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ETHANOL SENSING BEHAVIOUR OF TIO_2-PVK THIN FILMS

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ABSTRACT

The aim of these research is to investigate the effect of poly(n-vinylcarbozale) (PVK) additions on microstructures and ethanol sensing behaviour of TiO_2-PVK composites thin films. Five different ratios of TiO_2:PVK solutions were prepared for this experiment. Spin coating technique was employed for deposition of films. SEM and AFM characterization was used for microstructural characterization of the films. For gas sensing test the concept of variation in conductivity of the film was applied. All sensors were exposed towards nitrogen followed by ethanol vapour for gas sensing test. SEM and AFM micrographs indicated that the surface morphology of the films was governed by the amount of PVK additions. Sensor with 4 vol% of PVK was the only device exhibited gas sensing ability. The stability of the sensor reduced with the increment number of exposure cycle. These studies confirmed that composite between TiO_2 and PVK able to detect ethanol vapour at room temperature for certain amount of PVK.

Keywords: TiO_2; PVK; composite; sensing behavior;

INTRODUCTION

The development of sensitive and stable gas sensors to detect Volatile Organic Compounds (VOCs) has assumed a growing importance, owing to their wide range of application. Gas sensor with low operating temperature better selectivity and stability with optimization of other parameters is an issue of prime importance in the field of scientific research. Recent creation of inorganic/polymer composites having unique physical and chemical properties have attracted attention of many researcher to improve the gas sensor performance. Complementary behaviours obtained from the composites are thought could improve the disadvantages of both pure materials. In recent years, many studies on hybridization of conducting polymer and metal oxides as gas sensor have been reported in order to produce better sensors [1-6].

Sieviro et. al (2007) reported that TiO_2-CuPc sensor is more sensitive and stable compared to TiO_2 alone as methanol sensor [1]. For PANi/TiO_2 thin films, Tai et al.

(2007) reported that these sensors exhibit faster response, shorter recovery time and higher sensitivity when exposed towards NH_3 at room temperature compared to PANi thin film [2]. Besides, potential usage of p-polyaniline/n-TiO_2 heterojunction thin film as LPG gas sensor at room temperature had been reported by Dhawale et al. (2008) [3]. In addition TiO_2-PANi as ethanol sensor at room temperature has been investigated in our previous report [4]. These findings proved that composite between these two materials had produced better gas sensor especially at lowering the operating temperature. Based on these reported findings, microstructure, surface morphology and surface roughness are among the factors that greatly influence the sensing performance of the films. In order to have a greater understanding of composites materials, TiO_2 and PVK were chosen as new materials for ethanol detection. TiO_2 was chosen as composite materials because it was widely used as gas sensor, easy to synthesis and has low fabrication cost. As for PVK, it is believed to be suitable for gas sensing application due to its excellent electronic characteristics [7, 8]. Effect of PVK additions on microstructure of TiO_2 based thin films and its ability to detect ethanol was reported in this paper.

EXPERIMENTAL DETAILS

Titania solution was chemically synthesized using sol gel method [12]. The precursors of the solution were sodium chloride (KCl), titanium (IV) ethoxide (TEOD) and ethanol. KCl was first dissolved in 5 mL deionized water. Then 0.02 mL of KCl were added into 5 mL ethanol and stirred for 60 minutes. Finally, 0.085 mL TEOD was dropped wisely into the precursor solution. To stabilize the solution small quantity of acetylacetone was added. Then solution was constantly stirred for about 4 hours. Approximately 7 miliMolar of PVK solution was prepared by dissolving PVK powder in toluene. Hybridization process was done by mixing both solutions for 24hr. TiO_2 based solution was prepared to act as control sample and labelled as S_0. The PVK: TiO_2 solutions volume ratios were fixed at 1 vol%, 2 vol%, 3 vol% and 4 vol% and were labelled as S_1, S_2, S_3, and S_4 respectively. 0.015ml of the solutions was deposited on quartz substrates to fabricate thin films using spin coating technique. The rotation speed and time were fixed at 2000 rpm and 30 s respectively followed by drying process in air at room temperature. The procedures were repeated twice in order to get 3 layers of thin films. Finally, the comb shapes of Au electrodes were deposited on the surface of the film using sputtering technique for fabrication of sensor device (Figure 1). Surface morphological studies of the films were carried out using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

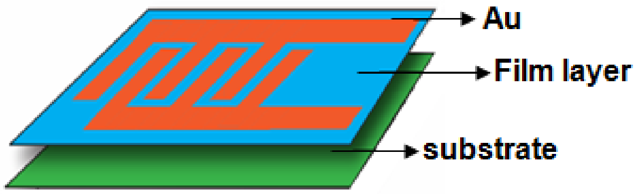


Figure 1: Schematic diagram of sensor device

For gas sensing test the concept of variation in conductivity due to interaction with analyte was applied and the measurement was performed at room temperature. The prepared device was put in a tight chamber and electrically connected to a power supply with constant voltage of 5 V. Nitrogen gas and ethanol vapour were alternately injected into the chamber for 3 minutes each and voltage variation across the sensor device during measurement was monitored by computerized data acquisition system (Figure 2). The devices exposure towards the gas was repeated for four cycles in order to investigate the stability of the sensor.

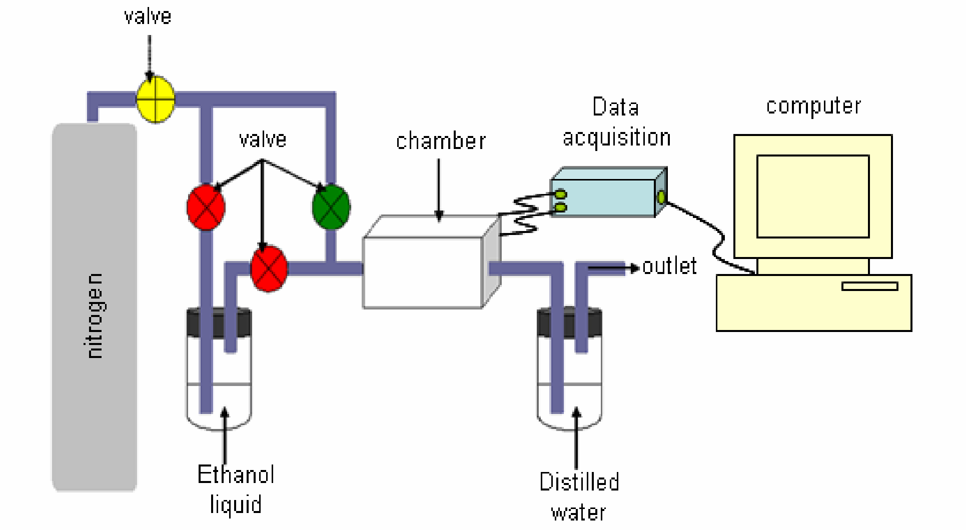


Figure 2: Sensor measurement setup

RESULTS AND DISCUSSION

SEM images for all films are presented in Figure 3. Film with no PVK addition showed agglomerated TiO_2 rich particles uniformly distributed over the surface of S_0. The TiO_2 particles has diameter in the range of 100 to 200 nm. Due to agglomeration, surface of TiO_2 film without PVK addition appears extremely rough. In contrast, composites films exhibited smoother surface. However, close observation revealed the additions of PVK systematically altered the microstructure and surface morphology of the films, from relatively smooth and even surface (S_1) to porous and uneven surface of samples S_4. Sample S_4 was also observed to exhibit the largest average pore diameter compared to other composite films. Cross-sectional SEM images for composite samples revealed that the films thicknesses are greatly influenced by the additions of PVK with S_4 is the thickest film, as a result from highest viscosity of solution (insets in Figure 3).

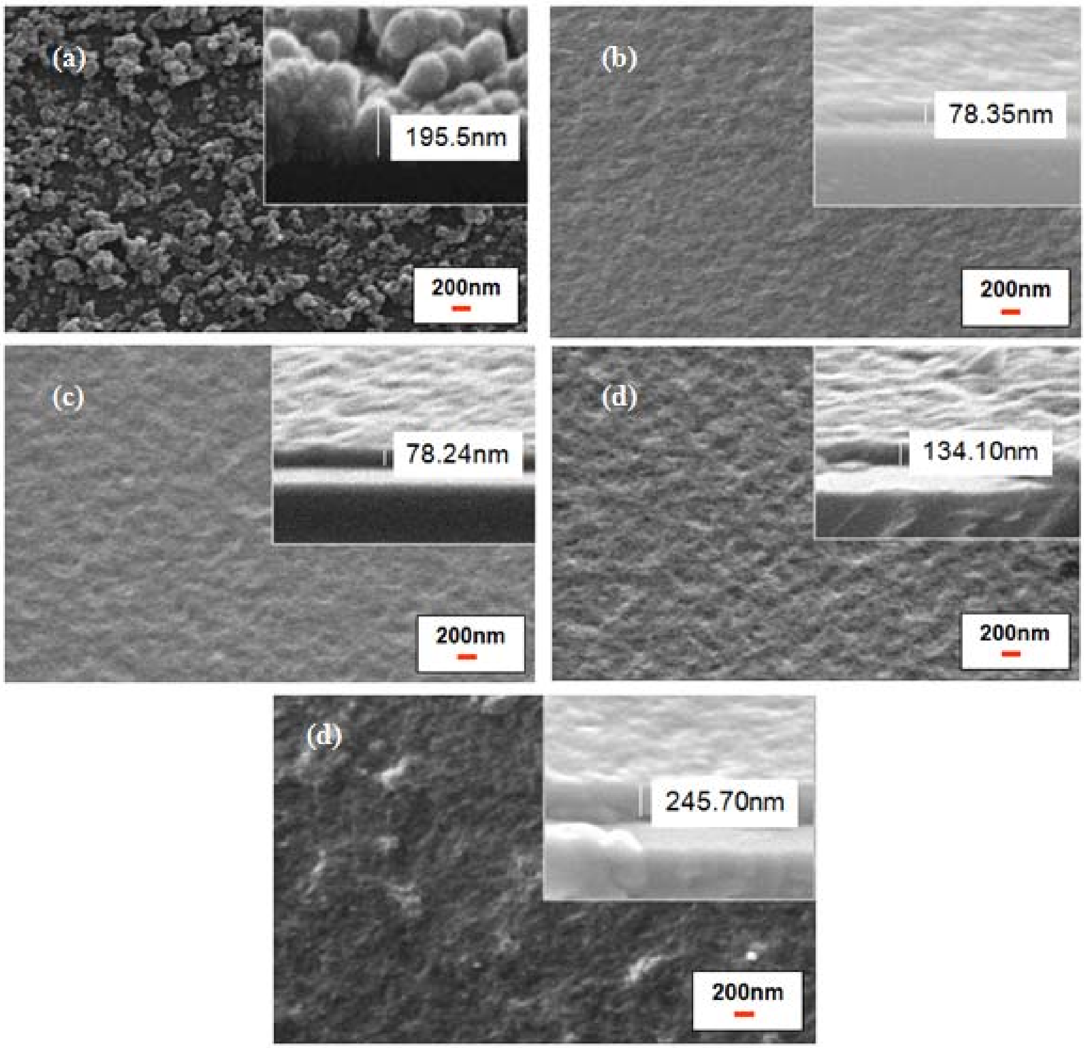
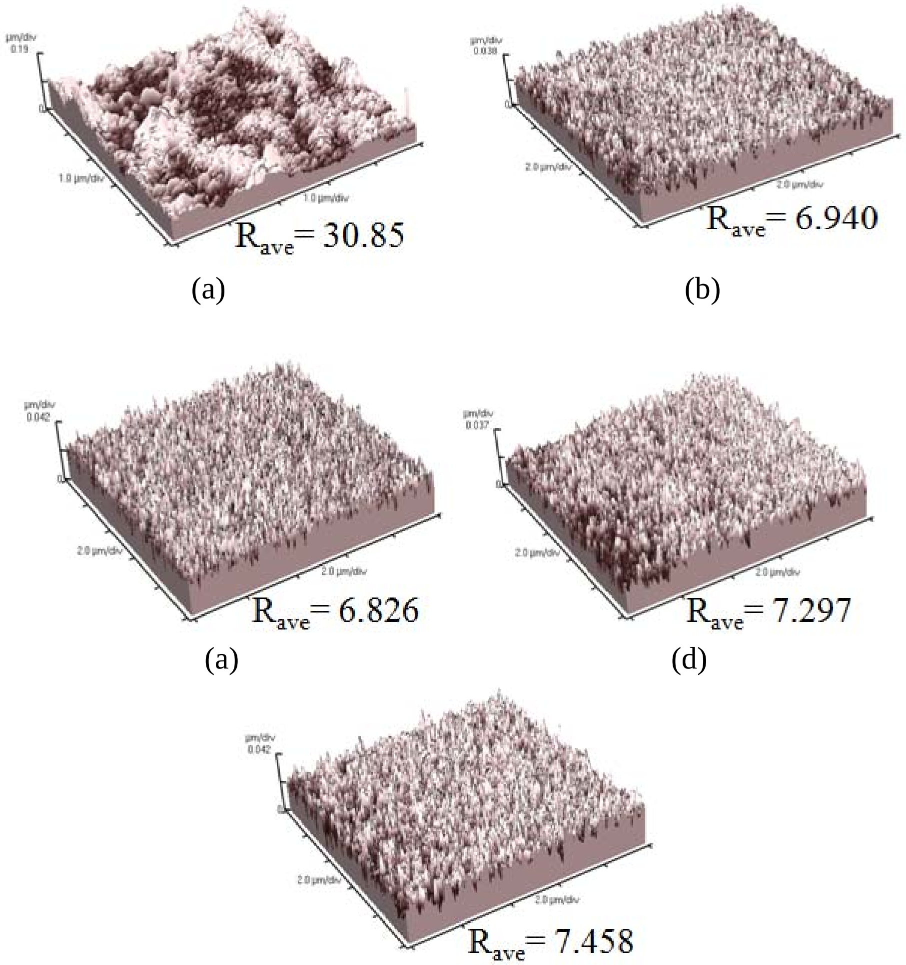


Figure 3: SEM micrograph for (a) S_0, (b) S_1, (c) S_2, (d) S_3 and (e) S_4

The AFM characterizations strongly support the findings from SEM micrographs (Figure 4) with S_0 have the highest average roughness (R_{ave}) of 30.85nm. As for the composites films, it was found that the average roughness for the whole area gradually increased with the increased amount of PVK in the starting charge. Since AFM describes the surface morphology of materials, more closely packed particles will results in low roughness. However, as the spacing between the particle increases due to higher PVK content, the surface morphology was translated as uneven, indicated by minor increment in roughness. Despite having approximately similar R_{ave} value, close investigation on samples S_3 and S_4 revealed that S_4 has more valleys which are broader and deeper than S_3 (Figure 5).



(a) (b)

(a) (d)

(e)

Figure 4: AFM images for (a) S_0, (b) S_1, (c) S_2, (d) S_3 and (e) S_4

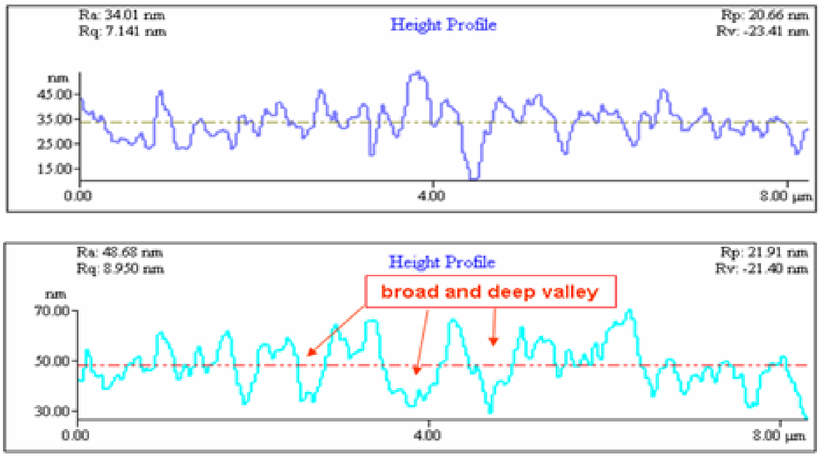
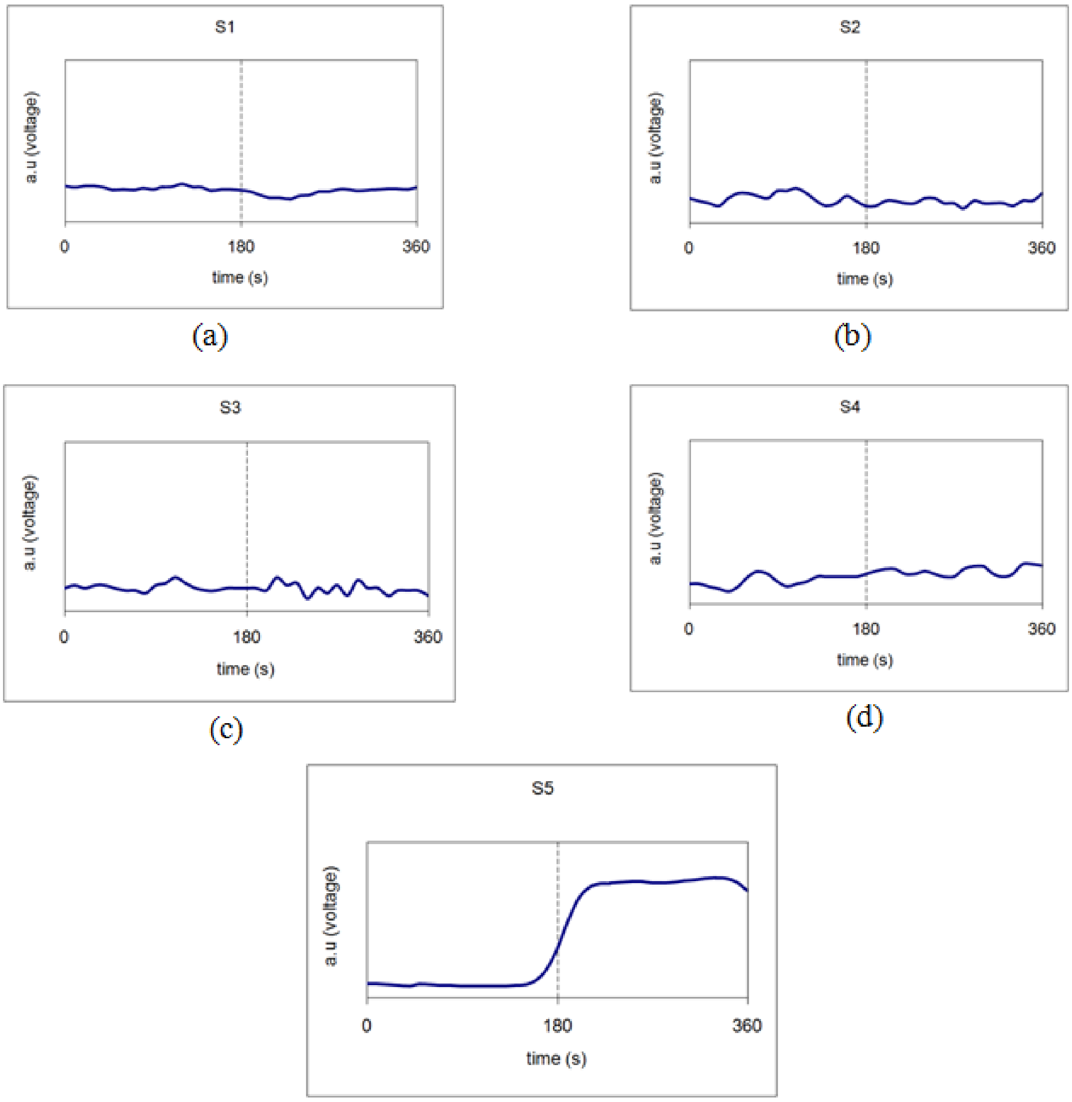


Figure 5: AFM cross section images for (a) S_3 and (b) S_4



(a) (b) (c) (d) (e)

Figure 6: Sensor (a) S_0, (b) S_1, (c) S_2, (d) S_3 and (e) S_4 response towards ethanol vapor at room temperature

Figure 6 shows the time dependence plot of the sensor voltage during ethanol sensing for all samples at room temperature. It was observed that sensors S_0, S_1, S_2 and S_3 showed no voltage variation when exposed towards nitrogen and ethanol vapour. However sensor S_4 showed significant voltage increment in ethanol ambience. This result was contributed by the presence of porous film with broad and deep valleys in S_4 enables better and longer entrapment of ethanol molecules. These entrapments allowed physisorption process between gas molecules and film to take place. As a result, the

PVK chains started to swell and consequently increased the electronic conduction path and thus contribute to higher resistance. These swelling processes may also break some of the electronic conduction path [9]. Sufficient period of physisorption process lead to chemisorption process which impedes electron delocalization thus increased the film resistance [10]. Increments of films resistance from both mechanisms during ethanol exposure was translated as higher response voltage. Moreover the rough surface of S_4 offered higher surface-to-volume ratio which allowed greater contact area. Even though S_0 have greater surface roughness and allowed better analyte entrapment compared to S_4, it couldn't give positive response towards the test gas because metal oxides require high temperature to operate effectively [11].

In order to check the sensing stability of sample S_4, the sensor was further tested for four cycles under the same condition. It was found that after 4 cycles the device still responded to the gas variation (Figure7). However, the sensor exhibited severe shift and failed to return to the initial baseline voltage.

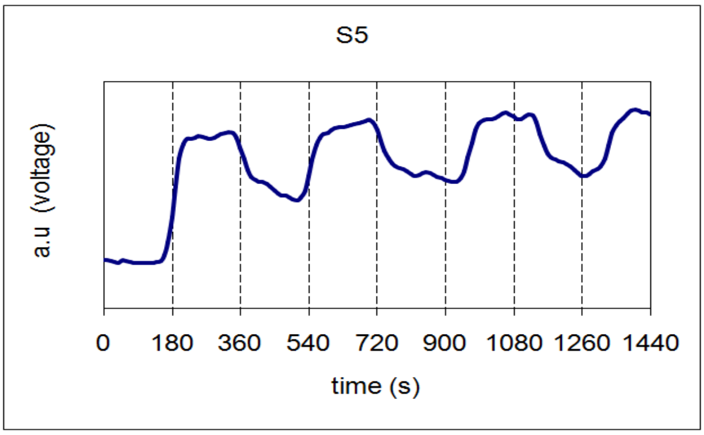


Figure 7: Sensing stability of S_4

CONCLUSION

A series of TiO_2-PVK composites has been prepared using wet chemical method. SEM and AFM studies shows that PVK amount have a strong effect on the surface morphology and porosity level of the films. Addition of 4 vol% PVK produces rough and porous film which exhibit reasonable sensing behaviour towards ethanol vapour. Two possible mechanisms namely physisorption and chemisorption between ethanol molecules and film simultaneously influence the resistance variations in the film. Most importantly, this study confirmed that composites of TiO_2 and PVK are able to detect ethanol vapour room temperature at certain amount of PVK. In addition, new material to detect ethanol vapour with low cost and easy fabrication was successfully synthesized.

ACKNOWLEDGEMENT

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