SYNTHESIS AND CHARACTERISATION OF ELECTROSPUN DOPED TIN(IV) OXIDE/ POLYANILINE/POLYHYDROXYBUTYRATE NANOCOMPOSITE FOR ETHANOL GAS SENSOR

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LIST OF SYMBOLS

µL	Microliter
Å	Angstrom
APS	Ammonium persulphate
cm	Centimeter
DAQ	Data acquisition
DMF	N,N- dimethylformamide
e	Electron
eV	Electronvolt
FTIR	Fourier Transform Infrared spectroscopy
g	Gram
hrs	Hours
HRTEM	High resolution transmission electron microscopy
K	Kelvin
kV	Kilovolt
M	Molar
mA	Miliampere
MFC	Mass flow controller
min	Minute
mL	Mililiter
Mol%	Mole percentage
nm	Nanometer
^{o}C	Degree Celsius
P3HB	Poly-3-hydroxybutyrate

Pa	Pascal
PANI	polyaniline
R_0	Sensor resistance in background gas
R^2	Correlation coefficient
R_g	Sensor resistance in target gas
s	Second
SAED	Selected area electron diffraction
sccm	standard cubic centimeter per minute
SEM	Scanning electron microscopy
T_{rec}	Recovery time
T_{res}	Response time
UV-vis DRS	Ultraviolet-visible diffuse reflectance spectroscopy
v/v	Volume per volume
W	Walt
Wt%	Weight percentage
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
PVP	Polyvinylpyrrolidone
PEG	Polyethylene glycol
SDS	Sodium dodecyl sulphate
MW	Molecular weight

SINTESIS DAN PENCIRIAN NANOKOMPOSIT STANUM(IV) OKSIDA TERDOP/POLIANILINA/POLIHIDROKSIBUTIRAT ELEKTROPINTAL SEBAGAI PENDERIA GAS ETANOL

ABSTRAK

Nanokomposit semikonduktor oksida logam/polimer konduktif ialah satu kelas baru bahan yang menggabungkan kelebihan oksida logam dan polimer. Penderia gas yang berasaskan oksida logam sering memerlukan suhu operasi yang tinggi dan menyebabkan penggunaan kuasa yang tinggi dan tempoh hayat yang singkat. Sebaliknya, polimer konduktif sesuai untuk penggunaan suhu operasi yang rendah, tetapi ia mempunyai tempoh tindak balas yang panjang. Bagi mengatasi kekurangan ini, satu penderia gas baru berasaskan nanokomposit elektropintal telah berjaya dibangunkan dengan menggabungkan nanorod stanum(IV) oksida (SnO_2) dengan polianilina (PANI) dan polihidroksibutirat (P3HB). Bahan tersintesis ini telah diuji dengan gas etanol (C_2H_5OH) dengan gas nitrogen (N_2) sebagai gas pembawa. Suatu kaedah mudah hidrotermal telah digunakan untuk mensintesis SnO_2 dan SnO_2 terdop nanorod tanpa acuan organik atau pengaktif permukaan. Kesan daripada pelbagai parameter iaitu pH, kepekatan prekursor dan tempoh pemanasan telah disiasat. Bagi nanorod SnO_2 terdop, kesan daripada pelbagai jenis dopan logam (Fe, Co, Ni, dan Pd) dan kepekatan setiap dopan juga telah dikaji. Keadaan optimum untuk mensintesis SnO_2 adalah 180 ºC, pH 13 dengan kepekatan prekursor 0.12 M dan tempoh pemanasan selama 24 jam. Nanorod SnO_2 yang telah disintesis telah diuji dengan 1000 ppm gas C_2H_5OH pada suhu operasi yang berbeza (200 – 450 ºC) dan ia memaparkan tindak balas yang paling tinggi (R_a/R_g,1.1 $\times 10^3$) pada suhu 450 ºC dengan tempoh tindak balas, T_{res}, 60 s. Bagi SnO_2 terdop, perubahan pada parameter hablur menonjol

apabila kepekatan dopan meningkat, dengan struktur hablur tetragon rutil dikekalkan. Ujian pengesanan gas C_2H_5OH pada suhu operasi 450 ºC menunjukkan penderia SnO_2 didop dengan 5 mol% Ni (5Ni:SnO_2) dan SnO_2 didop dengan 5 mol% Pd (5Pd:SnO_2) memaparkan tindak balas yang agak tinggi terhadap gas C_2H_5OH (R_0/R_g, 1.4 × 104 and R_0/R_g,1.7 × 10_4) dengan tempoh tindak balas T_{res} (50 s and 40 s) dan tempoh kembali ke rintangan elektrik asal adalah pantas T_{rec}, (22 min and 12 min) berbanding dengan penderia gas nanorod SnO_2 tanpa didop. Apabila pengesanan dijalankan pada gentian nanokomposit 5Pd:SnO_2/PANI/P3HB, penderia gas mempamerkan ciri pengesanan gas C_2H_5OH yang sangat baik pada suhu 80 ºC dengan bacaan R_0/R_g, 1.6 $\times 10^3$, T_{res}, 90 s dan T_{rec}, 10 min. Ciri penderia gentian nanokomposit 5Pd:SnO_2/PANI/P3HB ini disebabkan oleh hetero-simpang p-n, bentuk geometri gentian, satu dimensi (1D) nanorod dan kehadiran atom-atom Pd sebagai mangkin yang aktif. Penderia gentian nanokomposit yang baharu ini bakal menjadi satu kejayaan dalam aplikasi penderia gas etanol yang terbiodegradasi dan berfungsi pada suhu rendah.

SYNTHESIS AND CHARACTERISATION OF ELECTROSPUN DOPED TIN(V/POLYANILINE/POLYHYDROXYBUTYRATE NANOCOMPOSITE FOR ETHANOL GAS SENSOR

ABSTRACT

Semiconducting metal oxide/conducting polymer nanocomposite is a new class of material that combined the advantages of both metal oxide and polymer. Metal oxide based gas sensors tend to require high operating temperature, leading to high power consumption and short life time. In constrast, conductive polymers fit for low operating temperature usage, but they have slower response time. In order to overcome the limitations, a new electrospun nanocomposite based gas sensors were successfully developed by incorporating as-synthesised SnO_2 nanorods into polyaniline (PANI) and polyhydroxybutyrate (P3HB). The as-synthesised materials were tested on ethanol (C_2H_5OH) gas using nitrogen (N_2) as carrier gas. A facile hydrothermal method without using any organic template or surfactant was employed to synthesise undoped and doped SnO_2 nanorods. The effects of various parameters namely pH, precursor concentration and duration of heat treatment were investigated. For the doped SnO_2 nanorods, the effects of different types of metal dopant (Fe, Co, Ni and Pd) and the concentrations of each dopant (0.5, 1.0, 3.0 and 5.0 mol%) were also studied. The optimum condition for the synthesis of SnO_2 nanorods powder was 180 ºC, pH 13, with a precursor concentration of 0.12 M and the duration of heat treatment of 24 hrs. The as-synthesised SnO_2 nanorods tested with 1000 ppm C_2H_5OH gas at different operating temperatures (200 – 450 ºC) and exhibited the highest response (R_a/R_g, 1.1×10^3) at 450 ºC with response time, T_{res} of 60 s. For doped SnO_2, the changes in crystallographic parameters were prominent as the concentration of dopant increased,

while maintaining the rutile tetragonal crystal structure. The C_2H_5OH gas sensing test showed that 5 mol% Ni doped SnO_2 (5Ni:SnO_2) and 5 mol% Pd doped SnO_2 (5Pd:SnO_2) sensors have demonstrated relatively high C_2H_5OH gas response (R_0/R_g, 1.4×10^4 and R_0/R_g, 1.7×10^4) with fast response time, $T_{res,}$ (50 s and 40 s) and recovery time, T_{rec}, (22 min and 12 min) at operating temperature of 450 ºC as compared to undoped SnO_2 nanorods sensor. When it is carried out on the 5Pd:SnO_2/PANI/P3HB, the nanocomposite sensor exhibited excellent gas sensing properties at 80 ºC with R_0/R_g, 1.6×10^3, T_{res}, *90 s and* $T_{rec,}$ 10 min, respectively. The good sensing properties of 5Pd:SnO_2/PANI/P3HB nanocomposite fibres sensor were mainly attributed to p-n heterojunction, the fibres geometry, one dimensional (1D) nanorods and the presence of catalytic active Pd atoms. This new nanocomposite sensor will be a breakthrough in biodegradable low temperature ethanol sensor applications.

CHAPTER 1

INTRODUCTION

1.1 Overview

In the past couples of decades, the innovation of nanomaterials has become a leading edge in the field of nanoscience and nanotechnology. The nanotechnology defined as the development of functional materials, devices and systems with a dimension in the range of 1-100 nm (Korotcenkov, 2013). With a reduction in size, nanostructured materials exhibit unique properties such as electrical, mechanical and chemical properties which are significantly different from those of their bulk counterparts. To date, a wide variety of nanoscale materials has been synthesised. Among nanostructured semiconductors, metal oxides have received broad attention due to their distinguished properties in optics, gas sensors, magnetics and in catalysis (Batzill and Diebold, 2005).

The application of metal oxides as gas sensors has attracted many researchers attention ever since Seiyama and the co-workers (1962) discovered that the adsorption and desorption of gases on the surface of zinc oxide (ZnO) film caused a rapid changes in electrical conductivity (Seiyama *et al*., 1962). Since then, various types of metal oxides have been extensively investigated for gas sensing applications. In the early years, gas sensors have been fabricated in the form of thin films, where the metal oxide nanoparticles were coated on electrodes followed by sintering at high temperature (Korotcenkov, 2007). Recently, the one-dimensional (1-D) metal oxide nanostructures are found to be very promising for gas sensing applications due to their very high surface to volume ratio is very high and which can subsequently improve their sensor sensitivity (Pal *et al.*, 2012). Various forms of 1-D metal oxide nanostructures have been synthesised such as nanowires (Qin *et al*., 2008), nanotubes (Wang *et al.*, 2011),

nanospheres (Tang and Wang, 2016), nanorods (Birkel *et al.,* 2010) and nanobelts (Fields *et al*., 2006).

Among them, 1-D nanostructured, SnO_2 have received a great deal of interest in gas sensing applications owing to remarkable characteristics such as wide band gap (3.6 eV at 300 K) and high mobility of conduction electrons (100-200 cm^2 Ve^{-1} S^{-1}) (Batzill and Diebold, 2005). It is well established that the properties of SnO_2 nanostructures mainly depend on the synthesis route. A number of methods such as thermal evaporation (Luo *et al.,* 2004), hydrothermal (Nasresfahani *et al*., 2017), chemical vapour deposition (CVD) (Kwoka *et al*., 2005), sol-gel (Marikutsa *et al*., 2010) and co-precipitation (Zhang *et al.,* 2005) have been employed to synthesise 1-D SnO_2 nanostructures. Among them, hydrothermal route was considered as a promising method widely used to synthesise homogeneous SnO_2 nanostructures with controlled shape and size. Hydrothermal method is one in which the formation and growth of nanocrystal occurred under high temperature and pressure *via* chemical reaction and the solubility of substances (Shi *et al.,* 2013). Studies showed that tuning the experimental parameters, for instance type of solvent, pH condition, concentration of the precursor, heating temperature and duration of hydrothermal reaction affect the final morphology of product (Shi *et al.,* 2013). Although 1-D SnO_2 nanostructures shows some encouraging results in gas sensor application, improving the poor gas sensing response and recovery time, and high operating temperature require more efforts and still remain as a challenge. Therefore, significant effort has been focused on the improvement of SnO_2-based gas sensors.

One of the most common techniques for enhancing the gas sensing performance is by introducing transition metals or noble metals as a dopant. Noble metals such as Pd and Pt are often used to dop SnO_2 because of their excellent

oxidation catalytic properties which in turn enhance the reaction on the sensor surface during the gas sensing process (Korotcenkov, 2007). Meanwhile, *3d* transition metals (e.g Ni, Cu, Co, Fe, etc), doped -SnO_2 have been observed to improve their sensor response, response time and recovery time by reducing the size of SnO_2 particles (Zhao *et al*., 2015). Nevertheless, those doping sensors still require relatively high operating temperature (above 300 °C).

On the other hand, organic materials especially conductive polymer sensors work very well at room temperature and they are easy to fabricate due to their flexibility (Bai and Shi, 2007). Polyaniline (PANI) is one of the most extensively studied conductive polymers because of its ease preparation, high conductivity, low operating temperature and good environmental stability (Quan *et al*., 2017). However, PANI alone exhibits a rather low sensitivity to target gas. Recently, Kondawar and co-workers have established SnO_2/PANI nanocomposite for ammonia sensing application (Kondawar *et al*., 2012). Interestingly, this material is found to demonstrate special properties which is generated from both metal oxide and conductive polymer.

Typically, the synthesis of nanocomposite was carried out by mixing the metal oxide nanopowders with PANI polymer which was later fabricated into thin film (Geng, 2009). In another study by Geng and co-researchers (2007), the hybrid SnO_2/PANI was prepared *via* hydrothermal treatment where PANI was polymerised *in-situ* (Geng *et al.*, 2007). However, these methods could decrease the surface area of sensor materials.

In order to increase the surface area (> 100 cm^2 g^{-1}) of the sensor materials, electrospinning technique is often an efficient and relatively simple method to produce nanocomposite fibres (Ding *et al.*, 2009). Subsequently, higher surface area of sensor

material leads to higher sensitivity. However, the low molecular weight of PANI is generally insufficient for it to be electrospun directly into the fibres (Zhang and Rutledge, 2012). Thus, to circumvent this problem, the material usually blends together with higher molecular weight polymer such as polyvinylpyrrolidone (PVP) (Song *et al*., 2009) and poly-3-hydroxybutyrate (P3HB) (Araujo *et al.,* 2011).

Hence in this study, poly-3-hydroxybutyrate (P3HB) is selected. P3HB is a high molecular weight biopolymer that belongs to polyhydroxyalkanoates (PHAs) polymer class which is produced from microbial. A number of studies has been reported on the synthesis of PANI/P3HB conductive polymer which eventually combines both characteristics of biodegradability and electrical semiconductivity with good mechanical properties (Fryczkowski and Kowalczyk, 2009; Araujo *et al.,* 2011; Macagnano *et al.,* 2016).

To date, gas sensor plays a key role in various areas, especially in public and environmental safety, medical therapeutics, pollutants motoring and transportation industries. Ethanol (C_2H_5OH) gas sensors were extensively used in many applications to monitor chemical reactions, biomedical productions as well as breath analyser. Generally, the operating temperature of gas sensor depends on the area of applications. For instance, the operating temperature of the C_2H_5OH sensor in breath analyser is relatively lower than that of the sensor employed in industrial application works.

Herein, this research is divided into two parts: The main part of this research focuses on the synthesis of SnO_2 nanorods using the hydrothermal method and explores the effects of synthesis parameters, namely pH condition, concentration of the precursor and the duration of heat-treatment. The effects of *3d* transition metals doping on the structural and morphological properties of SnO_2 nanorods are then

investigated. The results obtained are compared with those of noble metal (Pd) doped SnO_2 nanorods. The as-synthesised pure and doped SnO_2 nanorods are tested on C_2H_5OH gas sensing in order to relate the properties of sensor material with the C_2H_5OH sensor response. This study will provide a better understanding of the roles of dopants in sensor materials.

Meanwhile, in the second part of the research, inorganic-organic hybrid nanocomposite fibres are synthesised *via* electrospinning technique using as-synthesised SnO_2 nanorods powder, conductive polymer PANI and a biopolymer P3HB. The effect of applied voltage and the flow rate to the polymer solution during the formation of fibres is carefully investigated. Then, this novel nanocomposite sensor is tested on C_2H_5OH gas. The nanostructured sensor materials synthesised in this research have a potential application as C_2H_5OH gas sensor.

1.2 Problem statement

Despite the advantages of SnO_2, its real application in the gas sensor field is still limited and in need of improvement. One of the common routes to improve the sensor properties is to reduce the particle size of SnO_2 to nanoscale. Previous studies have shown that 1-D SnO_2 nanostructures are an excellent candidate for gas sensing applications due to high surface-to-volume ratio (Korotcenkov, 2013). A number of methods were developed to synthesise homogenous SnO_2 nanostructured with controlled shape and size. However, these methods usually involve high temperature, complicated procedures and expensive instrumentation, which consequently increase the cost of sensor materials. Recently, hydrothermal method has been widely used in synthesising 1-D nanostructure metal oxides. However, the usage of surfactants and organic templates such as sodium dodecyl sulphate (SDS) (Tan *et al.*, 2011) and

polyethylene glycol (PEG) (He *et al.*, 2013) can cause environmental problems, especially to aquatic system. Meanwhile, Matin and co-workers (2010) successfully synthesised SnO_2 nanostructures *via* hydrothermal route using neither alkaline solution nor organic templates at 160 °C; however, the samples have to undergo post calcination at high temperature of 350 °C. Thus, in this current research, 1-D SnO_2 nanorods were synthesised using a simple hydrothermal route without using an organic template, surfactant and post calcination (Matin *et al.*, 2010).

Besides 1-D nanostructures, doping with transition metals and noble metals also improve the sensor characteristics of SnO_2 nanostructures. It is well known that adding noble metal dopants such as Pd and Pt lead to tremendous improvement in SnO_2 gas sensing properties (Kappler *et al*., 1998). Nevertheless, their obvious cost restricts their potential in practical applications. Thus, it was essential to explore less expensive alternatives such as common *3d* transition metals (e.g. Fe, Co, Ni, Cu, etc) to reduce the operation cost as well as to enhance the sensing performance. However, transition metals are rarely used than noble metals, even though they could improve the sensing properties of SnO_2. Furthermore, it can be difficult to study the effect of different transition metals doping on the gas sensing properties between numerous studies since the synthesis routes and reaction conditions are different which precludes predicting the final optimised functionality of SnO_2 sensor material. To the best of our knowledge, there is not many comparative studies of sensing properties of transition metals doped SnO_2 has been reported.

On the other hand, although SnO_2 nanostructures are widely used in industrial applications, their crystalline structures are not suitable for fabricating on flexible substrates. In addition, the high operating temperature is the main drawback in pure and doped SnO_2 based gas sensors. PANI is one of the most used organic sensor

material, but its low sensitivity and poor solubility in organic solvent limits its applications (Kondawar *et al.*, 2012). Therefore, a novel electrospun sensor material, SnO_2/PANI/P3HB nanocomposite fibres is being proposed in this study, which can complement the properties of SnO_2 and PANI.

Presently, C_2H_5OH gas detecting and monitoring technologies have attracted increased attention due to their high demand in biomedical, chemical, food industries as well as traffic safety. Therefore, current research was focused on the development of low cost and high-performance C_2H_5OH gas sensor.

1.3 Research objectives

To address the aforementioned shortcoming, the main aim of this research is to develop an efficient and environmentally friendly gas sensor nanomaterial. In order to achieve this goal, it is essential to understand the fundamental relationship between sensor response and physico properties of SnO_2 nanorods. Therefore, the specific objectives of this research are as follows:

i. To synthesise and study the structural and morphological characteristics of pure SnO_2 nanorods under different reaction parameters *via* hydrothermal method.
ii. To study the effect of different dopants (Fe, Co, Ni and Pd) on the morphology and structure of SnO_2 nanorods.
iii. To conduct comprehensive studies on the ethanol gas sensing performance of as-synthesised pure and doped-SnO_2 samples.
iv. To fabricate SnO_2/PANI/P3HB nanocomposite fibres using electrospinning method and characterise these nanofibres using spectroscopy and microscopy techniques.

v. To investigate the ethanol gas sensing properties of these SnO_2/PANI/P3HB nanocomposite fibres and propose the gas sensing mechanisms of these samples.

1.4 Outline of thesis

This thesis consists of seven chapters and is presented as follows:

Chapter 1 gives an overview of the study. It mainly focuses on the problem statements, research objectives and outline of the content.

Chapter 2 is a detailed literature review related to SnO_2 nanostructures in gas sensor application, the doped SnO_2 sensor properties, gas sensing mechanism, the principle of hydrothermal method and electrospun polymer nanocomposite fibres. The justification for author's research rationale is explained.

Chapter 3 is concerned with the methodology used for this study. Firstly, the steps involve in the fabrication of the pure SnO_2 and doped nanorods sensor materials are laid out. In addition, the technique employed for the novel SnO_2/PANI/P3HB nanocomposite as well as C_2H_5OH gas sensing measurement are discussed. The basic principles of the instrumental characterisation methods by Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (SEM/EDX), high resolution transmission electron microscopy with selected area electron diffraction (HRTEM/SAED), ultraviolet-visible spectroscopy (UV-vis) was also explained in this chapter.

Chapter 4 discusses the characterisation results obtained for pure SnO_2 nanorods sample synthesised *via* hydrothermal method at different conditions (pH condition, concentration of the precursor and duration of heat treatment). The optimum condition for the SnO_2 nanorods synthesis was stated and a possible growth mechanism is described in detail.

Chapter 5 presents the results and discussion of (Fe^{3+}, Co^{2+}, Ni^{2+} and Pd^{2+}) doped SnO_2 nanorods samples prepared *via* hydrothermal method using various dosages of dopants. The experimental results obtained from C_2H_5OH gas sensing measurement are reported. The role of dopants on the sensor performance is discussed and the gas sensing mechanism is suggested.

Chapter 6 discusses the optimum condition for fabricating electrospun SnO_2/PANI/P3HB. The C_2H_5OH gas sensing performance of novel nanocomposite fibre SnO_2/PANI/P3HB is investigated. The characteristics of the best performed nanocomposite fibres are discussed.

Chapter 7 presents the conclusions and possible future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Metal oxide gas sensors

Metal oxides gas sensors are receiving much attention in both industrial and environmental fields. They are widely used in industrial productions, automotive industries, medical applications, indoor air quality supervision and environmental monitoring applications (Miller *et al.,* 2014). The selection of metal oxide for gas sensor applications depends on their electronic structure. Generally, metal oxides can be divided into two groups, namely transition metal oxides (e.g Fe_2O_3, NiO, Cr_2O_3, etc.) and non-transition metal oxides which include pre-transition metal oxides (e.g Al_2O_3, etc) and post transition metal oxides (e.g. ZnO, SnO_2, etc.) (Henrich and Cox, 1994). Pre-transition metal oxides are known as wide band gap insulators and are expected to be inert. This is because with large band gap (~6.7 eV) neither electrons nor holes can easily be formed. Thus, this group of metal oxides is seldom used as gas sensors due to poor electrical conductivity (Yurish, 2012). On the other hand, transition metal oxides behave differently because the energy difference between each oxidation state of cation (d^n, d^{n+1} and d^{n-1}) is considerably small, where they can exist in several different kinds of oxides. However, the structural instability and non-optimality of other parameters which are important in gas sensors limit their application (Wang *et al.,* 2010). Unlike transition metals, only transition metal oxides with d^0 and d^{10} electronic configurations could find the real applications in gas sensor field. The d^0 electron configuration found in binary transition-metal oxides such as TiO_2, V_2O_5 and WO_3. Whereas, d^{10} configuration is found in post-transition metal oxides, such as ZnO, In_2O_3 and SnO_2, which are active in redox reaction because the electron configuration may be altered (Korotchenkov, 2013).

In past few decades, many papers about metal oxide gas sensors have been published. They are used for detecting various oxidising and reducing gases. According to Choi and Jang (2010) survey, tin(IV) oxide (SnO_2) remains the most frequently employed metal oxide in gas sensor applications, which is about 42% of publication in the last three decades, along with ZnO (16%), TiO_2 (13%), WO_3 (9%) and In_2O_3 (7%), respectively. These metal oxides are followed by Fe_2O_3, CuO, NiO, Ga_2O_3 and V_2O_5 (Choi and Jang, 2010). The predominance of SnO_2 is due to the fact that this material is sensitive to practically all flammable or toxic gases.

2.2 One dimensional (1D) metal oxide nanostructured gas sensor

One dimensional (1D) metal oxide nanostructures including nanowires, nanorods, nanotubes, nanobelts and nanoribbons have been regarded as the most promising materials for gas sensor applications due to their high surface-to-volume ratio and high crystallinity (Pearton and Ren, 2013). In addition, single phase 1D nanostructures such as nanobelts and nanowires, a detail analysis of the gas surface interaction can be carried out because there are no necks and boundaries. In contrast, the sensor system consists of randomly aggregated metal oxide nanoparticles with non-uniform particle size distributions, making it difficult to study the gas sensing properties accurately (Korotchenkov, 2013).

Several studies of 1D metal oxides nanostructured gas sensor can be found in literature review. Qin and co-researchers (2008) stated that powdered polycrystalline SnO_2 sensors are less stable because of the growth and agglomeration of grains. Whereas this origin for instability should not be relevant to 1D SnO_2 morphology with single crystalline. Table 2.1 presents the stability result for SnO_2 nanowires prepared by Qin and co-researchers (2008). The result revealed that the SnO_2 nanowires exhibit

a stable resistance reading over an eight–days period in ambient air at 290 ℃. It was deduced that the annealing treatment process and the excellent thermal stability of 1D SnO_2 nanowires could attribute to good stability of the gas sensor (Qin *et al.,* 2008).

Table 2.1: Resistance variation over time at 290 ℃ in air (Qin *et al.,* 2008).

Day	1	2	4	7	8
Resistance (MΩ)	13.3	13.6	13.5	13.8	13.9

In another study Chen and co-researchers (2006), synthesised SnO_2 nanoparticles and nanorods with similar size (<6 nm) using hydrothermal route and conducted gas sensing test on ethanol gas. They observed that SnO_2 nanorods recorded high response (R_a/R_g = 83.3) towards ethanol gas at 300 ℃, but surprisingly no measurement signal was detected for SnO_2 nanoparticles. It was then suggested in SnO_2 the decreased in carrier mobility is due to the large amount of nanoparticle which interfaces caused an increase in resistance. Meanwhile, the high sensitivity of nanorods was related to the diameter of particle which is almost close to 2L (L, width of depletion layer) of SnO_2 (3 nm). Hence, more oxygen in the atmosphere adsorbed on the sensor surface and lead to almost complete electron depletion in the nanorods. This phenomenon caused a drastic improvement towards ethanol gas (Chen *et al.,* 2006).

On the same note, Xi and Ye (2010) synthesised ultrathin nanorods with average diameter of ~2 nm which is smaller than its exciton Bohr radius. They also evaluated the ethanol gas sensing performance with nanowires, nanobelts and microrods by maintaining the experiment parameters. It was found that the ultrathin SnO_2 nanorods exhibited the highest ethanol sensing response (R_a/R_g 62 to 200 ppm), among the other SnO_2 nanostructures (nanowires, R_a/R_g 45 to 200 ppm and nanobelts,

R_a/R_g 23 to 200 ppm). However, the authors did not mentioned the size of other nanostructures (Xi and Ye, 2010).

Furthermore, by controlling the faceting planes of metal oxide 1D nanostructures, one can improve the sensitivity, selectivity and decrease humidity effects in gas sensors (Korotchenkov, 2013). Maiti and co-workers (2003) reported that SnO_2 nanoribbons with exposed $(10\bar{1})$ and (010) surfaces demonstrated highly effective NO_2 sensing properties. The sensing mechanism was examined using first principles density functional theory (DFT) calculation (Maiti *et al*., 2003). In the preparation of polycrystalline metal oxides, it is difficult to control the grain facet. However, it is achievable for 1D nanostructures metal oxide gas sensors. It was reported that the planes and faceting in 1D metal oxides nanostructures are subjected to the synthesis parameters (Wang *et al.,* 2013).

Up to now, various 1D metal oxide nanostructures have been fabricated into gas sensors. Table 2.2 presents the most used 1D metal oxide nanostructures in gas sensor researches. In summary, 1D metal oxide sensing materials show several advantages, such as facile fabrication, high surface area (~100 $cm^2\ g^{-1}$) (Matin *et al.,* 2010), high sensitivity and long-term stability, which make them prospective material for high quality gas sensor.

Table 2.2: The gas sensing performance of 1D metal oxide nanostructures.

Material	Target gases	Sensitivity (concentration, ppm)	Average diameter (nm)	Operating temperature (°C)	Ref.
SnO_2 nanobelts	ethanol	6.2 (100)	50–100	210	(Huang *et al.*, 2017)
SnO_2 nanobelts	ethanol	41.6 (250)	~200	400	(Comini *et al.*, 2002)
SnO_2 nanobelts	NO_2	15.5 (0.5)	~200	400	(Comini *et al.*, 2002)
SnO_2 nanorods	ethanol	213 (100)	5–20	200	(Shi *et al.*, 2009)
SnO_2 nanowires	H_2	253.0 (1000)	3–200	100	(Shen *et al.*, 2009)
SnO_2 nanotubes	H_2S	22 (10)	12 – 14	300	(Cho *et al.*, 2017)
ZnO nanorods	H_2	53.7 (3000)	~66	150	(Sett and Basak, 2017)
ZnO nanowires	NO_2	90.9 (0.5)	N/A	225	(Ahn *et al.*, 2008)
ZnO nanobelts	NO	54 (50)	100–200	200	(Kaur *et al.*, 2017)
WO_3 nanorods	NO_2	3.39 (10)	200	300	(Park *et al.*, 2012)
WO_3 nanorods	CO	2.38 (30)	200	300	(Park *et al.*, 2012)
In_2O_3 nanowires	ethanol	80 (50)	100	200	(López-Aymerich *et al.*, 2017)

2.3 Tin(IV) oxide (SnO_2)

2.3.1 Crystal structure of SnO_2

In general, SnO_2 has several polymorphs which are rutile tetragonal, $CaCl_2$-type, α-PbO_2-type, pyrite-type, ZrO_2-type orthorhombic phase I, fluorite-type and cotunnite-type orthorhombic phase II (Das and Jayaraman, 2014). Gracia and team (2007) reported that as the pressure increased SnO_2 underwent a transition from rutile-type → $CaCl_2$-type → α-PbO_2-type → pyrite-type → ZrO_2-type orthorhombic phase I

→ fluorite-type and cotunnite-type orthorhombic phase II (Gracia *et al.,* 2007). Among all these structures rutile tetragonal found to be the most stable phase (Appendix 1). Figure 2.1 shows the simulated crystal structures of SnO_2. Naturally, rutile SnO_2 occurs in mineral form, called as Cassiterite. Rutile SnO_2 has lattice parameters of a = b = 4.737 Å and c = 3.186 Å (in the tetragonal structure, a = b) and a unit cell with a space-group symmetry of $P4_2/mnm$. The position of atoms in crystal structure is determined by the ratio of lattice parameters *c/a* as well as internal parameter *u*. The position of cations (Sn) are at (0 0 0) and $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ and are surrounded by a distorted octahedron of anions (O) (Wu *et al.,* 2010).

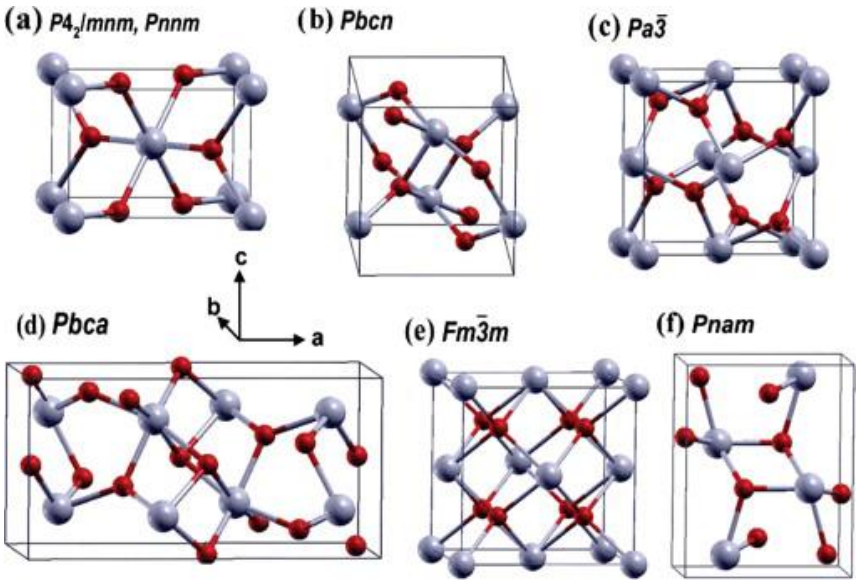

Figure 2.1: The crystal structures of SnO_2 (red: oxygen atom and blue: tin atom) : (a) rutile tetragonal (*$P4_2/mnm$*) and $CaCl_2$-type (*Pnnm*), (b) α-PbO_2-type (*Pbcn*), (c) pyrite-type (*$Pa\bar{3}$*), (d) ZrO_2-type orthorhombic phase I (*Pbca*), (e) fluorite-type (*$Fm\bar{3}m$*) and (f) cotunnite-type orthorhombic phase II (*Pnam*) Ref: (Gracia *et al.,* 2007).

2.3.2 Physical properties of SnO_2

Tin(IV) oxide (SnO_2) belongs to n-type semiconductor with wide band gap. It has been studied with great attention due to its high transparency in visible range of

electromagnetic spectrum, high reflectivity in infrared region and enhanced gas sensing properties that combine with low electrical resistance (Ahmad *et al.*, 2016). Table 2.3 presents a summary of physical properties of SnO_2.

Table 2.3: Summary of physical properties of SnO_2.

Properties	**Descriptions**
Mineral name	Cassiterite
Crystal structure	Tetragonal, rutile
Space group	$P4_2/mnm$
Lattice constant (nm)	a = 0.474 b = 0.319
Density (g cm^{-3})	6.99
Melting point (°C)	>1900
Heat of formation (eV)	6.0
Band gap (eV)	3.6
Exciton binding energy (meV)	130
Electron mobility	100 – 200 cm^2 V^{-1} S^{-1}

2.3.3 Gas sensing mechanism of SnO_2 gas sensor

Generally, the metal oxide gas sensors can be categorised into bulk-sensitive materials and surface-sensitive materials. Bulk sensitive materials in particular titanium dioxide (TiO_2) increases conductivity due to bulk oxygen vacancies (Batzill and Diebold, 2005).

On the other hand, SnO_2 is also grouped in the surface sensitive materials although bulk defects affect their conductivity. The direct band gap and high electron mobility of surface-sensitive materials resulted in large variation in electric conductance even with a slight change in charge carrier concentration. Consequently,

the conduction band bending induces strong conductivity changes in sensor material and eventually trigger the gas response signal (Wu *et al.,* 2010).

The fundamental gas sensing mechanism of SnO_2 is based on the electrical conductivity changes experienced by an n-type semiconducting metal oxide. When the surface chemisorbed oxygen reacts with a reducing gas (e.g. CO, H_2, H_2S, CH_3OH, C_2H_5OH, etc.), the sensor resistance decreases, whereas the resistance increases with oxidising gas (e.g. O_2, NO_2, O_3, etc). In the case of a p-type semiconductor the effect on the sensor resistance is *vice versa*.

Typically, oxygen molecules from the air are adsorbed on the surface of the SnO_2 sensing material. It was stated the form of chemisorbed oxygen either atoms or molecule depends mainly on the operating temperature of the SnO_2 sensor (Barsan and Weimar, 2001). Based on the results obtained from FTIR, temperature programed desorption (TPD) and electron paramagnetic resonance (EPR) spectroscopy, it was proven that the SnO_2 surface dominated by oxygen molecules at temperature below 150 °C, whereas ionic oxygen species dominates the SnO_2 sensor surface at higher temperature (Barsan and Weimar, 2001). The transfer of electrons from the SnO_2 sensor surface to the adsorbed oxygen molecules induced the bending of conduction band compared to the flat band. Figure 2.2 shows the schematic diagram of band bending near surface region of SnO_2 sensing material. A negative surface charged bends the bands upward, where the Fermi level was pushed into the band gap of SnO_2. Subsequently, it reduces the charge carrier concentration and resulting electron depletion region near the surface of the sensor particles. Electrons depletion leads a positive space charge region that compensates for the negative surface charge (Wang *et al.,* 2010).

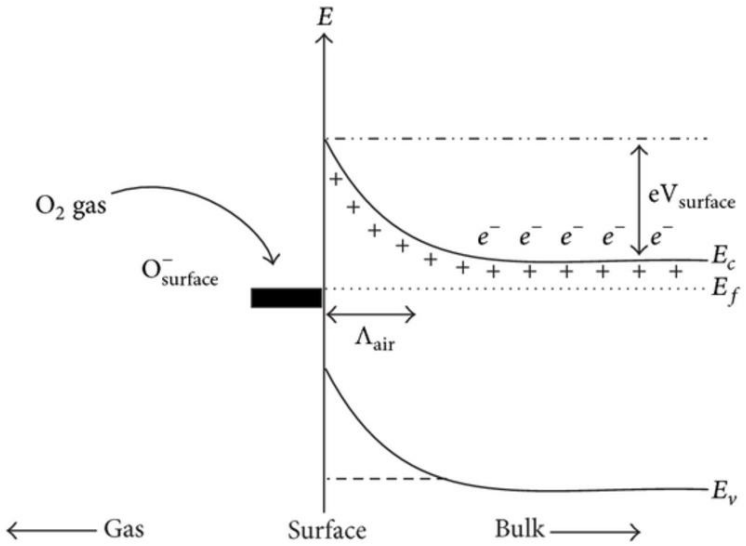

Figure 2.2: Schematic diagram of band bending near surface region of SnO_2 after the chemisorption of oxygen molecules from air. E_c, E_v and E_f respectively denote the energy of conduction band, valence band and the Fermi level. Meanwhile, Λ_{air} indicates the thickness of depletion of electron layer and $eV_{surface}$ signifies the surface potential barrier (adapted from (Yuliarto *et al.*, 2015).

During the gas sensing process, the SnO_2 sensor surface is exposed to the target gas (reducing or oxidising gases) and reactions between the chemisorbed oxygen ion species would take place. This phenomenon modifies the height of the surface potential barrier, eventually produce a variation in the electrical conductance of the SnO_2 sensor surface. The level of variation is dependent on the concentration of target gas. The reaction between the chemisorbed oxygen on the sensor surface and reducing gases causes release of electrons into the conduction band (Equations 2.1 and 2.2).

$$CO_{(g)} + O^-_{(g)} \rightarrow CO_{2(g)} + e^- \quad (2.1)$$

$$SO_{2(g)} + O^-_{(g)} \rightarrow SO_{3(g)} + e^- \quad (2.2)$$

The returning of electrons to the conductive band decreases the resistance (Korotcenkov, 2013). The schematic diagram of the gas sensing (reducing gas) mechanism on SnO_2 sensor surface is shown in Figure 2.3.

On the other hand, the reaction between oxidising gas and chemisorbed oxygen results in acceptance of electrons from the conduction band of the sensor (Equations 2.3 and 2.4). The caption of electrons during the reaction increases the resistance (Korotcenkov, 2013).

$$NO_{2(g)} + e^- \rightarrow NO^-_{2(g)} \quad (2.3)$$

$$O_{3(g)} + e^- \rightarrow O^-_{3(g)} \quad (2.4)$$

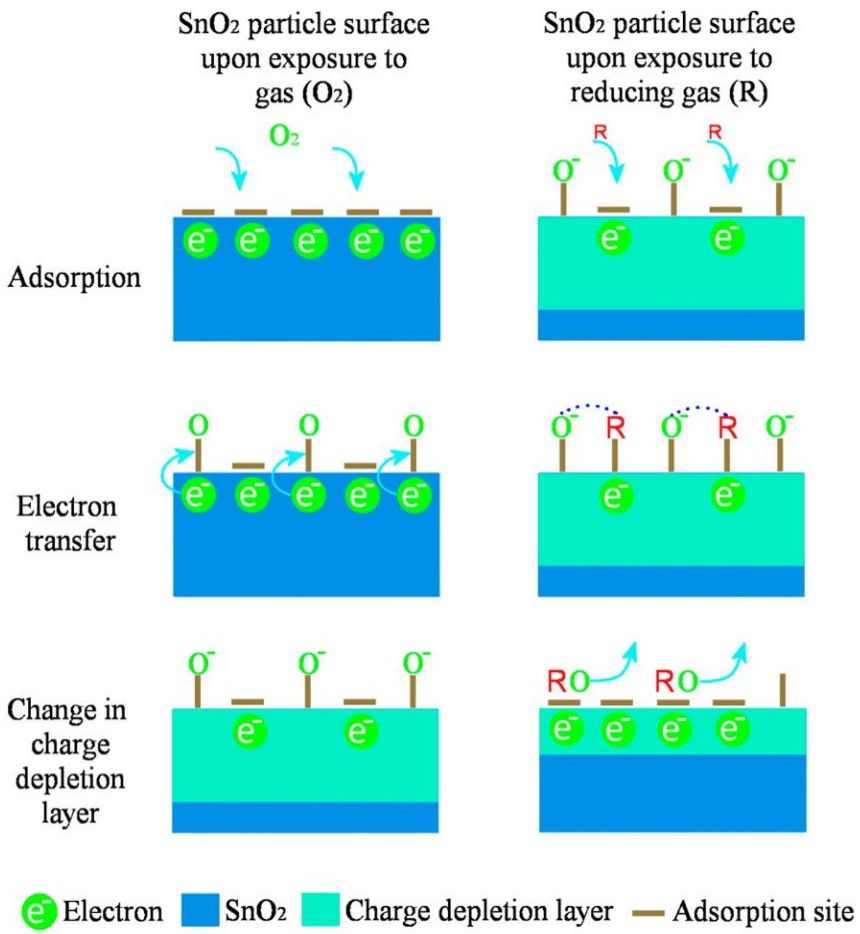

Figure 2.3: Schematic diagram of the reducing gas sensing mechanism on the SnO_2 surface (Tangirala *et al.*, 2017).

It is noteworthy that the pure SnO_2 sensor material surface has relatively less active sites available for oxygen adsorption compared to noble metals and transition metals, due to the formation of potential barriers on the particle surface (Liu *et al.*, 2014). Furthermore, it was found that in n-type semiconducting material such as SnO_2, electrons only contribute small fraction (<1%) to the total conductivity (Park and Akbar, 2003). Thus, two important efforts have been taken: firstly, reduce the size of SnO_2 particles to nano size scale and secondly, incorporating dopants which have relatively higher number of catalytic active sites compared to pure SnO_2. These two important efforts can have a significant impact on the SnO_2 sensor performance, as are discussed further in subsections 2.3.3(a) and 2.3.3 (b), respectively.

2.3.3(a) The effect of small grain size of SnO_2 sensor material

The effect of grain size of SnO_2 sensor material was explained by Xu and co-workers using a semi quantitative model (Xu *et al.,* 1991). According to this model, the SnO_2 particles are considered to be partially sintered crystallites which are connected to their neighbour particles by neck (Eranna, 2011) as shown in Figure 2.4. Figure 2.4 shows the schematic model of the effect of the crystallite size on the sensitivity of SnO_2 gas sensors. Basically, the relationship between the particle size (D) and the thickness of electron depletion layer (space-charge layer) around the particle surface may lead to three different phenomena. Firstly, when D is very much larger than L ($D >> 2L$), the conductivity is effectively controlled by the inner mobile charge carriers and the electrical conductivity depends exponentially on the barrier height. At this state, the sensor material is not so sensitive to the charge acquired from surface reactions. Based on the literature review it was estimated that the size of L for pure SnO_2 material is about 3 nm (Ogawa *et al.,* 1982; Yin *et al.,* 2009; Zhang *et al.,* 2009). While when $D \geq 2L$, the space charge layer region around the neck forms a constricted conduction channel within each aggregate. Thus, the conductivity of the SnO_2 depends on the grain boundaries and the cross-section area of those channels. Therefore, the SnO_2 particles are sensitive to the oxygen gas in atmosphere.

Lastly, if the D is less than 2L ($D < 2L$), the space charge layer region occupies the entire SnO_2 particle and the crystallites and the conductivity is determined by charge transport in the bulk. At this stage, the energy bands are nearly flat throughout the whole structure of the interconnected grains and there is no significant barrier for intercrystallite charge transport. Thus, a few charges from surface reactions will result in substantial changes in conductivity of whole structure, consequently SnO_2 becomes highly sensitive to oxygen in atmosphere (Geng *et al.,* 2010).

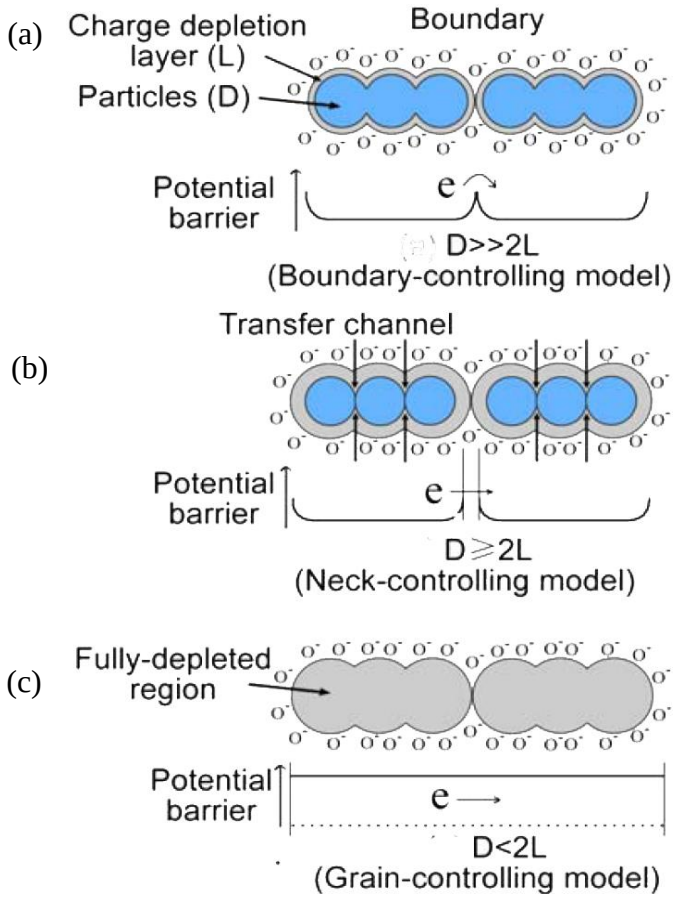

Figure 2.4: The schematic model of the effect of the crystallite size on the sensitivity of SnO_2 gas sensors: (a) Boundary-controlling model, (b) Neck controlling model and (c) Grain-controlling model (Sun *et al.,* 2012)

2.3.3(b) Mechanisms of gas sensing in metal doped SnO_2 nanostructures

Decreasing the size of SnO_2 particles to nanosize can significantly improve the gas sensing properties, achieving small dimensions remains as challenge in real applications. For example, the SnO_2 nanostructures with particle size less than 10 nm can have poor mechanical properties (Liu *et al.,* 2014). In addition, the size of SnO_2 crystallite can grow as the sensor is heat-treated to obtain good sensing properties during the gas sensing process, which can affect the performance of SnO_2 gas sensor (Miller *et al.,* 2006). Thus, doping is always considered as a traditional technology that can improve the physical and chemical properties of gas sensor (Lim and Oh, 1996; Liu *et al.,* 2011; Parthibavarman *et al.,* 2013; Jin *et al.,* 2015).

In general, the type of dopants may influence the gas sensing properties of SnO_2 mainly by inhibiting the grain growth and modifying the electron Debye length, eventually change the gas-surface interactions (Batzill and Diebold, 2005). Two different mechanisms are invoked to explain the sensitisation phenomenon of SnO_2 doped sensors: the electronic and the catalytic mechanisms. Figure 2.5 presents the schematic diagram of electronic and catalytic mechanisms in metal doped SnO_2 gas sensor. In the electronic mechanism, a reducing gas reacts on the surface of the metal dopant, releasing an electron that is transferred to SnO_2. The changes in the electron density near the surface of the SnO_2 leads to a decrease in resistance. In the catalytic mechanism which also known as spill-over mechanism, the metal dopant acts as a catalyst where the reducing gas is transported to the SnO_2 surface. When the reducing gas reacts with oxygen adsorbed on SnO_2 surface, the electrons release directly to the charge depletion layer of SnO_2 particle. The difference between these both mechanisms is that electrons transfer occurs in electronic mechanism, while atoms transfer occurs in the catalytic mechanism (Miller *et al.,* 2006).

Another role of doping in enhancing gas sensing properties is that by reducing the particle size SnO_2. This phenomenon was explained by Wu and co-workers (1999), due to the interaction on the boundaries between the host and dopant crystallites, the motion of crystallites is resisted, and the crystal growth stunted. As the result, the particle size is decreased by the metal doping (Wu *et al*., 1999).

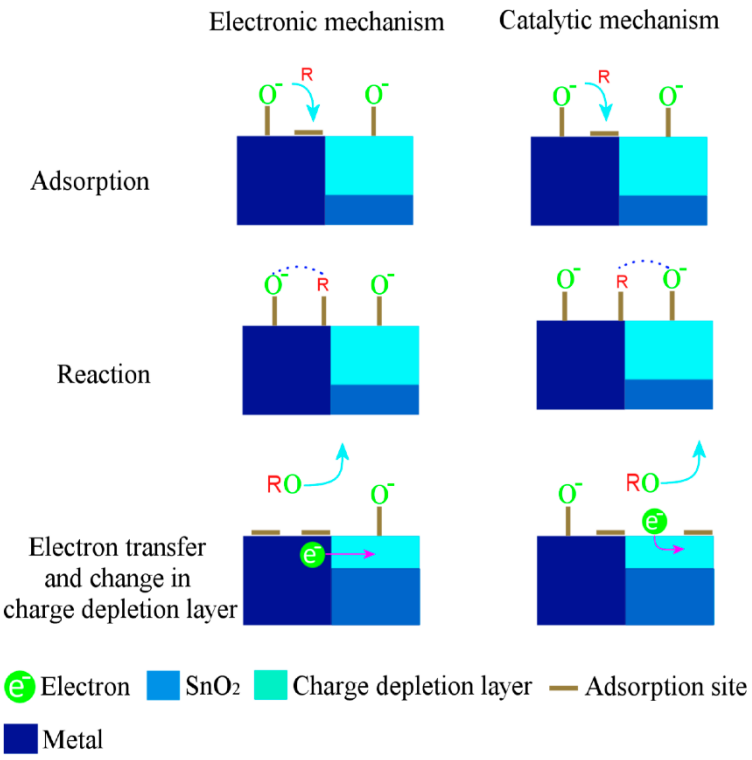

Figure 2.5: Schematic diagram of the electronic and catalytic mechanisms in metal doped SnO_2. R represents reducing gas (Tangirala *et al.*, 2017).

2.3.4 Metal additives (dopants) in SnO_2 gas sensors

The doping of tin(IV) oxide gas sensor is one of the traditional approaches used to enhance the gas sensitivity, selectivity and decrease the operating temperature. So far, various dopants including noble metals, transition metals, non-metals, alkaline earth metals and metalloid can be used. Among them, noble metals (Pd, Pt, Au, Ag, Rh) and transition metals (e.g. Fe, Co, Cu, Ni, etc.) are the most common metals used as dopants in gas sensor applications. Generally, noble metal dopants serve as "catalyst" (increase the rate of reaction) whereas transition metal dopants serve as "accelerator" (its presence cause an increase in the speed of chemical reaction) of various process (Korotchenkov, 2013). Doping can be categorised as bulk doping and surface doping. The bulk doping is normally carried out during the synthesis process of SnO_2, while surface doping can be performed following sensing layer deposition.