PREPARATION, CHARACTERIZATION AND PERFORMANCE OF TiO_2 BASED CATALYTIC PELLET FOR DETECTION OF VOLATILE ORGANIC COMPOUND UNDER UV LIGHT

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2009

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by

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Thesis submitted in fulfillment of the
requirements for the degree
of Master of Science

SEPTEMBER 2009

ACKNOWLEDGEMENTS

In the name of Allah, the Most Gracious and the Most Merciful.

Alhamdulillah, all praises to Allah for the strengths and His blessing in completing this thesis. Special appreciation goes to my supervisor, Associate Professor Dr. Mohamad Zailani Abu Bakar, for his supervision and constant support. His invaluable help of constructive comments and suggestion throughout the experimental and thesis works have contributed to the success of this research. Not forgotten, my appreciation to my co-supervisor, Dr. Ahmad Zuhairi Abdullah for his support and knowledge regarding this topic. You are my impression.

I would like to express my appreciation to the Dean School of Chemical Engineering, Prof. Abdul Latif Ahmad and also to the Deputy Dean School of Chemical Engineering, Dr. Zainal Ahmad for their support and help towards my postgraduate affairs. My acknowledgement also goes to all lecturers and staffs of School of Chemical Engineering, USM for their kindness and co-operations. Thanks to all laboratory technicians especially Mr. Shamsul Hidayat Shaharan for their technical assistance during this work.

I would like to extend my heartiest appreciation to Ministry of Science, Technology and Innovation (MOSTI) for providing me with National Science Fellowship (NSF) scholarship to assist my studies financially as well as the allocation for funding this research through SCIENCEFUND grant.

Sincere thanks to all my beloved friends especially Syura, Nora, Gaik Tin, Kak Siti, Mizah, Wan, Fiza, Aziah, Tijah, Syed, Jib, Fadhil, Kak Ida, Kak Midah,

Kak Huda, Kak Dila, Kak Unn, Kak Nida, Zulfakar and others for their kindness and moral support during my study. Thanks for the friendship and memories.

Last but not least, my deepest gratitude goes to my adored parents; Mr. Juhari Saad and Mrs. Siti Zaliha Abdullah and also to my sisters for their endless love, prayers and encouragement. Also not forgetting my beloved husband, Mohd Hilmi Abdullah for his invocation, warmness love, support and encouragement throughout this study. To those who indirectly contributed in this research, your kindness means a lot to me. Thank you very much.

- *Jusliha Juhari, September 2009* -

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LIST OF ABBREVIATIONS

a.u	Arbitrary unit
BJH	Barret-Joyner-Halenda
BET	Brunauer-Emmett-Teller
CO	Carbon dioxide
CO_2	Carbon monoxide
CB	Conduction band
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
EDX	Energy dispersion X-ray
EPA	Environmental Protection Agency U.S.A
FID	Flame ignition detector
FSP	Flame spray pyrolisis
FWHM	Full width at half maximum
GC	Gas chromatography
GHG	Green house gases
HC	Hydrocarbon
HCs	Hydrocarbons
HPC	Hydroxylpropylcelullose
IUPAC	International Union of Pure and Applied Chemistry
La	Lanthanum
LEL	Lower explosive limit
OH	Hydroxyl radical
N_2	Nitrogen
NMVOCs	Non-methane volatile organic compounds

NO	Nitric oxide / Nitrogen monoxide
NO_2	Nitrogen dioxide
O_2	Oxygen
O_3	Ozone
Ppm	Parts per million
PANI	Polyaniline
PM	Particulate matters
PVDF	Polyvinylidenfluoride
REO	Rare earth oxides
ROGs	Reactive organic gases
Sn	Tin
SEM	Scanning electron microscopy
SGS	Semiconductor gas sensors
SO_3	Sulfite
SO_2	Sulfur dioxide
TiO_2	Titanium dioxide
TB	Titanium (IV) butoxide
TCD	Thermal conductivity detector
TE	Titanium (IV) ethoxide
TEAM	Total Exposure Assessment Methodology
TEM	Transmission electron microscopy
TGA	Thermal gravimetric analysis
TPA	Triphenylamine
TTIP	Titanium (IV) isopropoxide
USP	Ultrasonic spray pyrolisis

UV	Ultra-violet
VB	Valence band
VOC	Volatile organic compound
VOCs	Volatile organic compounds
XRD	X-ray diffraction

LIST OF SYMBOLS

Symbols	Description	Unit
a, b, c	Lattice parameters	Å
d_p	Average pore diameter	Nm
e^-	Electron	Dimensionless
eVs	Energy barrier	kJ/mol
E_g	Band gap	eV
G, G_o	Conductance	Siemens (S)
h	Time	hour
h^+	Hole	Dimensionless
hv	Light of ultra-violet	Dimensionless
I	Current	Ampere
I_A	Intensity of anatase phase	Dimensionless
I_R	Intensity of rutile phase	Dimensionless
k	Boltzmann constant	$J. K^{-1}$
L	Crystallite size	nm
L_o, L_1	Depletion layer	Dimensionless
M	Concentration of solution	Molar
P	Pressure	Tons
P/Po	Relative pressure	Dimensionless
R, R_{air}, R_{VOC}	Electrical resistance	Ohm (Ω)
S	Sensitivity	Dimensionless
S_{BET}	BET surface area	m^2/g
T	Temperature	K
V	Voltage	Volt

$\mathrm{V_o^{\cdot\cdot}}$	Oxygen vacancies	Dimensionless
$\mathrm{V_{tot}}$	Total pore volume	cm^3/g
X_A (%)	Weight percentage of anatase in the sample	Dimensionless
X_R (%)	Weight percentage of rutile in the sample	Dimensionless
°C	Degree celsius	Dimensionless
λ	Wavelength of Cu Kα	Å
β	Full width at half maximum (FWHM)	Dimensionless
θ	Bragg angle	Dimensionless

PENYEDIAAN, PENCIRIAN DAN PRESTASI PELET BERMANGKIN BERASASKAN TiO_2 BAGI PENGESANAN SEBATIAN ORGANIK MERUAP DI BAWAH CAHAYA UV

ABSTRAK

Dewasa ini, peraturan alam sekitar ke atas sebatian organik meruap telah diketatkan di seluruh dunia, memandangkan penyejatannya yang cepat dan beracun serta sifat karsinogenik semulajadinya pada kepekatan yang tinggi di dalam udara menyebabkan ia berbahaya kepada kehidupan manusia. Oleh yang demikian, untuk mengesan sebatian organik meruap yang berbahaya dan beracun, sensor gas berprestasi tinggi yang diperbuat daripada kos bahan yang murah dan ringkas dalam fabrikasi adalah diperlukan untuk mengukur pelbagai jenis dan kuantiti sebatian organik meruap.

Dalam kajian ini, bahan pengesanan (La mengubahsuai TiO_2/ Sn mengubahsuai TiO_2) telah dibangunkan dengan menggabungkan lantanum (La) atau stannum (Sn) ke atas bahan asas TiO_2 melalui kaedah sol gel dalam turutan kaedah yang berbeza dengan kandungan julat aditif dan julat suhu pengkalsinan masing-masing di antara 0.0 % – 10.0 % berat atomic dan 500 °C – 900 °C. Kemudian, bahan pengesanan tersebut dimampatkan menjadi pelet bermangkin dengan bergaris pusat 20 mm dan ketebalan 2 mm. Bahan pengesanan yang berbentuk pelet bermangkin ini dicirikan dengan menggunakan analisis suhu gravimetrik (TGA), belauan sinar-X (XRD), mikroskop elektron sinaran (TEM), analisis permukaan (penyerapan-penyahserapan N_2), mikroskop elektron imbasan (SEM) dan spektroskop penyebaran tenaga sinar-X (EDX). Aktiviti pengesanan telah dijalankan menggunakan reaktor pengukur dengan kemudahan haba yang beroperasi pada julat suhu antara 50 °C hingga 400 °C. Prestasi pelet bermangkin yang telah terpilih seterusnya dikaji di bawah pelbagai keadaan operasi dengan kepekatan-kepekatan wap sebatian organik meruap (etanol, metanol dan aseton) yang berbeza di antara 1000 ppm dan 3000 ppm di bawah pengaruh sinaran cahaya UV.

Berdasarkan prestasi pengesanan dan kajian pencirian yang telah dijalankan, keputusan yang terbaik telah diperolehi apabila TiO_2 telah diubahsuai dengan aditif Sn manakala kandungan optimum bagi Sn dan suhu pengkalsinan adalah masing-masing 2.5 % berat atomik dan 600 °C. Prestasi pelet bermangkin yang telah terpilih (2.5-Sn-TiO_2-600) di bawah pelbagai keadaan operasi adalah optimum pada suhu operasi 250 °C dengan kepekaan yang tertinggi iaitu ~ 38.12 terhadap pengesanan 3000 ppm wap etanol. Kepekaan pelet bermangkin tersebut telah meningkat dengan banyaknya oleh sinaran cahaya UV dengan nilai kepekaan iaitu ~ 73.57 dan menurunkan suhu optimum operasi kepada 200 °C. Mekanisma pengesanan gas bagi pelet bermangkin ini dapat diklasifikasikan sebagai jenis kawalan permukaan dan sifat rintangan elektriknya menunjukkan jenis n-semikonduktor.

Kesimpulannya, pelet bermangkin 2.5-Sn-TiO_2-600 merupakan sensor pelet yang sesuai bagi pengesanan sebatian organik meruap di bawah sinaran cahaya UV kerana menggunakan kos bahan yang murah dan fabrikasi yang ringkas dengan menunjukkan kepekaan sebatian organik meruap yang tinggi walaupun pada suhu operasi yang rendah.

PREPARATION AND CHARACTERIZATION OF TiO_2 BASED THICK FILM CATALYTIC PELLET FOR DETECTION OF VOLATILE ORGANIC COMPOUND UNDER UV LIGHT

ABSTRACT

Nowadays, environmental regulations on volatile organic compounds (VOCs) have been tightened all over the world, as their rapid evaporation and toxic or carcinogenic nature at high concentrations in the air make them dangerous to human beings. Accordingly, in order to detect dangerous and toxic VOCs, high performance gas sensors made up from low cost materials and simplicity in fabrication are required to measure various kinds and quantities of VOCs.

In the present study, a sensing material (La-modified TiO_2/ Sn-modified TiO_2) was developed by incorporating lanthanum (La) or tin (Sn) onto TiO_2-based material by sol-gel method in different orders with additive loadings range between 0.0 at.% and 10.0 at.% and calcination temperatures range between 500 °C and 900 °C, respectively. Then, the sensing material was pressed into a catalytic pellet with a diameter of 20 mm and a thickness of 2 mm. The sensing materials (powders and catalytic pellets) were characterized using thermal gravimetric analysis (TGA), X-ray diffraction (XRD), transmission electron microscopy (TEM), surface analysis (N_2 adsorption-desorption), scanning electron microscope (SEM) and energy dispersive X-ray (EDX) spectroscopy. The detection activity was performed in a measurement chamber with heating facilities operated at temperatures between 50 °C and 400 °C. The performance of selected catalytic pellet under various operating conditions was further studied with different concentrations of VOC vapor (ethanol, methanol and acetone) between 1000 ppm and 3000 ppm under the influence of UV light irradiation.

Based on the detection performance and characterization study, the best result was obtained when TiO_2 was modified with Sn additive while the optimum loading of Sn and calcined temperature was 2.5 at.% and 600 °C, respectively. The performance of selected catalytic pellet (2.5-Sn-TiO_2-600) under various operating conditions was at the optimum when operating temperature was at 250 °C with the highest sensitivity of ~ 38.12 for 3000 ppm of ethanol vapor detection. The sensitivity of the catalytic pellet was greatly enhanced by the UV light irradiation to sensitivity values of ~ 73.57, while reducing the optimum operating temperature to 200 °C. The gas-sensing mechanism of the catalytic pellet was found to be a surface-controlled type and the electrical resistance-temperature characteristic indicated an n-type semiconductor.

In conclusion, the 2.5-Sn-TiO_2-600 catalytic pellet was a suitable pellet sensor for the VOC detection under UV light irradiation due to the low cost materials used and eases of fabrication with high VOC sensitivity even at lower operating temperature.

CHAPTER 1

INTRODUCTION

Air pollution caused by human beings goes hand in hand with civilization. Before industrialization, pollution of the air one breathes was mainly due to the use of open fireplaces which emitted smoke and gaseous organic combustion products, and the formation of urban structures then gradually led to a significant deterioration in the outdoor air quality in centre of population (Godish, 2001). The birth of the industrial era led to important sources of emission of polluting substances in the indoor and outdoor air, and reports of diseases caused by air pollution began to increase in number (Pearson, 2001).

Air pollutants from variety of sources keep contaminating the environment and thus threatening our life cycle system. Among the most dangerous air pollutants recognized globally in our atmosphere are oxides of nitrogen (NO and NO_2), oxides of sulfur (SO_2 and SO_3), oxides of carbon (CO and CO_2), ozone (O_3), volatile organic compounds (VOCs), lead and fine particulates. All these substances if present in the air in appreciable amount can cause harmful effects to human health, vegetation and human properties as well as the global environment (De Nevers, 2000). Therefore, high performance sensors and systems are required to detect and monitor various kinds and quantities of these pollutants.

Recently, the VOCs detection and monitoring has become a serious task due to stringent environmental standards and regulations on VOCs in many countries of the world. In United State, for example, approximately 50 % of the U.S Environmental Protection Agency’s (EPA’s) list of priority pollutants is composed of

VOCs. The Clean Air Act of 1990 calls for a 90 % reduction in the emission of 189 toxic chemicals over the next 8 years, 70 % of these being VOCs. Thus, in the present researcher work, particular attention on the detection and monitoring of volatile organic compounds is selected.

1.1 Volatile Organic Compounds (VOCs)

1.1.1 Definition

One of an important class of air pollutants, commonly found in the atmosphere at ground level in all urban and industrial centers is volatile organic compound and is abbreviated as VOC. The term volatile organic compound refers to those organic compounds which are present in the atmosphere as gases, but which under normal conditions of temperature and pressure would be liquids or solids.

The original definition of VOC is defined as organic compounds whose have vapor pressure less than 760 torr (101.3 kPa) and greater than 1 torr (0.13 kPa) at room temperature. However, effective as of December 29, 2004, the definition relies solely on any carbon-containing compound found in the atmosphere, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates and ammonium carbonate, which participates in atmospheric photochemical reactions (The United State Environmental Protection Agency, U.S. EPA, Definition of VOC: Code of Federal Regulations: Title 40, Part 51 Section 51.100). Other terms used to represent VOCs are hydrocarbons (HCs), reactive organic gases (ROGs), and non-methane volatile organic compounds (NMVOCs).

1.1.2 Emission Sources

There are two main sources of VOC emitted to the environment. 80 % of which comes from natural activities such as biogenic sources, vegetation and biomass. The other comes from human activities such as domestic activities, industrial activities, transportation and landfill (Wong, 2007). VOCs from the natural give rise to substantial ambient concentrations of organic compounds deriving from plants, trees, wild animals, natural forest fires, and anaerobic processes in bogs and marshes. The emissions of VOC by plants accounts for a significant fraction of the carbon fixed by photosynthesis, especially under stress conditions. These emissions reduce the amount of carbon that is fixed by vegetation. They take place on the continental scale and can therefore play a role in atmospheric chemistry even in remote areas (Hewitt *et al.*, 1995).

On the other hand, the anthropogenic VOC emissions come from motor vehicle exhausts, evaporation of petrol vapors from motor cars, solvent usage, industrial processes, oil refining, petrol storage and distribution, land filled wastes, food manufacture, and agriculture (Derwent, 1995). Some of the examples of human activities that directly emit VOCs are painting, varnishing, waxing, disinfecting, applying cosmetics, degreasing, storing fuels and using automotive products.

Figure 1.1 shows an example of human-made VOC emissions in one area. In 1985, Alberta is the fourth largest VOC emitting province in Canada. According to Environment Canada, the sources and percentage amounts of human-made VOCs generated in Alberta were transportation (motorcycles, cars, buses, trucks, boats/ships and aircraft); petroleum and petrochemical industry (petroleum refining plants); solvents, coating and miscellaneous sources (paints, paint strippers, wood preservatives, cleansers and disinfectants, moth repellents and air fresheners); fuel marketing (gasoline transfers from refinery to bulk stations, bulk stations to gas stations, gas stations to vehicles); electrical power generation (power plants); and others.

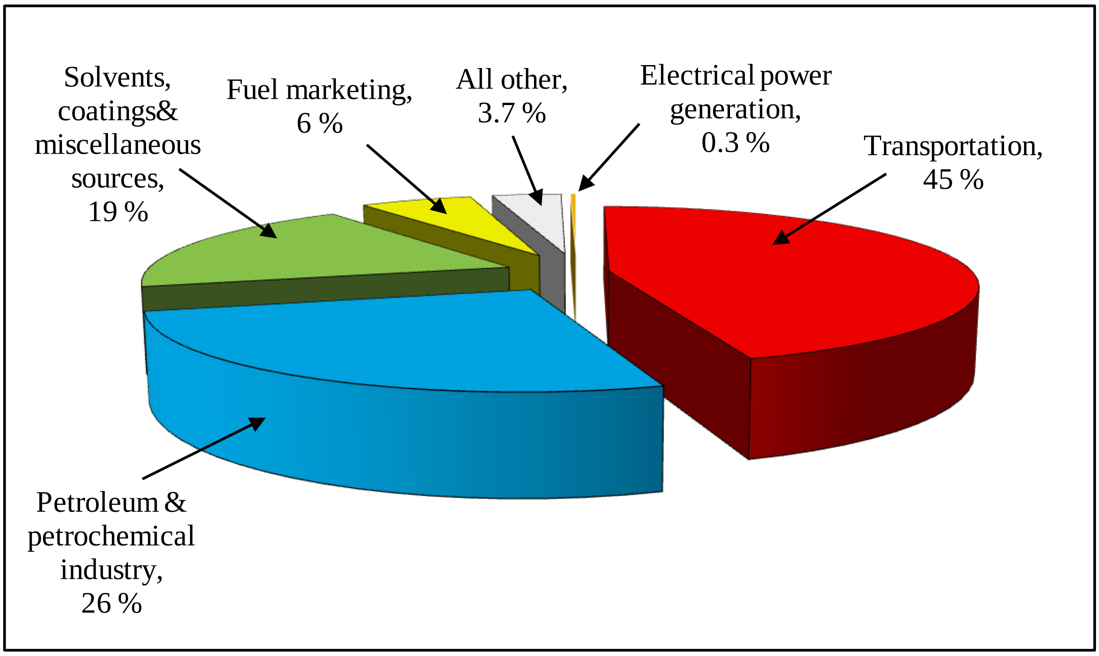

Figure 1.1: VOC emissions in Alberta, Canada in 1985 (Environment Canada).

EPA's Total Exposure Assessment Methodology (TEAM) studies found levels of about a dozen common organic pollutants to be 2 to 5 times higher inside homes than outside, regardless of whether the homes were located in rural or highly industrial areas. Additional TEAM studies indicate that while people are using products containing organic chemicals, they can expose themselves and others to very high pollutant levels, and elevated concentrations can persist in the air long after the activity is completed.

1.1.3 Human Health and Environmental Impact

According to Moretti and Mukhopadhyay (1993), most VOCs are 34 % aliphatic hydrocarbon, 28 % aromatic hydrocarbon, 26 % alcohols/ethers/ epoxides/phenols, 10 % halogenated hydrocarbons and 2 % others. These compounds are known for their carcinogenicity and mutagenicity, tropospheric photochemical oxidant production, stratospheric ozone depletion and climate change, global warming and odor problems (Chapman, 2004). The impact of VOCs on the environment depends on the concentration and properties of the individual compounds. VOCs can cause eye and respiratory tract irritation, headaches, dizziness, visual disorders, and memory impairment immediately after exposure to some VOCs. The extent and nature of the health effect depend on many factors, including level of exposure and length of time exposed.

VOCs have direct effect on human health by introducing ground level ozone, a common air pollutant which has been proven to be a public health hazard. Ground level ozone is a highly reactive gas that according to Environmental Protection Agency (EPA), it affects the normal function of the lung in many healthy human. Breathing air with ozone concentration above air quality standards aggravates symptoms of people with pulmonary diseases and seems to increase rates of asthma attacks. There is also evidence that prolonged exposure to ozone causes permanent damage to lung tissue and interferes with the functioning of the immune system. It can also adversely affect plants, animals and materials (Trimboli, 2005).

On a global scale, VOCs are Green House Gases (GHG) that contributes global warming by absorbing infrared radiation from the sun. The more complex structure of VOC is, the greater it's capacity to absorb infrared radiation. Many VOCs have a distinctive odor, which may become a localized nuisance. Certain VOCs may be highly odorous and are likely to be considered an annoyance under most circumstances, even if they are not necessarily harmful.

1.2 Gas Sensor Technology

A gas sensor is a device that creates an electrical signal in response to a chemical interaction with vapors. Because the information obtained from this process is useful, gas sensors have found widespread applications in both home and industry. Table 1.1 shows some applications of gas sensors. Despite its importance, there are challenges that exist in fabricating a reliable sensor before it can be deployed successfully. Ideal gas sensors exhibit high sensitivity to the vapor they are designed to detect. The sensor should produce an electrical response only when it is exposed to the gas of interest. Sensors should have stable, reproducible electrical signals to reduce the amount of time needed for calibration. Other practical concerns include minimization of size, weight, and power consumption, as well as the ability to place the sensor close to where the measurements are needed.

Table 1.1: Examples of applications for gas sensors (Capone *et al.*, 2003).

Applications	**Purposes/ Function**
Automobiles	▪ Car ventilation control ▪ Filter control ▪ Gasoline vapor detection ▪ Alcohol breath tests
Safety	▪ Fire detection ▪ Leak detection ▪ Toxic/flammable/explosive gas detectors ▪ Boiler control ▪ Personal gas monitor

Indoor air quality	▪ Air purifiers ▪ Ventilation control ▪ Cooking control
Environmental control	▪ Weather stations ▪ Pollution monitoring
Food	▪ Food quality control ▪ Process control ▪ Packaging quality control (off-odors)
Industrial production	▪ Fermentation control ▪ Process control
Medicine	▪ Breath analysis ▪ Disease detection

Despite some issues relating to the development of gas sensors, their roles are increasingly felt. For example, hydrogen sensors are needed in the rocket propulsion industry because hydrogen propellant leaks pose significant safety risks (Borodko *et al.*, 1999). In the automotive industry, the air to fuel ratio in vehicles is routinely monitored with oxygen sensors that utilize an electrochemical cell containing ZrO_2, which conducts oxygen ions at high temperatures (Spetz, 2006). In some industrial processes such as in the production of carbonated beverages, the presence of oxygen at ppm level must be detected and controlled (Sotter *et al.*, 2007).

NOx sensors are of high interest in industries that utilize combustion fuels or engines, because nitrogen oxides are formed when fuel burns at high temperatures. Approximately one-half of all NOx emissions into the environment are due to power plants and industrial boilers (Chen and Tsang, 2003). Nitrogen oxides are a unique danger because they can travel great distances from their emission source and result in acid rain, ozone, photochemical smog, and particulate matter far from the actual source of pollution. Beside O_2, H_2, NOx, CO, CO_2 sensor is another device that finds multiple uses needed for indoor air quality operations, early fire detection as well as for incubators for food storage and processing (Marsal *et al.*, 2003). Also, hydrocarbon or VOC sensors are needed for aeronautic and automotive exhaust monitoring, leak detection, and fire detection.

1.3 Types of Gas Sensor

Gas sensors can be divided into three big groups known as spectroscopic gas sensor, optic gas sensor and solid-state gas sensor.

1.3.1 Spectroscopic Gas Sensor

Spectroscopic systems are based on the direct analysis of the molecular mass or vibration spectrum of the target gas. These sensors can measure the composition of the different gases quantitatively with a good precision (Endres *et al.*, 1994). Mass chromatography, Nuclear magnetic resonance (NMR) spectroscopy and mass spectrometer are important gas sensor spectroscopic systems.

1.3.2 Optical Gas Sensor

Optical gas sensors measure absorption spectra after the target gas has been stimulated by light. This kind of sensors requires monochromatic excitation source and an optical sensor for the analysis of the absorbed spectra. Gas sensors based on optical absorption changes in thin films are for detection of various gases such as CO, NO, H_2. Optical gas sensors have several advantages over conventional electronic gas sensors, including the potential for higher sensitivity, reduced signal noise, and compatibility with combustible gases (Nam *et al.*, 2004). However, both of spectroscopic and optical systems are very expensive for domestic use, complex, large in size and sometimes difficult to implement in reduced spaces such as car engines. In addition, most analysis requires sample preparation, so that on-line, real-time analysis is difficult.

1.3.3 Solid-state Gas Sensor

Solid-state gas sensor based on a variety of principles and materials are favorable in the development of commercial gas sensors for a wide range of applications (Mandelis and Christofides, 1993; Moseley, 1997; Capone *et al.*, 2003). The preferences stem from their numerous advantages like ease of miniaturization, high sensitivities in detecting very low concentrations (at level of ppm or even ppb) of a wide range of gaseous chemical compounds, possibility of on-line operation and low cost (Capone *et al.*, 2003).

While solid-state gas sensors are favorable, they suffer from limited measurement accuracy and problems of life long stability. However, recent advances in nanotechnology has facilitated the production of novel classes of nanostructure materials with enhanced gas sensing abilities that increase the performances of solid-state gas sensors (Yamazoe, 1991; Yamazoe, 2005; Comini, 2006). This enables the solid-state gas sensors to have reversible interaction between the gas and the surface of a solid-state material, in addition providing conductivity/resistivity change of gas-sensing material, the detection of which can be performed by measuring the change of capacitance, work function, mass, optical characteristics or reaction energy released by the gas/solid interaction (Capone *et al.*, 2003). Table 1.2 provides the detection principle for solid-state gas sensors, which are strongly, depend on the development of technologies mainly driven by other than gas sensor applications.

Table 1.2: Types of solid-state gas sensors with the corresponding physical change used as gas detection principle (Capone *et al.*, 2003).

Type of devices	Physical change
Semiconductor gas sensors	Electrical conductivity/resistivity
Catalytic gas sensors: seebeck effect, pellistors, semistors	Heat or temperature
Electrochemical gas sensors (potentiometric or amperometric)	Electromotive force or electrical current in a solid-state electrochemical cell
Field effect gas sensors: diodes, transistors, capacitors	Work function (electrical polarization)
Piezoelectric sensors: Quartz crystal microbalances (QMB), surface acoustic wave (SAW), microcantilevers	Mass

1.4 Semiconductor Gas Sensors

Semiconductor gas sensors (SGS) known also as chemoresistive gas sensors, are typically based on semiconducting metal oxides such as SnO_2, TiO_2, ZnO, In_2O_3, WO_3, NiO, etc. These semiconducting metal oxides appear to be the best candidates for SGS owing to high sensitivity to pollutant gases, low cost, easy implementation, small size and good reliability for real-time control systems (Ruiz *et al.*, 2004a). These candidates also have non-stoichiometrics structures, so free electrons originating from oxygen vacancies contribute to electronic conductivity (Yu-De *et al.*, 2001).

SGS were originally commercialized in Japan (Taguchi, 1970) but, employing tin oxide as the sole sensitive component, were limited in application by a characteristic lack of specificity between gases. A range of more specifically reacting materials is now employed and all three of the categories of gas which need to be sensed; oxygen, flammable gases and toxic gases can now be monitored. This is the faster growing of the three main categories of gas of SGS at the present time.

The sensitivity of SGS is based on the dependence of the conductivity (resistivity) of semiconducting metal oxides on the surrounding atmosphere. Reactions involving gas molecules can take place at the semiconductor surface to change the density of charge carriers available (Yamazoe *et al.*, 2003). Hence, the conductance of the device changes progressively with changing atmospheric composition. The effectiveness of SGS prepared from semiconducting metal oxides depends on several factors including the nature of the reaction taking place at the oxide surface, the temperature, the catalytic properties of the surface, the electronic properties of the bulk oxide and the microstructure (Moseley, 1997).

1.5 Problem Statement

Gas sensors have a great influence in many areas such as environmental monitoring, domestic safety, public security, automotive applications, and air conditioning in airplanes, spacecrafts and houses, sensors networks. Due to this huge application range the need of cheap, small, low power consuming and reliable solid-state gas sensors has grown over the years and triggered a huge research worldwide to overcome their drawbacks, summed up in improving the well known “3S” which are sensitivity, selectivity and stability (Comini, 2006).

Currently, semiconductor gas sensors (SGS) or best known as metal oxide semiconductor gas sensors is widely used in industrial processes such as for detection of toxic pollutants and detection of hazardous gas leakages. So far the majority of research works have been carried out on the metal oxide semiconductor gas sensors using SnO_2. However, there are several problems associated with SnO_2 such as poor sensitivity at high operating temperature (> 200 °C), lack of selectivity and stability. Therefore, some new types of sensing materials are still being studied and exploited at present time.

One of the most innovative solutions to this problem has been recently proposed by Zakrzewska and Radecka (2007) who have realized that some metal oxides that are well-known for their gas sensing properties are extremely efficient in a photocatalytic decomposition of organic pollutants. The best example of this kind of a material seems to be TiO_2 in its combination of anatase and rutile form (Yu *et al.* 2002). Nevertheless, there is a great interest in sensing materials with different combinations of electronic and catalytic properties to achieve a considerable improvement in the performance of metal oxide semiconductor gas sensors. Therefore, it motivated many researchers to investigate the possibility of improving the gas-sensing properties of TiO_2 by loading with foreign additives (Ruiz *et al.*, 2005b). Moreover, one interesting approach for lowering the operating temperature is the exposure of TiO_2 to UV light irradiation (Anothainart *et al.*, 2003). Due to this, the development of reliable TiO_2-based gas sensors to detect VOC under UV light irradiation was carried out in this study.

1.6 Objectives

The present study has the following objectives:

a) To develop suitable catalytic pellets based metal oxide and their modified that can be used to detect VOCs at low temperature.

b) To characterize the catalytic pellets and their modified in order to elucidate the physicochemical properties for better performance in VOCs detection.

c) To design and fabricate the experimental rig for VOCs detection in order to measure the performance of developed catalytic pellets based on their conductivity/resistivity and sensitivity, and also to understand the reaction mechanism.

1.7 Scope of the Study

In the present study, titanium dioxide (TiO_2) was identified to be used as the substrate for the catalytic pellets. The selection was based on the high sensitivity, high chemical stability under harsh conditions, high photosensitivity, relatively low cost and successful application as sensing material by other researchers. The synthesis of TiO_2 powders was carried out by using titanium isopropoxide (TTIP) via sol-gel method. The selection of this method was made on the basis of their advantages reported by Chen *et al.* (2004) where is ability to improve homogeneity, stability, surface area and porosity of the sensing materials.

In order to enhance the gas sensing properties of the TiO_2-based sensor, several metal additives such as lanthanum (La) and tin (Sn) were incorporated to the TiO_2 powders. The modification of TiO_2 with metal additives was accomplished using an in-situ method. All synthesized gels were dried at 120 °C for 5 h and then further calcined at desired temperatures for 3 h in air. The pellet was prepared by pressing the powders and then further sintered at 850 °C for 2 h in air and cooled to the room temperature before been tested. The parameter studies at this stage as effect of different types of metal additive (La and Sn), metal additive loading (0 – 10 at.%) and calcination temperature (500 – 900 °C) was done in order to obtain the best catalytic pellet that can be used for further detection activity. The synthesis and preparation parameters which give the high porosity, high surface area and more crystallinity were chosen to obtain sensing materials with different physical and chemical characteristics for comparison of results. The resulted TiO_2, modified-TiO_2 powders and TiO_2, modified-TiO_2 catalytic pellets were subjected to comprehensive characterization techniques in order to find out their chemical and physical properties using TGA, XRD, TEM, N_2 adsorption/desorption analysis, SEM and EDX.

The gas sensing behavior of catalytic pellets was measured in a measurement chamber with heating facilities under controlled atmospheres. In the present study, the hazardous VOC vapors such as ethanol, methanol (alcohol group) and acetone (ketone group) were used as the model organic pollutant detection under the influence of UV light. The concentration of VOC vapors was analyzed by Hewlett Packard, Model 5890 series II gas chromatography, equipped with a packed column (Porapak Q, 3 m long x 2.33 mm ID) and a flame ionization detector (FID) before flowing into the measurement chamber. The parameter studies at this stage as effect of operating temperature (50 – 400 °C), different types of VOC vapor (ethanol, methanol, and acetone) and concentrations (1000 – 3000 ppm) and also UV light irradiation (with and without UV) were investigated. The course of the reaction can be monitored based on the electrical resistance and sensitivity of the catalytic pellets.

Exploration on the use of UV light to supply the energy for the reaction between VOC vapors and catalytic pellets was made, instead of providing high temperature.

1.8 Organization of the Thesis

There are five chapters covered in the thesis and each chapter describes the detail of the research study.

Chapter 1 (Introduction) gives a brief introduction and definition of VOCs, their emission sources and their impacts on human health and environmental. Then, the current gas sensor technologies to control and monitor the VOCs in domestic and industrial is described in general. This chapter also enclose with problem statements that provide some basis and rational to identify the clear direction of research objectives in the current studies. The scope of study covers the research work done to meet these objectives. Organization of the thesis winds up this chapter.

Chapter 2 (Literature Review) consists of the review conducted on semiconductor gas sensor researches. The brief explanation of semiconducting metal oxide based gas sensor as sensing material is introduced in the first section, followed by the exploration of sensing mechanism, sensing characteristics of TiO_2 including its advantage used as a sensing material, role of additives and ultraviolet (UV) light on sensing performance.

Chapter 3 (Materials and Experimental Methods) describes the chemicals and reagents used, preparation method and analysis required for the detection activity. It also explained on the details of the experimental setup, equipment used throughout the whole process of this study, detection analysis and analytical techniques for material characterization.

Chapter 4 (Results and Discussion) presents the result obtained from experimental runs and discusses on every effect of parameters on the preparation of sensing material and detection activity. Besides, the results from material characterization such as thermal stability, crystallinity, morphology, surface area, porosity, grain size and elemental compositions present also discussed.

Chapter 5 (Conclusions and Recommendations) gives the overall conclusions of the results obtained in the present study. Several recommendations for future studies as a continuation to the present one are also included in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Gas sensors are used for monitoring and controlling of industrial processes, analysis of gas compositions, for surveillance and many other applications. The development of gas sensor devices with optimized sensitivity and selectivity has been gaining prominence in recent years. Since the demonstration almost 50 years ago, that the adsorption of gas on the surface of metal oxides can bring about a significant change in the electrical resistance of the material, there has been a sustained and successfully effort to make use of this change for purposes of gas detection. Zakrzewska (2004) reported that the detection of toxic and flammable gases as well as humidity is a subject of growing importance in both domestic and industrial environments.

The present study is focused on the development of semiconductor gas sensors (SGS) based on metal oxides as functional sensing material and the role of incorporation additives on metal oxides that can be used to detect volatile organic compounds (VOCs) under UV light irradiation. These possible VOCs detection technologies have attracted the attention of many scientists and have been reviewed in recent reports (Paraguay D *et al.*, 2000; Sberveglieri *et al.*, 2000; Ruiz *et al.*, 2005a; Jiang *et al.*, 2006; Alessandri *et al.*, 2007; Rella *et al.*, 2007; Sasahara *et al.*, 2007; Teleki *et al.*, 2008; Vijaya *et al.*, 2008). Furthermore, Table 2.1 shows the summarized of metal oxides used in SGS for VOCs detection that have been studied by others authors.

Table 2.1: Summary of metal oxides used in SGS for VOCs detection.

Metal oxides	Method of preparation	Type of VOCs	Remarks	References
Polymer-TiO_2	Chemical precipitation	Alcohols, 500 ppm Benzene, 500 ppm	Maximum sensitivity observed at room temperature	Islam *et al.* (1999)
HPC-TiO_2	Sol-gel	Ethanol, 100-1000 ppm Methanol, 100-1000 ppm	Maximum sensitivity observed at operating temperature of 500 °C	Garzella *et al.* (2000)
ZnO	Chemical precipitation, emulsion and microemulsion	Isobutane, 1000 ppm Gasoline, 1000 ppm Ethanol, 1000 ppm	Maximum sensitivity observed at operating temperature of 300 °C	Xu *et al.* (2000)
La_2O_3-Pd-ZnO	Hydrolysis and impregnation	Ethanol, 1000 ppm	Maximum sensitivity observed at operating temperature of 175 °C	Rao (2000)
Pt/Nb-TiO_2	Sol-gel	Ethanol, 500 ppm Methanol, 500 ppm	Maximum sensitivity observed at operating temperature of 300 °C	Comini *et al.* (2000a)
TiO_2-WO_3	High-energy ball milling	Ethanol, 1000 ppm	Maximum sensitivity observed at operating temperature of 160 °C	Reddy *et al.* (2001)
WO_3	Commercial powder	Ethanol, 100 ppm	Maximum sensitivity observed at operating temperature of 200 °C	Yu-De *et al.* (2001)

Table 2.1: Continuous

Metal oxides	Method of preparation	Type of VOCs	Remarks	References
Polymer-TiO_2	Chemical precipitation	Benzene, 150-350 ppm Methanol, 150-350 ppm Ethanol, 150-350 ppm	Maximum sensitivity observed at room temperature	Mabrook and Hawkins (2001)
Pt-Ca-SnO_2	Chemical precipitation	Ethanol, 0-2000 ppm Toluene, 0-2000 ppm Acetone, 0-2000 ppm Benzene, 0-2000 ppm	Maximum sensitivity observed at operating temperature of 400 °C	Lee *et al.* (2002)
TiO_2-ZnO	Vapor-phase oxidation and mechanical mixing	Benzene, 10-200 ppm Toluene, 10-200 ppm Xylene, 10-200 ppm Acetone, 10-200 ppm Alcohol, 10-200 ppm	Maximum sensitivity observed at operating temperature of 370 °C	Zhu *et al.* (2004)
Sb-ZnO	Vapor condensation	Benzene, 100 ppm Toluene, 100 ppm Xylene.100 ppm Acetone, 100 ppm Alcohol, 100 ppm	Maximum sensitivity observed at operating temperature of 370 °C	Zhu *et al.* (2005a)
$ZnO/ZnFe_2O_4$	Wet-ball milling	Methanol, 0-8000 ppm Ethanol, 0-8000 ppm Propanol, 0-8000 ppm	Maximum sensitivity observed at operating temperature of 25 °C	Arshak and Gaidan, (2005)

Table 2.1: Continuous

Metal oxides	Method of preparation	Type of VOCs	Remarks	References
Tetrapod-shaped ZnO	Vapor-phase oxidation	Benzene, 100 ppm Toluene, 100 ppm Acetone, 100 ppm Alcohol, 100 ppm	Maximum sensitivity observed at operating temperature of 320 °C	Zhu *et al.* (2005b)
Anatase TiO_2	Flame spray pyrolisis (FSP)	Ethanol, 1-75 ppm Isoprene, 1-75 ppm Acetone, 1-75 ppm	Maximum sensitivity observed at operating temperature of 500 °C	Teleki *et al.* (2006)
$ZnO-Fe_2O_3$	Hydrolysis	Ethanol, 50 ppm Acetone, 50 ppm	Maximum sensitivity observed at operating temperature of 200 °C	Si *et al.* (2006)
CeO_2-ZnO	Sol-gel	Alcohol, 100 ppm	Maximum sensitivity observed at operating temperature of 320 °C	Ge *et al.* (2006)
TiO_2	Chemical precipitation	Ethanol, 20-200 ppm Acetone, 20-200 ppm	Maximum sensitivity observed at operating temperature of 350 °C	Rella *et al.* (2007)
$Pd/\gamma-Al_2O_3$	Mechanical mixing	Toluene, 10-1000 ppb	Maximum sensitivity observed at room temperature	Sasahara *et al.* (2007)
SnO_2	Chemical precipitation	Ethanol, 100-1000 ppm Propane-2-ol, 200-2000 ppm Acetyl acetone, 200-2000 ppm	Maximum sensitivity observed at operating temperature of 300 °C	Huang *et al.* (2007)

2.2 Metal Oxides as Sensing Materials

The development of new and more efficient materials for gas sensing is a challenge of the near future, as the market for these devices continues to grow. As first discovered in the early 60s, metal oxides are able to sense gases upon changes of their conductance. Gas sensors using metal oxide semiconductors have several advantageous features such as simplicity in device structure, reduced size, low cost for fabrication, robustness in practical applications and adaptability to a wide variety of reductive and or oxidative gases (Chung *et al.*, 1998). Simple metal oxides such as SnO_2, ZnO, WO_3 and TiO_2 are well known for their high sensitivity to changes in the surrounding gas atmosphere. The growing number of papers reporting on the successful application of these metal oxides in gas sensing devices shows the important role they play in the gas sensor research field (Moseley, 1997; Zakrzewska, 2001; Comini, 2006; Karunagaran, 2007; Herrán *et al.*, 2008).

Fairly extensive studies have been carried out on this group of gas sensors. Nevertheless, there are basic and technological problems yet to solve. One of such problems is that, so far the majority of investigations have been carried out on the metal oxide semiconductor gas sensors using SnO_2. Moreover, in spite of their high sensitivity, such gas sensors show usually poor selectivity and stability (Kocemba *et al.*, 2001). The other metal oxides should also be investigated more to get a comprehensive understanding about gas sensing-materials and sensing-mechanism. It is known that metal oxides can have either n- or p-type semiconductor of conductivity as shown in Table 2.2. For metal oxides with p-type semiconductor, the conductivity rises with oxygen pressure's growth, whilst for metal oxides with n-type semiconductor, the conductivity drops with oxygen pressure's growth.

Table 2.2: Classification of metal oxides based on type of conductivity (Korotcenkov, 2007).

Type of conductivity	Metal oxides
n-type	MgO, CaO, TiO_2, ZrO_2, V_2O_5, Nb_2O_5, Ta_2O_5, MoO_3, WO_3, ZnO, Al_2O_3, Ga_2O_3, In_2O_3, SnO_2
p-type	Y_2O_3, La_2O_3, CeO_2, Mn_2O_3, Co_3O_4, NiO, PdO, Ag_2O, Bi_2O_3, Sb_2O_3, TeO_2
n, p-type	HfO_2, Cr_2O_3, Fe_2O_3, CuO

The analysis of main gas-sensing materials in respect to their conductivity type shows that all the most effectively working gas sensors are designed on the base of metal oxides of n-type conductivity, such as SnO_2, TiO_2, WO_3, ZnO and In_2O_3 which providing the opportunity of oxygen's chemisorptions. Previous research has shown that, in general, all n-type metal oxides are thermally stable and have possibility to work at lower oxygen partial pressure in comparison with well known p-type metal oxides, for example such as CuO (Gordon *et al.*, 1996). It is known that many p-type metal oxides are relatively unstable because of the tendency to exchange lattice oxygen easily with air (Madou and Marrison, 1987).

Besides, the interaction with reducing gas decreases the resistance of n-type metal oxides and increases the resistance of p-type metal oxides as shown in Table 2.3. This is the preferred direction for sensor's resistance change during detection of reducing gases, contributing to simpler compatibility with peripheral measuring devices, and better reproducibility of output signal (Korotcenkov, 2007). However, it does not mean that p-type materials are not applicable for sensor design. For example, the previous research has shown that metal oxide $Cr_{2-x}Ti_xO_3$ ($x < 0.4$) (CTO), prospective for gas sensors design, is p-type material (Williams *et al.*, 2000).

Table 2.3: Resistance responses expected for reducing and oxidizing gases on n- and p-type metal oxides.

Metal oxides	Reducing gases	Oxidizing gases
n-type	Resistance falls	Resistance rises
p-type	Resistance rises	Resistance falls

Furthermore, the pretty big band gap (E_g) and small activation energy of the centers, responsible for metal oxides conductivity which is an optimal combination of parameters for the materials designed for solid-state semiconductor gas sensors (Korotcenkov, 2007). Such correlation of activation energies is necessary in order to avoid sensor's operation in the region of self-conductance. Kolmakov and Moskovits (2004) reported the influence of surrounding temperature on gas sensor parameters is reduced and as a rule, the higher operation temperature is, the bigger should be E_g. According to previous experimental results, the optimal band gap must be higher than 2.5 eV when operate at the operating temperatures exceeding T > 300 °C. Thus, it can be concluded that the well-known metal oxides satisfy this requirement as shown in Table 2.4.

It is necessary to note that an opportunity to operate at higher temperature is an important advantage of solid-state semiconductor gas sensors, because this fact allows reducing considerably the influence of air humidity on gas-sensing characteristics. It was established that, as a rule, the lower operating temperature is, the greater is the sensitivity of the sensor's parameters to relative air humidity (Korotcenkov, 2005). The big band gap also is a sufficient advantage for metal oxides with ionic conductivity, because the contribution of electron conductivity in sensing materials is being reduced especially at high operating temperatures

(Korotcenkov, 2007). On the other hand, there are n-type and p-type states that are formed in the band gap of the metal oxides as shown in Figure 2.1. The n-type metal oxides may act as donor band while the p-type metal oxides act as acceptor band.

Table 2.4: Band gap of metal oxides (Korotcenkov, 2007).

Metal oxides semiconductor	Band gap (eV)
MgO, CaO, Al_2O_3, SiO_2, TeO_2	> 6.0
SrO, Y_2O_3, HfO_2, ZrO_2	5 – 6
BaO, La_2O_3, CeO_2, Ga_2O_3	4 – 5
TiO_2, Nb_2O_5, Ta_2O_5, ZnO, In_2O_3, SnO_2	3 – 4
V_2O_5, Cr_2O_3, WO_3, NiO, Fe_2O_3	2 – 3
Co_3O_4, PdO, CuO, Sb_2O_3	1 – 2

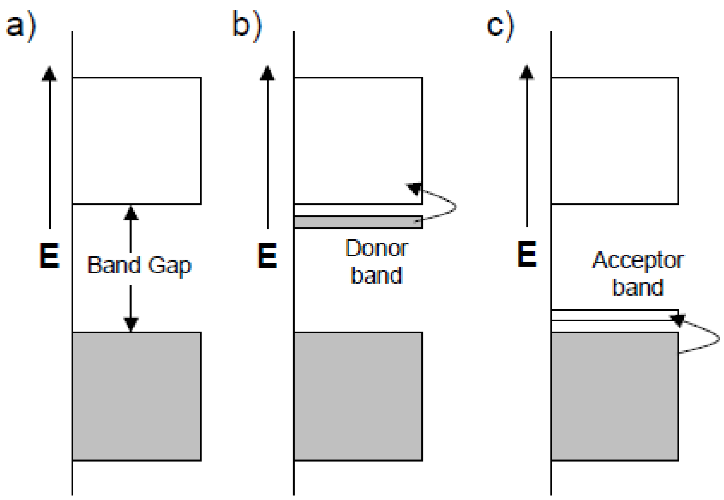

Figure 2.1: Band gap structure of (a) an insulator, (b) an n-type semiconductor and (c) a p-type semiconductor (Trimboli, 2005).

At present, there are three technologies used for the fabrication of SGS based on metal oxides devices viz. pellet-type (Bulpitt and Tsang, 2000), thin film-type (Mabrook and Hawkins, 2001) and thick film-type (Choi *et al.*, 2004). These types of