

**Magnetic, luminescence and gas sensing properties of
various zinc oxide nanostructures: The influence of surface
modification by gold on the gas sensing properties**

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Dedicated to the memory of my late grandfather

Ndabeni Hans Makhubela

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ABSTRACT

Various morphologies of zinc oxide (ZnO) including particles, spheres, flowers and sheets achieved by varying the pH from 7 to 13 were successfully synthesized using the microwave-assisted hydrothermal method. Effect of pH and annealing on morphological, optical and magnetic properties was investigated. Annealing altered the morphology of the ZnO structures obtained at pH levels of 9 and 13 whereby spheres and sheets were transformed into particles and platelets, respectively. The decrease in surface area and porosity of the ZnO structures was also observed with post-annealing. Green emissions assigned to oxygen vacancies (V_O) dominated the PL spectra of the as prepared ZnO structures. Whereas for annealed ZnO structures, green emissions only dominated the PL spectra of the ZnO structures produced at lower pH levels (pH 7 and 9) while those of the structures obtained at higher pHs were dominated by blue emissions assigned to zinc interstitials (Zn_i). The sensing performance of the ZnO nanostructures to CO, CH₄, NO₂, H₂ and NH₃ at temperatures ranging from room temperature (RT) to 450°C was investigated.

The study conducted on the influence of irradiation time to structural, luminescence, magnetic and sensing properties of ZnO nanorods revealed an increase in the surface area of the rods which correlated with the decrease of the lengths and widths with increasing irradiation time. High sensing response to CO at 350 °C was achieved. Surface defects on the ZnO nanorods were attributed for the high response to CO through the confirmation from PL and EPR analyses.

ZnO and Au loaded ZnO nanorods were also synthesized through the microwave-assisted hydrothermal method to study the effect of Au loading on sensing properties. The distribution of the Au nanoparticles on the surface of the ZnO nanorods was controlled by varying the Au concentration as 0.5, 1, 1.5, 2, 2.5 wt%. XRD, SEM, TEM and X-ray photoelectron spectroscopy (XPS) studies confirmed the presence of the Au nanoparticles on the ZnO nanorods surface. It was found that the sensors were selective to NH_3 and the 0.5 wt% sensor showed the highest response to NH_3 as compared to the other sensors. The mechanisms involved in the improved sensing response of the Au modified ZnO sensors were explained in detail.

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CHAPTER 1

Introduction

1.1 Overview

Various harmful and toxic gases are being emitted from different sources in people's living and working spaces and they are a threat to human life and the environment. The field of semiconductor based gas sensors experienced a great expansion and turned to be one of the most active research areas within the sensor community in the late 1980s. Since then, there has been a very high demand for high performance gas sensors with high sensitivity and selectivity, faster response, together with low power consumption and high device reliability. Researchers world-wide have therefore devoted a lot of efforts aiming at producing new sensing materials [1]. Currently, development of semiconductor metal oxide (SMO) based sensing materials is strongly dependent on the changes provided by new nanoscale technologies. Nanoscience which enables manipulation of matter at the molecular level has in fact become a central generator for innovations in materials processing. A wide range of studies have been focused on the production of new materials with unique structures and properties to enhance gas sensors performance in the nanoscale [2].

Among several types of gas sensors that have been developed lately, chemoresistive gas sensors have attracted extensive attention as they use SMOs as their sensing layer or material. These sensors are used in a wide range of

applications, such as environmental monitoring, fire detection, emission monitoring, and health monitoring [3, 4]. This technology has a huge potential in the development of sensor devices with unique properties and improved performance.

Nanostructured SMOs have been widely used in various applications including photocatalysts [5, 6], biosensors [7], and solar cells [6, 8] because of their unique optical, and electrical properties. They have also shown a lot of potential in gas sensing applications owing to their high sensitivity to several harmful gases, easy fabrication methods and low cost [9-12]. In addition, they are suited for sensing due to their high surface area as well as their good thermal stabilities under different operating conditions [13].

There are various SMO nanomaterials that have been fabricated for the detection of combustible and toxic gases such as CH_4 , H_2 , CO and volatile organic compounds (VOC's) [14]. SnO_2 [15, 16], WO_3 [17, 18], TiO_2 [19, 20] and ZnO [21] are some of the SMO employed for gas sensing. Among these oxides, ZnO is regarded as an important gas sensing material. This is due to its good thermal and physical stability, high electron mobility, low toxicity and affordability. It can be manufactured in various classes of morphology such as nanorods [22], nanowires [23], nanoparticles [24], nanospheres [25], nanoflowers [26], etc. Among several synthesis methods [27-29] used to prepare ZnO nanostructures, microwave-hydrothermal method is of interest owing to its simplicity of operation, low-energy consumption potential large scale industrialization. In a typical microwave-assisted method, variation of

preparation synthesis conditions such as reactants pH [30], annealing treatment [31], reaction time [22, 32] and additives such as surfactants, anions, polymers etc. [33] it is regarded as the most popular synthetic route of manipulating the morphology of the ZnO nanostructures.

Gas sensors based on nanostructured ZnO provide several advantages over current technologies for detecting both oxidation and reducing gases, such as low cost, long lifetime, and high selectivity and sensitivity [24]. At a present moment, the preparation and processing of nanostructured ZnO for sensing applications is limited in the ability to control the structural and morphological properties [14]. In addition, it has been established through various experiments that the size and morphology of ZnO nanostructures can affect its sensing performance [14, 34]. It has also been recently reported that both the surface state and morphology of the metal-oxides including ZnO play a major role in gas sensing performance [14, 35]. Hence, the ability to control their structures/morphology and size is essential for the improvement of their gas sensing capabilities. For instance, Hamedani *et al.* [14] synthesized ZnO nanorods, nanoparticles and flower-like morphologies and subjected them to the same concentration of CO, CH₄ and ethanol. It was discovered that the nanorods and nanoparticles were selective to CH₄ and ethanol, while the flower-like morphology was highly selective to CO. Liao *et al.* [36] on the other hand studied the dependence of gas sensitivity to the size of ZnO nanorods and have shown that the sensitivity of the thinner nanorods was higher than the thicker ones.

One of the important ways to improve the sensitivity, stability and selectivity of SMOs which has been used by several researchers is incorporation of noble metal nanoparticles on their surface [37-39]. Several noble metal nanoparticles including Au, Pt, Ag, and Pd have been used to modify the surface of SMO to improve their sensing capabilities [39-41]. Surface modification of the SMO with noble metal nanoparticles accelerates the sensing reactions on the surface of the semiconductor, thus improving response rate, response and recovery time, sensitivity and also selectivity [9]. For example, Hosseini *et al* [42] showed that Au modified ZnO nanorods showed higher response and selectivity to H₂S compared to unmodified ZnO nanorods.

1.2 Problem statement

Some of our everyday activities lead to release of gases. Some of these gases are dangerous to human life and to the environment. The human nose is regarded as highly sensitive; however, it is not sensitive to all the gases as some of these gases are odourless and colourless. Hence a reliable device which can detect gas leakage at very low concentrations is needed. ZnO based gas sensors have received much attention for being sensitive to various gases and for having a high surface area. However, the downside is that ZnO gas sensors suffer from poor sensitivity, selectivity and instability regardless of their high surface area. In an attempt to address these limitations several researchers have opted to dope or incorporate noble metal

nanoparticles in the surface of SMOs to improve sensing properties. Furthermore, methods and conditions of preparation have been found to have great effects on the microstructural properties of the materials, such as crystal size, orientation and morphology, and aspect ratio which strongly affect the sensing properties of ZnO. Hence, it is essential to develop a facile method to prepare high quality ZnO nanostructures with uniform morphologies. On the other hand, surface defects in ZnO are extremely important in gas sensing as they produce significant changes in the surface conductivity owing to variations in charge transfer and band bending caused by adsorbate species. Therefore, understanding defect structure of ZnO is of paramount importance.

Even though surface modified nanostructured ZnO with noble metals has become a hot topic of research recently, the ability to build and optimize the desired uniform shape of these nanostructures is of quiet importance. Up to date, control of the shape of ZnO nanostructures is rarely achieved and still remains a challenge. Different researchers are still trying to develop innovative methods for the preparation of ZnO nanostructures with specific morphologies for the application in gas sensing [22, 25, 30-32, 43].

1.3 Objectives

The objectives of this study are:

- Synthesis of various ZnO nanostructures and control of ZnO particle morphology through variation of reactants pH and irradiation time using the microwave assisted hydrothermal method

- Incorporation of Au nanoparticles to produce Au loaded ZnO nanostructures
- Characterization of both unloaded and Au loaded ZnO nanostructures using various techniques including X-ray diffraction (XRD), Scanning electron microscope (SEM), Transmission electron microscope (TEM), (BET), Electron paramagnetic resonance (EPR), Photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS).
- Fabrication of ZnO and Au loaded based sensors and investigate their gas sensing properties.
- Investigate the correlation between EPR, PL and gas sensing properties.

1.4 Thesis outline

Chapter 2: Literature review

This chapter gives general overview of gas sensors, followed by introduction to metal oxide semiconductor sensors, their characteristics and working principle. The chapter further focuses on the challenges faced by metal oxide sensors and how to overcome them. Also, the basic properties of ZnO are given.

Chapter 3: Synthesis method and characterization techniques

This chapter gives details on the experimental method and the characterization techniques used in this study.

Chapter 4: Microwave-assisted method derived ZnO with various morphologies: Effect of pH on PL, magnetic and sensing properties

In this chapter, the synthesis of ZnO nanostructures with various morphologies induced by variation of reactants pH using microwave-assisted hydrothermal method is reported. Details on effect of morphology on the optical, magnetic and sensing properties of ZnO nanostructures are provided.

Chapter 5: Tailoring the sensing properties of microwave-assisted grown ZnO nanorods: Effect of irradiation time on luminescence and magnetic

The effect of irradiation time on the morphological, optical, magnetic and sensing properties of ZnO nanorods is discussed in this chapter. A correlation between magnetic, PL and sensing properties is also discussed in detail.

Chapter 6: Highly selective NH₃ gas sensor based on Au loaded ZnO nanostructures prepared using microwave-assisted method

The effect of loading Au nanoparticles on the surface of ZnO nanorods is discussed in this chapter. The chapter explains in detail the 'spill over' mechanism induced by the addition of Au on the surface of ZnO nanorods.

Chapter 7: Conclusions and recommendations

This chapter gives the summary of the results, conclusions and recommendations for possible future work.

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CHAPTER 2

Literature review

2.1 Overview of gas sensors

A gas sensor is a device that is used to detect the change in concentration of certain gases in ambient air. The gas sensor device measures a physical quantity and transforms it into an electrical signal [1, 2]. Gas sensors date back to the 19th and 20th century when the detection of gas leakages became a concern after the effect of certain gases to the environment and human life was discovered. Mine workers were part of the first people to recognize the significance of detecting harmful gases in their working environments. Back in the early years, the miners would use songful birds such as the canary; the bird would stop singing and eventually dies in the presence of such harmful gases, signaling the miners to evacuate the mine [2]. Since then, a lot of sensing devices have been developed for monitoring and detecting gas leakages [3-10]

Gas sensors exist in three different categories namely: (i) optical, (ii) electrochemical and (iii) chemo-resistive gas sensors [11]. Electro-chemical sensors have a short lifetime and this has made them unpopular for many applications. Optical sensors on the other hand exhibit several unique characteristics including sensitivity, selectivity, adequate lifetime, and fast response. However, they are very expensive and are produced in large size. Even though chemoresistive sensors show poor gas selectivity, the low cost

and ease of fabrication has contributed a lot to their wide-spread use. More interestingly, chemo-resistive sensors are based on a sensitive material which is normally coated on a suitable support, in which the molecular recognition process takes place [11].

2.2 Chemo-resistive sensors

The resistive gas sensors are operated based on the change in their electrical resistance due to the interaction between the analyte gas molecules and the surface of the sensing material. This technology appears to be advantageous not only because of its good reliability for real time control systems, low cost, and simple completion but also the diversity for its practical use in environmental monitoring, transportation, security, defense, space missions, energy, agriculture, medicine, etc [12-14]. Chemo-resistive sensors can be categorized into three types namely: (i) Planar-type gas sensor, (ii) Flexible gas sensor, and (iii) Micro-machined gas sensor. Among these, Chemo-resistive types of gas sensors, the planar-type gas sensors which consist of a sensing thick/thin material/layer coated by either chemical or physical approaches onto a ceramic substrate support with interdigitated electrodes was used in this study. Figure 2.1 shows different configurations of chemo-resistive gas sensors.

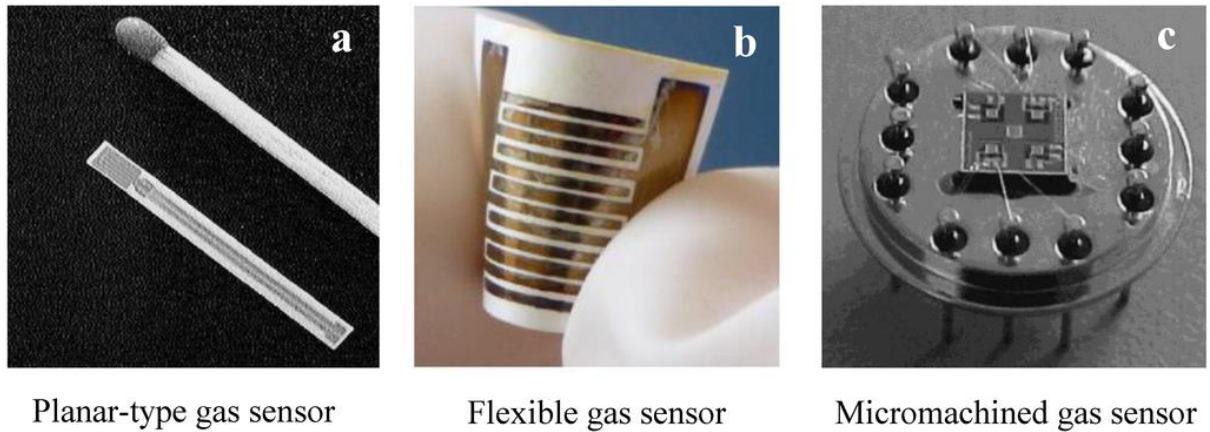


Figure 2.1: Chemo-resistive gas sensors with different configurations[11].

2.3 Characteristics of gas sensors

Generally, the fundamental principles that govern the operation of gas sensing devices are: (i) sensitivity, (ii) selectivity, (iii) fast response time and recovery time, (iv) stability, (v) low operating temperature, and (vi) detection limit.

- i. *Sensitivity* is the ratio of the change of measured signal to analyte concentration unit [15, 16]. Generally, sensitivity is calculated as the ratio of the absolute difference between the stabilized resistances of the device under dry air and under the specific gas (analyte) to the resistance under dry air [16-18].

$$\text{Sensitivity (\%)} = [(R_a - R_g)/R_a] \times 100 \quad (2.1)$$

Where R_a is the value of initial equilibrium resistance in dry air and R_g is the resistance in the presence of an analyte gas.

Furthermore, in some cases, it is also expressed as the ratio of resistance in air over resistance in gas for reducing gases: R_a/R_g and resistance in gas over resistance in air for oxidizing gases: R_g/R_a .

- ii. *Selectivity* refers to the ability of a sensor to respond to one gas in the presence of others [15, 16, 18, 19]. For instance, a methane sensor that is unable to detect other gas such H₂, NO₂ is considered to be selective.

This parameter can be assessed by the ratio of sensitivity between the gas of interest to be detected over the rest of gases that are not of interest for detection in equivalent concentrations.

$$\text{Selectivity} = (\text{Sensitivity of gas 1} / \text{Sensitivity of gas 2}) \quad (2.2)$$

- iii. *Response time* is a measure of the time taken by the sensor to achieve 90% of the response signal [16, 20-22].
- iv. *Recovery time* is the time it takes for the sensor signal to return to its initial value [16, 20-22]. The commercial usage of a gas sensor is highly dependent on its recovery time; a gas sensor that has a short recovery time will have greater applications in the commercial market than one with a long recovery time.
- v. *Stability* can be defined as the ability of a sensor to generate reproducible results for a certain period of time. This involves maintaining the sensitivity, selectivity, response, and recovery time [2, 16].
- vi. *Operating temperature* is the temperature that correlates to the maximum sensitivity of the sensor [15, 23].
- vii. *Detection limit* is expressed as the lowest concentration of the analyte that can be detected by the sensor under given conditions, mainly at a given temperature [15, 16]. According to the IUPAC definition, the detection limit is calculated as [24] :

$$3\left(\frac{noise_{rms}}{slope}\right) \quad (2.3)$$

The $noise_{rms}$ is determined by calculating the sensor noise using the fluctuation in the gas response at baseline using the root-mean-square deviation (rms), and the $slope$ is given by the first derivative of the response versus gas concentration graph [24, 25].

These parameters are utilized to characterize the sensing properties of a specific sensing material or device. A good semiconductor metal oxide (SMO) based gas sensor should exhibit high sensitivity, selectivity and stability; low detection limit; and small and response time and recovery time.

2.4 SMOs based gas sensors

As mentioned above, chemo-resistive sensors use semiconductors metal oxides (SMOs) as a sensitive layer which is often times coated on a suitable support. SMOs are considered as one of the most capable gas sensor candidates. The sensing effects of metal oxides were discovered by Seiyama in 1962 [11, 26]. Since then, metal semiconductor oxides have been extensively studied as gas sensors owing to their broad range of electronic, chemical and physical properties that are highly sensitive to changes in their chemical environment. Because of these properties, SMOs have become one of the most popular commercial sensors including chemo-resistive sensors [22, 27, 28]. SMOs range from n-type to p-type and they can interact with different gases as experienced in catalytic chemistry. However, not both kinds are often used for gas sensing. N-type metal oxide are mostly used, this is

because the mobility of main carriers (electrons) is of great importance than holes (p-type) in gas sensing [26].

To date, most of nanostructured SMO such as ZnO, SnO₂, TiO₂, In₂O₃, WO₃, TeO₂, CuO, CdO and Fe₂O₃ with different dimensions have been developed for resistive gas sensing applications owing to their reasonable sensitivities to various gases, such as NO₂, NH₃, CO, H₂, and C₂H₅OH [14, 29-34]. However, the most common SMOs used as sensing materials in chemo-resistive devices are SnO₂, ZnO, TiO₂. Figure 2.2 shows the flow chart demonstrating the research studies on both n- and p-type SMO used in chemo-resistive gas sensors. It is clear according to this flow chart that SnO₂ is the most SMO applied in practical commercial devices [14] followed by ZnO then TiO₂. However, in this study, the sensors that were fabricated are based on ZnO so its properties are discussed on the section below.

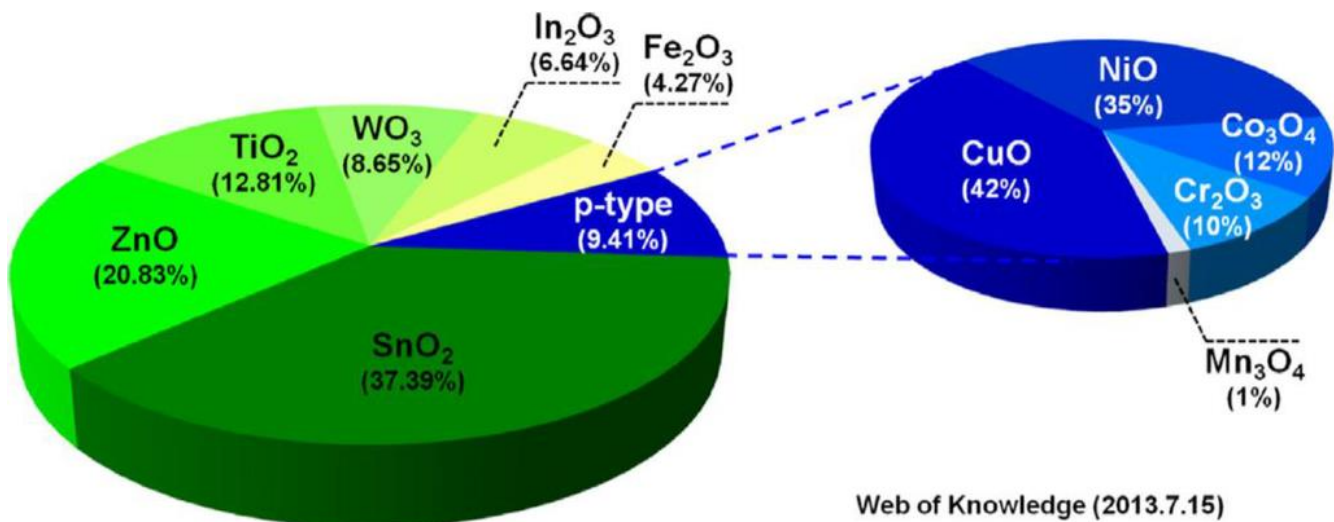


Figure 2.2: Research studies on n- and p-type SMO based gas sensors [11].

2.5 Structure of the sensing layer

A SMO sensor element generally comprises of a sensitive layer upon which the molecular recognition takes place and is deposited over a substrate that has electrodes for measuring the electrical characteristics. The sensor device gets heated up by its own heater which is separated from the electrodes by an insulator. The first SMOs sensors to be brought to industry is the Taguchi-type sensor which was discovered by Taguchi [35]. But most of the commercially available sensors these days are the ones which are manufactured by screen printing technique on small and thin ceramic substrates.[15, 35]. Screen printing involves printing a paste on a suitable substrate followed by a two-stage heat treatment to form a dense or porous layer with the chosen structure [36, 37]. The paste consists of powders mixed with an organic medium and a binder. The screen print technique is usually used to deposit layers of sensor materials, such as ZnO, SnO₂, TiO₂, and LaFeO₃ [36]. The technique is beneficial because thick films of SMOs can be deposited in batch processing, and this lowers the production cost.

2.6 ZnO: Basic Properties

ZnO is a II–VI semiconductor with a wide-band gap (3.37 eV) which shows n-type conductivity most probably due to the stoichiometric deviation in ZnO crystals which leads to a large number of surface defects [38, 39]. Abundance of several surface defects on this material allows it to provide flexibility to be exploited in several device applications. It can be produced in various forms of structures including nanowire [40, 41], tower-like structures [42], nanorods [43], nanobelts [44, 45], nanosprings [46], nanocombs [47, 48], nanorings [49]

and other interesting structures [50-56] and this allows various novel devices based on ZnO to be achieved. For the past few years, ZnO has gained a lot of attention due to its high transparency, room-temperature ferromagnetism, piezoelectricity, wide-band gap semiconductivity, and huge magneto-optic and chemical-sensing effects [57].

Furthermore, due to its large band gap, ZnO has emerged as a potential material for photonic applications in the UV or blue spectral region, including LED's [58, 59], photodetectors [60-62] and laser diodes [59, 63]. Its large exciton energy allows for excitonic emission processes at or above room temperature making it an excellent candidate for optical devices which are based on excitonic effects [63, 64]. It has also received a lot of attention in the field of gas-sensing due to its high chemical stability, suitability for doping, non-toxicity and low price rates [65-67]. According to various report, its sensing performance is influenced strongly by the microstructural parameters, including grain size and morphology [68-70]. For example, In a study conducted by Han *et al* [68], the effect of morphology on the sensing property of ZnO nanoflakes, nanocolumns and nanopyramids was investigated. The study made findings that the gas sensing of those three different ZnO nanostructures depended on the chemisorption of the crystal planes. It was further demonstrated that the crystal defects of ZnO were the key factor for determining gas sensing property [68, 71]. Different morphologies of ZnO nanomaterials have also been found to be sensitive to different gases, for example flower-like morphology with high sensitivity to CO [70], nanorods for detection of NO₂ [72], nanowires for selective sensitivity to H₂ [73], brush-like

structures with high sensitivity, selectivity fast response and low detection limit to ethanol [56], and successful detection of other gases by other ZnO morphologies have been reported so far [18, 33, 45, 74-86].

Structurally, ZnO has a relatively open structure consisting of a hexagonal close packed lattice where Zn atoms occupy half of the tetrahedral sites. It crystallizes preferentially in the stable hexagonal wurtzite structure at room temperature, with lattice parameters of $a = 0.3296\text{nm}$ and $c = 0.52065\text{ nm}$ belonging to the space group C^4_{6v} in the Schoenflies notation and $P6_3mc$ in the Hermann–Mauguin notation [87]. All the octahedral sites are empty and hence there are sufficient sites for ZnO to accommodate various surface defects and extrinsic dopants [57]. Figure 2.3 presents hexagonal structure of ZnO. The structure consist of alternating planes which are composed of tetrahedral coordination of O^{2-} and Zn^{2+} ions, alternately stacked along the c -axis. Its tetrahedral co-ordination results in piezoelectric and pyroelectric properties.

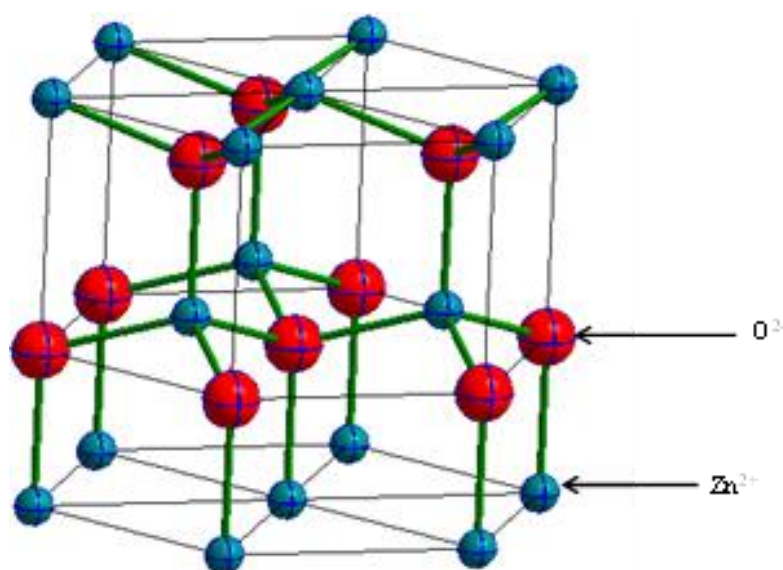


Figure 2.3: Hexagonal wurtzite structure of ZnO.

Defects in ZnO are one of the most discussed topics world-wide in condensed matter physics and material science nowadays. An elusive balance of various surface defects in this material has offered rise to fundamentally new and newer material properties [38]. Hence, control of defects or defects engineering is of importance in applications that exploit the wide range of properties of doped ZnO [57]. Furthermore, the small size and large surface-to-volume ratio exhibited by nanosized ZnO indicate that surface defects play a major role in controlling properties. At present, many efforts have been devoted to understanding defects and also to achieving an effective management of defects in ZnO either be of intrinsic or intentionally doped ions nature. It is therefore important to understand the relative dominance of carriers introduced by the doping over native defects. There are number of intrinsic defects within the bandgap of ZnO. Donor defects are Zn_i^x (neutral), $Zn_i^\bullet$ (single charged) $Zn_i^{''}$ (double charged) and V_o (neutral), $V_o^\bullet$ (single charged), $V_o^{''}$ (double charged) acceptor defects are $V_{zn}^{'}$, $V_{zn}^{''}$ and O_i [57]. Figure 2.4 shows the energy level diagram of ZnO defects.

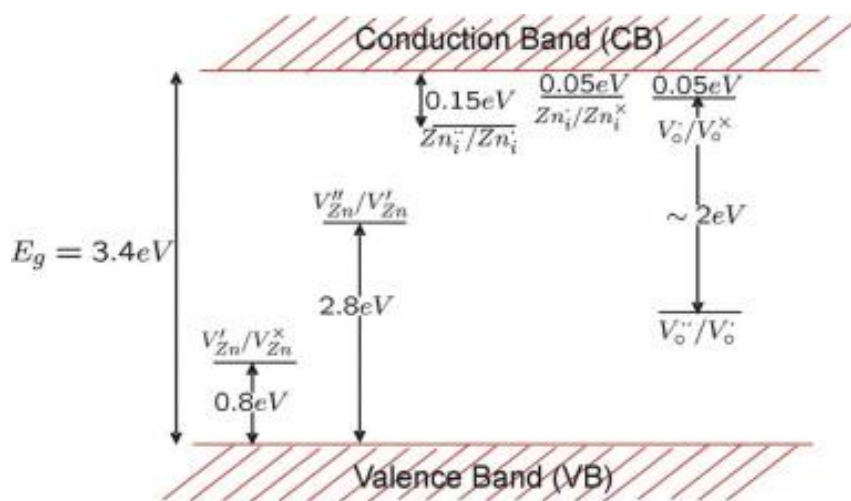
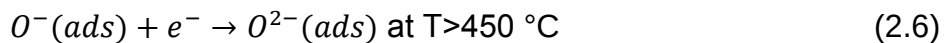


Figure 2.4: Energy levels of defects in ZnO [57].

2.7 Operating principle of SMO based gas sensors

Knowledge of the sensing mechanism and the understanding of the related processes have been improved considerably in the past few years. The detail explanation of the sensing mechanism of chemo-resistive sensors based on metal oxides was first described on the work originally reported by Wolkenstein [11] through the application of electron theory of chemisorption and catalysis on semiconductors. Gopel [88] later communicated a detailed report on the conditions of transport of electric charges through the metal oxide semiconducting layer in the presence of oxygen and reactive gases. Based on these theories, sensing mechanism in SMO based sensors basically involves the surface interaction between the analyte gas and sensing material. In fact, gas sensing of metal oxide sensors relies on the change of resistance of the sensing material due to chemical and electronic interactions between the target gas and the sensor material surface [89, 90]. In ambient air, metal oxide sensors adsorbs oxygen on its surface to form oxygen ions by withdrawing electrons from the conductance band, resulting in the formation of a depletion layer and an increase in resistance of the sensor material. The adsorbed (ads) oxygen species depend on the operating temperature. The oxygen ions form according to the following reactions [75]:



When ZnO gas sensor comes into contact with a target reducing gas such as CO, the reducing gas reacts with the oxygen ions leading to the release of trapped electrons back to the conduction band. This will increase the conductivity or reduce the resistance of the ZnO based sensor [16, 22, 39, 91, 92]. In the case of oxidizing gases such as NO₂ and O₂; after extracting the electrons from the conduction band, the depletion layer becomes thicker indicating a decrease in the electron concentration. The electrons don't get released back to the conduction band when an oxidizing gas is introduced, but more electrons are extracted from the conduction band, leading to a decrease in the conductivity or an increase on resistance of the ZnO sensor [16, 22, 39, 92]. The schematic diagrams for the gas sensing mechanism of ZnO when exposed to reducing and oxidizing gases are shown in Figure 2.5. The response of metal oxides is determined by how efficient the catalytic reactions taking place on the surface between the target gas and the oxygen species are. These catalytic reactions can be used as a way for estimating whether or not the material is suitable for gas sensing applications and also for determining the working temperature for the sensor [93]. The operating temperature of a sensor is defined as the temperature at which the sensor reaches its maximum response [15, 23] and is an important parameter of gas sensors and it influences reliability and stability of gas sensors. The operating temperature can also be used as a selectivity measure of gas sensors as the operating temperature varies depending on the specific target gas.

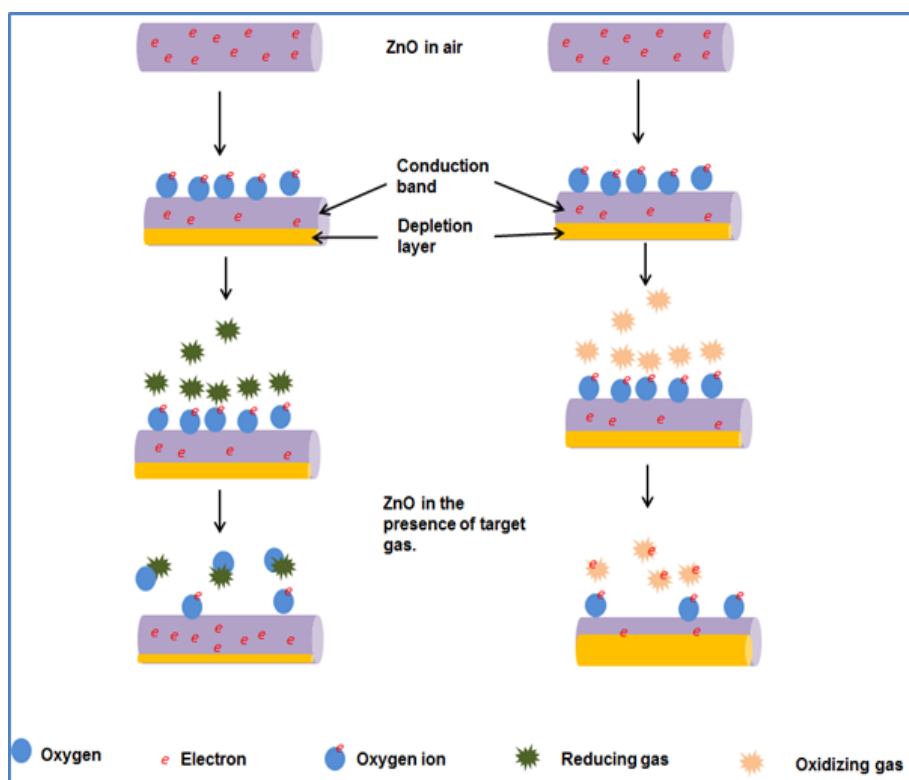


Figure 2.5: Schematic showing the sensing mechanism of ZnO sensor when in contact with reducing or oxidizing target gas.

2.8 Factors affecting SMO based gas sensitivity

Several studies have revealed that the sensing mechanism relies strongly on surface reactions therefore sensitivity, which is one of the most important parameters of SMO based gas sensors. Sensitivity changes with the factors affecting the surface reactions including (i) surface modification, and (ii) microstructure of sensing layers (i.e grain-size and shape). Sensor materials exhibiting high sensitivity and selectivity as well as low detection limit have always been of interest to many scientists and engineers. The following section discusses those parameters that influence the performance of gas sensors.

2.8.1 Surface modification

These days the basic efforts made in the science and research world-wide are devoted into optimizing the performance of gas sensors by improving their sensing performance. The sensor response of metal oxides is determined by the efficiency of catalytic reactions with the target gas on the sensor material surface. Thus, control of the catalytic activity of the sensor material is one of the most commonly employed way to improve the gas sensor performance [92]. However, in most cases the metal oxide surface is not catalytically active enough, so noble metals such as Pt, Au, Ag, etc. are used to improve this property [94-98]. Choi *et al* [94] fabricated undoped ZnO sensors which room temperature sensing of CO. After incorporating the Au into ZnO nanostructures, they observed that the response of the sensor to CO was improved when compared to that of the undoped ZnO. Rakeshi *et al* [99] also observed a catalytic activity improvement upon addition of gold on ZnO nanowires; the response improved as compared to that of undoped ZnO was phenomenal. It is important to control the size and dispersion of the noble metals on the metal oxide surface as the particle size can effectively control the temperature range and also the efficiency of a catalytic reaction [100, 101]. In a study conducted by Wang *et al* [102], the concentration of Au nanoparticles on the surface of the ZnO was varied from 2 to 14 wt% and the sensor response was low for the 2, 6 and 14 wt%. At low concentrations of Au there were insufficient Au particles on the surface of ZnO, and at 14 wt% the Au particles started to form a conduction channel because they were too many and connected to each other. Therefore the gas response was no longer controlled by the sensing properties of the most sensitive ZnO but

rather by the less sensitive conducting Au nanoparticles, resulting in the suppression of the gas sensing properties of the ZnO.

There are two types of interactions that happen between the noble metal and the metal oxide sensor surface namely the 'spill-over' and electronic sensitization mechanisms [89, 94, 97, 99, 101, 103]. The dispersed noble metals on the surface of the metal oxide sensor activate the spillover process as shown in Figure 2.6. In ambient air, oxygen molecules are adsorbed first on the catalyst and then spillover onto the metal oxide to react with the ionic adsorbed oxygen species, thereby inducing a change in conductance [26, 89, 104]. During second mechanism (electronic sensitization), the noble metal acts as a strong acceptor in its oxidized state, and accepts electrons from the metal oxide. In so doing, a surface space charge layer is induced; this strongly depletes electrons in the metal oxide near the interface. When the noble metal gets in contact with the target gas, it gets reduced and releases the electrons back to the metal oxide [26, 89]. Experimental researches have shown that the noble metals can improve gas sensing parameters such as response, response and recovery time and selectivity [104-107].

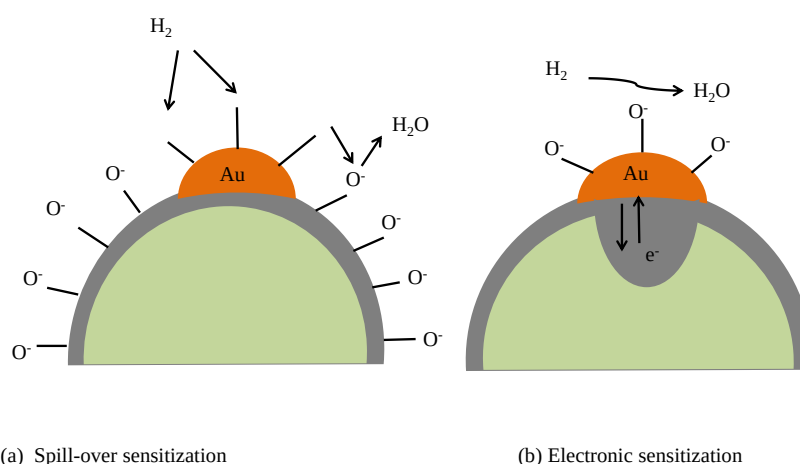


Figure 2.6: Schematic diagram showing the spill-over and electronic sensitization, using H_2 as the target gas.

2.8.2 Grain-size and shape

Many research efforts are directed to synthesizing sensing materials with small sizes, because small particle size exposes more surface area and hence will increase the sensitivity of the SMO [19, 45, 71]. Generally a sensor is considered to be composed of partially sintered crystallites that are connected to their neighbours by necks as shown in figure 2.7. The interconnected grains form larger aggregates that are connected to their neighbours by grain boundaries [91, 108]. Small grain sizes bring about high sensing sensitivity due to their large surface area [71].

To explain the effect of grain size on the sensitivity of SMO, a semiquantitative model was proposed by Xu *et al* [71, 91, 108]. The model explains the sensing ability of SnO_2 nanoparticles by comparing the grain size (D) and space charge layer (L). The model suggests that a higher response is obtainable when the grain size is much lower than twice the space charge layer. When $D \gg 2L$, the sensitivity is independent of D and the whole

structure is not so sensitive to the charges acquired from the surface but to the inner charges. When $D \geq 2L$, the space charge layer region around each neck forms a conducting channel, since the number of necks is much bigger than the grain contacts, they influence the conductivity of the sensing material and define the size-dependence of gas sensitivity [15, 91, 108]. Because of this model, extensive research has been dedicated to the development of new SMO materials with novel nanostructures and excellent properties to improve gas sensing performance [29, 109-112].

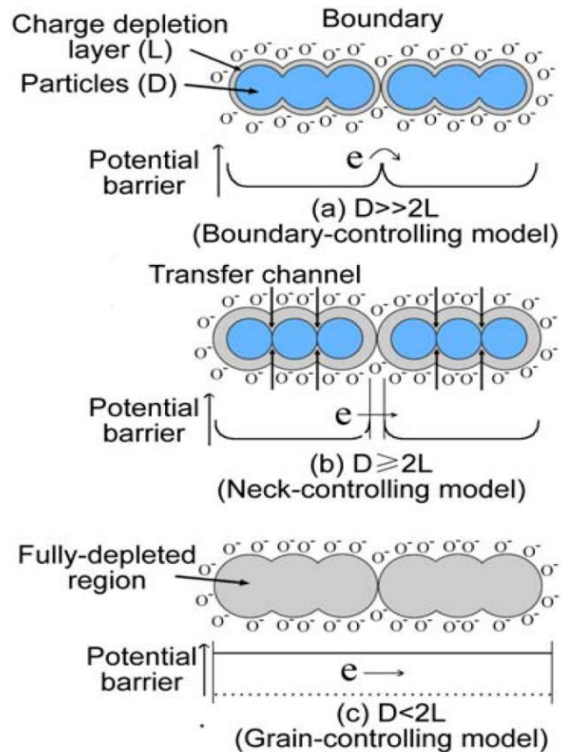


Figure 2.7: Schematic effect of the influence of grain size on the sensitivity of metal oxide gas sensors [91].

2.9 Challenges of SMO based gas sensors

There are several technological issues of SMO based gas sensors that limit their commercial use including (i) long-term stability, (ii) gas selectivity, (iii) long-term stability, and (iii) low operating temperature.

2.9.1 Stability:

One challenge that the SMO based gas sensors are faced with is the issue of low stability which has been found to result in frequent replacement of sensors, uncertain results, and false alarms. An ideal gas sensor should be able to provide long-term usage even at their being in corrosive mediums [93]. However, long-term stability remains a challenge for metal oxide sensors. For practical use, a sensor device should have a stable reproducible signal for a longer period. SMOs in nanoscale exhibit small grain size, therefore they are subject to degradation due to their high reactivity. At this stage, extensive research is still being conducted to improve the stability of SMO based sensors. However, to some extent previous reports have demonstrated that stability can be increased by post-annealing [113] and by lowering the operating temperature of the sensing material. Furthermore, doping metal oxides with metal particles [114] or mixed oxides [115] have been also demonstrated to improve the sensor stability.

2.9.2 Selectivity:

As mentioned earlier, a good gas sensor should be able to respond to only specific target gas molecules. Regrettably, SMO based gas sensors tend to sense the same way toward various reducing or oxidizing gases. For an example, a typical sensor designed for the detection of NH_3 , may respond to

H₂ and NO₂. So when these other two gases are present in the area that the sensor has to monitor, the sensor would respond as if its NH₃ that is present, whereas it's the other gas. The cross-sensitivity challenge is actually worse in real applications. To try resolve the challenge, researchers are doing more research on how to develop new devices that can overcome this challenge such as functionalizing the metal oxide surface with additives [107, 116, 117].

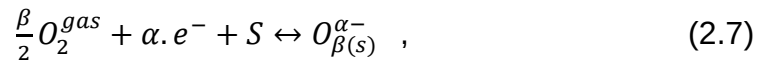
2.9.3 Operating temperature:

There are three processes that happens on the surface of SMO sensor, i.e. adsorption, desorption and the activity of the oxygen species [16]. These processes depend on temperature as they are thermally activated processes [16, 118]. The response is usually low at low temperatures, because gas molecules do not have enough thermal energy to react with the adsorbed oxygen species, hence the chemical reaction will be slow. So as the temperature increases, the response increases as well, but the response will decrease at higher temperatures as the sensor response is controlled by the speed of diffusion of gas molecules. The kinetics of the two processes eventually reaches equilibrium at some intermediate temperature, and the sensor response reaches its maximum [16, 18, 118, 119]. Researchers have shown that illuminating the SMO sensors with ultra-violet (UV) radiation can lower the operating temperature of the sensors [120, 121]. The UV light is used to activate the surface chemical reactions without having to heat up the sensors, and it is beneficial as it would reduce explosion hazards and also improve the device lifetime [122]. It was reported from previous studies that ZnO chemiresistor sensors can detect gases at room temperature when

illuminated with UV light of energy higher or equal to that of the band gap of ZnO [122-124].

2.10 Gas Sensitivity nature in nanostructured SMOs

Oxygen molecules adsorbs on the surface of the SMO by trapping electrons from the conduction band, thereby resulting in the formation of oxygen ions. The ions formed on the surface of the SMO are either in molecular (O_2^-) and atomic (O^- , O^{2-}) forms at temperatures between 100 and 500 °C. Below 150 °C the molecular form dominates and above 150 °C the ionic form dominate [15, 125, 126]. The general chemisorption equation can be written as:



where O_2^{gas} denotes an oxygen molecule in the ambient atmosphere, e^- is an electron which can reach the surface, which has enough energy to overcome the electric field resulting from negative charging of the surface. The concentration of the electrons is given by n_s ; $n_s = [e^-]$. S is an unoccupied chemisorption site for oxygen, $O_{\beta(s)}^{\alpha-}$ is a chemisorbed oxygen species with $\alpha = 1$ or 2 for singly or doubly ionized form and $\beta = 1$ or 2 for atomic or molecular form.

The existence of charged species on the surface of the SMO encourages band bending and the formation of a space charge layer [15, 125]. The concentration of the charge carriers on the surface layer can either be increased or decreased, depending on whether the SMO is n-type or p-type. The space charge layer is described by the thickness L_s and surface potential

V_s [15, 125]. The conductance dependence can be found using the mass action law which is given by:

$$k_{ads}[S]n_s^\alpha p_{O_2}^{\beta/2} = k_{des}[O_{\beta(S)}^{-\alpha}] \quad (2.8)$$

The total concentration of available surface sites for oxygen adsorption sites (occupied or unoccupied) can be denoted as $[S_t]$ so that:

$$[S_t] = [S] + [O_{\beta(S)}^{-\alpha}] \quad (2.9)$$

By defining the surface coverage θ with chemisorbed oxygen as:

$$\theta = \frac{[O_{\beta(S)}^{-\alpha}]}{S_t} \quad (2.10)$$

Equation (2.8) can be rewritten as:

$$(1 - \theta)k_{ads}n_s^\alpha p_{O_2}^{\beta/2} = k_{des}\theta \quad (2.11)$$

Equation (2.11) gives the relationship between the surface coverage with ionsorbed oxygen and the concentration of electrons with enough energy to reach the surface.

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CHAPTER 3

Material synthesis and characterization

3.1 Introduction

Zinc oxide (ZnO) nanostructures of different sizes and shapes have been synthesized through the microwave-assisted hydrothermal method. Gold (Au) nanoparticles were incorporated on the surface of the ZnO nanostructures to prepare Au loaded ZnO nanocomposites. These ZnO nanostructures were then characterized through different characterization techniques to study their structure, optical, magnetic and sensing properties. This chapter presents a detailed overview on the synthesis method used to prepare ZnO and Au-loaded ZnO nanostructures and the techniques used to characterize the nanostructures.

3.1.1 Microwave assisted synthesis method

Since 2007, the number of publications on the synthesis of ZnO using microwave-assisted method have been significantly growing significantly [1]. Microwave-assisted synthesis is a material synthesis method that applies microwave radiation to chemical reactions as a heat source. Microwave heating is based on two conversion mechanisms of the electromagnetic radiation to heat energy, which are dipolar rotation and ionic conduction, and are directly related to the chemistry composition of the reaction mixture. This behaviour allows selective heating of compounds in the reaction since different compounds have different microwave absorbing properties [1, 2]. It therefore interacts with reaction mixtures on a molecular level leading to a faster rate of reaction and shorter reaction time. Microwave-assisted method

offers simple, clean, fast, efficient, and economic synthesis of a large number of organic molecules. It can also provide a high degree of morphological control during the synthesis of the ZnO nanostructures by applying an almost direct and dynamic control over reaction temperature [2]. The technique offers process parameter control such as the power, temperature and irradiation time. Other advantages of this technique are (1) accelerated reaction rate due to high heating rates, (2) reaction selectivity due to different microwave absorbing properties, (3) control over reaction conditions, (4) improved reaction yield; (5) High purity of products, (6) it is a simple technique to handle, allowing simple optimization of experimental parameters and (7) it offers shorter reaction time [1-3].

In this work, ZnO nanostructures were synthesized by the microwave-assisted method.

3.1.2 Preparation of ZnO nanostructures with various morphologies: variation of pH

The chemical materials used for the synthesis of ZnO nanostructures were zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), hexamethylenetetramine (HMTA), sodium hydroxide (NaOH) and hydrazine hydrate (N_2H_4). All the chemicals were purchased from Sigma Aldrich, South Africa. Deionized water (DIW) was used as a solvent. The microwave used in the synthesis is EM-G430, 2.45 GHz, maximum output power 1000 W, SANYO Electric, UK.

0.1 M Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.1M NaOH were prepared in separate containers using distilled water as a solvent. The pH of the ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) solution was controlled to 7, 9, 11 and 13 by dropwise

addition of NaOH under vigorous stirring. The stirring was continued for 15 minutes and the reaction mixture was transferred to Teflon vessels and microwave irradiated for 10 minutes at a power of 150 W and temperature of 100 °C. Figure 3.2.1 shows the schematic of the experiment for the synthesis of the different ZnO nanostructures with various particle morphologies.

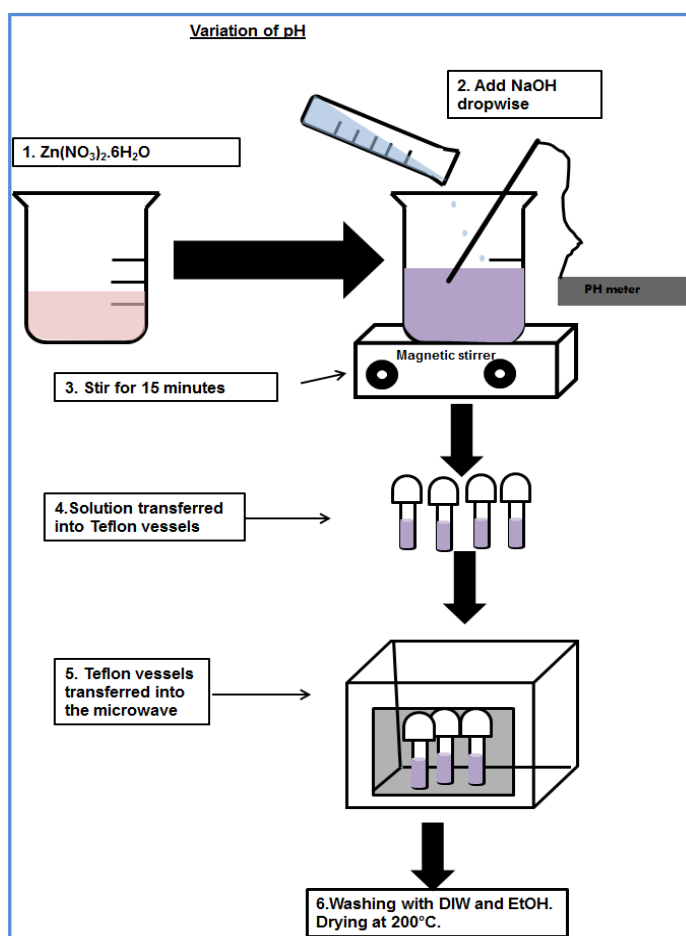


Figure 3.1: Schematic diagram showing the synthesis of different ZnO nanostructures by varying pH of the reaction mixture.

3.1.3 Preparation of ZnO nanorods: variation of irradiation time.

ZnO nanorods were prepared by mixing 0.1 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 0.1 M hexamethylenetetramine (HMTA) to form a homogeneous mixture. N_2H_4 was added dropwise until pH 10 under vigorous stirring. The stirring was continued for 15 minutes and the reaction mixture was transferred to Teflon vessels and microwave irradiated at a power of 150 W at 100 °C and the irradiation time was varied between 10-30 minutes.

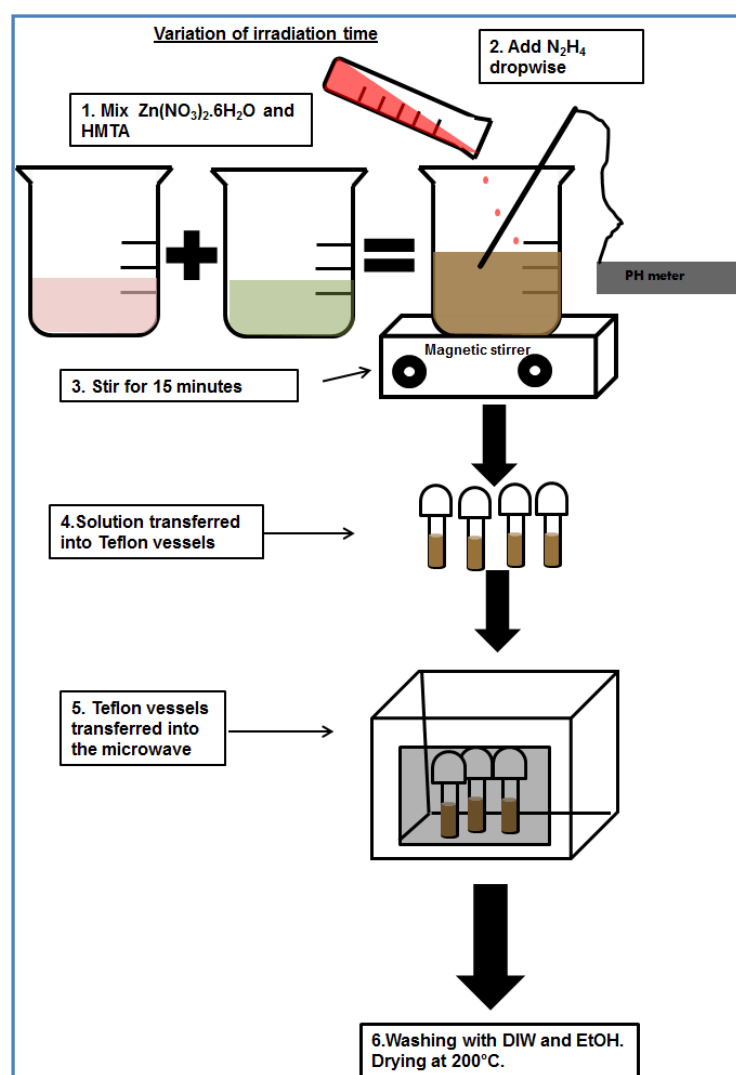


Figure 3.2: Synthesis of ZnO nanorods through variation of irradiation time.

3.1.4 Preparation of Au loaded ZnO nanostructures

The Au loaded ZnO nanostructures were prepared by first preparing ZnO by the method discussed above. 0.5-2.5 wt% of HAuCl_4 aqueous solution was added into deionized water, N_2H_4 was then added dropwise to the solution until the solution changed to a purplish color while stirring. The final solution was then mixed with the as-prepared ZnO suspended in ethanol. This solution was then transferred to Teflon vessels and irradiated in the microwave oven at a temperature of 100 °C at a power of 600 W.

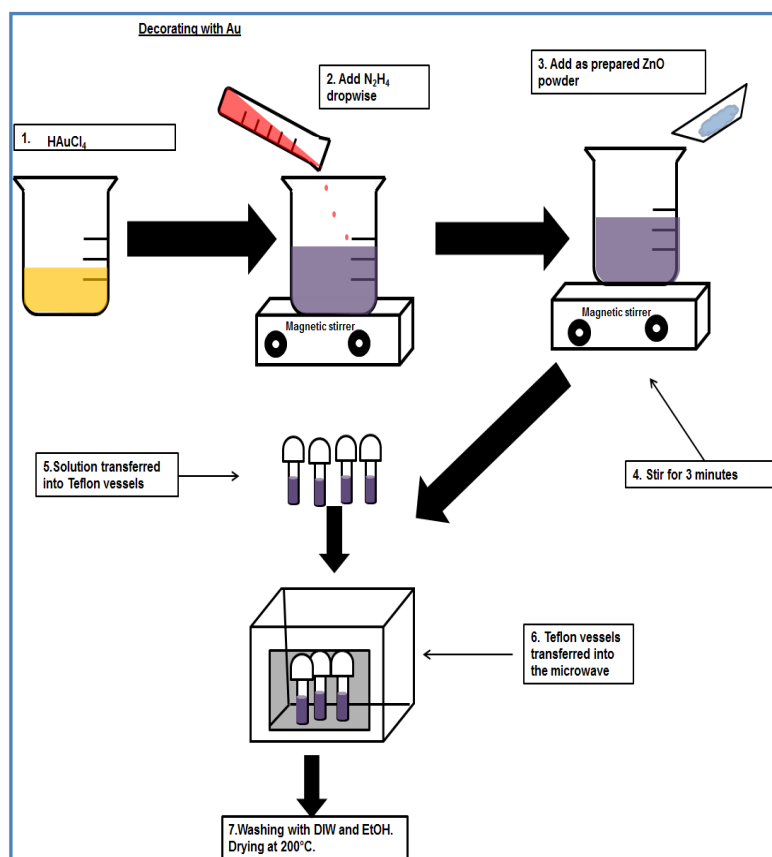


Figure 3.3: Schematic diagram of the experiment for the synthesis of Au loaded ZnO nanostructures.

In all the above experiments, the resulting products were allowed to cool down at room temperature and washed with DIW and EtOH to remove ionic impurities. The washing was followed by drying at room temperature then oven drying at 200 °C.

3.2 Characterization techniques

Different characterization techniques were used to determine the structural, morphological, chemical composition, optical, magnetic and surface properties of the synthesized materials using X-ray diffraction (XRD), scanning electron microscopy (SEM), transition electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, photoluminescence (PL), electronic paramagnetic resonance (EPR), and Brunauer-Emmet-Teller (BET). Gas sensing measurements were conducted using the Kinesistec testing station to investigate the sensing properties.

3.2.1 Structural characterization

3.2.1.1 X-ray diffraction (XRD)

In this study, the XRD technique was used to study the structural properties of the synthesized materials including orientation of a single crystal or grain, crystallite size, phase structure and composition, strain as well as lattice parameters. It is an effective non-destructive characterization technique used in material sciences for the identification of crystalline structure of compounds by their diffraction pattern [4]. Every crystalline solid has its distinctive XRD pattern to identify its crystal structure. When a monochromatic beam of x-rays with a wavelength (λ) is incident on a crystal with set of planes $h k l$, at an

angle θ as shown in Figure 3.4, the reflected wave patterns of the beam reinforce to form constructive interference, provided the reflected waves are in phase, and the constructive interference produces X-ray diffraction peaks. The production of the diffraction peaks must satisfy the Bragg's condition [5]:

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

where $n = 1$ d is the interplanar spacing of the crystal, θ is the angle of incidence and λ is the incoming x-ray radiation Cu K α emission ($\lambda = 1.5418$ Å). Variations of the angle, the polycrystalline materials interplanar spacing are satisfied by the Bragg's condition [6]

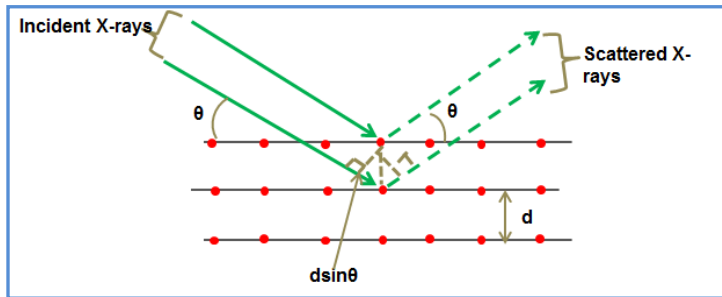


Figure 3.4: Conditions for Bragg's law.

In this study, PANalytical X'Pert PRO diffractometer with CuK α at $\lambda = 0.15405$ nm was used to analyse the synthesized ZnO powders. The schematic diagram for the XRD system is shown in Figure 3.5.

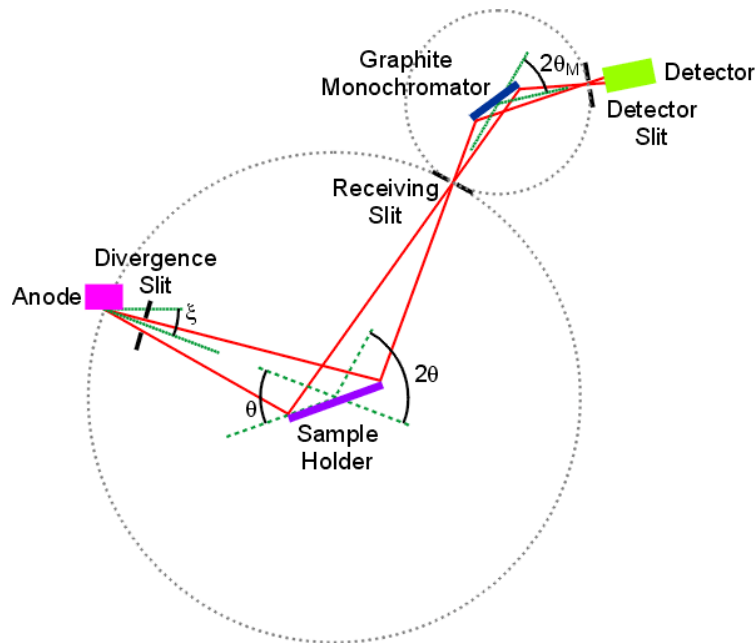


Figure 3.5: Schematic representation of X-Ray spectrometer, demonstrating X-rays from the Anode incident into the sample which is set at a desired angle to the incident beam. The detector measures the scattered rays which are constructively interfered [7].

3.2.1.2 Scanning electron microscopy, SEM

SEM is the most useful tool that uses electron beam to obtain surface image of a material. SEM depends on finely focused electron beam that is scanned across the sample [8]. The image resolution obtainable by SEM relies not only on the property of the electron probe, but also on the interaction of the electron probe with the sample. To obtain an image from this technique, the incident electron beam is scanned in a raster pattern across the sample's surface [9]. When a beam of primary electrons from the anode collides with the sample, it transfers some of its energy to the sample, which produces secondary electrons or backscattered electrons, and are attracted and collected by a positively biased secondary electron detector and converted into an image. It is important when performing microscopy analysis to get the apparatus resolution right.

Resolution can be described as that distance at which two objects are observed as two separate entities [10]. While magnification of the image is the ratio of the image display size to the sample area scanned by the electron beam [11]. Finding the best magnification but lacking appropriate resolution will not yield a desired outcome when operating the SEM, since no information of value will be gathered from such images. Field Emission SEM produces high resolution images that can be used to examine surface morphology, surface defects, particle size and distribution in materials. This technique offers exceptional image resolution, unique image contrast and a large depth of field. Qualitative and quantitative chemical or elemental analysis can also be obtained using an energy dispersive x-ray spectrometer (EDS) with the SEM [12] Figure 3.6 shows the schematic diagram of SEM. In this study, JEOL-JSM 7500F Field Emission Scanning Electron Microscope (FESEM) coupled with energy dispersive X-ray spectrometer (EDX) was used for SEM imaging. The samples are covered with an electrically conductive coating before the SEM analysis.

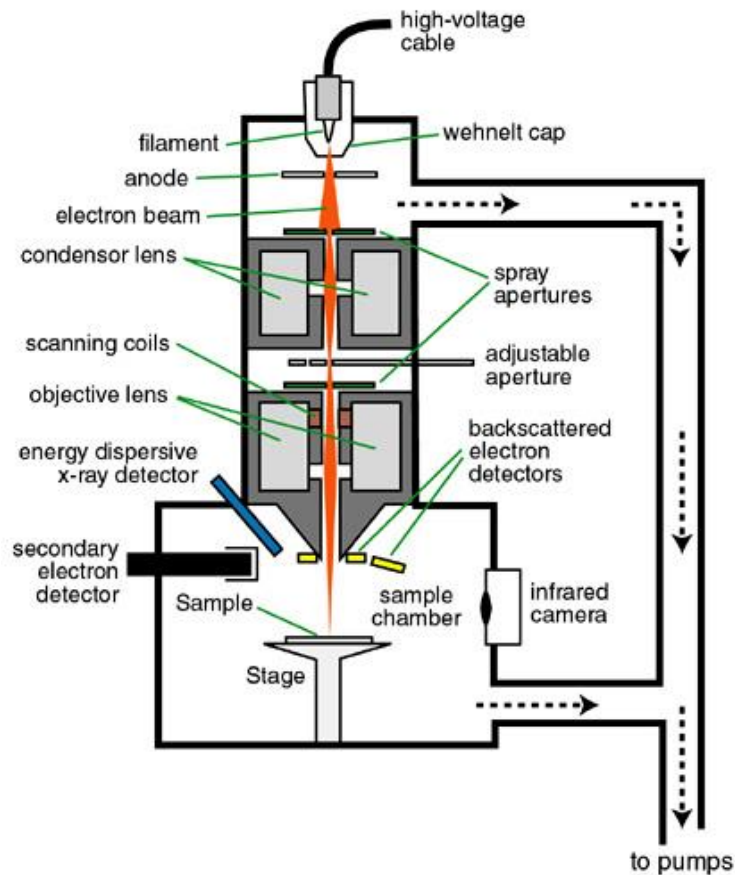


Figure 3.6: Schematic diagram of SEM [13].

3.2.1.3 Transmission electron microscopy (TEM)

TEM is a high spatial resolution imaging tool whereby a beam of electrons is transmitted through a specimen, and then an image is produced. The image is then magnified or enlarged and focused to appear either on a fluorescent screen or layer of photographic film, or to be detected by a sensor such as a CCD camera. This state of the art technique is often used to investigate the size, shape and arrangement of the particles which make up the specimen as well as their relationship to each other on the scale of atomic diameters. It can also be used to investigate the electron diffraction patterns of the crystalline structures. A general TEM schematic diagram is shown in Figure 3.7. In this

study, JEOL TEM-2100 transmission electron microscopy (TEM) with an accelerating voltage of 200 kV was used. The powder samples were prepared by dispersing a very small amount of powder in ethanol and ultrasonication until a full dispersion of the powder was achieved. A copper grid was then dipped in the dispersed homogeneous solution then transferred to the copper grid for TEM examination.

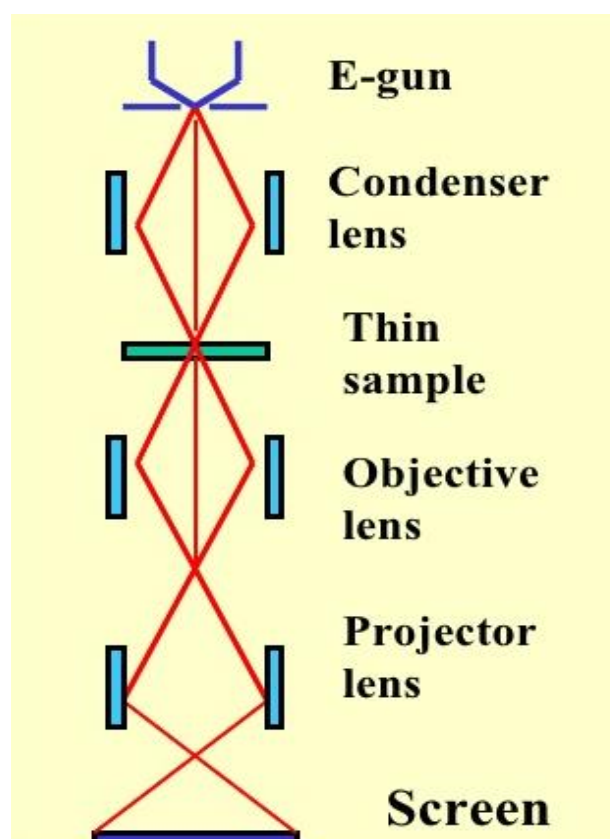


Figure 3.7: Schematic diagram of TEM [14].

3.2.2 Surface characterization

3.2.2.1 X-ray photoelectron spectroscopy (XPS)

XPS which is also known as electron spectroscopy for chemical analysis (ESCA) is a surface technique widely used for obtaining chemical information

at surfaces of different materials. It is commonly used to measure the elemental composition, chemical state, and electronic states of the elements that exist within a sample [15]. It uses highly focused monochromatised X-rays to examine the material. Its mechanism involves the ejection of a photoelectron from the K level of an atom by X-rays in vacuum. This phenomenon is based on the photoelectric effect where the concept of the photon was used to explain the ejection of electrons from a surface when photons impinge upon it [11, 16].

The energy of the photo-emitted electrons is specific to the chemical state of the elements and compounds present [17]. A photoelectron spectrum is then recorded by counting ejected electrons over a range of electron kinetic energies. Peaks appear in the spectrum from atoms emitting electrons of a particular characteristic energy. The energies and intensities of the photoelectron peaks assist in the identification and quantification of all surface elements. Figure 3.8 shows the schematic diagram of the XPS technique. X-ray excitation ejects electrons from the core level of the atoms, which will be accelerated to the detector via the cylindrical mirror analyzer.

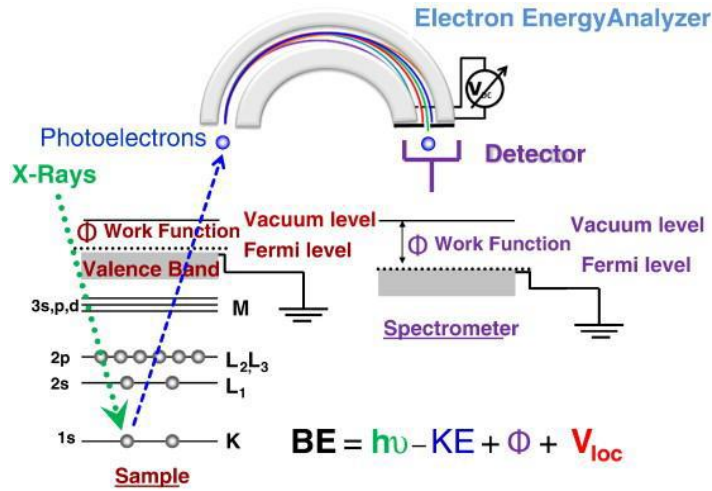


Figure 3.8: Schematic diagram of the XPS setup [18].

Determination of the energy spectrum of the emitted photoelectron is done using a high resolution electron spectrometer. The x-ray energy of an atomic binding energy (B.E.) is can be related to the kinetic energy of the emitted photoelectron by Einstein's equation for photoelectric effect:

$$B.E. = h\nu - K.E. - \phi_{spec} \quad (3.2)$$

Whereby h is the energy of the primary x-ray photons, $K.E.$ is the kinetic energy of the electron measured by the instrument and ϕ_{spec} is the work function of the spectrometer [18]. The sample analysis is conducted in an ultra-high vacuum (UHV) chamber, because electron counting detectors in XPS instruments are few meters away from the material irradiated with X-rays.

The XPS measurements in this study were performed using PHI 5000 Versaprobe-Scanning ESCA microscope with a monochromatic Al-Ka X-ray source (1486.6 eV).

3.2.2.2 Brunauer-Emmett Teller (BET)

The BET is a technique used to measure the specific surface area of a material. The theory of BET relies on physical adsorption of a gas on the surface of the solid. Because the interaction between gaseous and solid phases is usually weak, the surface of the sample is cooled using liquid Nitrogen to obtain detectable amounts of adsorption, in case of porous materials, the adsorption happens also on the surface of the pores [19, 20]. Adsorption of nitrogen at a temperature of 77 K leads to a so-called isotherm, usually referred to as BET isotherm [19], and is commonly measured over porous materials. Monolayer formation of gas molecules on the surface is used to determine the specific surface area, while the principle of capillary condensation can be applied to assess the presence of pores, pore volume and pore size distribution. The data is treated according to the BET adsorption isotherm equation:

$$\frac{1}{[V_a(\frac{P_0}{P}-1)]} = \frac{C-1}{V_m C} \times \frac{P}{P_0} + \frac{1}{V_m C} \quad (3.3)$$

Where V_a is the volume of gas adsorbed at standard temperature and pressure, V_m is the volume of gas adsorbed at standard temperature and pressure to produce an apparent monolayer on the sample surface, P is the partial vapour pressure of adsorbate gas in equilibrium with the surface at 77.4 K and is measured in pascals, P_0 is the saturated pressure of adsorbate gas, C is the dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the powder sample. The plot of $\frac{1}{[V_a(\frac{P_0}{P}-1)]}$ against $\frac{P}{P_0}$ results in a BET straight line. From the resulting BET linear plot, the slope, which is given by [21]:

$$S = \frac{C-1}{V_m C} \quad (3.4)$$

and the intercept, which is equal to

$$intercept = \frac{1}{V_m C} \quad (3.5)$$

V_m can be calculated as

$$V_m = \frac{1}{slope} + intercept \quad (3.6)$$

and C can be calculated as

$$C = \frac{slope}{intercept} + 1 \quad (3.7)$$

The surface area is calculated using the equation:

$$S_{BET} = \frac{V_m N_s}{V_a} \quad (3.8)$$

where V_m is the monolayer adsorbed gas, N_s is Avogadro's constant ($6.022 \times 10^{23} \text{ mol}^{-1}$), V is molar volume of adsorbate gas and a is the mass of the adsorbent. BET measurements in this study were performed using a Micromeritics TRISTAR 3000 surface area analyzer (USA). The samples were degassed at 200 °C for 12 h under a continuous flow of N_2 gas to remove adsorbed contaminants prior to analysis. Figure 3.9 shows a typical schematic diagram of BET setup.

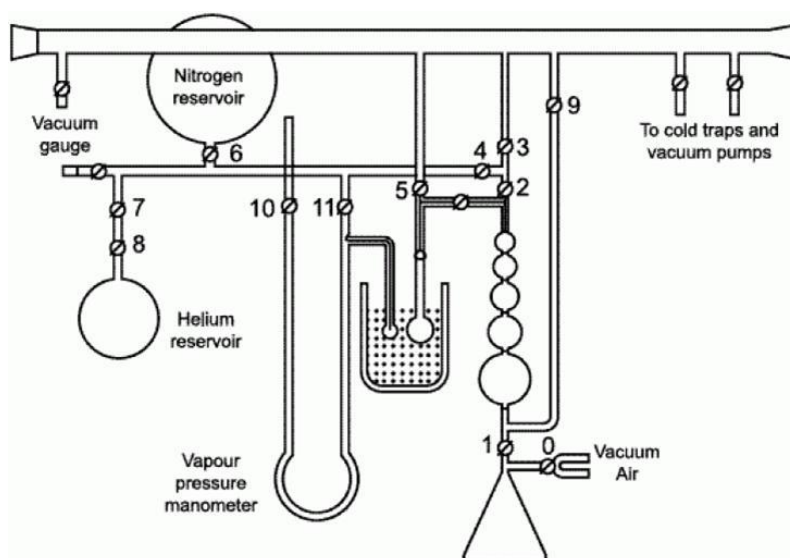


Figure 3.9: Schematic diagram of BET setup [21].

3.2.3 Optical characterization

3.2.3.1 Raman spectroscopy

Raman spectroscopy is a unique technique commonly used in chemistry or in solid state physics to observe vibrational modes of the molecule or crystal under study. In crystals, vibrations are usually referred to as phonons which are quantum of energies caused by the collective vibration of the atoms in the lattice, and they have large impact on properties like transportation of electricity, heat and sound. During the Raman experiment, a monochromatic laser radiation with a single wavelength/frequency is incident upon a sample, the light will interact with the sample and it may be reflected, absorbed or scattered. It is the scattering of the radiation that occurs which can give information about the sample's molecular structure. Furthermore, the change in wavelength of the scattered photon provides the chemical and structural

information. Light scattered from a molecule has numerous components namely; the Rayleigh scattering; the Stokes and Anti-Stokes scattering [22].

In molecular systems, these frequencies are principally in the ranges associated with rotational, vibrational and electronic level transitions. The scattered radiation occurs over all directions and may also have observable changes in its polarization along with its wavelength. Rayleigh scattering is the scattering without a change of frequency (wavelength). While Raman scattering happens when there is a change in the frequency (wavelength) of the light. Raman shifted photons of light can be of higher or lower energy, subject upon the vibrational state of the molecule. The Stokes scattering is a light scattering process whereby the photon is scattered at lower energy (longer wavelength). Whereas Anti-Stokes Raman scattering is a light scattering process whereby the photon is scattered at higher energy [22]. In this study, a Horiba Jobin-Yvon HR800 Raman microscope with 514 nm excitation laser and a spectral resolution of 0.4 cm^{-1} was used to perform Raman analyses. Figure 3.10 shows the schematic diagram of a typical Raman spectrometer.

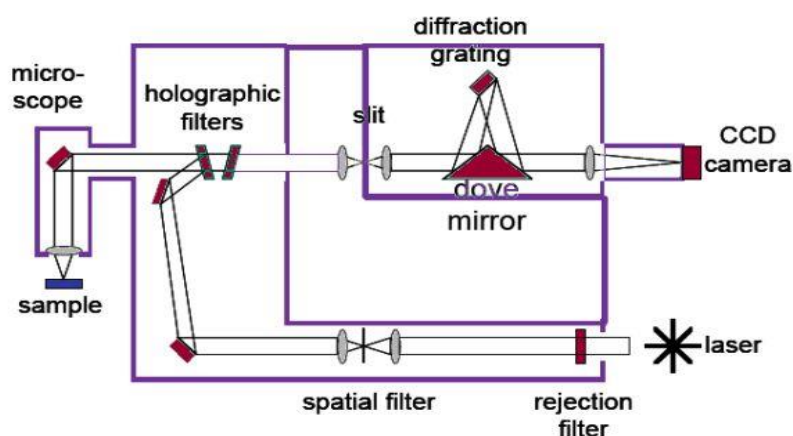


Figure 3.10: Raman spectrometer schematic diagram [23].

3.2.3.2 Photoluminescence (PL)

PL is a non-destructive characterization technique used for examining photo-excitation and optical transition in the electronic configuration of materials. A beam of light incident on a sample is absorbed and imparts excess energy into the material in a process called photo-excitation [24]. Photo-excitation causes electrons within a material to move into allowed excited states. When these electrons return to their ground state, the excess energy is released and may include the emission of light (radiative process) or may not (non-radiative process). The excess energy can be dissipated by the sample through light, or luminescence, and this luminescence is called photoluminescence and is usually observed from III-V semiconductor materials [25].

With regard to the semiconductor materials, when energy of incident photon is equal or larger than the energy bandgap, it will excite the electron of the valence band which will then move into conduction band. A recombination radiation from excited state to ground state will be generated. Absorption will also happen when an electron is excited to higher energy level from neutral acceptor energy level and it can also travel to ionization donor energy level from valence band or travel to conduction band from ionization acceptor energy level. Those occurrences can explain the energy band defects in the semiconductor [26].

For the PL studies, the Horiba Jobin-Yvon iHR 320 Nanolog spectrometer with Symphony® cryogenic detector using a Xenon lamp as a continuous energy

supply excited at 325 nm was used at room temperature. Figure 3.11 shows a schematic diagram of the PL spectrophotometer.

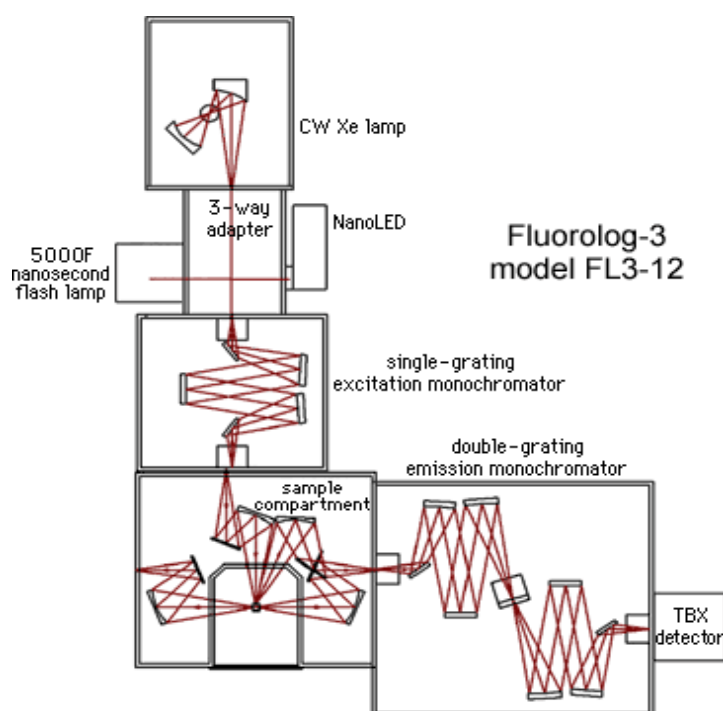


Figure 3.11: Schematic representation of a typical PL setup [27].

3.2.4 Magnetic measurements

3.2.4.1 Electron Paramagnetic Resonance (EPR)

EPR which is also known as electron spin resonance (ESR) spectroscopy, is the resonant absorption of microwave radiation by an unpaired electron of an atom or molecule (paramagnetic species) when placed in a strong magnetic field. It is a powerful technique used to study atoms, molecules or ions containing one unpaired electron either in solid, liquid or gaseous phase, point defects in solids and used to study systems with conducting electrons such as semiconductors and metals. EPR spectra are given as the first derivative of their absorption spectra.

When a molecule or compound with an unpaired electron is placed in a strong magnetic field, the spin of the unpaired electron can align in two different ways creating two spin states $m_s = \pm 1/2$. The alignment can either be along the direction parallel to the magnetic field which corresponds to the lower energy state $m_s = -1/2$ or antiparallel to the direction of the applied magnetic field $m_s = +1/2$. The two alignments have different energies and this difference in energy lifts the degeneracy of the electron spin states. The energy difference is given by:

$$\Delta E = E_{+1/2} - E_{-1/2} = h\nu = g_e \mu_B B_0 \quad (3.9)$$

This equation suggests that the splitting of the energy levels is directly proportional to the magnetic field's strength [28], as shown in figure 3.12

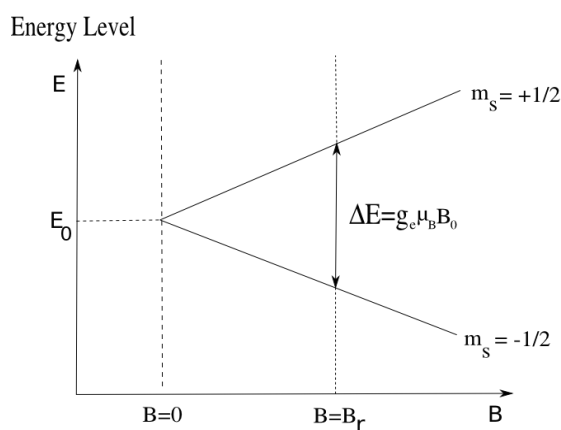


Figure 3.12: Energy levels for an electron spin ($m_s = \pm 1/2$) in an applied magnetic field B .

h is Planck's constant ($6.626 \times 10^{-34} \text{ J s}$), ν is the frequency of radiation, μ_B is Bohr magneton ($9.274 \times 10^{-24} \text{ J T}^{-1}$), B is the strength of the magnetic field in Tesla, and g is the g-factor. During the experiment the values of h , ν and

μ_B do not change and g value decrease with an increase of B . The g -factor is a measure of the intrinsic magnetic moment of the electron and it doesn't have a unit, and its value for a free electron is 2.0023. The EPR spectrum is given by the plot of the absorption of microwave frequency radiation against the magnetic field intensity.

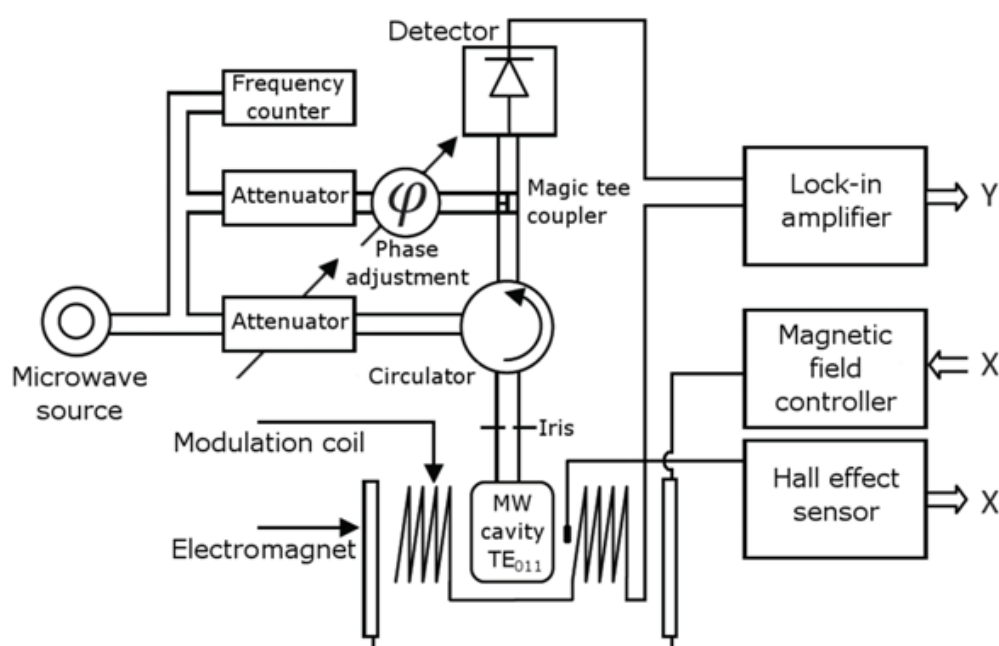


Figure 3.13: Schematic diagram of the EPR [29].

3.2.5 Sensing measurements

3.2.5.1 Gas sensing station

The gas sensing instrument was used to test the prepared nanostructures for sensing properties towards different gases. In this study, KENOSISTEC UHV and Thin film Equipment gas station (Figure 3.14) was used for the gas sensing experiments. The set-up of the system comprises of a sensing chamber, two thermostatic baths, eight gas inlets for different test gases,

twelve mass flow controllers which are meant to control the gas capacity reaching the chamber. It also consists of a sample stage, an air mixer and a dry air inlet which carries dry air into the mixer. Thermostatic bath 1 supplies wet air into the air mixer to make the dry air humid. There are six heaters included for the supply of voltage across the sample. It also includes six KEITHLEY picoammeter for the measurements of conductance.

The sensing films were prepared by dispersing the sample powder in ethanol to make a paste; the paste was then drop-coated onto the surface of alumina substrates interdigitated with Au/Pt electrodes. These sensing films were dried at room temperature and followed by annealing at 400-500 °C. The prepared sensing films were then fixed on the sample stage in the sensing chamber. Gases and humidity lines are directed to the chamber, heater supplies voltage across the sensing films and the picoammeters record the concentration of gas and humidity. Figure 3.14: shows the Schematic diagram of a gas sensor station set up [30].

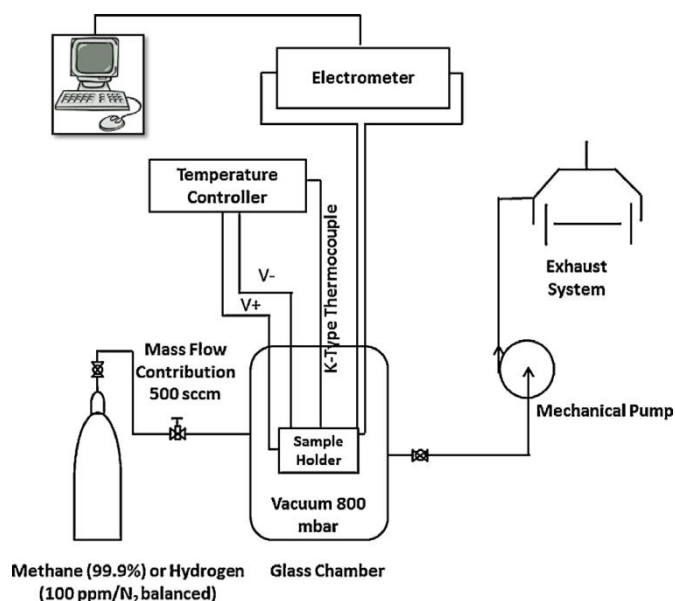


Figure 3.14: Schematic diagram of a gas sensor station set up [30].

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CHAPTER 4

Microwave-assisted method derived zno with various morphologies: effect of pH on PL, magnetic and sensing properties

4.1 Introduction

Gas sensing technology has been widely explored for gas detection in industrial areas, mines, households, medical applications and etc. The most common sensing materials used are metal oxide semiconductors such as SnO_2 [1], TiO_2 [2], ZnO [3-5], WO_3 [6], etc. This is due to their sensitive electrical conductivity towards ambient air, which ascends from charge transfer interactions with reactive gases such as H_2 , CO , and volatile organic compounds [7]. Among the mentioned metal oxides, ZnO is the most attractive semiconductor with a band gap of 3.37 eV at room temperature and a large binding energy of 60 meV [8-11]. It crystallizes in both the cubic and hexagonal form and exhibits n-type electric conductivity [12, 13]. ZnO is widely used as a gas sensor material owing to its advantages of stability, high sensitivity and low cost [14].

In this chapter, the change in morphology of ZnO nanostructures induced by the variation of pH using NaOH as a morphology directing base precursor and annealing of the final product is reported. Effect of pH and annealing on structural, optical, and magnetic properties has been investigated. Gas sensing properties were examined in detail.

4.2 Experimental

4.2.1 Sample preparation

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and sodium hydroxide (NaOH) were all procured from Sigma-Aldrich and utilized as received without further purification. The reaction solution was prepared by mixing 0.1 M Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.1M NaOH in separate containers using distilled water as a solvent. These two solutions were then mixed with continuous stirring in one beaker to form a zinc nitrate homogeneous solution. For variation of pH, four separate beakers with each containing the above zinc nitrate solution were prepared. Few drops of NaOH were added on each beaker under vigorous stirring to maintain the pH at 7, 9, 11 and 13, respectively. After being continuously stirred for 15 minutes, the mixtures were transferred into Teflon vessels, then placed in a microwave oven (EM-G430, 2.45 GHz, maximum output power 1000 W, SANYO Electric, UK) and finally subjected to irradiation for 10 minutes at a power of 150W. After being cooled at RT, the white precipitates were collected by centrifugation and washed several times with absolute ethanol and distilled water to get rid of undesirable impurities. The final products were divided into two parts; one part was dried at room temperature and the other was annealed at 450 °C for 2 hours.

4.2.2 Sample analysis

The identification of the phases was performed by X-ray diffractometer (XRD) using as Panalytical X'pert PRO PW 3040/60 equipped with a $\text{Cu-K}\alpha$ ($\lambda=0.154$ nm) monochromatized radiation source. The morphology of the synthesized products was examined by Scanning electron microscopy (SEM) using ZEIS-AURIGA Focused Ion Beam Scanning Electron Microscopy (FIB-

SEM). A Horiba Jobin-Yvon HR800 Raman microscope with 514 nm excitation laser and a spectral resolution of 0.4 cm^{-1} was used to perform Raman analyses. The specific surface area studies of the nanostructures were measured using a Micromeritics TRISTAR 3000 surface area analyser. Prior to the analysis, the samples were degassed at $150\text{ }^{\circ}\text{C}$ for 12 hours under continuous flow of N_2 gas to remove adsorbed impurities. The Photoluminescence (PL) spectra were recorded at room temperature following excitation at 325 nm using Jobin-Yvon Nanolog spectrometer. Electron paramagnetic resonance (EPR) spectra were measured at room temperature using a JEOL X-band EPR spectrometer at a constant frequency of 9.4 GHz.

4.2.3 Gas sensor fabrication and measurements

Gas sensing measurements were done using a Kinesistec testing station. The as-prepared and annealed ZnO products were dispersed in ethanol and coated onto alumina substrates with integrated Pt electrodes to prepare ZnO based sensor films. These films were then annealed at $400\text{ }^{\circ}\text{C}$ for 2 hours prior to sensing measurements. The sensing measurements were carried out using a computer-controlled KSGGAS 6S Kenosistec testing station for CH_4 , H_2 , CO and NH_3 gases. A constant flux of 500 ml/min of synthetic air and targeted gas was maintained during the measurements. Various concentrations ranging from 5 to 100 ppm of each targeted gas in a sensing chamber were achieved by controlling the mass flow rate ratio using a pre-calibrated mass flow meter (MKS Instruments Deutschland GmbH). All the sensor films were first measured at different temperatures (room temperature, 250, 300, 350 and $400\text{ }^{\circ}\text{C}$) and sensor films measured at revealed enhanced sensing response compared to other temperatures. Therefore sensing

measurements were conducted at an optimized operating temperature of 250 °C. The change in the current across the electrode in the presence or absence of targeted gas was measured using Keithley 6487 Picoammeter/voltage source meter. The gas response of the ZnO based sensors in this case can be defined as $S = R_a/R_g$ (reducing gases), where R_a and R_g were the resistance in air and test gas, respectively.

4.3 Results and discussion

4.3.1 X-Ray diffraction (XRD) analysis

In order to establish the phase of the prepared products, XRD analyses were conducted. Figure 4.1 shows the representative XRD patterns of the as-prepared and annealed ZnO nanostructures. The diffraction peaks of all the ZnO products are intense and are in good agreement with the wurtzite hexagonal structure of ZnO (JCPDS card no.36-1451). No diffraction peaks from impurities were observed, indicating that the ZnO nanostructures are of high purity. As shown in Figure 4.1(a-b), the diffraction patterns of all the products for both as prepared and annealed were alike, except for the minor variation in peak intensities which could be assigned to the structural changes with pH variation.

4.3.2 Scanning electron microscopy (SEM) analysis

The morphologies of the as-prepared ZnO products revealed SEM are presented in Figure 4.2 (a-h). It can be seen that for as-prepared products, when the pH of NaOH was 7, spherical particles were formed (see Figure 4.2 (a-b)). However, with the pH increase to 9, the spherical particles evolved into

homogeneously dispersed sphere-like structures as shown in Figure 4.2 (c). Higher magnification of the SEM image in Figure 4.2 (d) revealed that these sphere-like structures consist of tiny particles which aggregated to form the spherical hierarchical nanostructures. At a pH value of 11, sphere-like structures were completely transformed into flower-like structures (see Figure 4.2 (e)). HRSEM image in Figure 4.2 (f) revealed that every individual flower-like structure is composed of bunch of multi-nanorods made up of small particles nucleating from one centre forming structures of flower-like hierarchical structure. This structure was not maintained as it evolved into uniform roses-like structures with good dispersion with further increase of pH to 13 (see Figure 4.2 (g)). A clear observation from HRSEM presented in Figure 4.2 (h) showed that these roses-like structures are composed of several thin sheets that are stacked close to each other.

When the ZnO products were subjected to high temperature annealing, no obvious morphology change for structures obtained at pH levels of 7 and 11 (see Figure 4.3 (a-b) and (c-d)), except that the particles that were produced at pH 7 became bigger with annealing. However, the sphere-like structures obtained at a pH of 9 transformed into particles with smoother surface after annealing (see Figure 4.3 (e-f)). While roses-like structures assembled with several thin sheets prior annealing were disassembled into platelets composed by small particles (Figure 4.3 (g-h)). It can therefore be concluded based on these SEM observations that variation of pH and annealing treatment plays a significant role in altering the shape of various structures of ZnO.

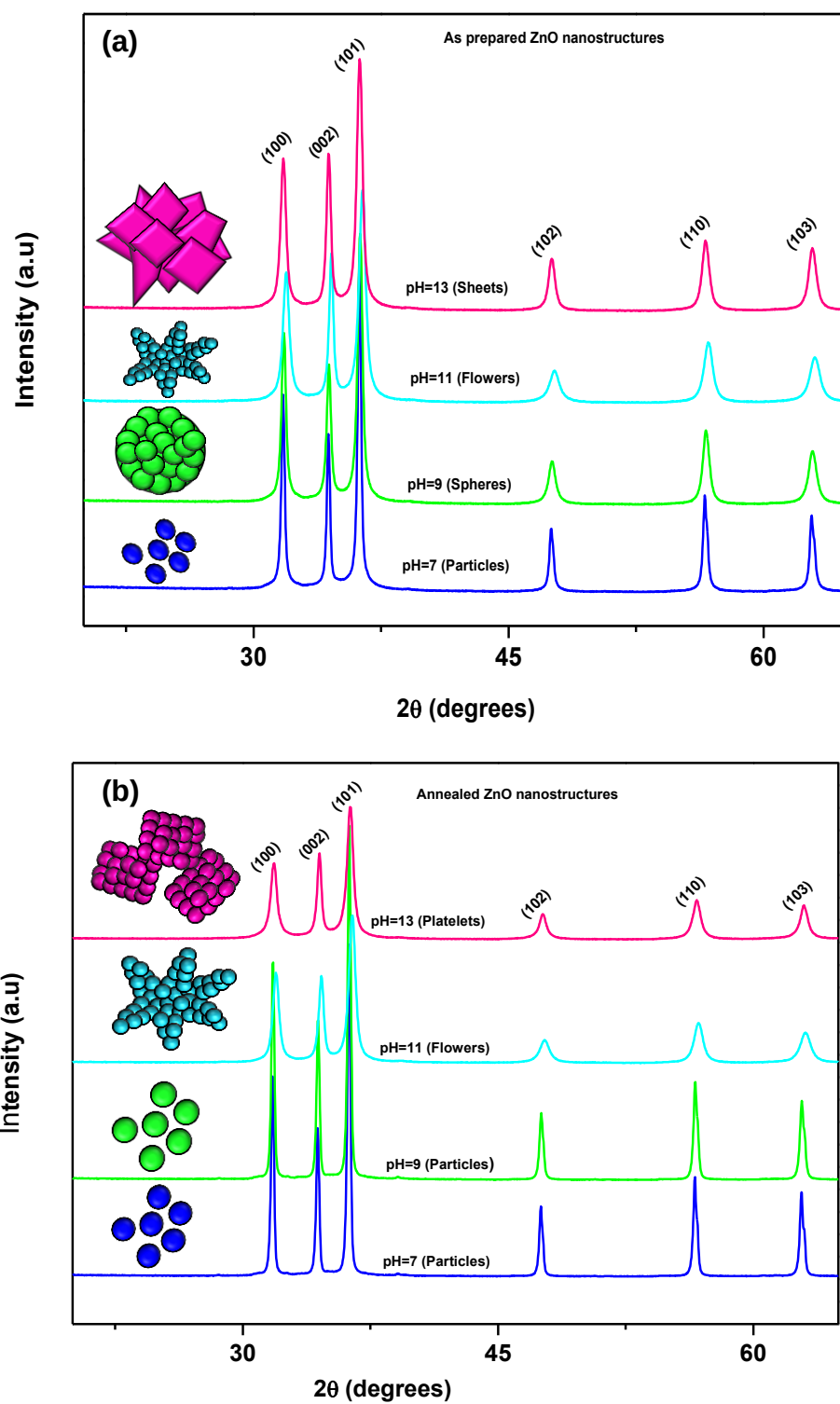


Figure 4.1: The XRD patterns of the (a) as prepared and (b) annealed ZnO nanostructures obtained after variation of pH from 7 to 13.

4.3.3 Brunauer Emmett Teller (BET) analysis

To gain more information about the porous nature of the ZnO structures, nitrogen adsorption and desorption were carried out. Figure 4.4 (a-b) shows the nitrogen adsorption and desorption isotherms of the ZnO nanostructures which gives a comparison on the surface area and the pore structure of the ZnO nanostructures before and after annealing. All the plots exhibited type IV isotherm with type H1 hysteresis loops which is the characteristic of mesoporous structures [15]. According to the IUPAC classification, type H1 hysteresis loop observed in these plots is indicative of the formation of nanoparticles clusters with a narrow distribution of the resultant pore size [16]. For annealed samples, the hysteresis loops are found to shift down for all the nanostructures (Figure 4.4(b)), indicating a reduction in surface area. Table 4.1 summarizes the measurement data showing the pore structure parameters including porosities, surface area and pore size of several ZnO nanostructures prior and after annealing. It can be noticed that of all the nanostructures from this table that, the rose-like structures reveal the largest surface area before and after annealing.

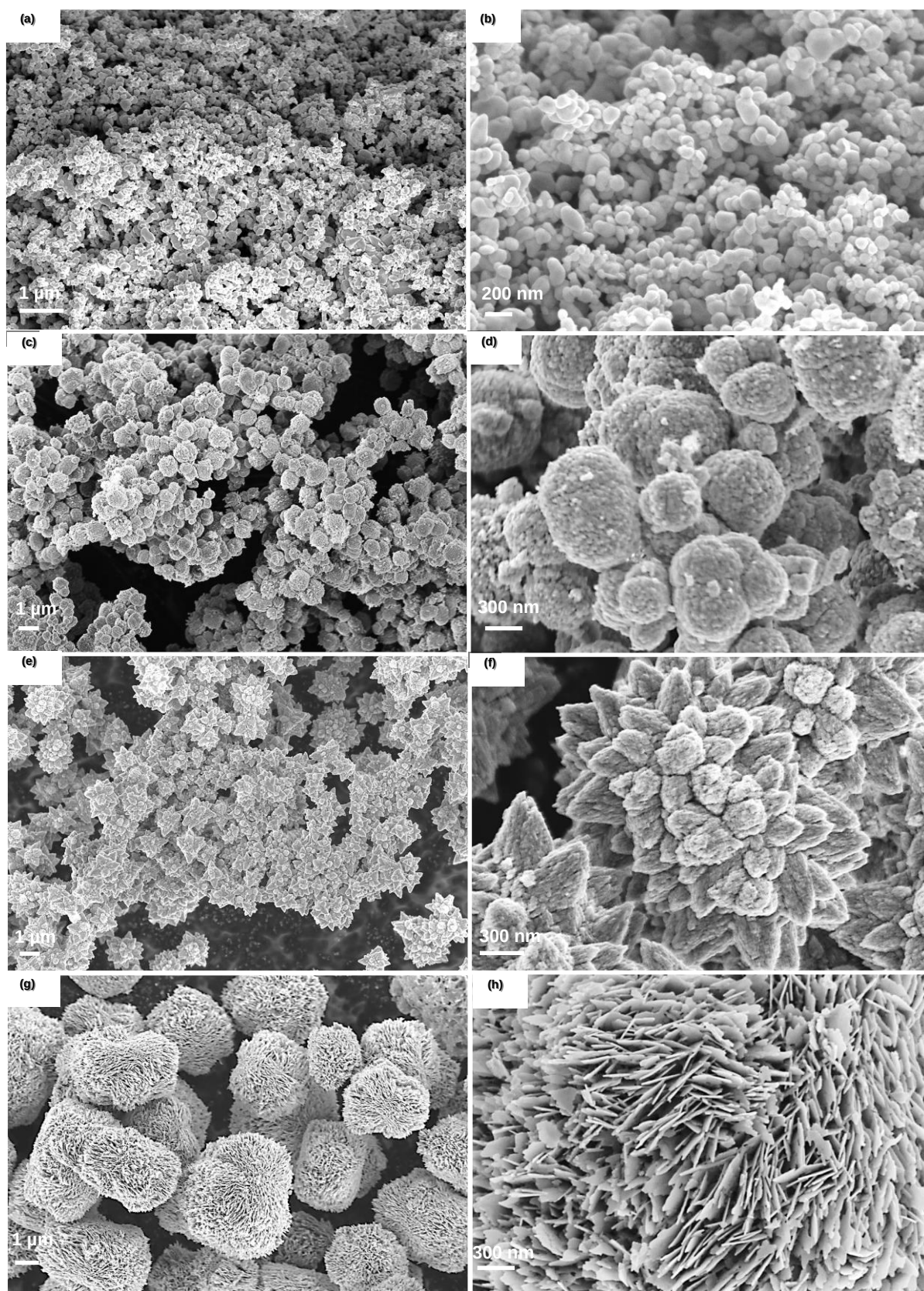


Figure 4.2 (a-h): SEM images of the as prepared ZnO nanostructures obtained after variation of pH from 7 to 13.

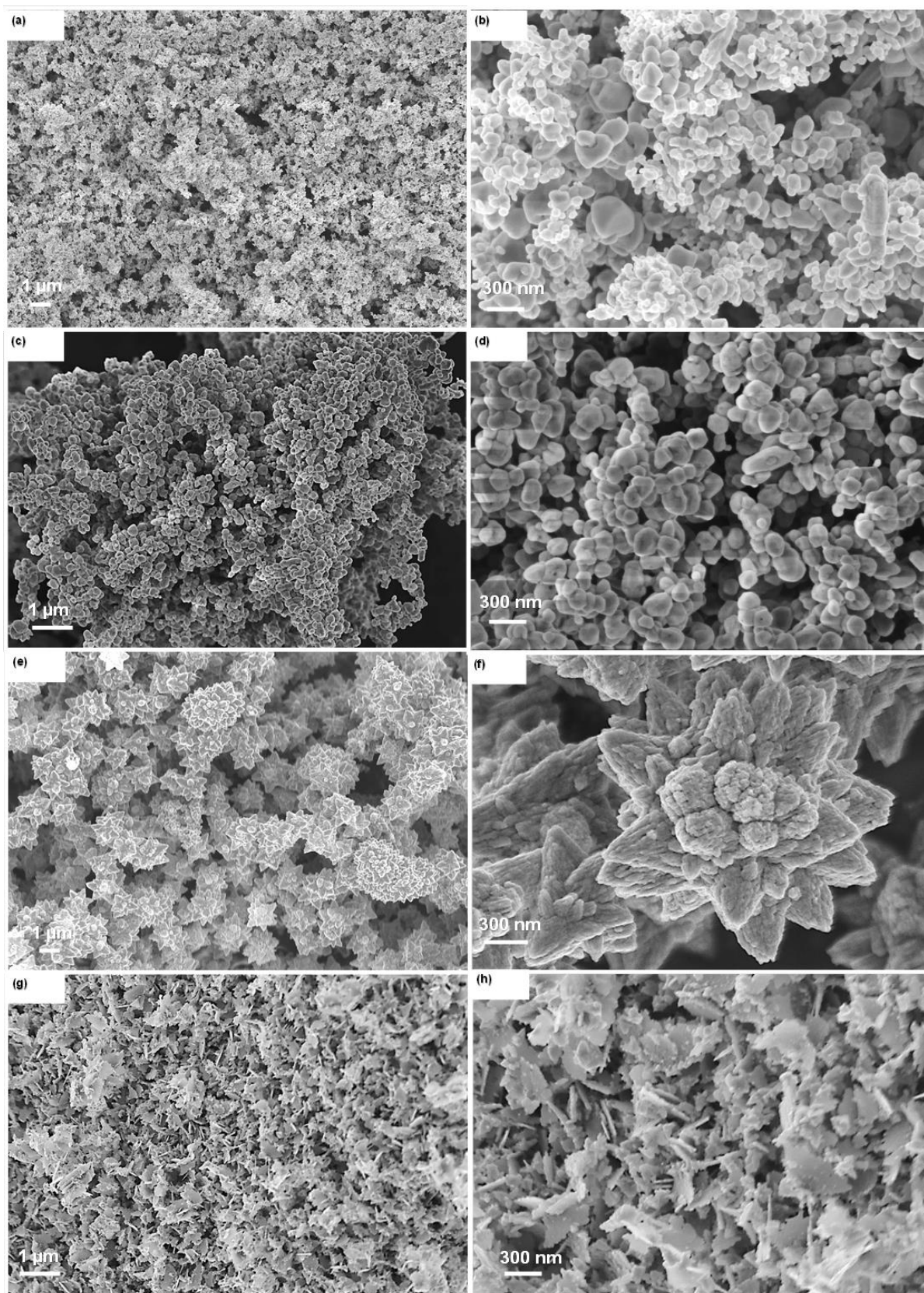


Figure 4.3 (a-h): SEM images of the annealed ZnO nanostructures obtained after variation of pH from 7 to 13.

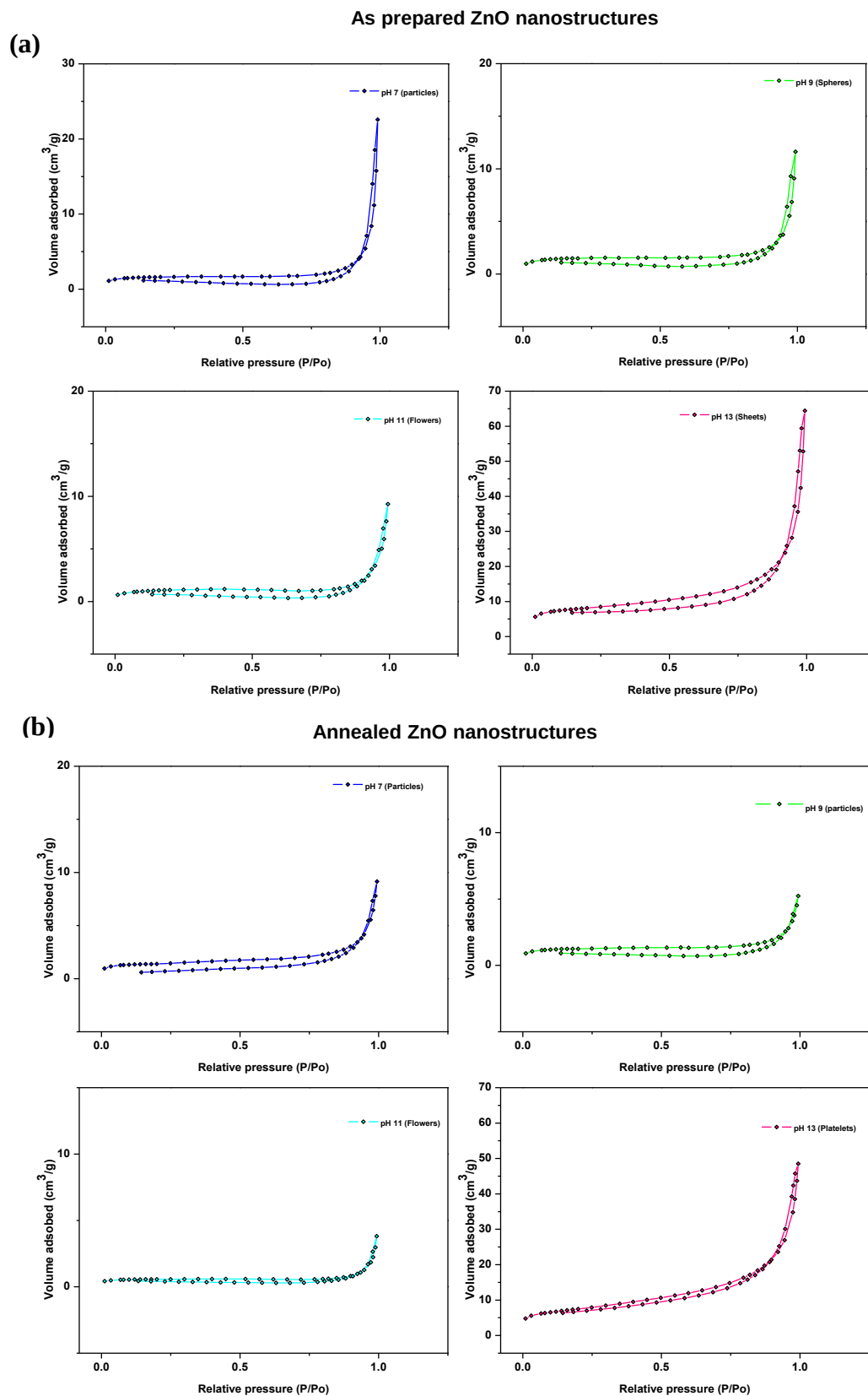


Figure 4.4: Nitrogen adsorption isotherms for the (a) as prepared and (b) annealed ZnO nanostructures obtained after variation of pH from 7 to 13.

Table 4.1: Summary of the BET specific surface area, pore volume (V_{pore}) and pore diameter (d_{pore}) of the ZnO nanostructures before and after annealing.

Morphology	As prepared			Annealed		
	Surface area (m^2/g)	V_{pore} (cm^3/g)	d_{pore} (nm)	Surface area (m^2/g)	V_{pore} (cm^3/g)	d_{pore} (nm)
Particles	5.62 ± 0.1000	0.035	55.31	4.76 ± 0.0881	0.013	22.52
Spheres	5.17 ± 0.1054	0.016	48.98	4.29 ± 0.0828	0.006	37.70
Flowers	3.95 ± 0.0582	0.014	42.98	1.92 ± 0.0373	0.005	51.65
Roses/sheets	28.30 ± 0.2444	0.096	24.18	26.49 ± 0.0584	0.0739	14.11

4.3.4 Raman analysis

To further investigate the phase and purity of the ZnO nanostructures, Raman spectroscopy was employed. Figure 4.5 (a-b) shows the room temperature Raman spectra of ZnO nanostructures before and after annealing. The spectra consist of several peaks located at 333, 378, 438, 574 and 590 cm^{-1} corresponding to E_{2H} - E_{2L} , $A_{1(TO)}$, E_{2H} , $A_{1(LO)}$ and $E_{1(LO)}$ modes of ZnO, respectively [16]. The prominent E_{2H} mode positioned at 438 cm^{-1} correlated with the vibrations of oxygen atoms is the characteristic of ZnO wurtzite hexagonal structure [17]. The band at 590 cm^{-1} can be associated with the zinc and oxygen related surface defects [18, 19].

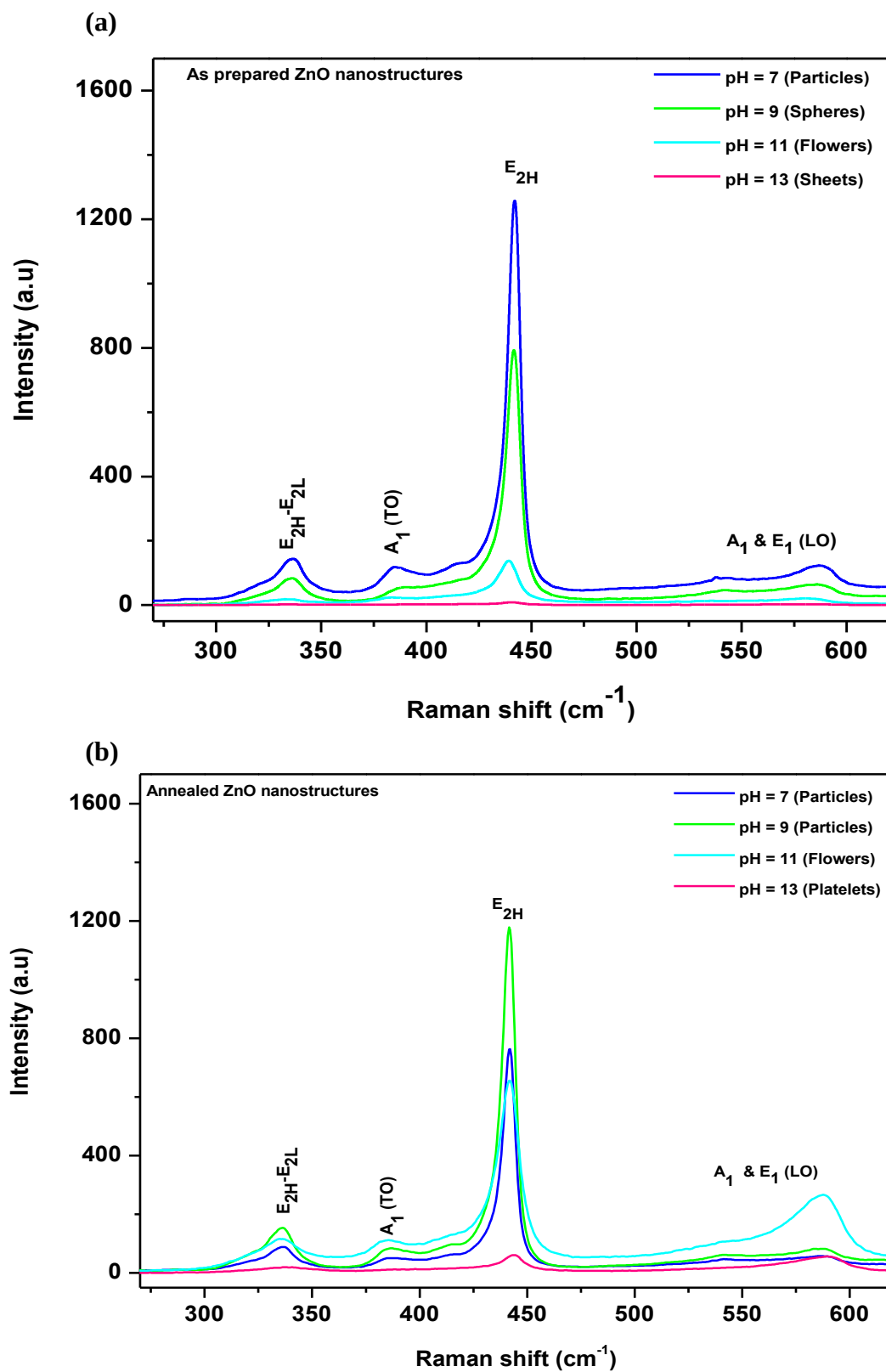


Figure 4.5: Raman spectra of the (a) as prepared and (b) annealed ZnO nanostructures obtained after variation of pH from 7 to 13.

4.3.5 Photoluminescence (PL) analysis

In nanostructured metal oxides, the small length scales and large-to surface volume ratio indicates that surface defects play a significant part in controlling material properties [20]. As mentioned earlier, surface defects are regarded as one of effective strategies to improve the gas-sensing properties. On the other hand, morphological and structural variations have a considerable effect on the defects structure in ZnO. To verify this effect, the PL spectra of the as prepared and annealed nanostructures were measured at room temperature with an excitation wavelength of 325 nm and are shown in Figure 4.6 (a) and (b). As observed in Figure 4.6 (a), the PL spectra of the as-prepared ZnO nanostructures exhibited considerable differences with variation of pH. For instance, a broad asymmetric feature consisting of two wide bands, the weak one in the blue region and a distinct one in the green region centred at 570 nm was observed. With the increase of pH from 7 to 13, the PL intensities of these bands were shown to increase with increasing pH up to 11, and then decreased when the pH was further increased to 13. After annealing at 450 °C (see Figure 4.6 (b)), the green emission band remained strong while the blue one was weakened for ZnO nanostructures obtained at pH of 7 and 9. Further increase of pH to 11 and 13 led to a significant drop in the PL intensity of the green emission band while the blue emission was pronounced

To understand the origin of individual defects, the observed several peaks were well-fitted with a Gaussian function for all spectra including those of the as-prepared (see Figure 4.6 (c) and annealed nanostructures (see Figure 4.6 (d)). At lower wavelengths, the UV emission peaks located at 388 nm and 390

nm usually attributed to the conduction band to valence band (CB-VB) recombination [18, 21] were observed. Violet-blue emissions ranging from 406 to 436 nm in this work can be assigned to zinc interstitials (Zn_i) with different charges, including neutral, single and double [22, 23].

Blue emissions in the region of 450 to 460 nm originate from zinc vacancies (V_{Zn}) [3, 24]. Emission peaks located in the blue-green region from 480 to 555 nm can be ascribed to singly charged oxygen vacancies (Vo^+) [3, 9, 25] while those in the yellow (550-610) are mostly attributed to doubly charged oxygen vacancies (Vo^{++}) [3, 9, 25]. Orange-red emission peaks between 610 and 750 nm could be due oxygen interstitials (O_i) [3, 8, 9, 26].

The enhancement and quenching of the intensity of both green and blue emissions of the as prepared ZnO nanostructures with increasing pH suggest the increase and decrease in the concentration of zinc and oxygen related defects with pH increase. Furthermore, the prominence of the green broad emission indicates that V_O defects exist in large quantities on the ZnO surface for samples produced prior annealing. For structures obtained at lower pH values of 7 and 9 after annealing, the PL spectra were dominated by V_O defects since strong green emissions were observed. In the case of ZnO structures obtained at pH values of 11 to 13, blue emissions were pronounced and this indicates that large quantities of Zn_i were formed on ZnO surface with post-annealing process. The decrease in the PL intensity with annealing in this case can be associated with the decrease in the concentration of both zinc and oxygen related defects in ZnO surface.

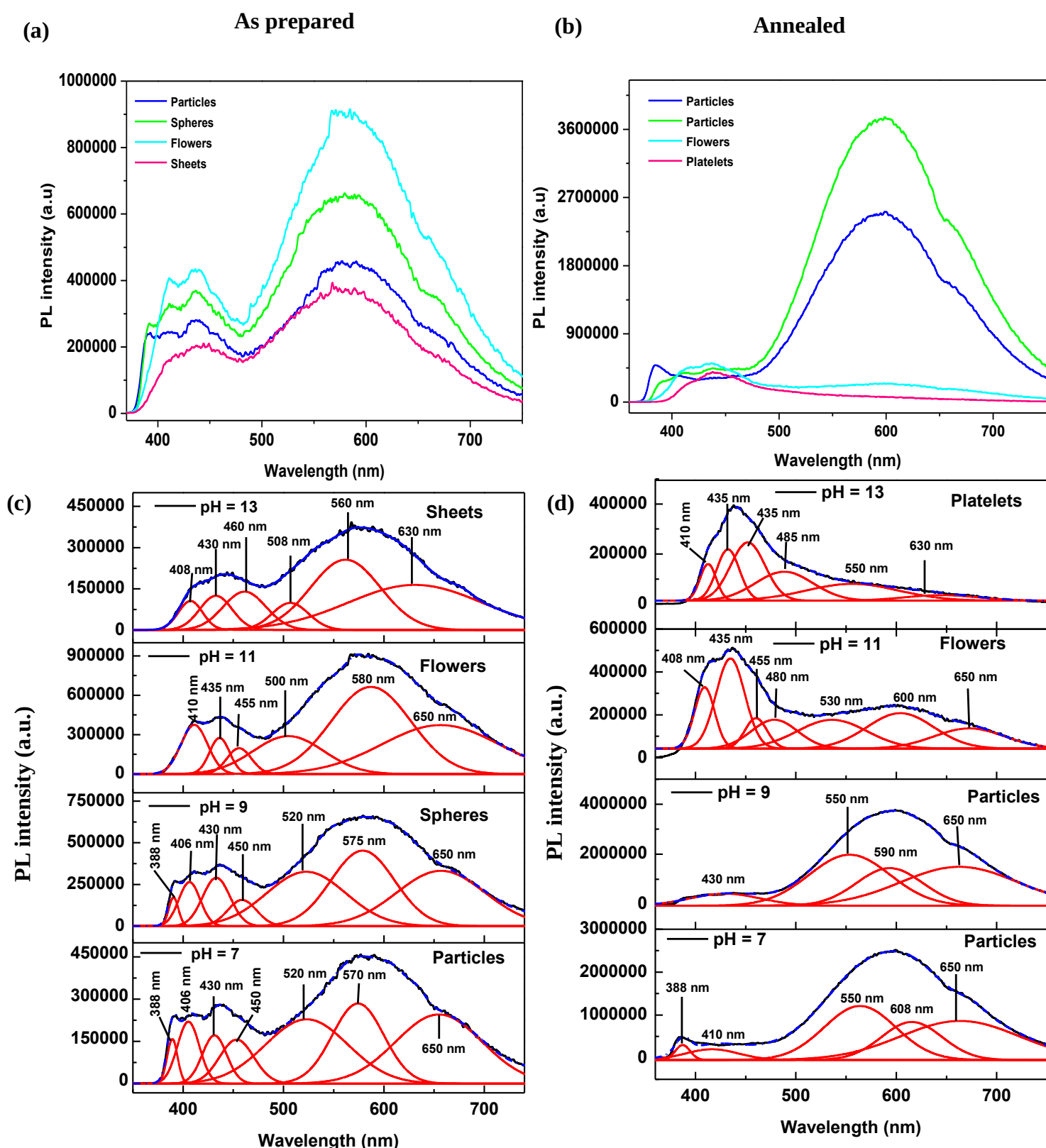


Figure 4.6: Comparison PL and de-convoluted spectra of the (a) and (c) as prepared and (b) and (d) annealed ZnO nanostructures obtained after variation of pH from 7 to 13.

4.3.6 Electron paramagnetic (EPR) analysis

To identify and understand the nature of impurities and surface defects in ZnO, EPR studies were conducted. Figure 4.7 (a-b) presents the EPR spectra of the as-prepared and annealed ZnO nanostructures. Prior to annealing, the EPR spectra (Figure 4.7 (a)) revealed two absorption peaks, the broad and prominent one at 270 mT followed by the weak and narrow one at 330 mT for all samples. The broad one at 270 mT can be associated with ferromagnetic resonance (FM) [3, 13], while the narrow one at 330 mT could be due to paramagnetic resonance (PM) [3, 27]. The PM feature became weaker with increasing pH and it was completely quenched and transformed into very small hyperfine structure for flower-like structures obtained at a pH of 11 and hence only one broad FM feature could be observed. After annealing, only one broad band associated with FM could be seen with increasing pH to 11. The PM feature was transformed into very small hyperfine structure after annealing for structures produced at pH levels of 7, 9, and 11. At pH of 13 (platelets-like structures) the intensity of the FM dropped and the PM appeared again. The presence of hyperfine structures in this case indicates the interactions between electronic state and nuclear spin momenta in Zn^{2+} [13].

According to several experimental reports, ferromagnetism in undoped ZnO nanostructures is related to several paramagnetic defects such as V_{Zn} , Zn_i and V_{O} present in the surface of ZnO [13, 27]. This agrees well with our PL results presented above in which co-existence and variation of blue and green emissions associated with Zn_i and V_{O} defects prior and after annealing was

observed. For as-prepared ZnO nanostructures V_O are dominant defects whereas for annealed ZnO nanostructures V_O are only dominant for structures obtained at lower pH levels (7 and 9). For pH of 11 and 13, Zn_i are of large quantities. The observed variations (decrease and increase) in the intensities of the EPR signals implies the variations in the concentration of the above mentioned defects on the surface of ZnO with increasing pH which correlates with our PL results. Most interestingly, no shift on the EPR signals occurred with structural transformation induced by variation of pH prior and after annealing which correlates well with the PL results. Based on these observations, the observed FM signal is therefore associated with combination of Zn_i and V_O defects on ZnO surface in the current study [3, 13, 28]. The PM signal is believed to be arising from different magnetic clusters of defects positioned near the surface of ZnO [4].

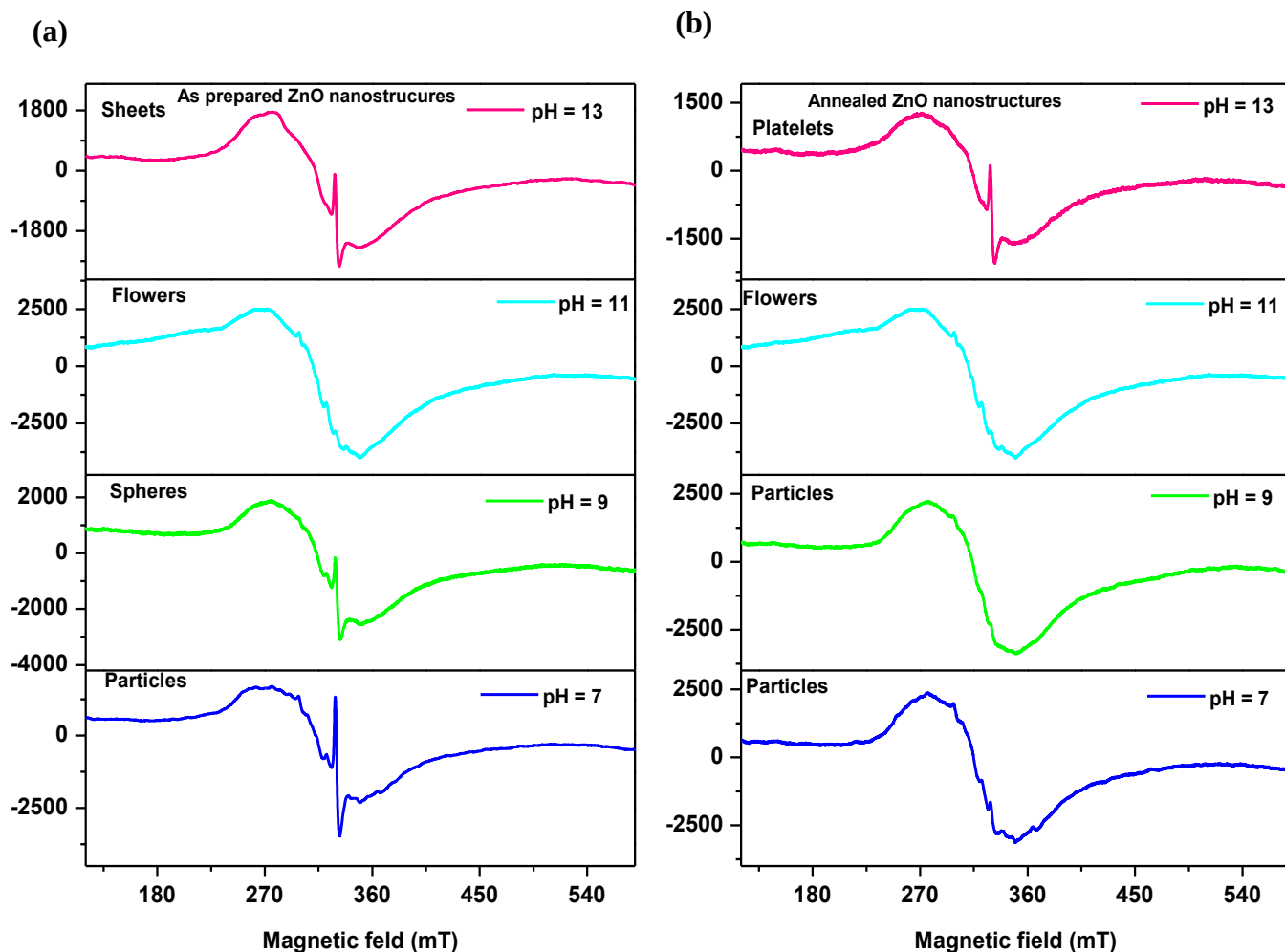


Figure 4.7: EPR spectra of the (a) as prepared and (b) annealed ZnO nanostructures obtained after variation of pH from 7 to 13.

4.3.7 Sensing properties

Gas sensor response of metal oxide based sensors is mainly determined by the interaction between the target gas and oxygen species in the surface of the sensor material. Hence the morphology, surface area and defects are important for gas sensing. To investigate the effect of morphology, surface area and defects on sensing properties, sensors based on the as-prepared and annealed ZnO nanostructures obtained at various pH levels were tested

at different gases including CH₄, CO, NH₃ and H₂. Figure 4.8 (a-d) shows the response characteristics of the ZnO sensors based on pH 7, 9, 11 and 13 towards various concentrations (5 to 100 ppm) of CH₄, CO, NH₃ and H₂ at 250 °C.

For as prepared ZnO nanostructures, response values of 27.7 (40 ppm), 27.1 (40 ppm), 16.3 (60 ppm) and 32.9 (100 ppm) were obtained when the ZnO sensors based on pH 7, 9, 11, and 13 were expose to CH₄ (a), respectively. After exposing the nanostructures to CO (b), the responses obtained were, 159.7, 86.3 and 136.6 at 100 ppm for pH 7, 11 and 13 based sensors, respectively whereas the maximum response obtained for ZnO sensor based on pH 9 was 79.7 at 40 ppm. With exposure to NH₃ (c), the maximum responses were 220.3 and 25.2 at 100 ppm for pH 7 and 13 based sensors and 28.7 and 12.8 at 40 ppm for pH 9 and 11 based sensors, respectively. Upon exposure to H₂ (d), the pH 7, 9, 11, and 13 based sensors gave the highest response of 62.4, 90.1, 85.5, and 118.9 at 80, 5, 5 and 100 ppm, respectively. Based on these results it is clear that the sensing performance of the ZnO nanostructures is influenced by the morphology, while the morphology depends on the pH variance.

Annealing of materials induce a change in the microstructural and stoichiometry of materials [29]. The morphology change of the ZnO structures was observed for pH 9 and pH 13, whereas pH 7 and pH 11 didn't show any obvious morphology change, but the PL and EPR studies showed that there is stoichiometry change in these structures.

As prepared ZnO nanostructures

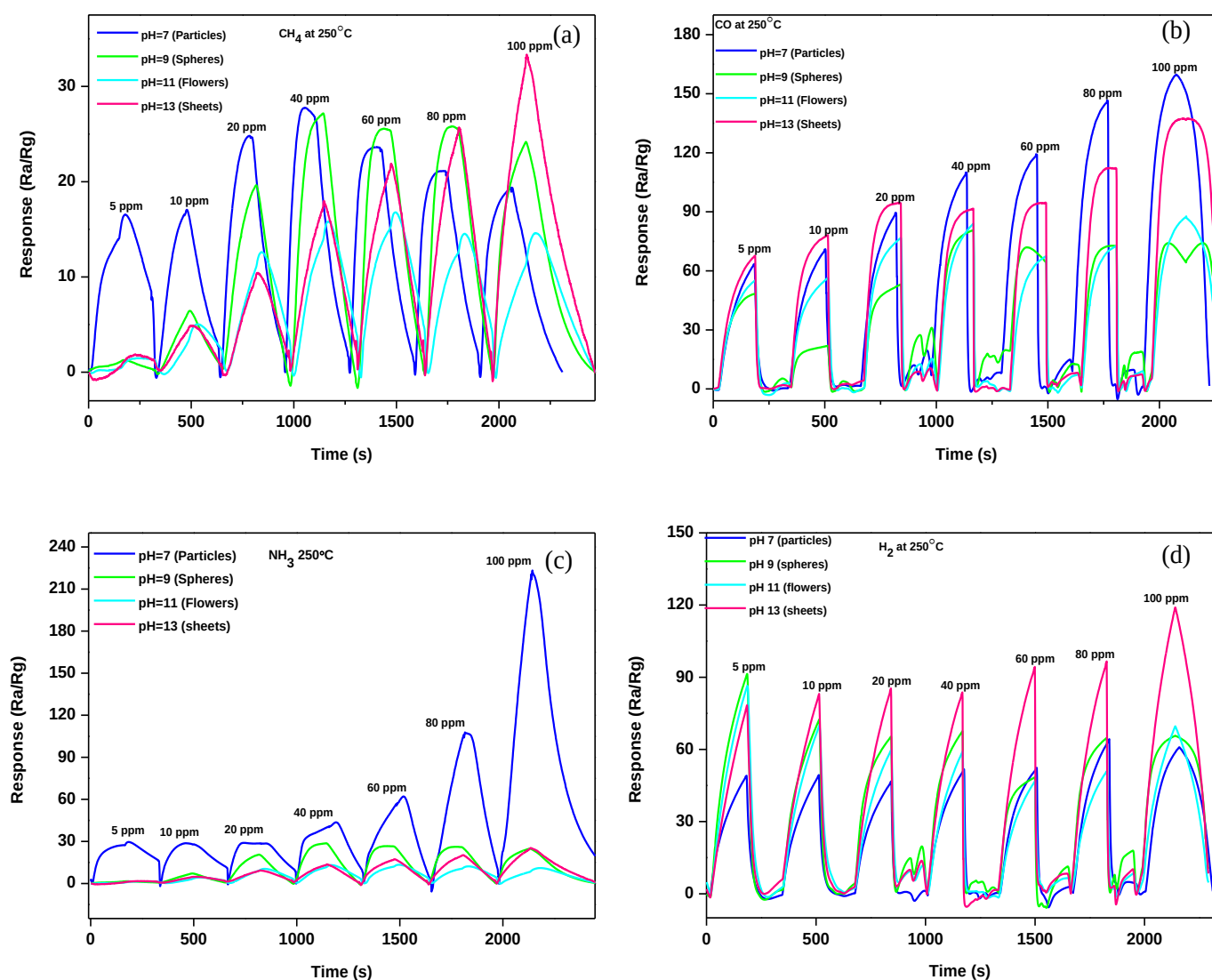


Figure 4.8: Response curves of the ZnO structures based sensors before annealing to different concentrations of (a) CH₄, (b) CO, (c) NH₃ and (d) H₂.

Figure 4.9 shows the response curves of the ZnO structures after annealing at 450 °C. When the sensors were exposed to CH₄ (a), the particles (pH 7 and 9) and the platelets (pH 13) based sensors showed their maximum responses of 30.1, 27.6 and 71.5 at 100 ppm, respectively while flowers at pH 11 showed maximum response of 10.1 at 80 ppm. For CO (b), maximum responses of 119.3, 57, 71.2 and 136.4 at 100 ppm for pH 7, 9, 11 and 13 based sensors,

respectively were obtained. Maximum responses of 130.1, 105.1, 80.8 and 191.7 at 100 ppm for pH 7, 9, 11 and 13 based sensors respectively were obtained with introduction of NH_3 (c) in a chamber. Upon H_2 (d) exposure, pH 7 and 11 sensors showed a maximum response of 90.6 and 55.8 at 100 ppm, respectively whereas the pH 9 sensor showed a maximum response of 92 at 80 ppm, and 123.5 at 10 ppm for pH 13 sensor.

Annealed ZnO nanostructures

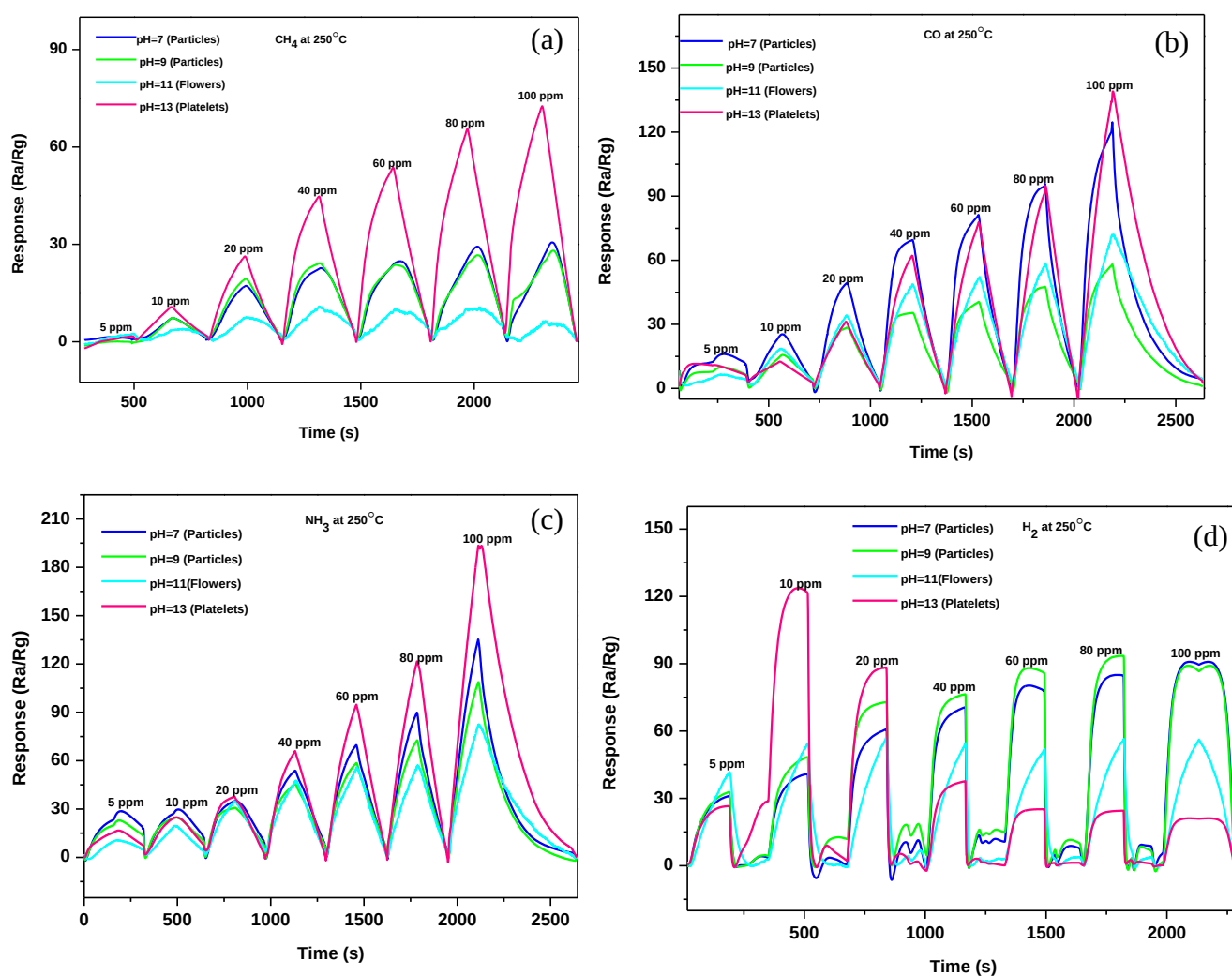


Figure 4.9: Response curves of the ZnO based sensors after annealing to different concentrations of (a) CH_4 , (b) CO , (c) NH_3 and (d) H_2 .

N₂ adsorption measurements revealed the reduction in the surface area and porosity of the ZnO structures with annealing at 450 °C. It is clear based on these observations that higher temperature annealing produced an obvious decrease of surface adsorption positions and reacting area for oxygen and target gases. It is therefore expected that the sensor response becomes lower with the decrease of porosity as a result of post annealing. However, in this work, the sensors became more stable after annealing showing improvement in the crystallinity and structural stability of the ZnO based gas sensors [30].

The sensing properties of ZnO are greatly influenced by the following factors: additives, morphology, grain size, working temperature, and porosity. On the other hand, micro-structural parameters including morphology, grain size, surface-to-volume ratio, porosity, and agglomeration [31] of undoped oxides have also been demonstrated to play an important role in gas sensing properties. However, surface-to-volume ratio and grain size have been found to have a major effect on adsorbed oxygen and gas–solid reaction [31]. Other reports have indicated that porosity has a big influence in sensitivity due to the fact that higher porosity will provide more percolation paths of gas molecules [31]. The pores having dissimilar sizes play different parts in transportation of gas molecules. It is therefore believed that both the grain size and porous microstructure play a significant role in increasing the sensing properties via helping gas percolation.

Furthermore, it is generally accepted that the gas response of metal oxide sensors usually involves two processes namely; diffusion and chemisorption

of gases [14]. Having nanostructures with high porosity offers a direct pathway for the gases to diffuse into the inner part of the sensor material [14, 32]. The specific surface area of the sensor material plays a vital role on the adsorption of oxygen molecules on the surface of the sensor, so a higher surface area leads to more chemisorbed oxygen species on the sensor surface. Small surface area reduces both oxygen and the adsorbing capacities of target gases, thus lowering gas response. In addition, surface defects on ZnO such as Zn_i and V_o also play an important role in the gas sensing properties of ZnO. This is because more oxygen molecules can be easily adsorbed and ionized on the surface of ZnO [3, 18]. It can therefore be concluded that according to SEM, N_2 adsorption, PL, and EPR analysis in current study, changes in morphology, porosity, surface area and structural defects induced by change of pH play a major role in variation of sensor response observed for both the as-prepared and annealed ZnO structures.

4.3.7.1 Response vs concentration

The sensor response is expected to increase with increasing concentration of the target gas. This is because the sensor response highly depends on the removal of the adsorbed oxygen species through a reaction between these oxygen species and the target gas, which will generate electrons. So when the sensor is exposed to low gas concentration, there will be a low coverage of the target gas on the surface of the sensor material, resulting in a low response. The surface reaction increases with increasing target gas concentration as there will be more surface coverage which will result in a higher sensor response. However, the surface reaction will be slow when the saturation point on the coverage of molecules is reached [33].

Figure 4.10 shows the variation of response of the as-prepared ZnO structures to CH₄, CO, NH₃ and H₂ concentration. When exposed to the four test gases, the ZnO nanostructures based gas sensors exhibited a rapid increase with increasing gas concentration until they reached a point where the response started decreasing with increasing concentration, which indicates that the sensors have reached their saturation limit. Upon exposure to CH₄, pH 7 and 9 based sensors reached their saturation limit at 40 ppm, whereas pH 11 saturated at 60 ppm and pH 13 showed an increase in response up to 100 ppm without reaching saturation. In the case of CO (b), all the sensors except for pH 9 sensor showed an increase in response with increasing CO concentration until 100 ppm. This kind of sensor behaviour suggests that these three sensors can respond at both low and high concentration of CO. Meanwhile the pH 9 sensor saturated at 40 ppm CO. For NH₃ (c), pH 7 and 13 sensors showed an increase in response without saturating until 100 ppm, whereas the pH 9 and 11 based sensors saturated at 40 ppm. When the sensors were exposed to H₂ (d); pH 9 and 11 based sensors saturated at 5 ppm, this behaviour shows that these two sensors are not suitable for detecting high concentration of H₂. The pH 7 and 13 based sensors showed saturation at 80 and 100 ppm H₂.

As prepared ZnO nanostructures

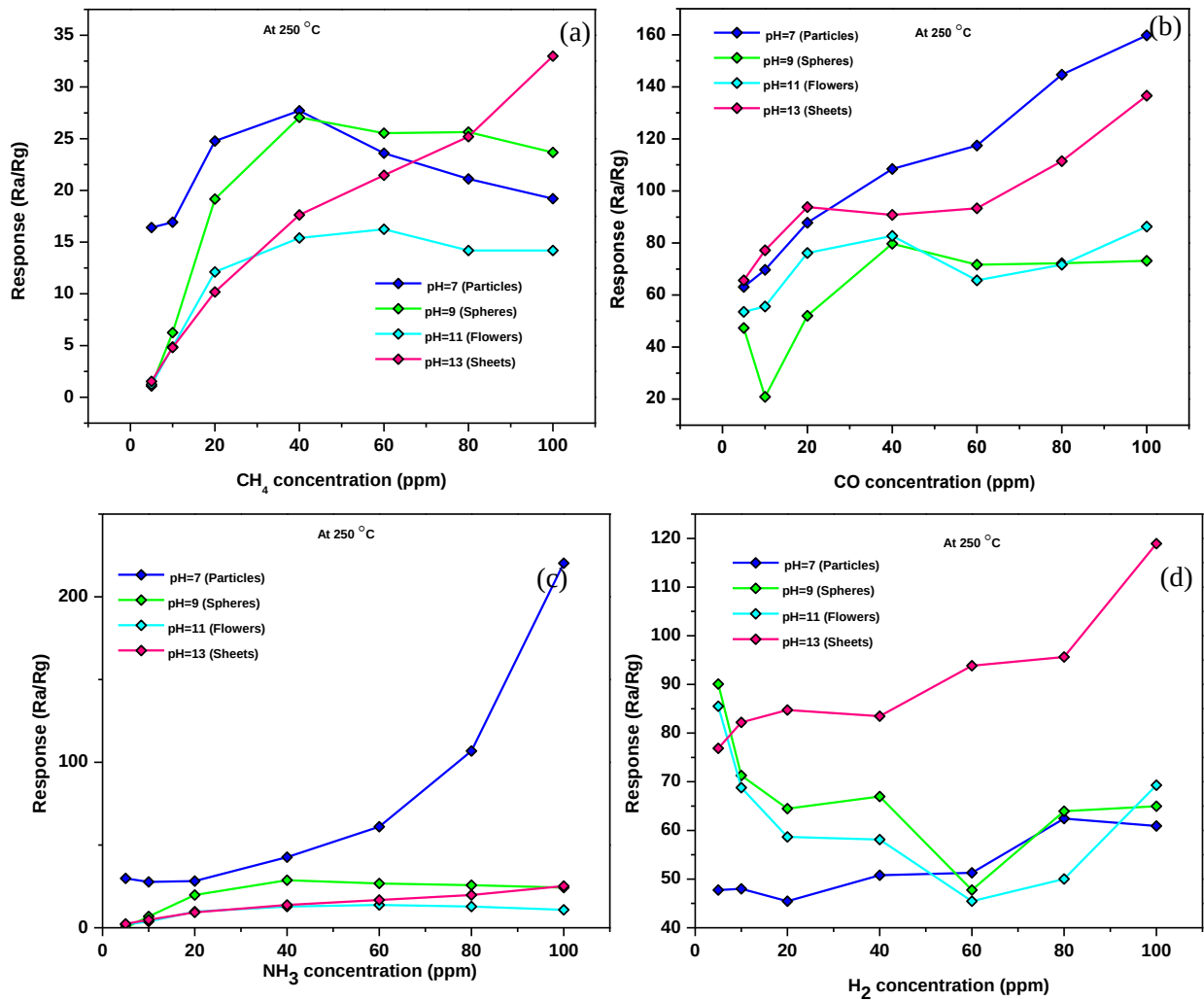


Figure 4.10: Sensing response of the ZnO structures before annealing to different concentration of (a) CH₄, (b) CO, (c) NH₃ and (d) H₂ at 250 °C.

After annealing the sensors showed improved trend as now the sensors were showing more of a dependence on the gas concentration as the response was increasing with increasing gas concentration (shown in Figure 4.11). However, the platelets (pH 13) showed a different trend from the other sensors when exposed to H₂. The sensor based on pH 13 showed its maximum response to

H₂ at 10 ppm, and started to have a decrease in response with increasing H₂ concentration. The platelets reached saturation at 10 ppm of H₂, which is different from the behaviour observed before annealing. This change of behaviour could be due to the morphology change and the nature of the gas. As much as the morphology influences the response of the sensor material; the nature of the gas does as well. Gas sensor response is governed by adsorption and reactions of the detected gases on the surface of the sensor material. For ZnO sensor materials, the surface adsorption of the detected gases depends on the nature of the gas such as the polarity, molecular weight and structures of the detected gas molecule. These properties determine whether the gas will be easily absorbed on the surface of the sensor material or not [14, 34]. So since the platelets are showing a saturation point at 10 ppm of H₂, the morphology change can be the cause of that.

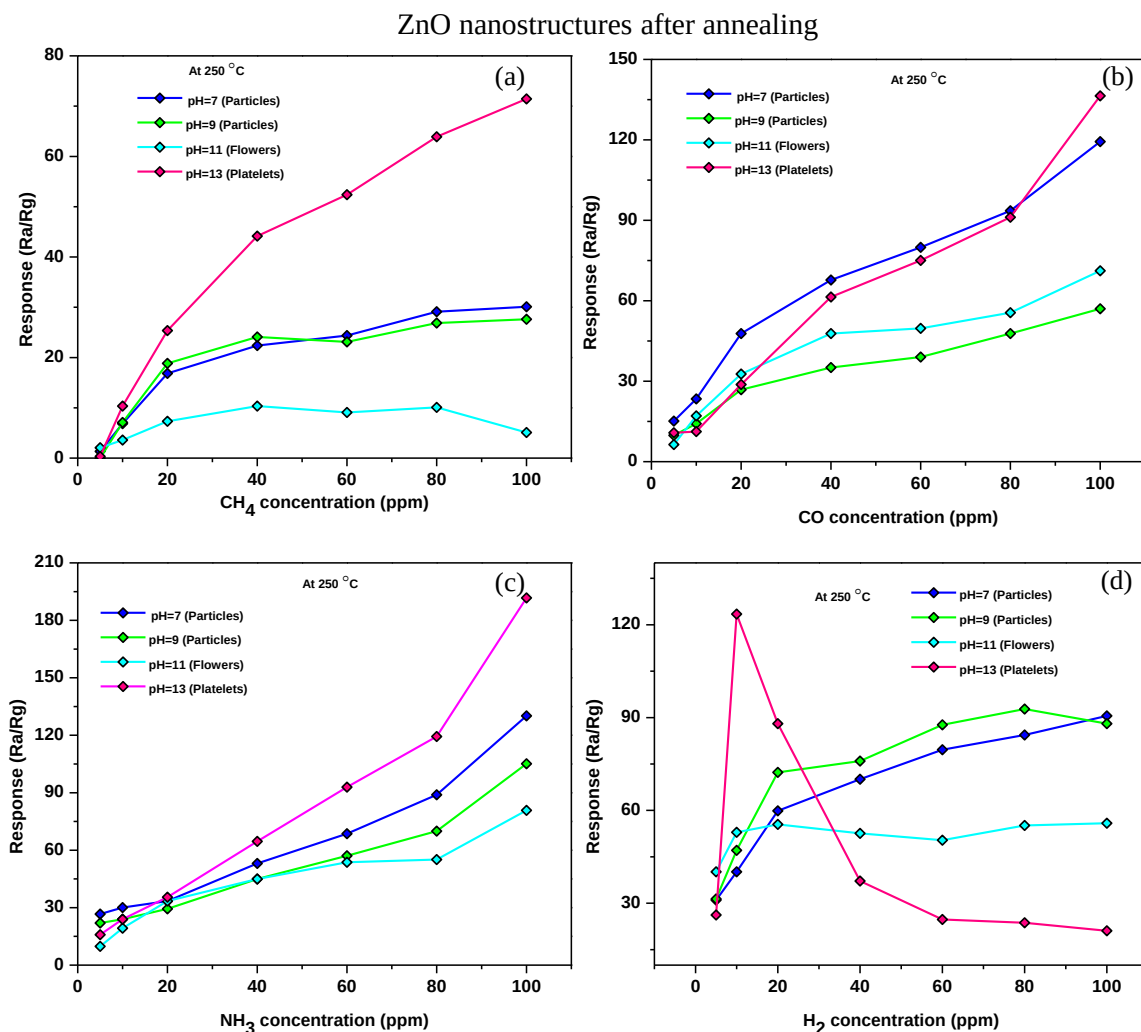


Figure 4.11: Sensing response of the ZnO structures after annealing to different concentration of (a) CH_4 , (b) CO , (c) NH_3 and (d) H_2 .

4.3.7.2 Response-recovery property

Prior annealing, the sensors respond more to CO , and after annealing they respond more to NH_3 . This means that the sensors based on the ZnO structures before annealing can be applied for the detection of CO and the annealed structures can be applied for the detection of NH_3 at 250 °C. Figure 4.12 shows the response and recovery time plots for the CO and NH_3 at 250 °C. The response and recovery times are important parameters for gas sensors as they determine the commercial usage of a sensor. The response

times (a) for the ZnO based sensors before annealing to CO ranges between 28-79 seconds, with the flowers (pH 11) and particles (pH7) showing longer response time at low concentrations of CO. The recovery times (b) of the sensors to CO ranges from 3-54 seconds.

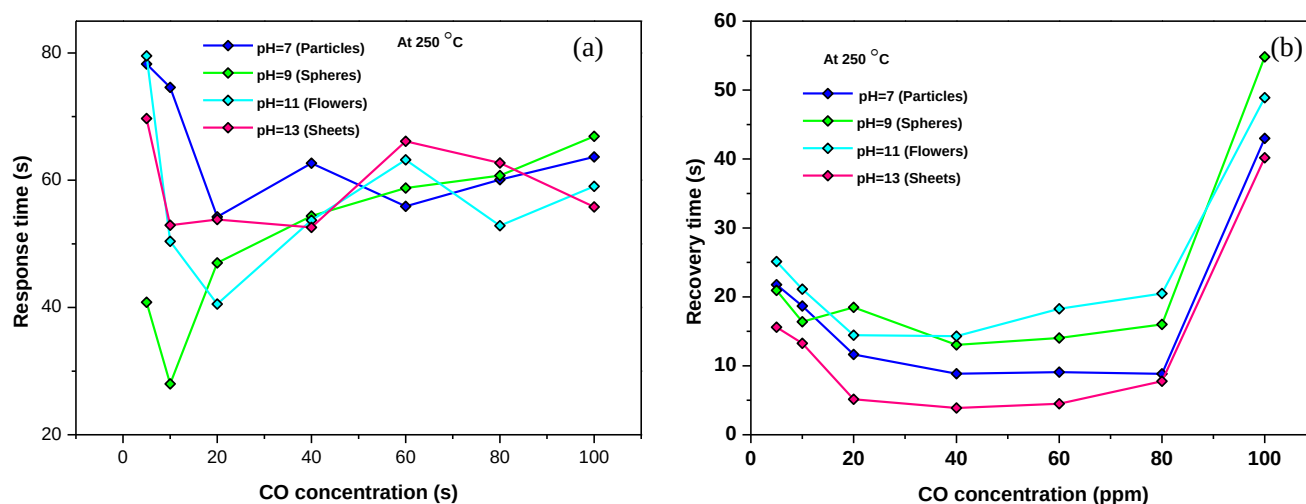


Figure 4.12: (a) Response and (b) recovery times for the ZnO structures before annealing based sensors to different concentrations of CO at 250°C.

The annealed ZnO structures show longer response times (a) ranging from 36-164 seconds and recovery times (b) ranging from 12-407 seconds when exposed to NH_3 (Figure 4.13). It is noticed that for both gases the ZnO based sensors show an increasing recovery time with increasing gas concentration. This can be because more gas is adsorbed on the surface of the material and the desorption gets delayed by the bonding between the ZnO sensors and the gas molecules [35].

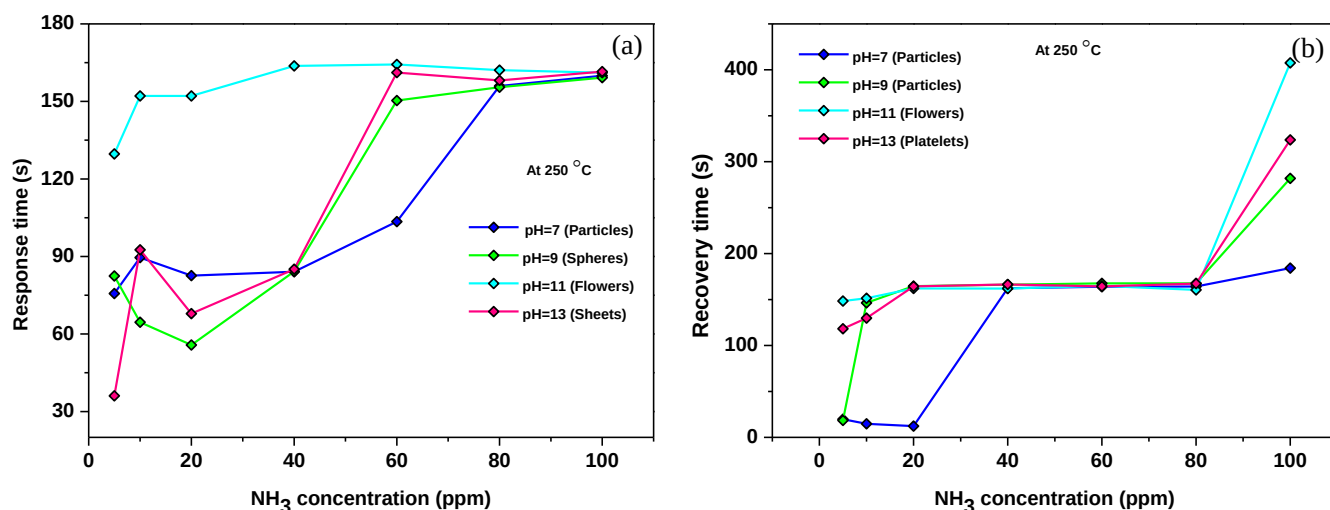


Figure 4.13: (a) Response and (b) recovery times for the ZnO structures after annealing based sensors to different concentrations of NH_3 at 250°C .

4.3.7.3 Gas selectivity

The ability of a sensor to single out a certain gas in the midst of other gases is one important parameter for a gas sensor, and it is called selectivity. Gas sensing response of the ZnO structures to 100 ppm of CH_4 , CO , NH_3 and H_2 at 250°C is presented in Figure 4.14 (a-b). The results indicate that the response of the ZnO structures without annealing to CO is higher than that to other gases, except for the structures at low pH of 7. However, after being subjected to annealing, results for the annealed structures indicate that the ZnO structures show high response to NH_3 . So the change of selectivity of the structures after annealing might have to do with the structural changes that the ZnO structures went through.

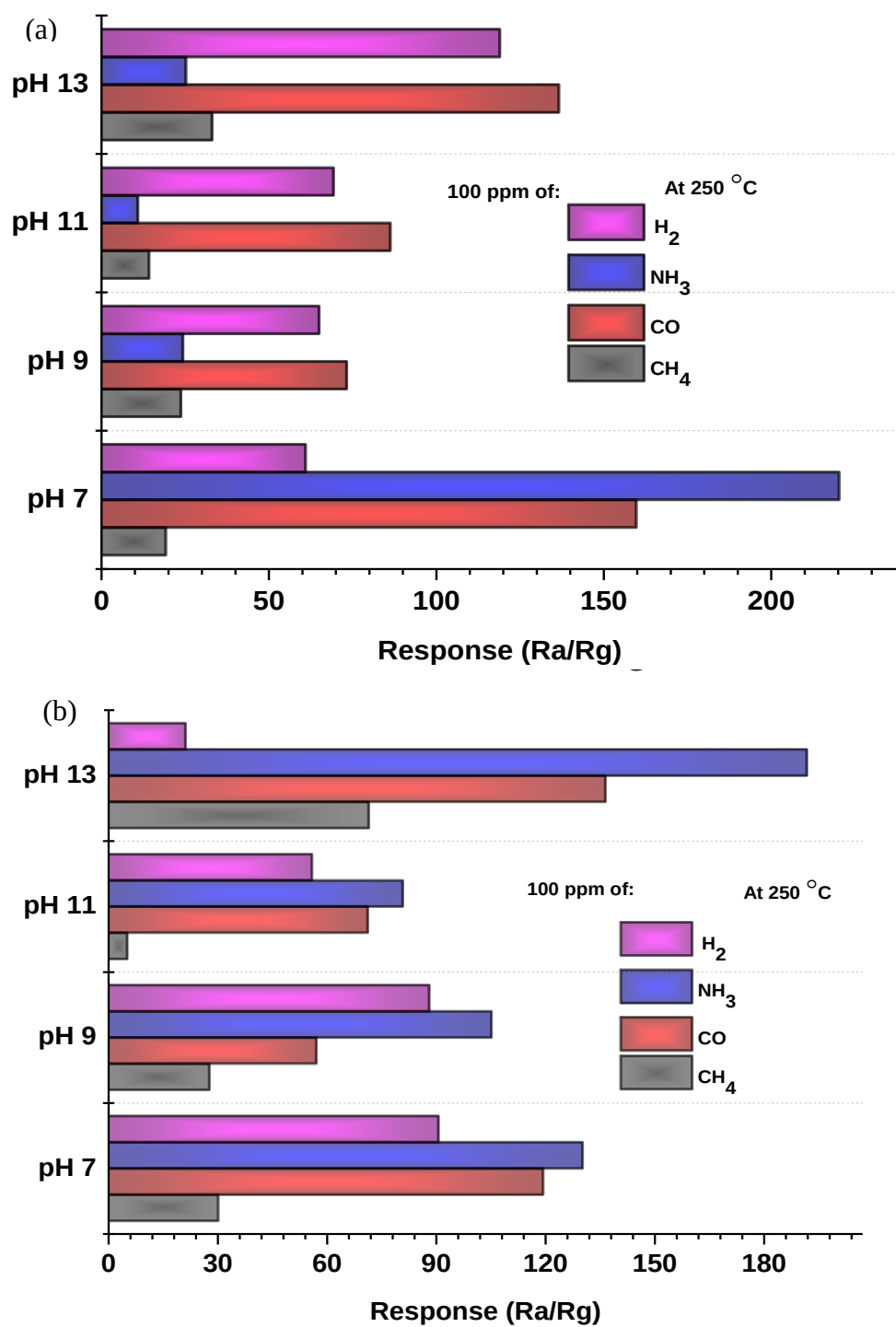
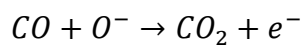


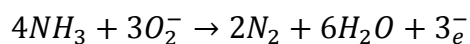
Figure 4.14: (a) Response of the as-prepared ZnO structures towards 100 ppm of different gases and (b) Response of the ZnO structures after annealing towards 100 ppm of different gases.

4.3.8 CO and NH₃ sensing mechanism

Owing to its n-type conductivity, ZnO has more electrons on its surface and its sensing mechanism is governed by changes of electrical resistance when in contact with reductive or oxidizing gases. When a ZnO based sensor is in air, oxygen molecules get adsorbed on its surface, the oxygen molecules then captures the electrons from the conduction band, resulting in the formation of oxygen ions and resistivity of the ZnO sensor. The oxygen species formed depends on the operating temperature of the sensor. At temperatures less than 150 °C the ions forming are O_2^- , O^- forms at a temperature between 150 and 450 °C, and above 450 °C forms O^{2-} [18, 36]. Since the operating temperature for the ZnO sensors in this study is 250 °C, the oxygen ions involved in the sensing mechanism will be O^- . When the as prepared ZnO nanostructures based sensors get into contact with CO, the oxygen ions on the surface of the ZnO based sensor will react with CO to form carbon dioxide and release the captured electrons back to the conduction band, the reaction happens as follows:



When the annealed ZnO nanostructures based sensors comes into contact with NH₃, the reaction between the oxygen ions and NH₃ will generate nitrogen and the captured electrons will be released back to the conduction band. The reaction is as follows:



Both reactions leads to a reduction in the resistance of the ZnO based sensor due to the increase of electrons in the ZnO nanostructures.

4.4 Conclusion

As-prepared and annealed ZnO nanostructures with different morphologies achieved by variation of pH were successfully synthesized using the microwave-assisted hydrothermal method. Effect of pH and post-annealing on structural, surface area and porosity, luminescence and magnetic properties was investigated. SEM showed morphological transformation with pH variation and post annealing. BET measurements revealed a drop in surface area and porosity with annealing at 450 °C. Correlation between PL and EPR studies showed that Zn_i and V_O are responsible for ferromagnetism observed from as prepared and annealed ZnO structures. Variation in surface area and porosity, morphology as well as surface defects caused by change of pH is the main reason for observed variation of ZnO sensors responses upon exposure to various concentrations of CO, CH₄, NH₃ and H₂ at 250 °C. The as prepared sensors showed high response to CO, whereas the annealed nanostructures showed the highest response to NH₃.

4.5 References

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CHAPTER 5

Tailoring the sensing properties of microwave-assisted grown ZnO nanorods: effect of irradiation time on luminescence and magnetic behaviour

5.1 Introduction

Detection of chemical gases is an increasing area of research for keeping our environment unpolluted. Nanorod-like structures are the ideal system for studying the transport process and are of benefit for developing new generation of nanodevices with high performance. Furthermore, ZnO nanostructures have attracted much attention due to their great miniaturization potential and large surface to volume ratio at the nanoscale level which allows quick diffusion of gas molecules, thereby leading to a faster response and recovery time [1, 2]. As a result, a higher sensitivity with a fast response and recovery time can be achieved even at low working temperatures [1]. It is well known that ZnO properties rely on its shape, size and orientation [3, 4], however, obtaining well defined shape and size of the ZnO nanostructures still remains a challenge . With the aid of scanning electron microscope (SEM), high-resolution transmission electron microscope (HRTEM) with selected electron diffraction (SAED), X-ray diffraction (XRD), Raman scattering, and electron paramagnetic resonance (EPR) measurements, the correlations between microstructural, optical, and magnetic properties in terms of defects and crystallinity induced by prolonged irradiation exposure of the nanostructures were investigated in detail. Detailed comparative study on the defect related emission and magnetic behaviour of pure ZnO nanorods is carried out to understand the sensing behaviour of the ZnO nanostructures.

5.2 Experimental details

5.2.1 Preparation of ZnO nanostructures

The chemical materials used for the synthesis of ZnO nanostructures were zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), hexamethylenetetramine (HMTA) and hydrazine hydrate (N_2H_4). All raw chemicals were purchased from Sigma Aldrich, South Africa. Deionized water (DIW) was used as a solvent. In a typical experiment, 0.1 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 50 ml deionized water under magnetic stirring at room temperature for 5 min to form an aqueous solution. At the same time, 50 ml of 0.1 M hexamethylenetetramine (HMTA) was prepared separately and combined with the solution containing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to form a homogeneous mixture. Hydrazine hydrate was then added dropwise to maintain the pH of an aqueous solution at 10 while stirring for 15 minutes. The final mixture was transferred to Teflon vessels, and irradiated in a microwave oven (EM-G430, 2.45 GHz, maximum output power 1000 W, SANYO Electric, UK) at different irradiation times ranging from 10 to 30 min (in steps of 5). The hot solution with a white precipitate was left to cool down naturally to room temperature. Subsequently, the solution was washed several times with de-ionized water and ethanol to remove some impurities. The obtained ZnO products were first dried at room temperature then annealed at 500 °C for 2 hours.

5.2.2 Characterization

Structure and phase analyses were conducted using a Panalytical X'pert PRO PW3040/60 X-ray diffractometer with a Cu-K α ($\lambda = 1.5405 \text{ \AA}$) radiation source. JEOL JSM-7500F Field emission scanning electron microscope and Oxford Energy Dispersive X-ray Spectroscopy were used to study the surface morphology and elemental composition, respectively, of the ZnO nanostructures. Transmission electron microscopy images and selected area electron diffraction images were captured using JEOL TEM-2100 microscope with an accelerating voltage of 200 kV. Photoluminescence spectra were measured on a Jobin-Yvon NanoLog spectrometer at an excitation wavelength of 320 nm at room temperature. The total specific surface area of the nanostructures were measured by nitrogen (N_2) physisorption at 77 K using a Micromeritics TRISTAR 3000 surface area analyzer (USA). The samples were degassed at 200 °C for 12 h under a continuous flow of N_2 gas to remove adsorbed contaminants prior to analysis. Raman spectra were recorded using a Horiba Jobin-Yvon HR800 Raman microscope with a 514 nm excitation Ar^+ laser and a spectral resolution of 0.4 cm^{-1} . The microwave absorption measurements were performed using a JEOL X-band electron paramagnetic resonance spectrometer JES FA 200 (JEOL, Japan) equipped with an Oxford ESR900 gas-flow cryostat and a temperature controller (Oxford Scientific Instruments 9700, UK). For sensing measurements, the ZnO nanostructures were first dispersed in ethanol and drop-coated on the top surface of alumina substrates with a size of $2 \text{ mm} \times 2 \text{ mm}$ with two Pt electrodes and a micro-heater on its bottom surface. Figure 5.1 shows the schematic of the fabricated ZnO sensors. Prior to analyses the samples were

analysed at various temperatures (room temperature, 250, 300, 350 and 400 °C), the samples analysed at 350 °C showed improved sensing response compared to other temperatures; hence this temperature (350 °C) was adopted for analyses. A flow through technique with a constant flow rate of 250 ml/min was used to test the electrical and gas-sensing properties of the thin films. A constant flux of synthetic air of 0.5 L/min was used as a gas carrier into which the desired concentration of CO, NH₃, H₂ or CH₄. Electrical characterization was carried out by volt-amperometric technique while the film resistance was measured by a Keithley 3706 source meter using a Kinesistec testing station

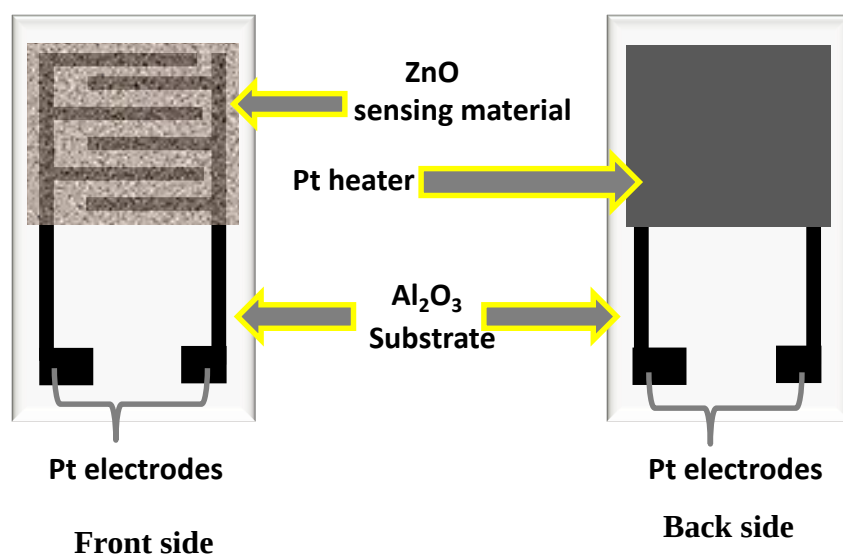


Figure 5.1: Structure representation of the fabricated ZnO sensor.

5.3 Results and discussion

5.3.1 Structural properties, XRD

Figure 5.2 (a) shows the XRD patterns of the ZnO nanostructures. All the diffraction peaks could be perfectly indexed as standard hexagonal wurtzite structure of ZnO which are in accordance with the JCPDS card (No. 36-1451). No other characteristic peaks of impurities arising from reactants of intermediate products were observed, implying the high purity phase of ZnO was crystallized. The sharpness and high intensity of the diffraction peaks of the ZnO samples indicate that the samples were highly crystalline. A noticeable shift on the position of the diffraction peaks towards lower angles at irradiation time of 15 min time was observed as demonstrated in Figure 4.2 (b) using the (101) diffraction peak. With an increase in irradiation time from 15 min to 30 min, the diffraction peaks were shown to shift towards high 2θ angle side. The shifting of the diffraction peaks depends on several factors such as inter-planar distance (d), average crystallite size (D), and lattice strain. Although the average crystallite size and strain are calculated as a function of both angular peak width at half maxima (β) and peak position (2θ), the role of 2θ in determining these values is very minimal compared to β . The inter-planar distance has inverse proportional relationship with diffraction peak position and hence it plays a major role in the shifting of the diffraction peak positions. The observed increase in d -value at 10 min led to a diffraction peak position shifting to lower 2θ side and a subsequent decrease in d -value shifted the diffraction peaks to higher 2θ angle side. A slight decrease in full width at half maxima (FWHM) of major diffraction peak confirms the crystallite size growth. The crystallite size of the ZnO nanostructures were calculated from

the broadening of the (101) diffraction plane using the Debye-Scherrer formula [5, 6] :

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (5.1)$$

where λ is the wavelength of the X-ray used; β is the FWHM; and θ is Bragg's diffraction angle. The crystallite sizes values are shown in table 5.1. The crystallite size was shown to increase from ~33 nm to ~36 nm with an increase in irradiation time to 15 min, and then decreased to ~ 34 nm at 20 to 30 min irradiation times. This increase in crystallite size with irradiation time can be explained by Ostwald ripening phenomenon [5, 7]. Ostwald ripening is an occurrence which can be observed in solids or liquids describing the change of an inhomogeneous structure over time. During this process, molecules from the surface of the small particles get removed and diffuse into the solution. Diffusion of these molecules increases the number of free molecules in the solution. Eventually the free molecules will get supersaturated and condense on the surface of the larger particles causing growth of the larger particles and a shrink of the smaller particles [5, 7]. Although the Debye Scherrer method is a well-known method that it uses XRD patterns to estimate the crystal size based on FWHM of the diffraction peaks, it does not take into account the peak broadening which result from the inhomogeneous strain and instrumental effects. To obtain more detailed information about the crystal size of the studied ZnO nanostructures, Williamson–Hall plot which provide information about lattice strain and effective particle size, particle size with zero strain, present in the sample was also used.

In the current study, the strains in synthesized ZnO nanostructures at irradiation times from 10 to 30 min were estimated and compared using the W–H equation [8]:

$$\beta \cos \theta = \frac{k\lambda}{L} + 4\varepsilon \sin \theta \quad (5.2)$$

where ε represent the strain associated with the nanostructures. Figure 5.3 represents the plot between $\beta \cos \theta / \lambda$ versus $4 \sin \theta / \lambda$ (W-H plot). It can be seen from this Figure that the obtained linear relation has a positive slope which can be attributed to tensile strain in the ZnO nanostructures [9]. The lattice parameters were also calculated [10] and are presented in table 5.1. BET surface area (see Table 5.1) was shown to gradually increase with an increase in irradiation time which correlated with the decrease in rods dimensions with increasing irradiation time.

Table 5.1: Crystallite size, strain, BET surface area and lattice parameters at different irradiation times

sample	2 θ	d ₁₀₁	D-W-H method (nm)	D-Scherrer (nm)	BET Surface area (m ² g)	Strain (X10 ⁻⁴)	a (Å)	c (Å)
10 min	36.35 ±0.01	2.47 ±0.006	30 ±1.65	31 ±1.69	0.03 ±0.02	17 ±1.1	3.24 ±0.004	5.19 ±0.006
15 min	36.10 ±0.04	2.49 ±0.010	33 ±3.42	36 ±1.94	0.05 ±0.03	15 ±0.1	3.26 ±0.003	5.22 ±0.001
20 min	36.40 ±0.03	2.47 ±0.008	33 ±3.39	34 ±2.89	0.99 ±0.17	13 ±1.9	3.23 ±0.001	5.18 ±0.001
25 min	36.50 ±0.01	2.46 ±0.008	32 ±3.06	34 ±1.86	1.69 ±0.17	17 ±0.9	3.23 ±0.002	5.17 ±0.002
30 min	36.38 ±0.02	2.47 ±0.007	32 ±3.04	34 ±1.85	2.58 ±0.14	14 ±1.1	3.24 ±0.001	5.19 ±0.003

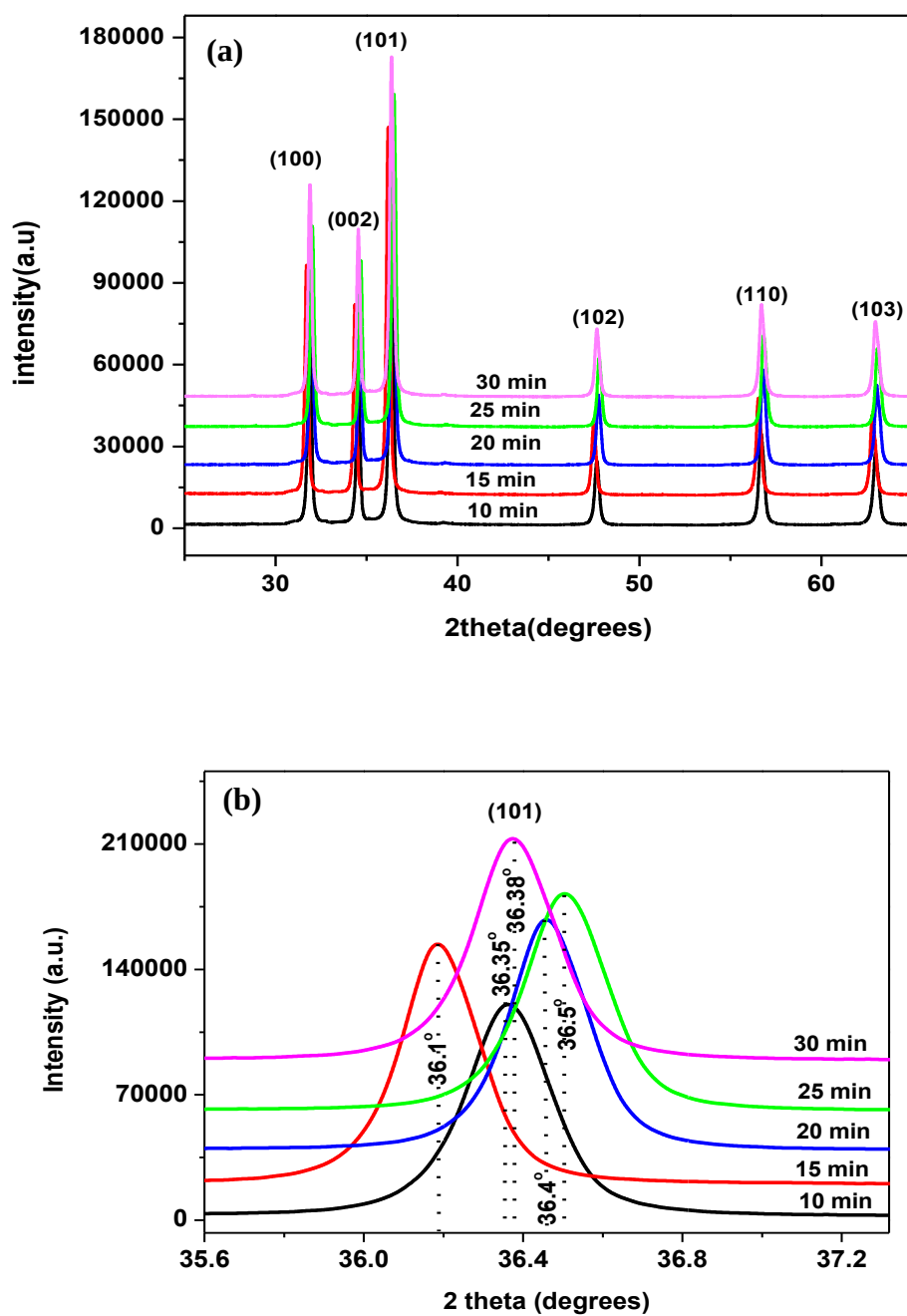


Figure 5.2: (a) XRD diffraction patterns of the ZnO nanostructures at different irradiation times (10-30 minutes), (b) magnified view of (101) diffraction peak.

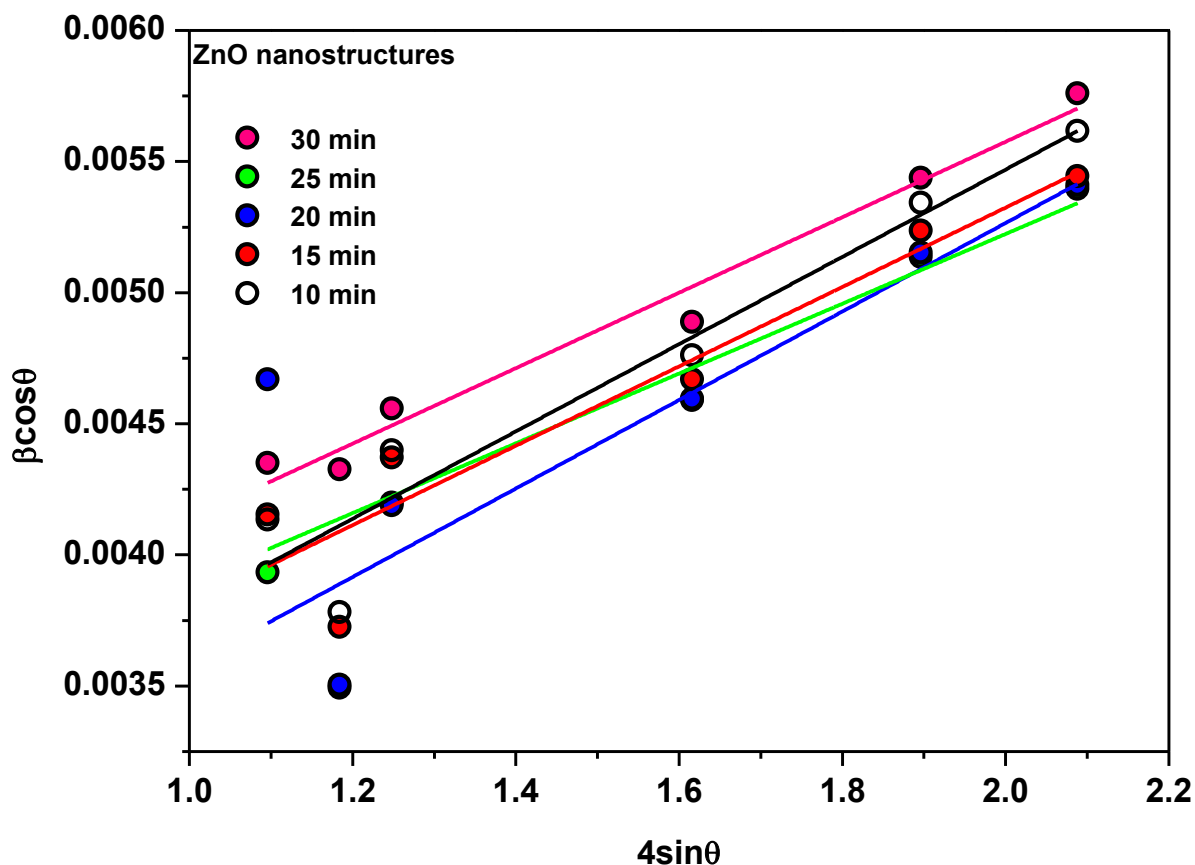


Figure 5.3: Williamson-Hall plots of the ZnO nanostructures at different irradiation times.

5.3.2 Morphology, FESEM and TEM

Figure 5.4 shows the SEM images of the ZnO nanostructures synthesized at irradiation times of: (a) 10 min, (b) 15 min, (c) 20 min, (d) 25 min and (e) 30 min. It is obvious from the images that irradiation time influenced morphology of ZnO particles. All the samples clearly exhibit the formation of rod-like structures. The average lengths and diameters of ZnO nanostructures are shown in Table 5.2. At irradiation time of 10 min (Figure 5.4 (a)), the SEM image reveals clustered multi-nanoparticles forming smooth rod-like structures. Upon increasing irradiation time to 30 min (Figure 5.4 (e)), the rods became thinner and shorter as compared to those prepared at 10 min irradiation time. The EDS spectrum in Figure 5.4 (f) confirms the presence of

all the elements (Zn and O) in our samples. The weak C peak is from the carbon tape on which the samples were mounted. The HRTEM images presented in Figure 5.5 (a-e) revealed very clear and well-defined lattice fringes of ZnO. The inter-planar spacing of the rod-like structures obtained at irradiation time of 10 min (Figure 5.5 (a)) was 0.28 nm corresponding to the d-spacing of the (100) plane of wurtzite structured ZnO. The selected area electron diffraction (SAED) pattern of the ZnO nanorod shown in the inset of Figure 5.5(a), illustrates that the individual nanorod is single crystalline in nature and preferentially grew along the [100] direction. For structures obtained after irradiation times of 15 to 30 min (Figure 5.5 (b-e)), a lattice spacing of about 0.26 nm was observed, which corresponds to an interlayer spacing of the (0002) planes in the ZnO crystal lattice. Using the HRTEM and SAED patterns of ZnO (irradiated for 15-30 min), it was confirmed that all the nanostructures (inset of Figure 5.5 (b-e)) had a [0001] direction, the polar c-axis of the ZnO crystal lattice.

Table 5.2: Rod dimensions obtained at varied irradiation times

Sample	Length (nm)	Diameter (nm)
10 min	909 $\pm$ 3.49	240 $\pm$ 6.62
15 min	575 $\pm$ 10.79	151 $\pm$ 3.57
20 min	706 $\pm$ 11.18	131 $\pm$ 0.48
25 min	627 $\pm$ 7.56	140 $\pm$ 3.77
30 min	579 $\pm$ 6.00	116 $\pm$ 1.49

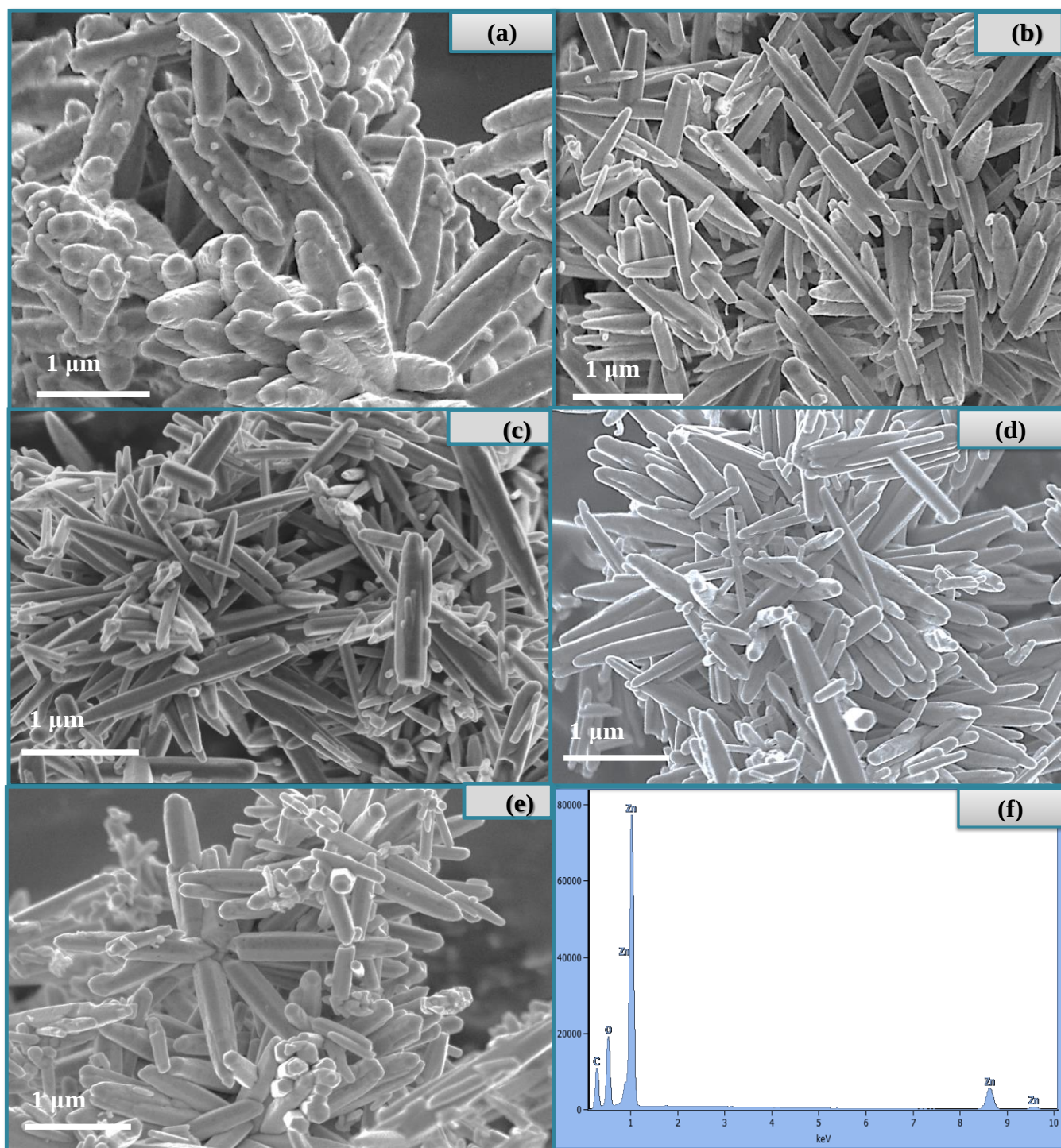


Figure 5.4 (a-e): FESEM images of ZnO nanostructures at different irradiation times (10-30 min respectively) and (f) EDS spectrum of the ZnO nanostructures.

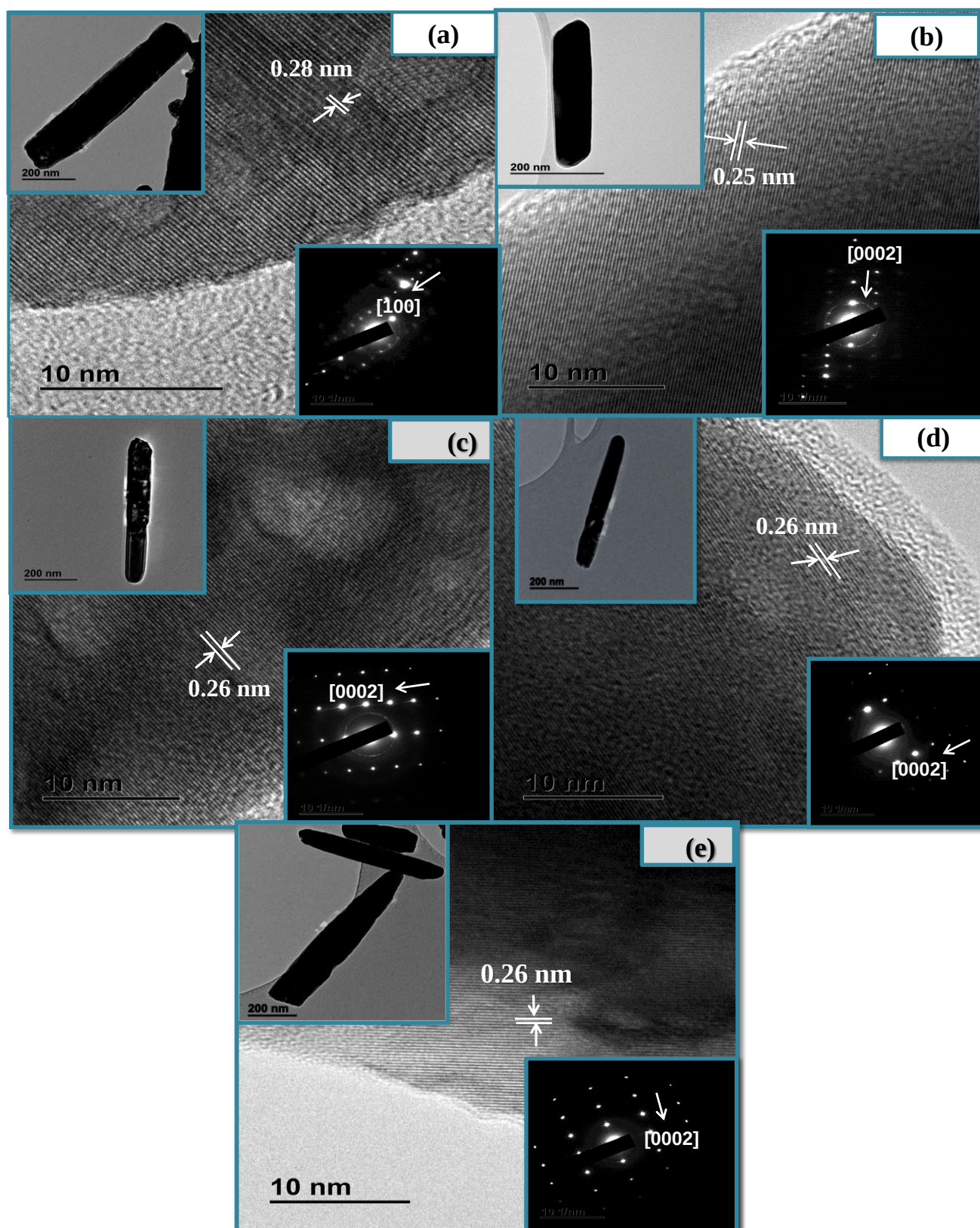


Figure 5.5 (a-e): TEM and HRTEM images of the ZnO nanostructures at different irradiation times.

5.3.3 . Raman scattering studies

To investigate the vibrational modes and the phase purity of the ZnO nanostructures, the Raman scattering method was employed. Figure 5.6 shows the Raman scattering spectra of the ZnO nanostructures prepared at different irradiation times. The sharp dominant peak observed at 438 cm^{-1} is known as the Raman-active dominant E_{2H} mode of the wurtzite hexagonal phase ZnO [11]. Other peaks observed at 332 and 380 cm^{-1} can be assigned to $E_{2H}-E_{2L}$ (multiphonon) and A_{1T} modes respectively [12, 13]. A broad peak at 582 cm^{-1} corresponding to superimposition of A_1 (LO) and E_1 (LO) [13] was also observed. This peak is believed to be caused by defects in ZnO such as oxygen vacancy, zinc interstitial and/or their complexes [14, 15].

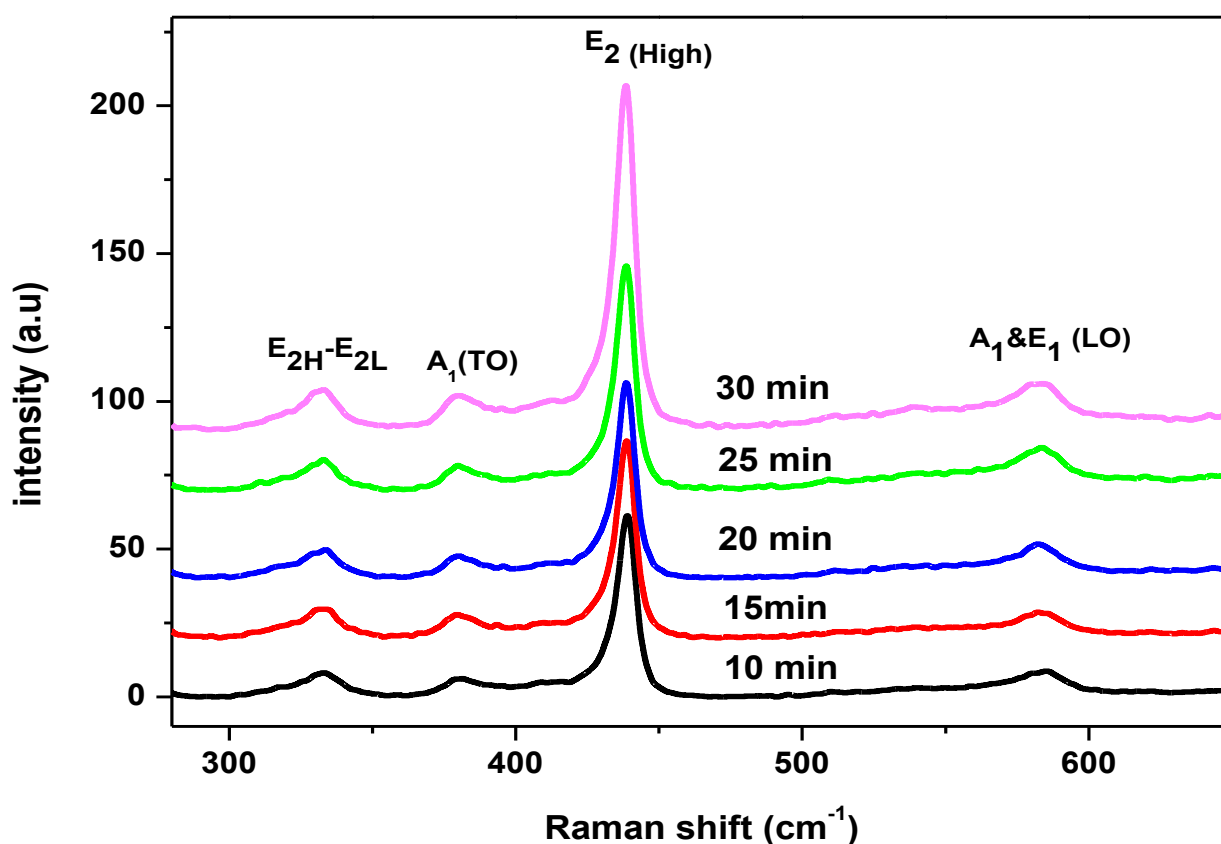


Figure 5.6: Raman spectra of ZnO nanostructures at different reaction times.

5.3.4 Photoluminescence (PL) studies

To identify point defects in ZnO nanostructures, PL and EPR measurements were performed. Figure 5.7 (a) compares the PL spectra of the ZnO nanostructures prepared at different irradiation times measured after excitation at 320 nm. The PL emission spectra of all the ZnO nanostructures exhibited the asymmetric curve in the visible region, pointing to the superposition of multiple emission bands. These spectra were de-convoluted using Gaussian fit (see Figure 5.7 (b-f), and the resulting peaks were assigned according to the nature of defects (zinc and/or oxygen vacancies) as shown in the fitted data. The emission band between 400 and 450 nm, can be assigned to Zn_i [16-19] while that observed in the range of 450 to 460 nm could be due to V_{Zn} [16, 20]. The green emission peak centred in the range of 500 to 540 nm originates from the singly ionized oxygen vacancy (V_O^+) [21-23] whereas that in the range of 550 to 610 nm is usually attributed to doubly ionized oxygen vacancy (V_O^{++}) [21]. The bands located between 610–750 nm may be due to oxygen interstitials (O_i) [18, 21, 24-26].

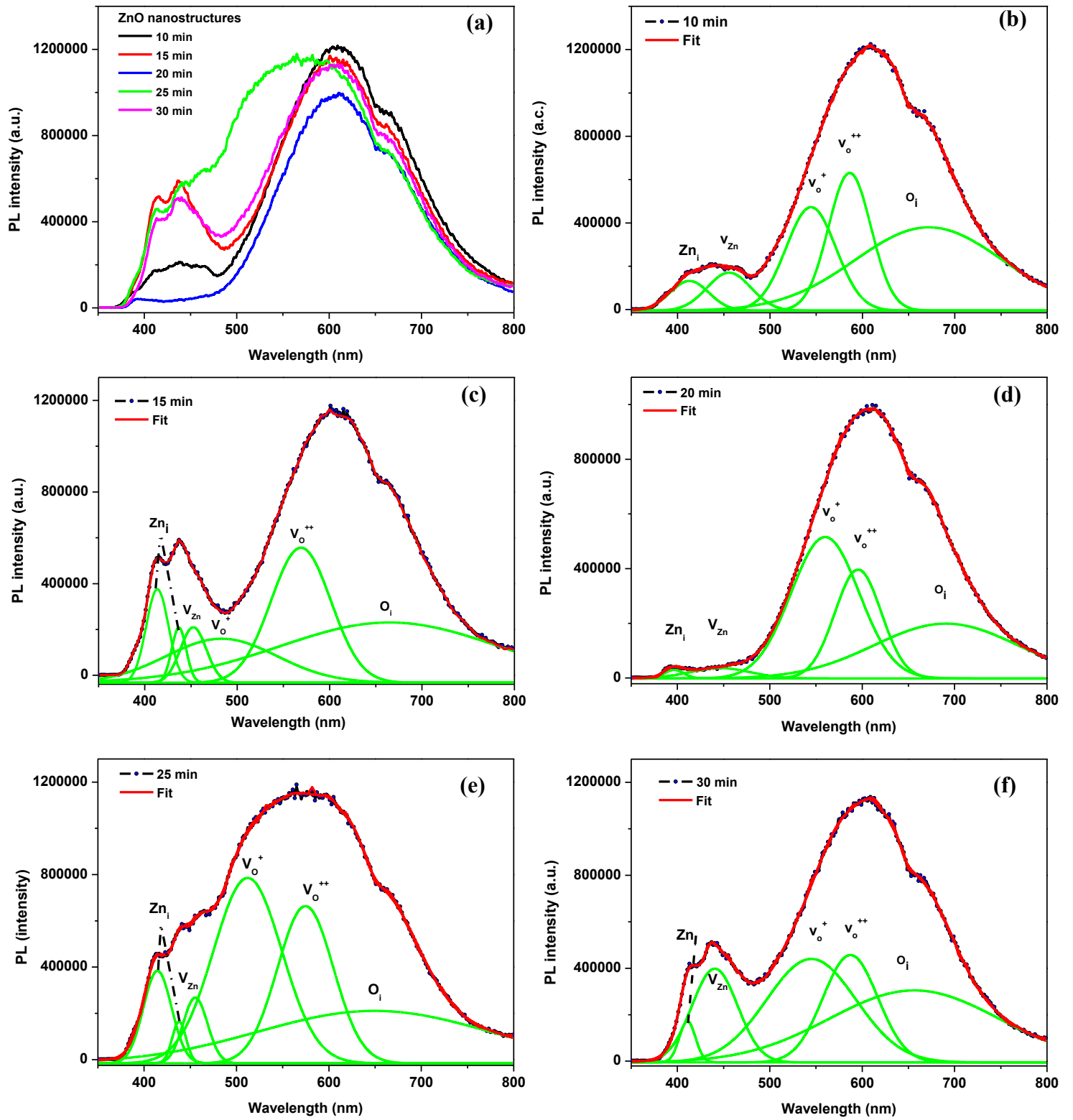


Figure 5.7: (a) Comparison and (b-f) Gaussian deconvolution of the PL spectra of ZnO nanostructures obtained at different irradiation times from 10 to 30 min.

5.3.5 Electron paramagnetic resonance (EPR) studies

Figure 5.8 (a) shows the EPR spectra of the ZnO nanorods prepared at different irradiation times. In general, nanostructured ZnO shows a S-shape single sharp feature due to the presence of V_O (unpaired electrons), which is one of the characteristics of ferromagnetic semiconductors [27]. As observed in Figure 5.8 (a), all ZnO nanostructures showed a broad single EPR signal together with a narrow EPR signal overlapping (see figure 5.8 (b)). This broad signal in this case is associated with a ferromagnetic (FM) resonance [12] while the overlapping narrow feature arises from the paramagnetic (PM) resonance [13, 22]. The presence of the PM feature which was found to slowly disappear at prolonged irradiation times is believed to result from different magnetic clusters of defects situated near the surface of ZnO nanostructures [24]. A very slight shift towards lower field which was more obvious at higher irradiation times (25 and 30 min) was also noted. This slight shift correlates with the PL results. Furthermore, the extensive broadening of the FM feature at irradiation time of 25 min compares well with the broadening of the PL emission assigned to co-existence of various defects which resulted in asymmetrical broad emission. Furthermore, it is worth noticing that the ZnO nanostructures obtained at irradiation time of 25 min exhibited a higher number of spins compared to the rest (see Table 5.3), implying higher concentration of defects at this irradiation time. It is clear from these results that there is a correlation between the PL and EPR results. Table 5.3 presents the g-factor values for samples prepared at different irradiation times. All the ZnO nanostructures show the effective g-factor values ≥ 2 which can be attributed to the combination of V_{Zn} and Vo^+ [12, 28]. The EPR resonance

signals with g-factors between 2.0024 and 2.0165 were previously reported by Galland *et al.* [29], which they attributed to V_{Zn} . Taylor *et al.* [30] reported the EPR signals with g-factors ranging from 2.0018 to 2.056 and also attributed them to V_{Zn} . For 25 and 30 min irradiation times, the g-factor values ≥ 2.5 were obtained and their origin is not known yet. A g-factor of ≥ 2.5 was also reported by Reddy *et al.* [31]. Room temperature ferromagnetism (RTFM) has also been observed in various undoped ZnO nanostructures [12, 27, 32-34] even though the origin of the d^0 ferromagnetism (FM) is still debatable. For instance, Panigrahy *et al.* [27] demonstrated a correlation between the FM and the oxygen vacancies (V_O) by tuning the oxygen deficiency in ZnO nanorods. On the other hand, Zhang *et al.* [34] recently claimed that the FM in undoped ZnO nano-films may be attributed to the existence of zinc interstitials (Zn_i). Most recently, Motaung *et al.* [12], reported the induced FM in ZnO nanostructures by altering defect concentration of zinc and oxygen vacancies. Phan *et al.* [32] prepared a high RTFM in pure ZnO nanoparticles by mechanical milling and showed that zinc vacancies (V_{Zn}) may be more effective in inducing FM. Based on these, it can be concluded that the FM in undoped ZnO is directly related to several intrinsic defects including V_O , Zn_i , and V_{Zn} , etc. Our results demonstrate that both Zn_i and Vo^+ defects play an important role in introducing the room temperature FM order in ZnO nanostructures.

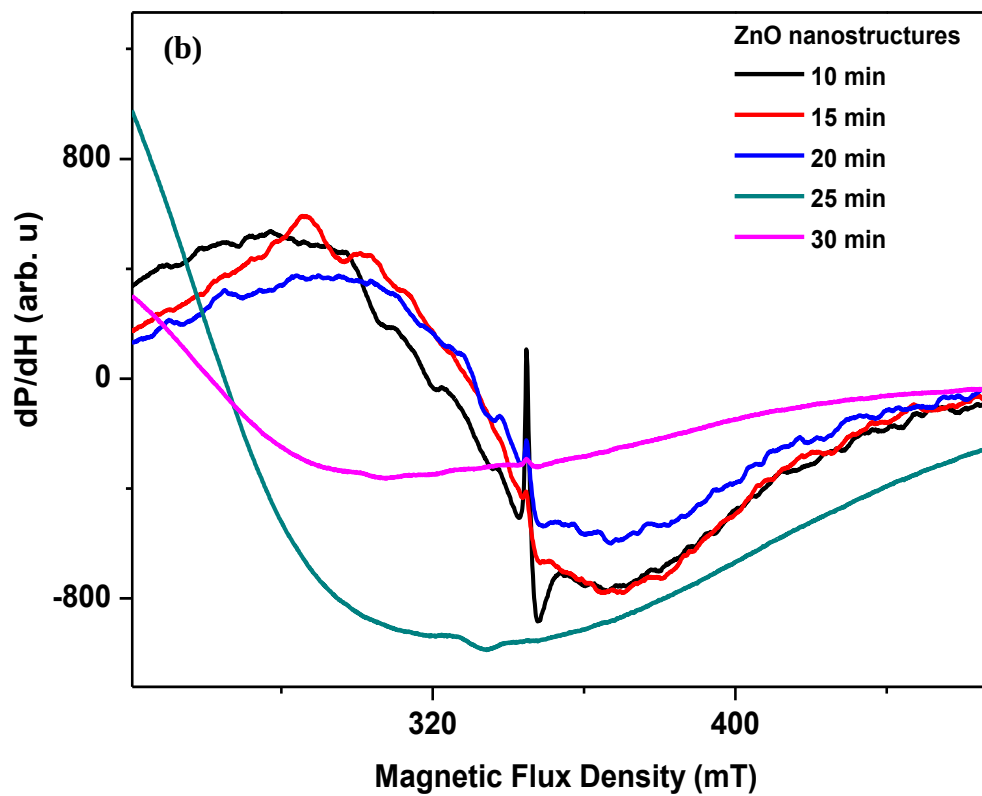
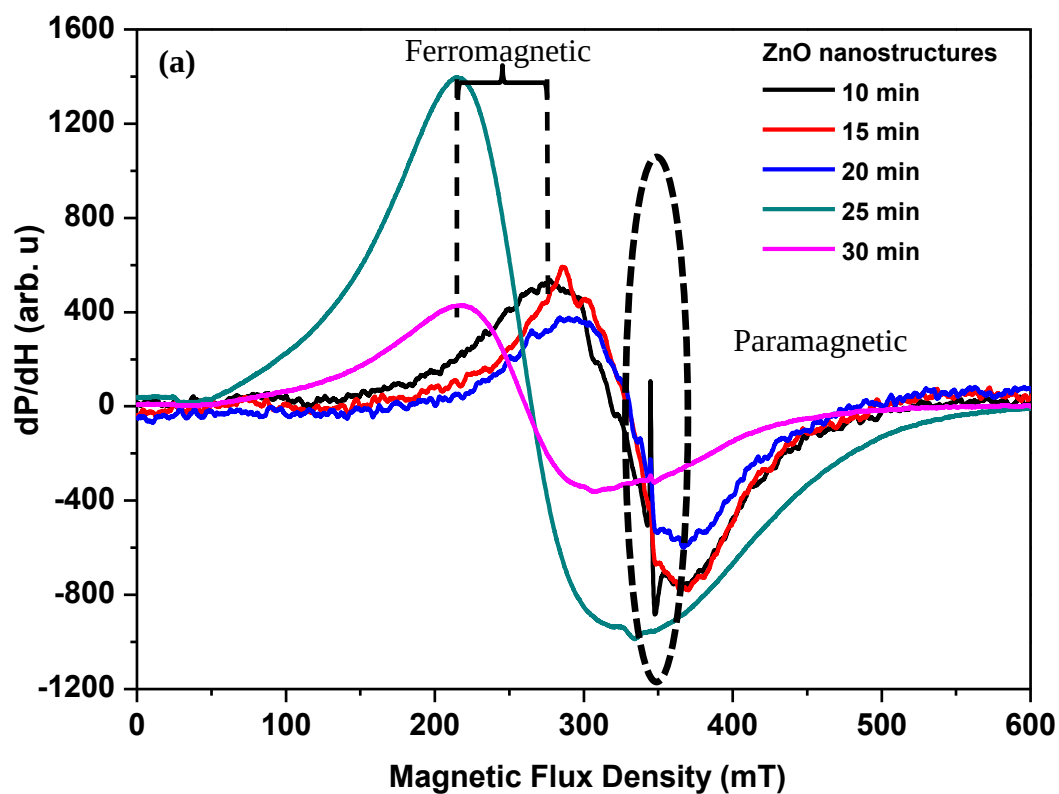


Figure 5.8: (a-b) EPR spectra of the ZnO nanostructures at different irradiation times.

Table 5.3: Representative of g-factor, line width (ΔH) and no. of spins (N_s) of the ZnO nanostructures

Sample	g-factor	FMR field (mT)	ΔH_{EPR} (mT)	$N_{\text{spins}} (\times 10^6)$
10 min	2.11 ± 0.0001	303 ± 0.03	79 ± 2.01	2.3 ± 0.08
15 min	2.05 ± 0.0004	313 ± 0.08	78 ± 1.34	2.4 ± 0.07
20 min	2.03 ± 0.0025	315 ± 0.38	72 ± 1.91	1.4 ± 0.08
25 min	2.57 ± 0.0053	249 ± 0.51	115 ± 0.96	8.9 ± 0.18
30 min	2.60 ± 0.0054	246 ± 0.51	92 ± 0.91	1.9 ± 0.04

5.3.6 Sensing studies

In principle, gas sensing behaviour depends on the surface redox reaction between the target gases and chemisorbed oxygen species on the metal oxide surfaces, leading to rapid change in conductance in the sensing material [35]. In order to investigate the effect of irradiation time on gas sensing properties of ZnO nanostructures, gas response to various concentrations of CO at 350 °C was measured. In this case, gas response (S) was designated $S = R_a/R_g$ [24, 36, 37], where R_a and R_g denote the sensor resistances in air and detected gas, respectively. Figure 5.9 shows the representative response-recovery curves of the ZnO nanostructures to CO in the testing range of 5 ppm to 100 ppm at 350 °C. When the sensors were exposed to a certain concentration of CO in each dynamic cycle, the corresponding response increased rapidly and reached almost its saturation point, then declined to the starting point once the analyte gas was released. All the sensors exhibited good response even at low 5 ppm of CO. From this observation, it suffices to say that the sensors show a reversible response to

these test gases. ZnO sensors based on 10 and 15 min exhibited a rapid increase in response with increasing gas concentration of CO (10-40 ppm). However, above 40 ppm, the response gradually decreased suggesting that the sensors have exceeded their saturation limit. ZnO sensors based on 20 to 30 min revealed a gradual increase in response with increasing CO concentration up to 100 ppm without reaching any saturation. Such behaviour indicates that this ZnO sensor can respond not only at low concentrations but also at high concentrations of CO.

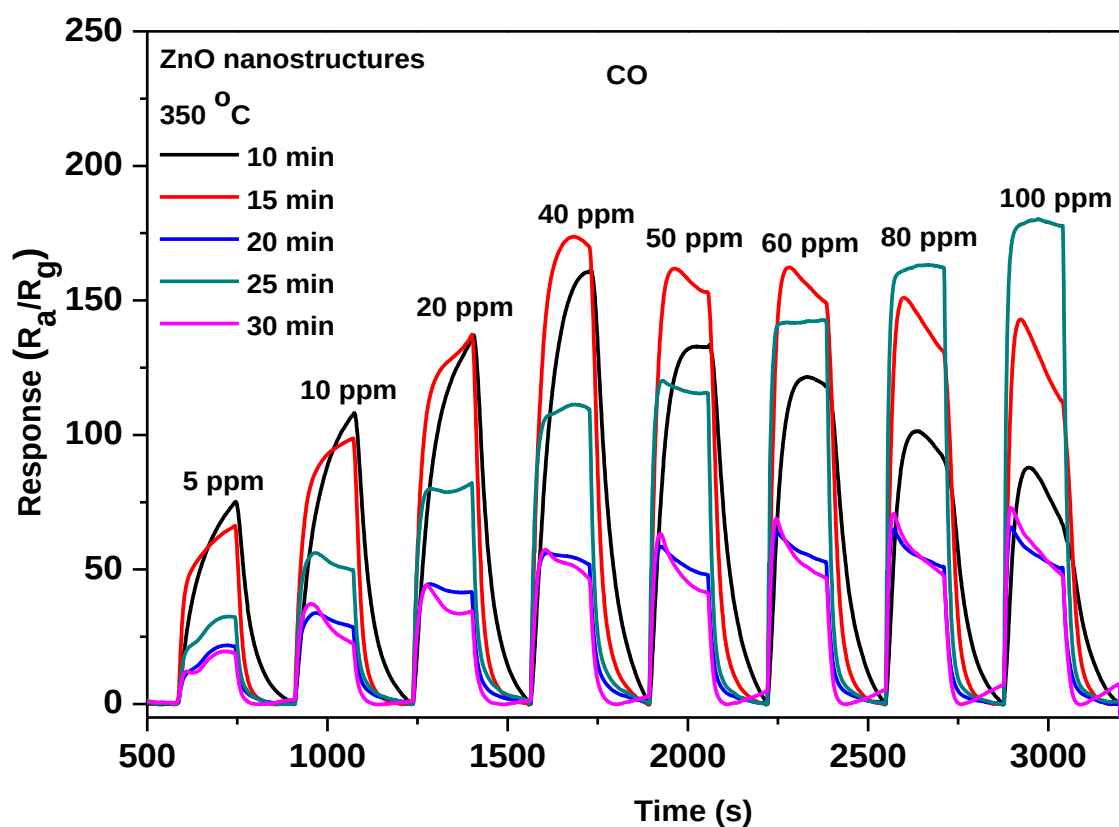


Figure 5.9: Gas response curves of 10 to 30 min based nanostructured ZnO sensors towards different CO concentrations at 350 °C.

As mentioned earlier, the sensitivity of the metal oxide semiconductor sensor such as ZnO is mainly determined by the interaction between the target gas and the surface of the sensor. Therefore, the observed differences in response maximum values with varying irradiation times in this case can be related to differences in surface area and surface defects of the ZnO nanostructures. It is well known that more chemisorbed oxygen molecules on the ZnO surface indicate better sensor performance [38, 39]. The adsorption of oxygen species is closely related to specific surface area. In most cases, a larger specific surface area will lead to more chemisorbed oxygen species on the surface. Furthermore, sensors with different morphologies exhibit different surface to volume ratio, thus different sensor performance because the more O ions are adsorbed on the surface of the ZnO nanostructures the higher will be the sensitivity of the sensor. For instance, Liao *et al* [38] demonstrated that the thinner nanorod based sensors showed better sensing performance due to larger effective surface area resulting in a larger quantity of adsorbed oxygen compared to thicker nanorod based sensors. Surface defect is an important factor for gas-sensing properties of nanostructured ZnO gas sensors. It is well known that gas response can be also enhanced remarkably with increasing surface defects such as Zn_i and V_O since more oxygen atoms can be easily chemisorbed and ionized on the surface of metal oxide semiconductor [20]. Han *et al* [40] tailored the defects of ZnO prepared using plasma enhanced chemical vapour deposition by annealing at different atmospheres and investigated the relation between the intrinsic defects and gas sensing properties of ZnO nanorods. Based on this study, it is safe to conclude that gas sensor response can be enhanced remarkably by more

donor defects of ZnO than acceptors which strongly suggest that donors and acceptors in ZnO crystal play different roles in electron transport. According to gas sensing results obtained from five ZnO sensors results presented above, it is obvious that the 15 min based sensor showed better response to CO concentrations up to 60 ppm while the 25 min based sensor exhibited better response to higher CO concentrations than 60 ppm. Based on BET surface area studies, 30 min based ZnO nanostructures with much thinner diameter were found to have higher specific surface area than the rest of the ZnO products, followed by the 25 min irradiation time. In this case, one would expect the sensor based on 30 min to adsorb more oxygen to form chemisorbed oxygen and thus exhibit a higher response than other sensors. However, it is obvious from this observation that the specific surface area did not play a major role in improving the sensors response (30 min). On the other hand, the EPR and PL analyses conducted on ZnO nanostructures based on 25 min revealed a broad signal related to ferromagnetic feature and defects related visible emission, respectively suggesting the dominance of surface defects at this sample. Furthermore, high concentration of surface defects was also confirmed by a higher number of spins observed in the case of 25 min followed by 15 min based ZnO nanostructures. This therefore explains the improved response observed for both the 15 and 25 min based ZnO sensors. Besides sensitivity or response, response–recovery and selectivity are also very important factors for evaluating the gas sensor performance. The related response and recovery times of the ZnO sensors to different CO concentrations were also calculated and are shown in Figure 5.10 (a-b). The response time can be defined as the time required for reaching 90% of the

equilibrium value of the resistance after gas exposure while the recovery time is the time required for the resistance to return to 10% below the original resistance in air after the test gas is released. It can be seen from Figure 5.10 (a-b) that the 10 and 15 min based sensors took longer to respond and recover as compared to those based on 20 to 30 min. This behaviour suggests that the adsorption process is faster than the desorption process as the gas molecules are quickly adsorbed on the surface, and the desorption process gets delayed by the bonding between the gas molecules and the semiconductor sensors [41].

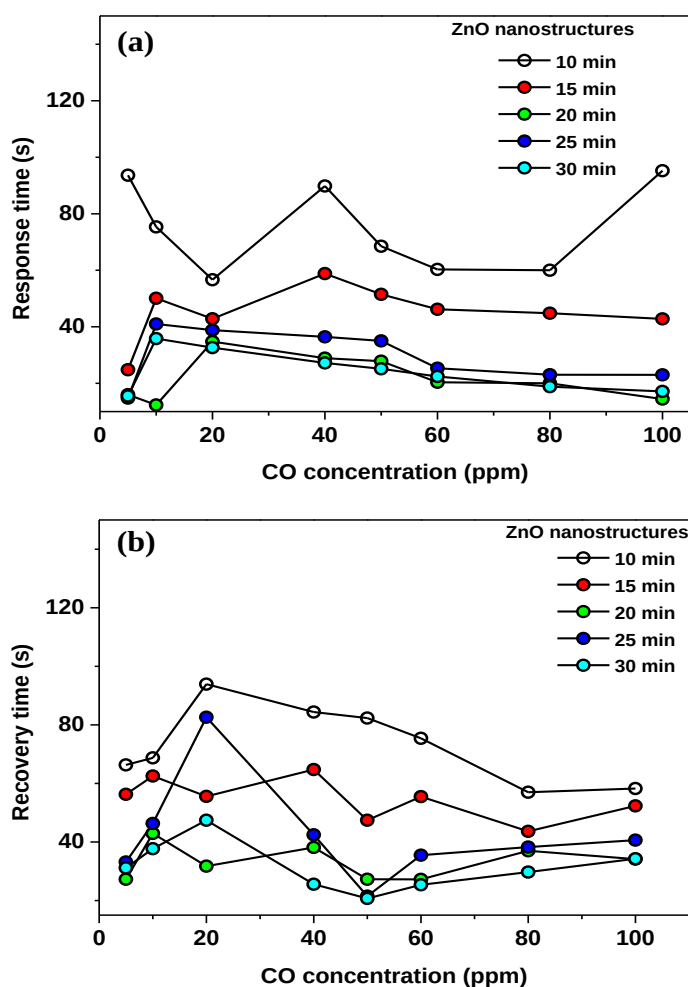


Figure 5.10: (a-b) Gas sensing response and recovery times of 10 to 30 min based nanostructured ZnO sensors to 5-100 ppm of CO at 350 °C.

The gas sensing mechanism taking place on the surface of the ZnO nanostructures when exposed to CO gas can be explained by the schematic representation in figure 5.11. In general, ZnO is a typical n-type semiconducting material and its gas sensing properties are predominantly controlled by the change in surface resistance [33]. Exposure of ZnO nanorods in air atmosphere would lead to adsorption of free oxygen molecules on the surface of the ZnO sensor. Thereafter, oxygen from the atmosphere captures electrons from the surface of ZnO nanostructures resulting in the formation of oxygen ions (O_2^- , O^- and O^{2-}) on the surface of the ZnO nanorods [35, 41]. After sufficient adsorption of oxygen, depletion layers were formed on the surface regions of the ZnO nanorods resulting in an increase in electrical resistance. When the ZnO nanorods were exposed to a certain concentration of CO, a relevant reaction on the surface of the ZnO sensor involving O^- and CO occurred. This then led to a decrease in the concentration of the oxygen ions on the ZnO sensor surface by producing CO_2 molecules, resulting in an increase in the concentration of electrons on the surface of the ZnO sensor and making the depletion layer thinner and thus leading to an increase in conductivity.

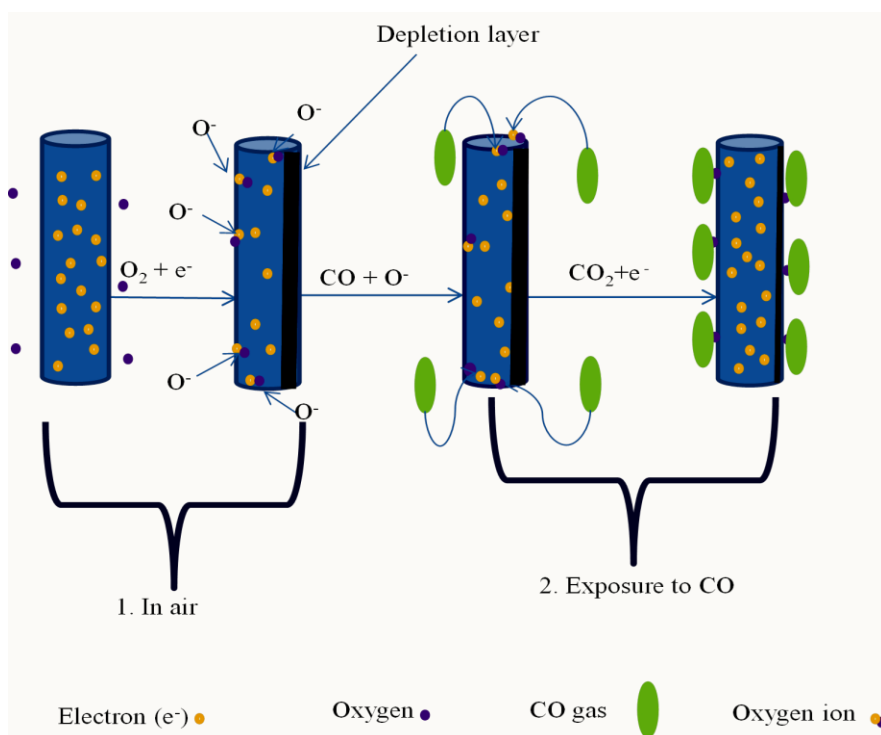


Figure 5.11: Schematic diagram showing a sensing mechanism of CO on the ZnO nanostructures surface.

Apart from CO, the ZnO nanostructures based sensors were tested for CH_4 , NH_3 , and H_2 to assess selectivity of five sensors. Figure 5.12 shows the comparison of the five sensors response to 60 ppm of the different gases. The sensors show response to all the test gases; however they show higher response to CO, indicating that the sensors are more selective and sensitive to CO.

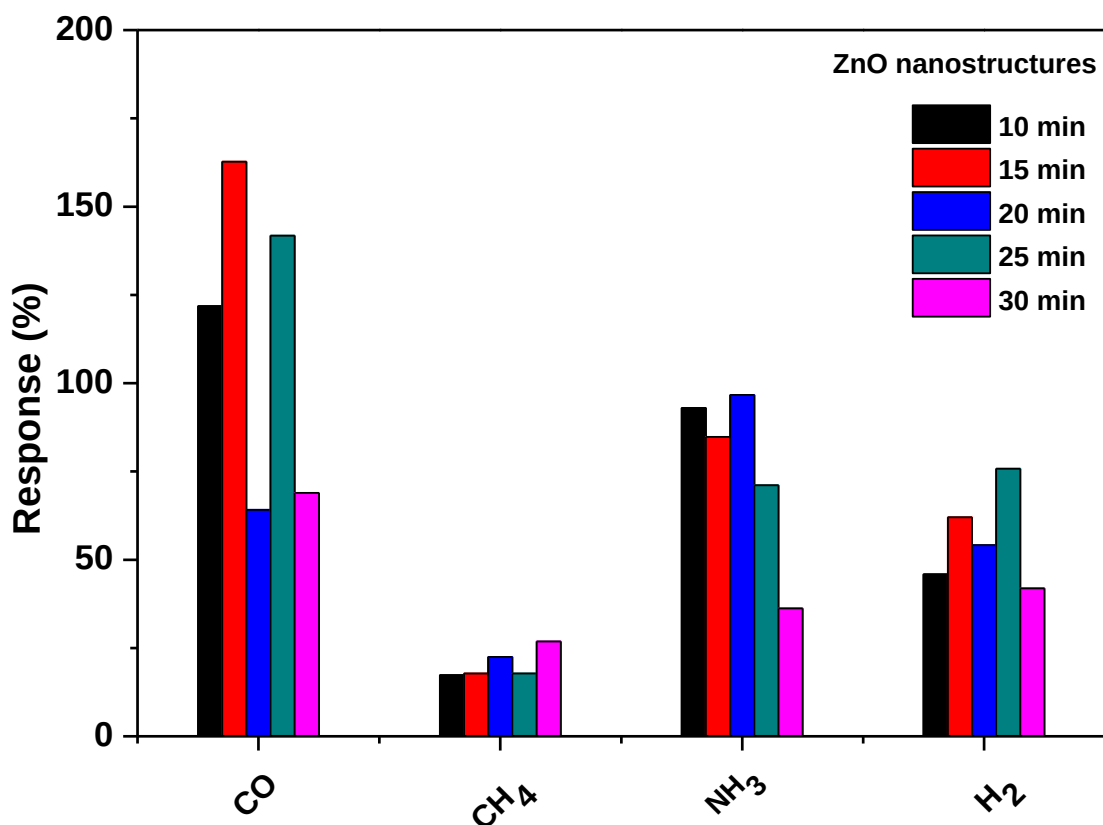


Figure 5.12: Response of the ZnO sensors to various gases.

5.4 Conclusion

ZnO nanorods with different lengths and widths depending on the irradiation time were successfully synthesized via microwave-assisted hydrothermal method. When evaluated as gas sensing materials, rod-like ZnO nanostructures manifested a notable high response to 60 ppm of CO at an operating temperature of 350 °C. A correlation between PL and EPR analyses revealed that Zn_i and V_O surface defects are responsible for observed room temperature ferromagnetism (FM) which resulted in improved sensing response. Thus our findings indicated that the prepared ZnO nanostructures may be used for the development of gas sensing devices.

5.5 References

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CHAPTER 6

Highly selective NH_3 gas sensor based on Au loaded ZnO nanostructures prepared using microwave-assisted method

6.1 Introduction

As gas sensing materials, semiconductor oxide materials have received a lot of attention owing to their high sensing performances including high sensor response, selectivity, fast response and recovery, non-toxicity [1-3]. In particular, ZnO as a n-type semiconductor oxide material having a wide-band gap of 3.34 eV [1-3] has recently received considerable attention in sensing application because of its low preparation cost, high electron mobility, and thermal stability under operating conditions of the sensors [4-6]. Au has been reported to be the most useful catalyst for detection of several reductive gases, such as H_2 [7], CO [3, 8] and VOC's [5, 9], through chemical sensitization [10, 11]. Furthermore, it has been demonstrated to effectively increase gas sensing properties including gas selectivity and response of several reductive gases as well as short response and recovery times for ZnO based gas sensors [9, 12].

In this chapter, several characterization techniques have been utilized to examine the structure, morphology, luminescence properties and defects of the ZnO and Au loaded ZnO (Au/ZnO) nanostructures. Comparison of the

gas-sensing properties of ZnO and Au/ZnO nanorods with various Au concentrations towards various concentrations of NH_3 was also conducted. Finally, the gas-sensing mechanism of Au loaded ZnO nanorods is explained.

6.2 Experimental details

6.2.1 Preparation of ZnO and Au loaded ZnO (Au/ZnO) nanorods

ZnO nanorods were produced using zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), hexamethylenetetramine (HMTA) and hydrazine hydrate (N_2H_4) as starting materials while de-ionized water (H_2O) has been used as a solvent. The synthesis procedure of the ZnO nanorods can be summarized as follows: 1M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to 0.1M (HMTA) with continuous stirring until a homogenous solution was formed. Subsequently, N_2H_4 was slowly added drop-wise to the solution while continuously stirring until the pH value of the solution reached 10. The solution was further stirred for 15 minutes. The final solution was then transferred into Teflon vessels and irradiated in a microwave oven (EM-G430, 2.45 GHz, maximum output power 1000 W, SANYO Electric, UK). After the solution was cooled down to RT, the final product was then washed several times with ethanol and de-ionized water to remove unwanted impurities. This was divided into two parts: the first part was transferred to the watch glass for drying while the second part was suspended in ethanol.

For preparation of Au nanoparticles, gold (III) chloride solution (HAuCl_4) was used as a precursor. In a typical experiment, a suitable amount of HAuCl_4 aqueous solution was added into 20 mL of deionized water. N_2H_4 was then used as the reducing agent by adding it dropwise the above mentioned solution. The final solution was then mixed with the as-prepared ZnO suspended in ethanol and further stirred for 3 minutes. This solution was then transferred into Teflon vessels and irradiated in the microwave oven at 100 °C. The resulting final product was washed several times with de-ionized water, dried at RT and annealed at 500 °C. The final weight percentages of Au were 0.5, 1, 1.5, 2 and 2.5 wt% obtained by controlling the amount of Au precursor (HAuCl_4).

6.2.2 Materials characterization

The crystalline structure of ZnO and Au/ZnO nanorods were examined using a Panalytical X'pert PRO PW3040/60 X-ray diffractometer (XRD) with a Cu-K α ($k = 1.5405$) radiation. The morphologies of the nanostructures were determined by JEOL JSM-7500F field emission scanning electron microscope (FESEM) and JEOL TEM-2100 transmission electron microscopy (TEM). The luminescence properties of the nanostructures were studied using Jobin-Yvon NanoLog spectrometer at an excitation wavelength of 325 nm at RT. Raman spectra were recorded using a Horiba Jobin-Yvon HR800 Raman microscope with a 514 nm excitation Ar^+ laser. Electron paramagnetic resonance (EPR) measurements were carried out on a JEOL X-band spectrometer-JES FA 200 equipped with an Oxford ESR900 gas-flow. For chemical states identification, by X-ray photoelectron spectroscopy (XPS) using a PHI 5000 Versaprobe-Scanning ESCA Microprobe was used.

6.2.3 Gas sensor fabrication

The sensing films were prepared by dispersing ZnO with and without Au in ethanol to form pastes which were coated drop-wise onto alumina substrates interdigitated with Au electrodes. These sensor films were dried for 2 hours and subsequently annealed at 400 °C for 2 hrs at a heating rate of 20 °C/min. The gas-sensing measurements of the sensors were performed towards CO, NH₃, H₂ or CH₄ using a Kinesistec testing station. A synthetic air with a continuous flow of 250 ml/min was used as a carrier gas. Desired concentrations of CO, NH₃, H₂ or CH₄ were achieved by mixing synthetic air with a specific target gas source at different flow rate ratios using mass flow controllers. The working temperature was varied from RT (25) to 400 °C. The electrical characterization was carried out by volt-amperometric technique while the electrical resistance of the films was recorded by a Keithley 3706 source meter.

6.3 Results and discussion

6.3.1 Structure analysis, XRD

Figure 6.1 shows the XRD patterns of the ZnO and Au/ZnO nanorods. All the diffraction peaks of ZnO exhibited a hexagonal phase of wurtzite ZnO corresponding to JCDs Card No. 36-1451. The intense diffraction peaks demonstrate that the ZnO materials are highly crystalline. As shown in Figure 6.1, when the Au was loaded, the diffraction peaks shift to lower angle probably due to alteration of the ZnO surface induced by Au loading. Furthermore, the XRD patterns of Au/ZnO nanorods revealed the appearance of new diffraction peaks at 38.37°; 44.44° and 64.66° which can be assigned

to (111), (200) and (220) planes of face-centered cubic (fcc) phase of Au (JCPDS Card No. 04-9748), respectively. The intensity of the diffraction peaks identified as Au became stronger with the increase of Au concentration indicating that more Au particles were formed on the surface of the ZnO nanostructures. This behaviour might also suggest a possible agglomeration of Au particles at higher loading due to poor dispersion.

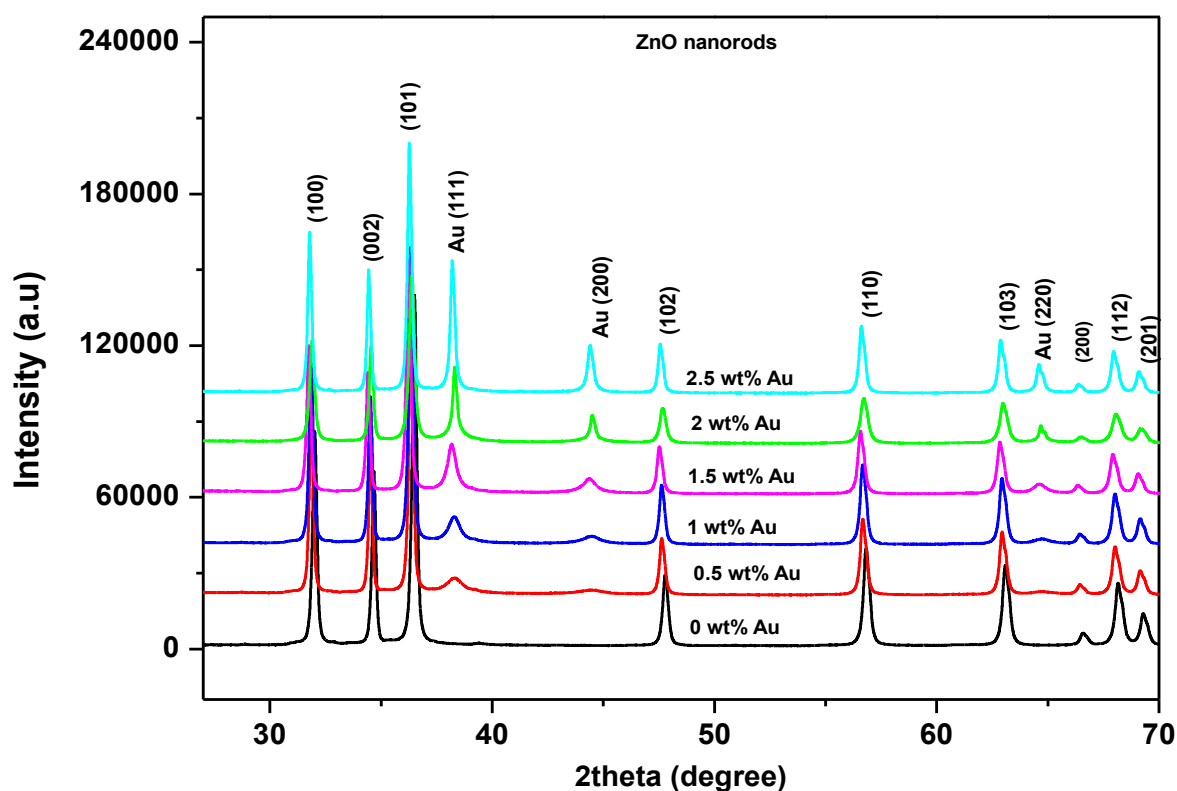


Figure 6.1: XRD patterns of the ZnO and the Au/ZnO nanorods with different loading concentrations of Au.

6.3.2 Morphology analysis, SEM and TEM

The SEM images of the ZnO and Au/ZnO nanorods at different Au concentrations are presented in Figure 6.2 (a-f). It can be seen from Figure 6.2 (a) that prior to ZnO surface modification by Au, randomly oriented rod-like structures with average width and length of ~140 nm and ~626 nm, respectively were formed. Upon addition of the Au particles on the surface of ZnO, additional bundles of rods grew from different angles on the core rod mimicking brush-like hierarchical structures. These structures were encrusted with spherical Au nanoparticles on the surface with particle diameters ranging from 11 to 36 nm and they were homogeneously distributed on the surface of each rod. It was further noticed that the ZnO nanorods surfaces were significantly coarsened after loading of the Au nanoparticles. The coarsening of the ZnO nanostructures surface may be due to the corrosion caused by the Au precursor (HAuCl_4). The coarse surface indicates that the Au loaded ZnO nanostructures have an enhanced surface area and more surface defects which is beneficial for gas sensing [9].

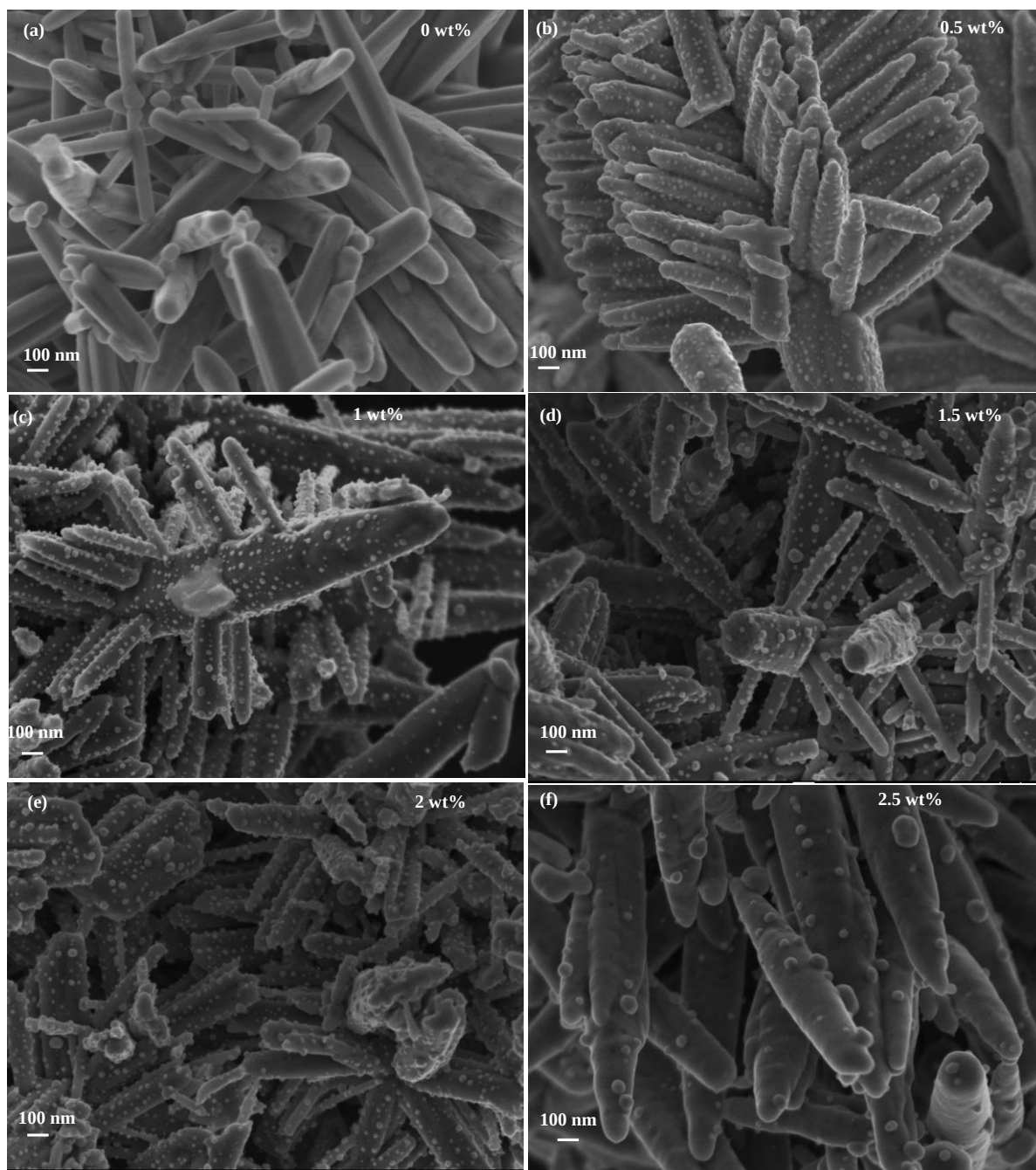


Figure 6.2: (a-f) SEM images displaying the ZnO and Au/ZnO nanorods.

To further verify surface modification of the ZnO nanorods by addition of Au particles TEM analyses were done. Figure 6.3 (a-f) shows the TEM images of ZnO nanorods with and without Au nanoparticles with different Au concentrations. It is obvious from the TEM images displayed that Au nanoparticles are dispersed on the surface of the ZnO nanostructures .

Histograms displaying particle size distribution are presented as insets of each figure. The average particle size of the Au nanoparticles in diameter was determined to be 11, 14, 15, 17, and 36 nm, for 0.5, 1, 1.5, 2, and 2.5 wt%, respectively. It was also observed that the average particle size of the Au nanoparticles significantly increased with increasing loading concentration of Au. The process at which these nanoparticles grow can be explained in terms of four steps which are as follows: (i) rapid formation of nuclei, (ii) Oswald ripening into bigger particles, (iii) continuous slow diffusion growth of the particles from the precursor, (iv) rapid consumption of the Au precursor resulting in a rapid growth of the particle size [13]. HRTEM images of the pure and Au loaded ZnO nanoparticles are presented in Figure 6.4 (a-f). A closer examination of HRTEM images (Figure 6.4 (b-f)) revealed fringes in both the particles and the rods for each sample. The measured d-spacing between adjacent fringes of 0.25 nm corresponding to the d-spacing of (002) plane of hexagonal wurtzite ZnO was obtained for unloaded ZnO single rod (Figure 6.4 (a)). On the other hand, the HRTEM images (Figure 6.4 (b-f)) of a single Au loaded ZnO rod revealed the lattice fringes of Au with d-spacing of 0.22 and 0.23 nm which can be indexed to cubic Au (111) lattice spacing. In addition, the lattice fringes of 0.25 and 0.24 nm corresponding to (002) and (101) crystal planes of ZnO were also measured.

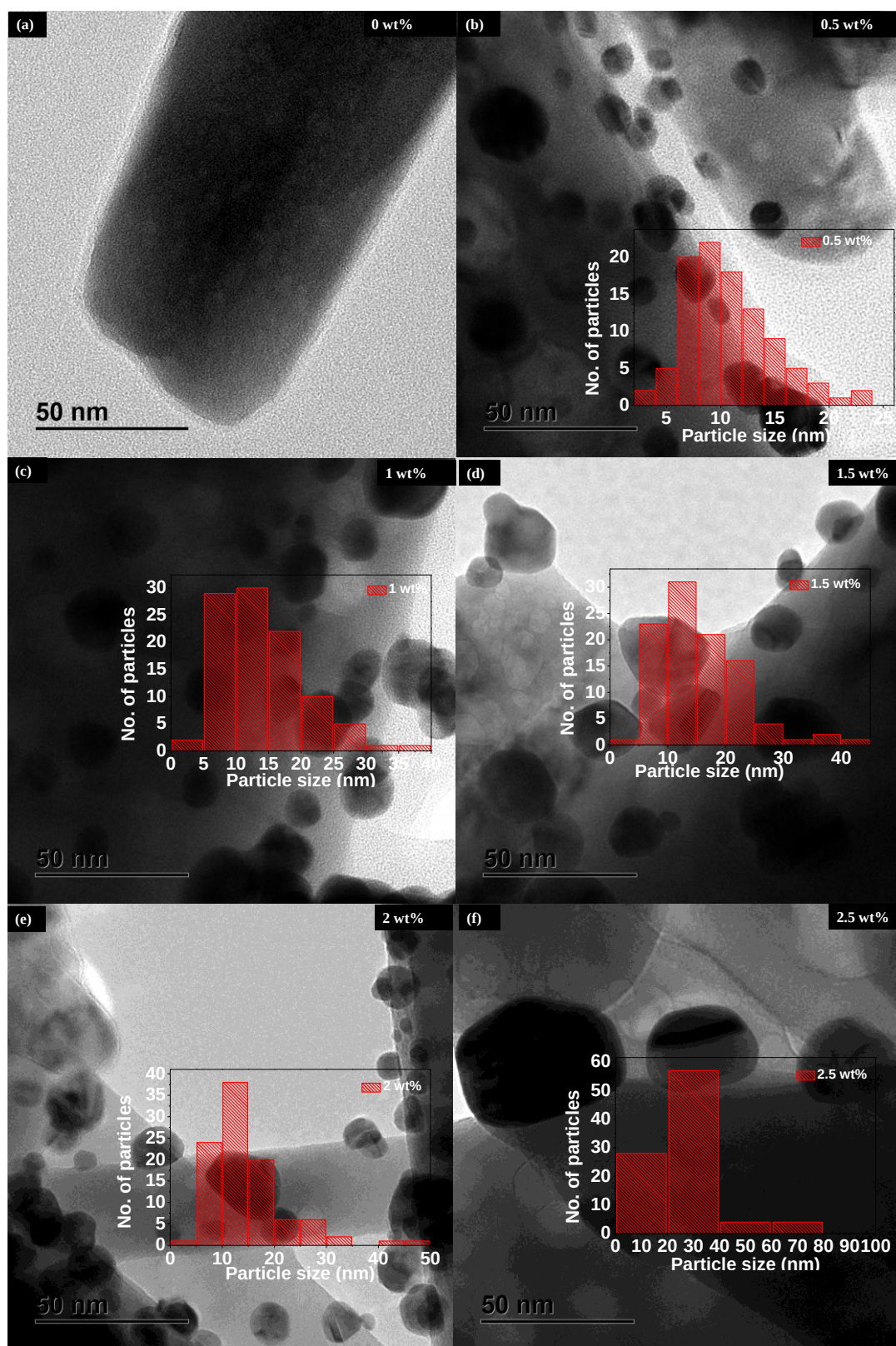


Figure 6.3: TEM images of the (a) ZnO and (b-f) Au/ZnO nanorods with insets of the size distribution histograms of Au nanoparticles (b-f).

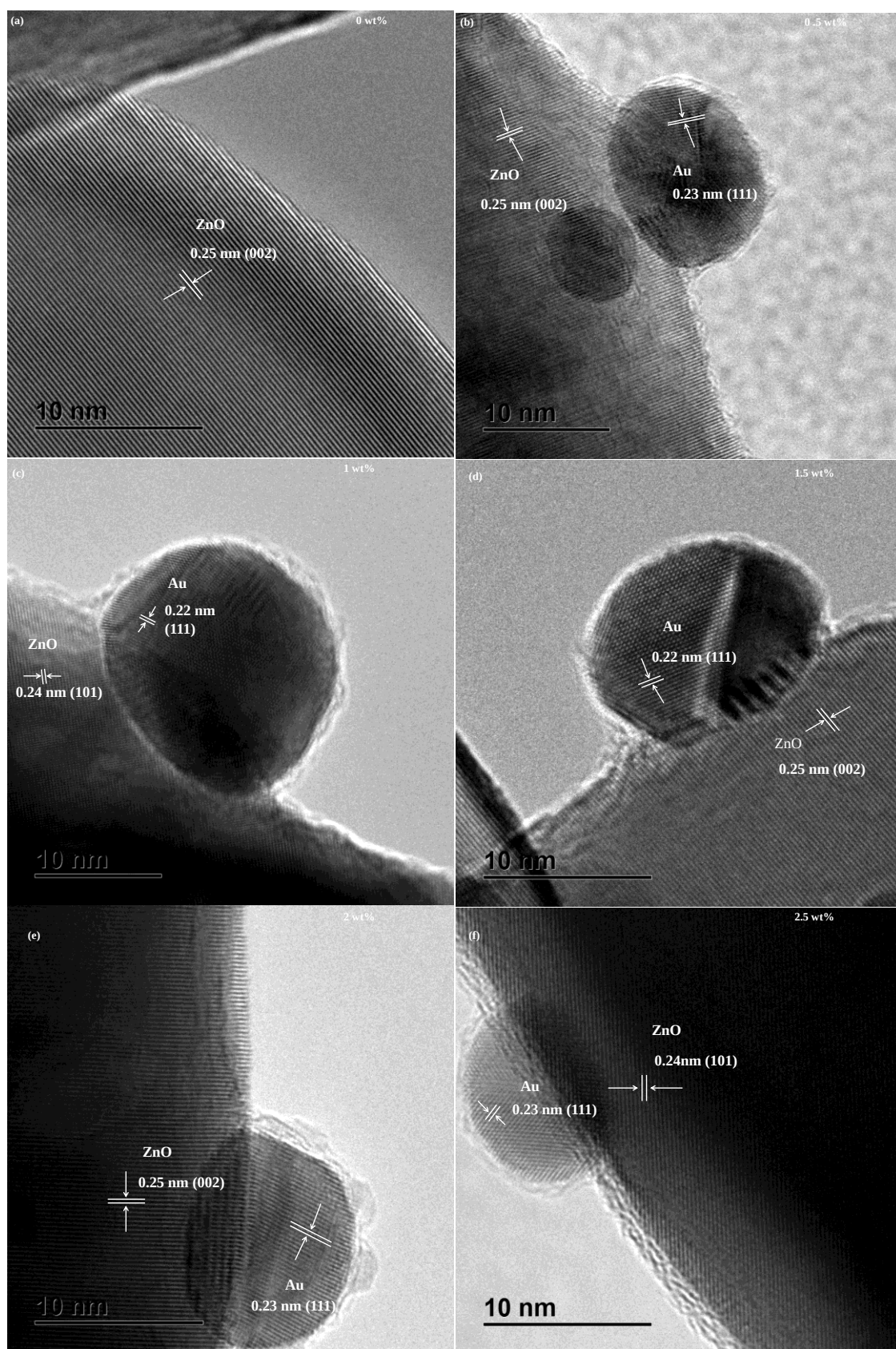


Figure 6.4: HR-TEM images of the (a) ZnO and (b-f) Au/ZnO nanorods with various Au concentrations.

6.3.3 Chemical composition analysis (XPS)

To further clarify the existence of Au metal nanoparticles on the surface of the ZnO nanorods, XPS analyses were performed. The XPS survey spectra of both ZnO with and without Au loaded nanoparticles in Figure 6.5 confirm the presence of Zn, O, Au and C elements. The adventitious carbon peak (C 1s) located at 285 eV was used to calibrate the binding energies scale.

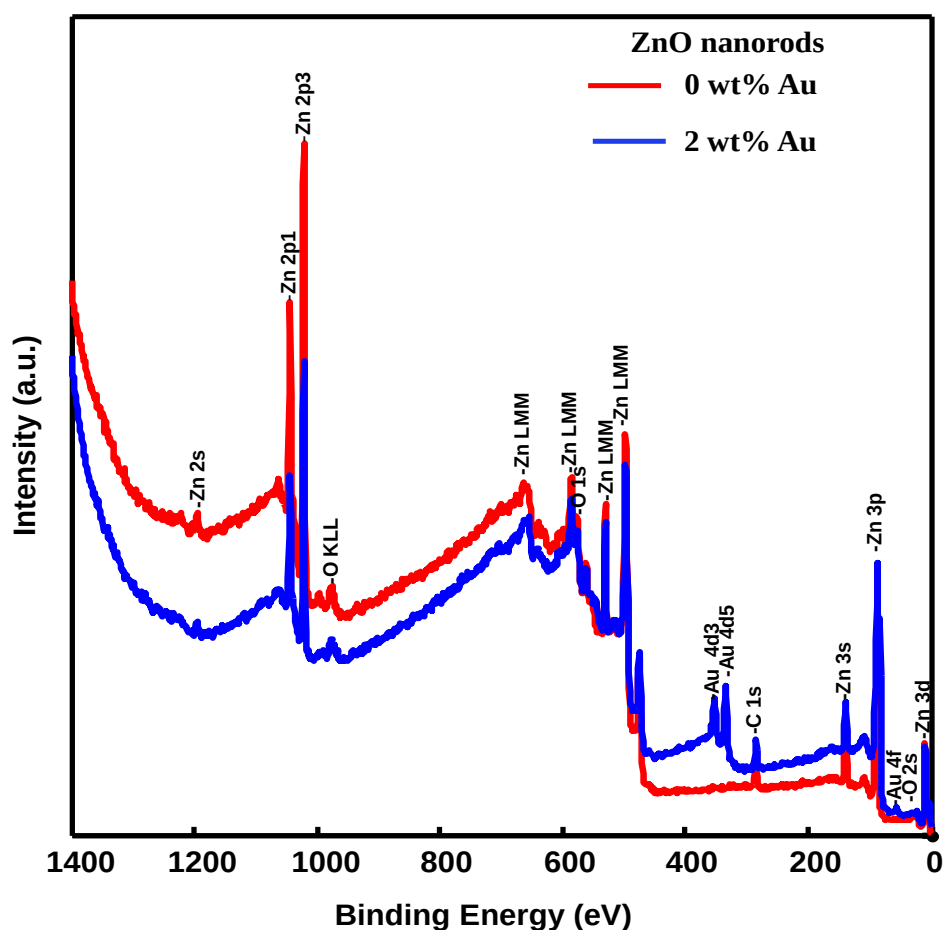


Figure 6.5: XPS survey spectra of the ZnO and Au/ZnO nanorods.

The high resolution spectra of the O 1s, Zn 2p, and Au 4f photoelectron lines of ZnO and Au/ZnO nanorods are presented in Figure 6.6 (a-d). As observed from Figure 6.5 (a) both ZnO and Au/ZnO nanorods consist of two

photoelectron peaks identified as Zn 2p_{1/2} and Zn 2p_{3/2} with binding energies of 1044.9 and 1021.8 eV, respectively [14]. The difference in binding energy between the two lines is 23.11 eV and this is within the standard reference value of ZnO [15]. This suggests that the Zn atoms are in +2 oxidation state. The two peaks centered at 83.5 and 87.23 eV in Figure 6.6 (b) can be attributed to Au 4f^{7/2} and Au 4f^{5/2}, respectively [9]. The appearance of these peaks confirms the presence of Au in ZnO nanostructures. A slight negative shift of 0.3 eV to lower binding energy in peak position of Au 4f^{7/2} compared to 83.8 eV of bulk Au (4f^{7/2}) [15] was also observed. This binding energy shift may be related to the strong electronic interaction between Au and ZnO which is believed to result from electron transfer from ZnO to Au [16]. It is also important to note the presence of two extra interference or overlapping shoulders at 88.3 and 91.7 eV assigned to Zn 3p confirming co-existence of Au and ZnO. Figure 6.6 (a-d) shows the deconvoluted O 1s peaks of the pure and Au loaded ZnO nanorods. The O1s peak for the pure ZnO can be classified into three peaks, namely: O_a, O_b and O_c whose binding energies are 529.9, 530.3 and 531.9 eV. The O_a peak can be attributed to O²⁻ ions on the wurtzite structure of hexagonal Zn²⁺ ion array, surrounded by Zn atoms with their full complement of nearest neighbor O²⁻ ions [17]. This means that the intensity of this peak is the measure of the amount of oxygen atoms in a fully oxidized stoichiometric surrounding. O_b can be associated with O²⁻ ions that are in oxygen deficient regions within the matrix of ZnO and/Zn-OH groups [17-20]. Any change in the intensity of O_b suggests variations in the concentration of oxygen vacancies. O_c is usually associated with loosely bound oxygen on the surface belonging to chemisorbed species such as CO₃,

adsorbed H_2O or O_2 on the surface of the ZnO [14]. For the Au loaded sample, O_a , O_b and O_c were observed at 530.4, 531.1 and 532.2 eV, respectively. Furthermore, it is worth noting that the intensity of the oxygen deficient peak (O_b) showed a decrease after the addition of Au, suggesting a reduction in the oxygen vacancies concentration.

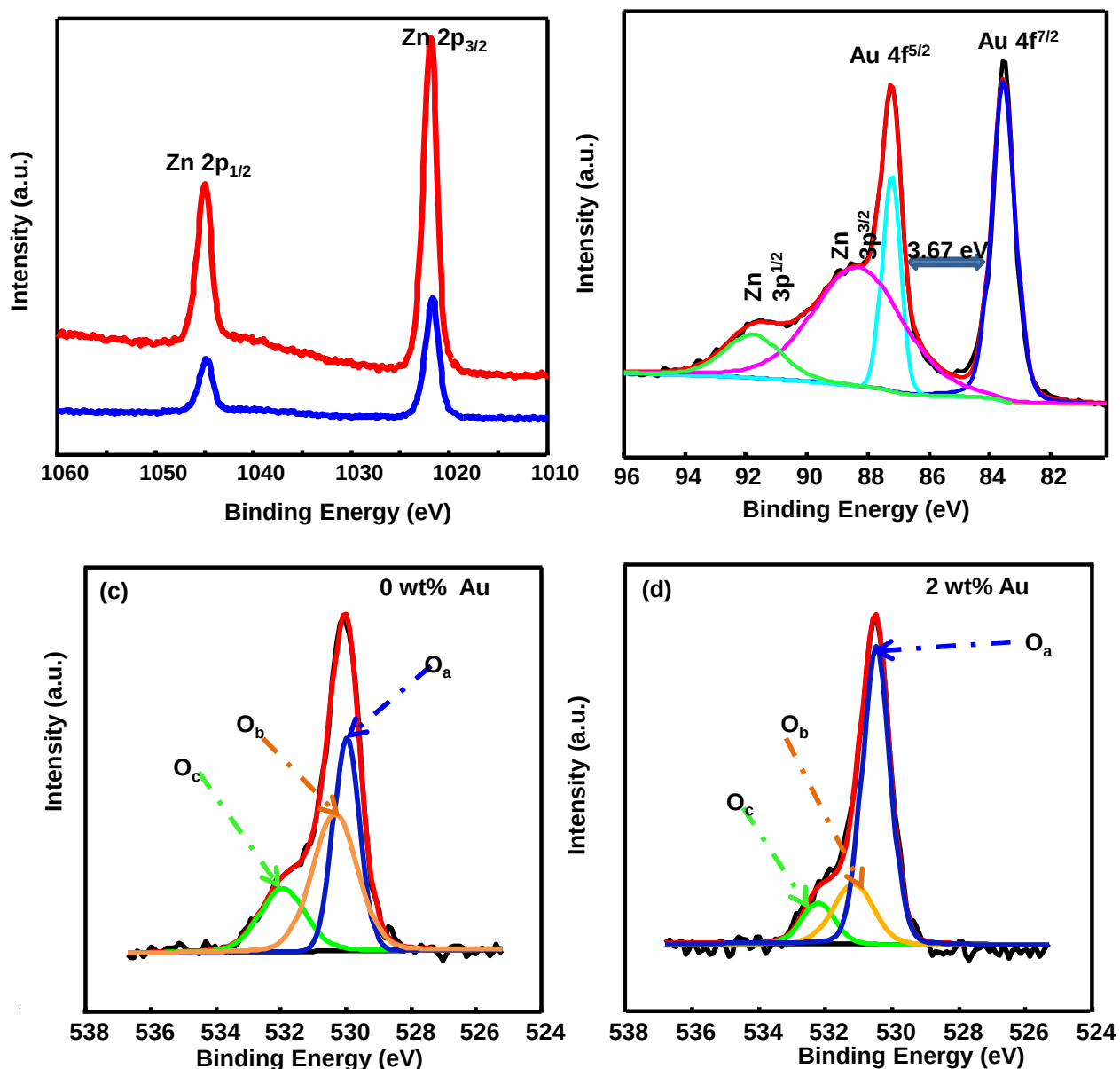


Figure 6.6: (a) XPS spectra of Zn 2p peaks for the ZnO and Au/ZnO nanorods, (b) Au 4f spectra, O1s spectra of (c) ZnO and (d) Au/ZnO nanorods.

6.3.4 Luminescence (PL) study

Since defects play an imperative role in sensing and magnetic properties, PL and EPR measurements were carried out. Figure 6.7 displays the PL spectra of the ZnO, Au/ZnO nanorods and Au nanoparticles after excitation at 320 nm. The PL spectrum for Au nanoparticles in this case was recorded for comparison. For ZnO, the PL spectra show two emission bands, the violet-blue emission in the 390 to 450 region and the strong broad deep level emission band in the range of 470-730 nm with a maximum at 580 nm. It is clear from the PL spectra that there are different emission colours due to either excitonic recombination or intrinsic defects. Violet-blue emissions are normally associated with zinc interstitials (Zn_i) and zinc vacancies (V_{Zn}) [18, 21]. Deep level emissions (DLE) in the visible region in ZnO often times take place in the green, yellow and orange-red regions between 480–550 nm, 550–610 nm, and 610–750 nm, respectively [22, 23]. Even though there is ongoing debate about the origin of the defects in the visible region, it is generally agreed that the oxygen vacancies (V_O) are responsible for the visible emission of ZnO [24-26]. The broad emission band observed from ZnO in the range of 470 to 730 nm in this study can therefore be attributed to oxygen vacancies (V_O) and oxygen interstitials (O_i) [23, 27, 28]. While the violet-blue emission in the 390 to 450 region can be associated with zinc interstitials (Zn_i) and zinc vacancies (V_{Zn}), respectively [18, 21]. In the case of Au nanoparticles, the PL spectrum showed a strong blue emission band centered at 470 nm dominating the PL spectrum with three peaks at 424, 435 and 452 nm, respectively. Excitation of Au nanoparticles at 320 nm led to excitation of the surface plasmon coherent motion as well as the d electrons.

Consequently, relaxation of these electronic motions followed by the recombination of the sp electrons with holes in the d band resulted in emission [29-31] of visible photons. It is also important to note that at low concentrations of Au (0.5 and 1 wt%), the PL spectra of the Au loaded ZnO samples resembled that of the unloaded ZnO, suggesting emission from ZnO dominated that of Au in ZnO/Au system. However, at higher content levels of Au (1.5 and 2 wt%), small contributions from Au appeared in the blue region. However, the PL intensity of their emission spectra remained weak in comparison with that of unloaded ZnO. Similar drop in the PL intensity with addition of Au was also observed by Ruiz Peralta *et al* [32] for Au decorated ZnO nanorods. They attributed the quenching of the PL emission from ZnO to the electron trapping capacity of Au in which Au on the surface of the ZnO nanostructures traps photogenerated electron which lead to quenching of the PL [32]. Furthermore, a shift of the PL emission spectra towards higher wavelengths was also noted with increasing content of Au. This shift could be due to Au electron deficiency which shifts the surface plasmon band to longer wavelengths [33].

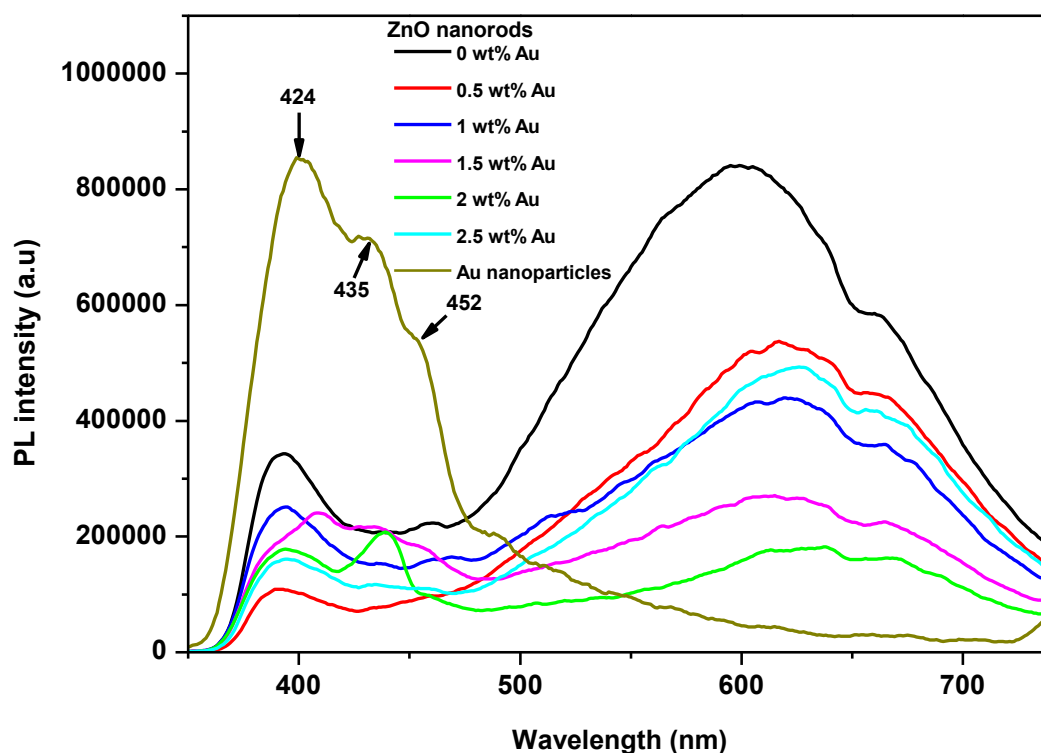


Figure 6.7: PL spectra of the Au nanoparticles, ZnO and Au/ZnO nanorods.

6.3.5 Magnetic properties

The paramagnetic properties of the ZnO and Au/ ZnO nanorods with different Au contents of 0.5, 1, 1.5, 2 and 2.5 wt% were determined using EPR analyses and the spectra are shown in Figure 6.8. The EPR spectrum of Au/ZnO displayed a single broad signal which is usually associated with ferromagnetic (FM) resonance [34-36]. FM in ZnO nanostructures has been widely reported to originate from paramagnetic defects including V_{Zn} , Zn_i , and V_O [18]. The similar broad EPR signal related to FM was also observed when Au nanoparticles were loaded on the surface of ZnO. This FM signal was shown to shift towards higher field with increasing Au loading concentration. Such shift in the FM signal suggests that Au metal nanoparticles affect the

local disorder on the FM exchange interaction [37]. Furthermore, the shift towards higher field with increasing Au loading concentration is consistent with the shift observed on the PL results. Such correlation between EPR and PL results suggests that the nanostructures possess the same type of paramagnetic defects responsible for observed room temperature FM. We observed previously that the existing paramagnetic defects on the pure ZnO are V_O [44]. Most importantly, the paramagnetic (PM) feature superimposed on the FM feature with higher Au loading concentrations (1, 1.5 and 2.5 wt%) appeared (see the circled area). Such PM feature is believed to result from different magnetic clusters of defects located near ZnO surface [21, 35]. This PM feature was completely suppressed at 2 wt% Au. However, heavily loaded ZnO sample (2.5 wt% Au) revealed several absorption peaks at low magnetic fields and the FM feature was slowly compromised. Such behavior could probably be due to the fact that at higher Au loading levels (above 2 wt%), tiny deposited Au particles tend to agglomerate together on the surface of ZnO and suppresses the amount of Zn_i and V_O which then resulted in the formation of Au-Au short range orders [35].

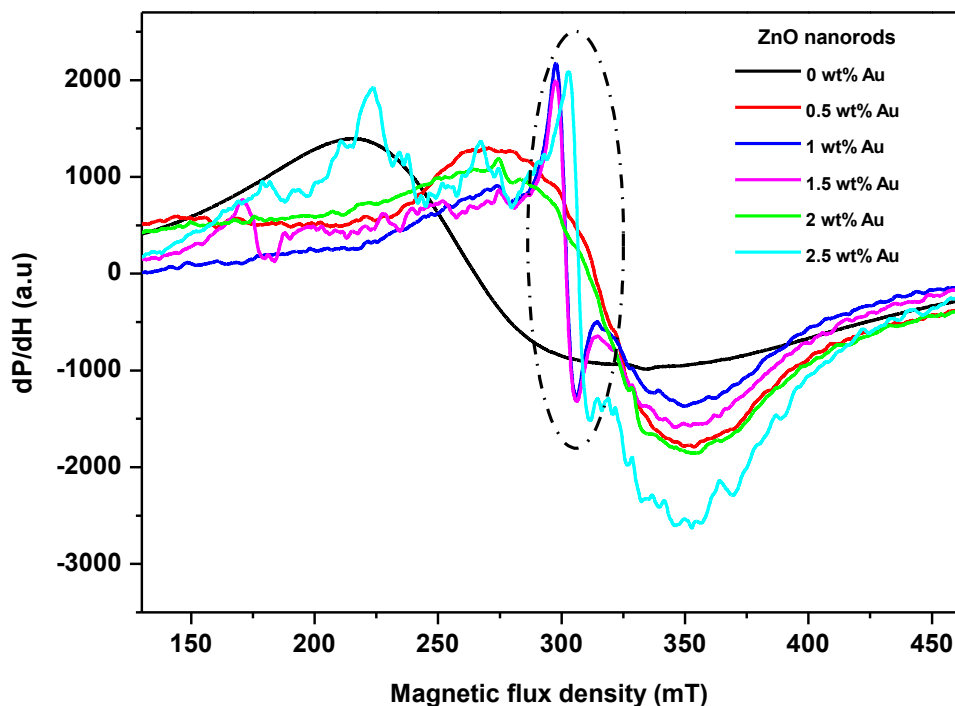


Figure 6.8: EPR spectra of the ZnO and Au/ZnO nanorods.

6.3.6 Gas sensing properties

6.3.6.1 NH_3 , CO, CH_4 and H_2 vs operating temperature

To examine the performance of ZnO and Au/ZnO based sensors, four gases were tested, namely, methane (CH_4), ammonia (NH_3), hydrogen (H_2) and carbon monoxide (CO). Gas sensing performance including sensor response, response and recovery times can be greatly influenced by the crystal structure and particle morphology, Au loading concentration, as well as operating temperature. Furthermore, it is a well-known fact that the operating temperature greatly impacts the response of metal oxide based sensors, since it controls the electrical conductivity and electrons mobility [38, 39]. Hence, the sensors were exposed to 100 ppm of each of the test gases at different

operating temperatures ranging from room temperature (RT) to 450 °C. In the current study, the sensing performance of the ZnO and Au/ZnO based sensors was evaluated in terms of sensor response as well as response and recovery time whereby sensor response (S) is defined as the ratio of the electrical resistance in air (R_a) to that in the tested gas (R_g), ($S = \frac{R_a}{R_g}$) [40]. While response time (T_{res}) is the time required to reach 90% of the response signal and recovery time (T_{rec}) signifies the time needed to reach 90% of the original baseline. Figure 6.9 (a-d) shows sensor response versus operating temperature for pure and Au loaded ZnO based sensors with different Au loading levels toward 100 ppm of CO, CH₄, H₂ and NH₃. From Figure 6.9 (a and c), the exposure of the sensors to 100 ppm of CO and H₂ led to an increase in sensor response with increasing temperature. Upon exposure to H₂, the sensors showed an optimum operating temperature at 350 °C for all sensors except for the 2 wt% sensor which showed its maximum response at 250 °C. For CO (Figure 6.9 (a)), all sensors revealed a linear relationship of the response to the temperature, except for the 2 wt% based sensors which showed their maximum responses at 300 °C. When the sensors were exposed to CH₄ and NH₃ gases, they showed their maximum response at RT. However, with exposure to NH₃, the ZnO sensor loaded with the lowest Au concentration (0.5 wt %) exhibited the most enhanced NH₃ response at a maximum value of ~1600 at RT. The sensor response was reduced when the operating temperature was further increased. The observed enhanced sensor response with 0.5 wt% loading level at this operating temperature could be due to the small particle size of Au nanoparticles which resulted to improved surface area owing to well-dispersed Au incorporation on ZnO support. As a

result, Au catalytic effect of NH_3 oxidation turns out to be extremely effective at RT [64]. As mentioned earlier, Au loading level is one of the important factors that significantly affect response and operating temperature. It is evident that unloaded ZnO based sensor and other sensors loaded with higher Au levels (1, 1.5, 2, 2.5 wt%) showed much lower response at RT and was reduced considerably at operating temperatures of 250 and 300 °C.

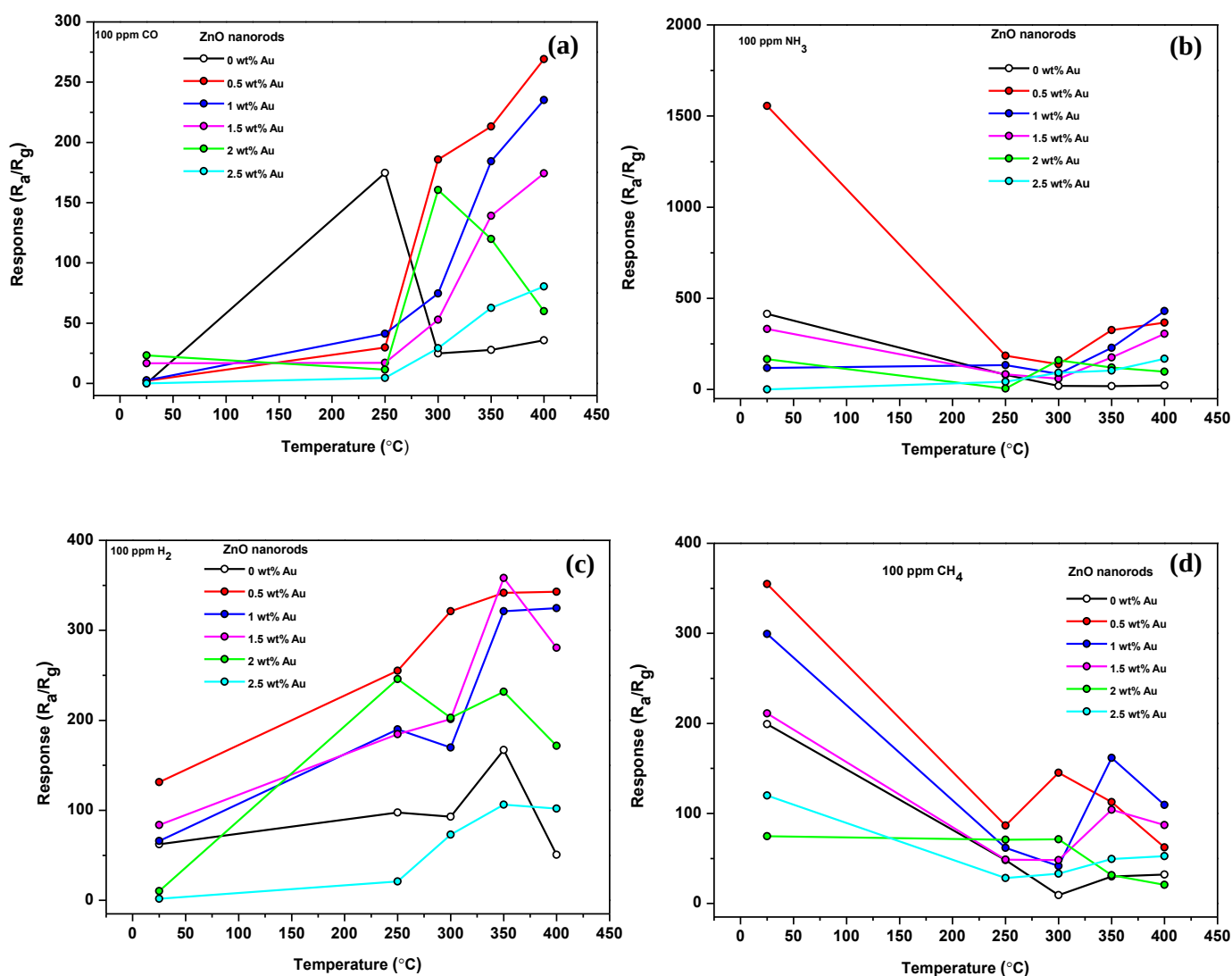


Figure 6.9: (a-d) ZnO and Au/ZnO based sensors response to 100 ppm CO , NH_3 , H_2 and CH_4 recorded at temperature range from RT to 450 °C.

The drop in sensor response with increasing Au loading level may be arising from clustering of Au nanoparticles resulting to larger Au agglomerates thus leading to lower surface area. It is clear from these results that the sensors show more sensitivity to NH_3 as compared to the other gases; therefore all the gas performance tests were done on NH_3 .

6.3.6.2 NH_3 sensing properties

Figure 6.10 (a) shows the plots of response curves of the ZnO and Au/ZnO based sensors at RT to different concentrations of NH_3 . The response values of all the sensors were shown to increase with the increase of NH_3 concentration. The 0.5 wt% Au loaded ZnO based sensor exhibited more enhanced response when compared to the rest of the sensors under the same concentration of NH_3 . In general, Au act as a catalyst that fast tracks the reaction rate as it plays a major part in improving sensing performance.

The enhanced sensor response with Au loading on ZnO surface in this work can therefore be explained in terms of spill-over effect [11, 41-44] which relies strongly on variations in the size and distribution of the Au nanoparticles loaded on ZnO nanorods support [44, 45]. The term spill-over in this case refers to the process whereby the Au, as a metal catalyst dissociate the molecule that can spill-over the surface of the ZnO support [3, 46]. During this process, the molecules are first adsorbed on the surface of Au nanoparticles, followed by migration to the ZnO surface to react with oxygen species on the surface thus changing electrical conductivity [47, 48].

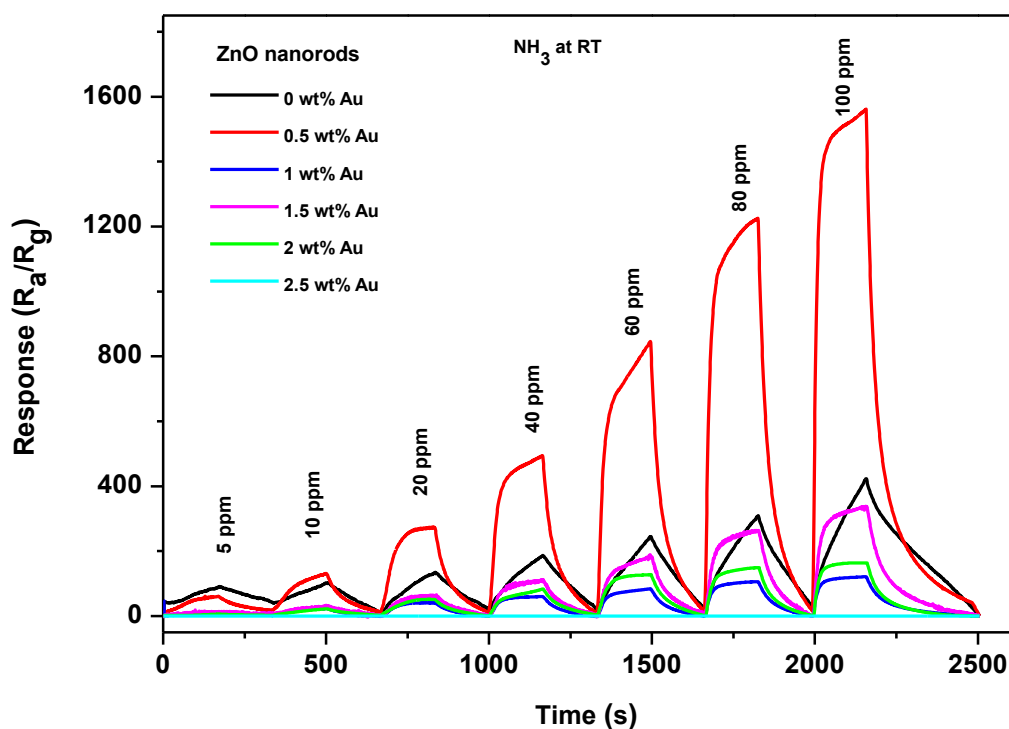


Figure 6.10: Response-recovery curves of the pure and Au loaded ZnO sensors to various concentrations of NH_3 at RT.

However, for such a process to effectively occur, Au nanoparticles must be homogeneously or well dispersed on the ZnO nanorods surface such that the Au nanoparticles exist close to all contacts so that the interparticle resistance can be controlled effectively [48]. Based on TEM analysis, for low Au loading level (0.5 wt%), Au nanoparticles were homogeneously distributed on ZnO support and their particle size was less than the rest of the loading levels. To understand the effect of Au metal catalyst in the current study, the response of Au loaded ZnO based sensor vs Au loading levels was plotted (see Figure 6.11). It can be seen from the plot that Au loaded ZnO based sensors exhibit response dependence on catalyst loading level in which a very sharp initial increase in response up to optimum maximum value at 0.5 wt% was observed. This is followed by a rapid decrease in response slightly below and

above the response value of the unloaded one as the loading content was increased up to 2.5 wt%. It is clear from this observation that the amount and distribution of Au particles on the surface of ZnO are the most important parameters governing the response of Au loaded ZnO. Excess of Au particles on the ZnO support tend to convert the nucleation types from homogeneous to heterogeneous which then results in agglomeration or clustering of Au particles on the surface of ZnO. As a result, the spill-over process then becomes less effective since less target gas molecules can be dissociated and spilled-over the surface of ZnO, hence deteriorated NH_3 sensing response with increasing Au loading level. In addition to spill-over effect discussed above as the main reason for observed enhance NH_3 response with Au loading in this study, it is also important to mention that optimal Au loading can enhance the surface area of the sensing materials thus enhancing the sensor response by providing more active sites on Au for adsorption of NH_3 gas molecules [9, 49]. However, excessive Au loading as a result of agglomeration lowers the surface area leading to reduced sensor response signal. Poor NH_3 responses observed for Au loading levels from 1 to 2.5 wt% could therefore be associated with the particle size growth of Au nanoparticles which later form Au agglomerates with increasing loading levels. Also, the increase in number of the Au particles at the surfaces of ZnO can cause blockage of NH_3 adsorption sites in the catalyst thus lowering the sensor response [7, 50]. It is therefore clear from these results that more loading of Au particles on the ZnO nanostructures surface leads to lowering of the gas sensor response.

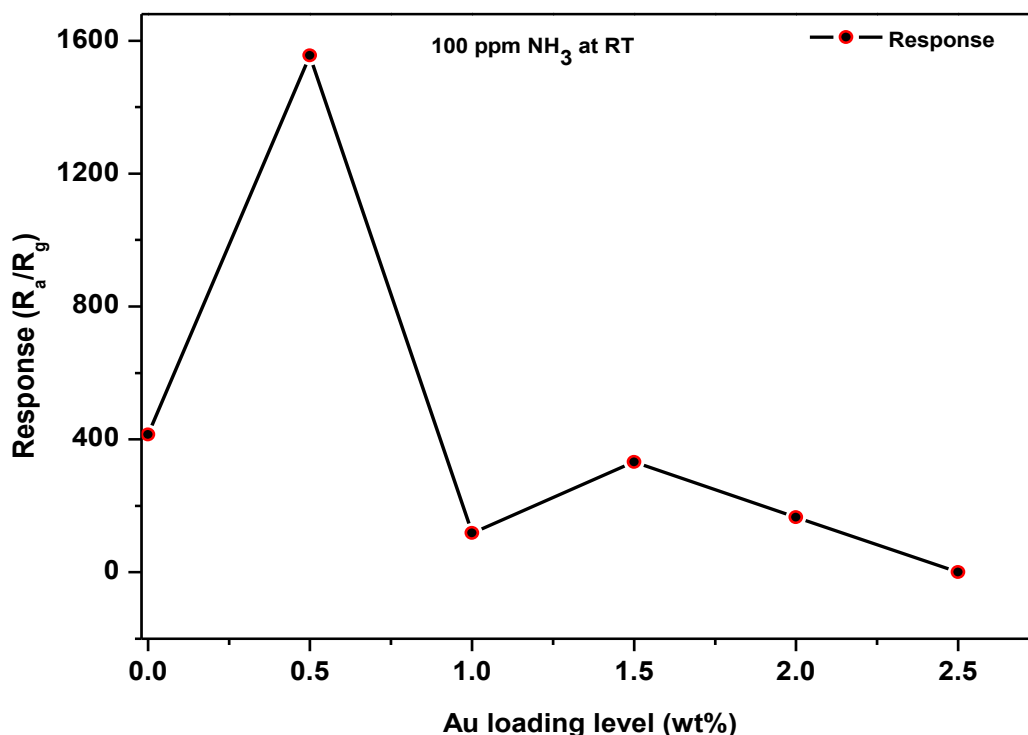


Figure 6.11: Response vs Au loading level of Au/ZnO based sensors to 100 ppm of NH_3 at RT.

6.3.6.3 Sensor response vs NH_3 concentration

Figure 6.12 shows the variation of sensors response with different NH_3 concentrations. The plots show that the responses of all the sensors increase with increasing gas concentration showing the dependence of response in gas concentration. The main reason behind such a linear relationship is that the response of sensors strongly relies on the removal of adsorbed oxygen molecules by reaction with a target gas and generation of electrons. Therefore, when the sensor is exposed to low concentration of NH_3 , the coverage of the NH_3 molecules on the surface of the sensor material will be low, leading to lower surface reaction and hence the low response. With

increasing gas concentration, the surface reaction also increases due to a larger surface coverage thus increasing sensor response [47].

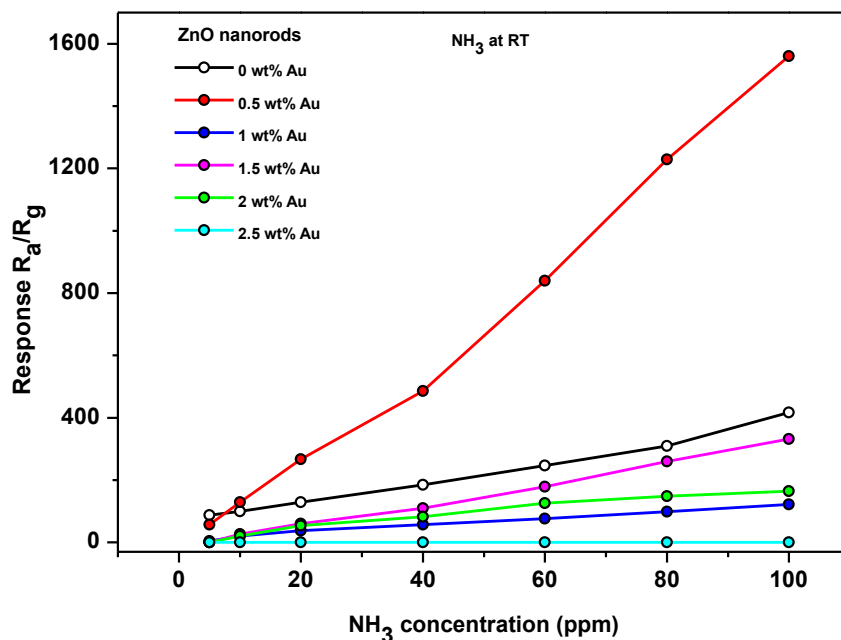


Figure 6.12: Variation of sensors response of ZnO and Au/ZnO to various concentrations of NH₃ at RT.

6.3.6.4 Response and recovery times vs NH₃ concentration

The response and recovery properties of the Au loaded ZnO sensors were also compared to those of the unloaded ZnO sensor, and are shown in Figure 6.13. Unloaded ZnO had response times of 122, 159, 165, 161, 162, 164 and 165 seconds and recovery times of 158, 159, 160, 170, 167, 167 and 346 seconds for concentrations of 5, 10, 20, 40, 60, 80 and 100 ppm, respectively. It is noticeable from Figure 6.13 (a-b) that the sensors based on the Au/ZnO had faster response and recovery times when compared to the ZnO. This can be attributed to the addition of the Au particles, which as a catalyst, acted as

the specific sites to promote the dissociation of the absorbed oxygen to oxygen ions.

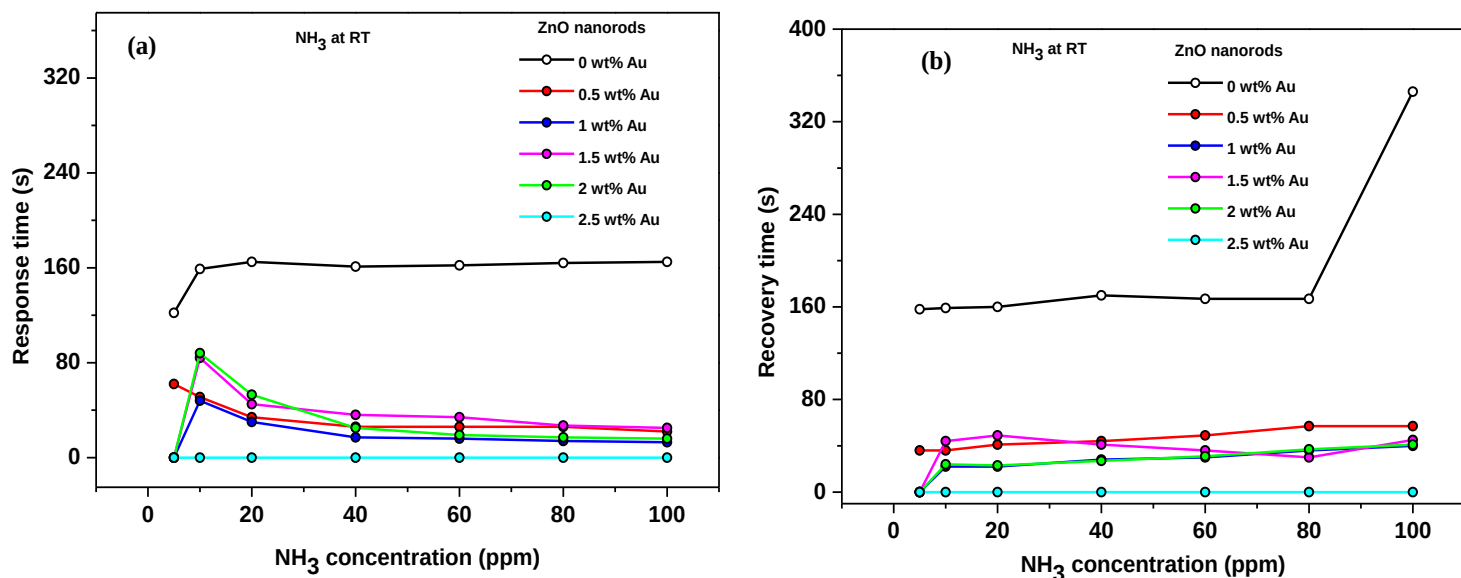


Figure 6.13: (a) Response times and (b) recovery times of the six sensors to different concentrations of NH₃ at RT.

6.3.6.5 NH₃ sensing mechanism

ZnO as an n-type semiconductor belongs to a surface-controlled type. Therefore its gas sensing mechanism involves a surface phenomenon which is due to the change of resistance of the sensing material resulting from the surface interaction between the target gas and the sensing material [3]. Figure 6.14 shows a schematic representation of the proposed mechanism for adsorption of NH₃ gas molecules after loading Au nanoparticles on surface of ZnO. It is generally accepted that in ambient air, oxygen molecules gets adsorbed to form O_2^- below 100 °C, or O^- between 100 and 300 °C, or O^{2-} at temperatures above 300 °C by capturing conductive electrons from the sensor

surface [51, 52]. Therefore, the adsorbed oxygen species at RT is mainly $O_{2(ads)}^-$. Au catalyst reaction process on ZnO surface comprising of oxygen species on the surface in ambient air at low operating temperature in the current study may be defined through the following reaction pathways:

(i) Direct adsorption and desorption of NH_3 and oxygen on ZnO surface



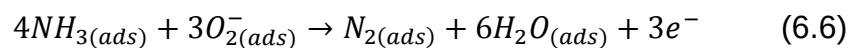
(ii) Adsorption of oxygen ions formed by dissociation and adsorption of oxygen gas at active sites of ZnO surface



(iii) Adsorption of negatively charged O^- ions $O_{2(ads)}^-$ formed after reaction of adsorbed oxygen ions with surface electrons



Upon NH_3 exposure over Au loaded ZnO surface, adsorption of NH_3 and adsorbed formate species can be described using the following reactions [53]



Therefore, exposure of Au loaded ZnO nanorods to NH_3 at low working temperature led to the release of electrons trapped in adsorptive states causing a decrease in sensor resistance.

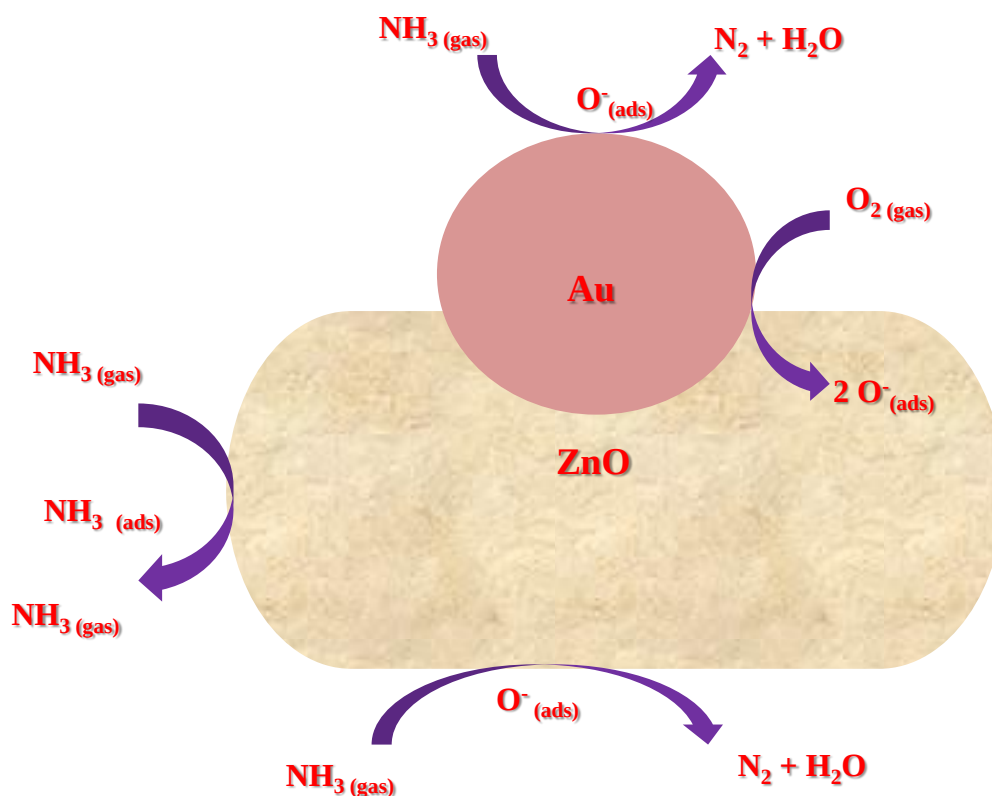


Figure 6.14: Proposed NH_3 sensing mechanism for Au/ZnO nanorods.

Previous studies have shown that the loading of a noble metal has an effect on the sensing performance of a sensor [4, 7, 9, 50, 54]. Table 6.1 shows a literature survey on the NH_3 gas sensing properties of various ZnO nanostructures compared to our current work based on ZnO nanorods. As shown in Table 6.1, our sensing material shows improved sensing response at room temperature when compared to other sensors tested even at higher temperature and higher gas concentration.

Table 6.1: The summary of gas sensing performances of ZnO and Au/ZnO based sensors produced by different synthesis procedures.

Methods	Materials	Gases	Concentration (ppm) and temperature (°C)	Sensing performances				Ref.
				Selectivity	Response (S)	t _{res} (s)	t _{rec} (s)	
Vapor phase transport	ZnO	CO, CH ₄ ,	3-6 H ₂ S	H ₂ S	128.4	600	780	[29]
	Au/ZnO	H ₂ S,	1000		475.3 ppm (6 nm)	660	1200	
		NH ₃ ,	250 NH ₃					
		acetone, ethanol	R.T					
hydrothermal	ZnO	CO ₂ ,NO,	50	Ethanol	-	-	-	[5]
	Au/ZnO	NH ₃ ,	325°C		1.335 ppm	5	20	
		CO, CH ₄ , ethanol			Au/ZnO (10 nm layer)			
hydrothermal	ZnO	H ₂ S,CO ₂ ,	5, 50	H ₂ S	5	-	860	[26]
	Au/ZnO	CH ₃ OH,	R.T		79.4	-	170	
		NH ₃ , Cl ₂ ,			(1.2 at %)			
		CH ₄ ,						
		C ₂ H ₅ OH						
hydrothermal	ZnO	CO,CH ₄ ,	100 ppm, RT	NH ₃	414.4	165	346	Current
	Au/ZnO	H ₂ ,NH ₃			1564.5 (0.5 wt %)	22	57	work

6.3.6.6 Selectivity of Au loaded ZnO based sensors

Gas selectivity is one of key parameters of a gas sensor. A sensor device comprised with a noble semiconductor-based sensor can detect an individual gas selectively when it is exposed to an atmosphere containing various gases with similar physicochemical properties. The selectivity study was carried out by exposing the six sensors to 100 ppm of different gases namely CO, CH₄,

H₂, and NH₃ at RT. The selectivity histogram of the sensors is shown in Figure 6.14. The sensors are highly selective to NH₃, and 0.5 wt% sensor shows the highest selectivity towards NH₃ with $S=1551.4$. This is higher than the response to other gases, indicating its excellent selectivity toward NH₃. It is therefore safe to conclude that 0.5 wt% sensor is a promising candidate for highly sensitive and selective detection of NH₃ at RT.

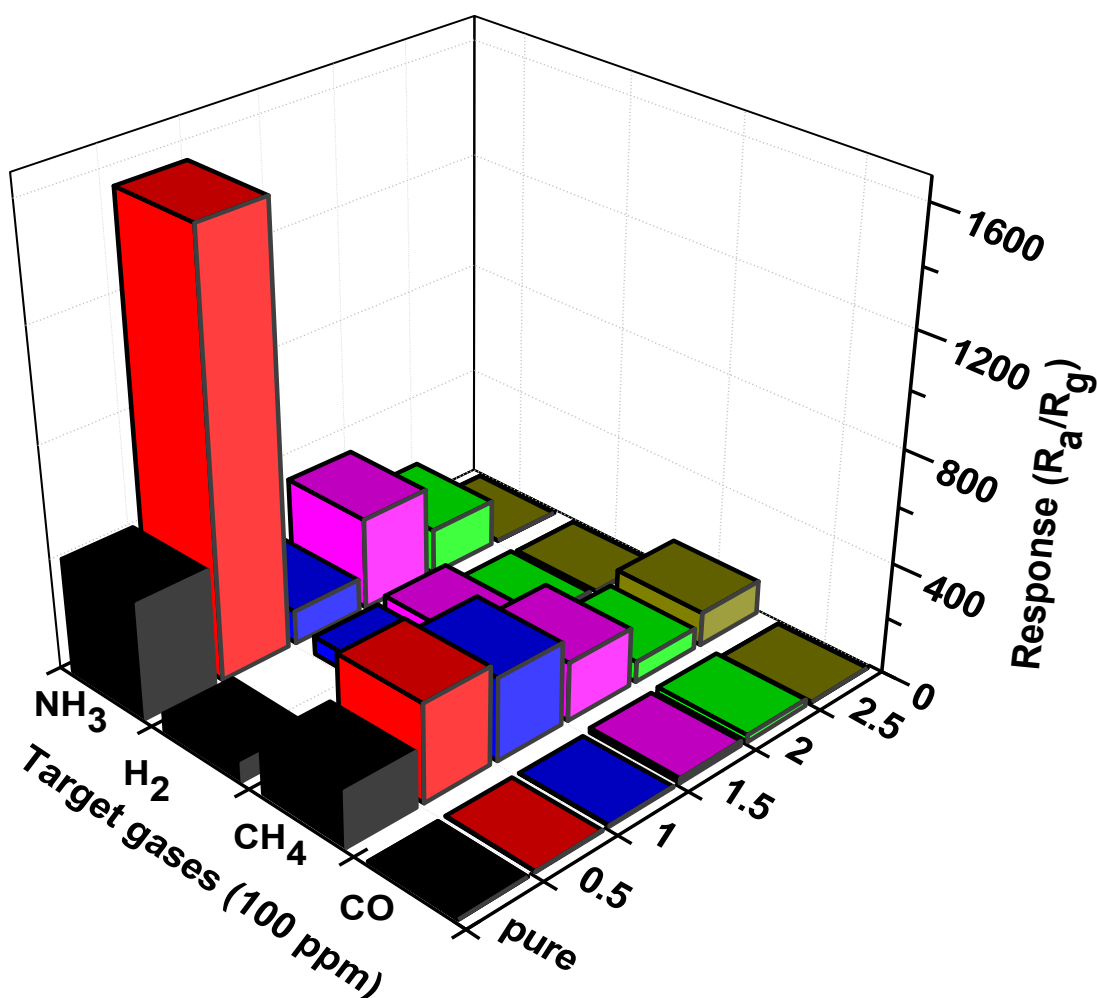


Figure 6.15: Selectivity histogram of the six sensors tested to 100 ppm of CO, CH₄, H₂ and NH₃ at RT.

6.4 Conclusion

Unloaded and Au loaded ZnO nanorods based sensors with different Au loading levels synthesized using microwave-assisted method have been investigated for selective detection of NH_3 gas from 5 to 100 ppm at RT. A 0.5 wt% Au loaded ZnO sensor showed highest sensing performance and selectivity to NH_3 gas at RT. Improved NH_3 response was explained by spill over mechanism which is highly effective when the Au catalyst is homogeneously dispersed on the surface of ZnO. The excellent sensing performance suggests that Au loaded ZnO nanorods sensor is a promising candidate for the detection of NH_3 gas for both lower and higher concentrations.

6.5 References

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Chapter 7

Conclusion

This thesis reports on the preparation of the ZnO nanostructures with various morphologies induced by variation of pH, ZnO nanorods controlled by variation of irradiation time and Au loaded ZnO nanostructures using microwave-assisted hydrothermal method. Non-destructive techniques such as XRD, SEM, TEM, XPS, BET, Raman, PL and EPR were used to study their microstructural, elemental, optical, and magnetic properties. Gas sensing properties of these ZnO nanostructures were also studied. Their sensing mechanisms are discussed in detail.

For ZnO nanostructures with various morphologies induced by variation of pH, SEM analysis revealed changes in morphology with variation of pH and annealing. PL studies showed decrease in the concentration of surface defects with annealing while the blue and green emissions were found to vary with increasing pH indicating variation in concentration of surface defects with change of pH. As prepared ZnO sensors exhibited high response to CO while the annealed ones showed high response to NH₃ at 250 °C.

ZnO nanorods whose lengths and widths were found to be influenced by variation of irradiation time showed high response to CO at 350 °C. PL and EPR studies demonstrated that the high sensing response was due to Zn_i and V_o surface defects.

For unloaded and Au loaded ZnO nanorods, 0.5 wt% Au loaded ZnO nanorods showed the highest selectivity and response to NH_3 at RT. The enhanced sensing performance of the 0.5 wt% sensor was due to the 'spill-over' mechanism which is highly effective when the Au nanoparticles are homogeneously dispersed on the surface of the ZnO nanorods.

List of publications

1. K. Shingange, G.H. Mhlongo, D.E. Motaung, O.M. Ntwaeaborwa, Tailoring the sensing properties of microwave-assisted grown ZnO nanorods: Effect of irradiation time on luminescence and magnetic behaviour.

Journal of Alloys and Compounds Vol. 657 (2016) 917–926

2. K. Shingange, G.H. Mhlongo, D.E. Motaung, Z.P. Tshabalala, O.M. Ntwaeaborwa Highly selective NH₃ gas sensor based on Au loaded ZnO nanostructures prepared using microwave-assisted method.

Journal of Colloid and Interface Science (under review)

3. K. Shingange, G.H. Mhlongo, D.E. Motaung, Z.P. Tshabalala, O.M. Ntwaeaborwa Microwave-assisted method derived ZnO with various morphologies: Effect of pH on PL, magnetic and sensing properties.

Journal of Material Research Bulletin (submitted)