SYNTHESIS AND PERFORMANCE OF ORDERED MESOPOROUS SnO_2 USING KIT-6 NANOCASTING FOR DETECTION OF HYDROGEN SULPHIDE GAS

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by

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Thibbaganesh A/L Sattigamurti

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LIST OF SYMBOLS

Symbol	Description	Unit
α_0	Pre-exponential constant	ppm^{-1}
a_o	Unit cell parameter	nm
α	Sensitivity coefficient	ppm^{-1}
$C_{A,s}$	Gas Ccncentration outside the film	ppm
C_A	Gas concentration inside the film	ppm
d_{hkl}	d-spacing	Å
D	Average pore size	Nm
D_k	Knudsen diffusion constant	m^2/s
E_a	Reaction activation energy; gas-dependent	kJ/mol
E_k	Reaction activation energy; temperature dependent	kJ/mol
E_g	Band gap	eV
k_o	Pre-exponential constant	s^{-1}
k	Arrhenius equation constant	-
L	Film thickness	Nm
M	Molecular weight	g/mol
R	Gas Constant	J/mol.K
r	Pore radius	nm
S	Sensitivity of sensor	-
S_{BET}	BET specific surface area	m^2/g
T	Operating temperature of sensor	K
V_T	Total pore volume	cm^3/g

LIST OF ABBREVIATION

Symbol	Description
AC	Alternate current
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CO	Carbon Monoxide
CEM	Conventional evaporation method
HCL	Hydrochloric acid
H_2S	Hydrogen sulphide gas
IUPAC	International Union of Pure and Applied Chemistry
In_2O_3	Indium Oxide
KIT-6	Korean Institute of Technology
MEMS	Microelectronic mechanical system
NO_2	Nitrogen Dioxide
NaOH	Sodium hydroxide
N_2	Nitrogen
O_3	Ozone
OMS	Order mesoporous silica
OMMO	Order mesoporous metal oxide
PM_x	Particulate matters
SO_2	Sulphur dioxide
SnO_2	Tin Oxide
SGS	Semiconductor gas sensor
SEM	Scanning Electron Microscopy
SLM	Solid-liquid method

WO_3	Tungsten trioxide
XRD	X-ray powder diffraction
3-D	Three-dimensional

SINTESIS DAN PRESTASI SnO_2 BERLIANG MESO TERSUSUN YANG MENGGUNAKAN TEMPA NANO KIT-6 UNTUK PENGESANAN GAS HIDROGEN SULFIDA

ABSTRAK

Dalam bidang pengesanan gas berbahaya, penderia berasaskan timah oksida(SnO_2) telah mendapat banyak minat kerana kepekaan yang tinggi, tindak balas pantas dan kestabilan jangka panjang. Walau bagaimanapun, sensitiviti dan prestasi penderia berasaskan SnO_2 masih memerlukan kajian lanjut. Kerja ini memberi tumpuan kepada sintesis dan prestasi nanocasted mesoporous SnO_2 menggunakan silika mesopous KIT-6 untuk pengesanan gas hidrogen sulfida. Sintesis KIT-6 dilakukan menggunakan pluronic P-123 triblock copolymer, HCL dan tetraethoxysilane, diikuti dengan rawatan hidroterma menggunakan mandi minyak pada suhu 80°C dan 100°C. Suhu penuaan hidroterma 80°C mempamerkan struktur liang dan luas permukaan yang lebih baik kemudian 100°C. SnO_2 mesoliang yang dihasilkan dibandingkan dengan menggunakan dua jenis penyusupan yang berbeza iaitu kaedah pepejal-cecair dan kaedah sejatan konvensional. Berdasarkan sifat struktur yang diperoleh daripada pencirian XRD, BET dan SEM, ia menunjukkan kaedah penyejatan konvensional mempamerkan struktur yang lebih baik. Seterusnya, pengesanan gas hidrogen sulfida telah dijalankan menggunakan MATLAB berdasarkan sifat fizik yang diperolehi dari SnO_2 mesoporus yang telah dibangunkan. Pengaruh kepekatan hidrogen sulfida dan suhu operasi ke atas kepekaan penderia gas telah diterokai dengan bantuan model mekanisme resapan untuk menemui kaedah paling berkesan untuk mengoptimumkan sifat penderiaan gas yang mengunakan SnO_2 mesoliang. Keputusan yang diperoleh untuk kepekatan gas pada kepekaan menunjukkan lengkung yang diselesaikan dengan baik apabila kepekatan meningkatkan kepekaan

meningkat sehingga titik tepu yang sesuai dengan keputusan eksperimen daripada kertas penyelidikan. Dengan membandingkan suhu operasi terhadap kepekaan dengan kepekatan penderia yang berbeza-beza, ia mempamerkan lengkung berbentuk loceng yang berkorelasi dengan data eksperimen daripada kertas penyelidikan. Akhir sekali, analisis sensitiviti bergantung pada ketebalan filem, L, dan saiz liang, r, telah dijalankan. Kedua-dua analisis menunjukkan bahawa lengkung simulasi dengan data eksperimen yang dijalankan berdasarkan penyelidikan ini berkorelasi dengan data eksperimen hasil penderiaan gas daripada kertas penyelidikan yang diterangkan secara terperinci dalam kajian ini. Berdasarkan 17 Matlamat Pembangunan Lestari, matlamat 13 sesuai dengan kajian ini. Matlamat 13 adalah mengenai perubahan iklim, di mana ia adalah untuk meningkatkan kemampuan negara untuk menahan dan pulih dari bencana alam dan bahaya. Untuk mempunyai langkah berjaga-jaga awal yang disebabkan oleh gas hidrogen sulfida yang berbahaya kepada alam sekitar, sensor ini akan menjadi cara terbaik untuk memantau jumlah pencemaran hidrogen sulfida.

SYNTHESIS AND PERFORMANCE OF ORDERED MESOPOROUS SnO_2 USING KIT-6 NANOCASTING FOR DETECTION OF HYDROGEN SULPHIDE GAS

ABSTRACT

In the realm of harmful gas detection, tin oxide(SnO_2) based sensors have garnered a lot of interest because of their sensitive, quick response and stable over the long run. However, the sensitivity and performance of SnO_2 based sensor still require further research. This work focuses on the synthesis and performance of nanocasted ordered mesoporous SnO_2 using KIT-6 mesoporous silica for detection of hydrogen sulphide gas. Synthesis of the KIT-6 was done using pluronic P-123 triblock copolymer, HCL and tetraethoxysilane, followed by hydrothermal treatment using oil bath at temperature 80°C and 100°C. Hydrothermal aging temperature 80°C exhibits better pore structure and surface area then 100°C . The produced ordered mesoporous SnO_2 was compared using two different types of infiltration which are the solid-liquid method and conventional evaporation method. Based on the structural properties obtain from XRD, BET and SEM characterization, it shows that conventional evaporation method exhibits better structure. Subsequently, the detection hydrogen sulphide gas was carried out using MATLAB based on the obtained physical properties of the developed ordered mesoporous SnO_2. The influence of hydrogen sulphide concentration quantity and operating temperature on the sensitivity of a gas sensor was explored with the help of a diffusion mechanism model in order to discover the most effective methods for optimising the gas sensing trends of mesoporous SnO_2. The result obtained for the gas concentration on the sensitivity shows a well resolved curve as concentration increases the sensitivity increases until a saturation point which suits the experimental result from the research paper. By comparing the

operating temperature against the sensitivity with varying concentration of the sensor it exhibits a bell-shaped curve which correlates with experimental data from the research papers. Finally, sensitivity analysis was performed based on the film thickness (L), as well as pore size (r).Both of the analysis showed that simulated curve with experiment data conducted based on this research correlates with experimental data of gas sensing results from the research papers which are explained detailed in this study. Based on the 17 Sustainable Development Goals, goal 13 suits the studies. Goal 13 was about climate changes, where it’s about increasing countries' ability to withstand and recover from natural disasters and climate related hazards. To have early precaution caused by the hazardous hydrogen sulphide gas to environment, this sensor will be a perfect way to monitor the hydrogen sulphide pollution amount.

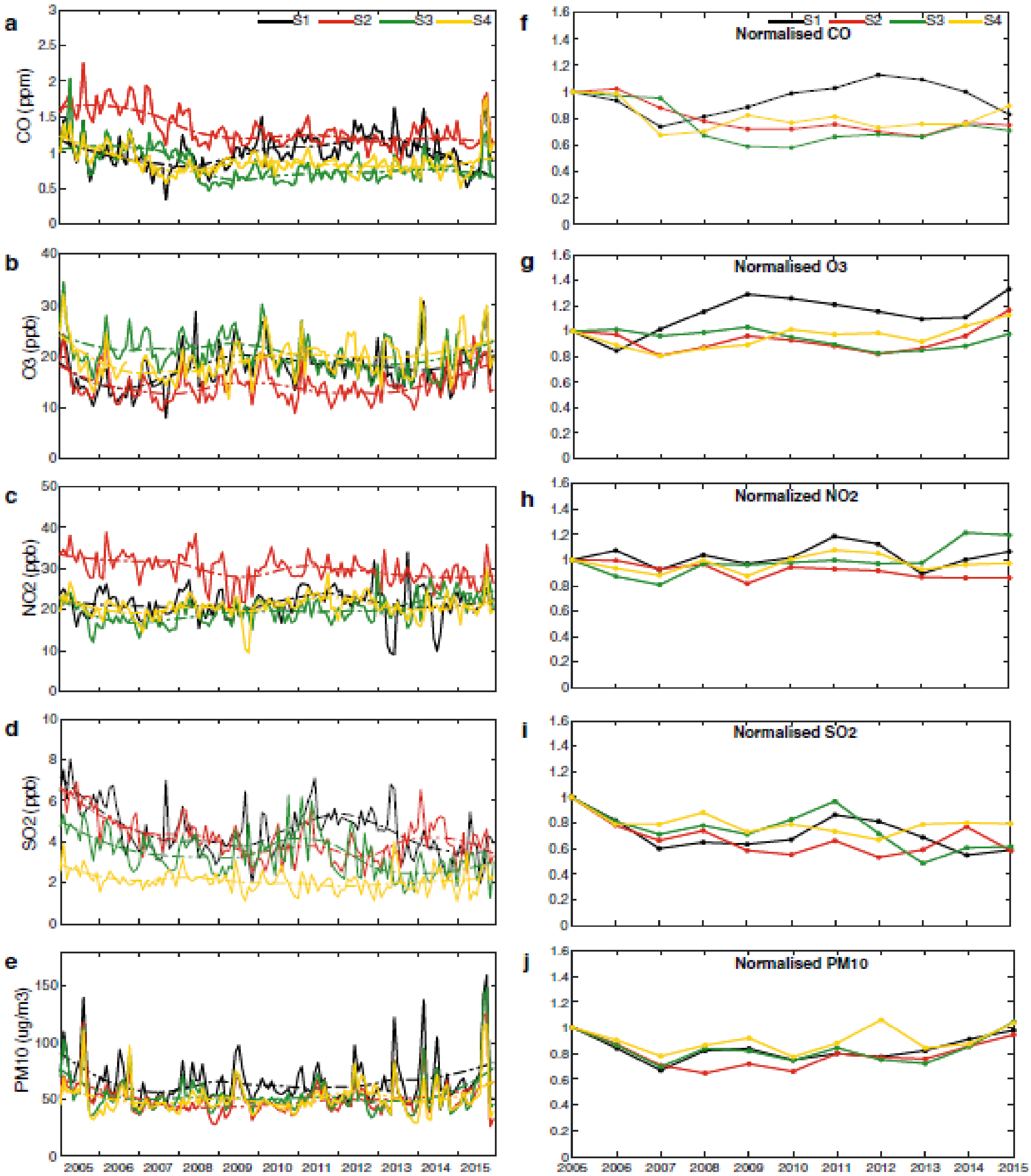
CHAPTER 1 : INTRODUCTION

1.1 The Importance of Monitoring Air Pollutants

The expansion of human demand for commodities produced in factories has accelerated in recent years. A lot of waste was being discharged directly into the environment throughout the manufacturing process. Mainly usage of fossil fuels creates exhaust fumes, which are eventually damaging the natural ecosystem, this has a direct influence on the environment. The effects of air pollution may be harmful even if they are not immediately apparent. According to new findings study, many pollutants are capable of negatively impacting community health and wellness even at extremely low concentrations. (Yuliarto, 2021) For instance, Figure 1.1 a-e shows the monthly mean concentrations of air pollutants with the estimated trend for the 11 years from January 2005 to December 2015 and f-j shows the normalised annual mean of air pollutants of 2005 at Selangor, Malaysia. (Klang (S1), Petaling Jaya (S2), Shah Alam (S3) and Cheras (S4)) (Mohtar et al., 2018) The levels of CO, O_3, NO_2, SO_2 and PM_{10} are quite high, these gases are classified as dangerous gases, so they need to be within the adequate levels. (Mohtar et al., 2018) This proves that Malaysia still faces issues on the air pollution levels.

Moreover, the pollutant known as hydrogen sulphide was generally acknowledged to be hazardous. The value of its threshold level was 10 parts per million. Hydrogen sulphide, often known as H_2S, a colourless gas that most well-known for the smell of rotten eggs that it gives off. The extraction of oil and natural gas, as well as their processing, are the most prominent sources of emissions. There are also paper mills, coke oven facilities, and petrochemical factories that fall within the category of industrial sources. Even at low concentrations, H_2S capable of causing irritation to the respiratory and cardiovascular systems, with early symptoms including eye irritation as well as headaches, nausea, and vomiting.(Bhomick et al., 2014)

Figure 1.1: Monthly mean concentrations of air pollutants with the estimated trend for the 11 years from January 2005 to December 2015 and f-j shows the normalised annual mean of air pollutants of 2005 at Selangor, Malaysia. (Klang (S1), Petaling Jaya (S2), Shah Alam (S3) and Cheras (S4)) (Mohtar et al., 2018)



The consequences due to air pollution not only affects human health but also harm the environment. Acid rain was one of the significant examples of the harmful effect of air pollutants. Acid rain was especially harmful to lakes, streams, and forests, as well as the flora and animals that reside there. Rain was one of the most important elements for human and animal survival. It formed by a chemical reaction from sulphur dioxide and nitrogen oxide content that was released into the air. (Burns, 2016) Exposure to pollutants for extended periods of time can make these problems much worse by causing chaos on the nervous, reproduction, and respiration systems. It can also lead to cancer and, in extremely rare instances, even cause death. The implications in the long run are chronic, which means they can last for lifetime, and they can even lead to death. In addition, the chronic toxicity of many different air pollutants has been linked to the development of a wide variety of cancers. (Mohtar et al.,) This emphasises the need of determining the most efficient method for assessing air pollutants in both the outdoor and indoor environments. As a result, a detection system was vital for identifying and controlling air pollution emissions. To be precise, specific gas sensors play a major role.

The sensors used to assess air pollution can be broken down into two categories: monitor the concentration of gas species and measure the concentrated mass of particle matter (PM). All sensor systems are made up of a few fundamental components, which include the sensory part that reacts to target in interest and varies with the particle mass in a sampling airflow; the device that translates responses into electrical impulses; a source of power, such as a battery, and data storage capabilities or a connection to a communication device. (Snyder et al., 2013)

Currently, there are certain conventional analytic equipment that were used for monitoring and detecting the gases. These types of equipment are normally located in the laboratory, for example, gas chromatography. The outcome will give an exact and precise reading, but these equipment's need specific skills to be operated. Besides, that it's high cost, very time consuming and high maintenance. (Snyder et al., 2013) Unquestionably, solid-state gas sensors are cheap production costs, great sensitivity, quick reaction and recovery times, a simple electronic interface, ease of use, low maintenance, and the capacity to detect huge volumes of gas. (Yuliarto, 2015) In conclusion, importance of monitoring air pollutant gives huge impact to goal 13 of sustainable development goals where climate change can be identified earlier to secure the precautions and action need to take.

1.2 Semiconductor Gas Sensors Based on Mesoporous Metal Oxides

Semiconductor gas sensors, also referred to as chemoresistive gas sensors due to their primary composition of metal oxides, are employed for the purpose of determining the presence of gases in the air. Recent applied studies and product launches in the field of mesoporous metal oxide sensors have shown some key trends in the use of nanotechnologies and gas-sensing layers, which will be implemented in the future. These trends include the use of micromachined silicon platforms as substrates for the sensitive layers of sensing devices in order to achieve low-cost, reliable, smart, and small sensing devices that use less power and are more reliable. (Capone et al., 2004) This trend demonstrates the significance of micromachined silicon platforms as substrates for the sensing layers of devices.

Electrically transduced gas sensors, also known as semiconductor gas sensors, are semiconductor gas sensors in which gas molecules interact directly with the sensor material. These interfaces are crucial in defining sensing device sensitivities, durability, and even biocompatibility. For a long time, single-gas applications relied on semiconducting gas sensors because of the flexibility and low power consumption they offer in terms of customising sensitivity and measuring concentrations of specific elements. However, disadvantages like high cross-sensitivity and poor selectivity to specific gases tend to offset the benefits. Low precision and selectivity can be overcome by employing a variety of sensing materials and techniques. (Nikolic et al ., 2020)

In terms of their ability to conduct electricity, semiconductors are defined as materials that have a conductivity that was higher than that of non-metals but lower than that of metals. Impurities are introduced to the materials that make up semiconductors in order to increase the conductivity of the materials. When a pentavalent impurity was supplied, a semiconductor was said to be of the N-type, but when a trivalent impurity was injected, it was referred to as a P-type semiconductor. (Wisitsoraat et al., 2009) The major difference between N-type and P-type are that Anthracene, Antimony, Phosphorous, and Bismuth (elements with five valence electrons) are examples of impurities that are introduced into N-type semiconductors while P-type semiconductors contain impurities such as aluminium, gallium, and indium (elements with three valence electrons), which are introduced to increase their conductivity. In an N-type semiconductor, most of the charge carriers move from low potential to high potential. In a P-type semiconductor, most of the electric charge carriers move from high potential to low potential. (Wisitsoraat et al., 2009)

The electrical resistance of a semiconductor gas sensor was created by a porous assemblage of small crystals of an n-type metal oxide semiconductor, generally SnO_2, In_2O_3, or WO_3. (Nikolic et al ., 2020) Mesoporous transition metal oxides are particularly important among non-silica mesoporous materials because they have d-shell electrons that are constrained to nanoscale walls, redox-active interior surfaces, and interconnected pore networks. As a result of these characteristics, they exhibit a wide range of fascinating features in energy conversion and storage as well as sensing, adsorption, and separation. Semiconductor gas sensors are categorized into two subtypes which are surface sensitive sensors that operate at temperatures below 500 °C. and bulk sensitive sensors that operate at elevated temperatures (usually more than 800 °C). (Yamazoe and Shimanoe, 2009)

An oxide refers to a type of molecule that has a chemical formula that contains at least one oxygen atom and one other element in addition to that element. Crystalline solids that are composed of a metal cation and an oxide anion make up metal oxides. It possesses an oxygen anion that has a state of oxidation equal to -2. Metal oxides are well-known for their usefulness as a chemical sensing material. The fundamental concept behind the application of crystalline semiconductor metal oxides as gas detectors was predicated on the surface-chemical interaction that takes place between the molecules of the gas and the surface of the sensing metal oxide. (Waitz et al., 2010) As a result, variations in electrical resistance may be used to determine the detection and quantification of a specific gas. Carbon and metal oxide semiconductors such as SnO_2, ZnO, WO_3, and In_2O_3 have gained research and engineering importance and are widely used to detect air polutants. Detection of combustible and explosive gases as well as environmental monitoring are all possible with the SnO_2 gas sensor's capabilities. (Li et al., 2020) In this research, SnO_2 was the chosen metal oxide due to its sensitivity for many types of gases species and low cost.

Metal oxides have a lot of different electrical properties that can be changed and changed again. This makes them a good material for things like solar cells, optoelectronics, spintronics, piezoelectric, and gas sensors. The responsiveness and sensitivity of metal oxide gas sensors can be improved by reducing the grain size and adjusting the operational temperature and humidity in line with metal additions and doping. In addition, the precision of a detector in relation to the type of gas being measured (oxidising or reducing), the electrical properties of the semiconductor materials, the action of dopants, and the natural order of the oxides being chosen are all important characteristic parameters to consider. (Shankar and Rayappan)

Tin(IV) oxide was used for functional sensing materials for semiconductor gas sensors in the field of chemical sensing because their electrical conductivity or resistivity changes with the composition of the gas environment surrounding them. (Mohtar et al., 2018) Metal oxides can be divided into two categories: non-transition and transition. Metal oxide semiconductors are divided into two types: n-type (where electrons are the majority of carriers) and p-type (where holes are the majority of carriers). (Yuliarto, 2015) SnO_2 was classified into the n-type semiconductor with favoured output signal due to electrons are the major carrier. SnO_2 metal oxide has been the choice in chemical sensing industry but several key parameters such as synthesis techniques used, chemical characteristics of SnO_2, sensor properties and the atmosphere are still being highlighted as problem. (Thorsten et al., 2006)

Moreover, one of the important characteristics of SnO_2 was shown by the porosity. Sensing materials having a high surface to volume ratio are sought at after their high sensitivity and rapid response, which are directly related to porosity. Microporosity was essential in this context because combination of larger specific surface area (usual range at 100–500m2 g-1) together strong diffusion into gasses molecule. (Waitz et al., 2010) Metal oxide particles with diameters range in few nanometres was created by a traditional sol–gel synthesis technique and bonded together to create a porous network. Mesoporous metal oxide materials are more durable and thermally stable, and they can preserve their integrity and mechanical strength even at extremely high temperatures. (Waitz et al., 2010)

Generally, there are three primary synthetic strategies for the production of mesoporous metal oxides with a large specific surface area and porous surface, which are standard sol-gel technique, utilization of amphiphilic structure directors (soft templating) and structure replication (hard templating). (Yang and Zhao, 2005) However, mesoporous metal oxides produced using traditional sol-gel processes have poor thermal stability and are prone to porosity loss at high temperatures. Synthesis using soft templating approach's challenge was that after removal of the soft template, the mesoporous metal oxide exhibits poor mesoporous structure, amorphous inorganic walls, and thermal stability. In hard templating method mesoporous silica material was used, which in this research KIT-6 was used. This approach gives out high crystalline framework, thermal stability, high surface area and stable mesopore structure. (Yang and Zhao, 2005) (Ren et al., 2012)

1.3 Detection and Monitoring System

Detection and monitoring systems of gas sensor have been revolving through these years which are being improved as time goes on based on further research. Traditional analytical instruments and solid-state gas sensors are the most commonly used identification systems for identifying and analysing dangerous gases. As an example, gas chromatography-mass spectrometry (GC-MS), mass spectrometry (MS), gas phase chromatograph (GC), and fourier transforms infrared (FTIR) equipment that are classified under traditional analytical instruments. Traditional analyses have the disadvantage of being expensive, sophisticated, and wide in scope. Furthermore, because the majority of analyses necessitate sample preparation, on-line, real-time analysis were challenging. (Capone et al., 2004)

Solid state gas sensors, which are based on a variety of principles and materials, are the most promising prospects for the development of commercial gas sensors for a wide range of applications in the gas detection field. (Capone et al., 2004) Solid state gas sensors have piqued the interest of the industrial and scientific groups due to their numerous advantages, which include small sizes, high sensitivities in detecting very low concentrations (at the level of ppm or even ppb) of a wide range of gaseous chemical compounds, the possibility of on-line operation, and low cost due to the possibility of bench production.(Nikolic et al ., 2020) They are one of the most important technologies in contemporary society. Solid-state chemical sensors have been widely utilised; however, they have a restricted measurement precision and have problems with long-term stability, which makes them less than ideal. However, it could be resolve by relating to the synthesising of material with new properties through the controlled modification of their microstructure on a nanometre scale, which would result in the production of novel classes of nanostructured materials with enhanced gas sensing properties, providing the opportunity to dramatically improve the performances of solid state gas sensors in this manner. (Zhao, 2013)

Furthermore, solid state gas sensors can be divided into three categories based on the sensing principles used and the sensor configurations which are the solid electrolyte-based gas sensors, resistive gas sensors based on semiconducting metal oxides, and impedance metric gas sensors. A dominating ionic conductivity was observed in solid electrolytes, which caused by the migration of ions through point defect sites in the crystal lattice. These sensors have only a minor contribution (usually less than 1 %) from electronic conduction (electrons or holes) to the total conductivity. (Liu et al., 2014) In solid electrolyte-based gas sensors has three types of sensors which are the Equilibrium potentiometric gas sensors, non-equilibrium potentiometric (mixed potential) gas sensors and Amperometric gas sensors.

Impedancemetric gas sensor, a sensor that uses AC measurements at a specified frequency. It was similar to solid-state impedance spectroscopy, which an electrochemical characterization technology that evaluates the cell response across a wide range of frequencies. (Pasierb and Rekas, 2008) When measured in the frequency domain, impedance was determined as the relationship between voltage and current. It was possible to investigate the frequency-dependent behaviour of individual electrochemical components using a technique called 'equivalent circuit analysis,' which are based on frequency-dependent behaviour. (Liu et al., 2014)

Next, the resistive gas sensors based on semiconducting metal oxides was widely used solid state gas sensors in various types of fields. The electrical resistance changes of semiconducting oxides caused by the contact between the sensing material and analyte gas, which was preceded by an electron transfer, measured by the resistor-type sensor. (Liu et al., 2014) This type of solid state gas sensor possesses numerous advantages than the previous two types of sensors which are the simple setup, cheap production, and cost effectiveness, as well as advancements in miniaturisation and MEMS technology (microelectronic mechanical system). Depending on the interactions between the sensing element and the analyte gas, semiconducting metal oxide-based sensors can be divided into three groups: bulk conduction-based sensors, surface conduction-based sensors, and metal/oxide junction-based sensors.(Liu et al., 2014)

1.4 Problem Statement

In many different sectors, gas sensors are essential for monitoring and detecting harmful inert gases, as well as assuring safety, air quality, and assessing surroundings. These are the conventional type of gas sensing equipment, which were high cost, time consuming and requires large size. Recently, research was being done that gas sensors with exclusive structure such like mesoporous metal oxides have better performance.

(Ren et al., 2012) There are some portable hydrogen sulphide gas sensors which often uses n-type metal oxide (e.g., SnO_2) but it possesses low response, moderate sensitivity against the pore size, film thickness and operating temperature. Ordered mesoporous SnO_2 have the potential for accurate and fast detection of gas. However, the ordered mesoporous SnO_2 sensing method was still plagued by a lack of sensitivity due to material's poor diffusion and chemisorption activities. The diffusion and chemisorption activities of a material are heavily influenced by its physicochemical parameters, such as porosity, surface area, grain size, and crystallite size. In this work, KIT-6 was used as the hard template to replicate the nanocasted ordered SnO_2 mesoporous structure due to its high crystalline framework, thermal stability, high specific surface area and stable mesoporous structure for hydrogen sulphide gas sensor.

1.5 Research Objective

I. To synthesize and characterize nanocasted mesoporous SnO_2 materials using KIT-6 as pre-synthesized ordered mesoporous silica (OMS).

II. To investigate the influence that varying nanocasting parameters have on the formation of nanocasted mesoporous SnO_2.

III. To study the hydrogen sulphide gas-sensing performances of nanocasted mesoporous SnO_2 by using MATLAB simulation under different operating temperature, gas concentrations, pore size and film thickness.

1.6 Sustainability

In the context of the production of products, goods, and services, the idea of sustainability refers to serving the demands of the current generation without jeopardising the ability of future generations to satisfy their own. The idea in sustainability involves acknowledging that the natural world was a resource that can be depleted. Therefore, it was essential to make efficient use of the environment and the resources it provides while also working to preserve it for the benefit of the Earth, our environment, humanity, and all other forms of life. One of the 17 Sustainable Development Goals that were set in place by the United Nations General Assembly in 2015, Sustainable Development Goal 13 focused on acting related to climate change. The stated objective statement for accomplishing this goal was to take rapid action to fight climate change and its negative effects. (Hák et al., 2016) As in this research mesoporous SnO_2 were used to detect the hydrogen sulphide gas in the atmosphere correlates to the goal 13 where action related to climate change. This sensor will be an ideal method for determining the level of hydrogen sulphide pollution that were present in an area in order to take preventative measures against the harmful effects of hydrogen sulphide gas on the surrounding environment.

CHAPTER 2 : LITERATURE REVIEW

2.1 Ordered Mesoporous Silica

Porous matter, which was ubiquitous in nature for structural and functional reasons, has lately resurfaced in chemistry. As a result of their vast surface area, substances with small pores lend themselves well to surface reaction and adsorption. Mesoporous materials are of significant interest to the materials community because their pore structures, as well as their catalytic, adsorption, conductive, and magnetic properties, may be easily controlled. Mesoporous materials can be utilised for a wide range of purposes. Considering that the morphology and texture of mesoporous silica are particularly significant for industrial applications, it has been discovered that acid-based synthesis can be used to produce mesoporous silica films, spheres, hollow spheres, fibres, and other materials for this purpose, among other things. (Lin et al., 2005)

Ordered mesoporous silica(OMS) was the most known class of mesoporous material. There are several advantages to employing mesoporous silica as the rigid template in nanocasting. Mesoscopically, it has a well-ordered mesopore structure, a large surface area, and a large volume of mesopores. It was crucial that the application of mesoporous silica that the particle size be reduced to the nanometre range for intracellular delivery since the majority of reaction occurs in the nanometre region when the material was used. The predominant phase of porous materials should be voids, either with a random character, as in disordered pore systems, or with a high degree of regularity, as in ordered pore systems. (Polarz and Antonietti, 2002) The diameter of the pore system was used to classify pore systems. According to IUPAC terminology, porous materials are divided into three categories: microporous (pore size less than 2 nm), mesoporous (2–50 nm), and macroporous (pore size greater than 50 nm) as shown in Figure 2.1 with the structure. (Chaudhary and Sharma, 2016) The size of these mesopore may be determined by the type of surfactants used, as well as the auxiliary chemicals used, and the synthesis conditions used.

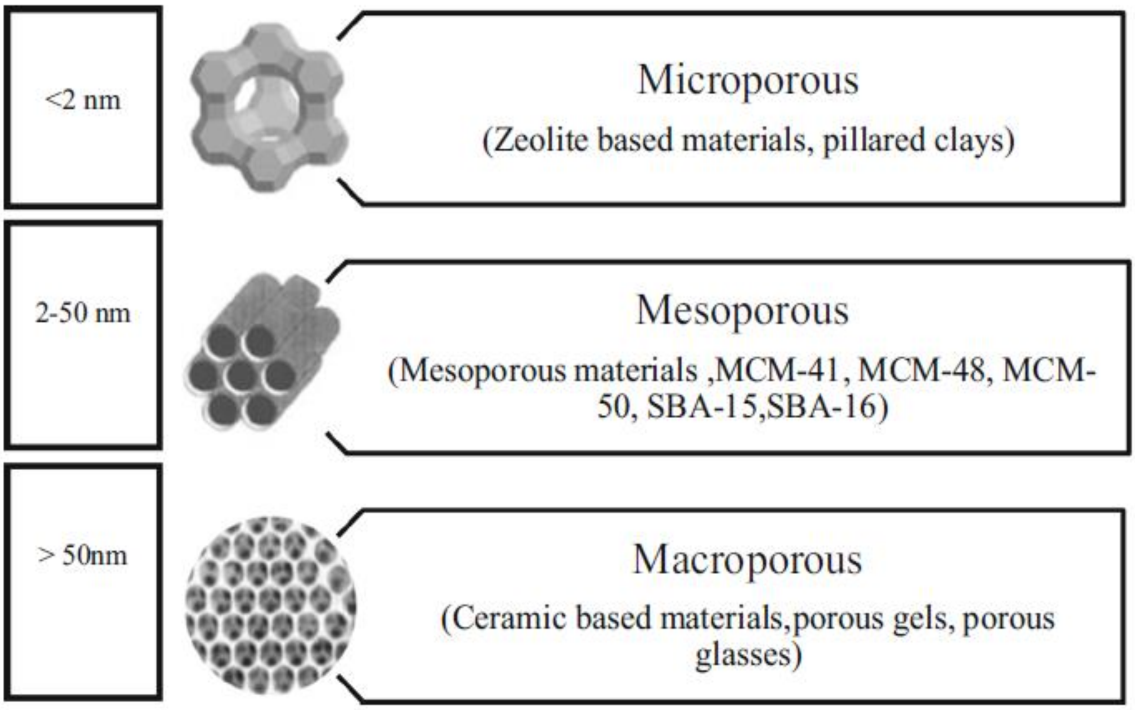


Figure 2.1: International Union of Pure and Applied Chemistry (IUPAC) classification of porous materials. (Chaudhary and Sharma, 2016)

Over the course of the past few decades, a large amount of research effort has been directed into controlling the pore architecture of ordered mesopore material and adjusting the morphology of these structures. So far, there have been few reports on tuning mesostructures and other physical properties of the KIT-6, owing to the fact that the KIT-6 synthesis process must be closely monitored to ensure the formation of Ia3d-type cubic mesostructures rather than p6 mm (e.g., SBA-15) or mixed mesophases of Ia3d & p6mm. (Wang et al., 2013) KIT-6 has an interpenetrating cylindrical pore system and a bicontinuous cubic structure. In contrast to other mesoporous materials, KIT-6, which were a three-dimensional cubicmesoporous silica, composed of two continuous and interpenetrating systems of chiral channels, resulting in an intricately interwoven 3D network of cylindrical open mesopores (pore size >5 nm) with a structure that corresponds to the Ia3D symmetry. (Lee et al., 2013)

Moreover, synthetic circumstances affect the synthesis of ordered mesoporous silica. The competition between surfactant–surface and surfactant–surfactant interactions govern surfactant assembly at the solid/liquid interface. This was also impacted by the surface's hydrophilic/hydrophobic characteristics. The final mesostructure was governed by a surfactant/silicate liquid-crystal like phase, which were controlled by the interfacial curvature surrounding the surfactant micelles, in the production of ordered mesoporous silica particles via a cooperative self-assembly technique. The meso-phase change being achieved by controlling the interfacial curvature. The interfacial curvature of surfactant micelles in the synthesis of highly ordered mesoporous silica might be influenced by the local concentration of surfactant, which differs with the bulk concentration of surfactants. (Lee et al., 2013)

2.2 Ordered Mesoporous Metal Oxide

Ordered mesoporous metal oxide (OMMO) was well known in multiple industry due to its unique physicochemical properties. OMMO have piqued the interest of researchers Because of their unique characteristics and vast range of uses. The use of soft and hard templating paths to prepare these materials has been reported in the literature. (Wang et al., 2013) The use of soft and hard templating paths to prepare these materials has been reported in the literature. Hard templating, or nanocasting, was superior to soft templating for the creation of strong meso-structures with good crystallinity and has now been applied to a variety of transition metal oxides. (Waitz et al., 2010)

Transition mesoporous metal oxides are fascinating materials having applications in optoelectronics, superconductors, chemo-resistive gas sensors, and field emission devices, among others. Tin dioxide (SnO_2), a mesoporous metal oxide with a wide band gap (Eg =3.6 eV at 300 K). (Waitz et al., 2010) The electrical conductivity of mesoporous SnO_2 grains varies as a result of the interaction between oxygen and gas reduction, which was the operating principle of SnO_2 as a gas sensor. In general, mesoporous SnO_2 has a better sensitivity on gas sensors due to its wide surface area. (Yuliarto et al.,2015) Ordered mesoporous transition metal oxides have emerged as excellent choices as materials for a wide range of applications, including catalysis, adsorption, sensor, lithium ion batteries, supercapacitors, and drug delivery, due to advantages such as high surface area, open pore system, controllable pore size and morphology, and high thermal/chemical stability of the rigid framework over conventional bulk and nanoparticulate counterparts. (Waitz et al., 2010)

2.3 Synthesis Methods & Routes for Ordered Mesoporous Metal Oxides

Synthesis methods and routes for Ordered Mesoporous Metal Oxide goes through physical and chemistry processes. The sol-gel process refers to a novel approach to the creation of new materials. This method allows for greater control over the entire set of reactions involved in the synthesis of solids. By modifying the surface of substrates, it has possibility of obtaining a stable surface and high surface area. (Yilmaz and Soylak, 2020) The nanocasting's synthesis technique have two key paths which are the Soft-templating and hard-templating. Soft templating was separated under cooperative self-assembly, real liquid crystal templating, and evaporation-induced self-assembly which was based on the application of surfactants or co-block polymers (EISA). The hard templating pathway, on the other hand, was closely similar to the macroscopic casting process: a stiff mould having voids as in correct form (morphology, surface curvature) will be first loaded with materials or precursors. (Deng et al., 2016)

2.3.1 Soft-Templating Method

Soft-templating (sometimes referred as that of the endotemplate approach) method seeks for the co-assembly of surfactant molecules and foreign species it into an ordered mesoporous structure once the template was removed. (Marcos-Hernández and Villagrán, 2019) This templating refers to supramolecular entities such as self-assembled arrays comprising structure-directing molecules such as surfactants that result in small mesopores as 30 nm. As shown in Table 2.1 different pore size have different method of nanocasting. (Sierra-Salazar et al., 2019)

Table 2.1: Mesoporosity tailoring with soft templating (Sierra-Salazar et al., 2019)

Pore Size (nm)	Method
2–5	Surfactants with diverse chain lengths Long chain quaternary cationic salts Neutral organoamines
5–8	Charged surfactants combined with organic swelling agents
2–8	Nonionic surfactants
4–20	Triblock-copolymer-based surfactants
10–30	High molecular weight block-copolymers Triblock-copolymers combined with swelling agents

Soft templating has evolved into a broad synthetic pathway for ordered mesoporous materials, with two separate synthetic procedures improving and refining it with cooperative self-assembly and a "real" liquid-crystal templating process. (Sierra-Salazar et al., 2019) The term "template" refers to a substance that was utilised to induce porosity inside a matrix in material science. (Marcos-Hernández and Villagrán, 2019)

Furthermore, this technology has evolved into a broad synthetic pathway for ordered mesoporous materials, with two different synthetic procedures improving and refining it which are the cooperative self-assembly and a "real" liquid-crystal templating process. (Marcos-Hernández and Villagrán, 2019) Figure 2.2 shows the scheme of the two different soft-templating method strategies for the synthesis of mesoporous materials: (A) cooperative self-assembly and (B) "true" liquid-crystal templating process. (Sierra-Salazar et al., 2019) Cooperative self-assembly have one extra step compared to "true" liquid-crystal templating process which was the condensation of inorganics before the template removal. According to current research, the soft-templating approach isn't completely applicable to all mesoporous metal oxides. Due to soft templating the removal of template will affect the mesoporous metals porosity. This process cannot produce most metal oxides of sufficient structural grade. (Deng et al., 2016)

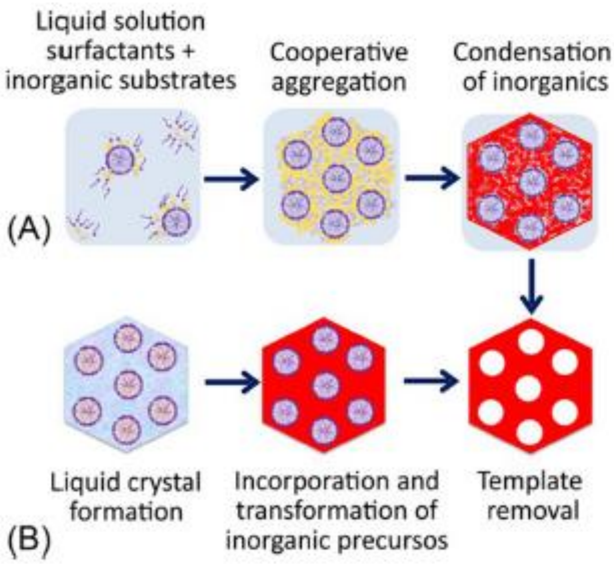


Figure 2.2: Scheme of the two different soft-templating method strategies for the synthesis of mesoporous materials: (A) cooperative self-assembly and (B) "true" liquid-crystal templating process (Sierra-Salazar et al., 2019)

2.3.2 Hard-Templating Method

A further simple method for obtaining mesoporous structures was the hard-templating synthetic approach, commonly known as "nanocasting." Based on the research, preformed templates comprised of nanoparticle aggregates, carbon, or mesoporous silica are used in this process. (Marcos-Hernández and Villagrán, 2019) Hard templating method was also known by endotemplating method . Based on Sierra-Salazar et al., 2019 the porosity that results are determined by the hard template's properties. The synthesis of carbon using a silica template was a good example. Figure 2.3 shows the ordered mesoporous carbons (OMC) preparation with mesoporous silica templates.

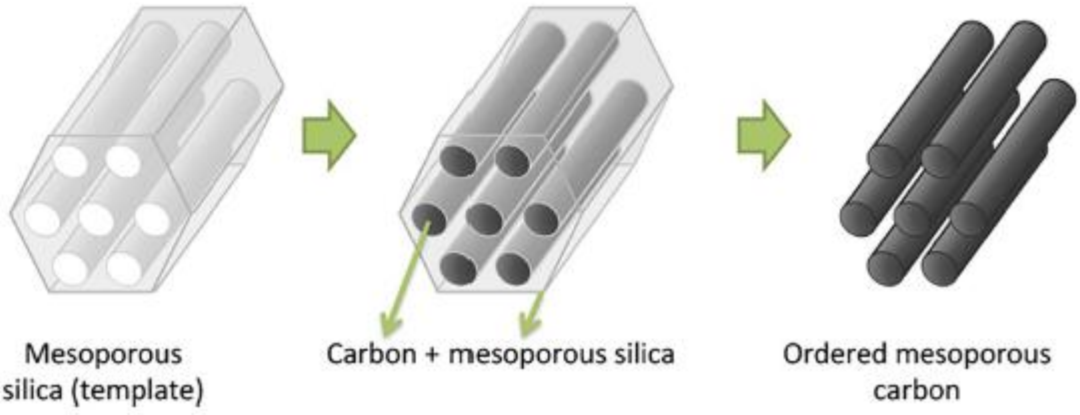


Figure 2.3: Ordered mesoporous carbons (OMC) preparation with mesoporous silica templates.

The use of hard templates to synthesise mesoporous materials opens up new possibilities for creating ordered mesostructured materials. Through this approach, large surface area and highly ordered mesostructure with a crystalline framework of mesoporous SnO_2 material can been obtained. Nanocasting method give the promising strategy of producing ordered mesoporous SnO_2. Nanocasting was the ideal method for producing ordered mesoporous powders due to the features of the parent template, commonly mesoporous silica, or carbon, may be customised on-demand by modifying the kind of precursor and its concentration, heat treatment temperature, and reaction time. (Kumar and Chowdhury, 2015) (Polarz and Antonietti, 2002)

In general, the nanocasting route consists of three steps: precursor infiltration, casting step or heat treatment of the impregnated template under a controlled atmosphere to convert the infiltrated precursor to inorganic material, and template removal by dissolution or oxidation at high temperatures. (Kumar and Chowdhury, 2015) The infiltration process in nanocasting were divided into four sub-steps: (1) precursor selection, (2) solvent selection, (3) template selection, and (4) precursor solution/gas infiltration into the pores of the template. The most crucial part was the precursor selection because it determines the stability. A metal-containing precursor were ground with a mesoporous silica template and predicted to migrate into silica pores. (Polarz and Antonietti, 2002) Improved pore occlusion necessitates collaboration between the solvent and the metal precursor. The volatile solvent should have a strong dissolving activity, a limited ability to coordinate, and little interaction with the silica surface. (Kumar and Chowdhury, 2015)

2.4 Gas Sensing Mechanism

It was commonly known that such a mechanism of gas diffusion through a porous material were proportional to the size of the pores concerned. Even gas diffusion through a porous material was proportional to the size of the pores concerned, and even surface diffusion, Knudsen diffusion, and molecular diffusion all take place in this order when the pore size grows as a result of this. (Sakai et al., 2001) Literature describes the overall mechanism of conductance caused by pressed powders of n-type semiconductors with oxygen or other acceptor surface states, as well as the specific process.

The SnO_2 sensor refer to a gas sensor with a surface-controlled response. In order for the gas sensing process to work, certain parameters, such as the surface conductivity of the semiconductor, must modify. The oxygen molecules will be adsorbed to the surface of SnO_2 nanostructures when exposed to air, and they would collect electrons from the conduction band of SnO_2 to form chemisorbed oxygen species based on the temperature of environment. The following chemical processes can be used to illustrate the chemical adsorption process: (Zhou et al., 2018)

$$O_2(gas) \leftrightarrow O_2(ads) \quad (2.1)$$

$$O_2(ads) + e^- \leftrightarrow O_2^-(ads)(T < 150°\mathrm{C}) \quad (2.2)$$

$$O_2^-(ads) + e^- \leftrightarrow 2O^-(ads)(150℃ < T < 400℃) \qquad (2.3)$$

$$O^-(ads) + e^- \leftrightarrow O^{2-}(ads)(T > 400℃) \qquad (2.4)$$

The chemiresistance principle, which describes the change in electrical conductivity or resistivity of thin films as a result of exposure to a target gas, was used to operate the metal oxide gas sensor. In other words, when gas molecules contact with metal oxides, they either operate as a donor or acceptor of charge carriers (Receptor function), and the resistivity of the metal oxide changes as a result of the interaction. (Shankar and Rayappan, 2015) Figure 2.4 shows the schematic of metal oxide thin film gas sensor which describes on how the metal oxide sensor detects the gas. The type of majority carriers in the semiconducting film, as well as the nature of gas molecules (whether oxidising or reducing) in the surrounding environment, determine whether the resistance of a metal oxide thin film increases or decreases. When the SnO_2 sensor comes into touch with the measured gas, its resistance changes depending on the oxidation or reduction tendencies of such gas. (Zhou et al., 2018)

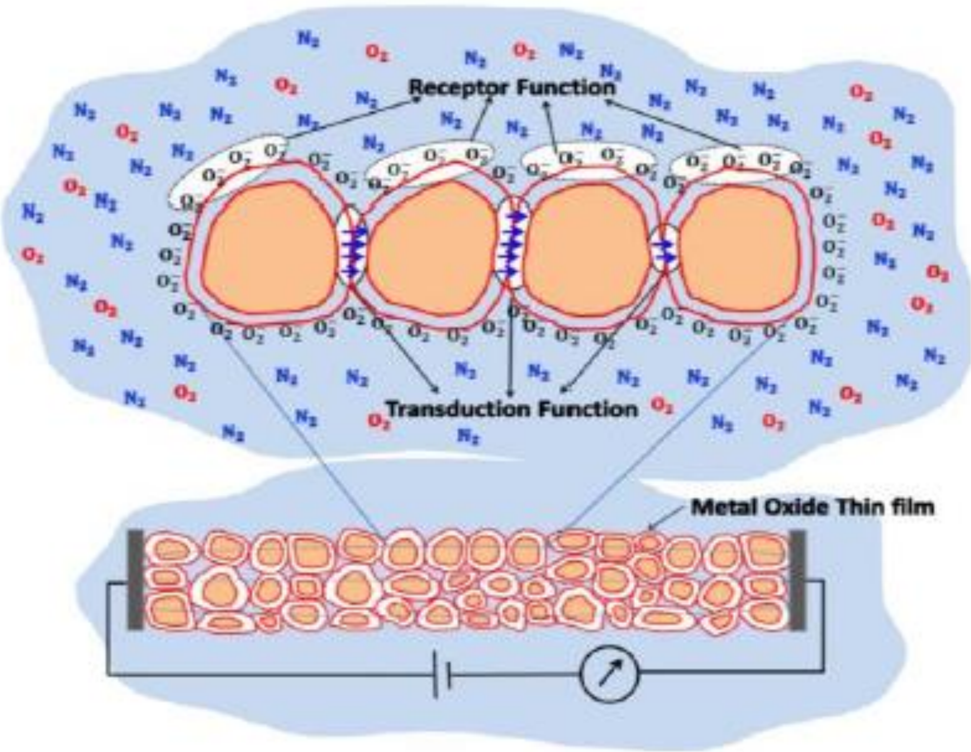


Figure 2.4: Schematic of metal oxide thin film gas sensor. (Shankar and Rayappan, 2015)

2.6 Mathematical Modelling and Reaction Kinetics of The Gas Sensor Parameters.

The model of gas diffusion was used to develop the relationship between the concentration of the target gas, the operating temperature of the sensor, the size of the pore, and the film thickness of a mesoporous SnO_2 gas sensor. Sakai and Gong studies show the development of the gas diffusion theory based on the steady-state of Knudsen diffusion and first-order reaction. (Sakai et al., 2001)(Gong et al., 2009) To explain the dynamics of gas diffusion in the response process, a Knudsen diffusion equation that was based on a first-order reaction of the gas has been developed.

$$D_K = \frac{4r}{3}\sqrt{\frac{2RT}{\pi M}} \qquad \text{Equation 2.5}$$

The formula for the Knudsen diffusion constant was shown in Equation 2.5. In this formula, D_K represents the Knudsen diffusion constant, T represents the temperature, R represents the gas constant, r represents the pore radius, and M represents the molecular weight. The Knudsen diffusion constant was used in the process of determining the link between the sensitivity of a mesoporous SnO_2 gas sensor and the concentration of the target gas, the size of the pore, and the film thickness of the sensor. (Sakai et al., 2001)

Based on the Knudsen diffusion equation a diffusion equation was developed with first-order surface response. Assumption was made that the adsorbed oxygen in the sensor and the surface reaction was first order kinetics. Equation 2.6 shows the diffusion equation in related to the Knudsen constant. (Gong et al., 2009) Here (C_A) refer to concentration of target gas A, (t) refer to time, (D_k) refer to Knudsen diffusion coefficient, (x) refer to distance or depth from the top surface of the sensing layer and (k) refers to rate constant.

$$\frac{\partial C_A}{\partial t} = D_K \frac{\partial^2 C_A}{\partial x^2} - kC_A \qquad \text{Equation 2.6}$$

At steady state, $\frac{\partial C_A}{\partial t}$ = 0, equation 2.6 was transformed to equation 2.7 :

$$D_K \frac{\partial^2 C_A}{\partial x^2} - kC_A = 0 \qquad \text{Equation 2.7}$$

Considering the boundary conditions where C1 and C2 represent integral constants enable to formulate the general solution to this equation as follows. Equation 2.8 show the concentration equation where x was the thickness of sensor film. (Gong et al., 2009)

$$C_A = C_1 \exp\left(x\sqrt{\frac{k}{D_K}}\right) + C_2 \exp\left(-x\sqrt{\frac{k}{D_K}}\right) \qquad \text{Equation 2.8}$$

C1 and C2 are the integral constant which are solved by two boundary conditions based on Sakai's research paper.

i. $C_A = C_{A,s}$ when x = 0 which was at the surface of the sensing layer.

ii. $\frac{\partial C}{\partial x} = 0$ when x = L (bottom)

$$C_A = C_{A,s} \frac{\cosh\left[(L-x)\sqrt{\frac{k}{D_K}}\right]}{\cosh\left(L\sqrt{\frac{k}{D_K}}\right)} \qquad \text{Equation 2.9}$$

Equation 2.9 shows the concentration equation of target gas A.

The Arrhenius equation was then used to determine the rate constant, which was dependent on the temperature. As stated in Equation 2.10 below, the E_k represents the first-order reaction activation energy, and the k_0 represents the pre-exponential constant. (Sakai et al., 2001)

$$k = k_0 \exp\left(-\frac{E_k}{RT}\right) \qquad \text{Equation 2.10}$$

Furthermore, it was assumed that the film composed of a series of uniformly extremely thin sheets, and it was also presumed that the conductance σ of an extremely thin sheet varies linearly as a function of the gas concentration [C(x)] using the coefficient of α (sensitivity coefficient). It was classified that the film was stacked in this manner in order to achieve the desired effect. Equation 2.11 shows that under gas exposure, σ(x) and normalised by that in air (σ_0). (Sakai et al., 2001) (Gong et al., 2009)

$$\sigma(x) = \sigma_0(1 + \alpha C_A) \qquad \text{Equation 2.11}$$

The α present in the equation 2.11 was the sensitivity coefficient where it can be found out using the equation 2.12.

$$\alpha = \alpha_0 \exp\left(-\frac{E_a}{RT}\right) \qquad \text{Equation 2.12}$$

Where E_a was apparent activation energy for the transduction process and a_0 was pre-exponential constant.