SYNTHESIS AND FABRICATION OF DROP-COATED SnO_2 THICK FILM SENSOR VIA SOL GEL METHOD FOR ETHANOL GAS DETECTION

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2017

SYNTHESIS AND FABRICATION OF DROP-COATED SnO_2 THICK FILM SENSOR VIA SOL GEL METHOD FOR ETHANOL GAS DETECTION

by

LOW KOK WEI

Thesis submitted in partial fulfillment of the requirement for the degree of

Bachelor of Chemical Engineering

May 2017

ACKNOWLEDGEMENTS

Firstly, I would like to express my utmost gratitude to my supervisor, Assoc. Prof. Dr. Mohamad Zailani Abu Bakar, who guided me through this final year project. I sincerely appreciate his recognition on my relentless effort and I am grateful for his support throughout the whole process to project completion.

Next, I would also like to thank Muhammad Yusri bin Ahmad, my post-graduate senior. He actively offered helps to me on my experiment from time to time. His generosity to share his precious knowledge and ideas in every stage of this project has been rewarding for me to complete the project on time.

In addition, School of Chemical Engineering and School of Materials and Mineral Resources, Universiti Sains Malaysia have my special thanks as well for providing me the facilities needed for the experiment. I am also indebted to all staff and assistant engineers of School of Chemical Engineering for their kindness and assistance in handling the equipment while completing the project.

Lastly, I would like to thank my beloved family and friends for their unceasing support and encouragement throughout the whole project completion.

Low Kok Wei

May 2017

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LIST OF SYMBOL

Symbol	Description	Unit
β	Full angular width at half-maximum of the peak	length
θ	XRD scattering angle of peak	-
D	Average particle size	nm
e^-	Electron	-
λ	X-ray source wavelength	length
R_a	Resistance of the gas sensor in the reference gas	Ohm
R_g	Resistance of the gas sensor in the reference gas containing target gas	Ohm
S	Sensitivity of the gas sensor	percentage

LIST OF ABBREVIATIONS

Al	Aluminum
Al_2O_3	Aluminum oxide
NH_3	Ammonia
BET	Brunnauer-Emmett-Teller
Cl	Chlorine
CO	Carbon monoxide
CVD	Chemical Vapor Deposition
Cr	Chromium
EDX	Energy Dispersive X-ray
C_2H_5OH	Ethanol
H_2	Hydrogen
H_2S	Hydrogen sulphide
In_2O_3	Indium (III) oxide
IUPAC	International Union of Pure and Applied Chemistry
Fe	Iron
La	Lanthanum
Mn	Manganese
CH_2	Methylene
N_2	Nitrogen
NO_2	Nitrogen dioxide
NO_x	Nitrogen oxide
O	Oxygen
O_2	Oxygen

ppm	Parts per million
SEM	Scanning Electron Microscope
SnO_2	Tin (IV) oxide
TiO_2	Titania
Ti	Titanium
VOC	Volatile organic compound
H_2O	Water
XRD	X-ray Diffraction Spectroscopy
ZnO_2	Zinc cxide
ZrO	Zirconia

SINTESIS DAN FABRIKASI BAGI TEBAL FILEM SnO_2 SENSOR MELALUI KAEDAH SOL-GEL DAN SALUTAN JAUTHAN UNTUK MENGESAN GAS ETANOL

ABSTRAK

Tin dioksida (SnO_2) telah berjaya disintesiskan melalui kaedah sol-gel dengan melarutkan tin (IV) klorida dalam air suling dan seterusnya menambahkan ammonia seterusnya; sementara kaedah-kaedah tersebut adalah lebih mudah dan murah. Bahan pengesan etanol yang dihasilkan ini telah dicirikan dengan Belauan Sinar-X, Imbasan Elektron Mikroskop, Tenaga Serakan Sinar-X and Brannauer-Emmett-Teller analisis. Berdasarkan keputusan analisis Belauan Sinar-X, saiz kristalit bertambah apabila suhu pengklasinan meningkat; di mananya saiz kristalit yang diperolehi dengan suhu pengklasinan dalam 400 ^oC, 500 ^oC dan 600 ^oC ialah 11.28 nm, 13.06 nm dan 18.17 nm masing-masing. Pencirian Imbasan Elektron Mikroskop menunjukkan sebaran SnO_2 zarah yang homogen dan tanda-tanda gumpulan pada suhu pengklasinan yang lebih tinggi. Analisis Tenaga Serakan Sinar-X telah mengesahkan komposisi SnO_x serbuk yang disintesiskan ialah SnO_2. Seterusnya, hasilan SnO_2 serbuk telah disalutkan pada permukaan substrat alumina melalui kaedah salutan jatuhan dalam proses fabrikasi. Untuk memahami pengaruh ketebalan filem terhadap sensitiviti, sensor-sensor tersebut telah difabrikasi dengan 3, 5 dan 7 lapisan salutan bahan pengesan. Suhu operasi yang antara 200 ^oC dengan 400 ^oC dan pelbagai kepekatan gas etanol (200 ppm - 1000 ppm) telah digunakan untuk mengaji tentang tindakbalas sensor dalam keadaan yang berbeza. Sensor SnO_2 yang disintesiskan didapati berfungsi terbaik pada 300 ^oC dan sensitiviti sensor-sensor berkadar terus dengan kepekatan gas etanol. Keseluruhannya, sensor yang menunjukkan sensitiviti dalam pengesanan gas etanol yang tertinggi ialah sensor yang difabrikasi dengan 5 lapisan

salutan serbuk SnO_2 yang diklasinkan pada 500 ^oC. Pengesanan gas etanol bagi sensor ini juga adalah lebih baik daripada sensor yang difabrikasikan dengan meggunakan serbuk SnO_2 komersial. Ini disebabkan oleh saiz kristalit serbuk sistesis yang lebih kecil dan jumlah kawasan permukaan serbuk sintesis yang lebih besar. Berdasarkan analisis XRD dan BET, SnO_2 serbuk komersial adalah 70.64 nm saiznya dan mempunyai luas permukaan 4.55 m^2/g manakala SnO_2 serbuk terbaik yang disistesiskan adalah hanya 13.06 nm saiznya and mempunyai jumlah luas permukaan yang lebih besar iaitu 36.74 m^2/g.

SYNTHESIS AND FABRICATION OF DROP-COATED SnO_2 THICK FILM SENSOR VIA SOL-GEL METHOD FOR ETHANOL GAS DETECTION

ABSTRACT

Tin dioxide (SnO_2) nanopowders has been successfully synthesized via sol-gel method by dissolving the precursor, tin (IV) chloride pentahydrate in distilled water and adding ammonia solution afterwards; in which the methods are relatively simpler and cheaper. The obtained ethanol sensing materials were then characterized with X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX) and Brannauer-Emmett-Teller (BET) analysis. From the XRD result, the crystallite sizes increase with the rise in calcination temperature; where the crystallite size obtained at calcination temperature of 400 ^oC, 500 ^oC and 600 ^oC are 11.28 nm, 13.06 nm and 18.17 nm respectively. SEM characterization shows homogenous distribution of SnO_2 nanoparticles and hints agglomeration at higher calcination temperature. It was found through EDX analysis that the chemical composition of the SnO_x synthesized is confirmed to be SnO_2. After that, the synthesized SnO_2 powders were deposited on alumina substrates through drop coating method for sensor fabrication. To understand the effect of film thickness on the sensitivity, the sensors were fabricated at 3, 5 and 7 drop layers of sensing materials. Operating temperature ranging from 200 ^oC to 400 ^oC and different ethanol gas concentrations (200 ppm to 1000 ppm) were also used for sensor testing to study the gas sensing behavior at different conditions. It was found that the as-prepared SnO_2 sensors work best at 300 ^oC and the sensitivity of the sensors exhibits linear dependency on the ethanol gas concentration. In all, the sensor that showed highest sensitivity to ethanol gas was the one fabricated using 5 drop layers of SnO_2 nanopowders calcined at 500 ^oC. This sensor also outperformed the sensor fabricated with commercial SnO_2 nanopowders by having a higher sensitivity, ascribed

by the former having smaller crystallite size and higher surface area. From the XRD and BET analysis, the commercial SnO_2 powder is 70.64 nm in size and have an average surface area of 4.55 m^2/g whereas the best synthesized SnO_2 powder is only 13.06 nm in size and have a higher average surface area of 36.74 m^2/g.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

1.1.1 Ethanol gas sensors

One of the most talk-about severe issues in 21st century is environmental pollution which contributes to various hazards not only to human but also to other living organisms. The demand for gas sensors has been higher than ever for more stringent emissions regulations. Metal oxide semiconductors such as ZnO_2, In_2O_3 and SnO_2 have been widely employed as the sensing materials in the last ten years for their simplicity and high sensitivity to the target gases (Chen et al., 2006). For instance, with the succession over the prior technology, passive colormetric sensors, tin dioxide (SnO_2) based carbon monoxide gas detectors have become a standard regular instalment in most residence and workplace (Bakrania & Wooldridge, 2009).

A lot of volatile organic pollutants are broadly used in industries and are the key effluent that negatively affect the environment; one of those organic pollutants is ethanol, which is the most common volatile organic compounds (Khan et al., 2012). The most popular alcohol, ethanol is best known as the alcohol used in alcoholic beverages (Arafat et al., 2012). For human, inhalation of concentrated ethanol vapor most likely to inflict headache, nausea and confusion whereas skin contact with ethanol vapor might cause mucous membrane irritation, weakens physiological functions and more (Gardner & Varadan, 2013). Ethanol has been identified as one of the organic pollutants which cause severe harmful effect on environment and human health due to its toxicity, carcinogenicity and hazardous properties, hence monitoring

and detecting ethanol vapors are very important (Khan et al., 2012). Therefore, there is a vital role for ethanol gas sensor to detect and prevent the damage caused by ethanol.

On that note, one of the widely studied vapor gases by metal oxide gas sensors, is ethanol vapor. High sensitivity, short response-recovery time and good selectivity detection of ethanol vapor is important and ethanol gas often found in food industry, environmental monitoring of leakage detection in industrial distribution lines, and in breath alcohol detector in exhaled drivers' breath (Guo et al., 2011; Ho et al., 1998; Vaezi & Zameni, 2012). Other than that, application of ethanol gas sensors also can be found in food industries such as the control of fermentation process and safety of food packaging (Zhan et al., 2013), since ethanol is a major breakdown product of food such as fruits and grains when fungi or bacteria develops and that could lead to infection and spread of diseases (Nirmala, 2011).

1.1.2 Tin (IV) Oxide (SnO_2) as ethanol sensing materials

It has been long established and proven that solid state gas sensors based on semi-conducting metal oxides, such as tin dioxide (SnO_2), zirconia (ZrO), titania (TiO_2) as the active sensing material are very promising in monitoring the hazardous gases emission into the atmosphere; where they have sensor response to few parts per million gas concentration and selectivity even at low operating temperatures (Bakrania & Wooldridge, 2009; Bittencourt et al., 2003). Among those solid state gas detecting devices, metal oxide gas sensors have a lot of advantages, for instance, low cost, compact size and easy production; hence these gas sensors have dominated the domestic, commercial and industrial applications (Sun et al., 2012).

1.1.3 SnO_2 sensors

Tin dioxide, gas sensor is a n-type semiconducting sensor with a wide band gap of 3.6eV in its pure and undoped form, which has a tetragonal lattice crystalline structure (Arkadiy & Aleksander, 2004; Guo et al., 2011; Luo et al., 2013). In this wide band-gap with six oxygen atoms surrounding every tin atom in its stoichiometric form offers a good insulating properties for the gas sensors (Naturwissenschaften, 2007). It has several other advantages like higher chemical, mechanical and thermal stability and lower cost (Kadhim & Abu Hassan, 2015; Vaezi & Zameni, 2012).

High sensitivity, short response–recovery time and good selectivity are equally important to detect ethanol in the practical application. In addition, a high sensitivity with compact structure ethanol gas sensor to be equipped in a car or as a breath analyzer are very interesting for these applications for preventing car accident from drivers over the legal drink-drive limit (Guo et al., 2011; Ho et al., 1998).

1.1.4 SnO_2 sensing mechanism

The gas sensors operation is based on the principle of measuring the change in resistance of the sensing material surface in exposed to the target reducing gas. The reversible redox reaction of oxygen vacancies within the tin oxide layers with atmospheric oxygen is the main response mechanism.

In air, oxygen gases are adsorbed on the SnO_2 sensing material surface, forming a layer of oxygen ions or oxygen adsorbates (either atomic O^-, O^{2-} or molecular O_2^-). The adsorbate oxygen layer captures and traps the electrons from the conduction band in inner SnO_2 film, reducing the electron density and leaving positive charges in a space charge layer near the metal oxide surface layer. The negative charge trapped in the oxygen adsorbates creates a surface potential, a potential barrier against electron flow and causes an electron-depletion layer; and this thus increases the resistance and reduces the conductivity (Ivanov, 2004; Sun et al., 2012).

The trapped electrons in oxygen adsorbate will return to the SnO_2 film once the sensor is exposed to reducing gases such as ethanol gas. Then the associated potential barrier with the depletion layer decreases in height. This leads to the increase in the electron density in the SnO_2 layer surface and then resistance decreases hence the conductivity of the sensor increases back (Miller et al., 2006; Sun et al., 2012). Figure 1.1 shows the schematics diagram for the mechanisms leading to SnO_2 gas sensing mechanism in response to reducing gas.

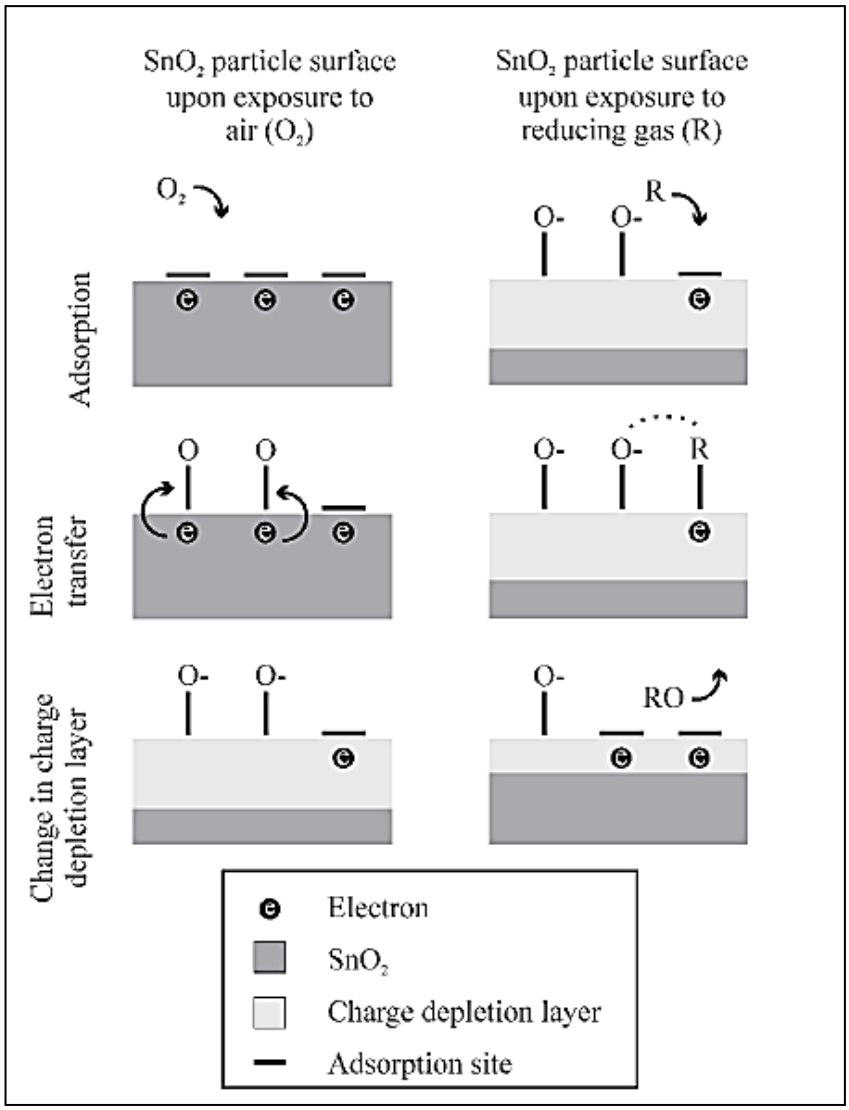

Figure 1.1: Schematics indicating the SnO_2 gas sensing mechanisms in presence of reducing gases (Miller et al., 2006).

The amount of chemisorbed oxygen on the surface and the species heavily affects the change of resistance in the gas-sensing mechanism; those factors are highly dependent on the microstructure of the SnO_2, such as specific area, particle size and the porosity (Bittencourt et al., 2003; Guo et al., 2011). The surface conductivity for the metal oxides is heavily influenced by the surface stoichiometry where oxygen vacancies acts as donors that increases the surface conductivity and oxygen adsorbate acts surface acceptors that binds electrons and reduces the surface conductivity.

Amount of a specific gas present is directly related to the change in conductivity of the sensor hence the quantitative determination of gas present in the exposed environment can be done by exploiting the relation (Sun et al., 2012).

1.1.5 SnO_2 synthesis methods

There are many processes developed to synthesize SnO_2 nanostructures, thermal evaporation, chemical vapor deposition, spray pyrolysis, sol-gel method, solvothermal method, hydrothermal and more (Naje et al., 2013; Taylor et al., 2010; Ullah et al., 2017). Generally, these methods can be classified into vapor phase deposition and solution-based crystal growth. Vapor phase deposition such as thermal evaporation and rapid oxidation, produces high quality nanostructure but costs relatively more. On the other hand, solution-based crystal growth synthesis like co-precipitation, sol-gel method and hydrothermal, is simpler and cheaper whereby these methods often generate nanomaterial with control of particle sizes and structures at lower temperature (Srivastava, 2014).

1.1.6 SnO_2 synthesis via sol-gel method

Sol-gel is a simple chemical method to synthesize homogeneous nanoparticles at a low temperature. Sol-gel method is favored for its simplicity in just mixing precursor in solution for desired composition and structure modification at molecular level which often produce nanoparticles with high porosity and large surface area (Ang et al., 2011). In this process, the precursor solution is transformed into inorganic solid. This can be done by firstly dispersion of the colloidal particles of the precursor in a liquid, forming sol then conversion of the sol into a rigid phase, namely gel by the means of hydrolysis and condensation. After that, typically amorphous precipitate is obtained. To promote particle growth and to alter particle morphology, heat treatment or calcination is then applied to the precipitate and metal oxides nanoparticles can be

obtained thereafter (Bhagwat et al., 2015). The sol-gel method can also be applied for synthesis of oxides nanoparticles for various metals such as Ti, Fe, Cr, Mn, Al and many more (Adnan et al., 2010).

1.1.7 Fabrication of SnO_2 sensor

Sensor fabrication is a complex process that restrict, limit and define sensor performance (Bakrania & Wooldridge, 2009) where different morphologies and composition can be produced from different fabrication methods. In fabrication, metal nanoparticles are dispersed on the surface of the substrate to increase the surface area to volume ratio so to favor the adsorption of gases (Khanna, 2012). SnO_2 sensing material can be fabricated into thin-film, thick-film and pellet form. There has been quite a lot techniques developed to fabricate SnO_2 thick films, for instance, screen printing, drop-coating, sputtering, sol-gel methods and more.

On the other hand, electron beam evaporation, thermal evaporation, sputtering and chemical vapor deposition are some of the important method for thin film sensor generation. Thin and thick SnO_2 films share a great similarity in the general architecture where both techniques incorporate a substrate (typically alumina) containing printed electrodes (typically platinum or gold) (Miller et al., 2006). An annealing or calcination step is often included in most of the sensor fabrication process to drive off the impurities that may be present in SnO_2 sensing material, such as chlorine.

When it comes to selecting the fabrication technique, factors like cost, purity, porosity and reproducibility must be taken in account for consideration (Fine et al., 2010). Screen-printing are quite popular for thick film technologies used in industries whereas sol-gel deposition, spin coating and sputtering are widely employed for thin

film technologies. Due to lower power consumption and better sensor performance, thick or thin film SnO_2 sensors are typically preferred to pellet, sintered block and porous plug sensors (Miller et al., 2006).

1.1.7.1 Chemical vapor deposition

One of the thin film fabrication is chemical vapor deposition (CVD) where a heated substrate is exposed to a precursor or mixture of precursors in vapor phase. A film of the desired sensing material is then formed by the reaction or decomposition of the precursor vapor on the heated substrate. Vital properties of the gas sensing material such as grain size, thickness and porosity can be well controlled with CVD and CVD also offers an advantage in film growth speed with a typical rate up to 1 μm per minute for processes that occur even only under atmospheric pressure. Different CVD techniques includes rapid thermal CVD, aerosol assisted CVD and atmospheric pressure CVD. Precursors must be volatile enough for successful delivery to the heated substrate; while non-volatile precursors must be made into an aerosol before deposition or else rapid thermal CVD is used (Fine et al., 2010).

1.1.7.2 Screen printing

Screen printing is one of the thick film deposition techniques and its technologies has been widespread and popular in gas sensors field. In the deposition process, an ink is pushed through a porous layer or mesh which is masked to produce the desired layout on the substrate (Fine et al., 2010). Conventional ink incorporates a binder paste which improves the mechanical strength and adhesion of sensing material onto the substrate surface (Viricelle et al., 2005). After that, the print is calcined for vehicle removal, leaving a solid material on the target substrate.

1.1.7.3 Drop coating

Another thick film deposition techniques is drop coating in which the fabrication is carried out by depositing a paste onto a substrate surface with controlled injection using pipette (Fine et al., 2010). The paste is made of desired metal oxide powder and a solvent. Thickness of the sensing material film can be varied with different number of drops deposited and this is very dependent on the viscosity and density of the paste solution (Bakrania & Wooldridge, 2009). Then it is followed by a heating step to remove the solvent thus improving adherence of sensing material to the substrate.

1.2 Problem statement

Metal oxide sensors have been widely used for the last ten years when it comes to toxic and combustible gases detection, for their low cost production. High sensitivity, selectivity and stability are the criteria for a great metal oxide gas sensor with high performance. Much attention has been put to improve the sensors in terms of those criteria. It has been reported that the performance of a metal oxide gas sensor is related to the preparation method and the operating conditions of the sensors. Particle size, sensing film morphology and film thickness can be affected by the sensor preparation route and those sensor properties directly influence the performance of the sensor. Nevertheless, the study on a simple and low-cost preparation method without using complicated equipment for SnO_2 sensors towards ethanol gas is vital. Therefore, sol gel method was used to synthesize SnO_2 nanoparticle and drop coating method was used to fabricate the SnO_2 sensor. Then, the surface structure of the sensing material and the performance of the sensor are studied and compared with the sensor fabricated using commercial SnO_2 powders.

1.3 Research objectives

The main objectives of this study are:

i. To synthesize SnO_2 nanopowders by sol-gel method and to fabricate SnO_2 gas sensor by drop coating method.

ii. To study the effect of operating temperature and concentration of ethanol gas on the SnO_2 thick films sensing performance.

iii. To develop an understanding of the relationship between the morphology of the SnO_2 nanoparticles and the gas sensing performance.

iv. To compare the sensing performance of sensors fabricated using synthesized and commercial SnO_2 powders in terms of sensitivity.

CHAPTER TWO

LITERATURE REVIEW

2.1 Tin (IV) Oxide (SnO_2) Sensor

Studies has proved that the structural features with different morphologies and compositions dramatically affects the properties and performance of SnO_2 based sensors; and the structural features are heavily influenced by the precursor synthesis process and the deposition techniques (Bittencourt et al., 2003; Guo et al., 2011). Hence, the synthesis of nanostructured SnO_2 materials, like nanotubes, nanoribbons or nanobelts, macroporous films, nanowires, hollow spheres and mesoporous SnO_2, has been the focus of considerable amount of studies where mesoporous SnO_2 has been paid great attention to meet the ever-increasing demand of gas sensors (Guo et al., 2011). On the other hand, wide investigation also shows that nanostructures of SnO_2 show high sensitivity to acetone gas, with short response times (Tan et al., 2015). Hence, the degree of selective detection of ethanol in the presence of acetone using gas sensors fabricated with as-prepared and commercial SnO_2 precursors is also compared (Hieu et al., 2008).

SnO_2 has been the most popular sensing material for its higher sensor response to oxidizing and reducing gases simultaneously, showing high sensitivity to a wide variety of reducing gases, such as H_2, CO, NO_2, H_2S, CH_2 and ethanol (Bittencourt et al., 2003; Vaezi & Zameni, 2012). As ethanol gas sensing material, SnO_2 holds many advantages like low cost, shorter response and recovery time and also simple manufacturing technique (Sun et al., 2012). Traits of this material, such as high chemical stability in acids and bases, good electrical conductivity with transparency in the visible optical spectrum, high corrosion resistance (Arkadiy & Andriiko, 2004) and

its natural non-stoichiometry properties (Delgado, 2002), has been the reason for its frequent usage for the ethanol sensing.

2.2 Sensor substrate material

Sensing film is important for the receptor function (the reactions between the gas and the metal oxide surface), whereas the response of the complete device depends on the choice of the transducer and the operation mode. Alumina or silicon based substrates are the most used materials for gas sensors. The substrate used for gas sensors should be chemically inert and have excellent thermal stability and good dielectric properties. There must be no undesirable reactions between the substrate and the gas-sensitive layer (Comini et al., 2008). Good adhesion of gas sensing layer deposited on substrates is essential while thermal coefficient of the gas sensing layer is very important for great adhesion. Alumina and silicon based substrates typically could withstand temperature up to 1000 ^{o}C. Those substrates also offers several advantages such as good mechanical strength, good surface finish for uniformity, less visual defects like pits or burr and low cost in large production (Korotcenkov, 2013).

2.3 Sensing material synthesis via sol-gel method

Amongst different synthesis methods for preparation of tin oxide, sol gel method offers several advantages over other methods, such as ambient processing conditions, does not need complicated equipment, better homogeneity and controlled stoichiometry, flexibility of forming dense monoliths, thin films, and nanoparticles (Basu et al., 2013; Bhagwat et al., 2015; Kose et al., 2015; Pawar et al., 2012). Sol gel method is a relatively novel process in preparation of material which needs precise microstructural control (Shiomi et al., 2000). For example, Hyodo et al. (2002) prepared mesoporous structure SnO_2 powders by utilizing the self-assembly of a cationic surfactant and investigated their gas-sensing properties to H_2 and NO_x. Also,

a new sol–gel route with neutral sol in preparing SnO_2 films using tin oxalate as the precursor and water as the solvent (Luo et al., 2015). Nevertheless, precursor used in the conventional sol–gel method to prepare SnO_2 is materials such as chloride ($SnCl_2 \cdot 2H_2O$), sulfates and so on. The solvent always used is ethanol.

Through sol-gel route, the particles synthesized typically have a relatively better uniformity of size (Altavilla & Ciliberto, 2011). Sol-gel method has a relatively lower temperature sintering capability, usually 200 – 600 ^oC and it has been reported to produce high quality coatings through simple, economic and efficient method (Comini et al., 2008). According to Choudhary et al. (2012), the average SnO_2 particles sizes synthesized using sol gel method was 14.68 nm; it can be concluded that small particles, which is generally better for sensing application for higher active surface area thus higher sensitivity, can be obtained through sol gel method. In addition, flexibility was also shown where several works reported different SnO_2 crystallite sizes obtained through sol gel route. For instance, Tripathi et al. (2016) obtained SnO_2 nanopowders of 3.8 – 4.8 nm using polyethylene glycol assisted sol gel method while Zhang & Liu (1999) obtained SnO_2 nanopowders with sizes of 2.6 to 10.2 nm using a sol gel route based on tin tetrachloride and ethylene glycol. Kose et al. (2015) synthesized SnO_2 nanopowders with crystallite sizes ranging from 6.03 nm to 9.65 nm by varying the sol concentrations. Also, Hassanzadeh et al. (2008) used sol gel route with propanol and isopropanol mixture instead of ethanol to synthesize SnO_2 nanopowders and crystallite sizes from 6 – 80 nm were obtained.

On the other hand, SnO_2 nanopowders synthesized through thermal evaporation method at 1000^oC had diameter ranging from 200 to 600 nm, according to the work by Li et al. (2011). Patil et al. (2012) synthesized SnO_2 particles using a simple

hydrothermal route in the presence of surfactant hydrazine and obtained an average size of 22.4 nm. In this study, the SnO_2 precursors were synthesized using a sol-gel method proposed by Bhagwat et al. (2015) since sol gel method is relatively simple and have comparable results with other common synthesis route. A comparative study between sensors prepared using as-prepared and commercial SnO_2 powders is to be conducted.

2.4 Fabrication of SnO_2 sensor

Sensor performance can be restricted, limited and defined by sensor film fabrication, which is a complex process (Bakrania & Wooldridge, 2009). Thick film technology is an easy and simple technique for low-cost devices fabrication where the powder selection and firing step are crucial. Paste of semiconducting metal oxide powder with or without the inorganic additives and/or binder is fabricated to produce thick film gas sensors (Comini et al., 2008). Among the typical fabrication methods for SnO_2 thick films sensor, drop-coating method is used for its better sensor performance in terms of sensitivity compared to sputtering and screen printing Bakrania & Wooldridge (2009) showed that drop-coated sensors yielded excellent sensor response compared to binder-paste screen-printed sensors. Bittencourt et al. (2003) reported that drop-coating method outperformed sputtering method to grow more sensitive active SnO_2 films, in which the sensitivity of drop-coated sensors was higher than that of sputtered sensor by five times.

Drop-coating is used in this study also for its ability to yield repeatable sensor performance and its simpler instrumentation compared to that of other methods, such as screen printing or sputtering (Bakrania & Wooldridge, 2009; Bittencourt et al., 2003). To mitigate the effect of different fabrication methods, only drop-coating

method is used to investigate the relationship between the sensor performance and the material properties.

2.5 Factors affecting the sensitivity of SnO_2 sensor

Sensitivity is mainly dependent on the chemical reaction rate on the sensor-gas interface and the speed of the gas diffusion to the sensor-gas interface and these two processes can be affected by various factors (Basu et al., 2013). The sensitivity of the sensor towards reducing gas, such as ethanol gas, can be defined as followed (Liu et al., 2009):

$$S = \frac{\mathbf{R_a}}{\mathbf{R_g}} \tag{2.1}$$

where S = sensitivity of the gas sensor

R_g = resistance of the gas sensor in the reference gas containing target gas

R_a = resistance of the gas sensor in the reference gas (usually air)

Crystallite size is one of the dominant factors for sensing performance for SnO_2 sensor where sensitivity would be higher with lower crystallite size; and the crystallite size can be controlled with different calcination temperature for SnO_2 nanopowders synthesis (Xu et al., 2012). A small particle size, a large surface-to-volume ratio and high crystallinity are required to enhance the sensitivity of gas sensors (Muthuvinayagama & Viswanathanb, 2015). Llobet et al. (2000) studied drop coated tungsten oxide films and showed that formation of particles agglomeration can be a consequence from long solvent evaporation temperature. In short, there are a few important factors affecting the sensitivity of the SnO_2 sensors towards ethanol vapor to be noted, for example, thickness of the sensing film, calcination of SnO_2 sensing

material, operating temperature of the sensor, concentration of target ethanol vapor, presence of other volatile organic compound and the addition of additives.

2.5.1 Thickness of sensing film

Thickness of the sensing material film of the sensor has been reported to have an influence on the sensitivity of the sensor. As the film thickness or the particle size of the metal oxide decreases, the sensitivity increases or the response time decreases (Khanna, 2012). According to Hossein-babaei & Orvatinia (2003), the sensitivity would be higher when the film thickness is lower as shown in Figure 2.1 and gas sensor made of SnO_2 films with thickness less than 300 nm are prone to have lower stability and reproducibility.

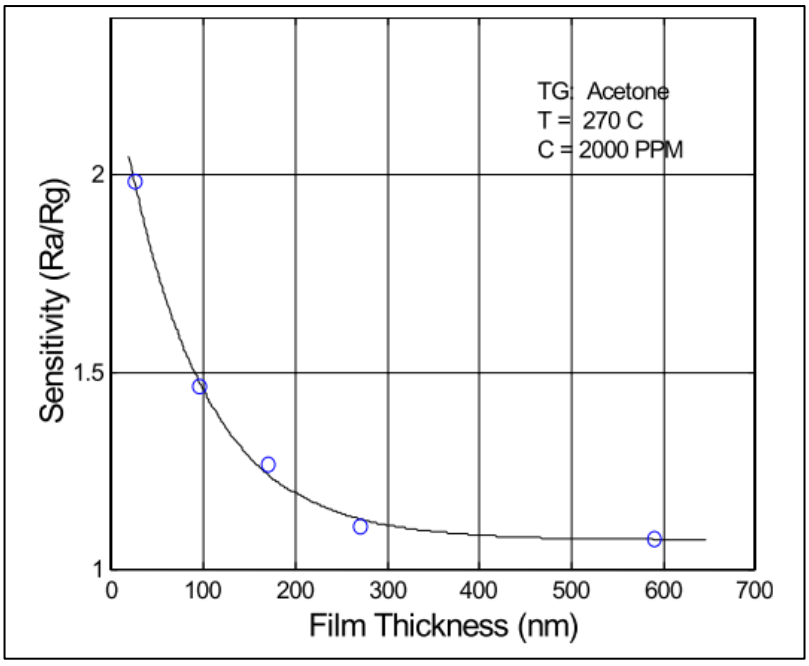

Figure 2.1: Experimental relationship observed between the sensitivity of the gas sensors and effective thickness of the tin oxide layer.

In the work done by Liewhiran & Phanichphant (2007), ZnO thick film sensors fabricated on Al_2O_3 substrate were also found to have better sensitivity toward ethanol gas for thinner sensing film, as shown in Figure 2.2. They found that film thickness

increases when number of cracks increases, as a result of agglomeration of small grains at cooling after calcination; these cracks decrease the surface area and deteriorates film properties of the sensing materials, causing a decline in sensitivity.

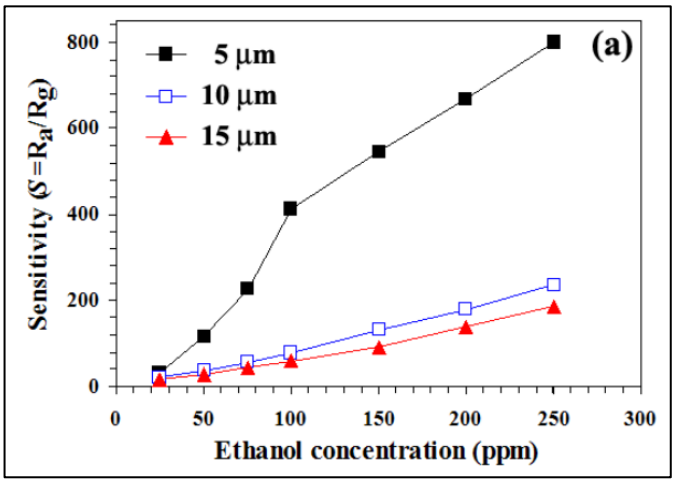

Figure 2.2: Comparison of sensitivity of ZnO thick film sensors with various film thickness dependence on ethanol concentration.

2.5.2 Calcination temperature

Calcination temperature plays a vital role in controlling crystallinity and particle size of the sensing materials produced and it was reported that crystallinity and crystallite size generally increases as aging heat time increases. Figure 2.3 shows that the crystallinity increases with calcination temperature (Pawar et al., 2012; Zhong et al., 2012). Calcination also increases the number of charge carriers and reduces the optical transmittance (Ikhmayies, 2016).

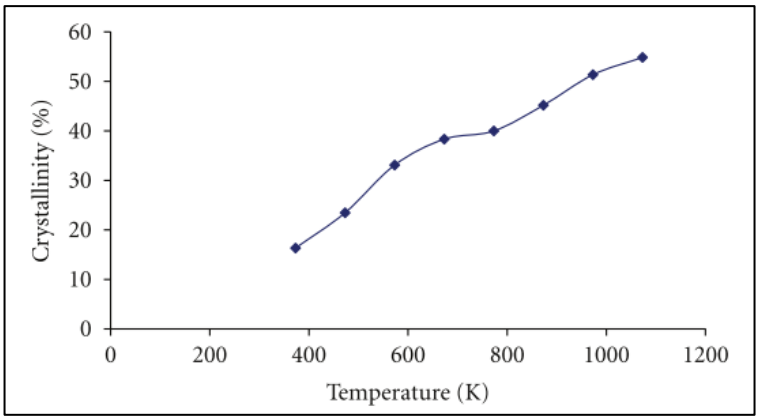

Figure 2.3: Variation of the crystallinity of SnO_2 nanoparticles with calcination temperature.

Cabot et al. (2000) reported in their work that as the annealing temperature increases, the grain size obtained for various doped SnO_2 nanopowders also increases, as shown in Figure 2.4. Several works characterized SnO_2 thin films calcined at 400 ^oC, 500 ^oC and 600 ^oC, obtaining crystallite sizes of 8.3 nm, 33.19 nm, and 33.20 nm respectively (Ke et al., 2011; Li et al., 2012). Another work by Köse et al. (2014) also reported similar trend where the grain size of SnO_2 particles calcined at 350 ^oC to 750 ^oC with 100 ^oC increment were obtained at 15 nm, 17 nm, 22 nm, 36 nm and 41 nm respectively.

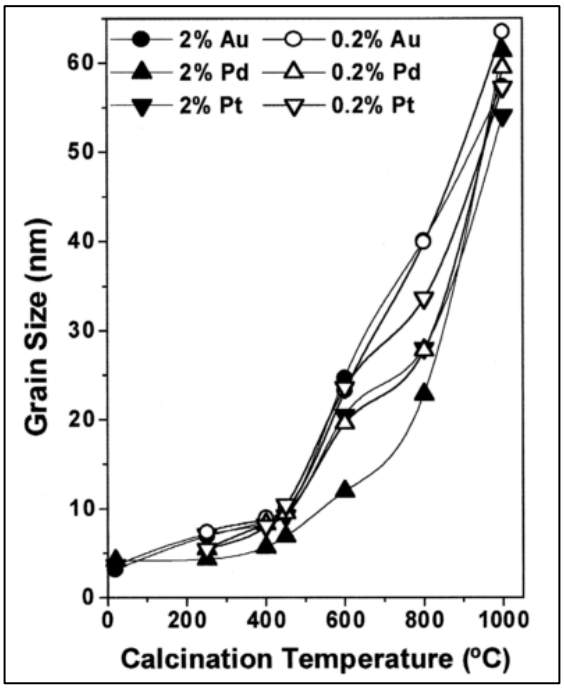

Figure 2.4: Crystallite size evolution with calcination temperature for different modified SnO_2 nanopowders.

Nanoparticles with higher crystallinity have improved properties like higher stability which offers an advantage for gas sensor (Pawar et al., 2012). Sensitivity is enhanced by high surface area which could provide high amount of active sites for oxygen adsorption and surface reaction. When the crystallite size of the sensing material decreases, the porosity and the surface area for the surface sensing reaction would increase hence higher sensitivity towards target gases. Sintering as a result of annealing can cause the number of pores to decrease while increase the pore size, then reducing the surface area and sensitivity with increasing calcination temperature (Guo et al., 2011).

In the case of sol gel method, higher calcination temperature is preferred to remove chlorine ions and also to promote ions adsorption on powder surface (Kose et al., 2015). The calcination temperature employed could not be too high as it could promote agglomeration and decrease the specific surface area of the sol-gel-obtained

nanocrystalline SnO_2. Therefore, balance must be kept between grain sizes and stability using different calcination temperature because small grains could agglomerate at high temperature thus reducing surface areas though it offers a higher surface area (Pawar et al., 2012; Wang et al., 2010).

Furthermore, resistivity of SnO_2 sensors has been reported to decrease with increasing calcination temperature (Jeng, 2013; Lee et al., 2014) as shown in Figure 2.5. Sensitivity is proportional to the change in the resistance of the material on exposure to the target gas (Altavilla & Ciliberto, 2011). When the calcination temperature is higher, the crystallite size is larger and number of grain boundaries is lower, as a result the conductivity increases and resistivity decreases (Mehraj et al., 2016). Besides, the stability of the sensing material could be improved with a lower resistance of the sensors (Xu et al., 2012). Hence in this study, different calcination temperatures of the deposited films at 400 ^oC, 500 ^oC and 600 ^oC are used, correlating the sensor performance and the microstructure of the sensing material deposited.

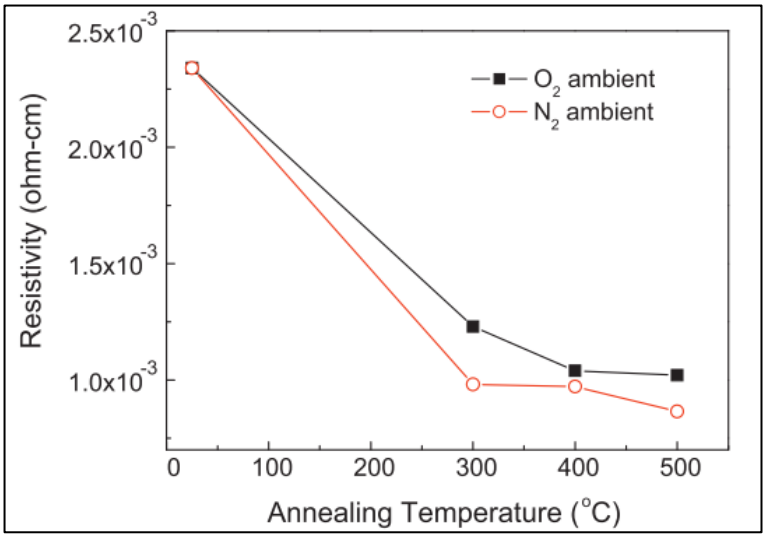

Figure 2.5: Relationship between resistivity of SnO_2 films and calcination temperature in O_2 and N_2 ambient.

2.5.3 Operating temperature

The relationship between the operating temperature and metal oxide sensor response is generally a bell shape curve, with a maximum sensitivity at a certain temperature. As the temperature increases, there would be an increase in sensitivity until the optimum temperature is reached and the sensitivity would fall on further increase in temperature. Sensitivity increases from temperature rise because the external heat energy contributes to overcome the activation energy barrier for the adsorption and sensing surface reaction; the exothermic vapor adsorption on the metal oxide surface could be disrupted for extra heat energy supplied, then the sensitivity of the sensor decreases (Ang et al., 2011).

A high number of studies showed that SnO_2 sensors work best at an operating temperature of 300 ^oC to detect ethanol vapor (Ang et al., 2011; Guo et al., 2011; Xu et al., 2012). As reported by Guo et al. (2011), the ethanol gas sensors prepared with SnO_2 nanopowders calcined at 300 ^oC and 400 ^oC had an optimum sensitivity of 70.3 and 100.4 at operating temperature of 300 ^oC whereas sensors prepared with commercial SnO_2 nanopowders reached optimum sensitivity at operating temperature of 350 ^oC as shown in Figure 2.6. Therefore, operating temperatures of 200 ^oC, 300 ^oC and 400 ^oC for SnO_2 sensors were used to study the performance of the sensors for detecting ethanol gas.

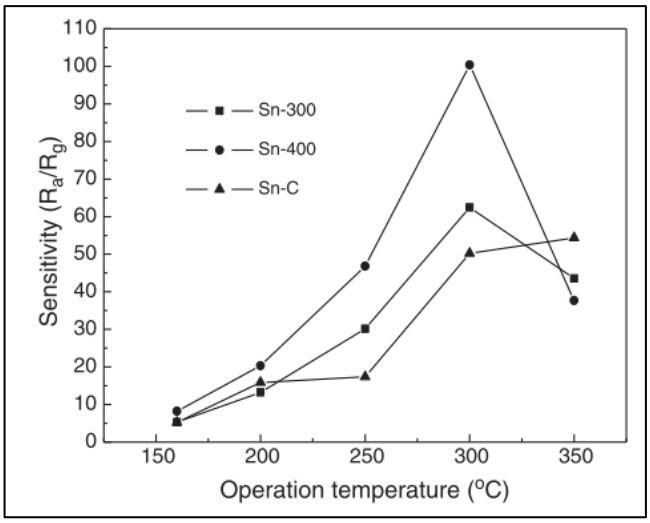

Figure 2.6: Sensitivities of the SnO_2 sensors to 0.1 vol.% ethanol at different operating temperature.

2.5.4 Concentration of ethanol

There have also been many studies on the effect of concentration of ethanol vapor on the sensitivity of the sensor. Generally, ethanol vapor concentration has a linear relationship with the sensitivity of the sensor, in which an increase in ethanol concentration provides more ethanol molecules available, and more ethanol molecule would be adsorbed on the metal oxide surface per unit time (Basu et al., 2013).

For example, Chen et al. (2006) fabricated 20 SnO_2 sensors with nanoparticles of 80 – 180 nm and tested them for the sensitivities of the sensors towards ethanol at different ethanol concentration from 10 to 300 ppm, and obtained a linear dependence of the sensitivity on the ethanol concentration as shown in Figure 2.7.

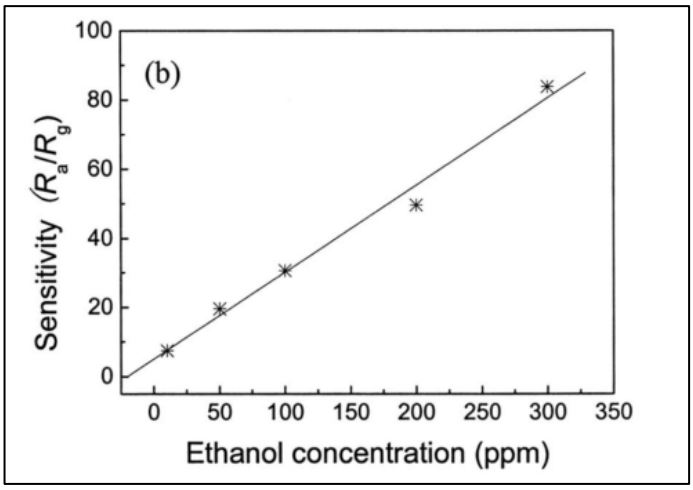

Figure 2.7: Sensing properties of SnO_2 sensors exposed to ethanol gas with different concentrations.

On the other hand, Figure 2.8 shows that the sensitivity of SnO_2 thin film sensor towards ethanol gas was also found to increase with ethanol concentration, and saturates after 1150 ppm of ethanol (Mishra et al., 2002). At low concentration, sensitivity increases linearly with concentration as there should be sufficient number of surface states available to react with ethanol vapor molecules; while the adsorbed oxygen species might not be enough for reaction thus sensing mechanism (Mishra et al., 2002). In this study, the concentration of ethanol gas from 200 ppm to 1000 ppm was used so to correlate the concentration of ethanol with the sensitivity of the sensor.

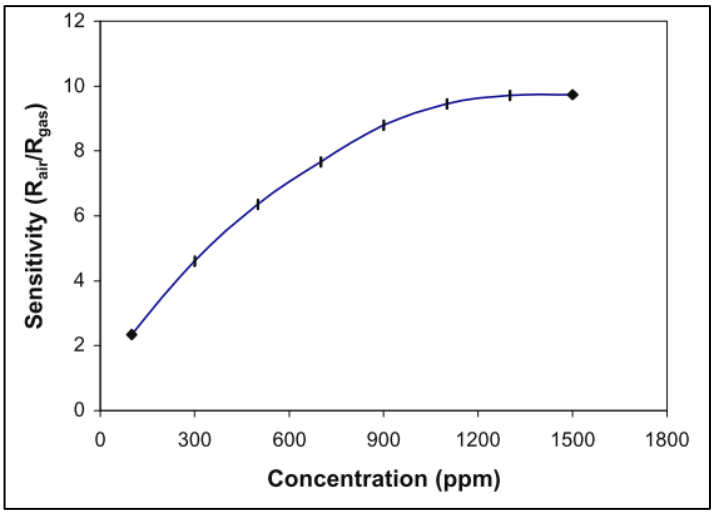

Figure 2.8: Variation of sensitivity of tin oxide sensor with ethanol concentration at 623 K.

2.5.5 Effect of different volatile organic compounds

Acetone is typically the major disturbing volatile organic compound for ethanol detecting sensors. The sensitivity of SnO_2 sensor towards ethanol or other volatile organic gases is found to be highly temperature dependent and hence different temperatures can be used to render the films sensitive to different gases. The reaction of ethanol vapor with the chemisorbed oxygen on the metal oxide surface is related to decomposition or oxidation reaction, with a chemical reaction as shown:

$$C_2H_5OH + O^- \rightarrow CH_3CHO + H_2O + e^-$$

According to Ang et al. (2011), SnO_2 sensor is sensitive towards ethanol and acetone at 300 ^oC and towards methanol at 250 ^oC, as shown in Figure 2.9. An article reported that SnO_2 sensors showed the highest selectivity of ethanol over acetone at 300 ^oC where the selectivity was 6.5, 5.9 and 7.9 for sensors prepared using SnO_2 nanoparticles calcined at 400 ^oC, 600 ^oC and 800 ^oC respectively (Xu et al., 2012).