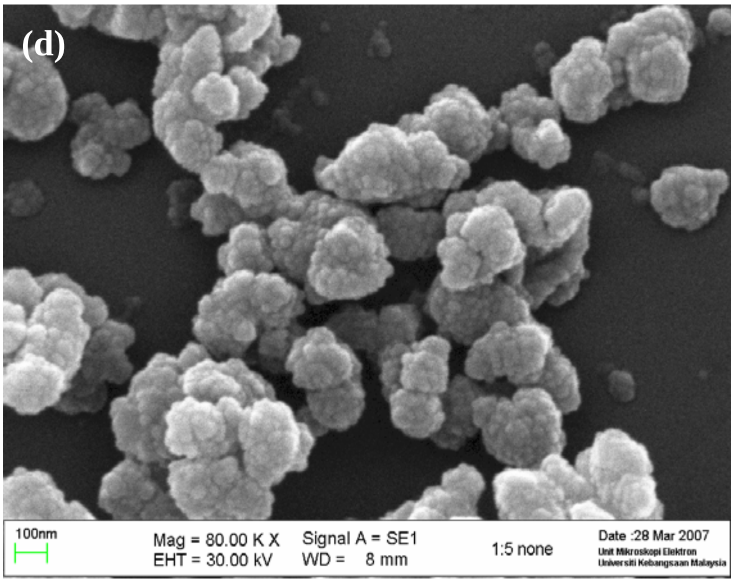

Figure 2: SEM images of thin films TiO_2 nanoparticles coated porphyrin with ratio of (a) 1:2, (b) 1:3, (c) 1:4 & (d) 1:5.

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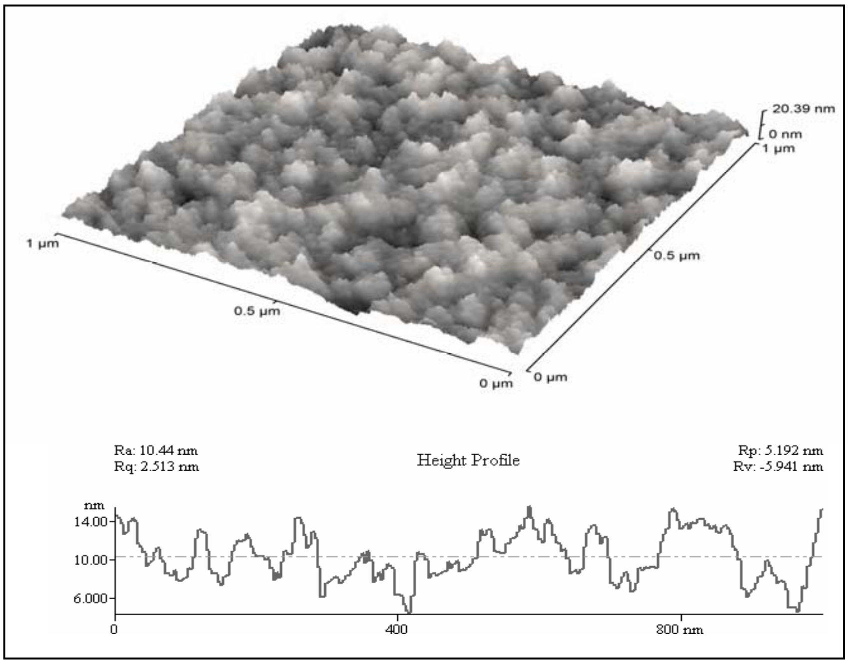
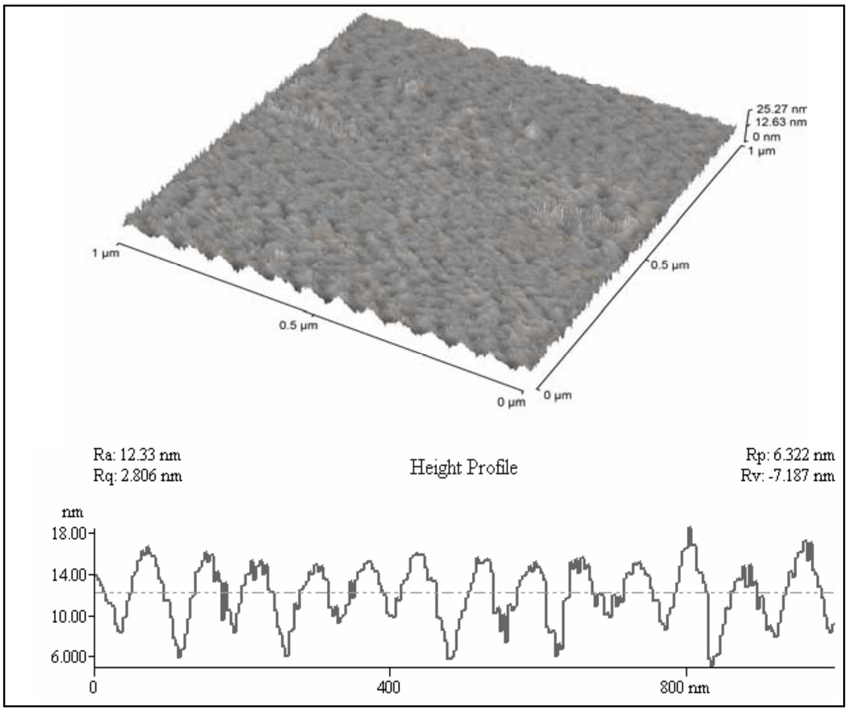


(a)



(b)

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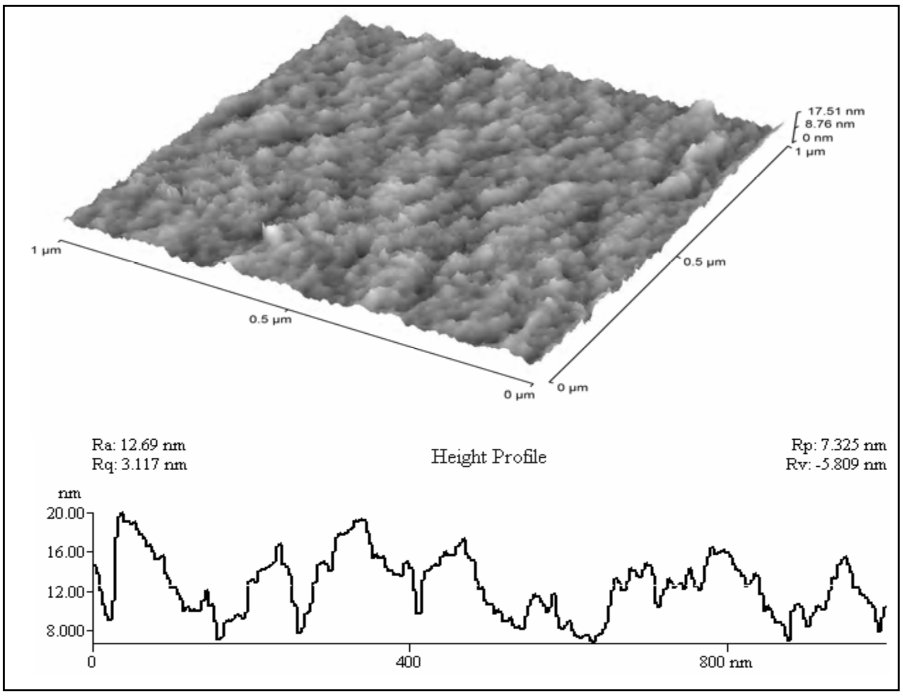

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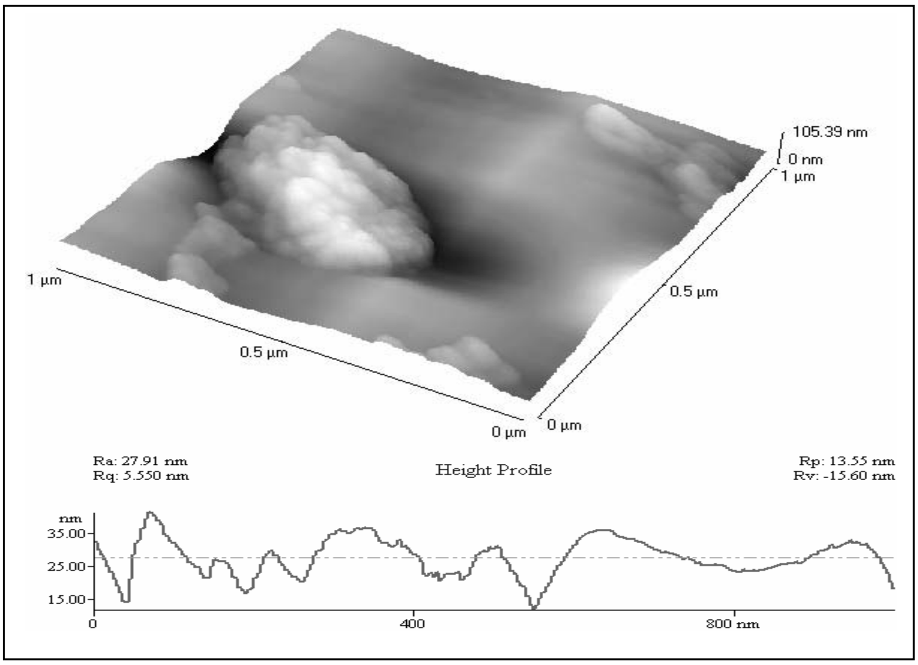

(d)

Figure 3: A three-dimensional images of thin films TiO_2 nanoparticles coated porphyrin with ratio of (a) 1:2, (b) 1:3, (c) 1:4 & (d) 1:5.

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Table 1: Summarized the average grain size and surface roughness of all thin films.

Thin film	Grain size (nm)	Roughness (nm)
TiO_2 coated porphyrin ratio 1:2	15.21	10.44
TiO_2 coated porphyrin ratio 1:3	20.35	12.33
TiO_2 coated porphyrin ratio 1:4	39.36	12.69
TiO_2 coated porphyrin ratio 1:5	50	27.91

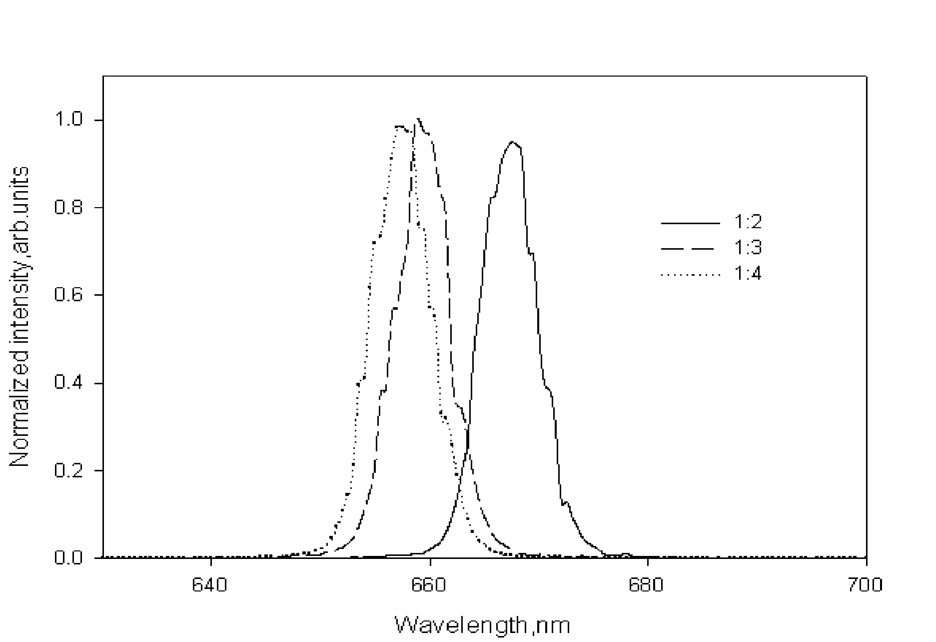

Figure 4: Emission spectra of thin films TiO_2 nanoparticles coated porphyrin with ratio of 1:2, 1:3 and 1:4.

Figure 4 compares the emission spectra of thin films TiO_2 nanoparticles coated porphyrin with ratio of 1:2, 1:3 and 1:4. It was found that, the emission spectra of the thin films are move to the blue shift with increasing amount of porphyrin volume. The emission spectra of thin film TiO_2 nanoparticles coated porphyrin with ratio of 1:5 cannot be recorded due to the higher of porphyrin volume. So, the thin film was not used for the sensing experiment.

When exposed to volatile organic compounds, thin films of TiO_2 nanoparticles coated porphyrin with ratio of 1:2, 1:3 and 1:4 undergoes change in their fluorescence emission spectra. Figure 5 (a), (b) & (c) shows emission spectra of the thin films in presence of volatile organic compounds that can be determined from their distinct emission peaks.

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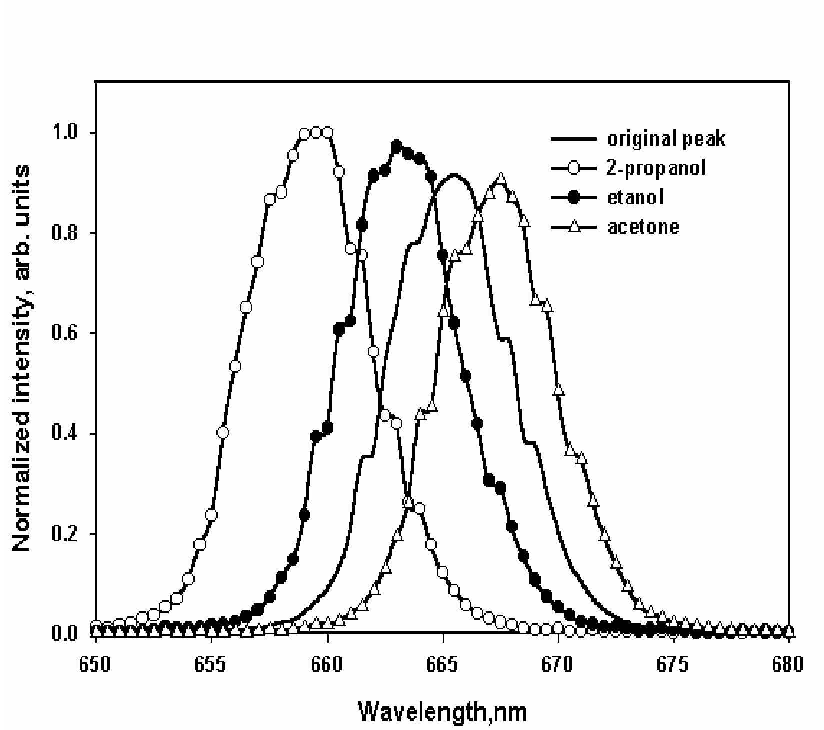
The changes emission peak of the thin films from the original either to red shift and blue shift depended on changes in electronic states between the ground state and excited state of the porphyrin molecules. This change could be due to the interaction of porphyrin molecules with volatile organic compounds molecules that causes rearrangement of the electrical dipole in the porphyrin compounds of the thin film [12]. A certain circumstance may be created by this activity is the changes on the energy gap between highest occupied molecular orbital (HUMO) and lowest unoccupied molecular orbital (LUMO). Thin films before interacting with VOCs molecules possesses a gap between these two orbital that determines its initial emission upon the excitation light due to the excited transition of the electrons to the ground state. When an excitation light source absorbed by the thin films molecules which interact with gas molecules, it may emits light at different wavelength peaks.

It was found that, the thin film of TiO_2 nanoparticles coated porphyrin with ratio of 1:2 shows more intensive interaction and exhibit good sensitivity than other thin films. The thin film has the smallest size; it will give the larger surface area and increase the interaction with VOCs. The sensing experiments using the same thin films were repeated for many times. It was found that no significant different of the results when it was repeated for many times. This means that the sensor has repeatability property and suitable to be use as sensing material for identify type of volatile organic compounds.



(a)

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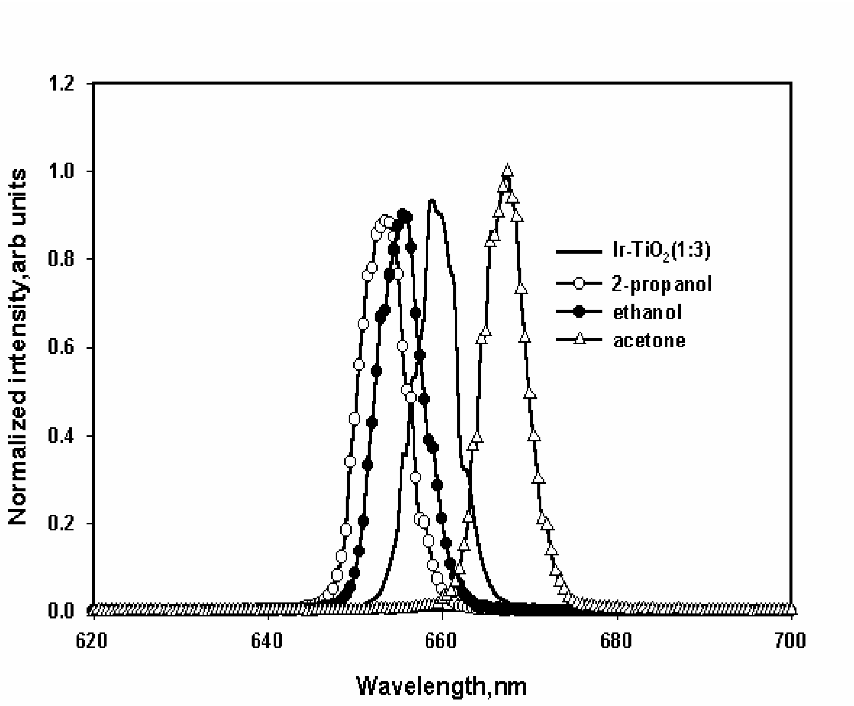
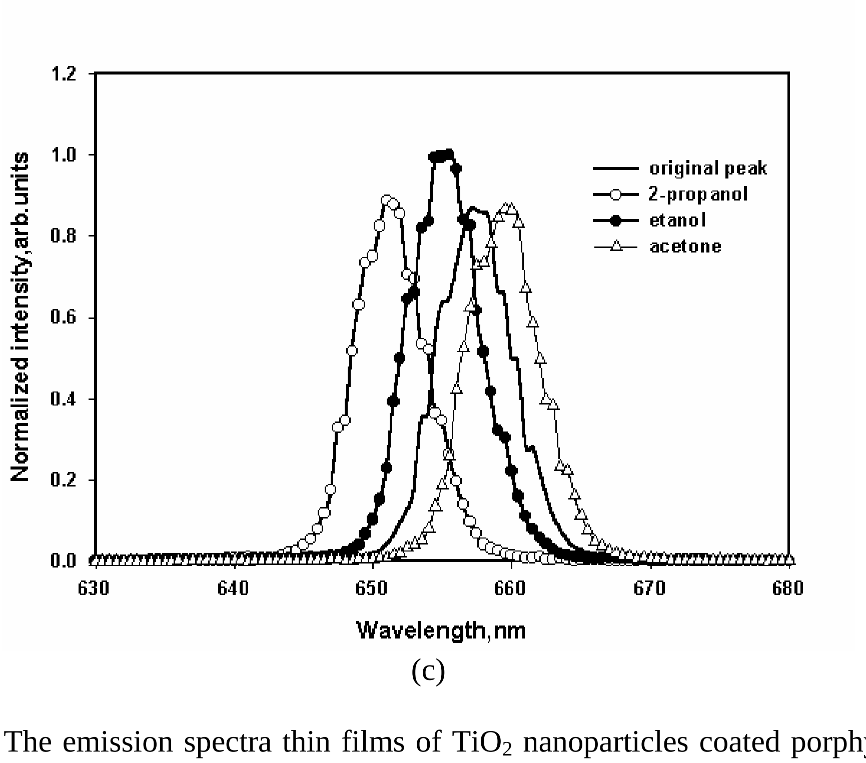


(b)



(c)

Figure 5: The emission spectra thin films of TiO_2 nanoparticles coated porphyrin with ratio of (a) 1:2, (b) 1:3, (c) 1:4 at the original peak and in present of 2-propanol, ethanol and acetone.

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(a) (b)

CONCLUSION

Thin films of TiO_2 nanoparticles coated porphyrin with ratio of 1:2, 1:3, 1:4 and 1:5 were succsessfuly fabricated. All thin films produce fluorescence spectra except for ratio 1:5. In presence of air and volatile organic compounds, thin films produced different emission spectra and ease for chemical identification process. The thin film of TiO_2 nanoparticles coated porphyrin with ratio of 1:2 produced more intensive interaction and exhibit good sensitivity than other thin films. Hence, it potentially be use as fluorescence gas sensor.

ACKNOWLEDGEMENT

This project has been carried out with support of Malaysian Ministry of Higher Education under Research University grant UKM-OUP-BTT- 26 / 2007.

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