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Detection of Ethanol Vapours Using Titanium Dioxide (TiO_2) Catalytic Pellet by Conventional and Modified Sol Gel Dip-Coating Method

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ABSTRACT

The present investigation deals with the development of ethanol-vapour-sensing materials coated with the semiconducting oxide TiO_2. Thick films of anatase TiO_2 were deposited using the sol-gel dip-coating technique on alumina substrates by conventional alkoxide sol and modified sol added with Degussa P-25 as the sensing medium. It was shown that crystallised TiO_2 anatase was obtained at the annealing temperature of 500ºC. The fabricated TiO_2 sensors exhibited highest sensitivity at the sensing temperature of 350 ºC. Sensitivity towards the ethanol vapour was further increased with UV light effect. The enhancement of the sensitivity of the modified catalytic pellet can be explained by the crystallite of anatase TiO_2 and the effect of the photocatalytic of TiO_2. The high sensitivity of the TiO_2 film deposited with modified sol revealed that the modified sol could be a new alternative in the development of a TiO_2 ethanol sensor.

Keywords: Dip coating, Sol gel, TiO_2, VOCs sensor

INTRODUCTION

Metal-oxide semiconductor (MOS) gas sensors have been extensively studied to improve the sensing properties towards combustible and toxic gases. The advantages of the MOS are their low cost, easy implementation and reliability (Ruiz *et al.,* 2004). Among the metal oxides, TiO_2 is one of the mostly investigated materials in a wide range of applications e.g. in the field of optics, electrical insulation, solar cells, antibacterial coatings and polluting gas sensing (in the anatase phase) (Taurino *et al.*, 2004).

Homoudi *et al.* (2007) reported that the TiO_2 semiconductor is markedly inert and has stable a crystalline structure. Anatase and rutile are different in the opacity and physical properties. Anatase phase is an n-type

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semiconductor and its resistance has been found to decrease on reduction with gases. On the other hand, rutile phase exhibits p-type conductivity. An anatase TiO_2 thick film was developed for the alcohol sensor that operated at 400 and 500ºC (Garzella *et al.,* 2000). The improvement of the TiO_2 as an effective ethanol sensor was carried out in this research.

TiO_2 can be obtained by different deposition techniques such as chemical vapour deposition (CVD), sputtering and sol-gel (W. Chen *et al.*, 2004; Garzella *et al.*, 2000; Zhang, Zhou, & Lei, 2005). Sol-gel techniques were studied in this research due to the simple low-cost synthetic route, excellent compositional control and the feasibility of producing sensing film on the pellet shapes when dip coating is used (Mohammadi & Fray, 2007). In this research, the conventional sol and modified sol for the fabrication of a good ethanol sensor based on sensitivity was carried out. Other than that, the effect of UV light on the sensitivity of the sensors was studied to understand the photocatalytic properties of TiO_2.

METHOD

In this work, the conventional TiO_2 sol preparation is adapted from Takahashi *et al.* (Takahashi & Matsuoka, 1988). A 0.5 M solution of titanium isopropoxide (TTIP) in isopropanol was prepared and subsequently Diethanolamine (DEA) with molar ratio of DEA/TTIP = 4 was added to the solution. The solution was stirred at room temperature for 2 hours and subsequently water with molar ratio of H_2O/TTIP = 2 was added drop by drop under vigorous stirring. A clear sol was obtained, sealed and left for ageing for at least one day. The modified TiO_2 sol was adapted from Balasubramanian *et al.* (Balasubramanian *et al.,* 2004). The modified sol-gel solution was prepared by addition of a calculated amount of TiO_2 Degussa P-25 to the sol solution. The powder was added slowly with vigorous stirring to prevent the formation of agglomerates. A thick, white, viscous solution was obtained.

The substrate used is the alumina disk pellet with diameter 2cm and thickness 2mm. The alumina disk substrate was prepared by pressing 1.5g of advanced alumina powder (Sumitomo Chemical AA05) with a hydraulic press. The substrate was dried and sintered at 1200ºC for 4 hours. The substrate was rinsed with DI water and dried in an oven at 100ºC for 4 hours before it was deposited by TiO_2. The sensing film was deposited on the substrate by dip coating in conventional and modified sol for 15 seconds. The coated pellet was dried for 10 minutes in ambient temperature. The completely dried pellet was then dipped in sol for 15 seconds again. The dip-coating procedure was repeated 5 times to obtain 5 layers of coating. The selection of 5 layers of TiO_2 coating was based on the literature that 5 layers of TiO_2 gave a better response in sensing hexanol (Katarzyna *et al.,* 2005). The dried, coated pellet was then calcined at 400ºC, 450ºC and 500ºC respectively. The synthesised metal oxide gas sensor was characterised by Scanning Electron Microscope SEM (JSM-6460 LV) and X-ray Diffraction (Philips PW 1710).

The DC resistance of the pellet sensor was measured using the multimeter (Keithley 6517A) with an applied voltage range of 5V in a laboratory-fabricated experimental setup as shown in Fig.1. Mass flow controllers were used to control the flow rate of the purified air into the gas chamber and to evaporate the ethanol from the water bath. The ethanol vapour concentrations were determined using an offline gas chromatograph. An external heater was used to heat and control the working temperature of the sensors. The catalytic sensor was examined by measuring

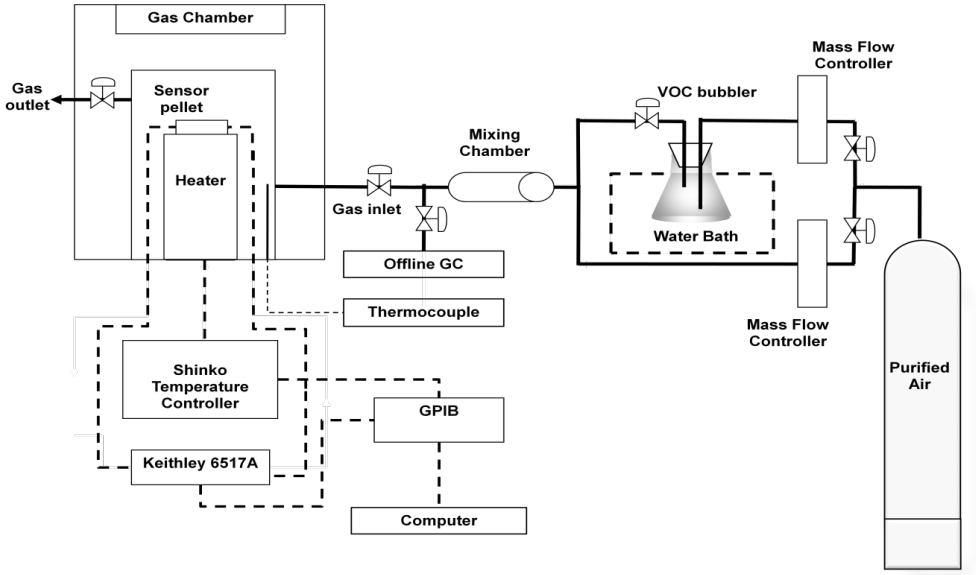

Fig.1: Schematic of the gas sensor testing measurement rig

electrical resistance in the air and followed by the ethanol vapour flowing through the gas chamber within the operating temperature range of 100°C to 400°C. Ethanol sensitivity was defined as $S=R_A/R_V$, where R_A and R_V are the electrical resistance of the pellet in air (ohm) and in ethanol vapour (ohm) respectively (Ang *et al.,* 2011). The sensitivity of the pellets towards 1000ppm ethanol at different operating temperatures was performed. The effect of the UV light on the gas sensor sensitivity was studied accordingly.

RESULTS AND DISCUSSION

Fig.2 shows the XRD patterns of the TiO_2 catalytic pellet with conventional sol (CO5) and modified sol (MO5) annealing at 500°C. XRD was used to study the crystalline structure and phases of TiO_2 catalytic pellet. The observed peaks in Fig.2 could be indexed based on the TiO_2 anatase phase structure. The peak at 25.4° corresponds to the TiO_2 anatase (1 0 1) reflection and other small peaks at 37.7° and 47.8° correspond to (0 0 4) and (2 0 0) respectively (Al-Homoudi *et al.*, 2007). There is no significant evidence for the rutile phase of TiO_2 in the XRD patterns. The transition from anatase to rutile required higher annealing temperature. The annealing temperature of 500°C was suitable to achieve complete anatase of TiO_2 (Y. Chen & Dionysiou, 2006; Kermanpur *et al.,* 2008), which is an n-type semiconductor that is suitable for gas-sensing application.

According to Senguttuvan *et al.* (2007), gas-sensing properties of a metal oxide strongly depend on the gas' morphological features. A high surface area facilitates the chemisorptions process by increasing the adsorption and desorption rates (Alterkop *et al.,* 2003). Fig.3(a) and Fig.3(b) show the SEM micrograph of TiO_2 films as grown and after annealing at 500°C by conventional sol and modified sol respectively. Fig.3(a) clearly shows that the surface of film prepared without Degussa P-25 in the sol is smooth with less grain formed whereas the surface of the film prepared by modified sol exhibit a lot of clusters or grains due to the incorporation

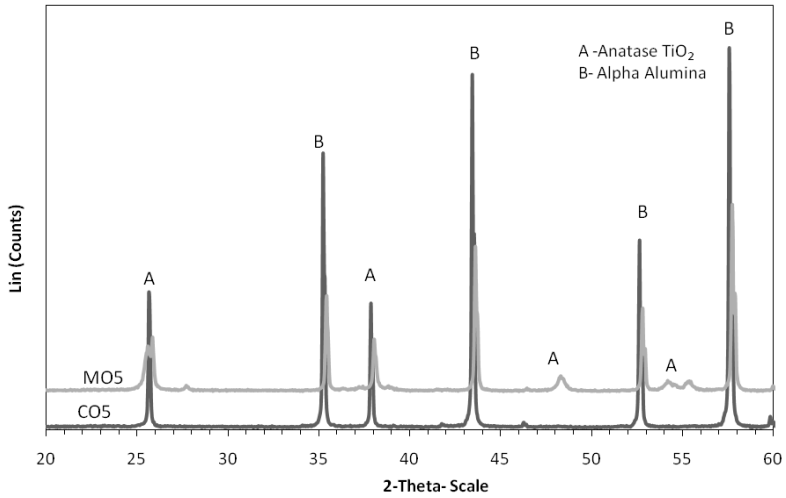

Fig.2: XRD patterns of TiO_2 pellet with conventional sol (CO5) and modified sol (MO5) annealing at 500°C

of P-25 powder in the films (Chen & Dionysiou, 2006). More grains tend to give a higher surface area for the chemisorptions during the detection of ethanol.

Fig.4 shows the sensor resistance in the air as a function of operating temperature for the catalytic pellet CO5 and MO5. Pellet CO5 gives higher resistance, reflecting that the grain (cluster of crystallites from P-25 particles and alkoxide hydrolysis) growth in CO5 is lower. When the grains formed are fewer, the surface area that facilities the chemisorptions process will be reduced and the electrical conductivity will be reduced (Ruiz *et al.,* 2004). When O_2 is adsorbed onto the TiO_2 surface, it traps electrons from the TiO_2 material due to the strong electronegativity of the oxygen atom to produce the negatively charged and chemisorbed oxygen adsorbates as shown in the reaction (1) below. When the concentration of electrons in the n-type semiconductor is decreased according to (1); the resistance of the material increases.

$$O_2 + e^- \rightarrow O^-_{2\,(ads)} \tag{1}$$

When ethanol vapour is introduced to the TiO_2 catalytic pellet, Alessandri *et al.* (2007) propose that the interaction of ethanol vapour with the surface chemisorbed oxygen can take place in the following surface reactions (2) and (3). Therefore, after the ethanol vapour is introduced to the sensor pellet, the resistance of the pellet decreases due to the increment of the electrons from the reaction (3).

$$C_2H_5OH_{(g)} + O_2 \rightarrow CH_3CHO + H_2O \tag{2}$$

$$C_2H_4O + O^-_{ads} \rightarrow CO_2 + H_2O + e^- \tag{3}$$

The response sensitivity for the catalytic pellet coated with modified sol and conventional sol is shown in Fig.5. The sensitivity for the MO5 is higher than for the CO5. The maximum

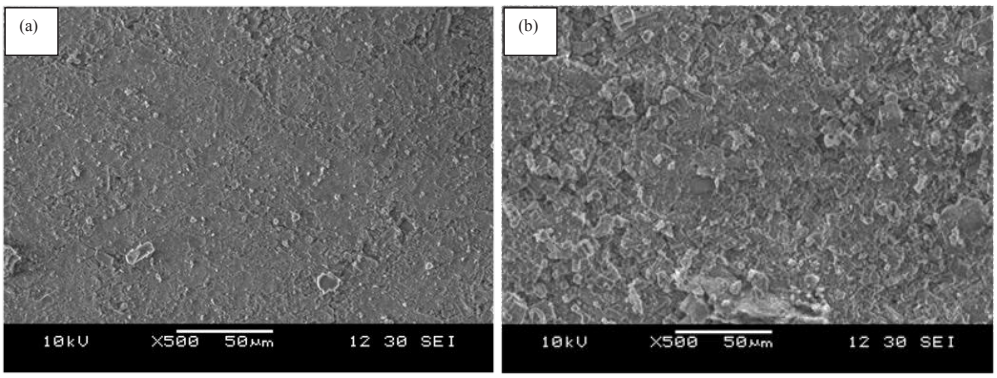

Fig.3: SEM micrographs of the TiO_2 catalytic pellet of (a) Conventional Sol (b) Modified sol over the calcination temperature of 500°C (bars: (a) and (b) 1micron)

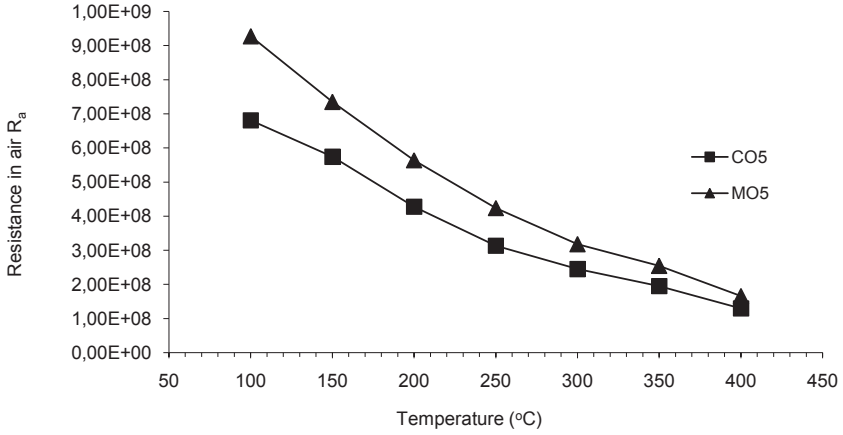

Fig. 4: Sensor resistance in air as a function of operating temperature for catalytic pellet by conventional sol (CO5) and modified sol (MO5)

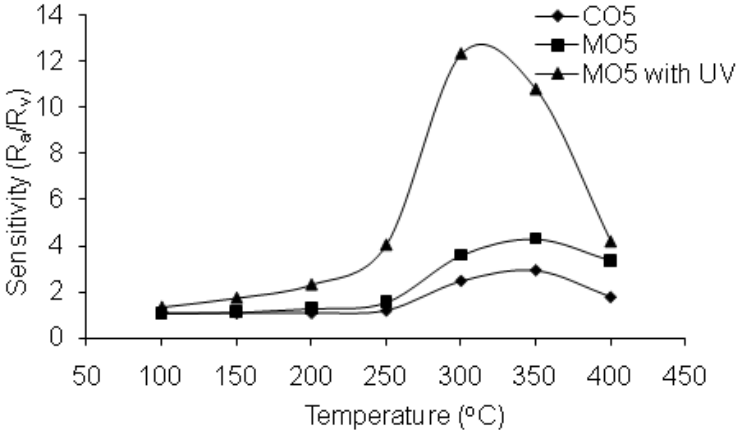

Fig.5: Sensor response to 1000ppm ethanol as a function of temperature for TiO_2 catalytic pellet

sensitivity to ethanol is achieved by the MO5 ~1.97 at the 350°C operating temperature. However, the maximum sensing response for CO5 only reaches ~1.83 at 350°C operating temperature. With the higher surface area of the MO5, the surface reaction between the ethanol vapour and the oxygen adsorbates is higher and, therefore, the sensitivity of the MO5 is higher than that of the CO5.

Other than that, the sensitivity of the TiO_2 sensor towards the ethanol vapour of MO5 in the presence of UV light was also studied. The sensitivity of the MO5 is increased gradually when the UV light is provided. It was clearly shown that the sensitivity of the MO5 in the presence of UV light is achieved at ~12.32 at operating temperature 300°C with an increment of 3 times compared to the MO5 without UV light. This result implies that UV light stimulates surface defects and enhances the catalytic properties of the sample, leading to a dramatic increase in the sensitivity of ethanol.

According to Yang *et al.* (2003), the major process occurring at the surface of the TiO_2 is the reduction of the electron acceptor ($O^-_{2\ ads}$) by photo-generated electrons, as shown in the Eq. (1). For an n-type semiconductor oxide, the adsorption increases the charge carrier density at the interface and decreases the depletion region. The absorption of UV light increases the density of ionic oxygen on the TiO_2 surface and, hence, provides more active sites for further reaction with ethanol vapour. With the UV light, the interaction between the surface and the oxygen molecules can be enhanced, speeding up the reactions and shifting the equilibrium of the reaction to a lower operating temperature.

The results suggest that the Degussa P-25 had modified the physical characteristics of the sensor, that is, the forming of anatase crystallites TiO_2 with more grains and increasing the active sites on the surface of the catalytic pellet, resulting in better interaction with ethanol vapours.

CONCLUSION

Catalytic pellets were successfully developed for detection of ethanol vapour by sol-gel dip-coating method. From the XRD, the single anatase phase of TiO_2 was formed at the annealing temperature of 500°C. The active surface for the reaction between the target gases and the oxygen adsorbates on the MO5 was increased with the increased growth of the grain on the MO5. With the higher active surface area, the sensitivity of the MO5 was increased compared to the CO5. With the addition of UV light, the maximum sensitivity of the MO5 was achieved at the 300°C operating temperature. This suggests that the Degussa P-25 in modified sol is beneficial to improve the performance of the gas sensor compared with the use of the conventional alkoxide sol by improving the grain growth and the anatase TiO_2 crystalline. Further work on the optimisation of sensitivity to ethanol based on the structure of catalytic pellets such as number of layers of TiO_2 coating and thickness of substrates can be carried ou t .

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