

**DESIGN, FABRICATION AND TESTING OF
AMPEROMETRIC HYDROGEN GAS SENSOR BASED ON
PALLADIUM NANOPARTICLES MOUNTED ON MULTI-
WALLED CARBON NANOTUBES**

BY

ISMAIL ADENIYI BULIYAMINU

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This thesis, written by **ISMAIL ADENIYI BULIYAMINU** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN PHYSICS**.



Dr. Abdulaziz H. Al-Aswad
Department Chairman

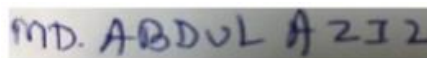


Dr. Suliman Saleh Al-Homidan
Acting Dean of Graduate Studies

Date



Dr. Zain H. Yamani
(Advisor)



Dr. Md. Abdul Aziz
(Co-Advisor)



Dr. Nabil Maalej
(Member)



Dr. Muhammad Baseer Haider
(Member)



Dr. AbdelKarim Mekki
(Member)

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[This thesis is dedicated to my beloved mother and the memory of my late father, may Allah grant him highest place in Jannah. It is also dedicated to my wife, my son and my siblings. The final dedication is to Almighty Allah for his mercy on me.]

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LIST OF ABBREVIATIONS

AGS:	Amperometric Gas Sensor
Ag/AgCl:	Silver/Silver Chloride
BCC:	Body-Centered Cubic
CE:	Counter Electrode
CGS:	Conductometric Gas Sensor
CNTs:	Carbon Nanotubes
EC:	Electrochemical
EDS:	Energy Dispersive Spectroscopy
EGS:	Electrochemical Gas Sensor
FCC:	Face Centered Cubic
FESEM:	Field Emission Scanning Electron Microscopy
f/MWCNTs:	Functionalized Multi-Walled Carbon Nanotubes
FWHM:	Full Width at Half Maximum
HRTEM:	High Resolution Transmission Electron Microscopy
LOD:	Limit of Detection
MFC:	Mass Flow Controller
MOS:	Metal Oxide Semiconductor
MOx:	Metal Oxide
NaBH₄:	Sodium Borohydride
Pd:	Palladium

Pd-H:	Palladium Hydride
Pd(NO₃)₂:	Palladium Nitrate
PdNPs:	Palladium Nanoparticles
PdNPs- f/MWCNTs:	Palladium Nanoparticles mounted on Functionalized Multi-Walled Carbon Nanotubes
PGS:	Potentiometric Gas Sensor
Pt:	Platinum
PTF:	Palladium Thin film
PTFE:	Polytetrafluoroethylene
RE:	Reference Electrode
SAED:	Selected Area Electron Diffraction
SE:	Sensing Electrode
TCD:	Thermal Conductivity
WE:	Working Electrode
XPS:	X-ray Photoelectron Microscopy
XRD:	X-ray Powder Diffraction

ABSTRACT

Full Name : Ismail Adeniyi Buliyaminu
Thesis Title : Design, Fabrication and Testing of Amperometric Hydrogen Gas Sensor Based on Palladium Nanoparticles Mounted on Multi-Walled Carbon Nanotubes
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Monitoring hydrogen gas leakages to provide safety against any accidents that might occur in the process of production or transportation of hydrogen gas is of utmost importance. Amperometric gas sensing is an excellent candidate for safety and industrial monitoring of hydrogen. In this thesis, a simple design and fabrication of an amperometric hydrogen gas flow sensor is developed. The active sensing material was synthesized based on palladium nanoparticles decorated on the tubular walls of carboxylic acid functionalized multi-walled carbon nanotubes and deposited on polytetrafluoroethylene membrane sheets for fabricating the working electrode. The sensing material was characterized by X-ray powder diffraction, field emission scanning electron microscopy, energy dispersive spectroscopy, high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy. Field emission scanning electron microscopy and high-resolution transmission electron microscopy showed evidence of successful formation of the palladium nanoparticles on the wall-surface of the functionalized multiwalled carbon nanotubes. High resolution transmission electron microscopy and X-ray powder diffraction confirmed the polycrystallinity and face-centered cubical properties of the sensing material with an average crystallite size of 2.7 ± 0.8 nm. The amperometric hydrogen gas detection measurements were carried out to confirm the response to different flow rates of both H₂

and N₂. It was confirmed that our sensor is sensitive to H₂ flow. The fabricated amperometric hydrogen gas flow sensor showed rapid response and good stability for a long period of time with maximum percentage deviation of 2.6%. It showed a sensitivity of 2.78 $\mu\text{A}/\text{sccm}$, limit of detection of 3.2 sccm at 1% H₂, and a good linear response, with maximum percentage deviation of 6.1%, over a flow range of 0-50 sccm. It was also found to be reproducible with maximum percentage difference of 7.9%. |

ملخص الرسالة

الاسم الكامل: إسماعيل عديني بوليامينو

عنوان الرسالة: تصميم، و تصنيع، وإختبار مستشعر غاز الهيدروجين الأمبيرومترى المعتمد على جسيمات البلاديوم النانوية الموضوعة على أنابيب الكربون النانوية متعددة الجدران.

التخصص: الفيزياء

تاريخ الدرجة العلمية: أبريل، 2020 م.

إنّ مراقبة تسرّب غاز الهيدروجين لتوفير السلامة ضد أي حوادث قد تحدث أثناء عملية إنتاج أو نقل غاز الهيدروجين لأمر في غاية الأهمية. تعتبر حساسات الغاز الأمبيرومترية مرشحاً ممتازاً للسلامة والرصد الصناعي للهيدروجين. في هذه الأطروحة، تم تطوير و تصنيع تصميم لمستشعر تدفق غاز الهيدروجين الأمبيرومترى. تم تصنيع مادة الإستشعار من جسيمات البلاديوم النانوية، الموزعة على أنابيب الكربون النانوية متعددة الجدران والموظفة عن طريق حامض الكربوكسيل، وترسيبها على صفائح غشاء البولي ترافلوروايثيلين لتصنيع القطب المستشعر. تم تحليل مادة الإستشعار عن طريق حيود الأشعة السينية، والمجهر الإلكتروني الماسح، والتحليل الطيفي المشتت للطاقة، والميكروسكوب الإلكتروني النافذ عالي الدقة، والمطيافية كهروضوئية بالأشعة السينية. أظهر كل من المجهر الإلكتروني و المجهر الإلكتروني عالي الدقة دليلاً على نجاح تكوين الجسيمات النانوية للبلاديوم المعدني على سطح جدران أنابيب الكربون النانوية. أكد الفحص المجهرى الإلكتروني النافذ عالي الدقة وأشعة الحيود السينية للمسحوق على وجود تعددية بلورية، و التي تحتوي على خصائص المكعب مركزي الوجه، لمواد الاستشعار بمتوسط حجم بلوري 2.7 ± 0.8 نانومتر. تم إجراء القياسات الأمبيرومترية للكشف عن غاز الهيدروجين للتأكد من الاستجابة لمختلف معدلات التدفق لكل من غاز الهيدروجين و النيتروجين. أظهر مستشعر تدفق غاز الهيدروجين الأمبيرومترى إستجابة سريعة واستقرار جيد لفترة طويلة من الزمن مع أقصى نسبة انحراف تبلغ 2.6%. أظهر المستشعر حساسية تدفق بمقدار 2.78 مايكرو أمبير لكل سنتيمتر مكعب في الدقيقة ($\mu A / sccm$)، و حد أدنى للاستشعار بمقدار 3.2 sccm عند 1% H_2 ، واستجابة خطية جيّدة، مع أقصى نسبة انحراف تبلغ 6.1%، على مدى تدفق 0-50 sccm. كما وجد أنه يمكن أن تتم إعادة تصنيع المستشعر مع اختلاف طفيف في الأداء بنسبة 7.9% كحد أقصى

CHAPTER 1: INTRODUCTION

1.1 Sensors

Generally, sensors are devices that convert physical or chemical inputs into electronic output signals. They are typically connected to external electronic devices, like a computer, which receive information and/or feedbacks from the sensors during the detection process. [1, 2]. The essential modules and components of a sensor are grouped as depicted in figure 1.

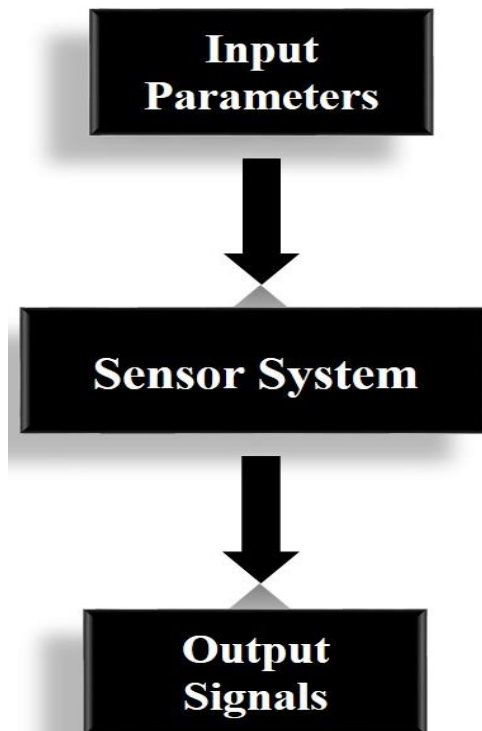


Figure 1 Block diagram showing the main components of sensor

Sensors can be classified into two different types: physical and chemical sensors [2-5]. The physical sensors are basically used to measure physical quantities including temperature, resistance, pressure, moisture, density, thickness etc. They are used in various industrial applications like health, agriculture, military and aerospace [3, 5].

The chemical type sensor converts the chemical analytes concentration into electrical signals through the chemical reactions [6]. The feedback from the sensor is received by the receptor which changes the chemical reaction into the energy to be analyzed by the transducer [2, 4]. Figure 2 shows a commercial chemical sensor.

Sensors may also be categorized based on the physical parameters they measure. For example, temperature sensor is used mostly for the industrial temperature control. Likewise, the chemical sensor, pressure sensor, photodetector, magnetic switch sensor, optical sensor and speed sensor [2, 5] etc. Some other applications include active and passive infrared (IR) sensor used in different devices such as for television remote control [3, 4].

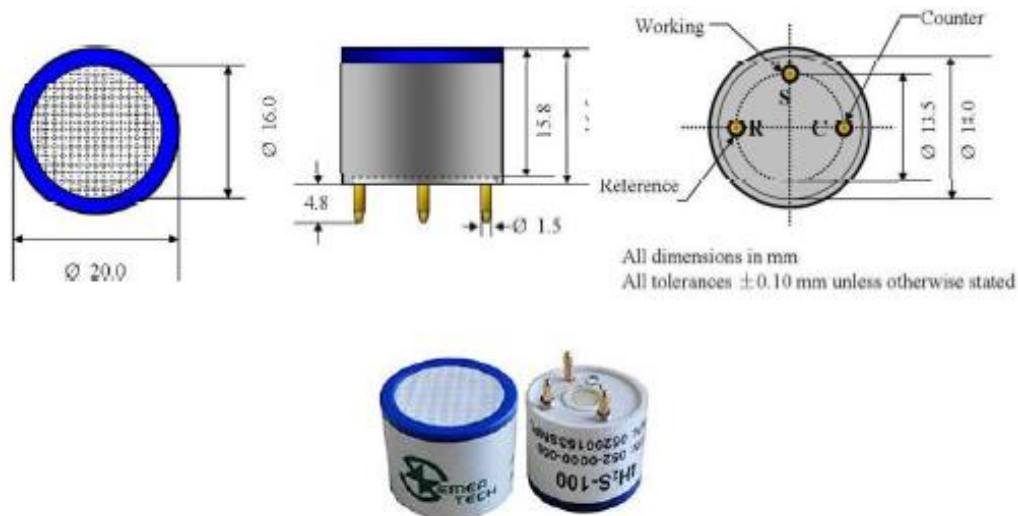


Figure 2 Real device chemical sensor [3]

In addition to low cost and portability, sensors are chosen for a specific application depending on certain features and requirements such as the sensing parameter and mechanism, selectivity, linearity, detection limit, stability, accuracy, sensitivity, ruggedness, operating conditions, response time and reproducibility [4, 5].

Chemical sensor has been demonstrated to be one of the highly effective sensor technologies [7, 8]. This includes high effective discrimination of target gases and possible cross-reactivity performance towards multi-analytes [8]. This makes it a highly recommended sensor with high selectivity when compare with selective biosensors [2, 9]. It covers multidisciplinary application in chemistry, physics, optics, semiconductor, and membrane technology [2, 6]. It also responds to certain chemical activities in a medium and transform it into electrical signals [2]. Generally, chemical sensors may be categorized into biosensor and gas sensor. It may also be categorized, based on the principle of operation, into optical, semiconductor and electrochemical sensor [6].

The biological sensor is the type that interacts with the analyte in the form of enzyme-like or antibody to generate electric signals [4, 6]. They are prevalently used in plant biology and biomedical applications [3, 5, 10, 11]. Biosensor may be divided into three categories according to the principle of operation; the enzyme-based sensor, microbial based sensor, and immuno-based sensor [3, 5, 6, 10, 12, 13]. Gas sensors are meant to detect the flow and/or the concentration of certain gases through various sensor technologies. The gas flow and/or concentrations are converted into electrical responses. The electrical responses of the gas sensors correspond to the flow and/or concentration of the target gas. They are widely used in different industries such as medical and food [6, 14]. Since the environmental monitoring is so important to human lives, gas sensors are imperative and play a pivotal role in safety.

1.2 Gas sensor

There are numbers of combustible, flammable and toxic gaseous substances in the atmosphere that need to be monitored. Most of these dangerous gases are used in the industry, and these gases can escape unknowingly, which is dangerous to the workers and people living nearby. This brings the need for the gas sensors to monitor the air we breathe.

The main parameters that define the performance of gas sensor are sensitivity, stability, selectivity and repeatability [2-5]. Gas sensors are applicable in aerospace to monitor some flammable, combustible and toxic gases like H_2 , CO_2 , and O_2 . Other fields of use include petrochemical industry (e.g. for quality control and leakages alarm for conventional pollutants), food quality control (e.g. detection of food molecules like humidity and CO_2 when food is no longer good for consumption), agriculture (e.g. checking of ammine and ammonia in the soil and/or water), security (for detection of dangerous gases for public safety) [2, 4]. According to the principle of operation, gas sensors can be grouped into semiconductor-type, electrochemical-type and optical-type [2, 6, 14, 15].

1.3 Amperometric Gas Sensor

Electrochemical-type gas sensors (EGS) are gas detectors that operate by measuring the flow and/or the concentration of analyte gases by creating redox reaction at the surface of a suitable sensing electrode and producing electric signals proportional to the amount of analyte gas. They are categorized into three main classes: (i) amperometric [16, 17], (ii) conductometric [16-18] and (iii) potentiometric [16, 17, 19] according to their mode of actions. Amperometric sensors employ a fixed potential applied between a reference electrode and a working electrode to measure the current responses based on the

electrochemical reactions. Conductometric gas sensor employs a series of frequencies for the conductivity measurement. Potentiometric gas sensors employ the potential applied between two electrodes for the measurement of electrode potential based on the established local equilibrium at the sensor interface [16, 18, 20]. Specifically, amperometric gas sensors (AGS) are promising owing to their capability to work under atmospheric pressure, room temperature and in a rugged environment [16, 18, 21, 22].

AGS have properties that make them attractive to researchers for gas detection applications. Specifically, they are reliable and capable of producing electrical signals at ambient air and temperature, with low power consumption [23, 24]. They play an imperative role in environmental applications including safety, health and security [16, 18, 22]. AGS can be designed to operate accordingly at temperatures ranging from about -30 °C to over 1000 °C [16, 18, 19]. The choice of operating temperature determines which types of sensing materials and electrolytes will be used in the fabrication process. A liquid electrolyte or polymer is required for room-temperature AGS while a solid electrolyte is highly recommended for high-temperature AGS. The former is commonly used industrially for safety and medical applications while the latter has been primarily developed for stack gas monitoring [2, 16, 19, 25, 26]. AGS are not so difficult to design, low cost, and rugged enough for long-term applications. Unlike potentiometric gas sensors, in which the generated signal (voltage) depends not on the sensing electrode size, AGS generates a signal (current) which is proportionate to the active area of the sensing electrode [16, 18, 19, 22, 27, 28].

Ideally, gas sensors are required to be simple, portable, fast in response, selective, sensitive, stable, low cost and able to undergo miniaturization [16, 29, 30]. To accomplish these

properties, AGS technology could be an appropriate option owing to their usual intrinsic sensitivity and selectivity [16, 29, 31, 32]. They are regarded as the most popular types of sensors in various practical applications ranging from food safety to environmental monitoring [16, 17, 19]. The choice of the sensing materials depends on the choice of the analyte gas. In the present work, hydrogen gas H_2 is the analyte gas of interest.

1.4 Importance and Uses of Hydrogen Gas

Hydrogen is the lightest of all chemical element and is 14.5 times lighter than air. It is the most abundant substance in the Universe. It is regarded as a clean energy carrier [9, 33, 34]. Hydrogen has density of 0.08988g/L at standard conditions for temperature and pressure (STP), a low boiling point of $-252.8\text{ }^{\circ}\text{C}$, a low melting point of $-259.2\text{ }^{\circ}\text{C}$ at atmospheric pressure [17, 35]. It is colorless, odorless, and tasteless [17, 18, 35]. Contrary to the behavior of other gases, the temperature of H_2 rises above room temperature when its pressure decreases as a result of the gas expansion [36, 37]. This can be best explained according to the principle of thermodynamics; it means that the intermolecular force of repulsion dominates the intermolecular force of attraction [36-40]. Otherwise, cooling of hydrogen take place during expansion which is like other gases as well [40].

Hydrogen gas is a clean energy carrier used in various chemical processes and industries for a variety of applications including petrochemical production, transportation, oil and fat hydrogenation, medical, fertilizer production and aerospace [16, 18, 35]. Hydrogen has been widely used in fuel cell and power generation applications because of its low polluting effect because the byproduct is basically water [18, 23, 35, 41, 42]. It is highly flammable and can explode at volume concentrations ranging from 4 to 75% in air. Due to its high

flammability, hydrogen ignition will spontaneously occur in air at a temperature of about 520-580 °C and, at a minimum ignition energy of about 0.02 mJ [17, 18].

Due to these uncommon properties that make hydrogen different from traditional fuel, proper care must be taken in dealing with hydrogen because any leakages are extremely dangerous in transportation, power transformer systems, and in chemical production. Hence, a proper and effective method for detection of hydrogen gas leakage is required. Therefore, effective hydrogen gas sensors are highly needed to monitor its leakage at very low amounts for safety operation in various applications[43, 44].

There are several gas sensors available commercially [16, 18, 19, 45, 46]. Many attempts have been made with different detection principles to develop hydrogen gas sensors based on electrochemistry, catalytic combustion, electrical conductivity, thermal conductivity, semiconductors and optical properties [18, 24, 43, 47]. Most of these methods are costly, time consuming in sensing materials preparation and some of them exhibit poor response when it comes to sensing hydrogen gas at low concentrations [48-52].

The active components of an amperometric gas sensor are sensing materials, electrolyte, membrane, counter (and reference) electrodes. More importantly, mass transportation of hydrogen gas towards the working (sensing) electrode is imperative in dealing with amperometric gas sensing measurements [53, 54]. However, the success in amperometric hydrogen sensors depend on the working electrode materials and the pore size of the membrane to provide long-term stability, high sensitivity and selectivity, in addition to linear response. As a result, research on development of working electrode materials is an active subject of research.

1.5 Motivation and Problem Statement

Amperometric gas sensors are important in both research and industry due to the high demand in various applications such as health, medical, safety, security and environmental monitoring. Hence, much research has been carried out to develop novel nanomaterials to achieve the requirement for sensors to be highly sensitive, specific and fast response.

Carbon nanotubes CNTs, prepared by several techniques, received considerable attentions for several applications due to their unique chemical and physical properties. Among the known CNTs, multiwalled carbon nanotubes MWCNTs stood out as the most used catalyst support due to the thermal and mechanical stability exhibited over SWCNTs [55-57], in addition to its conductive properties. Henceforth, the motivation for using MWCNTs as a support for electrochemical sensing material fabrication.

Selection of catalysts which can adsorb and desorb the analyte gas at a high rate is a big challenge [2, 6]. Palladium-based nanoparticles, among other pure metal nanoparticles, are an excellent candidate to realize a high H_2 sensing performance because of the ability of palladium to adsorb high volume of hydrogen [58].

Therefore, we designed and fabricated an amperometric sensor cell with a suitable sensing electrode based on PdNPs-f/MWCNTs. Establishing a workable amperometric gas sensing setup to produce the results that enhance the sensor performance is the main challenge of this research. Fabricating good working electrodes is also one of the key aspects of the research presented in this thesis. The choice of hydrogen gas H_2 as the analyte comes since it is used in petrochemical industry and it is by far a better candidate to traditional fossil fuels to meet the global energy demands.

1.6 Research Objectives

This research project aims to develop a portable and sensitive amperometric hydrogen gas H₂ sensing cell. The objectives of this research include the following:

1. Design and fabrication of the amperometric gas sensor cell or housing.
2. Synthesis of the sensing materials that serve as good catalysts for hydrogen sensing.
This will be achieved by mounting palladium on carboxylic functionalized multi-walled carbon nanotubes.
3. Morphological and chemical composition characterization of the electrode material.
4. Fabrication of the sensing electrode by vacuum filtration method.
5. To analyze the electrochemical behavior of the electrode material.
6. To check the amperometric response of the sensor upon exposure to different concentrations of hydrogen gas.

1.7 Thesis Outlines

This work entails five chapters, the first chapter introduces the research topic (sensors and their various types), the importance of hydrogen gas, provides the motivation and lists the objectives of the research.

Chapter two is a literature review and gives the fundamental background of amperometric sensor by describing the classes of electrochemical gas sensors, the operating principles, components, sensor requirements, and its general characteristics and performance. This

chapter also details the sensing mechanism as a surface reaction process taking place between the sensing material and target gas.

Chapter three presents the experimental aspect of this study including the sensing material preparation, instrumentations, material and electrochemical characterization techniques with physical explanations, working electrode fabrication, explanation of the design and fabrication of the sensor cell, and amperometric gas sensing setup.

Chapter four gives the results of structural and morphological characterization of the sensing material using XRD, FESEM, XPS and HRTEM. Then, amperometric tests are described in detail. By analyzing the results, we calculate the sensitivity and the response time of the fabricated amperometric hydrogen gas sensor.

Chapter five summarizes the thesis and concludes with possible work in the future.]

CHAPTER 2: LITERATURE REVIEW

This chapter begins by introducing the fundamental principle behind the amperometric H₂ gas sensor. The discussion includes the detection mechanism and features of electrochemical gas sensing including sensitivity, selectivity, response time, stability and cost-effect. Finally, this chapter will focus on the materials for sensing electrode and the current detection challenges.

2.1 Principle of Operation of the Amperometric H₂ Gas Sensor (AGS)

Amperometric gas sensor (AGS) is one of the significant types of the electrochemical gas sensor for current measurement. Other electrochemical gas sensors are conductometric sensor for conductivity measurement and potentiometric gas sensor for voltage measurement [16, 18, 22]. As shown in figure 3, AGS follows the concept of a normal electrochemical system with two or three different electrodes. A typical two electrodes sensor system mainly consist of a CE and a WE connected by an ionic conductive electrolyte for transfer of charges. The CE and/or WE cannot totally maintain the constant potential simultaneously with the flow of current. In a typical electrochemical measurement, an additional third electrode known as the RE is introduced to complete the circuit without any flow of current via it and maintaining the constant potential [59, 60]. This serves as the standard potential reference for the WE. With this kind of electrochemical set up, the CE can still polarize without affecting the performance of the WE [59].

The detection process consists of the following four steps: (i) diffusion of the analyte gas (e.g. H₂) through a gas permeable membrane on which working/sensing material is

deposited, (ii) adsorption process of the analyte gas takes place on the WE surface, (iii) followed by the electro-reaction on the WE and (iv) the reaction products desorb from the surface of the sensing electrode. A current signal that measures the rate of chemical reaction on the WE surface, is acquired with the help of a potentiostat as shown in figure 3 [16, 18, 22, 59, 61, 62].

In detail, the hydrogen gas is transported by diffusion through the WE support (porous membrane). The sensing material adsorbs H_2 gas where the H_2 dissociates into its atoms. When a fixed potential is applied, an electrochemical hydrogen oxidation reaction takes place at an appropriate potential between the RE and the WE. In this regard, the hydrogen atoms are oxidized into hydrogen ions at the sensing electrode surface. Next, desorption of the product takes place and diffuse into the electrolyte. Reduction reaction occurs at the CE surface which is configured to balance the charges added or removed from the electrolyte during the electrochemical reaction process. The electrochemical system is connected to an external circuit, such as potentiostat circuit, where the current is generated as a function of electrons generated during the electrochemical reaction.

The flow of current through the sensor system is controlled by the rate of electrode reaction known as the kinetic rate as well as by diffusion rate of H_2 onto the WE surface [18, 22]. The flow of electrons produces the current signal as a function of the amount of H_2 gas adsorbed and reacted at the WE surface. Meanwhile, the charge is related to the number of the detected molecules [18, 59]. This section provides a brief understanding of the principle of operation of AGS. More details about the general principle of operation of AGS and other types, mentioned in chapter one, can be found elsewhere [2, 7, 16, 18, 21, 63-71].

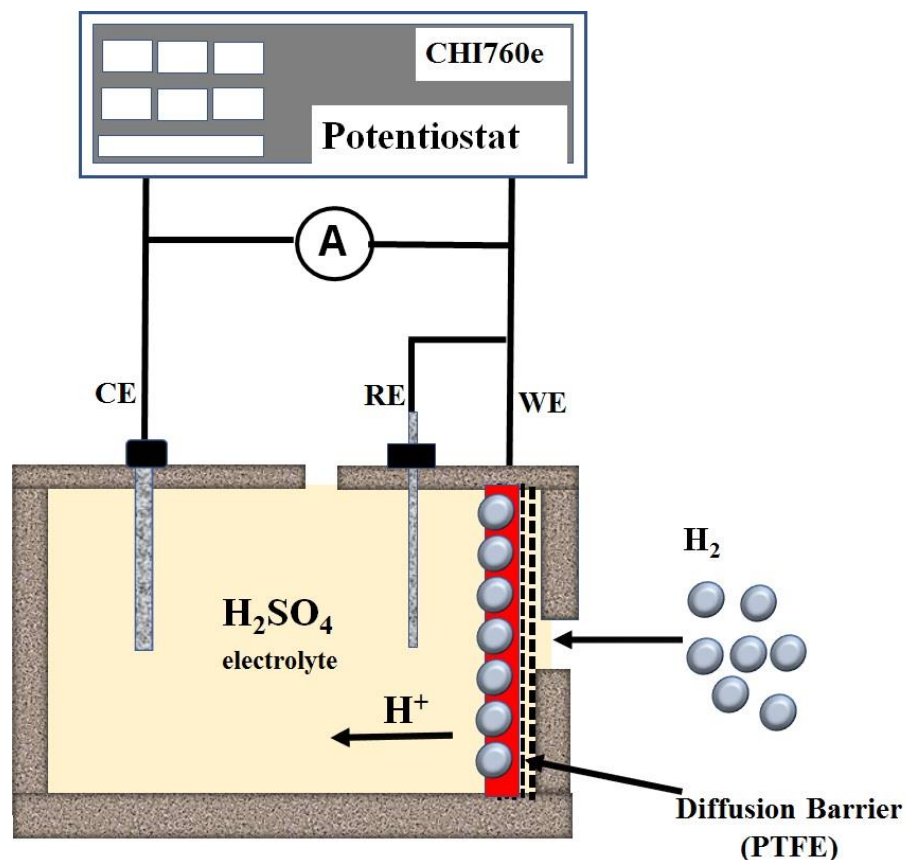


Figure 3 The principle of operation of an amperometric hydrogen gas sensor

2.1.1 Mass Transport

One of the key aspects of amperometric gas sensing is the redox reaction occurring at sensing electrode surface. Three significant steps are involved in achieving the electrode reaction. First, the analyte gas moves towards the sensing electrode interface (mass transport). Second, transfer of electrons occur by means of the quantum mechanical tunneling between the sensing electrode and the H₂ analyte gas that is adsorbed on the electrode surface. Third, the reaction product desorbs from the sensing electrode surface and diffuses to the electrolyte in order for the sensing electrode to accommodate fresh analyte gas [72-77]. In general, the overall electrode reaction is the net transfer of electrons in terms of the H₂ oxidation reaction that takes place on the sensing electrode surface.

However, the overall sensing electrode reaction depends on the rate of transfer of electron and the rate at which the analyte gas is transported (Mass Transport) to the electrode surface via the porous membrane [78]. Therefore, the main pillar in the subject of analyte transport is the mass transport that describes the transfer rate of the H₂ gas to the sensing electrode surface. Gas sensor fabrication is usually configured in such a way that the mass transport is limited by diffusion.

2.1.2 Diffusion

Herein, we investigate the movement of the H₂ analyte gas from the region of higher concentration to the region of lower concentration through the porous membrane. When the analyte gas diffuses through the membrane, the electro-active species (analyte gas) adsorbed by the electrode are consumed to cause the reaction to occur. Hence, the concentration of the analyte gas on the electrode surface are reduced and diffusion layers are formed which is a depends of the concentration gradient [79-81]. The existence of this concentration gradient leads to the occurrence of the so-called diffusion [79, 82, 83]. Hence, the movement of the analyte gas through the membrane under the influence of the concentration gradient can be described by Fick's First Law [82].

$$\dot{V} = \frac{\Delta P \times A \times D}{x} \quad (2.1)$$

Where $\dot{V}$ is the rate of the molecules moving via the porous membrane (mol/s), P is the pressure (atm), A is the membrane surface area (m²), x is the thickness of the porous membrane (m) and D is the diffusion coefficient (m²/s). In Fick's law of diffusion, we are interested in the amount of molecules that pass through the membrane over some period which determines the kinetic rate of reaction and the amount of current generated. How to

maximize the amount of the molecules that pass through the membrane is the main concern to achieve a better sensing response. The idea is to reduce the thickness of the membrane for faster rate of diffusion. The smaller the thickness of the membrane the easier for molecules to diffuse. Having more molecules is also achieved by increasing the pressure or concentration, of the incoming analyte gas. Increasing the membrane surface area also improves the diffusion through the membrane. Equation (2.1) can also be written with regard to the flux and the pressure or concentration gradient as shown in equation (2.2)

$$J = \frac{\dot{V}}{A} = \left(\frac{\Delta P}{x} \right) \times D \quad (2.2)$$

Where $\frac{\dot{V}}{A}$ is the flux, J ($\text{molm}^{-2}\text{s}^{-1}$), which is the net rate of molecules passing through an area, ΔP is the pressure drop across the porous membrane, x is the membrane thickness, and $\left(\frac{\Delta P}{x} \right)$ is the pressure gradient which is the change in pressure over the thickness of the membrane. Equation (2.2) may be represented by a one dimensional differential equation which relates the diffusional flux J (which is the gas molecule per unit time across the given area) normal to the membrane, with the diffusion coefficient D in which we have assumed the isotropic and homogeneous media and the pressure gradient $\frac{\partial P}{\partial x}$ as shown in equation (2.3) [82, 84]

$$J = -D \frac{\partial P}{\partial x} \quad (2.3)$$

The negative sign in equation (2.3) indicates the movement of the analyte gas is down the pressure gradient (i.e. from the higher concentration region to the lower concentration

region). In some experimental measurement, it is required to know how the flow and/or the concentration of the analyte gas varies as function of time. This can be defined by the Fick's second law (equation 2.4) [82] of diffusion which can be derived from the first law of diffusion. Hence,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2.4)$$

In this case, diffusion is in x-direction normal to the sensing electrode surface. Equation (2.4) relates the rate of change of concentration and/or pressure as a function of time with the concentration gradient.

2.1.3 Migration

In electrochemical measurements, charged particles move in reaction to the electric field generated by the potentiostat. This also contributes to the total flux of the analyte sample which depends on the following parameters: (i) diffusion coefficient, (ii) charge and number of ions and (iii) the magnitude of the electric field gradient experienced by those ions. This transport due to the electric field gradient is regarded as “Migration”, which is due to the electrostatic effect due to applied potential on the working electrode. When a constant potential is supplied, an electric field is generated. This occurs by means of electrostatic force. The migratory flux induced by the electric field is expressed as shown in equation (2.5) [84, 85] as

$$\frac{\partial C}{\partial t} = -UC \frac{\partial \phi}{\partial x} \quad (2.5)$$

2.1.4 Convection

Convection is regarded as the forced movement of the solution by mechanical force such as stirring or any other means of mechanical force. In electrochemical measurement, the rate at which the electrolyte solution is disturbed can greatly affect the convection contribution to ions in the electrolyte [86]. Convective transport can occur in two ways: the first is a natural convectional force which could be introduced into the electrolyte solution by gravity. The second is the forced vibration which could be attributed to the stirring or any other means to disturb the solution. Hence, the velocity created as a result of the movement of electrolyte in the cell can be described by equation (2.6) [84, 85]

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} \quad (2.6)$$

Where v_x is the hydrodynamic velocity which is obtained in any experimental situation by solving Naiver-Stokes equation [85]. The convective flux transport may be expressed as:

$$J = C v_x \quad (2.7)$$

Where v_x in this case is a solution velocity

2.1.5 Total Mass Transport in Electrochemical Measurement

To account for the total current passing through the electrode surface, we are required to add the three transport effects of diffusion, convection and migration that take place in the system kinetic. Mathematically, this is defined by Nernst-Planck equation [85] in one dimension.

$$J(x, t) = -D \frac{\partial C(x, t)}{\partial x} - \left(\frac{ZF}{RT} \right) DC(x, t) \frac{\partial \phi(x, t)}{\partial x} + C v_x(x, t) \quad (2.8)$$

Where D (m^2/s) is the diffusion coefficient, J ($\text{molm}^{-2}\text{s}^{-1}$) is the total flux, v_x (ms^{-1}) is the hydrodynamic velocity and ϕ is the electrostatic potential. Equation (2.8) shows that the total flux is related to the concentration gradient from diffusion term, electrostatic potential from migration term and the hydrodynamic velocity from the convection term. Equation (2.8) requires an exact solution as to be able to predict the amount of current flowing in the system. This can be very difficult to deal with, even for a modern computer, because of some non-linear terms in the equation [85]. Yet, in electrochemical measurements, various experimental conditions can be controlled and minimized to eliminate some complex terms from this intricate equation. This limits the overall mass transport basically to only the contribution from the diffusion part.

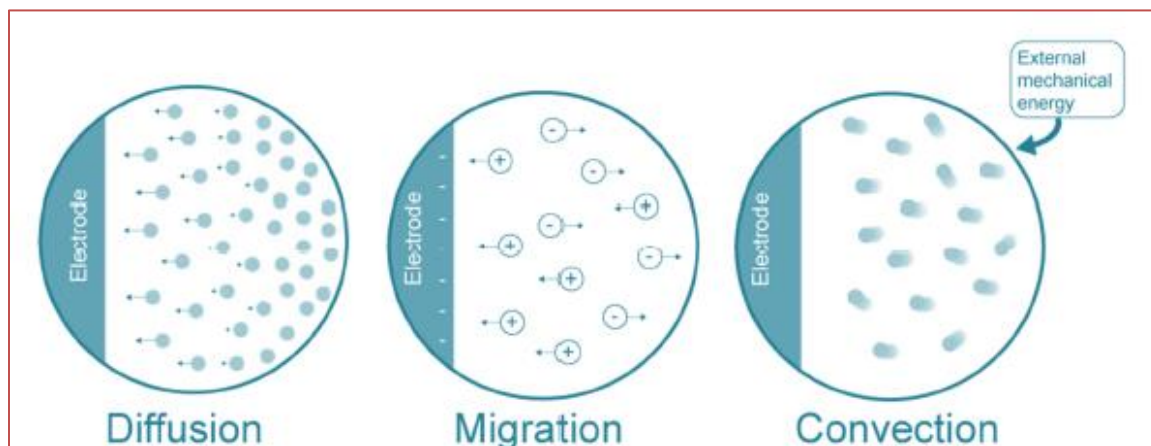


Figure 4 Schematic diagram [170] of mass transport (i) diffusion, (ii) migration, and (iii) convection

To start, the migration term, is due to electrostatic interaction on the electrode surface that comes from the application of electric potential on the electrode surface. This migration part of the equation is notoriously difficult to solve accurately for real solutions. Hence, minimization of the electric field subjected to the electrode surface is highly required. This is achieved by adding more inert solution to the electrolyte involved in the experiment. Not only will this minimize the electrostatic interaction on the electrode interface by removing

the migratory effect but will also improve the passage of current through the solution. In this regard, the electric field is dissipated not only over the electroactive species but also over the ions, so that the migratory effect is minimized to < 1% [85].

Secondly, to get rid of the mechanical vibration due to the convective transport term, total control of any vibrations from the surroundings is ensured by. (i) maintaining undisturbed electrolyte solution and (ii) ensuring that the sensing environment is unperturbed. Hence, equation (2.8) can be limited to the remaining term attributed to diffusion. Hence, the current observed at the working/sensing electrode surface can be written in terms of the flux as shown in equation (2.9) [85].

$$I_t = nFAD \frac{\partial C_i}{\partial x} \quad (2.9)$$

Where n is the number of electrons transferred during the sensing process, F is the Faraday's constant, and all other parameters are as defined earlier.

2.2 Components of an Amperometric Gas Sensor (AGS)

Typically, an AGS is composed of the working electrode attached to a gas permeable membrane, counter electrode, reference electrode and an electrolyte for ions transportation.

2.2.1 Gas Membranes

The use of membranes has been recognized for a long period of time in terms of industrial applications such as its use as a filter paper filtration in food industry [87, 88], desalination of sea water to produce drinking water [88, 89], as well as tissues and artificial lung engineering in medical industry [88, 90]. The membrane mechanism for hydrogen transport depends mainly on whether it is porous or dense. Dense membranes are widely used for

hydrogen transport in gas separation technique [88]. Porous membranes find their use in electrochemical gas sensors. They serve as diffusion barriers that control analyte gas to reach the sensing electrode surface where the redox reaction takes place [88].

The porous hydrophobic gas-permeable membrane, in figure 5, can aid the selectivity of the electrochemical sensor (i.e. allow the passage of only the analyte gas and sieve the interferences) [16, 18, 22, 88]. The permeability of the analyte gas through the membrane depends on some specific properties such as diffusivity of the gas and porosity of the membrane [91]. Also, the response time and the sensitivity of the AGS depends on the pore size, diffusion rate and thickness of the membrane [18, 22, 88]. Therefore, the choice of gas membrane depends on the nature of the analyte in consideration.

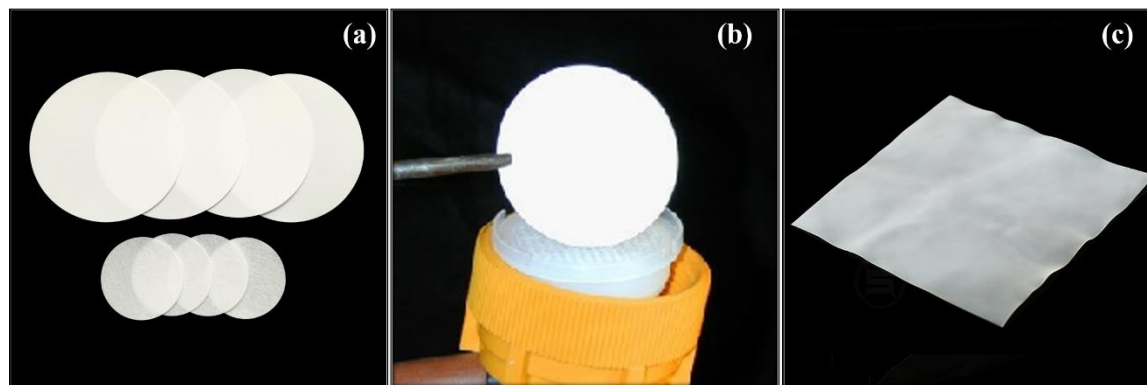


Figure 5 Picture of gas permeable (a) PTFE [171], (b) Teflon [172], and (c) Nafion membranes [173]

The membrane also serves as a diffusion barrier to prevent the leakage of the liquid electrolyte (aqueous solution) from the electrolyte chamber. Therefore, the use of hydrophobic type of membrane is highly recommended as its surface is not wetted by the aqueous electrolyte solution [16, 18, 22, 61, 88]. Instead, it only allows the flow of the incoming gas to the working electrode-electrolyte interface. For example, for a low-concentration analyte gas to generate a very high sensitivity, a highly porous permeable

gas membrane is required to allow more flow of analyte on the surface of the electrode per unit time to achieve high sensitivity [16, 18, 22, 32, 92-94]. Yet, the electrolyte should not be allowed to leak out of the chamber. Hence, preference should be on the permeability, thickness and hydrophobicity. Durability and manufacturability are also important [18].

Various types of commercial membranes are available which could be made from polymeric or inorganic materials. Examples of such commercially available membranes are thin solid Teflon membrane, Polytetrafluoroethylene (PTFE) membrane, microporous Teflon membrane, and the silicon membrane [18]. In amperometric hydrogen gas sensing based on liquid electrolyte, the most commonly used membranes are PTFE [47, 95-102], and Teflon [61] membranes. For amperometric hydrogen gas sensing based on solid polymer electrolyte, the most commonly used membranes are Nafion-117 [61, 101, 103], Nafion-177 [102] and ionic polymer membrane [103]. In the present work, PTFE membrane was used due to its unique properties such as hydrophobicity, chemical stability, high temperature resistant, and high permeability of analyte gas with no leakage of aqueous electrolyte.

2.2.2 Electrolytes

One of the imperative components of AGS is the electrolyte with the role of transporting charge between the sensor electrodes. It could be a solid or liquid electrolyte and allows the flow of ions between the electrodes. It has to be chemically stable and form a stable and constant potential with the reference electrode [16-19, 22]. It should support electrode reaction mechanism occurring on both the counter and working electrodes [16, 18, 22] and compatible with the sensing material (i.e. sensing material has to be active in such electrolyte medium) [18, 52]. In amperometric hydrogen gas sensing research, the most

commonly used electrolyte is the proton conducting type which is the main reason for the wide use of sulfuric acid (H_2SO_4) [47, 52, 61, 95-102, 104] for ambient-temperature H_2 gas sensors. Also, proton conducting solid polymer electrolytes such as Nafion electrolyte have been used [61, 101-103, 105] at high temperatures. However, ceramic materials are the most preferably used electrolyte for high temperature sensors [18]. These solid electrolyte materials do not have leakages and corrosion problems [106]. This is the main advantage over the liquid electrolyte.

2.2.3 Electrode Material Selection

Working (Sensing) Electrode (WE): This is the main electrode used in conjunction with the counter and reference electrodes. There is a transfer of electrons on working electrode-electrolyte interface during the electrode reaction of interest. The selection of the sensing electrode (SE) is important to achieve a successful sensing experiment. The selection depends on the type, design and methodology of the sensor in question. The working electrodes must be porous enough to allow the target gas to diffuse to the electrode/electrolyte interface if it has a reasonably high surface area. Noble metals nanoparticles have been known to be promising gas sensing materials due to their unique properties including excellent stability and electrocatalytic properties [30, 107-111]. The use of platinum (Pt) has attracted the attention of researchers due to its indispensable properties including chemically inertness and electrocatalytic properties [22, 30]. Palladium has great adsorptive affinity for hydrogen compared to platinum [22].

However, for synthesizing metal NPs with huge surface area, high conductivity and electrocatalytic activity, it is important to support the metal nanoparticles with carbonaceous materials such as graphite, carbon nanotubes or glassy carbon [30, 107, 109].

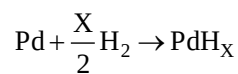
This prevents nanoparticles from agglomeration and improves the conductivity and stability performances. Multi-walled CNTs have been reported in many works as good metal supporting materials to achieve high conductivity and high stability [17, 32, 47, 95-98, 112]. This is as a result of their unique properties like high chemical stability [32, 98, 112, 113], excellent electrical properties [17, 32, 55, 112], high surface to volume ratio [32, 55, 60, 112] and high mechanical strength [32, 59, 113-116]. In this platform, acid treated functionalized MWCNT was used due to its ability to provide more attachment sites and support for the catalysts [112, 117]. Untreated MWCNTs are well known for their poor dispersibility and aggregation formation [118, 119]. Functionalization helps promoting the dispersion and surface activation to overcome self-aggregation [119]. Also, to improve the interfacial interaction and the homogeneous dispersion feasibility of MWCNTs [55, 120]. Because of the high surface area, carbon nanotubes decorated with noble metal nanoparticles are recommended for amperometric gas sensing to achieve rapid response and high sensitivity [47, 95-98, 121]. Besides, CNT doped noble metal nanoparticle films on membranes allow the diffusion of the gas into the sensing cells. This is important for fabricating amperometric hydrogen sensors. In this thesis, we have grown palladium nanoparticles (PdNPs) on the surface of acid-treated commercial functionalized multiwalled carbon nanotubes (f/MWCNTs). The use of palladium is due to its high affinity to hydrogen.

Various sensor technologies have been established for the hydrogen leak detection [25, 47, 61, 95-98, 104, 105, 122-125]. This detection mechanism is often based on the features of the type of sensing material. To enhance the hydrogen gas interaction with the sensing material, an electrocatalytic based material is required [16, 18, 19, 52]. The use of catalytic-

based sensing materials, like metals and their oxides, have been reported [20-26]. Among them, the most popular and deeply investigated is the platinum catalytic-based sensing material because of its high electrocatalytic activity [25, 47, 52, 61, 90, 95-97, 105]. However, platinum cannot adsorb hydrogen as much as palladium. Hence, palladium nanoparticles are a good substitute for the well reported platinum catalytic-based material in hydrogen sensor applications. Also, because of the high surface area-to-volume ratio of nanoparticles which provide large surface area for interaction to take place between hydrogen gas and the Pd metals [52, 58]. This same noble metal material often acts as the catalyst for the hydrogen oxidation reaction to take place [16, 18, 19, 58]. Apart from the sensing electrode, the other major constituent of AGS is the counter electrode. For a basic AGS, only the sensing electrode and the counter electrode are most important. A third electrode, reference electrode, is to measure the potential of the working electrode with no current passing through it, but rather through the counter electrode.

The fundamental processes of sensing can be described in four steps:

- 1.** Diffusion of the analyte gas to the sensing electrode through the porous PTFE membrane. This diffusion process has been discussed early in Chapter 1. The use of the membrane here enhances the selectivity and diffusion limit working mode [18, 22, 88].
- 2.** When the hydrogen gas molecule diffuses through the membrane, it is adsorbed on the Pd surface where it interacts with the Pd atoms via van der Waals force [18, 19, 22, 52, 58]. Pd reacts reversibly with hydrogen to form Palladium Hydride according to the reaction below:



Where PdH_X is the palladium hydride and X is the ratio of hydrogen atom to palladium atom metal which depends on the temperature and pressure of the hydrogen gas [126]. Hence, it is required to investigate the palladium-hydrogen interaction mechanism.

When the adsorption of hydrogen gets to some saturation level, the ratio X of hydrogen atom to palladium atom can be as high as 0.6 as shown in the phase diagram of Pd-H (figure 6) according to reference [126]. The high affinity and high ratio are the main reasons for the use of palladium in hydrogen storage and separation [126]. Pure palladium bulk is known to expand during adsorption of hydrogen and shrinks during its desorption. But this deformation is irreversible because the metal does not return to its original shape after desorption. This irreversible shape deformation has been reported in several papers [126-130]. The expansion of the pure palladium, when hydrogen is adsorbed, is due to the bulk palladium being changed from the FCC structural lattice into α - and β -phases and into their mixed ($\alpha + \beta$) phases as in the figure 6. The only difference in the two phases, α and β , is in the concentration of hydrogen atoms to palladium atoms, with a difference in the lattice constants of the two phases (α -phase = 3.89 Å and β -phase = 4.02 Å). Hence, this simply means the increase in volume of the Pd lattice during the adsorption of hydrogen atoms and decrease in volume during the desorption of the product. This irreversible deformation maybe attributed to the stress that is produced by the adsorption-desorption process over a long period of time. The expansion and contraction can be traced to ordinary elasticity while the so-called irreversible deformation can be attributed to the phenomenon known as the super-plasticity [126]. This is, in solid state, a situation when crystalline materials

expand beyond their limits which results into deformation and cannot return to their original shape. Several research have reported the deformation of palladium metal during the adsorption and desorption of hydrogen in terms of the super-plasticity [130-132].

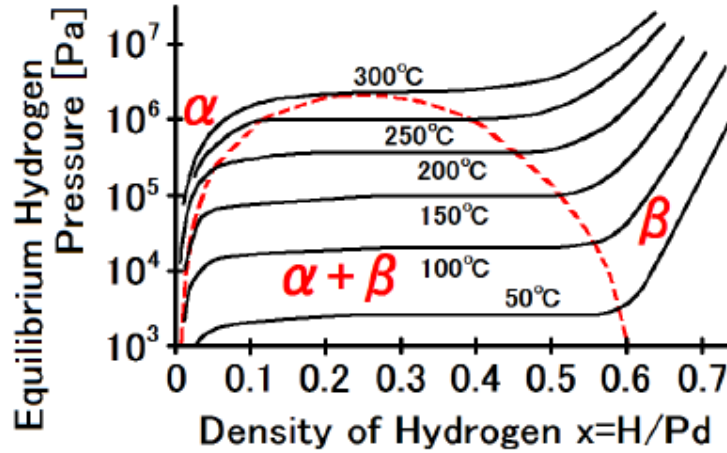
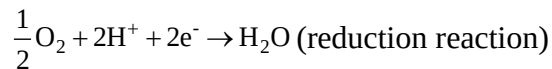
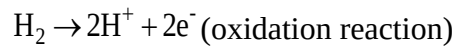


Figure 6 Phase diagram of the Pd-H system: the α -, β - and ($\alpha + \beta$)-phases are indicated together with a phase boundary by a broken curve [126]

3. Electrochemical redox reactions take place: (i) oxidation reaction takes place on the working electrode surface where hydrogen is oxidized to donate its electron to form hydrogen ion. (ii) reduction reaction occurs on the counter electrode surface where the electrons are consumed.



4. The reaction product of the oxidation reaction desorbs from the sensing electrode surface and diffuse into the electrolyte.

Counter (Auxiliary) Electrode (CE): This electrode is used to complete the electric current path and allow the flow of electric current. It is usually made up of materials such

as carbon, glassy carbon and platinum wire. In a two-electrode system, it is regarded as the auxiliary electrode which may serve as the reference electrode. Unlike the reference electrode, the potential of CE is not constant during the electrochemical measurements [16, 18, 19, 22]. The most commonly used counter electrode in amperometric hydrogen gas sensing is the platinum wire [47, 61, 95-98, 100-102]. Figure 7 shows the image of the counter electrode.



Figure 7 Picture of the counter electrode (platinum wire) [174]

Reference Electrode (RE): This electrode is used to complete the electric circuit necessary for an electrochemical measurement, and no flow of electric current through it. In electrochemical H_2 gas sensing, saturated Ag/AgCl [47, 61, 95-98, 100-102, 105] has attracted the attention of researchers because of its portability, stability and longevity [16, 18, 19]. In some cases, pseudo-reference electrodes like Pt-air electrode [133] are also used as the reference electrode. Figure 8 shows the image of the reference electrode.

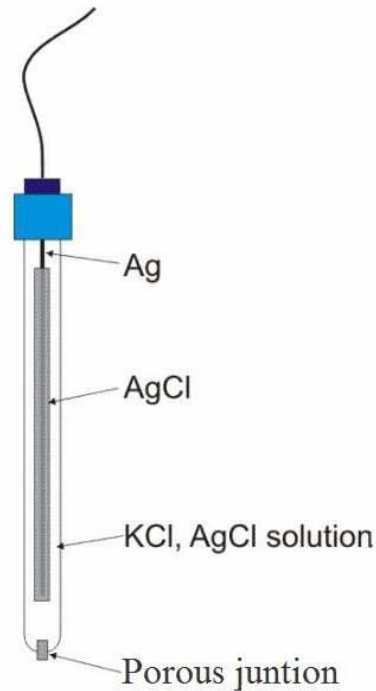


Figure 8 Picture of the saturated reference electrode (Ag/AgCl) [175]

2.3 Features of Amperometric Gas Sensor

2.3.1 Sensitivity and Selectivity

The development of hydrogen gas sensor is necessary for alerting about leakages to prevent any kind of harmful situations which may occur by the hydrogen gas usage. The main concern of the end-users is the sensor performance and reaction when exposing the sensor to different species of gases which can interfere with the behavior of the sensor towards the target gas. Exposing the sensor to the gases other than the target gas may cause undesirable effects including a false positive response [16, 18, 32, 92] in which the sensor gives a similar response to other species of gas present, thereby giving a wrong impression to the users that there may be a leakage of the target gas. Also, a false negative response, whereby sensors give a reduced response when exposed to the target gas, as may cause the user to be at high risk without knowing. If care is not taken, all these malfunctions such as

poor sensitivity and insufficient selectivity may cause accidents in industries or sectors in which hydrogen gas is used.

Ideally, a gas sensor established for hydrogen should not respond to other forms of gases apart from hydrogen. That is, there should be selectivity and sensitivity towards the main target gas (hydrogen) in the presence of other species of gases (interferents e.g. carbon (IV) oxide, methane or carbon monoxide). Being selective only to the target gas will prevent false alarm or undetected harmful situations. So, it is important to eliminate, or at least reduce the cross-sensitivity towards other species of gas.

The cross-sensitivity has been evaluated for five sensor platforms (metal oxide (MO_x), Electrochemical (EC), Thermal conductivity (TCD), Palladium thin film (PTF) and Metal oxide semiconductor (MOS) sensors towards methane, carbon-dioxide and carbon-monoxide [134, 135]. Many other sensor platforms can be found in the literature [136-140]. Our major interest in this thesis is basically on the amperometric hydrogen sensor platform that makes use of some catalysts which are specific to hydrogen (e.g. platinum and palladium) and are most common commercial sensors [32, 94, 134, 135]. Varieties of design strategies have been used in sensor platform to improve the sensor selectivity [32, 134, 135, 141]. Overall, the working electrode material plays a significant role for providing good properties including sensitivity, selectivity, stability and low operating temperature of amperometric hydrogen gas sensor.

Mostly, as shown in figure 9, sensitivity is obtained from the slope of the signal (response) versus the flow or concentration of the analyte gas [16, 18, 19, 22, 47, 61, 95-98, 103, 105]. This is known as the calibration curve in amperometric gas detection.

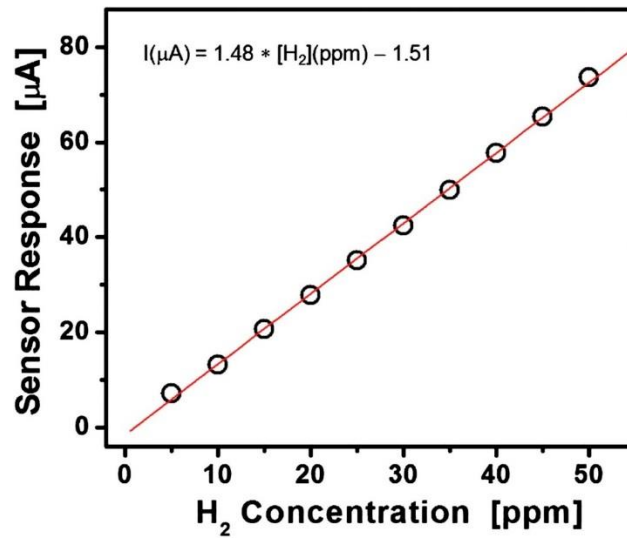


Figure 9 The calibration curve for amperometric measurement [98]

2.3.2 Stability and Reproducibility

In AGS, stability of the sensing material relates to its ability to withstand normal environmental condition, giving the same output over a long period of time [61, 101]. Availability of little change in the output over a short or long period of time is regarded as drift, which may be due to the degradation of the sensing material, electrolyte contamination or defect in any of the sensor components. To provide correction to any of the problems which may cause instability, sensor operating conditions need to be properly studied to ensure accuracy in the measurement. Various amperometric hydrogen gas sensors have been fabricated and reported based on nanoparticle sensing electrode in either solid or liquid electrolyte [47, 66, 71, 95, 97, 98, 104]. One of the reported pitfalls is instability over a long period of time due to the change in the environmental condition [61]. In general, improving the stability of the sensing material will improve the sensor performance. Also, an appropriate support, such as MWCNTs, is required for a strong attachment of the working electrode materials to the membrane.

Reproducibility in an amperometric gas sensing is the ability of the sensing material, synthesized in different batches under the same circumstances, to produce similar output response. If all proper conditions are taken into consideration, sensor should give a very close results if not completely accurate.

2.3.3 Response Time and Recovery Time

In amperometric sensing, the surface of the sensing electrodes is usually chemically modified with some catalysts added to facilitate the oxidation or reduction reaction. The transfer electron or response current occurs when a constant potential is applied. Experimentally, relative response change is the ratio of the change in the response current to the current in the absence of the analyte gas:

$$\text{Relative Change in Response} = \frac{\Delta I}{I_o} = \frac{(I - I_o)}{I_o} \quad (2.9)$$

Where I is the current in the presence of the target gas, and I_o is the initial current in the absence of the analyte gas. ΔI is the change in current signal. A large relative change in response indicates that the AGS is highly sensitive.

Figure 10 shows the response curve of the sensor when exposed to the flow of an analyte gas. When the sensor is exposed to the analyte gas, the response time is the time taken by the sensor to reach 90 % of its steady state response current. This is referred to as T_{90} , as in figure 10. The recovery time is the time taken by the sensor to return by 90% to the original baseline current when the target gas is shut off. This is denoted by T_{10} , as shown in figure 10.

Response and recovery times basically depend on how fast the catalyst components adsorb and desorb the analyte gas [52]. The other way to achieve a shorter response time is to ensure rapid diffusion through the membrane via a fast mass transport process [16, 18, 19, 142, 143]. The thickness and pore size of membrane can also catapult the rate of diffusion of the analyte gas to the sensing catalyst. Hence, selection of a good membrane is important to decrease the response time. The best possible way to minimize the response time is by direct exposure of the sensing material to the analyte to get rid of a diffusion barrier completely [21, 31]. This will give the sensor a better response, and higher sensitivity [144]. However, neglecting the diffusion barrier leads to uncontrollable diffusion rates, and may finally end up in nonlinearities in the sensor response [145].

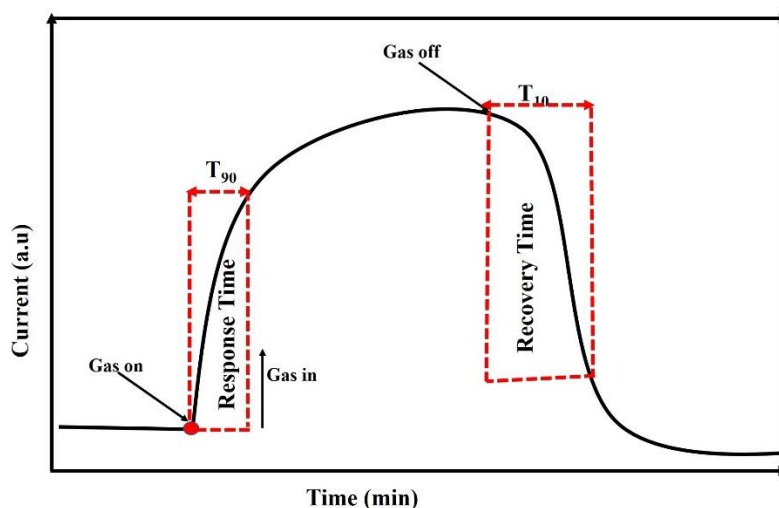


Figure 10 A graph of the response/recovery time of an amperometric gas sensor response

CHAPTER 3: EXPERIMENTAL

This chapter describes the experimental section of this thesis. It details the preparation method used for the sensing material, instrumentations and characterization techniques with physical explanation. This will be followed by discussion on the design and fabrication of the amperometric hydrogen gas sensor cell. The discussion includes the process employed in the fabrication of the working/sensing electrode. The AGS setup system is shown with clear explanation and arrangement.

3.1 Synthesis of the Sensing Material (PdNPs-f/MWCNTs)

All chemical reagents including palladium(II) nitrate $\text{Pd}(\text{NO}_3)_2$ (ACS reagent, $\geq 99.99\%$), sodium borohydride (NaBH_4 , ACS reagent, $\geq 97.0\%$), sulfuric acid (H_2SO_4 , ACS reagent, $\geq 98.0\%$) and carboxylic acid functionalized multi-walled carbon nanotubes (f/MWCNTs, purity $> 95\%$) were used directly as purchased from Sigma-Aldrich without any further purification. Polytetrafluoroethylene PTFE porous membranes (thickness: 0.21 mm, pore size: 1 μm , and porosity: 51%) were purchased from Goodfellow, USA. Gold wire, Platinum wires and saturated Ag/AgCl reference electrode were purchased from Sigma-Aldrich. Scotch tape-898 (one-sided adhesive) premium grade was obtained from 3M, United states.

Initially, various amounts of the materials were used during the material preparation. After rigorous experiment with variation in the amounts of precursors used during the preparation of the materials, optimum amount was found and is reported in this thesis.

First, 5 mg of carboxylic acid functionalized multi-walled carbon nanotube (f/MWCNTs) was added directly into 20 ml of water. The mixture was treated under homogeneous

suspension in ultrasonic (Branson Ultrasonic cleanser: 5510E-DTH) agitation bath for 4 hours.

Next, 25 mg of $\text{Pd}(\text{NO}_3)_2$ was added directly into 20 ml of water and ultrasonicated for 1 h, to prevent agglomeration. The mixture of the two solutions was sonicated for another 1 hour to achieve a homogeneous mixture. Afterward, the mixture was transferred to a beaker with a magnetic stirrer for rigorous stirring at 300 rpm. Under the vigorous stirring, a 20 mM NaBH_4 solution in 50 ml of water was prepared and injected into the mixture using a drop-wise addition method for about 30 minutes. The resultant mixture was further stirred for the next 1 hour for proper reduction of the palladium salts.

Furthermore, the total mixture (90 ml PdNPs-f/MWCNTs) was treated again under sonication for another 1 hour to disperse the reaction product and uniform decoration of f/MWCNTs with Pd nanoparticles. Finally, the reaction product, PdNPs-f/MWCNTs, was collected by centrifuging at a speed of 12000 min^{-1} at room temperature, of 27°C , for 1 hour. This is the material which was used to fabricate the sensing or working electrodes. A step by step method used in decorating f/MWCNTs with PdNPs is illustrated in figure 11. The reaction scheme of the material preparation is shown in figure 12.

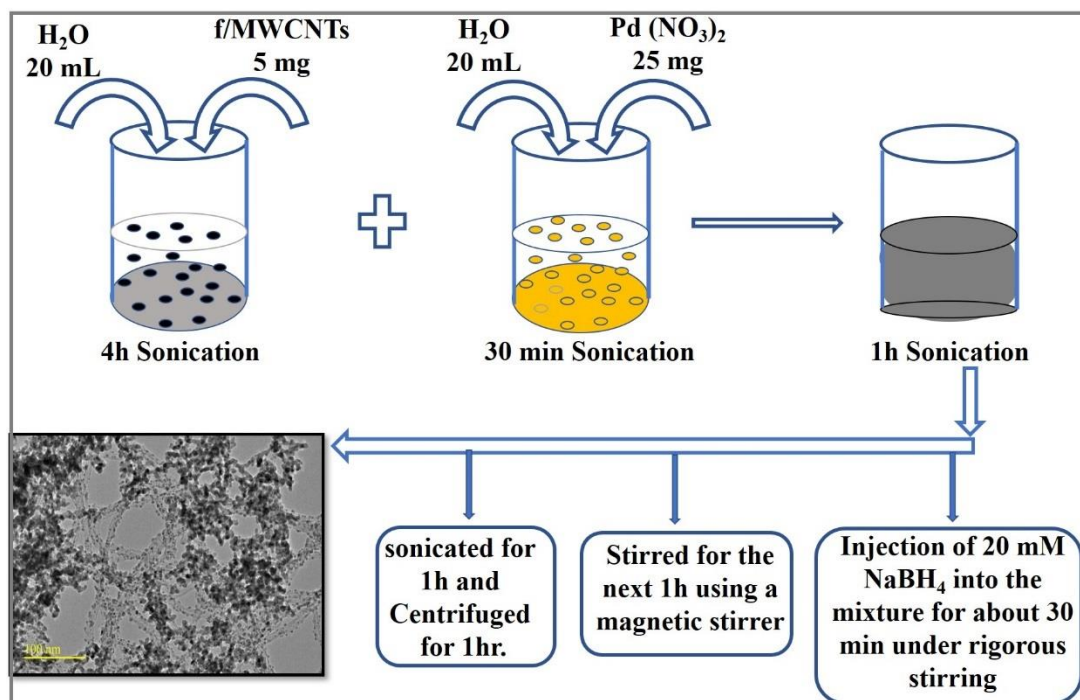


Figure 11 A step by step method for the preparation of PdNPs-f/MWCNTs

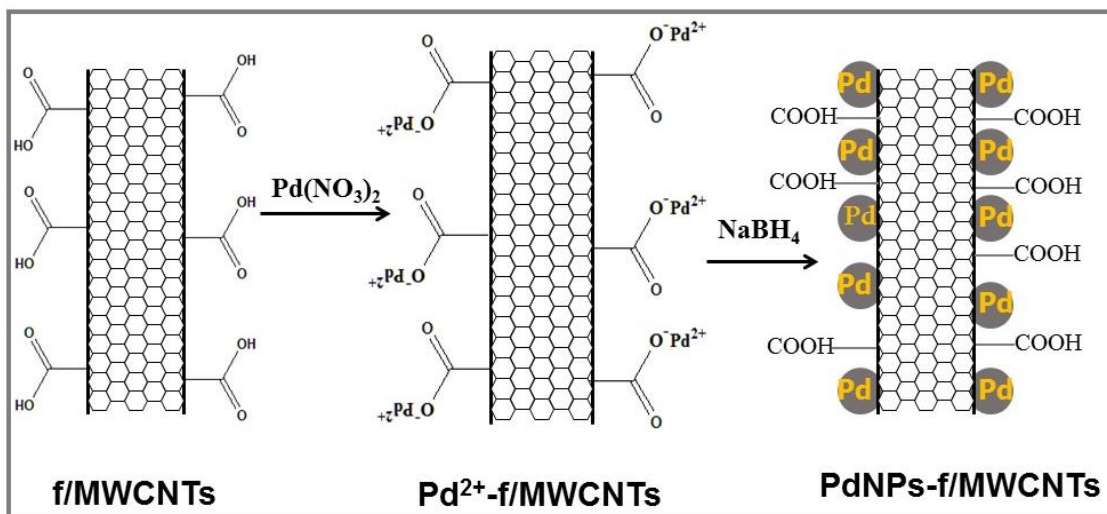


Figure 12 Reaction scheme of the preparation of PdNPs-f/MWCNTs

3.2 Instrumentations

X-ray photoelectron spectroscopy (XPS) analysis was carried out at the physics department. Transmission electron microscopy was done at the center for engineering research. All other material characterizations were accomplished with the equipment at the Center of Excellence in Nanotechnology (CENT), King Fahd University of Petroleum and Minerals (KFUPM). The X-ray powder diffraction (XRD) patterns of f/MWCNTs and PdNPs-f/MWCNTs were recorded at a scan rate of 0.2° per min in the 2θ -range from 5° to 100° using a Rigaku Miniflex II diffractometer equipped with Cu K-alpha radiation. The morphological properties of the two samples (f/MWCNTs and PdNPs-f/MWCNTs) were recorded using a field emission scanning electron microscope (FESEM) (Tescan Lyra-3). The energy dispersive X-ray spectroscopy (EDS) spectra were also recorded using Oxford Instruments Xmass detector mounted on the FESEM machine. Further morphological properties of the f/MWCNTs and PdNPs-f/MWCNTs were recorded using a transmission electron microscope (JEOL JEM 2100F). Finally, X-ray photoelectron spectrometer (XPS) (ESCALAB 250Xi XPS Microprobe, Thermo Scientific, USA) was applied for chemical composition analysis as well as to identify the oxidation state of the different elements in the prepared samples.

3.3 Material Characterization Techniques

This section discusses the physical explanations and the working principles of all the characterization techniques used in this thesis.

3.3.1 Principle of Operation of X-ray Diffraction (XRD)

X-ray powder diffraction analysis is a nondestructive technique for material characterization. It employs X-rays to provide information about the crystallographic structures, phase identifications and other structural parameters such as strain, crystal defects and grain sizes of crystalline materials on atomic scale.

When the monochromatic X-rays are produced from cathode ray tube and are directed towards the sample. They interact with electrons in the atoms and elastically scattered. If the scattered waves from atoms are in phase, they interfere constructively. These diffracted X-rays carry information about the electrons in the sample in a specific direction (θ), which is governed by the Bragg's law:

$$n\lambda = 2d\sin\theta \quad (3.1)$$

Equation (3.1) relates the wavelength of the incident X-rays (λ) with the crystal lattice spacing (d) of the sample. Where n is any integer number and θ is the incident angle between the X-rays and the planes of atoms.

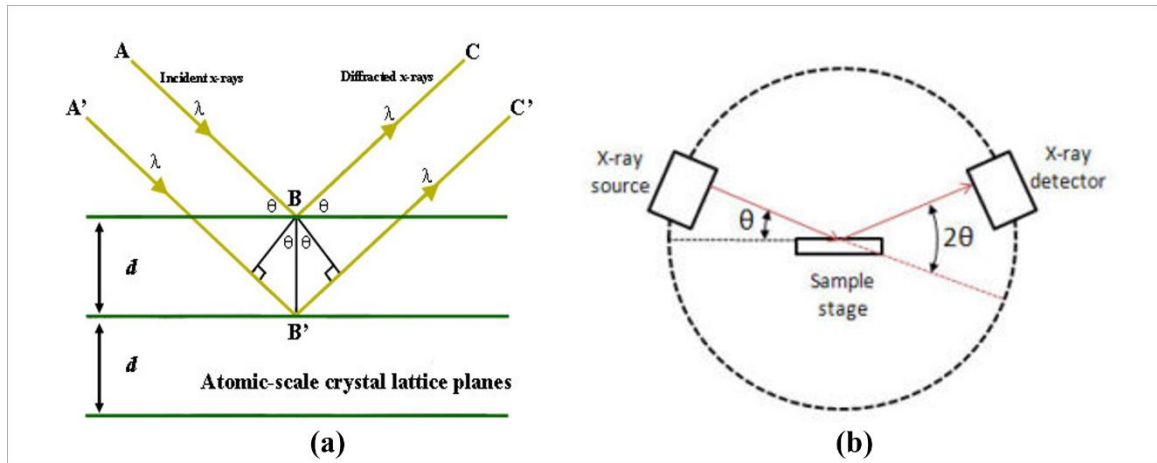


Figure 13 (a) Diffraction pattern of X-rays at crystal lattice (b) Schematic diagram of a diffractometer in X-ray Powder diffraction [176]

In XRD analysis as arranged in figure 13, the experimental setup comprises of three main components: (i) X-ray tube, (ii) sample holder and (iii) detector which may be either a photographic plate or a Geiger/Scintillation counter. The sample, usually in powder form, is placed in the sample holder at the center of the instrument. The X-rays ($\lambda=1.54 \text{ \AA}$ for Cu K_{α} radiation) are collimated and directed onto the sample at angle θ , the crystallites in the powdered sample are expected to be oriented such that the Bragg's condition can be satisfied. In this type of arrangement, both the detector and sample holder are rotated such that the diffracted X-rays are received by the detector at an angle of 2θ . Then, the detector processes the diffracted X-rays and converts it to intensities which can be received by the computer. Typically, XRD data is recorded at various angle of 2θ ranges and the scan speed depending on how long the measurement is required to take.

3.3.2 Principle of Scanning Electron Microscopy

Scanning electron microscopy (SEM) employs electron beams to provide information about the morphology of the sample at nanoscales. High energy accelerated electrons are focused on the sample by applied potential difference and magnetic fields as shown in figure 14(a). When the highly focused and energetic electrons interact with the sample, the incident electron beams-matter interaction produces a variety of signals (figure 14 b) such as diffracted electrons, secondary electrons, backscattered electrons, backscattered diffracted electrons, auger electron, characteristic x-ray, continuum x-ray etc. All these classes of transformed electrons give information about different properties of samples. For surface morphology which is the key objective of SEM imaging, backscattered and secondary electrons are important. Hence, SEM detectors are meant to detect only

backscattered and secondary electrons. Furthermore, characteristic x-ray can also be detected to identify elemental composition of the sample which is regarded as the energy dispersive spectroscopy (EDS).

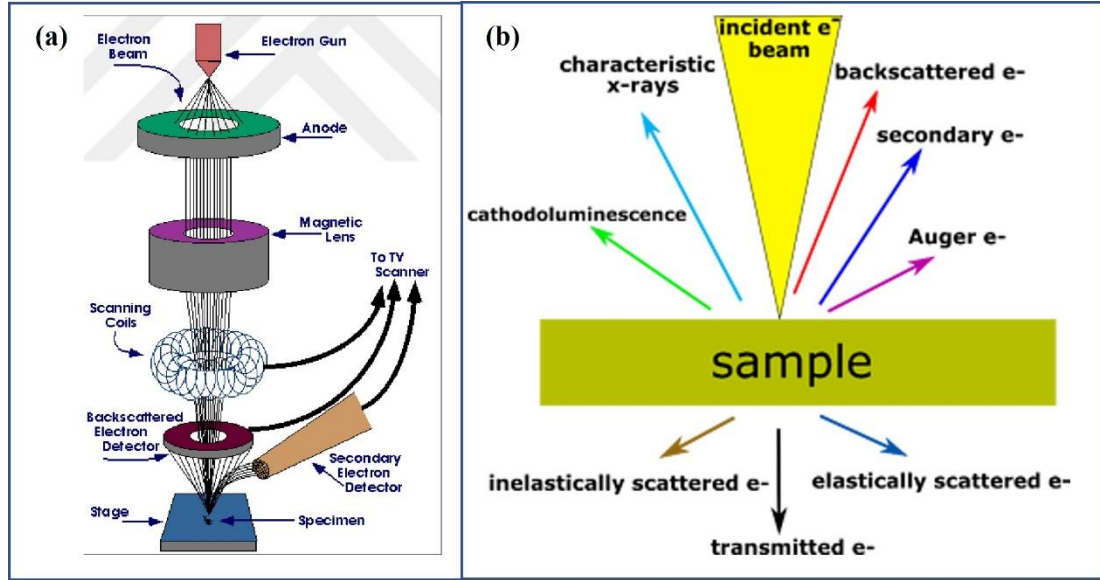


Figure 14 (a) Schematic diagram for working principle of SEM, and (b) Illustration of electron-matter interaction in SEM [177]

3.3.3 Principle of X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy analysis is a surface spectroscopic technique used to investigate chemical composition of a sample up to about 2-5 nm depth. XPS can detect all the chemical elements (except the elements with atomic number less than 3) on the sample surface. XPS works based on the principle of photoelectric effect, originally explained by Hertz [5] and later explained by Einstein using quantum nature of light [6]. According to figure (15a), when an incident X-ray bombards the crystal surface, core electrons are ejected to escape from the material with a maximum kinetic energy E_k as explained in equation (3.2):

$$E_k = h\nu - E_B - e\phi \quad (3.2)$$

Where E_k is the maximum kinetic energy, E_B is the binding energy of the electron, ν is the photon frequency and the $e\phi$ is the work function.

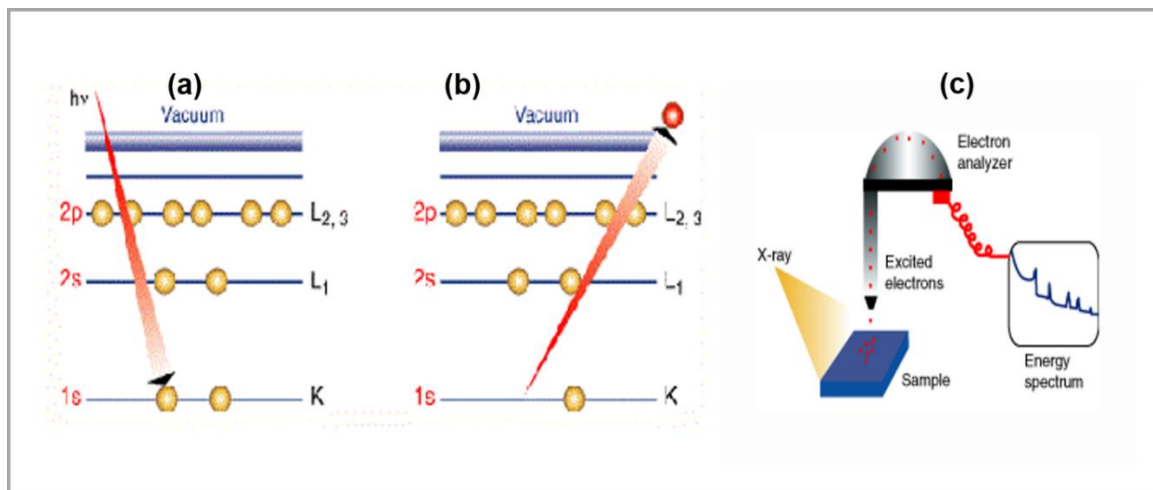


Figure 15 (a & b) Working principle and (c) Schematic diagram of XPS [178]

According to figure (15c), when the surface of a sample is irradiated by X-rays of enough energy ($h\nu$), the resulting electrons are knocked out of atoms. Some of the ejected electrons will undergo prompt emission, escape to the surface of sample and then to the vacuum area while some of the electrons ejected are inelastically scattered and unable to find their way to the surface. Those photo-ejected electrons in the vacuum area are received by the electron analyzer which first measures their kinetic energies and later generates an XPS spectrum of intensities against binding energies. The binding energies are the energies that bound the electrons together just before they escaped from the atoms while the intensities are the number of photoelectrons ejected per unit time. In a typical XPS spectrum, each prominent energy peak is attributed to a specific element and the intensity of each energy peak can tell how much of that element is present in the sample. Also, the area of each peak is proportional to the number of atoms in each element.

3.3.4 Principle of Transmission Electron Microscopy

Transmission electron microscopy employs a high energy electron up to 300 kV accelerating voltage, which can be accelerated to nearly the speed of light. The electron beam has similar behavior as wave front having a wavelength about a million time shorter than light wavelength. TEM works on the same principle of the light microscopy. But electrons are involved unlike in the light microscope where light is required.

When the tungsten filament is heated, electrons are emitted. The emitted electrons are enclosed by the negative cap into a loosely focused beam. When an electron passes through the thin section of the sample specimen, electrons are scattered. Electromagnetic lenses are used to focus on the scattered electrons to change into image form, diffraction patterns or nano-optical spectrum depending on the principle of operation of the system.

The imaging section consist of two electromagnetic lenses and the screen. One of the lenses is for refocusing after electrons have passed through the specimen while the other lens is for the image magnification and projecting on the screen.

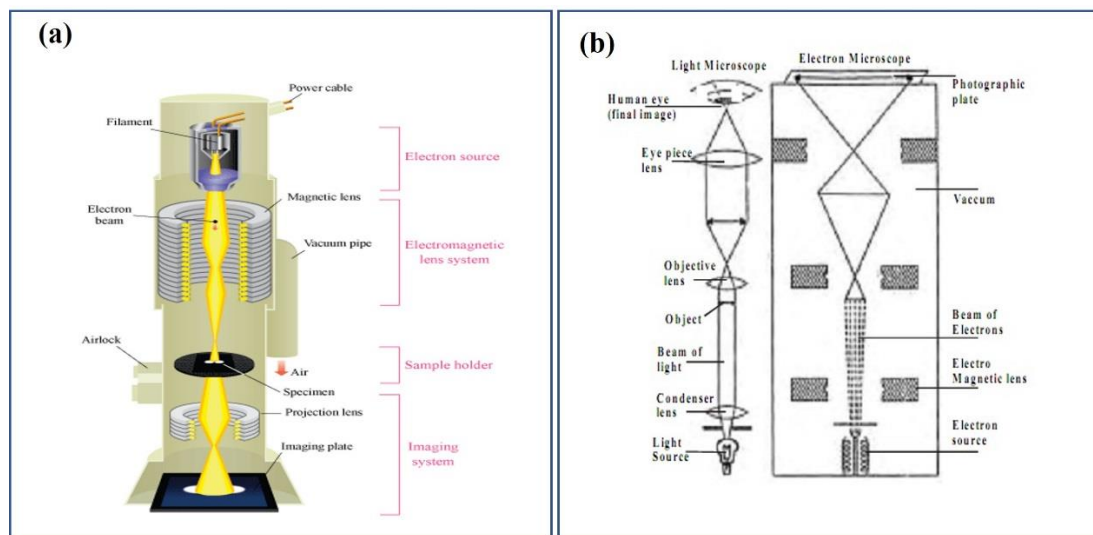


Figure 16 (a) Block diagram [179] (b) Schematic diagram of working principle of TEM [180]

3.4 Electrochemical Characterization Technique

A typical potentiostat requires an electrochemical cell with three electrodes: (i) the reference electrode (RE), (ii) the counter electrode (CE), and (iii) the working electrode (WE). The reference electrode is used, without any flow of current through it, to maintain electrochemical potential. It also measures the potential on the working electrode surface. The CE is employed to complete the cell circuit and to balance the current observed at the working electrode. It receives the current from the solution after the transfer of current from the working electrode to the solution. The working electrode is where the reaction of interest takes place, the potential is controlled, and the current is measured. All electrodes are confined in an electrolyte. Hence, potentiostat refers to as an electronic device which controls the voltage difference between the working electrode and the reference electrode, thereby implementing this control of voltage and injecting current into the CE. Mostly, the potentiostat measures the current between the working electrode and the counter electrode. Meanwhile, the cell potential is the control variable while the cell current is the measured variable. Since the reference electrode current is negligible, then the potential drop between the sensing and reference electrodes is also negligible. Hence, the high possibility for the constant potential to be more stable and compensation for voltage drop across the solution.

The schematic circuit diagram in figure 17 shows the working principle of a potentiostat. It is designed to sense/control (i) the voltage difference between the WE and RE, so that the potential difference between the working electrode and reference electrode remain constant (ii) to control the electro-reaction, and (iii) to release an output signal that is proportional to the working electrode current. When an input voltage is applied between the reference and working electrodes. The actual potential difference between the reference

and working electrodes is measured by a differential amplifier known as the electrometer in figure 17 (a). Ideally, electrometer has infinite impedance, hence zero current. Therefore, current does not flow via the reference electrode.

The measured voltage is compared with the input voltage by a second differential amplifier (known as control amplifier). In the case of any differences between the input voltage and the potential difference between the RE and WE, the control amplifier will drive current into the cell to increase/decrease the voltage to balance with the input voltage. It works on the principle of negative feedback such that the measured voltage from the electrometer enters via the negative input of the amplifier. The cell current is measured by I/E converter by forcing the cell current to flow through the resistor R. The resulting voltage across the R is a measure of the cell current.

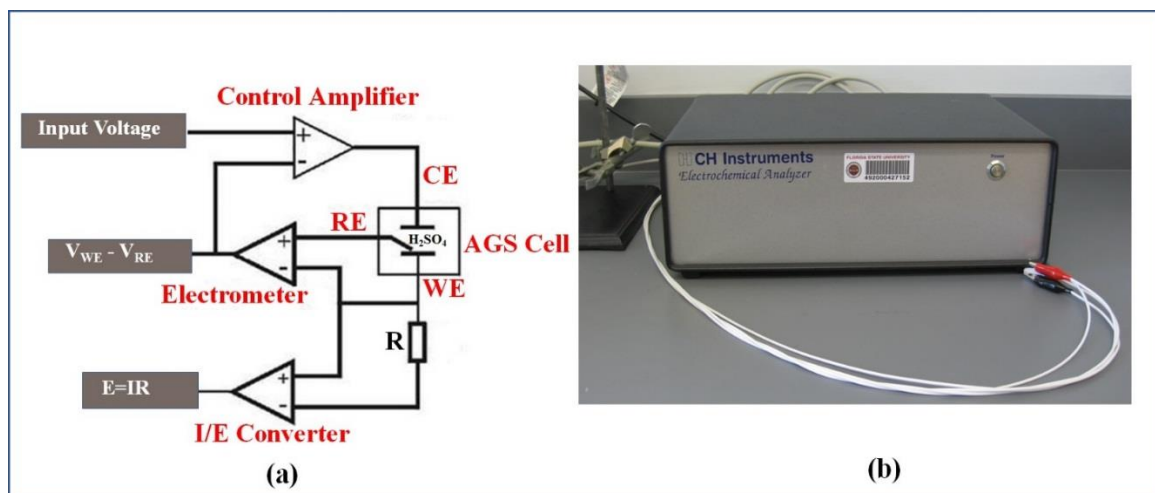


Figure 17 (a) Schematic circuit [181] and (b) Photograph of Potentiostat [182]

3.5 Fabrication of Sensing Electrodes (PdNPs-f/MWCNTs/PTFE)

The sensing material PdNPs-f/MWCNTs in figure 18 (a) was deposited on a circular PTFE membrane as shown in figure 18 (b). Initially, PTFE porous membrane was prepared by cutting into a circular shape of diameter of 4.5 cm. The sensing electrode material was prepared by adding 1 ml of PdNPs-f/MWCNTs into 25 ml of ethanol. The mixture was sonicated for 2 hours. This was deposited on the porous PTFE membrane sheet through a vacuum filtration method, washed with ethanol several times to wash away the impurities. The fabricated sensing electrode (PdNPs-f/MWCNTs/PTFE) was dried in an oven at a temperature of 100 °C for 1 hour. figure 18 (c) shows the photograph of the fabricated sensing electrode.

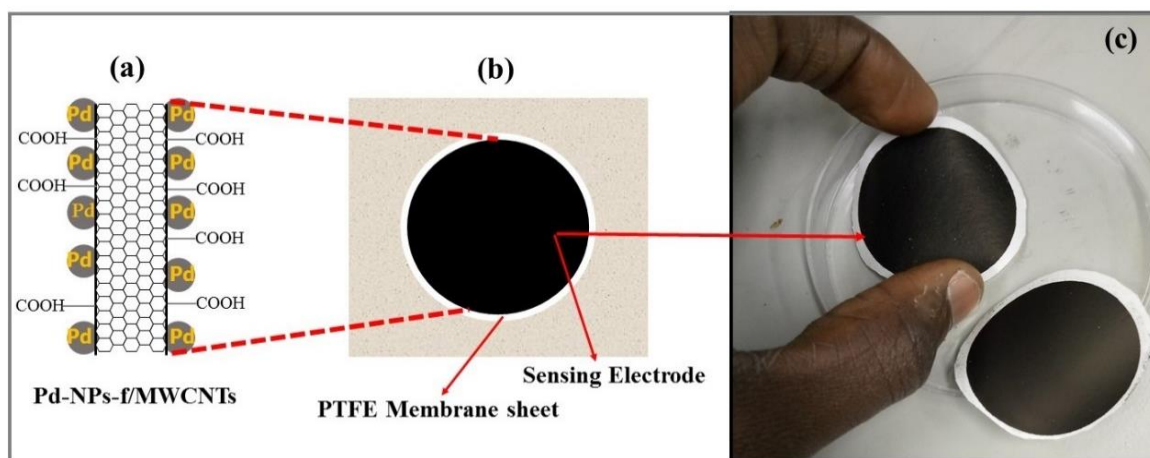


Figure 18 (a) Reaction scheme of PdNPs-f/MWCNTs, (b) Design of the working electrode, and (c) Photograph of the fabricated working electrode

3.6 Design and Fabrication of the Amperometric Hydrogen Sensor Cell

According to figure 19 (a), a teflon rectangular hollow cuboid (7.5 cm x 5.2 cm x 5.2 cm) design was fabricated for the amperometric gas sensor cell at the research institute machine shop. The sensor cell is configured such that there is a circular opening of diameter 2.5 cm, where the sensing electrode membrane is placed. The sensing side faces the inner part of the sensor cell for proper connection through the electrolyte. The cap in the figure 19 (a) can be used to cover the cell opening (diameter: 2.5 cm) with help of the four thread screws. Hence, an inlet is made available on the cap for the gas to flow into the sensor. The side circular cover (diameter: 3.0 cm) of figure 19 (a) possesses three holes. One of the holes is for the gas outlet and the other two holes are for the counter and reference electrodes. figure 19 (b) shows the dimensions of the sensor cell, its inner view and how it is positioned during the sensing operation.

Figure 20 (a) presents the photograph of the fabricated gas sensor cell. The cell is now positioned such that the side opening is the circular hole (2.5 cm) where the sensing electrode is fixed. The top circular opening (3.0 cm) is for the cover with three holes. The cap is shown with the working electrode and the four thread screws. figure 20 (b) presents a complete sensor cell connected with the three electrodes. A gold wire was connected to the surface of sensing electrode with the help of a scotch tape. The other two electrodes are suspended into the liquid electrolyte which allows the transport of ions between the electrodes.

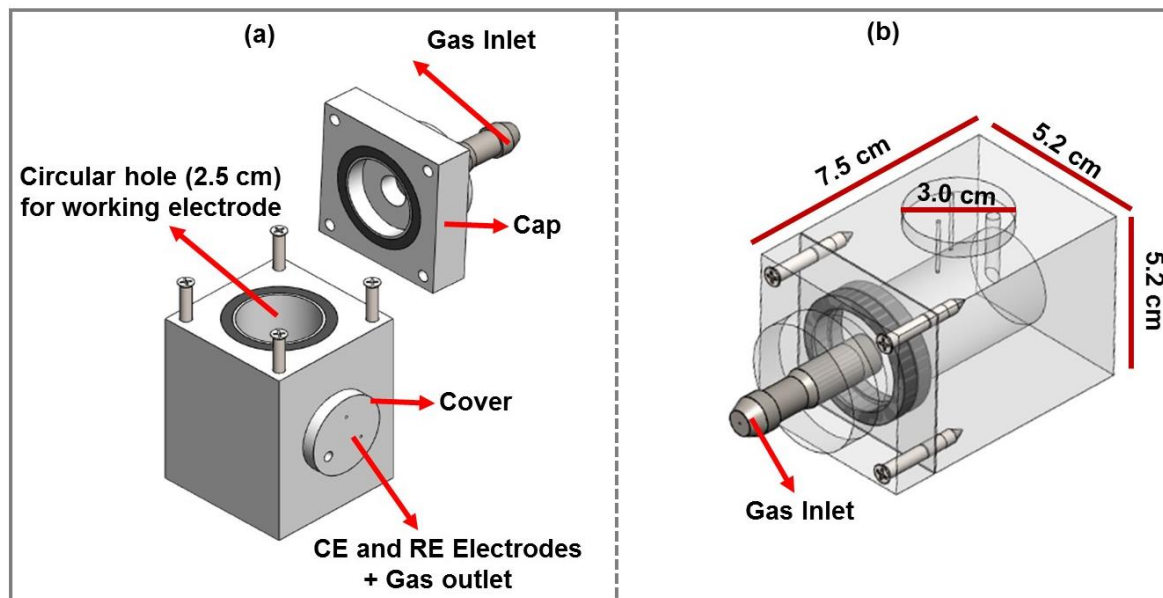


Figure 19 Design of an amperometric gas sensor cell

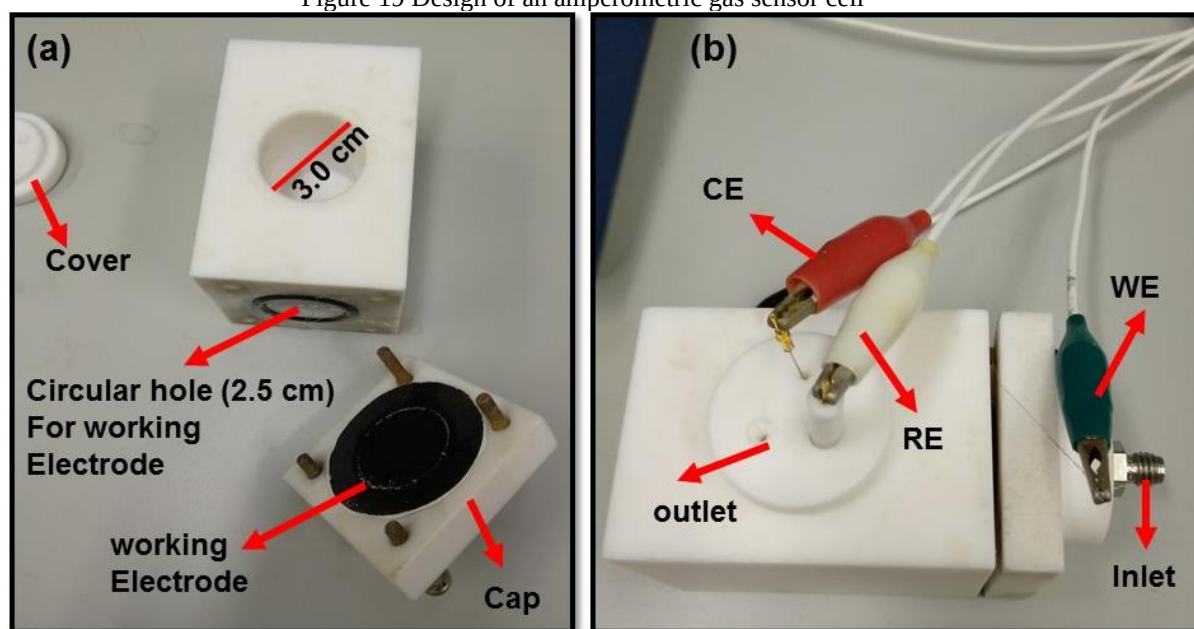


Figure 20 Photograph of the fabricated amperometric gas sensor cell

3.7 Amperometric Gas Sensing Setup

Gas sensing measurement was performed with an experimental setup (figure 21) composed of two standing cylinders. One cylinder is filled with 1% H₂ with nitrogen balance. The other cylinder is 99.999% nitrogen. In some experiments, the H₂ cylinder was just 0.1% H₂ in nitrogen balance. Two mass flow controllers (MFC) are connected to the two gas cylinders to control the flow rate of the gases, and a gas mixer chamber is connected to the MFCs for homogeneous mixture of gases.

The fabricated AGS housing is composed of the working electrode (PdNPs-f/MWCNTs/PTFE), and electrolyte (1M H₂SO₄), with the two other electrodes (CE and RE). The sensor housing is connected to the mixer chamber and also to the potentiostat with the screen for output signals.

When the gas cylinder knobs are turned anticlockwise, the flow of gas will reach the MFC and the gas can be controlled depending on the desired flux needed. The gases then proceed to the mixer for homogeneous mixture before it reaches the sensor. Electrochemical reactions take place on the surface of the working electrode. The resulting electrons are received by the potentiostat. Hence, the potentiostat converts the generated electrons into the output signals that is recorded digitally for further data processing. Various voltage strengths were applied to obtain the optimum operating voltage for our sensor

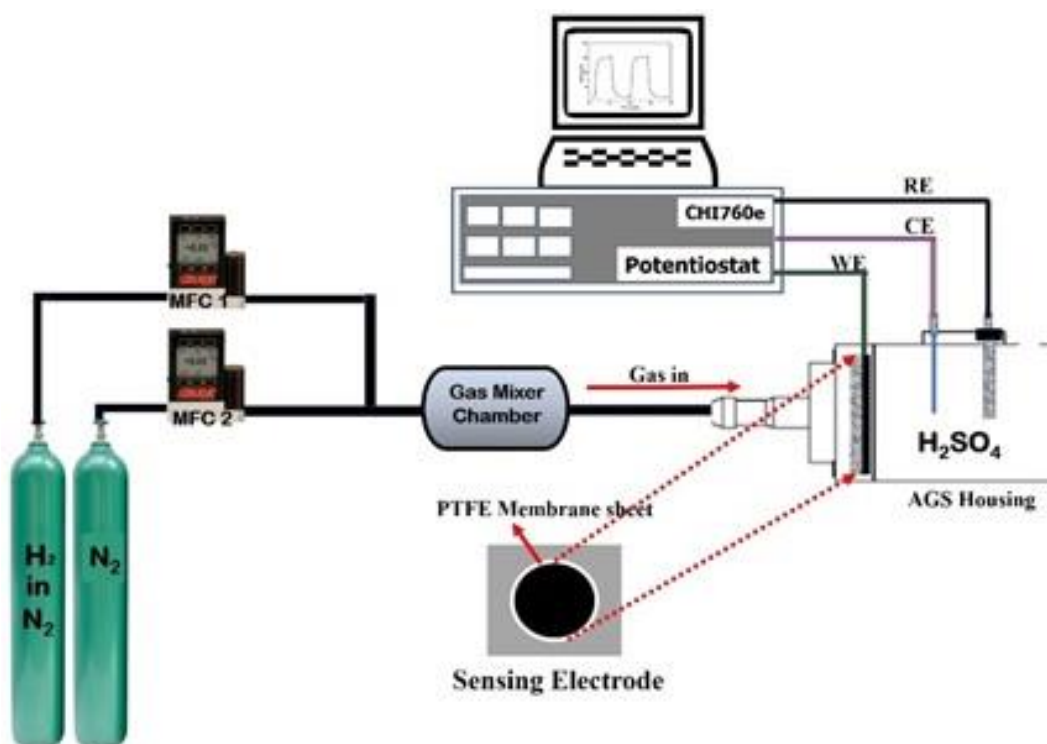


Figure 21 Experimental set up for the amperometric hydrogen gas sensor measurement

CHAPTER 4: RESULTS AND DISCUSSION

This chapter will provide interpretation of results based on the characterization of the sensing material and the amperometric hydrogen gas sensing measurement. The characterization section entails XRD, SEM, EDS, TEM and XPS of f/MWCNTs and PdNPs-f/MWCNTs. The AGS measurement, based on PdNPs-f/MWCNTs details the hydrogen flow test towards 0.1% and 1% H₂ in nitrogen flow. This will be followed by the sensor characteristics measurements such as sensitivity, stability, reproducibility, limit of detection, and response and recovery times towards H₂ exposure at room temperature.

4.1 Material Characterization Results

4.1.1 X-ray Diffraction Analysis of f/MWCNTs and PdNPs-f/MWCNTs

The X-ray powdered diffraction analysis of the f/MWCNTs and PdNPs-f/MWCNTs were taken to observe the purity, crystallite size and the crystalline structures of the samples. From the XRD analysis of the f/MWCNTs (figure 22 a), the two peaks at 25.5° and 42.9°, corresponding to the (002) and (100) crystal planes respectively, are attributed to the graphitic peaks of carbon atoms [118, 119, 146-152]. The other diffraction peaks at the angle 2 θ values of 53.2° and 78.5° are indexed (004) and (110) crystal planes respectively [151, 152]. The recorded XRD patterns of PdNPs-f/MWCNTs, in figure 22 (b), can be assigned to the (111), (200), (220) and (311) of Pd which occurred at the 2 θ values of 39.4°, 45.6°, 67.0°, and 80.7° respectively [153-156]. The PdNPs is found to be the face-centered cubic (fcc) crystal structure. The disappearance of the carbon peak in the PdNPs-f/MWCNTs may be the consequence of the difference in the number of electrons in the

carbon and palladium. Hence, the low intensity of a lighter element may be suppressed by the high intensity of the heavier element.

The crystallite size of the PdNPs-f/MWCNTs was obtained from the Debye Scherrer equation (equation 4.1) [157].

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (4.1)$$

Where D is the crystallite size, K is the Scherrer's constant (~ 0.9), λ is the wavelength (1.5406 Å) for Cu K-alpha, and β is the full width half maximum (FWHM) of the peak at angle θ . Hence, the crystallite size was calculated for each of the Pd peaks as shown in table 1. The average crystallite size was obtained to be about 2.7 ± 0.8 nm.

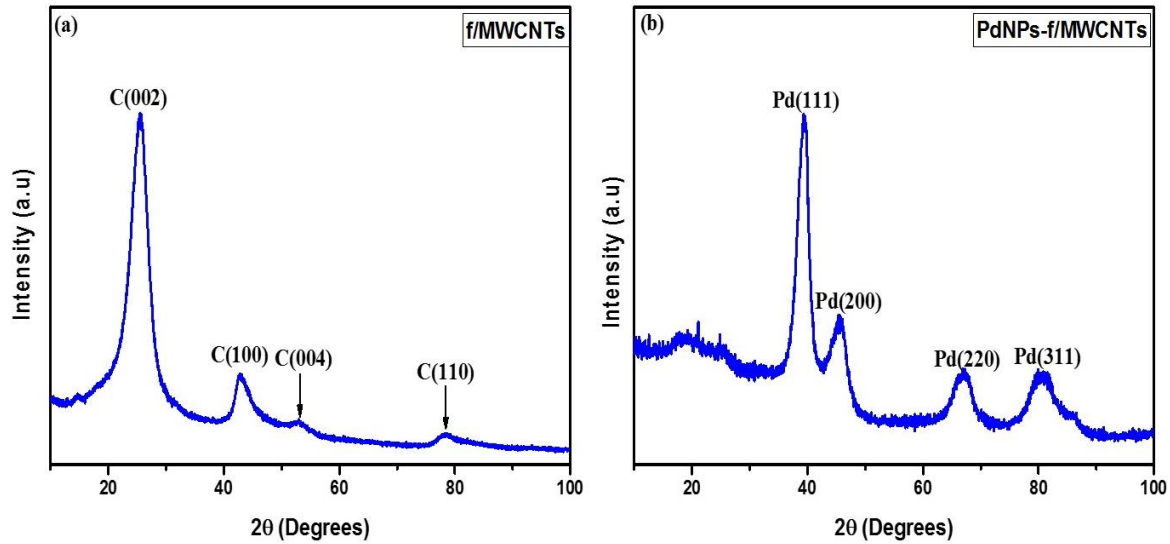


Figure 22 XRD diffraction pattern of the (a) f/MWCNTs and (b) PdNPs-f/MWCNTs

Table 1: XRD analysis results for PdNPs

S/N	Peak Positions	FWHM (degrees)	Crystallite Size (nm)
1	39.4	2.2	3.8
2	45.6	3.2	2.7
3	67.0	3.9	2.4
4	80.7	5.2	2.0
			$A_v = 2.7 \pm 0.8 \text{ nm}$

4.1.2 Scanning Electron Microscopy (SEM) of f/MWCNTs and PdNPs-f/MWCNTs

The morphology and composition of the f/MWCNTs and PdNPs-f/MWCNTs were investigated by Field Emission Scanning Electron Microscope (FESEM) and Energy-dispersive X-ray spectroscopy (EDS) measurements. For SEM and EDS analysis, 5 mg of f/MWCNT was added to 40 mL of DI-water and sonicated for 4 h. After which 50 μL of the solution was dropped on an aluminum substrate and dried in an oven at 50 $^{\circ}\text{C}$ for 1 h.

Figure 23 (a) shows the SEM micrographs images of functionalized MWCNTs. It is observed that f/MWCNTs are curled and display interconnecting tubes entangled with one another. Figure 23 (b) shows the morphological properties of PdNPs-f/MWCNTs nanocomposite. Pd-nanoparticles are evident on the surface of interconnected f/MWCNTs tubular networks.

EDS elemental analysis presented in figure 24 (a) confirms the presence of the principal elements in the PdNPs-f/MWCNTs, as expected. The presence of the carbon and oxygen are from the functionalized MWCNTs while the Pd is from the PdNPs. No impurities can

be recorded on the surface of PdNPs-f/MWCNTs. The existence of Aluminum (Al) comes from the surface of the substrate. The corresponding elemental mappings with the homogenous distribution of C, O and Pd are displayed in the figure 24 (b-d) respectively.

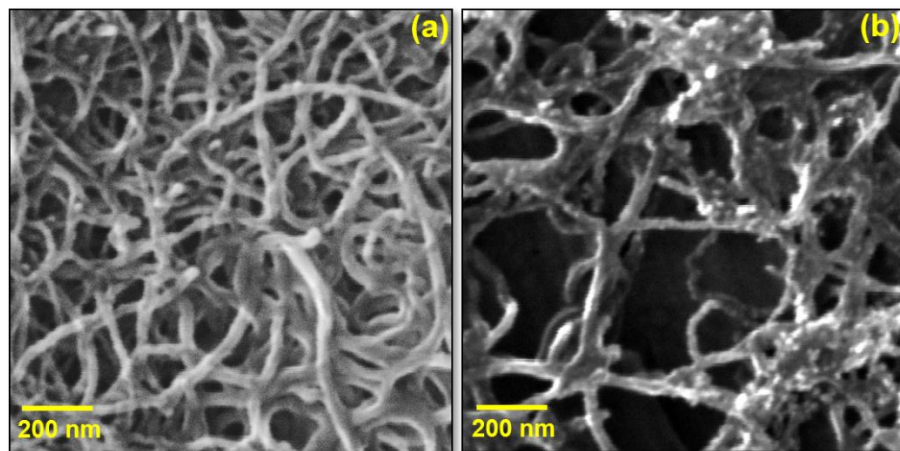


Figure 23: FESEM images of the (a) f/MWCNTs and (b) PdNPs-f/MWCNTs

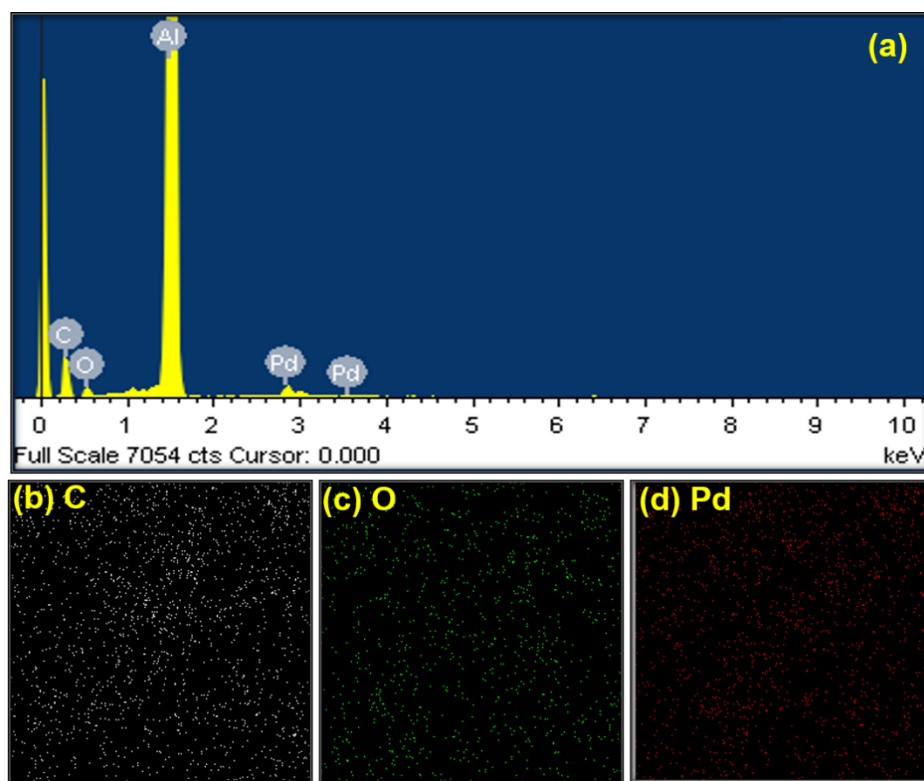


Figure 24 (a) EDS elemental analysis of PdNPs-f/MWCNTs and Elemental Mapping of (b) Carbon C, (c) Oxygen O, and (d) Palladium Pd

4.1.3 Transmission Electron Microscopy (TEM) of f/MWCNTs and PdNPs-f/MWCNTs

TEM analysis of the f/MWCNTs and PdNPs-f/MWCNTs is shown in figure 25. Figure 25 (a) reveals the presence of interconnected tubular networks of the f/MWCNTs. The evidence of decoration of spherically shaped Pd nanoparticles over the f/MWCNTs is clearly shown in figure 25 (b), as we have seen in SEM images. The insets in figures 25 (a & b) are the selected area electron diffraction (SAED) patterns which provide information about the composition of crystalline structures in the f/MWCNTs and PdNPs-f/MWCNTs samples. The ring diffraction shape indicates the polycrystallinity of the material which is composed of many single crystals with discrete spots. The spots are a result of the Bragg diffractions. The HRTEM image of f/MWCNTs in figure 25 (c) shows well aligned fringes with the d-spacing of 0.35 nm which is ascribed to the C (002) crystal plane [150, 158] in XRD results. Similarly, the HRTEM image PdNPs-f/MWCNTs in figure 25 (d) shows fringes in different directions with the d-spacings of 0.35 nm and 0.23 nm. These correspond to the C (002) and Pd (111) crystal planes [153, 159] of f/MWCNTs and PdNPs respectively, in agreement with XRD results. figure 25 (e) shows the 20 nm scale box of the HRTEM image with well dispersed Pd nanoparticle on f/MWCNTs. All particles are within the range of 1.5-6 nm with the maximum number of particles in the size range of 3-5.5 nm as can be observed in the histogram of average particle size in figure 25 (f). This agrees with XRD results, as discussed earlier.

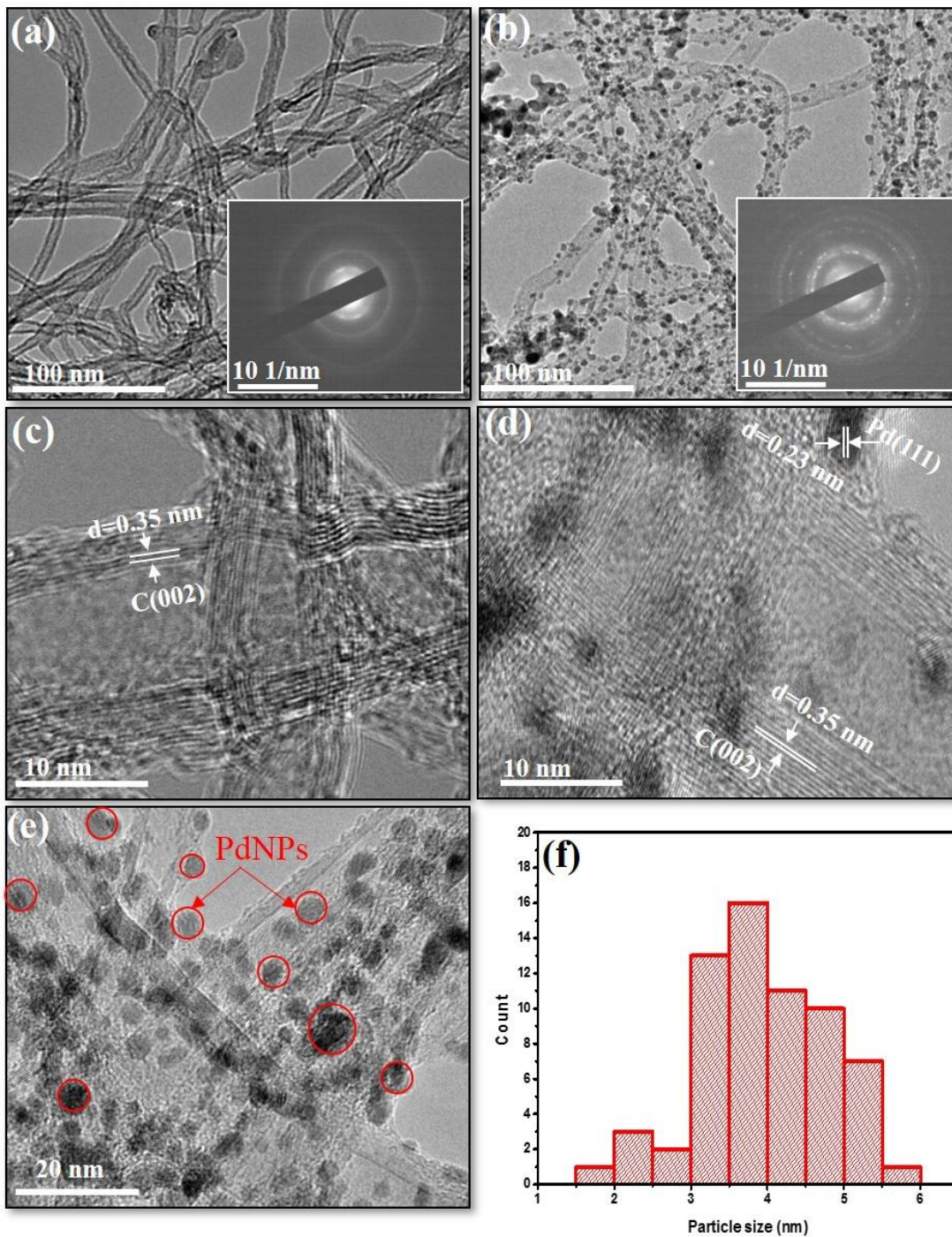


Figure 25 TEM image of the (a) f/MWCNTs and (b) PdNPs-f/MWCNTs. HRTEM of the (c) f/MWCNTs and (d) PdNPs-f/MWCNTs. (e) HRTEM at 20 nm and (f) Histogram of average particle size.

4.1.4 X-ray Photoelectron Spectroscopy Analysis of f/MWCNTs and PdNPs-f/MWCNTs

The chemical information of the f/MWCNTs and PdNPs-f/MWCNTs was investigated by the X-ray photoelectron spectroscopy (XPS). The XPS samples were prepared by dropping 50 μ L of f/MWCNT and PdNPs-f/MWCNTs solutions separately on a clean glass substrate and were dried in an oven at 50 °C overnight. Figure 26 (a) presents the XPS survey spectrum of the f/MWCNTs which displays two distinct binding energies at 284.6 and 531.9 eV corresponding to the carbon C1s and oxygen O1s core level peaks respectively. Similarly, in the survey spectrum of the PdNPs-f/MWCNTs in figure 26 (b), there is, in addition, palladium (Pd3d, Pd3p and Pd3s) signals. In the high-resolution scan, peaks of Pd3d, in figure 26 (c), were deconvoluted, displaying a doublet composed of two main peaks, corresponding to Pd3d_{5/2} and Pd3d_{3/2} spin orbit splitting. There is the existence of metallic Pd⁰ and Pd²⁺ with binding energies at Pd3d_{5/2} (335.6eV, 337.2eV) and Pd3d_{3/2} (340.8eV, 342.2eV) respectively [153, 155, 160-167]. The contribution of Pd²⁺ is due to some oxidized species of palladium (PdO). The appearance of the 284.6 and 286.2 eV peaks (figure 26 d) in the high resolution of C1s resemble the C-C and C=O respectively [161, 168, 169].

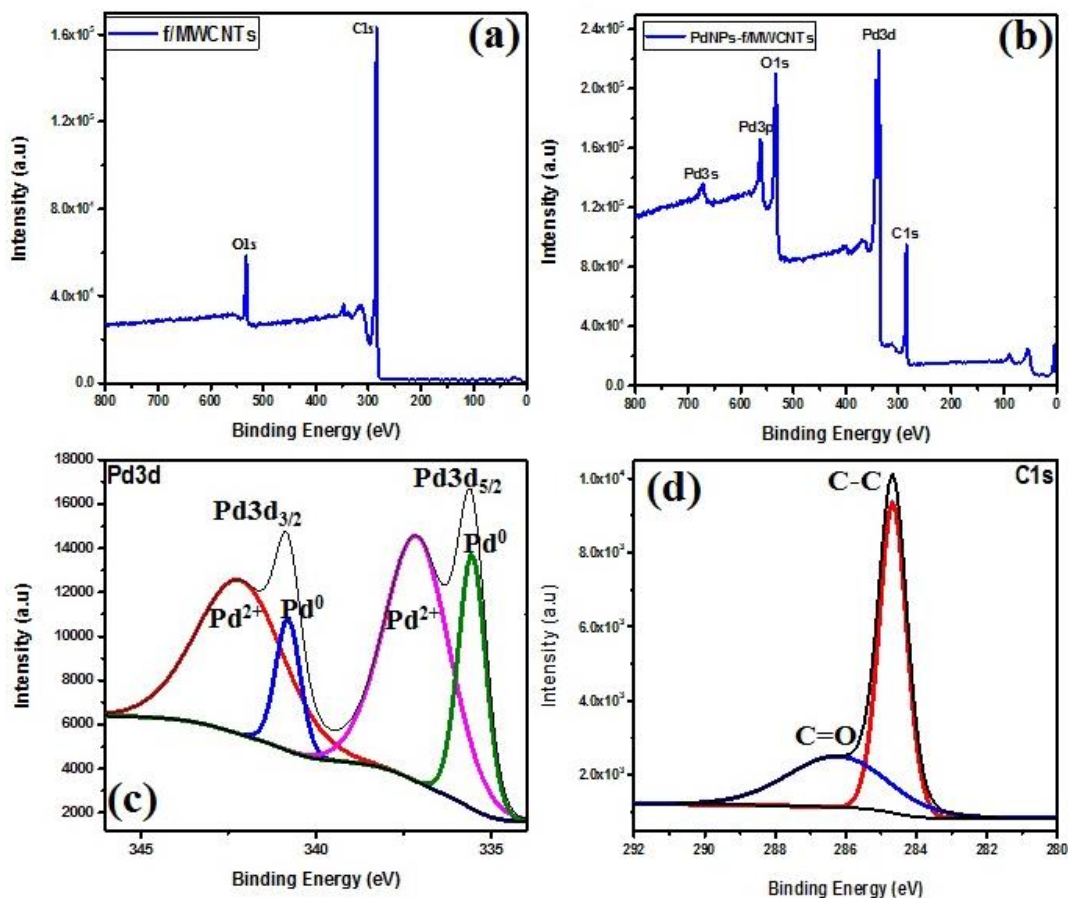


Figure 26: XPS survey spectrum of the (a) f/MWCNTs and (b) PdNPs-f/MWCNTs. High resolution spectrum of (c) Palladium, and (d) Carbon

4.2 Amperometric Hydrogen Detection

The amperometric measurements were performed using a CHI (760e) electrochemical workstation. The fabricated PdNPs-f/MWCNTs/PTFE membrane was used as the working electrode for the amperometric hydrogen gas detection measurements in 1 M of H_2SO_4 at room temperature. The active surface area of the PdNPs-f/MWCNTs/PTFE in the electrolyte medium is 4.9 cm^2 . Saturated Ag/AgCl and platinum wire were used as the reference electrode and the counter electrode respectively, to complete the three-electrode system. Two different concentrations of hydrogen gas were used throughout this

experiment; 0.1% H₂ in N₂ (1,000 ppm) and 1% H₂ in N₂ (10,000 ppm) while the flow was controlled by an MFC. Nitrogen gas was introduced as a carrier gas, as needed, throughout the experiments.

4.2.1 Optimization of Sensing Materials and Sensor Parameters

In order to determine an appropriate working condition of our sensor, an array of data was recorded with the help of the potentiostat by conducting various trials. Some of the results from the trial and error method are shown in figure 27.

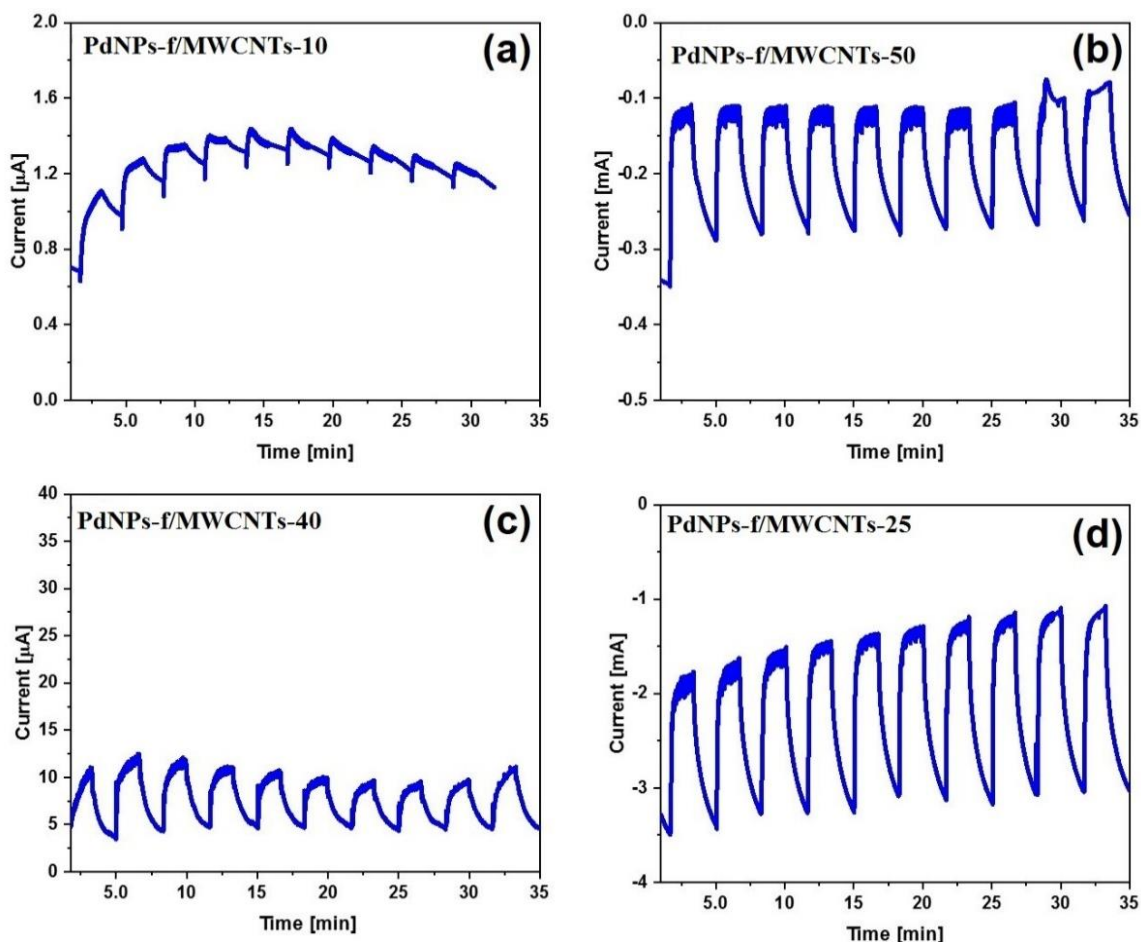


Figure 27 Amperometric response profile graph of the PdNPs-f/MWCNTS at various trial and error method during the optimization of the sensor materials and parameters

Initially, we began by varying the amount of the two precursors in the material preparation as well as the amount of the reducing agent. The list of the variations in the precursors is shown in the Table 4.1, and it is numbered in the order of preparation. The material preparation method was fully discussed earlier in chapter 3.

Table 2: List of the prepared samples by varying the amount of precursors for the optimization performance

S/N	f/MWCNTs (mg)	Pd(NO ₃) ₂ (mg)	NaBH ₄ (mM)	Name
1	25	10	10	PdNPs-f/MWCNTs-10
2	5	50	30	PdNPs-f/MWCNTs-50
3	5	40	30	PdNPs-f/MWCNTs-40
4	5	25	20	PdNPs-f/MWCNTs-25

The PdNPs-f/MWCNTs-10, in the Table 4.1, was deposited on the membrane to obtain the hydrogen detection result, shown in figure 27 (a). The time-dependent profile was obtained when the sensor was exposed to mixtures of H₂ and N₂ flows with concentrations in the range of 1000-10000 ppm. For example, for the 1% H₂ source, this was calculated by the concentration dilution formula in equation (4.2) [20-25].

$$H_2 \text{ Conc.} = \frac{\dot{V}_{H_2}}{\dot{V}_{H_2} + \dot{V}_{N_2}} \times 10,000 \text{ ppm} \quad (4.2)$$

Where $\dot{V}_{H_2}$ is the volumetric flow of hydrogen containing cylinder, while $\dot{V}_{N_2}$ is the volumetric flow of nitrogen cylinder. When a constant voltage is applied and the valve is opened to allow the sensor to detect the gas, this is the ON state of the sensor which is a

measure of increase in response current. Closing the valve is regarded as the OFF state of the sensor, which returns the response current back to the baseline.

The result in figure 27 (a) shows that the sensor responses were not able to recover the baseline current and the entire response was non-linear. After many trials by adjusting parameters and components of the sensor, there was no significant improvement.

The assumption was that the material with a large amount of the f/MWCNTs: (i) will be highly dense on the membrane, (ii) might affect the diffusion limited of gas flow, and (iii) lower the performance of the catalysts by blocking the hydrogen from reaching the surface of the catalyst. After lengthy variations in the amounts of the precursor, we proceeded to synthesize a modified sensing material, named PdNPs-f/MWCNTs-50 as shown in the Table 4.1. This behaved better as can be seen in figure 27 (b). The adsorption and desorption seem to occur very fast to achieve a fast response time and a quick recovery time but the noise effect in the saturation state is comparatively high. This noise effect was attributed a result of a high pressure of the hydrogen gas from the gas cylinder. Also, the stability of the sensing material on the membrane surface was also a challenge which was attributed to the fact that the f/MWCNTs, acting as a binding material, was not enough to support the high amount of Pd nanoparticles.

To maintain 5 mg of f/MWCNTS, we reduced the amounts of the $\text{Pd}(\text{NO}_3)_2$. Hence, we obtained another material (PdNPs-f/MWCNTs-40) which also behaved like that of PdNPs-f/MWCNTs-50. Further optimization was done to achieve a suitable sensing material PdNPs-f/MWCNTs-25. Hence, it was used throughout the experiment. The first result recorded with this material is shown in figure 27 (d). This also displays some issues like

the negative current. However, this can be corrected by adjusting the applied voltage. Hence, we obtained the time profile graph in figure 27 (d). To control the non-linearity effect in this figure 27 (d), the pressure at which the gas reaches the membrane was regulated and stabilized at 14 psi throughout the experiment.

Alongside the optimization of the material, we investigated the effect of the material deposition on the membrane, we tried by varying the amounts of the material deposited on the electrode surface. Finally, 500 μL of the suitable sensing material (PdNPs-f/MWCNTs-25) was dissolved 35 mL ethanol, and apply on the PTFE membrane, for the working electrode fabrication.

4.2.2 Operating potential difference of the PdNPs-f/MWCNTs based sensor

For an amperometric gas sensor, it is required to confirm the sensor operating potential between the working electrode and the reference electrode. The essence of the constant applied potential is to force electrons to flow through the sensor and power the rate of electrode chemical reaction. Several measurements were carried out by checking the effect of the applied voltage on the baseline current and the sensor response at large.

A range of potential differences of 0.0-0.60 V were tested to determine the preferred working potential of our sensor, as shown in figure 28 (a). The applied potential of 0.0V displayed no response but noise throughout the measurement. This suggests that at 0.0 V, the sensor does not respond to the flow of H_2 , but the noisy signal. Hence, the baseline current of -1000 A is not real, it is instead regarded as the current which is due to the

reduction effect of oxygen present in the material. The negative potential was also tested and behaved like that of zero potential.

Figure 28 (b) shows the magnification of the response obtained for the potentials of 0.4-0.65 V. As we increased the applied potential, the baseline current also increased. The potential range between 0.5 and 0.55 V are chosen as the working potential range of our sensor. They are found to give limited level of baseline currents. Further increase in potential (e.g. 0.7 V) led to disconnection of the working electrode due to excessive current flowing through the working electrode. This suggests that the applied potential is too high for the working electrode to withstand the resulting current.

We repeated the effect of the concentration of the precursor of the sensing materials, for this potential range. Various concentrations were subjected to test, at this operating potential to know the optimum concentration of the Pd salts required for good sensor response.

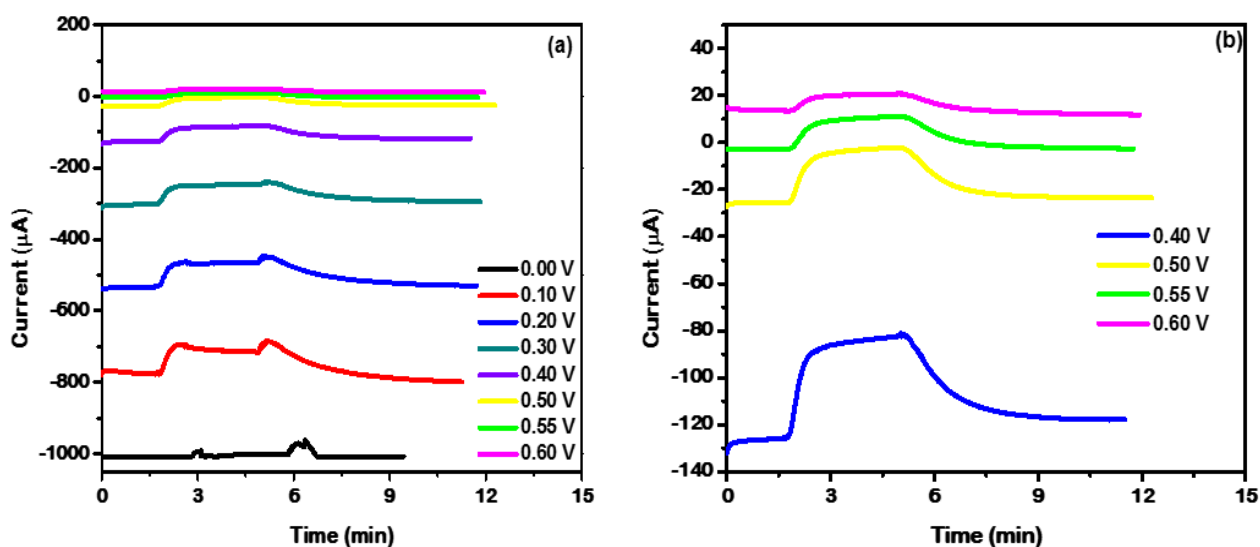


Figure 28 (a) Response of the PdNPs-f/MWCNTS at various voltages (0.0-0.60 V) and (b) Magnification of the response between (0.4-0.6 V)

4.2.3 Testing and Confirmation of the Flow of H₂ Gas (0.1% H₂ gas)

This section presents the confirmation of our sensor response to the flow of hydrogen gas only and not to the flow of nitrogen. Figure 29 (a) shows the behavior of the sensor towards the constant flow of hydrogen (0.1% H₂ gas) while varying the flow of nitrogen. Initially, the sensor was exposed to 5 sccm of H₂ in the absence of nitrogen. Next, it was exposed to 5 sccm H₂ + 10 sccm N₂, 5 sccm H₂ + 15 sccm N₂, 5 sccm H₂ + 50 sccm N₂, and 5 sccm H₂ + 35 sccm N₂. The response of the sensor to nitrogen is insignificant as they all exhibit similar response in the range $14.5 \pm 0.5 \mu\text{A}$. In each step, removal of hydrogen gas from the mixture of the two gases was confirmed to recover the sensor back to its original baseline even with the steady flow of N₂. A sudden removal of nitrogen from mixture of the gases shows insignificant effect on the response.

Further experiments were conducted to confirm the variation of hydrogen gas ranging from 5-50 sccm in a constant 5 sccm flow of N₂ as shown in the figure 29 (b). The obtained response values are shown in the Table 4.2, and the increase in response is due to the increased amount of electrons generated when the flow of hydrogen gas is increased. The slightly increasing baseline current of the measurement in figure 29 (b) might be ascribed to the incomplete desorption of the gas ions from the electrode surface. Yet this effect needs further investigation. Hence, our sensor is assumed not to respond to nitrogen. Instead, it measures the flow of hydrogen into the membrane. This can be clearly understood from figure 29 (a), where constant flow of hydrogen maintains constant response current. Similarly, in figure 29 (b), an increase in the hydrogen flow rate increases the response current. This means the generated signal current is a measure of the charges generated on the working electrode surface which also depends on the flow rate of hydrogen. Hence,

various flow rate of hydrogen affects the signal currents, which give the possibility to detect the flow of hydrogen at constant concentration.

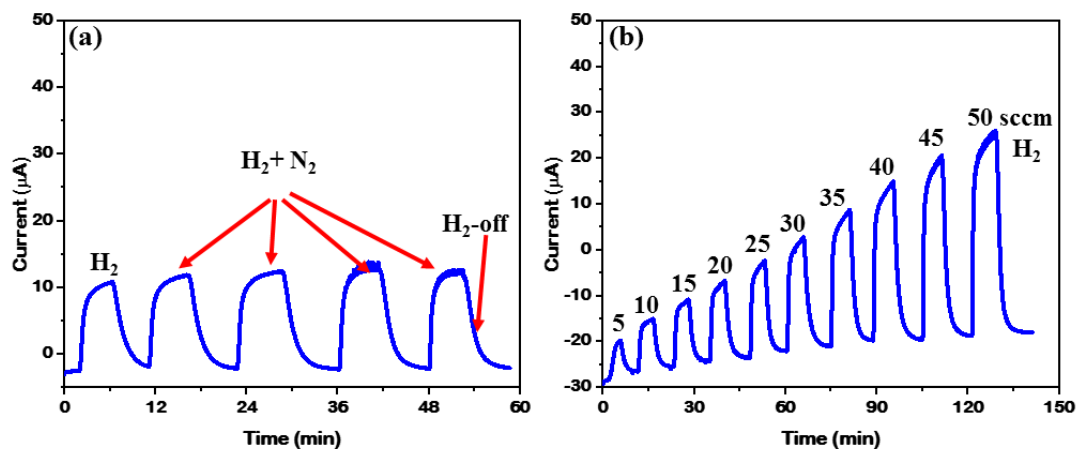


Figure 29 Response of the PdNPs-f/MWCNTS to 0.1% H₂ for the (a) constant 5 sccm of H₂ with variation in N₂ at 0.55 V and (b) Constant 5 sccm flow N₂ with variation in H₂ from 5-50 sccm at 0.50 V

Table 3: Response values of the graph in figure 29 (b): Constant 5 sccm flow N₂ with variation in 0.1% H₂ from 5-50 sccm at 0.50 V

H ₂ flow rate (sccm)	N ₂ flow rate (sccm)	Response height (μA)
5	5	8.50
10	5	11.30
15	5	14.60
20	5	17.30
25	5	21.20
30	5	24.60
35	5	29.40
40	5	34.10
45	5	39.70
50	5	44.50

4.2.4 Testing and Confirmation of the Flow of H₂ Gas (1% H₂ gas)

Further experiments were conducted by exposing the gas sensor to 1% of H₂ with the variation in the flow of H₂ gas (4, 6, 8, 8, and 10 sccm) in a constant 5 sccm flow of N₂. The repetition of the 8 sccm is to confirm the accuracy of the sensor and can be used to judge the stability of the sensor. Therefore, the response to 1% H₂ is considered to be normal and improved as compared to that of 0.1% of H₂. This is obvious by comparing the current responses in figure 30 with those in figure 29 (b). For example, 10 sccm H₂ + 5 sccm N₂ of 1% H₂ (figure 30) gives a current response of 32.80 μ A while that of 0.1% H₂ (figure 29 b) gives a current response of 11.30 μ A.

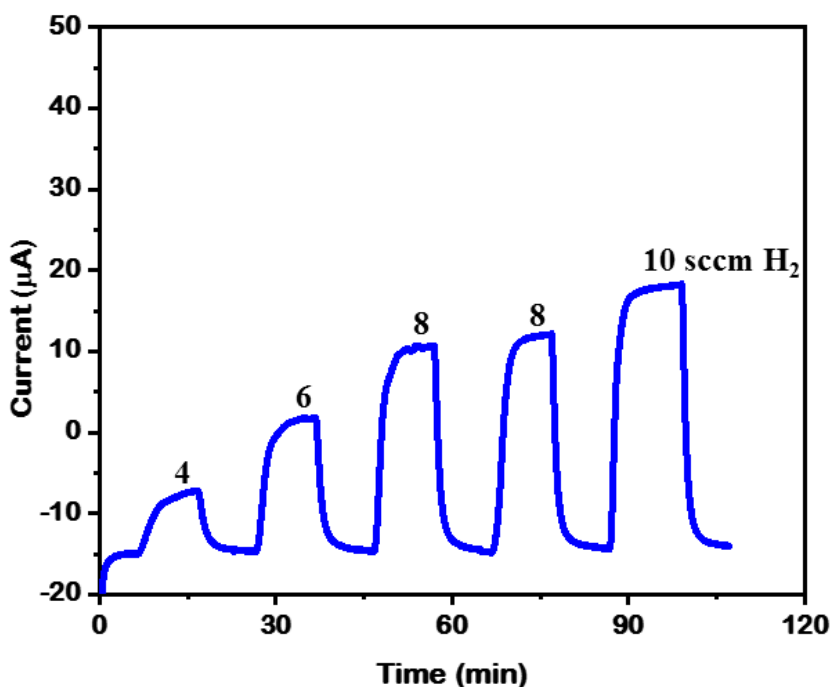


Figure 30 Response of the PdNPs-f/MWCNTS at various flow of 1% H₂ in the constant 5 sccm flow N₂ at 0.5 V

Table 4: Response values of the graph in figure 30; various flow of 1% H₂ in the constant 5 sccm flow N₂ at 0.5 V

H ₂ flow rate (sccm)	N ₂ flow rate (sccm)	Response height (μA)
4	5	7.30
6	5	16.40
8	5	25.50
8	5	25.60
10	5	32.80

4.2.5 Evaluation of Sensitivity of PdNPs-f/MWCNTs based sensor

Further measurements were recorded as in figure 31 (a). The calibration curve of this measurement was achieved by plotting the response value against different flow of 1% H₂. According to a linear regression analysis, the linear fit was accomplished with the correlation coefficient of $R^2 = 0.98$, showing good linear relationship between the flow of H₂ at a fixed concentration, over a flow range of 0-50 sccm, and the current response. The obtained linear equation of the linear regression line is $I [\mu A] = 2.78 H_2 \text{ (sccm)}$ at 1% H₂. The slope of the calibration curve is defined as the sensitivity of the sensor.

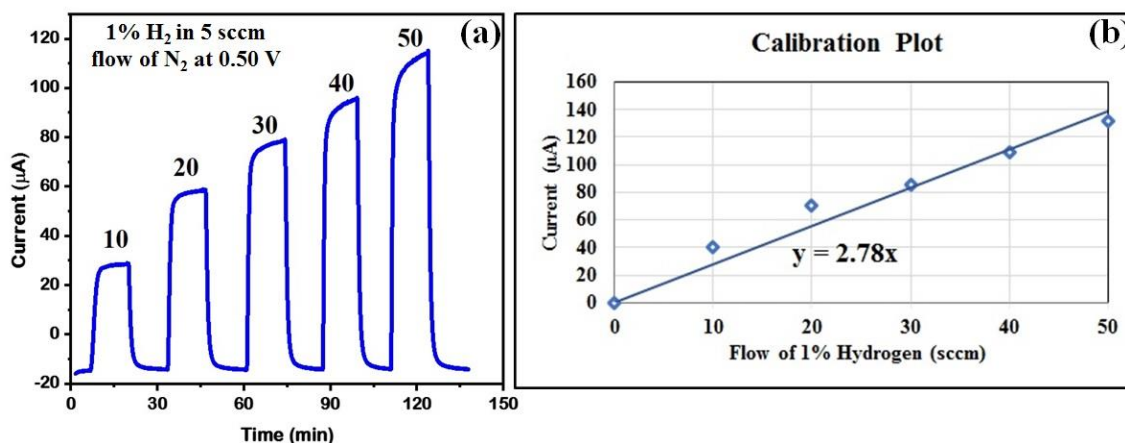


Figure 31 Response of the PdNPs-f/MWCNTS at (a) various flow of 1% H₂ with constant 5 sccm flow N₂ at 0.50 V, and (b) A typical calibration curve of the response against the H₂ flow

The obtained value of sensitivity is 2.78 $\mu\text{A}/\text{sccm}$ at 1% H_2 , which represents the ability of the sensor to detect a small flow of hydrogen gas. Furthermore, the background noise level of the sensor response was obtained to be 2.94 μA , which was determined by the standard deviation of the residuals of the response.

The limit of detection (LOD) was estimated by equation (4.3)

$$LOD = \frac{3\sigma}{S} \quad (4.3)$$

Where σ is the standard deviation of the residuals of the response (μA) and S is the slope of the calibration line ($\mu\text{A}/\text{sccm}$). Hence, the LOD was obtained to be about 3.2 sccm at 1% H_2 , which is defined as the lowest flow of 1% H_2 where the sensor gives credible response. The deviation of the data points from the best fit line, in figure 31 (b), was obtained to be 8.5 μA . The maximum percentage deviation in the sensor responses was obtained to be 6.1%, which is regarded as the linearity error.

The increase in the current response is related to the flow of the hydrogen which can be controlled by the diffusion rate of hydrogen into the diffusion barrier. Hence, the limiting current can be expressed by the equation (4.4) [20-26]

$$I_{\text{lim}} = \frac{2qAD}{x} [\text{H}_2]_{\text{gas}} \quad (4.4)$$

Where I_{lim} is the limiting current in μA , q is the quantity of charge of electron, A is the active surface area of the working electrode, x is the thickness of the diffusion barrier, D is the diffusion coefficient of hydrogen, and $[\text{H}_2]$ is the flow of hydrogen. Assuming all

other parameters are known, the response current should be proportional to the flow and/or concentration.

Table 5: Response values of the graph in figure 31 (a) various flow of 1% H₂ with constant 5 sccm flow N₂ at 0.50 V

H ₂ flow rate (sccm)	N ₂ flow rate (sccm)	Response height (μA)
10	5	42.50
20	5	72.10
30	5	91.80
40	5	108.0
50	5	125.70

4.2.6 Response time, Recovery times and Stability of PdNPs-f/MWCNTs based sensor

This section displays the response and recovery times of PdNPs-f/MWCNTs based sensor and shows its stability towards 15 sccm of 1% H₂ in 5 sccm of N₂. The response and recovery times were found to be 90 ± 1 s and 97 ± 1 s respectively towards 1% H₂, which indicates good reversibility due to its ability to return to the baseline level after exposure to hydrogen.

The traces of the measurement are shown in figure 32 (a). This quick response is related to the presence of active surface sites in PdNPs-f/MWCNTs which aid the interaction with hydrogen.

To confirm the stability performance of the PdNPs-f/MWCNTs based sensor, the response current was taken for again 15 sccm of H₂ in 5 sccm of N₂ after about 60 days storage of PdNPs-f/MWCNTs electrode. According to the response plot of stability profile in figure 32 (b), the response/recovery time of both runs are similar. Hence, the performance of our

sensor is demonstrated to be stable for a long period with percentage deviation of 2.6 % and in ambient operating conditions.

In general, among the problems which could cause the variation in the stability of operation of sensor are; (i) the design and fabrication errors, and (ii) presence of impurity in the sensing electrode.

We had adjusted the design during the calibration and optimization of the sensor parameters and components. Hence, the little variation in the stability of the PdNPs-f/MWCNTs based sensor could only be attributed to the variation of the surrounding environment, contamination of the electrolyte, and maybe the degradation in electrocatalytic activities as a result of the sensing electrode surface contamination.

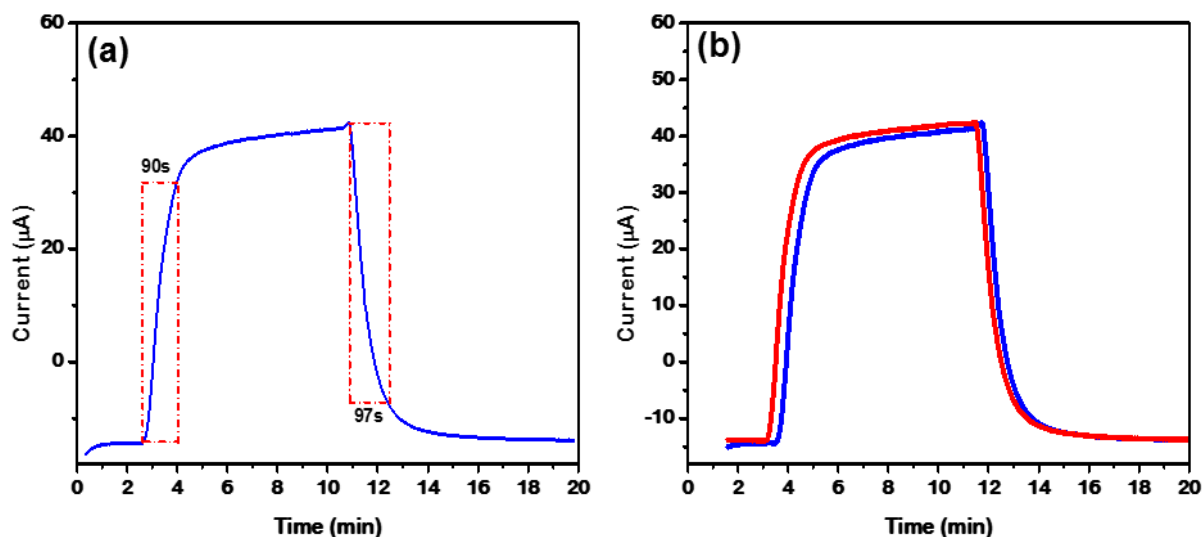


Figure 32 (a) Response/Recovery times of PdNPs-f/MWCNTs based sensor towards 15 sccm of 1% H_2 with 5 sccm of N_2 and (b) Stability of PdNPs-f/MWCNTs based sensor 15 sccm of 1% H_2 with 5 sccm of N_2 (November-Red and January-Blue) at 0.50 V

4.2.7 Reproducibility of PdNPs-f/MWCNTs based sensor

This section shows the reproducibility of the PdNPs-f/MWCNTs towards 5 and 10 sccm of H_2 in 5 sccm of N_2 flow. We investigated the reproducibility measurement by producing a new sensing material to fabricate new working electrodes using the same procedure as before. As depicted in figure 33, little variation of response, maximum percentage difference, was obtained to be 7.9%. This variation might have occurred in the process of the new sensing material preparation. With this little deviation in response, our sensor is classified to exhibit very good reproducibility characteristics.

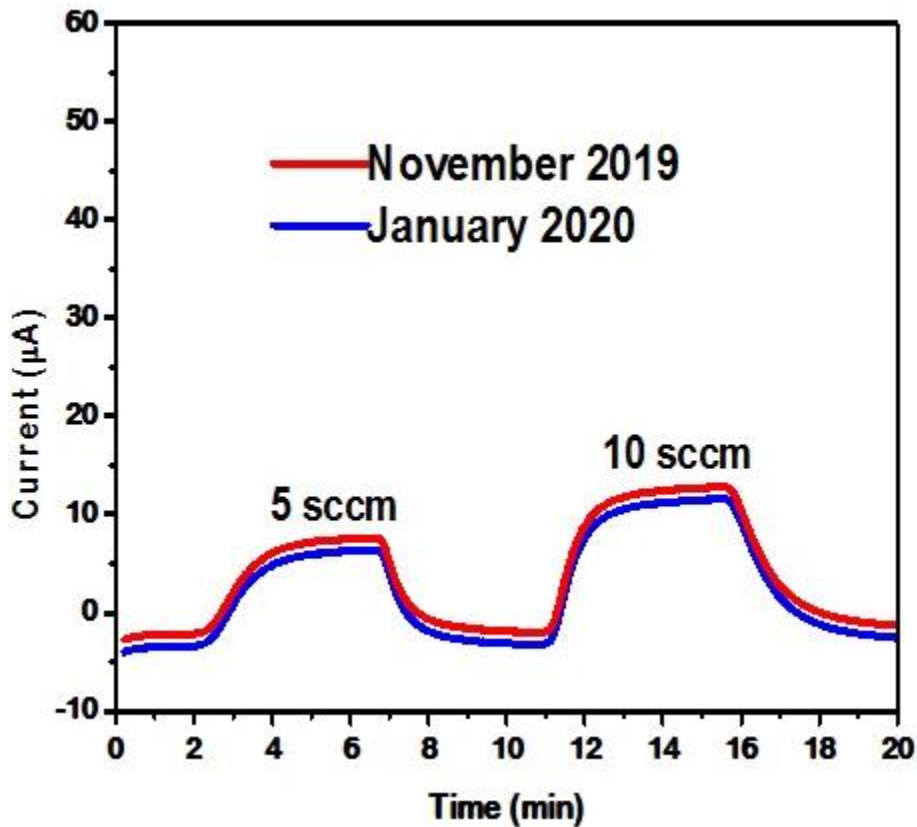


Figure 33 Response of the repeatability test of PdNPs-f/MWCNTs based sensor towards 5 and 10 sccm of 0.1% H_2 with constant 5 sccm of N_2 at 0.55 V

CHAPTER 5: CONCLUSION

5.1 Conclusion

An amperometric hydrogen gas flow sensor has been designed and fabricated based on PdNPs-f/MWCNTs to achieve rapid response, sensitive, and repeatable chemical gas sensing towards 0.1% and 1% H₂ flow. The morphological characterization of PdNPs-f/MWCNTs exhibited dispersed PdNPs on the tubular surface of the f/MWCNTs with an average crystallite size of 2.7 ± 0.8 nm. The presence of the elemental composition of the sensing material containing palladium, carbon and oxygen, was confirmed by EDS and XPS analyses. The amperometric gas sensing results indicated that the PdNPs-f/MWCNTs based sensor displayed good performance with a sensitivity of 2.78 $\mu\text{A}/\text{sccm}$, LOD of approximate 3.2 sccm at 1% hydrogen gas over a flow range of 0-50 sccm. The sensor exhibited good sensitivity and linear response, with correlation coefficient of 0.98, towards hydrogen flow in the presence of nitrogen gas. The sensor response and recovery times towards 15 sccm of 1% H₂ flow was obtained to be 90 ± 1 s and 97 ± 1 s, respectively, which indicates good reversibility. Furthermore, it exhibited good stability, with a maximum percentage deviation of 2.6% for about 60 days of storage at room temperature. It revealed reproducible result with a maximum percentage difference of 7.9%. In summary, the PdNPs-f/MWCNTs based sensor developed in this work shows good response characteristics to hydrogen gas at room temperature.

5.2 Future work

The amperometric hydrogen gas flow sensor developed in this thesis can further be extended by:

1. Testing the sensor at different operation temperatures.
2. Modifying the sensing material by decorating PdNPs on home-made carbon or other permeable substrates of large specific surface area.
3. Improving the catalysts by doping PdNPs with other active metal catalysts.
4. Studying the effect of particle size on the sensing response.
5. Carrying out the selectivity test.

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Vitae

Name	:Ismail Adeniyi Buliyaminu
Nationality	:Nigeria
Date of Birth	:7/1/1990
Email	:ismatech20009@gmail.com
Address	:140 Idioro Oke-ola Isale Oba Iwo, Osun State, Nigeria
Zip Code	232101

Academic Background

M.S. Physics, April 2020, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, Saudi Arabia

B.Sc. (Hons) First Class in Physics, 2015, University of Ibadan, Ibadan, Nigeria

West African Senior School Certificate Examination, June 2008, Islahudeen Community High School, Oke-afo Iwo, Osun State, Nigeria

Primary School Certificate, 2002, D.C. School Oke-ola Iwo, Osun State, Nigeria

Research Interests

Sensors

Nanomaterial and their Applications

Computational Physics and Material Science

Condensed Matter Physics

Publications

1. **Ismail A. Buliyaminu**, Md. Abdul Aziz, Syed Shaheen Shah, A.K. Mohamedkhair, Zain H. Yamani, Preparation of nano-Co₃O₄-coated Albizia procera-derived carbon by direct thermal decomposition method for electrochemical water oxidation, Arabian Journal of Chemistry, Volume 13, Issue 3,2020,Pages 4785-4796,ISSN 1878 5352, <https://doi.org/10.1016/j.arabjc.2019.12.013>.
2. Md. Aminul Haque, Md. Rajibul Akanda, Delwar Hossain, M. Aminul Haque, **Ismail A. Buliyaminu**, Shaik Inayath Basha, Munetaka Oyama, and Md. Abdul Aziz "Preparation and characterization of Bhant leaves-derived nitrogen-doped carbon and its use as an electrocatalyst for detecting ketoconazole" Electroanalysis10.1002/elan.201900474(2019).
<https://doi.org/10.1002/elan.201900474>.
3. **Ismail A. Buliyaminu**, Md. Abdul Aziz, Zain H. Yamani, Amperometric Hydrogen Gas Flow Sensor based on Palladium nanoparticles Decorated on the Carboxylic Functionalized Multiwalled Carbon Nanotubes- **Finalized**
4. **Ismail A. Buliyaminu**, Md. Abdul Aziz, Zain H. Yamani, Electrical and Electrochemical Properties of an Aluminum-Doped Zinc Oxide Electrode Decorated with Densely Gathered Palladium Nanoparticles-**Finalized**

Conferences

1. **IsmailA.Buliyaminu**^{1,2}, Md. AbdulAziz^{1, *}, ZainH.Yamani^{1,2} Preparation of nano-Co₃O₄-coated *Albizia procera* derived carbon by direct thermal decomposition method for electrochemical water oxidation” 11th International Conference and

Exhibition on Chemistry in Industry at the Gulf Convention center, Kingdom of Bahrain, October 29 – 31, 2019.

2. Md. Abdul Aziz, Syed Shaheen Shah, **Ismail A. Buliyaminu**, Mohammed Ameen Ahmed Qasem “Simple and straight-forward thermal preparation of metal oxide nanocatalysts from commercially available metal precursors for electrochemical water oxidation” Symposium on Insights into Gas Diffusion Electrodes: From Fundamentals to Industrial Applications, Magdeburg, Germany, September 23 – 25, 2019.

Patent

1. Md. Abdul Aziz, **Ismail A. Buliyaminu**, Zain H. Yamani, Preparation of nano-Co₃O₄-coated Albizia procera-derived carbon by direct thermal decomposition method for electrochemical water oxidation