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United Arab Emirates University

College of Engineering

Department of Electrical Engineering

DESIGN, FABRICATION AND CHARACTERIZATION OF LOW-POWER GAS SENSORS BASED ON ORGANIC-INORGANIC NANO-COMPOSITION

Ayah Faeik Salim Abu Hani

This thesis is submitted in partial fulfilment of the requirements for the degree of Master of Science in Electrical Engineering

Under the Supervision of Dr. Falah Awwad

November 2016
Declaration of Original Work

I, Ayah Faeik Salim Abu Hani, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this thesis entitled “Design, Fabrication and Characterization of Low-power Gas Sensors based on Organic-inorganic Nano-composition”, hereby, solemnly declare that this thesis is my own original research work that has been done and prepared by me under the supervision of Dr. Falah Awwad in the College of Engineering at UAEU. This work has not previously been presented or published, or formed the basis for the award of any academic degree, diploma or a similar title at this or any other university. Any materials borrowed from other sources (whether published or unpublished) and relied upon or included in my thesis have been properly cited and acknowledged in accordance with appropriate academic conventions. I further declare that there is no potential conflict of interest with respect to the research, data collection, authorship, presentation and/or publication of this thesis.

Student’s Signature: ___________________________ Date: 23-12-2016
Approval of the Master Thesis

This Master Thesis is approved by the following Examining Committee Members:

1) Advisor (Committee Chair): Dr. Falah Awwad
   Title: Associate Professor
   Department of Electrical Engineering
   College of Engineering
   Signature ___________________________ Date 11/12/2016

2) Co-advisor: Dr. Saleh T. Mahmoud
   Title: Professor
   Department of Physics
   College of Science
   Signature ___________________________ Date 11/12/2016

3) Member (Internal Examiner): Dr. Mousa Hussein
   Title: Associate Professor
   Department of Electrical Engineering
   College of Engineering
   Signature ___________________________ Date 11/12/2016

4) Member (External Examiner): Dr. Manos M. Tentzeris
   Title: Professor
   Department of Electrical and Computer Engineering
   Institution: Georgia Institute of Technology, Atlanta, USA
   Signature ___________________________ Date 01-12-2016

Dr. Mohammad Shoqeeb Lajhari on behalf of Prof. Manos M. Tentzeris
This Master Thesis is accepted by:

Dean of the College of Engineering: Professor Sabah Alkass

Signature ___________________ Date 29/12/2016

Dean of the College of the Graduate Studies: Professor Nagi T. Wakim

Signature ___________________ Date 10/1/2017

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Abstract

Lower power consumption and higher performance are compelling demands in the electronic systems motivating the search for new materials which are capable of fulfilling these demands. Recently, nanomaterial-based sensor technology has drawn considerable attention towards the development of sensing applications such as H$_2$S gas sensors. Development of H$_2$S gas sensors is crucial due to its extreme toxicity and damaging effects on both health and environment. This thesis aims to develop H$_2$S gas sensors with enhanced sensitivity, flexibility, lower operating temperature, and high selectivity.

The proposed sensors present a contribution to the field of nano-electronics. They are designed based on the integration of nanotechnology and conducting polymer technology. These sensors are consisting of oxide semiconducting nanomaterials (WO$_3$, ZnFe$_2$O$_4$ and CuFe$_2$O$_4$ nanoparticles) and a newly developed organic polymer with engineered conductivity ((poly (vinyl alcohol; PVA)-glycerol). The doped solutions are casted to form flexible membranes which are characterized and tested to investigate their gas-sensing performance. The sensing method of these membranes is only a measure of resistance/conductance change denoting that the signal conditioning circuitry of such sensors is relatively simple.

The results showed very good sensitivity and selectivity towards H$_2$S gas as well as excellent reproducibility and long-term stability; these are very important properties for a reliable sensor. Another interesting result of this study was the low operating temperature of the sensors, as they show noticeable responses at low temperatures in the range of 20°C - 40°C. The lower operating temperature means lower power consumption, which is an ultimate goal in the electronic applications
industry. The results reveal reasonably fast responses, with minimum average response times in the range of 19 - 22 s. This study encloses novel results since it is the first work, to the best of our knowledge, to incorporate WO$_3$, ZnFe$_2$O$_4$ and CuFe$_2$O$_4$ nanoparticles with a conductivity-controlled organic polymer for H$_2$S sensing applications.

**Keywords:** H$_2$S sensor, nanomaterial, organic polymer, WO$_3$, ZnFe$_2$O$_4$, CuFe$_2$O$_4$. 
تصميم وتصنيع ودراسة خصائص أجهزة استشعار غاز ذات استهلاك منخفض للطاقة، باستخدام مركب نانوي من مواد عضوية وغير عضوية

الملخص

يعد السعي إلى خفض استهلاك الطاقة ورفع الكفاءة من الضرورات الملحة في مجال تصنيع الأنظمة الإلكترونية، لذلك كان لا بد من البحث عن مواد وتقنيات جديدة كفيلة بتحقيق هذه الأهداف. ففي الأونة الأخيرة، كان لاستخدام تكنولوجيا النانو- （nanotechnology） في تصنيع أجهزة الاستشعار بمختلف أنواعها، أثر إيجابي ساهم في تطوير هذه الأجهزة. ومتالاً، على ذلك، أجهزة الاستشعار الخاصة بغاز كبريتيد الهيدروجيني (H2S) ، حيث يُولى هذا الغاز اهتماماً بالغاً وذلك لسميته الشديدة وتأثيره الضار على الصحة والبيئة. لذلك فإن هدف هذه الرسالة يتلخص في تحضير ودراسة أجهزة استشعار خاصة بغاز كبريتيد الهيدروجيني، تميز باستجابةها العالية للغاز مع درجة من الأنتقائية، وبمرونتها، وباستهلاكها المنخفض للطاقة.

تمثل هذه الدراسة على أجهزة الاستشعار إسهاماً في مجال الإلكترونيات المعتمدة على تقنية النانو- （nanotechnology） حيث تم تصميمها وتصنيعها باستخدام مزيج من أكاسيد المعدن شبه الموصلة دقيقة الحجم （nanometer） (CuFe2O4 و ZnFe2O4 و WO3) ، و بوليمر عضوي （Ionic Liquid） (PVA) تمت معالجته بسائل أيونيي (Ionic Liquid) بهدف تحويله إلى بوليمر موصول، وهو ما يمثل دماجاً ما بين تكنولوجيا البوليمرات الموصلة والناانو- （nanotechnology） ومن ثم تم تحويل المركبات السائلة إلى أغشية صلبة. وتمت دراسة خصائصها ومدى استجابتها لغاز كبريتيد الهيدروجين. تعتمد آلية قياس درجة استشعار الغاز على مدى التغير الحاصل في موصلية هذه الأغشية عند تعرضها للغاز، مما يدل على أن الدائرة الإلكترونية التي تستخدم لتحليل ومعالجة الإشارة الكهربائية الناتجة عن الاستجابة للغاز هي دائرة بسيطة التركيب.
أظهرت نتائج دراسة أجهزة الاستشعار هذه استجابة قوية لغاز كبريتيد الهيدروجين، مع درجة عالية من الانتقائية، بالإضافة إلى إمكانية استعمالها بشكل متكرر ونتائج دقيقة على المدى الطويل. وبشكل عام، تعتبر هذه الخصائص مهمة جداً؛ كونها معايير أساسية في الحكم على مدى فاعلية أجهزة الاستشعار. ومن النتائج الملموسة في هذه الدراسة هي إمكانية الاستجابة للغاز في درجات حرارة منخفضة نسبياً (20 - 40 درجة مئوية) مما يدل على استهلاك منخفض للطاقة وهو هدف أساسي ومطمح دائم في مجال صناعة الإلكترونات. أما فيما يخص المدة الزمنية التي تستغرقها أجهزة الاستشعار للاستجابة للغاز، فقد أظهرت النتائج استجابة سريعة من قبل هذه الأجهزة، حيث كان الحد الأدنى لمعدل الاستجابة هو (19 - 22 ثانية).

وبناءاً على ما سبق، تقدم هذه الدراسة نتائج جديدة من نوعها كونها المرة الأولى - على حد علمنا - التي يتم فيها تصنيع أجهزة استشعار خاصة بغاز كبريتيد الهيدروجين اعتماداً على مزيج من أكاسيد المعادن شبه الموصلة دقيقة الحجم (النانومتر) (ZnFe₂O₄ و WO₃ و CuFe₂O₄) و بوليمر عضوي (PVA) و موصل موصلي.

مفاهيم البحث الرئيسية: أجهزة استشعار، غاز كبريتيد الهيدروجين، مواد نانوية، بوليمر عضوي.
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Last, but certainly not least, I express my eternal appreciation and gratitude to my beloved parents and family who have always been there for me no matter where I am, for unconditional love, support and patience. I thank them for always believing in me and letting me find my own way.
Dedication

To my beloved parents and family
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<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>Copper ferrite</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-Dispersive x-ray Spectroscopy</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation Energy</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volt</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>Hydrogen Sulfide</td>
</tr>
<tr>
<td>$I_g$</td>
<td>Electrical current in presence of the target gas Nanoparticles</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic Liquid</td>
</tr>
<tr>
<td>$I_o$</td>
<td>Electrical current in absence of the target gas</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-Voltage Scanning Electron Microscopy</td>
</tr>
<tr>
<td>$K_B$</td>
<td>Boltzmann constant = 1.38064852 x 10$^{-23}$ m$^2$.kg.s$^{-2}$.K$^{-1}$</td>
</tr>
<tr>
<td>LabVIEW</td>
<td>Laboratory Virtual Instrument Engineering Workbench</td>
</tr>
<tr>
<td>NPs</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>PPM</td>
<td>Part per million</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly-vinyl alcohol</td>
</tr>
<tr>
<td>R</td>
<td>Rate constant</td>
</tr>
<tr>
<td>$R_0$</td>
<td>Arrhenius factor</td>
</tr>
<tr>
<td>SCCM</td>
<td>Standard cubic centimeters per minute</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>$S_%$</td>
<td>Gas-sensing response</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (Kelvin)</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>Tungsten Oxide</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>ZnFe$_2$O$_4$</td>
<td>Zinc ferrite</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

1.1 Overview

This thesis work highlights the integration of nanotechnology and conducting polymer technology in the fabrication of flexible sensing materials for H₂S gas detection, with enhanced sensitivity, flexibility, lower operating temperature, and high selectivity.

This thesis report starts with the literature review in chapter 2, which introduces facts about H₂S gas, a variety of applied materials and methods of H₂S detection, and proposed alternative sensing materials. Chapter 3 provides details about the materials, methods and the fabrication processes of the proposed sensing materials. The results are presented and discussed in chapter 4. Finally, chapter 5 concludes the outcomes of this thesis work and provides an insight to future works.

1.2 Statement of the Problem

H₂S gas is a silent killer which can lead to sudden death among workers in fields where this gas occurs naturally. Although H₂S gas sensors are available, they are generally in the rigid form and hardly meet the requirements of flexible electronic devices. Indeed, these sensors suffer from high power-consumption, and relatively long response time. Therefore, the inevitable risks of H₂S gas and the demand for a higher performance and lower power-consumption sensors urge the search of new materials which are capable of fulfilling these demands.
1.3 Research Objectives

This work is aimed to contribute to a growing research in the area of gas sensing technology, and the field of nano-electronics. Therefore, the main research objectives of this thesis are:

1) Designing and fabricating chemiresistive H₂S gas sensors based on metal oxide nanomaterials (ZnFe₂O₄, CuFe₂O₄ and WO₃ nanoparticles) doped in a newly developed conductivity-controlled polymer.

2) Investigating the electrical properties and gas-sensing performance of the proposed sensors.
Chapter 2: Literature Review

This chapter presents and discusses some facts and information related to this thesis work. It begins with providing some facts about H$_2$S gas, such as sources and risks. Then, it presents a variety of applied materials and methods that have been used in the fabrication of H$_2$S gas sensors. Finally, this chapter discusses the proposed alternative sensing-materials that will be used in this thesis work and are expected to enhance the quality of H$_2$S gas sensors.

2.1 Hydrogen sulfide gas (H$_2$S)

Hydrogen sulfide gas (H$_2$S) is considered a major air pollutant, which naturally occurs in large quantities in oil and natural gas industries, paper milling, sewage treatment, and landfills [1][2]. H$_2$S gas is colorless, corrosive, flammable, extremely toxic and potentially lethal in low concentrations, as low as few parts per million (ppm). The damaging effects of H$_2$S depend on the amount of gas inhaled and for how long. Exposure to very high gas concentrations can immediately lead to death. More details about the amount of inhaled gas and its corresponding symptoms/effect are shown in Table 3 in appendix [3][4][5][6]. Frequently, industrial workers face the risk of exposure to H$_2$S gas or even gas explosion. Therefore, saving the lives requires enhancing the quality of H$_2$S sensors.

2.2 Materials and methods for H$_2$S gas detection

Most of the available sensors are expensive and they suffer from different problems such as high power-consumption, poor stability, inflexibility, and malfunction in harsh environment [7][8][9]. Therefore, H$_2$S gas sensors have been
under constant development to meet the growing demands on highly efficient sensors. A variety of materials and methods have been used for real-time detection of H$_2$S gas. The four most common types of H$_2$S gas sensors are as follows [10]:

2.2.1 Electrochemical sensors

Electrochemical sensors are basically based on electrolytes; solid and liquid electrolyte sensors. For H$_2$S detection, solid electrolytes are commonly used. Based on their working principles, solid electrolytes are two types: amperometric and potentiometric. When amperometric-based electrolytes exposed to the target gas, they produce current signals corresponding to the gas concentration. Pt-electrode and ceramic are examples of amperometric-based sensing materials which have been used for H$_2$S gas detection. While in potentiometric-based sensors, a potential difference (voltage) is produced as a result of reaction with the gas [10][11]. For example, potential-based H$_2$S sensors were prepared based on sodium super ionic conductor (NASICON) and Pr$_6$O$_{11}$-doped SnO$_2$ sensing electrode.

However, most of the commercially available solid electrolyte sensors suffer from poor selectivity. Sensor arrays are employed to overcome the poor selectivity; they form a series of sensors (spots), and their measurements are used to produce a specific fingerprint for a specific target gas [11].

2.2.2 Optical sensors

The attenuation of light waves is the core principle of gas sensing technique of optical-sensors. Analyte information from these sensors are usually obtained by employing optical transduction techniques [12]. A waveguide (optical fiber) and a coating are frequently used to design such sensors. Therefore, placing the analyte at
the interface of the fiber and a coating, causes interaction with the light, with the fact that \( \text{H}_2\text{S} \) absorbs the ultraviolet (UV) light in deep UV region (\(<200 \text{ nm}) [13]. Thus, quantitative and qualitative analysis based on experimental signals can be recorded due to emission or absorption. Optical sensors are of two types: direct sensing and indirect sensing sensors. Direct sensing techniques include infrared, non-dispersive infrared, fourier transform infrared, ultraviolet absorption and diode laser sensing. While indirect sensing is in the form of optical-technique based arrays combined with sampling system and means of pattern classification [13] such as electronic noses (artificial sensors).

### 2.2.3 Piezoelectric sensors

Piezoelectric sensors are mass-change sensing devices [10]. Indeed, surface acoustic wave (SAW) sensor is a type of piezoelectric sensors [15]. The working principle of SAW device is based on the travel of Rayleigh wave over its surface or oscillation frequency that is caused by any change in its mass. SAW can sense changes up to 1 pico gram (pg) of mass. Another type of piezoelectric sensors is the quartz crystal microbalance (QCM) [16], where its working principle is based on frequency shift. This QCM is a resonating polymer-coated disk with metal electrodes. When this device is exposed to the target gas, the odor is absorbed by the polymer, thus, the mass of the devices increases which causes a reduction in the resonance frequency which is inversely proportional to the adsorbed mass of gas. This type of sensors can sense a mass change up to 1 nano gram (ng).

However, piezoelectric sensors are unable to measure in a true static way. A fixed amount of charge on the piezoelectric material will result when subjected to a static force. As pressure loads and temperature increases, a reduction in the
sensitivity happened due to “twin formation”, while at temperatures above 300°C, quartz sensors must be cooled during measurements [17].

2.2.4 Oxide-semiconductor sensors

Oxide-semiconductor materials have been widely investigated to find new functionalities of their chemiresistivity. Among their crucial roles in different fields and applications, oxide-semiconductor materials such as \( \alpha\-\text{Fe}_2\text{O}_3 \) [18], spinel ferrites [19][20], CuO [21], WO\(_3\) [22] have shown promising potentials to detect harmful and toxic gases such as H\(_2\)S. These materials are chemiresistive, where the change in the resistance governs their gas detection. In general, oxide-semiconductors exhibit poor electrical conductivity since most charge carriers are trapped in surface states. Those carriers are activated to the conduction when exposed to a target gas which increase the conductivity of the oxide-semiconductors. Controlling the resistance of the sensing material can be achieved by tuning the concentration of charge carriers in materials, and its optimum response can be found. In terms of conductivity, n-type semiconductors are found to be better than p-type, as the majority charge carriers in n-type materials are electrons. This suggests that n-type oxide-semiconductor materials will give better results as H\(_2\)S gas sensors. In this matter, a review study [23] suggests that the response of a p-type oxide semiconductor gas sensor to a given gas was equal to the square root of that of an n-type oxide semiconductor gas sensor to the same gas when the morphological configurations of both sensor materials were identical [24]. This concludes that oxide-semiconductor materials are the best candidate to be used in this work, and especially the n-type materials.
2.3 Nanomaterials

Nanotechnology has brought many great changes and new research opportunities in the fields of chemistry, physics, biology, material science, nanoelectronics and others. Nano-materials are defined as “material having one or more external dimensions in the nanoscale or which is nanostructured” [25]. Nanostructures can exhibit different properties than those of the same material without nanostructures. One of the important characteristics of nanomaterials is their large surface area to volume ratio compared to bulk materials, which opens many possibilities for creating new materials and facilitating chemical processes. For example, in the field of gas sensing technology, sensitivity of sensors is dependent on the surface to volume ratio; therefore, using nanomaterials with narrow size distribution for these applications would further promote the chemical reactivity of the nanomaterials because as the surface-to-volume ratio of the particle increases, the number of reactive sites increases [26].

2.4 Organic-inorganic nano-composite for H₂S detection

Fabrication of electronic devices based on organic materials and inorganic nanomaterials are very attractive to enable applications, such as transparent and flexible electronic devices, which are power saving, size compactable, and easily portable [26][28]. The properties of such nano-composite materials depend not only on the properties of their constituents but also on their combined morphology and interfacial characteristics, which brings synergistic effects. A wise choice of the constituents to be used for H₂S gas detection application would help achieving the optimum enhancement of H₂S sensors in terms of sensitivity, selectivity, response time, low power consumption, easy fabrication, and flexibility.
In the literature, oxide-semiconductor materials have been the most common and promising materials for \( \text{H}_2\text{S} \) gas sensing applications due to their easy and simple fabrication process, low manufacturing cost, and low detection limits [24]. Among these oxide materials, tungsten oxide (WO\(_3\)), which is an n-type metal oxide with a band gap in the range of 2.6–3.0 eV, attracts much attention because of its structure, surface morphology, defect structure, and active surface area of the WO\(_3\) material which have great influence on its surface properties including its gas sensing properties [29]. Therefore, WO\(_3\) has been used in many applications such as gas sensors [30][31][32]. \( \text{H}_2\text{S} \) gas sensors based on WO\(_3\) nanostructures have been reported to detect \( \text{H}_2\text{S} \) gas at very low concentrations [32][33][34]. Spinel-type oxide semiconductors with the formula (MFe\(_2\)O\(_4\)) such as zinc ferrite (ZnFe\(_2\)O\(_4\)) and copper ferrite (CuFe\(_2\)O\(_4\)) have been also reported for being highly sensitive and selective toward \( \text{H}_2\text{S} \) gas [19]. They showed reversible interaction of the gas with the pre-adsorbed ambient oxygen, therefore, their electrical resistance changes significantly upon exposure to \( \text{H}_2\text{S} \) gas [20]. Both ZnFe\(_2\)O\(_4\) and CuFe\(_2\)O\(_4\) behave as n-type metal-oxide semiconductors [35]. Although oxide materials have limited selectivity towards some interfering gases and lack flexibility, integrating them with conducting organic polymer would enhance their sensing properties and provide selectivity to the target gas. Therefore, the inorganic WO\(_3\), ZnFe\(_2\)O\(_4\) and CuFe\(_2\)O\(_4\) nanomaterials in corporation with conducting organic polymer will be considered in this thesis study.

Conducting organic polymers have been synthesized and used in the field of electronic applications including organic field effect transistors (FETs), light emitting diodes (LEDs), organic photovoltaics and gas sensing application [36][37][38]. A newly developed organic polymer ((poly(vinyl alcohol; PVA)-
glycerol) with engineered conductivity [39][40][41] will be considered in this study. The organic polymer would serve as a host for the oxide nanoparticles in the form of solid and flexible membrane. The electrical conductivity of the sensor’s membrane is controlled by doping the organic polymer (PVA) with a suitable ionic liquid (IL). In general, ILs serve as electrolytes and diffusion barriers, and they have low values of vapour pressure, wide potential windows, and low toxicity. In addition, ILs are suitable to be used for the fabrication of electrochemical sensors as they are environmentally friendly [42][43]. Due to their low-molecular-weight, when ILs are blended with polymers, the free volume of the material or the macro-molecular mobility of the polymer will increase, resulting in a decrease in the intermolecular forces, thus, the polymeric network becomes less dense, and consequently the extensibility and flexibility of the films are improved [44]. ILs/plasticizers such as glycerol have been incorporated into different polymers and they have been reported to improve the polymer properties such as ionic conductivity that is attained at room temperature, thermal and electrochemical properties of polymers for specific applications [45]. The sensing principle of the proposed sensing materials is based on conductance change when they interact with H₂S gas. Therefore, incorporating IL in NPs-doped PVA membranes for H₂S gas sensing applications will mainly enhance the conduction pathways, which is expected to improve the sensitivity especially at lower operating temperatures. For this study, 5% (weight percent) of IL (glycerol) will be used; following a previous study where the optimum conductivity was achieved at about 5 wt% of ILs/glycerol within a PVA matrix [46][47][48].

Information on gas sensing properties of WO₃, ZnFe₂O₄ and CuFe₂O₄ nanostructures to H₂S gas detection are still limited. Therefore, it is interesting to
investigate the gas sensing properties of these materials based on organic-inorganic nano-composite, which we believe it would be excellent choice towards fulfilling the objectives of this thesis.
Chapter 3: Materials and Methods

This chapter discusses the three stages of fabricating the sensing materials. First, this chapter provides the detailed processes of preparing the WO$_3$, ZnFe$_2$O$_4$ and CuFe$_2$O$_4$ nanoparticles. Then, it shows the production of the sensing materials where these nanoparticles are separately incorporated within a conducting polymer; followed by the methods that have been used to characterize the nanoparticles and the sensing material. Finally, the device fabrication and experimental setup are discussed.

3.1 Synthesis of WO$_3$ nanoparticles

Different experimental methods have been developed and used to prepare WO$_3$ nanomaterials with different morphologies, such as sol-precipitation [22], sol-gel [29], solvo-thermal synthesis [49], precipitation method [50], and others. Among these methods, the sol-gel method is more preferable because it is inexpensive, simple, and flexible in terms of controlling temperature and pressure.

In this study, WO$_3$ nanoparticles were synthesized using a sol-gel method following a protocol that was described by Wang et al [29]. In a typical experiment as illustrated in Fig. 1, 7 g of tungsten (VI) hexachloride WCl$_6$ were slowly added to 100 ml of absolute ethanol (C$_2$H$_5$OH), then stirred for around 10 minutes. Next, 10 mL of 0.5 M ammonia solution were added drop-wisely to the precursor solution using a syringe pump at a rate of 5 ml/h. The solution was kept under continuous stirring and ice cooling for 24 h. The precipitated WO$_3$ NPs were washed by deionized water and centrifuging in order to remove the chloride ions, and on average, a 100 mL suspension containing tungsten oxide nanoparticles containing sol...
was obtained. The obtained nanoparticles were dried in vacuum at 50°C for 12 h, and then calcined at 500°C for 1 h in air. Finally, WO₃ NPs suspension (10 wt%) in deionized water was prepared.

3.2 Synthesis of ZnFe₂O₄ and CuFe₂O₄ nanoparticles

ZnFe₂O₄ and CuFe₂O₄ nanoparticles were prepared separately using the co-precipitation method. In a typical experiment, the required weights of zinc and iron chloride with the ratio of Zn to Fe as 1:2 were dissolved in 100 mL distilled water to get mixed aqueous solutions. Similarly, copper and iron chloride with the ratio of 1:2 were dissolved in 100 mL distilled water. For each sample, 50 mL aqueous solution of 8M NaOH solution was used as the precipitating agent and was added drop wise into each reaction vessel solution at 90°C under continuous magnetic stirring. After 90 minutes, the resultant precipitations were collected and centrifuged at 3000 rpm and then washed with distilled water several times. The obtained ZnFe₂O₄ and CuFe₂O₄ nanoparticles were calcined at 500°C for 2 hours. Finally, NPs suspension (10 wt%) in deionized water for both samples was prepared. The following balanced chemical equations describe this formation of the nanoparticles [51]:

\[
\text{CuCl}_2 \cdot 6\text{H}_2\text{O} + 2 \text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 8 \text{NaOH} \rightarrow \text{CuFe}_2\text{O}_4 + 8 \text{NaCl} + 22 \text{H}_2\text{O} \quad \text{Eq. (1)}
\]

\[
\text{ZnCl}_2 + 2 \text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 8 \text{NaOH} \rightarrow \text{ZnFe}_2\text{O}_4 + 8 \text{NaCl} + 16 \text{H}_2\text{O} \quad \text{Eq. (2)}
\]

3.3 Preparation of the sensing materials

5 g of PVA granules were dissolved in 100 ml of deionized water, and then it was kept under continuous stirring at 90°C until a homogeneous PVA solution 5 wt% (by weight) was obtained. Then, this PVA solution was used to separately
prepare the sensing membranes: (PVA-IL-WO$_3$ NPs) with different WO$_3$ NPs concentrations by volume percent (2.5 vol%, 5 vol% and 7.5 vol% of the WO$_3$ NPs suspension). For each membrane, a PVA stock solution was doped with the desired vol% of WO$_3$ NPs suspension and a 5 vol% ionic liquid (glycerol). The doped polymer solutions were kept under continuous stirring condition at 90°C until transparent and homogenous solutions were obtained. Each of the resulting polymer doped solutions was then casted onto a petri dish to form a thin membrane. The membranes were then placed in a vacuum oven at 50°C for 12 hours, where the excess water was evaporated slowly. Further details on the solution casting method and its experimental details are described elsewhere [46][47][48]. Finally, uniform polymer membranes of around 200 µm thickness were obtained, as shown in Fig. 1.

![Figure 1: Sensing membranes](image)

3.4 Characterization

The crystal structures of the nanoparticles were characterized by X-ray diffraction (XRD) using a Shimadzu 6100 X-ray diffractometer, with a Cu-K$_\alpha$ radiation ($\lambda = 1.5406$ Å). The particle size and morphology of the nanoparticles and the sensing membranes’ surface were characterized using the scanning electron
microscopy (SEM, JEOL, JSM-5600) and transmission electron microscopy (TEM, FEI, Tecnai G20). A more precise measurement of the particle size was obtained using the Zeta-sizer (Malvern Instruments, Model ZEN360, England). The chemical compositions of the nanoparticles were determined by energy-dispersive X-ray spectroscopy (EDS) analysis apparatus on the same SEM. A Solartron 1260A Impedance/Gain-Phase Analyzer was used to investigate the ac impedance of the sensing membranes as a function of frequency (10 – 10^6 Hz) at 25°C. Z-60 and Z-view software package was used to control measurements. Finally, the electrical characterization and conductivity responses of the gas sensors were measured using a Keithley Instruments source measurement unit (KI 236). Control and measurements devices were interfaced to the computer using LABVIEW software.

3.5 Sensor fabrication and experimental setup

A (1 cm × 1 cm) square sample of each polymer membrane: (PVA-IL-9%WO3), (PVA-IL-5%ZnFe2O4) and (PVA-IL-5%CuFe2O4) depicted in Fig. 2, was inserted between two electrodes to form the sensor. The bottom electrode is in the form of a copper sheet (1.5 cm × 1.5 cm) of 0.15 μm thickness, while the top electrode was a (0.8 cm × 0.8 cm) stainless steel grid with a grid size of (250 μm × 250 μm). The three layers were fixed using a suitable adhesion; see Fig. 2(a). Then the fabricated sensor was electrically connected as illustrated in Fig. 2(b). The two electrical electrodes were fixed to the grid and copper contacts by a conductive silver paste. The sensor was then fixed on a test stage (heating element) inside a temperature-controlled Teflon chamber as shown in Figs. 2(c) and 2(d). H2S gas was diluted with N2 gas inside a gas mixer and injected into the chamber with controlled flow rates using Bronkhorst mass flow meters and controller. The test was conducted
inside a fume hood under an atmospheric pressure and at different temperatures 20°C, 40°C, 60°C and 80°C (measured from the copper sheet’s surface). During the test, N₂ flow rate was set to 300 sccm, and the H₂S gas was added with controlled concentrations, a schematic diagram of the experimental setup is shown in Fig. 3. For a gas-sensitivity test, a bias voltage was applied between the sensor electrodes, and its electrical current signal was measured with reference to time at different H₂S gas concentrations.

Figure 2: (a) Schematic diagram of the sensor and (b) The electrical measurement circuit. (c) and (d) Picture of the gas test chamber (the sensor is set inside the test chamber)
Figure 3: Experimental setup

1: Gas cylinders
2: Bronkhorst mass flow meters
3: Bronkhorst mass flow controller
4: Keithley Instruments source measurement unit (KI236)
5: Teflon gas test chamber
Chapter 4: Results and Discussion

The nanoparticles were first synthesized and then characterized to study their structural and morphological characteristics. Then, the sensing materials (where the nanoparticles are incorporated within the organic polymer membranes) were produced and electrically characterized. Finally, the gas sensing performance and gas sensing mechanism were investigated.

4.1 Structural and morphological characterization

Powder samples of the WO₃, ZnFe₂O₄ and CuFe₂O₄ nanoparticles were characterized by X-ray diffraction (XRD); the results are shown in Fig. 4. The position and relative intensity of diffraction peaks of the WO₃ sample were indexed according to JCPDS card No. 83-0950, and they match well with XRD fundamental peaks of the monoclinic structure. The peaks of ZnFe₂O₄ and CuFe₂O₄ samples match well with XRD fundamental peaks of cubic spinel-structure, according to JCPDS card No. 22-1012 and JCPDS card No. 01-077-0010, respectively.

The chemical contents of the samples were investigated by the (EDS) spectrum of the produced nanoparticles, as shown in Fig. 5. From the EDS spectra, it can be confirmed the presence of W and O in the synthesized sample of WO₃ nanoparticles (Fig. 5(a)). The EDS results also confirm the presence of both Zn and Fe elements in the ZnFe₂O₄ sample (Fig. 5(b)), as well as Cu and Fe in the CuFe₂O₄ sample (Fig. 5(c)). It should be noted the presence of Carbon (C), and this is true due to the use of carbon tape on the sample stub.
Figure 4: XRD characterization of (a) WO$_3$ NPs, (b) ZnFe$_2$O$_4$ NPs, and (c) CuFe$_2$O$_4$ NPs.
Figure 5: EDS spectra of (a) WO$_3$ NPs, (b) ZnFe$_2$O$_4$ NPs, and (c) CuFe$_2$O$_4$ NPs
Next, the morphologies of the nanoparticles were characterized by the SEM imaging as shown in Fig. 6, which shows agglomerates of these nanoparticles.

Figure 6: SEM images of (a) WO₃ NPs, (b) ZnFe₂O₄ NPs, and (c) CuFe₂O₄ NPs
A representative SEM image of the sensing membrane’s surface was taken for (PVA-IL-7.5%WO$_3$) membrane, see Fig. 7. The image reveals a uniform distribution of the nanoparticles inside the membrane.

![SEM Image](image.png)

**Figure 7:** SEM image of the (PVA-IL-7.5%WO$_3$) membrane

More precise measurement of the WO$_3$ nanoparticles size was determined using the Zeta-sizer. Figure 8 shows that the average particle size was 13.1 ± 3.8 nm. Moreover, the nanoparticle size of ZnFe$_2$O$_4$ and CuFe$_2$O$_4$ samples were estimated using their TEM images. The images demonstrate that the nanoparticles are uniform in size. The estimated sizes in each sample were 5 ± 1.4 nm and 7 ± 2.1 nm for ZnFe$_2$O$_4$ NPs (Fig. 9(a)), and CuFe$_2$O$_4$ NPs (Fig. 9(b)), respectively.
Figure 8: Size distribution of the WO$_3$ NPs measured using the Zeta sizer

Figure 9: TEM images of (a) ZnFe$_2$O$_4$ NPs, (b) CuFe$_2$O$_4$ NPs
4.2 Electrical properties

4.2.1 Impedance model of the sensing membranes

The AC impedance measurement of the sensing membrane provides a quantitative measure of the resistive and capacitive impedance as given by the following equation:

\[ Z(\omega) = Z'(\omega) - j Z''(\omega) \]  
Eq. (3)

where, \( Z'(\omega) \) and \( Z''(\omega) \) are the real and imaginary parts of the impedance, respectively. A small piece of each sensing membrane was placed between two stainless-steel electrodes, the top electrode’s area is \( 9.61 \times 10^{-6} \text{ m}^2 \) while the area of the bottom electrode is large enough to facilitate electrode alignment. Then, the AC impedance measurement was taken as a function of the frequency range from 10 to \( 10^6 \) Hz. Figure 10 shows the AC impedance spectrum (Nyquist plots) of the sensing membranes (PVA-IL-5%WO\(_3\)), (PVA-IL-5%ZnFe\(_2\)O\(_4\)) and (PVA-IL-5%CuFe\(_2\)O\(_4\)), measured at 25°C, where frequency is an implicit function. The two semicircles shown in the figures denoting that the membranes can be represented by two parallel RC circuits connected in series as shown in Fig. 11. The smaller semicircle (as pointed by an arrow) occurs at higher frequencies. It can be related to the resistive and capacitive components (\( R_m \) and \( C_m \)) of the membrane, and can be assigned to the charge transfer process (kinetic process) that occurs at high frequencies [47]. The larger semicircle which occurs at low frequencies corresponds to the interfacial charge transfer resistance and double layer capacitance (\( R_{ct} \) and \( C_{dl} \)), due to the contribution of mass migration process (diffusion) [47]. Table 1 provides the estimated values of \( R_m, C_m, R_{ct} \) and \( C_{dl} \).
Figure 10: AC impedance spectrum (Nyquist plots) measured at 25°C for: (a) (PVA-IL-5%WO$_3$ NPs), (b) (PVA-IL-5%ZnFe$_2$O$_4$ NPs) and (c) (PVA-IL-5%CuFe$_2$O$_4$ NPs)
Table 1: AC impedance results for the sensing membranes

<table>
<thead>
<tr>
<th>Sensing material</th>
<th>$R_m$ (Ω)</th>
<th>$C_m$ (F)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$C_{dl}$ (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA-IL-5%WO$_3$</td>
<td>2.31 E+04</td>
<td>1.42 E-11</td>
<td>3.60 E+06</td>
<td>1.09 E-07</td>
</tr>
<tr>
<td>PVA-IL-ZnFe$_2$O$_4$</td>
<td>1.73 E+05</td>
<td>1.25 E-11</td>
<td>1.05 E+07</td>
<td>2.97 E-09</td>
</tr>
<tr>
<td>PVA-IL-CuFe$_2$O$_4$</td>
<td>7.57 E+04</td>
<td>1.23 E-11</td>
<td>1.59 E+06</td>
<td>3.25 E-09</td>
</tr>
</tbody>
</table>

4.2.2 I-V measurements

The operating temperature has a significant effect on the gas sensing performance of the sensor. Therefore, the electrical conductance of each sensor was measured at different operating temperatures. Figure 12 shows the current-voltage (I-V) characteristics of the sensors obtained at (20°C, 40°C, 60°C and 80°C) just before performing the sensitivity tests. Typical I-V curves were obtained for the three sensing membranes as shown in Fig. 12. The representative I-V curves of the (PVA-
IL-5%WO₃) sample (Fig. 12(a)) are approximately linear, while a small nonlinearity is observed in I-V curves of (PVA-IL-5%ZnFe₂O₄) sample (Fig. 12(b)), and (PVA-IL-5%CuFe₂O₄) sample (Fig. 12(c)). Such I-V characteristics with small nonlinearity indicate low barrier between the contact and polymer membrane, which ensure easy transport of charge carriers to contact upon exposure with H₂S gas [52].

Based on these I-V curves, a constant voltage of 1 V was applied to the (PVA-IL-WO₃) sensor’s electrodes for gas sensitivity tests, and 2 V was used for (PVA-IL-5%ZnFe₂O₄) and (PVA-IL-5%CuFe₂O₄). Thus, the electrical response currents were measured as a function of time and gas concentration.
Figure 12: I-V curves as a function of temperature of the sensing membranes: (a) (PVA-IL-5%WO₃ NPs), (b) (PVA-IL-5%ZnFe₂O₄ NPs) and (c) (PVA-IL-5%CuFe₂O₄ NPs)
Figure 13 shows the plots of the natural logarithm of each sensor’s resistance versus the inverse of the temperature. Negative temperature coefficients of the resistances were revealed from these plots, where the resistance decreases as the temperature increases. Such decrease of the resistance with the temperature has been observed previously for different systems, and could be assigned to charge transport between metallic islands that is dominated by thermally assisted tunneling [53][54][55].

The activation energy (Eₐ) of the three sensing materials were determined based on these results and using the Arrhenius equation [56]:

\[ R = R_o e^{\frac{-E_a}{K_B T}} \]  

Eq. (4)

where, \( R_o \) is a constant, \( K_B \) is Boltzmann constant, and \( T \) is temperature. The activation energy values were determined to be 0.545 eV, 0.42 eV and 0.58 eV for (PVA-IL-5%WO₃ NPs), (PVA-IL-5%ZnFe₂O₄ NPs) and (PVA-IL-5%CuFe₂O₄ NPs) membranes, respectively.
Figure 13: The dependence of the natural logarithm of the resistance on the inverse of temperature for: (a) (PVA-IL-5%WO$_3$ NPs), (b) (PVA-IL-5%ZnFe$_2$O$_4$ NPs) and (c) (PVA-IL-5%CuFe$_2$O$_4$ NPs)
4.3 Gas sensing properties

Figure 14 shows representative responses of the sensors as functions of time and H₂S gas concentrations, measured at 80°C. The results reveal that the resistance changes in response to H₂S gas for all the three sensors, translated as a change in the measured current at a constant voltage. In addition, the response magnitudes are directly proportional to the gas concentration, in other words, the amount of change in the measured current increases as the gas concentration increases. Moreover, the results clearly show that the resistance almost recovers its initial value when the flow of H₂S gas is stopped, which indicates the reversibility of these sensors.

Small noise fluctuations were observed in the responses; for example, in the (PVA-IL-WO₃) sensor’s response (Fig. 14(a)), noise fluctuation was around 0.4 µA. Nevertheless, the sensing response is the variation in the electrical current signal (i.e. measured from the maxima or the minima of noise-signal). This variation in electrical current is dependent on H₂S concentration, where it changes in the figure from 0.15 µA (at 10 ppm) to 1.64 µA (at 300 ppm). Moreover, the variations of noise signals during response measurements were investigated for a number of cycles measured using a voltage of 1 V for the (PVA-IL-5%WO₃), and 2 V for both (PVA-IL-ZnFe₂O₄) and (PVA-IL-CuFe₂O₄) at blank sample N₂ gas (300 sccm) at 80°C, as shown in Fig. 15. The figure reveals limited variations in the noise with average values of 1.0 × 10⁻⁶ A, 1.30 × 10⁻⁶ A and 1.62 × 10⁻⁶ A for the representative sensors: (PVA-IL-5%WO₃) Fig. 15(a), (PVA-IL-5%ZnFe₂O₄) Fig. 15(b) and (PVA-IL-5%CuFe₂O₄) Fig. 15(c), respectively. These results indicate that the present sensors exhibit reasonable performance as they show low noise signal.
Figure 14: Representative current responses of the sensors as function of the time and H$_2$S concentrations, measured at 80°C, for: (a) (PVA-IL-5%WO$_3$ NPs), (b) (PVA-IL-5%ZnFe$_2$O$_4$ NPs) and (c)(PVA-IL-5%CuFe$_2$O$_4$ NPs)
Figure 15: The variation of noise signals as a function of measurement cycle at blank sample N₂ gas (300 sccm) at 80°C for: (a) (PVA-IL-5%WO₃), (b) (PVA-IL-5%ZnFe₂O₄) and (c) (PVA-IL-5%CuFe₂O₄)
The gas-sensing response (S%) is defined according to the following equation:

\[ S (%) = \left( \frac{I_g - I_o}{I_o} \right) \times 100 \tag{5} \]

where, \( I_g \) and \( I_o \) are the electrical current of the sensor in presence of the target gas and nitrogen gas only (reference current), respectively. Figure 16 shows the responses of (PVA-IL-WO\(_3\) NPs) with WO\(_3\) NPs concentrations of 2.5%, 5% and 7.5% as functions of temperature and H\(_2\)S gas concentrations. These results reveal that the response increases with the increase in temperature and H\(_2\)S gas concentration, and the highest responses were obtained at 80°C. It is very interesting to notice a reasonable response at low temperature of 20°C for all the three sensors, as depicted in Fig. 16. When WO\(_3\) NPs concentration increases from 2.5% to 5%, the response increases, while no further increase happens when the concentration increases to 7.5% (especially at 80°C). All the sensors showed good sensitivity to H\(_2\)S gas; thus, any of them can be used for sensitive detection to H\(_2\)S. However, at 80°C, the 5% sensor showed the highest response and its best linearity of response. In terms of linearity of response, only the 7.5% sensor showed linear responses at all different temperatures, while the 5% sensor has its best linearity at 80°C. These tests also showed that the lowest detection limit was 10 ppm starting from 60°C. The low operating temperature indicates the low-power consumption of the sensor. These sensors exhibit excellent sensing properties compared to the previously reported sensors (based on WO\(_3\) nanostructures) at similar temperatures for H\(_2\)S gas sensors [57][58].
Figure 16: Sensor’s response for H₂S gas at different temperatures for WO₃ based sensors: (a) (PVA-IL-2.5%WO₃ NPs), (b) (PVA-IL-5%WO₃ NPs) and (c) (PVA-IL-7.5%WO₃ NPs)
Figure 17 shows the response (S%) of (PVA-IL-5%ZnFe$_2$O$_4$) and (PVA-IL-5%CuFe$_2$O$_4$) sensors as a function temperature and H$_2$S concentration. The results reveal that ZnFe$_2$O$_4$ NPs based sensor has higher response than the CuFe$_2$O$_4$ NPs based sensor, at all different operating temperatures and H$_2$S concentrations. Both sensors showed reasonable response at low temperatures, as low as 40°C, and at low H$_2$S concentrations of 10 ppm for ZnFe$_2$O$_4$ based sensor (Fig. 17(a)), and 25 ppm for CuFe$_2$O$_4$ based sensor (Fig. 17(b)). For example, at 300 ppm and 80°C, the response of ZnFe$_2$O$_4$ NPs based sensor is 64.4% while 39.1% for CuFe$_2$O$_4$ NPs based sensor. This difference can be assigned to response saturation of CuFe$_2$O$_4$ NPs sensor with increasing the H$_2$S concentrations and temperature. The reason behind this saturation can be assigned to that the chemical affinity between copper and sulfur is higher than the affinity between zinc and sulfur [59]. This can be further rationalized by considering the solubility product constant (KSP) which is higher for CuS ($1 \times 10^{-36}$) compared to ZnS ($1 \times 10^{-23}$) [59], although this constant is for the solubility of a salt in water solution. As a result, H$_2$S is adsorbed more strongly onto CuFe$_2$O$_4$ NPs than ZnFe$_2$O$_4$ NPs leading to an increase in the poisoning rate of H$_2$S on CuFe$_2$O$_4$ NPs sensor as H$_2$S gas concentration increases, which causes fast response saturation. Therefore, it can be said that, the response increases with temperature and gas concentration for ZnFe$_2$O$_4$ based sensor, while it saturates at 60°C and 200 ppm for CuFe$_2$O$_4$ based sensor.
Figure 17: Sensor’s response for H$_2$S gas at different temperatures for: (a) (PVA-IL-5\%ZnFe$_2$O$_4$) and (b) (PVA-IL-5\%CuFe$_2$O$_4$)
The reduction in operating temperature is a reduction in the power consumed by the heater, therefore, it was found that reducing the operating temperature from 200°C to 80°C saves approximately 89% of power consumed by the heater used in this work. The power reduction was calculated as follows:

\[ P_{\text{reduction}} = \left( \frac{P_{200^\circ C} - P_{80^\circ C}}{P_{200^\circ C}} \right) \times 100 \quad \text{Eq. (6)} \]

where \( P_{200^\circ C} \) and \( P_{80^\circ C} \) are the power consumed by the heater to heat it up to 200°C and 80°C, respectively. \( P_{200^\circ C} = 33.75 \text{ W} \) and \( P_{80^\circ C} = 3.75 \text{ W} \).

The sensor’s response time is known as the time taken by the sensor to reach 90% of its maximum response. Figure 18 shows the average response times of the (PVA-IL-WO\(_3\)) based sensors. Each point in the figure is the average response times at different H\(_2\)S concentrations (for a particular WO\(_3\) NPs concentration). The error bars are taken as one standard deviation. The figure shows decrease in the response time when nanoparticles concentration increases from 2.5% to 5%. The minimum response time is 19.1 ± 3.4 s at concentration of 5%, which is very close to the response time of the 7.5% sensor (within the error bars). These response times are considered short when compared with the previously reported response times in the literature [58][60][61]. While, the average response times for ZnFe\(_2\)O\(_4\) based sensor and CuFe\(_2\)O\(_4\) based sensor are 20.1 ± 6.2 s and 21.9 ± 4.3 s, respectively. These response times are considered short response times compared with other reported H\(_2\)S sensors [62][63][64].
The (PVA-IL-WO₃) sensors were further investigated for their reproducibility and stability. Figure 19(a) shows a representative response of the reproducibility test of the (PVA-IL-5%WO₃) sensor, where 300 ppm H₂S gas was injected and released successively for five cycles at 80°C. The figure reveals almost no apparent change in the response over the 5 cycles. These tests were consistent for all measured samples. It should be noted here that the reference electrical currents in Figs. 14(a) and 19(a) are different since they belong to different samples. Nevertheless, the difference in the base current has no effect on sensor performance since what matter is the difference in the electrical current (see Eq. 5). Figure 19(b) shows error bars of the (PVA-IL-5%WO₃) sensor’s response when exposed to 300 ppm H₂S at 80°C for five cycles successively. The largest standard deviation was lower than 3%, which indicates an excellent reproducibility of the sensor.
Figure 20 shows the response signal of the (PVA-IL-5%CuFe₂O₄) sensor for 300 ppm H₂S gas diluted with air (99.999%) at 80°C. The figure reveals that the response curve is similar to that for H₂S diluted with N₂ gas, and the response is stable as well as reproducible.

Figure 19: Reproducibility analysis of (PVA-IL- 5%WO₃ NPs) sensor by successively exposing it to 300 ppm of H₂S gas at 80°C: (a) Reproducibility results and (b) Error bars of the sensor’s response when exposed to 300 ppm H₂S at 80°C
Figure 20: Response signal of the (PVA-IL-5%CuFe₂O₄) sensor for 300 ppm H₂S gas diluted with air (99.999%) at 80°C

The long-term stability of (PVA-IL-5%WO₃ NPs), (PVA-IL-5%ZnFe₂O₄ NPs) and (PVA-IL-5%CuFe₂O₄ NPs) sensors was investigated, where the response of each sensor was tested continuously over (20-25) days at 300 ppm H₂S gas and 80°C, as shown in Fig. 21. The highest deviation of the responses was less than 5%, indicating an excellent long-term stability of these sensors.
Figure 21: Long-term stability of the sensing membranes: (a) (PVA-IL-5%WO3 NPs), (b) (PVA-IL-5%ZnFe2O4 NPs) and (c) (PVA-IL-5%CuFe2O4 NPs) to 300 ppm H₂S gas at 80°C
The selectivity of the sensor to H$_2$S gas was also investigated. Figure 22 shows the response signals of the representative (PVA-IL-5%WO$_3$), (PVA-IL-5%ZnFe$_2$O$_4$) and (PVA-IL-5%CuFe$_2$O$_4$) sensors against H$_2$S (300 ppm), C$_2$H$_4$ (50000 ppm) and H$_2$ (50000 ppm) gases, measured at 80°C. The figure reveals weaker responses of the sensors towards H$_2$ and C$_2$H$_4$ gases compared to H$_2$S gas. Furthermore, the sensors did not show any response to C$_2$H$_4$ and H$_2$ gases when measured at temperatures below 80°C, and at concentrations equal or less than 50000 ppm. Therefore, the sensors have relatively high selectivity to H$_2$S gas, which make them promising for practical industrial applications.

![Figure 22: Selectivity histogram of the sensors when exposed to H$_2$S, C$_2$H$_4$ and H$_2$ gases, measured at 80°C](image-url)
The dependence of the sensor response on relative humidity inside the test chamber at 80 °C and 300 ppm for ZnFe$_2$O$_4$ based sensor is shown in Fig. 23. The figure reveals reasonable drop in the response when the relative humidity increases to 50%. Nevertheless, dramatic decrease in the response is observed for higher humidity. The humidity dependency results from the presence of PVA layer that is likely to absorb H$_2$O [10]. All the sensors were fabricated using this polymer matrix, as a result, they are best operational at low values of humidity.

Figure 23: Dependence of the sensors’ response on relative humidity inside the test chamber at 80°C and 300 ppm for ZnFe$_2$O$_4$ based sensor
4.4 Gas sensing mechanism

The change in the electrical conductivity of metal oxides-based semiconductors governs their gas-sensing performance. The exact fundamental gas sensing mechanisms are still controversial. A common hypothesis suggests that trapping of electrons at adsorbed molecules result in band bending which is mainly responsible for conductivity change of the sensing material once it is exposed to the gas [62]. Understanding the sensing mechanism for WO₃, ZnFe₂O₄ and CuFe₂O₄ nanoparticles based sensors should consider: (i) the high surface area of the WO₃ nanoparticles which result in more reactive sites, and (ii) the adsorbed oxygen species (O₂⁻, O²⁻ and O⁻) onto the nanoparticle surface. When the sensor is exposed to H₂S gas, the following reactions take place on the surface [61][66][67]:

\[
\begin{align*}
\text{H}_2\text{S} + 3 \text{O}^- \text{(ads)} & \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 3\text{e}^- & \text{Eq. (6)} \\
\text{H}_2\text{S} + 3 \text{O}^{2-} \text{(ads)} & \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 6\text{e}^- & \text{Eq. (7)}
\end{align*}
\]

According to the above equations, when the adsorbed oxygen interacts with H₂S gas, electrons are released and cause the increase in the conductivity (decrease in resistance) [35]. When the flow of H₂S is stopped, the number of free electrons is reduced which decreases the conductivity of the sensor causing a reversible sensing behavior.

It should be mentioned that the presence of glycerol in the matrix of the sensor material described herewith facilitates the conductivity throughout the mechanism described above [48]. The proposed sensors assembly, therefore, provides an enhanced pathway towards the sensing of H₂S gas by virtue of the high surface area of nanoparticles and glycerol as an ionic liquid, while the use of a non-expensive PVA provides a convenient matrix to accommodate these ingredients.
4.5 A comparison on gas-sensing performance with literature-reported sensors

Table 2 shows a comparison of the gas sensing-performance between our proposed sensors and several H₂S sensors based on oxides materials and conductive polymers that have been reported in the literature. These sensors share the same sensing principle (conductivity impedance), thus, the signal conditioning circuitry of such sensors is relatively simple, which means low-cost and simple production. Therefore, the most important criteria to evaluate and compare the performance of these sensors are: operating temperature, response time, detection limit, response, selectivity, and flexibility. Among these sensors, our sensors show a relatively excellent performance; as they operate at low temperatures with a relatively fast response and they are flexible. The sensors with lower detection-limits than our sensors suffer from either high operating temperatures or long response times.

Fortunately, our sensors have successfully met our expectations and goals of enhancing H₂S sensors by producing sensitive and selective sensors with lower operating temperatures, lower power consumption, more flexible, and faster response.
<table>
<thead>
<tr>
<th>Sensor/material</th>
<th>Operating temperature (°C)</th>
<th>Response time (s)</th>
<th>Detection limit (ppm)</th>
<th>Response</th>
<th>Selectivity to H$_2$S/Interfering gases</th>
<th>Flexibility</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our proposed sensors</td>
<td>20 – 80 Optimum: 60 &amp; 80</td>
<td>19-22</td>
<td>10 – 300 ppm</td>
<td>S%: 65% at 300 ppm</td>
<td>Very good/ H$_2$, C$_3$H$_4$</td>
<td>Flexible membranes</td>
<td></td>
</tr>
<tr>
<td>Polyaniline Nanofiber Composites with Metal Salts</td>
<td>25</td>
<td>66</td>
<td>10 ppm</td>
<td>S%: 20% at 10 ppm</td>
<td>-</td>
<td>Rigid thin films</td>
<td>[68]</td>
</tr>
<tr>
<td>Polyaniline nanowires-gold nanoparticles hybrid network</td>
<td>25</td>
<td>120</td>
<td>Sub-ppm</td>
<td>13.78% per ppb</td>
<td>Good/ NH$_3$</td>
<td>Electrodeposition bridging the gap between the gold micro-electrodes</td>
<td>[69]</td>
</tr>
<tr>
<td>Networks of WO$_3$ nanoparticles</td>
<td>300</td>
<td>&gt;2</td>
<td>10 – 200 ppm</td>
<td>S%: &gt;100% at 50 ppm</td>
<td>-</td>
<td>Drop cast or spin cast onto the micro-hotplate</td>
<td>[70]</td>
</tr>
<tr>
<td>Cu-doped ZnO nanocrystalline films</td>
<td>100 – 300 Optimum: 250</td>
<td>&gt;60</td>
<td>2.5 – 10 ppm</td>
<td>S%: 75% at 10 ppm</td>
<td>High/ CO$_2$, H$_2$, NH$_3$, SO$_2$</td>
<td>Rigid thin films</td>
<td>[71]</td>
</tr>
<tr>
<td>α-Fe$_2$O$_3$ nanoparticles</td>
<td>100 – 400 Optimum: 300</td>
<td>30</td>
<td>Sub-ppm</td>
<td>Rg/Ra: 1.25 at 6.05 ppm</td>
<td>-</td>
<td>Pasted/coated on aluminum tube</td>
<td>[72]</td>
</tr>
<tr>
<td>Partially inverse spinel zinc ferrite</td>
<td>200 – 360 Optimum: 260</td>
<td>8</td>
<td>1 – 100 ppm</td>
<td>Rg/Ra: 64 at 100 ppm</td>
<td>High/ Ethanol, Acetone, Formaldehyde, Ether, Butylamine</td>
<td>Drop casting ZFO powder on a gold-pattered alumina substrate.</td>
<td>[73]</td>
</tr>
</tbody>
</table>

Table 2: Comparison of the gas sensing performance of several conductivity impedance-based H$_2$S gas sensors.
Chapter 5: Conclusion and Future Work

5.1 Conclusion

The aim of this thesis work was basically to develop H₂S gas sensors with enhanced flexibility, lower operating temperature and high sensitivity and selectivity, in order to meet the compelling demand for a higher performance and lower power consumption. Therefore, sensors were fabricated based on organic-inorganic nano-composites.

The sensors were prepared by incorporating WO₃, ZnFe₂O₄ and CuFe₂O₄ nanoparticles separately in PVA-IL solutions. The casted doped-solutions form membranes which were tested, and their electrical and gas-sensing properties were investigated.

The results of this study showed that the proposed sensors possess very good sensing properties. The best response of all the sensors to H₂S gas was obtained at 80°C, yet a reasonable response was noticed at a low operating temperature of 20°C-40°C. This reduction in operating temperature saves 89% of the power consumed by the heater to heat up the sensor. The detection limit of the sensors was 10 ppm for WO₃ and ZnFe₂O₄ based sensors, while 25 ppm for CuFe₂O₄ based sensor. The results showed a reasonable average response time of 19-22 s, which was in good agreement with previously reported work in the field of H₂S gas sensing applications. Moreover, the sensors exhibited excellent reproducibility and stability, and were identified to be selective to H₂S gas. In addition to the aforementioned qualities, the sensors were characterized by their ease of fabrication, flexibility and low-power
consumption, thus, these sensors have the potential to be utilized for monitoring and control applications of H₂S.

5.2 Future Work

This work is a part of a research project, and the effect of humidity is well considered, therefore, new materials are to be developed in order to overcome the humidity-dependency of the current sensors. In addition, further enhancement is needed to reduce the threshold detection limit of the sensor down to sub-ppm gas concentrations, and this could be achieved by studying and investigating different surface-morphologies of the sensing materials.
References


[38] J.F. Morin, N. Drolet, Y. Tao, M. Leclerc, Syntheses and characterization of electroactive and photoactive 2,7-carbazolenevinylene-based conjugated.


[73] [f] Jiangtao Wu, Daojiang Gao, Ting Sun, Jian Bi, Yan Zhao, Zhanglei Ning, Guangyin Fan, Zhaoxiong Xie. Highly selective gas sensing properties of partially inversed spinel zinc ferrite towards H$_2$S, Sensors and Actuators B 235 (2016) 258–262.
List of Publications


Appendix

Table 3: H$_2$S concentrations and their corresponding symptoms/effects

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Symptoms/Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00011-0.00033</td>
<td>Typical background concentrations</td>
</tr>
<tr>
<td>0.01-1.5</td>
<td>Odor threshold (when rotten egg smell is first noticeable to some). Odor becomes more offensive at 3-5 ppm. Above 30 ppm, odor described as sweet or sickeningly sweet.</td>
</tr>
<tr>
<td>2-5</td>
<td>Prolonged exposure may cause nausea, tearing of the eyes, headaches or loss of sleep. Airway problems (bronchial constriction) in some asthma patients.</td>
</tr>
<tr>
<td>20</td>
<td>Possible fatigue, loss of appetite, headache, irritability, poor memory, dizziness.</td>
</tr>
<tr>
<td>50-100</td>
<td>Slight conjunctivitis (&quot;gas eye&quot;) and respiratory tract irritation after 1 hour. May cause digestive upset and loss of appetite.</td>
</tr>
<tr>
<td>100</td>
<td>Coughing, eye irritation, loss of smell after 2-15 minutes (olfactory fatigue). Altered breathing, drowsiness after 15-30 minutes. Throat irritation after 1 hour. Gradual increase in severity of symptoms over several hours. Death may occur after 48 hours.</td>
</tr>
<tr>
<td>100-150</td>
<td>Loss of smell (olfactory fatigue or paralysis).</td>
</tr>
<tr>
<td>200-300</td>
<td>Marked conjunctivitis and respiratory tract irritation after 1 hour. Pulmonary edema may occur from prolonged exposure.</td>
</tr>
<tr>
<td>500-700</td>
<td>Staggering, collapse in 5 minutes. Serious damage to the eyes in 30 minutes. Death after 30-60 minutes.</td>
</tr>
<tr>
<td>700-1000</td>
<td>Rapid unconsciousness, &quot;knockdown&quot; or immediate collapse within 1 to 2 breaths, breathing stops, death within minutes.</td>
</tr>
<tr>
<td>1000-2000</td>
<td>Nearly instant death</td>
</tr>
</tbody>
</table>