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New Hybridization Approach of Titanium Organometallic: PANi Thin Films as Room Temperature Gas Sensors

(Pendekatan Baru Penghibridan Filem Nipis Organologam Titanium: PANi Sebagai Pengesan Gas Suhu Bilik)

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ABSTRACT

The aim of this research was to investigate the ability of organometallic titanium-PANi hybrid materials as gas sensor at room temperature. To form the hybrid materials, commercially available polyaniline (PANi) powder were directly added into organometallic titanium sols which was synthesized using the sol gel method. The composite films were prepared via spin coating technique followed by electrode deposition for sensors fabrication. Five different organometallic titanium:PANi ratios namely 1 wt% to 5 wt% of PANi were prepared for this experiment. For gas sensing test, all samples were exposed to ethanol vapour. The sensing mode is based on the variation in the electrical conductivity due to the interaction between the gas molecules and the film. It was observed that the composite sensors required appropriate ratio to exhibit optimum sensing properties. This finding proved that the hybridization process is successful and offered much cheaper and easier method for fabrication of room temperature gas sensor.

Keywords: Ethanol; nanocomposite; PANi; thin film; TiO_2

ABSTRAK

Kajian ini dijalankan untuk mengkaji keupayaan bahan hibrid organologam titanium-PANi sebagai pengesan gas pada suhu bilik. Untuk penghasilan bahan hibrid, serbuk polianilina (PANi) komersial dicampurkan secara terus ke dalam sol organologam titanium yang disintesis menggunakan teknik sol-gel. Filem komposit telah disediakan menggunakan kaedah salutan berputar diikuti dengan pemendapan elektrod untuk fabrikasi sensor. Lima nisbah organologam titanium: PANi yang berbeza iaitu 1 wt% sehingga 5 wt% kandungan PANi telah disediakan untuk kajian ini. Bagi tujuan pengujian gas, kesemua sampel telah didedahkan kepada wap etanol. Mod pengesanan yang digunakan adalah berdasarkan variasi kekoduksian elektrik akibat interaksi antara molekul gas dan filem. Didapati, pengesan komposit memerlukan nisbah-nisbah tertentu untuk menunjukkan sifat pengesanan yang optimum. Hasil kajian membuktikan proses hibrid yang dilakukan dalam kajian ini berjaya menghasilkan pengesan gas pada suhu bilik dengan kos yang lebih murah dan kaedah penyediaan yang mudah.

Kata kunci: Etanol; filem nipis; nanokomposit; PANi; TiO_2

INTRODUCTION

Controlling and monitoring ethanol is important in some fields such as environmental monitoring, controlling some chemical process like fermentation and testing alcohol levels of drivers. For that, reliable sensor had been developed. Metal oxides based gas sensors were the earliest discovered and most widely applied sensors since they can detect a variety of gasses with high sensitivity, simple design, cost effective, easy implementation and compatible with microelectronic system (Hongyan et al. 2006; Korotchenkov et al. 1999; Tang et al. 1995). Up to now, many efforts have been done in order to improve the performance of these sensors especially in gas selectivity, working temperature and power consumption. One promising approach is the application of organic materials. Exploitation of organic materials such as conducting polymers as gas sensor had shown very promising result for gas sensors applications. Conducting polymers possess good tuneable electrical conductivity, operate at room temperature and are organic electrochromic materials with chemically active surface (Bai & Shi 2007; Javadpour et al. 2009; Manoj et al. 2005). However they are chemically sensitive, have poor mechanical properties and lack of selectivity, thus poses a processibility problem. For that, studies on hybrid materials have been done and the result proved that complementary behaviours obtained from hybridization process from both materials improved the disadvantages of pure materials (Desphande et al. 2009; Dhawale et al. 2008; Geng et al. 2007; Jumali et al. 2009; Savage 2009; Tai et al. 2007). Using the same approach, we have designed a new hybrid materials, a more cost effective and simpler method for gas sensor fabrication.

This paper reports on the ability of hybrid organometallic titanium and polyaniline (PANi) for ethanol detection at room temperature.

EXPERIMENTAL METHOD

The gas sensor of the present study was designed and fabricated to operate as conductometric gas sensor. It is made up of two important physical components: sensitive layer which interacts with the analite and tranducer which converts the chemical sensor to an electrical sensor. The active layers of sensor were composite of organometallic titanium and polyaniline. Organometallic titanium solution was prepared via sol gel method. The starting materials of the solution were sodium chloride (KCl), titanium (IV) ethoxide (TEOT) and ethanol. KCl was first dissolved in 5 mL of deionized water. Then 0.02 mL of dissolved KCl were added into 5 mL ethanol and stirred for 60 min. Finally, 0.085 mL TEOT was dropped into the precursor solution. Small amount of acetylacetone was added to stabilize the organometallic titanium solution.

To form the hybrid materials, commercially available polyaniline (PANi) powders were directly added into organometallic titanium sols. Five different composites solution with organometallic titanium: PANi ratios varied from 1 wt% to 5 wt% of PANi were prepared for this experiment. Composite thin films were prepared through spin coating technique on 25 mm × 25 mm quartz substrate. Organometallic titanium and PANi based films were also prepared as controlled samples. The prepared samples are summarized in Table 1. Surface morphological studies of the films were carried out using scanning electron microscopy (SEM). Gold sputtered interdigital electrodes were deposited on the top of the films surface to form a transducer. The structure of the device is shown in Figure 1.

For gas detection system the film was put in a chamber and electrically connected to a power supply with a constant voltage of 5 V. Electrical measurement was conducted at room temperature and flow through technique was used to expose the sensor towards alternating of N_2 gas and ethanol vapour. The gas exposure time was fixed at 3 min for each pulse of the test gas and followed by nitrogen exposure for recovery process of the sensor. The electrical response (voltage) during the experiment was monitored by a computerized data acquisition system. The sensor responses were displays in real time and save for off-line processing and analysis.

TABLE 1. Summary of prepared samples

Sample	Ratio (Organometallic titanium sol:PANi)	Organometallic titanium sol (mL) (1 mL ~ 0.01 g)	PANi (g)
S_1	1:0	3.00	0.00
S_2	0:1	0.00	0.03
S_3	1:1	3.00	0.03
S_4	1:2	3.00	0.06
S_5	1:3	3.00	0.09
S_6	1:4	3.00	0.12
S_7	1:5	3.00	0.15

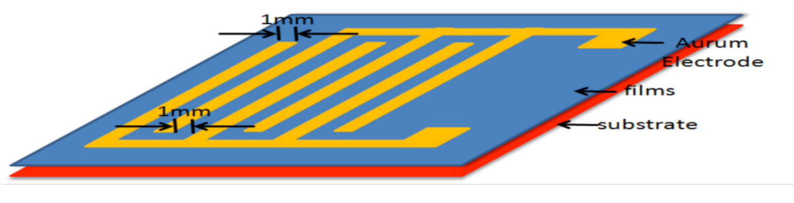

FIGURE 1. Sensor device

Results and Discussion

The microstructure of the films were characterized by SEM and shown in Figure 2. It can be seen that the organometallic titanium based film consist of agglomerated particles distributed on the surface (Figure 2(a)) while the PANi film had relatively flat and smooth surface morphology over a large area (Figure (2b)). For composites materials, the figure shows that the amount of PANi influenced the microstructure and surface properties of the films. As the amount of PANi was increased the small agglomerated structure tend to accumulate and form a network chain at the outer surface. This alteration can be seen clearly in samples S_3 and S_4. Besides that, the particles size became smaller and the films surface start to have porous structure (samples S_5 and S_6). However, this morphology changed with the highest amount of PANi. It clearly showed that the agglomerated structure changed to overlap flakey properties (Sample S_7).

The response of the devices towards test gas is shown in Figure 3. The results were expressed in terms of relative change in voltage as a function of time. Obviously, different surface morphology of the samples presented a different trend of the gas response. It was observed that both controlled samples showed no voltage variation when exposed towards nitrogen and ethanol vapour. PANi is a well known gas sensor at room temperature but in our research PANi alone was not responsive towards the test gas. This result was expected due to the smooth and flat surface which were not suitable for gas detection.

Even though organometallic titanium films have good surface morphology for gas detection, no significant changed was noticed in the film because this material is not a sensitive material for gas detection. Besides, to the best of our knowledge no research has been done on these materials. The main purpose of utilizing organometallic titanium in this research was to develop a better surface morphology for PANi so that it can enhance the gas detection. For composite materials, samples with small amount of PANi remained insensible towards the test gas. Appreciable changed was noticed in the S_4 sample. However the baseline drops off is clearly seen. Similar patterned was also observed for film with highest amount of PANi which belongs to sample S_7. These circumstances maybe due to incompatible surface morphology of the films. Samples S_5 and S_6 showed voltage increment within a minute indicating that these samples were sensitive towards the ethanol. We believe that surface morphology is one of the main factors that confered the good response because the presence of porous structure and rough surface of the films offered higher surface-to-volume ratio which allowed greater contact area between films and gas molecules. The plausible mechanism seems to fit with our observation maybe due to protonation and deprotonation of PANi as proposed by Deshpande et al. 2009. Another possible mechanism is because of the swelling of PANi chain (Arshak et al. 2007).

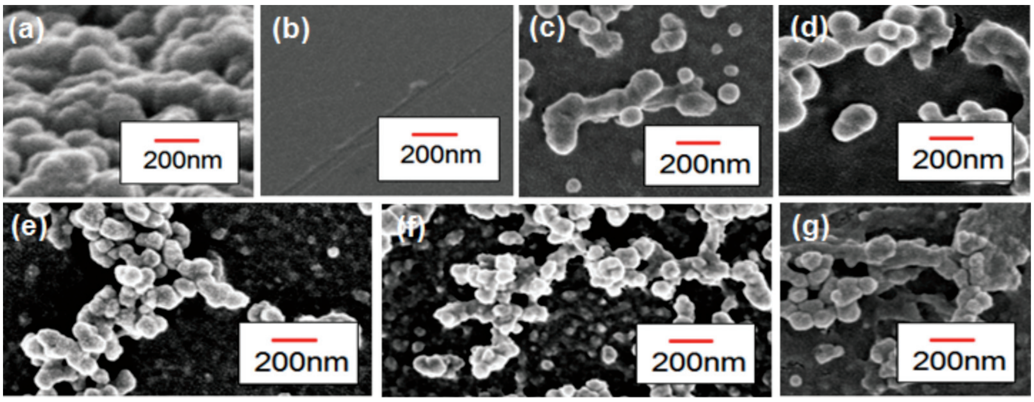

FIGURE 2. SEM images of (a) S1, (b) S2, (c) S3, (d) S4, (e) S5, (f) S6 and (g) S7

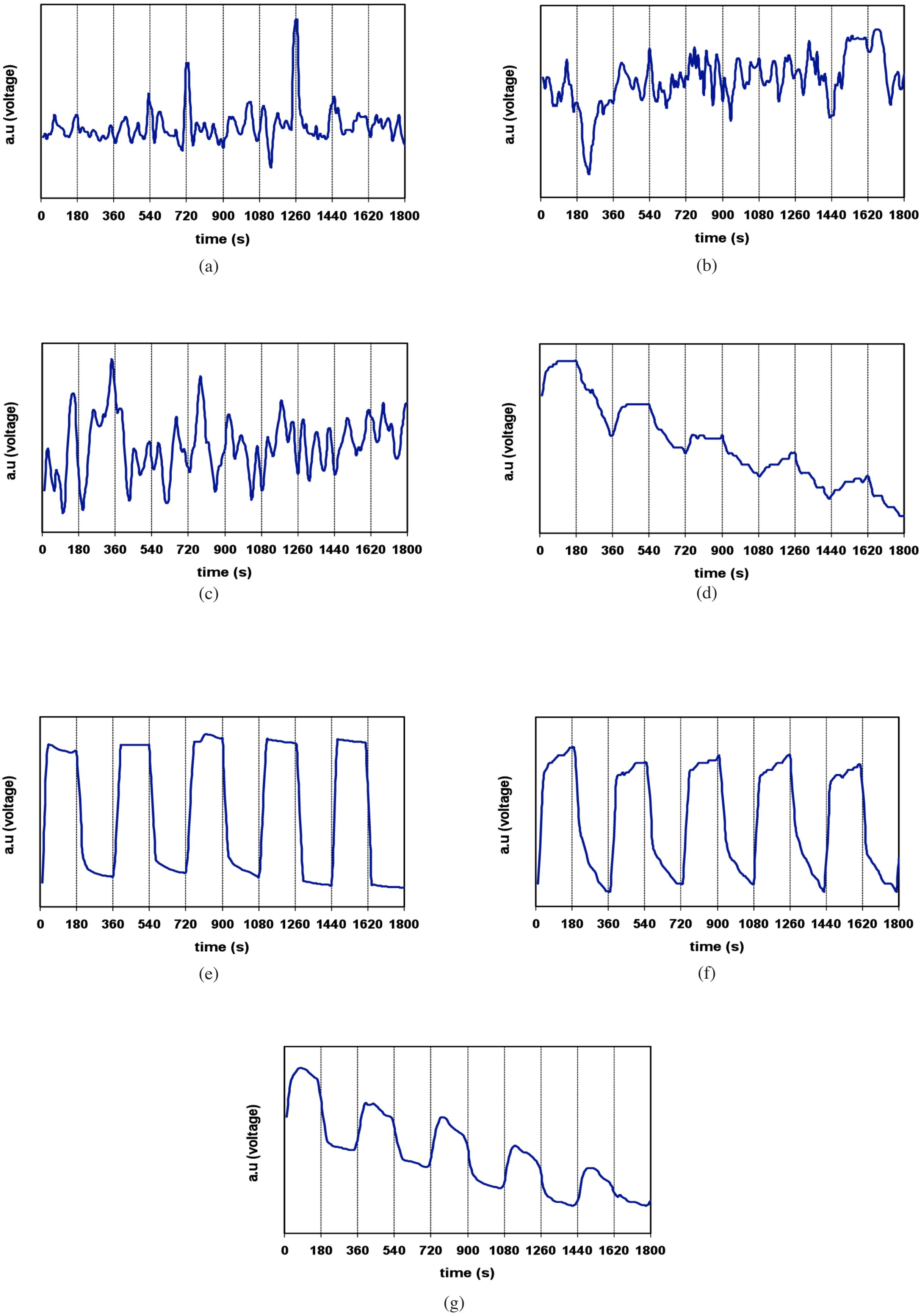

FIGURE 3. Sensor response of (a) S1, (b) S2, (c) S3, (d) S4, (e) S5, (f) S6 and (g) S7 towards ethanol vapor at room temperature

CONCLUSION

A series of organometallic titanium-PANi composites has been prepared using wet chemical method. SEM studies showed that PANi amounts have a strong effect on the surface morphology and porosity level of the films thus contributed to different finger prints of sensor response. In addition, a new material to detect ethanol vapour with low cost and easy fabrication was successfully synthesized.

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