THE ROLE OF TEMPERATURE AND POLYVINYL ALCOHOL CONCENTRATIONS IN THE SYNTHESIS OF ZINC OXIDE NANOPARTICLES

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Dedication

This work is dedicated to:

My father: Bekele Hirpha

My mother: Barke Kubache

My brothers: Ketema and Fekeda Bekele

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List of Abbreviations

NPs	Nanoparticles
UV/vis	Ultraviolet-visible
FT-IR	Fourier Transform Infra-Red
XRD	X-Ray Diffraction
PVA	Polly Vinyl Alcohol
ZnO	Zinc oxide
1D	One Dimensional
2D	Two Dimensional
3D	Three Dimensional
0D	Zero Dimension
NIR	near infrared

Abstract

The objective of this thesis is to study the role of temperatures and polyvinyl Alcohol concentrations in the synthesis of zinc oxide nanoparticles (ZnONPs). Zinc oxide nanoparticles weresynthesized using zinc nitrate hex-hydrate ($Zn(NO_3)_2.6H_2O$)and Polyvinyl Alcohol (PVA) concentrations (1.89M, 2.27M, 3.34M)at 400℃, 500℃, 600℃through wet-chemical precipitation methods. The effect of temperatures and concentrations were characterized using X-Ray Diffraction (XRD), Fourier-Transform Infrared (FT-IR), UV-Vis spectroscopy, Scanning Electron Microscopy (SEM) and Fluorescence Spectroscopy. The XRD results shows that the synthesized ZnONPs have wurtzite hexagonal structure with particles size 22nm, 24.1nm and 28.9nm at annealing temperatures of 400℃, 500℃, and 600℃ respectively. On the other hand, the sizes of ZnO NPs for PVA concentrations 1.89M, 2.27M, and 3.34M were 19.23nm, 21.82nm, and 23.84nm at temperature of 400℃respectively. The FT-IR measurements were carried out to indentify the presence of ZnO and its vibrational modes. The signal appeared around 400-600$cm^{-1}$was assigned for ZnO stretching vibration. The optical absorption of ZnO NPs of annealing temperatures indicatesred shift as the temperature increases.This characterization also revealed that band-gaps energy of ZnONPswas decreased as the temperatures and concentrations are increased. The morphology of ZnO NPs was characterized by SEM also indicated size increment as the temperature and concentration of PVA increases.

1. Introduction

The idea and concept of nanotechnology was first introduced by Richard P. Feynman in 1959 at the annual meeting of the American physics society. He gave lecturer titled, “There is plenty of room at the bottom” and he spoke about manipulating and controlling things on small scale. Due to his foresight, Feynman is often regarded as the first visionary of nanotechnology. Eric Drexler, yet another visionary of nanotechnology, stretched the imagination further and advocated that the power of chemistry be used to build molecular machine and predicted the tremendous impact that would have on a wide spectrum of technology. Nanotechnology is a technology that primarily deals with the synthesis, characterization, exploration and exploitation of nanostructure materials with structural features in between atoms and their bulk materials. In other words, it is a technology of design and application of nanoscale materials with their fundamentally unique properties and functions [1].

The application of nanotechnology have got attraction in the areas ofmedical, biomedical, healthcare, life science, agricultures, safety of food, security, energy production, energy conversion, energy storage, infrastructure, in building and constructions[2]. It also provides higher efficiency of device, and new approaches to diagnosis and treat of diseases, effective environmental monitoring and alternative ways for substantial energy development for better world [3]. Moreover, its applications also provide very fast response, low-cost, long-life and easy to use by unskilled user. This brings revolution in the life style and safety of human kind. Therefore, it is possible to say that nanotechnology is applied almost in every aspect of our present world.

Nanoparticles are a part of nanomaterials that are characterized by at least one dimension in the nanometer (1nm to 100nm) scale. These materials possess the structures known as nanostructures which constitute a bridge between molecules and infinite bulk systems. Structures and sizes have definite effects on the properties of nanoparticles [4]. As a result, the properties of nanomaterials are significantly different from those of a single atom (molecule) and those of bulk matter with the same composition. In line with this, they have also more mechanical strength, thermal stability, catalytic activities, electric properties, optical properties, etc. than that of the bulk one [5]. A suitable control of the properties and response of nanostructures can lead to the development of new devices and technologies [6]. Moreover, when the size of materials is in the nanoscale region, the large surface area to volume ratio exhibited by them improves their high surface reactivity with the surrounding environment. This property makes nanomaterials suitable candidates for many optoelectronic applications. Therefore, nanomaterials have opened up possibilities for new innovative functional devices and technologies. Nanomaterials that are based on metal oxide semiconductors have been on research due to their enormous use in diverse areas including electronics, piezoelectricity, optoelectronics, bio-sensors, catalysis, etc., [7].

Zinc oxide (ZnO), cobalt oxide (Co_3O_4), nickel cobalt oxide (NiCo2O4), Magnesium Oxide (MgO), Aluminum Oxide(Al_2O_3), Iron Oxide (FeO), Silicon oxide (SiO_2), Potassium Oxide (K_2O), and Calcium Oxide (CaO) are some of metallic oxide used in different research area. Among these different metal oxide semiconductor, ZnO NPs are the most promising metal due to their attractive physical and chemical properties as well as their low-cost, simplicity, environmental friendly and easy to grow. ZnO NPs are a highly attractive from research communities in the applications of modern optoelectronic technologies due to its relatively large

surface area to volume ratio, thermal stability, and larger band gap of 3.37 eV at roomtemperature, high exciton binding energy of 60 meV, high transparency, its high ionic and biocompatibility [8, 9]. Its higher band gap ensures a higher breakdown voltage, ability to sustain large electric field, lower electric noise, and higher temperature and higher power operation. Because of its high exciton binding energy, optically pumped lasing at room and above room temperature has been confirmed [10,11].

ZnO NPs are hydrophobic inorganic compound existing in white powder form and have three types of crystalline structures. These structures are wurtzite, cubic zinc blende and cubic rock salt. Wurtzite is the most stable structure among all. It is hexagonal and symmetrical in shape with the absence of symmetrical center. This structure contributes to the high piezoelectricity property. The various structures of ZnO NPs can be classified as among new materials with potential application in many fields of technology. Based on these structures, ZnO can occur in one dimensional (1D), two dimensional (2D) and three dimensional (3D) structures [12]. However, synthesis route is also very important to get different types of nanostructures with different properties. ZnO nanoparticles can be prepared by wet-chemical precipitation methods [13, 14].

In present case, the temperature and concentrationare factorsconsidered in chemical reaction in the synthesis of ZnONPs by the precipitation method. When theconcentrations of the reactants are raised, the reaction proceeds more quickly. This is due to an increase in the number of molecules that required the minimum energy. In other word, increasing the number of particles in a given volume affects the rate of reaction because cramming more particles into affixed volume increases the concentration of reactant and frequency of the collision leads to higher

reaction rate. Here increasing concentrations also increase the particle size. When solids and liquids react, increasing the surface area of the solid will increase the reaction rate. On other hand, decrease in particle size causes an increase in the solid's total surface area [13, 14].

Similarly, raising the reaction temperature can double or triple the reaction rate. This is due to an increase in the number of particles that have the minimum energy required. The reaction rate decreases with a decrease in temperature and vice versa. Increasing the temperature makes the reactant particles to move more quickly, more collision of particle and this cause the rate reaction to proceed. Reaction temperature is an important parameter which influences the structural morphology of the particles as well as the particle size. As the reaction temperature is increased, the particle size also increases. In heating process when the particles are formed, they collide with one another to form a larger particle. This process is depends upon the temperature and available energy, that’s why particle size increases with increasing temperature. Therefore, the change in the reaction temperature will certainly influence the morphology and structure of nanomaterials because particle morphology is strongly dependent up on the super-saturation which in turn is dependent upon the solution temperature. Thus, the synthesized ZnO nanoparticles with controllable temperature and concentration were prepared for designing nanotechnology devices.

The synthesized ZnO NPs have been characterized using various physical techniques such as X-rays diffraction (XRD), Scanning Electron Microscopy (SEM), UV-Vis Spectroscopy, Fluorescence Spectroscopy and Fourier Transform Infrared Spectroscope (FT-IR).

Therefore, the general objective of this research is to investigate the role of temperatures and Polyvinyl Alcohol (PVA) concentrations in the synthesis of zinc oxide nanoparticles. The

specific objectives are: 1. Synthesis ZnO nanoparticles by wet chemical methods, 2.Characterize the synthesizedZnO nanoparticles by XRD, FTIR, SEM, UV/Vis Spectroscopy, and Fluorescence Spectroscopy, 3. Calculate the size ZnO NPs by using Debye Scherrer formula, 4.Investigate the effect of temperature and PVA concentrations on the particle size, structure and morphology of ZnO NPs.

The thesis is organized as follows. Chapter 1 deals with introduction that contains short description of the research with specific and general objectives. In Chapter 2, Literature review related to the general properties of ZnONPswas explained.The crystal structures, piezoelectric, mechanical, optical and electronic properties, and synthesis ofZnO NPs, are described in details. The last part of this chapter, the characterization techniques of ZnONPs by X-ray diffraction, Fourier Transform Infrared Spectroscope, UV/vis spectroscope, Scanning Electron Microscope and Fluorescence Spectroscope were mentioned in details.

In Chapter 3, the materials and methods used in this work are presented. This chapter has two sections, the first section of this chapter deals with the description of various chemicals, apparatus,methods of sample preparation and the second section of this chapter deals characterization methods.In Chapter 4, the results and discussion of the thesis were presented. The effects of temperature and concentrations, the crystal structure, particle size and shapewere obtained from XDR, and SEM. The FT-IR measurements carried out toindentify the presence of ZnO NPs and its vibrational modes were described. Theabsorption spectra ZnO NPs were determined by UV-Vis Spectroscopyand transmission spectra of the sample by Fluorescence.

Finally, conclusion is given in Chapter5.

2. Literature Reviews

2.1. General properties of zinc oxide nanoparticles

Among inorganic metals, ZnO play a fundamental role in developing new devices as they present a considerable variety of structures, stoichiometry, chemical and physical properties that can be tailored to make use of a variety of suitable synthesis techniques [15- 17] . Zinc oxide is one of the most attractive materials in research due to its wide application in fields ranging from optoelectronics, photo-catalysis and optics to biology together with its exceptional properties of good stability, bio-compatibility and non-toxicity. It is also one of the most important and versatile functional properties due its wide spectrum of outstanding properties [18]. In addition, ZnO is a biocompatible and bio-safe which attracts it for chemical sensor and biosensors applications [3, 15].

Furthermore, ZnO possesses different nanostructures such as nano-tubes, nano-wire, nano-rods,nano-flower,nano-belts, nano-tetra pods, nano-ribbons, nano-rings, nano-combs which are made ZnO nanostructures to possibly be grown on cheap and flexible substrates as well as without substrates. Hence, ZnO nanostructures are attractive and promising material for some future nanotechnology applications [13,14]. However, most of these advantages are definitely utilized due to the fundamental properties of ZnOnanomaterials. Therefore, the basic properties of ZnO nanostructures were introduced in this study.

2.1.1 Crystal structures and bonding nature of ZnONPs

ZnO is an n-type semiconductor whose iconicity resides in between being covalent and ionic semiconductor. It has three kinds of crystal structures namely wurtzite (B4), zinc blende (*B*3) and

rock salt (B1) [19]. From these, wurtzite (B4) is thermodynamically stable phase at room temperature and all the discussion covered in this thesis is based on wurtzite crystal structure.

ZnO have crystalline usually in the hexagonal wurtzite type structure shown in Figure 2.1below. The hexagonal structure has a point group 6 mm (Hermann-Mauguin notation) or C6v (Schoenflies notation). The lattice constants are a= 3.25 Å and c= 5.2 Å; their ratio c/a~ 1.60 is close to the ideal value for hexagonal cell c/a= 1.633. The wurtziteZnOalso has four face terminations, with two are polar and other two are non-polar.

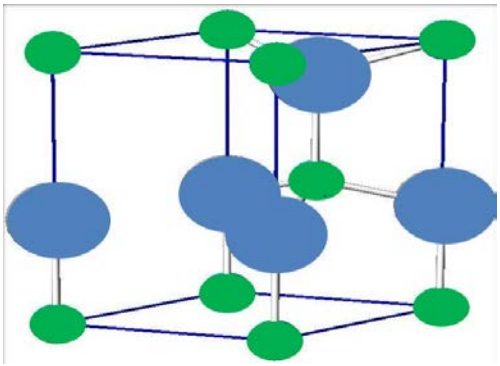

Figure 2.1Wurtzite structures of ZnO [19,20].

Both polar and non-polar faces have equal number of Zn and O atoms, but the chemical and physical properties of polar faces are different from non-polar faces [21].Another important feature of ZnO is its bonding nature. The bond between zinc and oxygen has firm ionic character, whereas the tetrahedral coordination of the ZnO crystal structure also points out the sp3 covalent bonding. That is why ZnO sorted out as covalent as well as ionic compound. It is well known that among all the semiconductors, which have tetrahedral bond andZnO holds the highest piezoelectric tensor. Due to these features ZnO become more important than others in applications where electromechanical coupling plays a role [19-21].

Properties	Values
Density	5.606 g/cm^3
Molecular weight	81.39
Stable phase	Wurtzite
Melting point	1975℃
Refractive index	2.008, 2.029
Band gap energy	3.37eV
Lattice constant	a_0 0.324995nm
	$c_0$0.52069nm
	c_0/a_0 1.602 or 1.633
Exciton binding energy	60meV

Table 2.1: Properties of ZnONPs [13-15]

2.1.2 Piezoelectric properties ZnONPs

ZnONPs are a promising piezoelectric material due to an effective accumulation of charges when mechanical stress is applied on it. Since ZnO has both semiconducting and piezoelectric properties, therefore it has enormous potential in energy harvesting applications. The polarity present in the ZnO tetrahedral crystal structure is oppositely charged ions produce positively charged zinc and negatively charged oxygen polar surfaces that creates conventional dipole moment. Therefore one can say that piezoelectricity initiates from the polarization of the tetrahedrally coordinated unit. In this principle the piezoelectric effect changes an applied mechanical stress into an electrical voltage or vice versa.

There are two possible ways to determine piezoelectric properties. One is called direct piezoelectric effect and the other is called converseor indirect piezoelectric effect. In the direct piezoelectric effect force is applied on the material in order to create strain in it, which generates

charges on the material's surface due to electrical polarization that results output voltage signal. In converse piezoelectric effect an external voltage is applied in order to generate strain in the material. Polarity in ZnO is also critical, because it has substantial influenced on different properties like growth direction, etching, piezoelectricity and defect generation. Moreover due to the absence of center of symmetry in the wurtzite crystal structure of ZnO, it exhibits pyroelectric behavior as well as besides being piezoelectric [22, 23].

2.1.3 Optical properties of ZnO NPs

ZnO holds some exceptional properties which make that an excellent luminescent material. These properties include direct and wide band gap, large excitons binding energy and deep leveldefect emission [1, 15, 25]. Today, ZnO has drawn much attention based on its unique and promising properties that makes it a promising candidate for short wavelength photonics.These properties arise from its direct wide band gap of 3.37 eV which corresponds to the energy of 3655 Å photons. ZnO is a material that strongly absorbs ultra violet light below 3655˚A and is transparent to visible wavelength of the electromagnetic spectrum [23].

Zinc oxide generally appears as white in the range of visible wavelengths with a typical refractive index of 2.008, 2.029. But due to unintentional doping of the grown crystals ZnO crystals usually appears as red, green or yellow colored. Under ultra violet (UV) light ZnO becomes photo-conductive. By the combination of optical and semiconductor properties, zinc oxide becomes acontender for a newgeneration of devices and is a promising material in solar cells because solar cells require transparent conductive coating for greater quantum efficiency [25].

According to Yang et al., both intrinsic and extrinsic effects are the contribution of optical properties in semiconductor. Intrinsic optical transition is described as the transition between the holes in valence band and electrons in conduction band where also an excitonic effect is concluded as the result of coulomb interaction [26].

The electronic states are created in the band gap when the impurities and complexes are added and influence optical absorption and emission processes. These kinds of properties can be related to extrinsic properties. Bound excitons are generally defined as excitons that can be bound to charged donors and acceptors. The electronic states of these bound excitons are highly dependent on the band structure of the semiconductor material. Due to the electron transition between the valence band and the conduction band, the ZnO nanostructures have been a promising candidate in implementing photonic devices [23, 26].

As direct band gap is good for short wavelength photonics, high excitons binding energy permits effective excitonic emission atambient temperature and deep level defect emission is responsible for covering the whole visible region beside ultra-violet emission. On the other hand, the optical properties rely heavily on intrinsic and extrinsic defects present in the crystal structure and it is possible to tune for optical/electrical properties just by manipulating the nature and quantity of defects present there. These defects can occur at the time of growth or annealing. The intrinsic defects (like vacancy) are those in which host atom is absent, while extrinsic defects are those in which foreign atoms (like impurities) are involved. ZnO have two most common defects known as oxygen vacancy and zinc vacancy [24, 25].

2.1.5 Electronic properties of ZnONPs

At ambient temperature and pressure, zinc oxide has a wide, direct band gap semiconductor of 3.37eV and excitation binding energy of 60meV. The large band gap gives ZnONPs the advantages of higher voltage breakdown, reduce electronic noise, ability to sustain large electric fields and higher power operation than smaller band gap materials. On the other word, the wide band gap and large exciton binding energy of ZnONPs also make it a potential candidate to be applied in chemical sensors, luminescence devices and solar cells. Due to the presence of vacancies and interstitial defects, ZnO is said to be n-type semiconductor [27].

2.2 Synthesis of ZnO NPs

The synthesis of nanoparticles is generally grouped into two main approaches, namely bottom-up and top-down approaches.

2.2.1 Top-down Approach

The top-down approach is a method that tears down larger building blocks into finer pieceslarger scale and then reduces to nanoscale. In short, top-down approaches occurs when large objects are modified to give smaller feature. All solid state route falls under this category. Film deposition and growth, nano-imprint (lithography), etching technology, mechanical polishing, etc are examples of top down approach. The main reason of alteration in different mechanical, thermal and other property is due to increase in surface to volume ratio. By nature, it is not cheap and quick to manufacture as well as it is not suitable for large scale production. Top-down techniques do not usually lead to individual nanoparticles; however, they can produce bulk nanostructure materials [27,28].

2.2.2 Bottom-up Approach

The bottom up approach is a method that builds nanomaterials from atomic or molecular precursors. In other word, it occurs when small building blocks are produced and assembled into larger structures. All the techniques that start with liquid and gas as starting materials falls under this category. In this case, the main controlling parameters are morphology, crystalline, particle size, and chemical composition. Chemical synthesis, laser trapping, self-assembly, colloidal aggregation, etc are examples of bottom up approach. Synthesis of nanoparticles by bottom up is cheap, fast and suitable to manufacture large scale nanoparticles. Thus, nanostructures can be synthesized either by bottom-up or top-down approaches. Many of the bottom-up approaches have difficulties in the scale up, while the top-down approach can easily scale up. Thus, one can see from figure 2.2 that both these approaches are complementary to each other.[28].

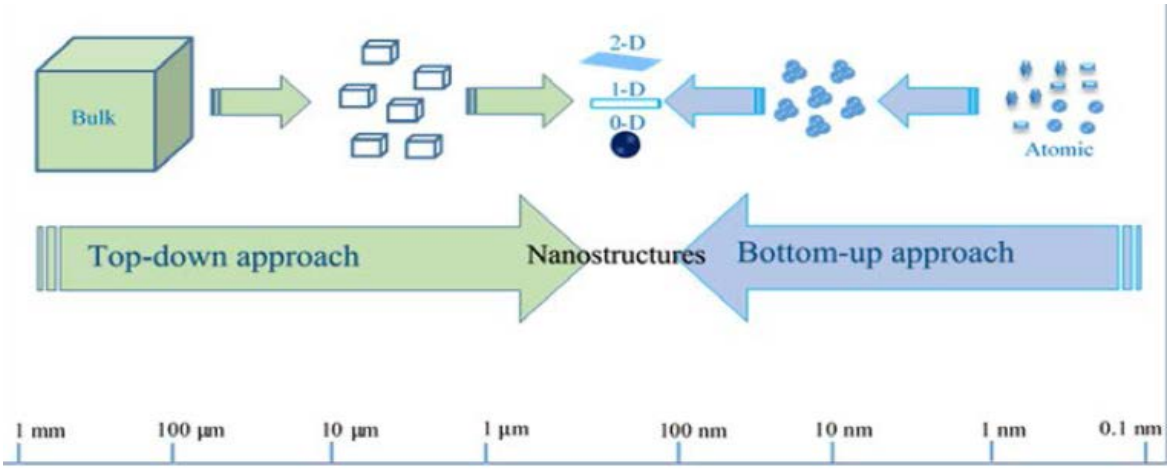

Figure 2.2: Top-down and bottom-up approaches[27-29].

2.2.2.1 Wet-chemical synthesis

Wet chemical synthesis is a solution based processing routes used for the synthesis of ZnO NPs include precipitation of solids from supersaturated solution, homogeneous liquid phase chemical reduction and ultrasonic decomposition of chemical precursors. On the other hand, chemical synthesis is one of the most important techniques which can be performed by using a range of precursors and different conditions like temperature, time, concentration of reactants, and so forth[29].

2.2.2.1.3 Precipitation methods

The fundamental study on kinetics of precipitation reaction is important to improve the industrial precipitation process. Precipitation is the creation of a solid from a solution. When reaction occurs in a liquid solution, the solid formed is called “precipitate” and the chemical that produce solid is called the “precipitant”. In other word, precipitation reaction is only the phase transformation from liquid to solid with chemical reaction. An important stage of the precipitation methods is the formation of the nucleation i.e., the precipitation reaction is a combination of two stage process, called nucleationand growth. Nucleation plays an important role in controlling the properties of the final product, size distribution and nature of the phase [30-32]

2.3 Characterization methods

Different characterization methods were used to gain deep understanding of the morphological characteristics, crystalline, functional group, optical property and particle size of the synthesized ZnO nanoparticles. The most common techniques used in this study are X-Ray Diffraction

(XRD), Scanning Electron Microscope (SEM), Ultra-Violet Visible Spectroscopy (UV-Vis), Fourier Transform Infrared Spectroscopy (FT-IR) and Fluorescence Spectroscopy. The crystal structure and particle size were determined using XRD, the optical effect was analyzed from the spectra data using UV-Vis spectroscopy and FT-IR indicate the presence of functional group present in the ZnO NPs. The characterizations of ZnO nanostructures using these instruments are presented as follows.

2.3.1 X-Ray Diffraction (XRD)

X-rays are electromagnetic radiations of wavelength1Å (10^{-10}m) which occurs between ultraviolet and gamma rays in the portion of the electromagnetic spectrum. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at atomic level [33]. X-ray diffraction (XRD) is a rapid, a non-destructive and a powerful technique used to study the phase of a crystalline material, information on unit cell lattice parameters, crystal structure, crystal orientation and crystallite size. XRD is widely used to characterize unknown crystalline materials [34].

The working principle of the XRD technique is relied on constructive interference of X-rays and a crystalline sample. In a crystal, the atoms distribute regular in space, which comes into being crystal lattices. These lattices form a series of parallel planes with spacing distance d. The x-rays are generated by a cathode ray tube (X-ray produced by the impact of accelerated electrons with heavy metal such as Cu), filtered (filtered and collimated by nickel filters) to produce monochromatic X-ray radiation which directed toward the sample. When X-rays light with wavelength λ is projected onto a crystal lattice at an angle θ, the interaction of the incident

X-rays with the sample provides constructive interference if the conditions satisfy Bragg's law [35, 36]:

$$n\lambda = 2d_{hkl} \sin\theta \quad (1)$$

where nis an integer 1, 2, 3, … (usually n =1 for consideration of first order), λis wavelength in angstroms (1.5418 Å for Cu-K_α), $d_{hkl}$is spacing between the planes called inter planar lattice constant, θ is the angle between the incident light and the lattice planes, the 2θ is angle between the incident and scattered beams, the angle 2θ of maximum intensity is called the Bragg angle. All diffraction directions of the lattice will be generated by scanning through a range of 2θ angles on the sample. Figure 2.3 illustrates the reflection of X-rays from two planes of atoms in a crystal solid. The direction of plane normal (hkl) is perpendicular to a plane of atoms and the diffraction vector **S** is the vector bisects of the angle between the incident and diffracted beam. The lattice constants 'a' and 'c' and the spacing distanced_{hkl} for the wurtzite structure of ZnO can be calculated using the Eq. (2)and (3) written below [37]:

$$a = \sqrt{\frac{1}{3}}\frac{\lambda}{\sin\theta} \text{ and } c = \frac{\lambda}{\sin\theta} \quad (2)$$

Spacing distance $d_{hkl}$is then given by:

$$d_{hkl} = \frac{ac}{2}\sqrt{\frac{3}{c^2(h^2 + hk + k^2) + \frac{3(al)^2}{4}}} \quad (3)$$

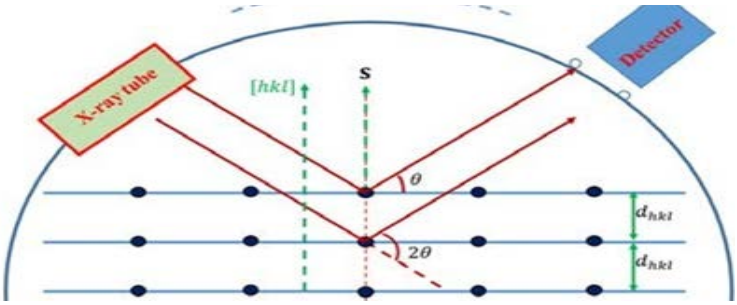

Figure 2.3:Typically, Bragg Brentano geometry [37]

. The average particles size of a crystalline is calculated from the Debye Scherrer formula as:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{4}$$

Whereβ is the full width at half maximum of the peak and D is the average grain size of the crystalline. The full width β is usually measured in radians at half of the maximum intensity [38, 39].

2.3.2 Scanning Electron Microscopy (SEM)

The scanning electron microscope is an optical instrument that uses a beam of high-energy electrons to produce a variety of signals at the surface of specimens used. This signals show information about the sample including chemical composition, crystalline structure, external morphology and orientation of materials which make up the sample. SEM analysis is normally considered to be non-destructive because the x-rays generated do not lead to loss of volume of the sample, so it becomes possible to repeatedly analyze the same materials. On other hand, scanning electron microscope is a kind of electron microscope which images a sample by

scanning it using a high-energy electron beam. The electrons then interact with the atoms making up the sample, thus producing signals which reveal information about the sample's composition, surface topography and other properties [40].

2.3.3 Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared spectroscopy is an important technique in organic chemistry. It is an easy way to identify the presence of certain functional groups in a molecule and one can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities. Analysis by infrared spectroscopy is based on the fact that molecules have specific frequencies of internal vibrations. These frequencies occur in the infrared region of the electromagnetic spectrum from 4000-400cm^{-1} wave number [39]. When a sample is placed in a beam of infrared radiation, the sample will absorb radiation at frequencies corresponding to molecular vibrational frequencies, but will transmit all other frequencies. Once the data has been obtained, it is converted into digital information using a mathematical algorithm known as the Fourier Transform.

The frequencies of radiation absorbed are measured by an infrared spectrometer, and the resulting plot of absorbed energy vs. frequency is called infrared spectrum of the material. Identification of a substance is possible because different materials have different vibrations and yield different infrared spectra. Furthermore, from the frequencies of the absorption it is possible to determine whether various chemical groups are present or absent in a chemical structure. In addition to the characteristic nature of the absorption, the magnitude of the absorption due to a given species is related to the concentration of that species [39, 40].

2.3.4 Ultraviolet Visible Absorption Spectroscopy (UV-Vis)

The instrument used in ultraviolet-visible spectroscopy is called UV/Vis Spectrophotometer. Spectrophotometer provides a means for analyzing liquids, gases and solids through the use of radiant energy in the far and near ultraviolet, visible and near infrared regions of the electromagnetic spectrum. Accordingly, the predetermined electromagnetic radiation wavelengths for ultra-violet (UV), visible (Vis) and near infra-red (NIR) radiation is defined as follows; UV radiation: 300 to 400 nm, Vis radiation: 400 to 765 nm, NIR radiation: 765 to 3200 nm. This instrument operates by passing a beam of light through a sample and measuring wavelength of light reaching a detector. Analytical information can be revealed in terms of transmittance, absorbance or reflectance of energy in the wavelength range between 160 and 3500nm. Light is quantized into tiny packets called photons, the energy of which can be transferred to an electron upon collision. However, transfer occurs only when the energy level of the photon equals the energy required for the electron to get promoted onto the next energy state, for example from the ground state to the first excitation state. This process is the basis for absorption spectroscopy [41].

The UV-Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of sample solution can be determined by measuring the absorbance at some wavelength. The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the solution [23]. This relation can be expressed as:

$$I = I_0 e^{-\alpha} \tag{5}$$

Whereα is the measured absorbance I_0 is the intensity of incident light at a given wavelength and I is the transmitted intensity. Hence, UV-Vis can also be used to determine the concentration of samples in solution[42].

The electronic band structure of semiconductors and metals is determined by their optical properties. The band gap energy of the sample was calculated by using the absorption edge relation [24]:

$$E_g = hv_g = \frac{hc}{\lambda_g} \quad (6)$$

Where h = $4.14x10^{-15}$evs $c = 2.99 \times 10^{8}\ {}^{m}/_{S}$ and λ_g is wavelength.

2.3.5 Fluorescence Spectroscopy

Fluoresce spectroscopy is a contactless, versatile, nondestructive, powerful optical method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. One way this excess energy can be dissipated by the sample is through the emission of light, or fluorescence. In the case of photo-excitation, this fluorescence is called photo fluorescence. Thus photofluoresenceis the spontaneous emission of light from a material under optical excitation. This light can be collected and analyzed spectrally, spatially and also temporally. The intensity and spectral content of this Fluorescence is a direct measure of various important material properties [40].

Photo excitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may

include the emission of light (a radiative process) or may not (a non radiative process). The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process. PL spectroscopy gives information only on the low lying energy levels of the investigated system. In semiconductor systems, the most common radiative transition is between states in the conduction and valence bands, with the energy difference being known as the band gap [41].

Fluorescence spectrum is quite different from absorption spectrum in the sense that absorption spectrum measures transitions from the ground state to excited state, while fluorescence deals with transitions from the excited state to the ground state. The period between absorption and emission is typically extremely short. An excitation spectrum is a graph of emission intensity versus excitation wavelength which looks very much like an absorption spectrum. The value of wavelength at which the molecules absorbs energy can be used as the excitation wavelength which provide a more intense emission at a red shifted wavelength, with a value usually twice of the excitation wavelength [42].

3. Materials and Methods

In this chapter the materials and methods of this thesis are presented. The first section of this chapter deals with the various chemicals, apparatus, instruments and methods of sample preparation were presented in details.In the second section methods sample characterization were discussed briefly.

3.1 Materials

3.1.1 Chemicals

The chemical used in this work are double distilled water, Nitric acid ($H(NO_3)_4$), Polyvinyl Alcohol (PVA) and Zinc nitrate hex-hydrate ($Zn(NO_3)_2.6H_2O$) as precursors to synthesis ZnO NPs in this research.

3.1.2 Apparatus and Instruments

The apparatus used in this experiment are: beakers, Volumetric flasks, Magnetic stirrer with hot plate, Thermometer, Analytical balance, Drying Oven, Spatula, What man filter paper, Muffle Furnace, puddle, crucible, 1cm quartz cuvette and small mortar and pestle.The instruments used are:X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM),FT-IR, UV-Vis Spectroscopy and Fluorescence Spectroscopy.

3.2 Methods of Sample Preparation

ZnO NPs were prepared by a precipitation method according to previously reported [43]. About 6gm of Polyvinyl Alcohol were dissolved in 6ml (2.26M) of double distilled water and stirred by

magnetic stirrer for 30min. Again 2gm of zinc nitrate hex-hydrate ($Zn(NO_3)_2.6H_2O$) also dissolved in 20ml of double distilled water and stirred by magnetic stirrer for 15 min. After this, zinc nitrate hex-hydrate ($Zn(NO_3)_2.6H_2O$) solution was added into Polyvinyl Alcohol (PVA) solution drop by drop touching the walls of container and stirred continuously for 2hrs. The aqueous solution turned into a milky white without any precipitation.After the reaction is completed, solution was allowed to settle and the supernatant solution was removed by washing with double distilled water for three times. The precipitate solution was allowed to dry in oven at 160℃ for 12hrs. The sample wascalcinated in muffle furnace for 8 hrs at the temperature of 400℃. By similar procedures, the other samples were prepared at annealing temperatures of 500℃ and 600℃ respectively. On the other hand, the PVAconcentrations (1.89, 2.27, and 3.34 M) dependent ofZnO NPs are also prepared in similar manner at the temperature of 400℃.

3.3 Characterization Methods for ZnO NPs

Various techniques have been used for characterization of ZnO NPs. The most common techniques used in this work were X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscope (FT-IR), UV-vis Spectroscopy and Fluorescence Spectroscopy.

3.3.1 X-Ray Diffraction (XRD).

The X-ray diffraction (XRD) pattern for ZnO nanoparticles were analyzed using XPERT-PRO X-ray diffractometer by generating Cu-K_α radiation (λ=1.5418Å). It is used to determine the crystalline phase of the synthesized nanoparticles. Small amount ofZnOnanopowders were used for characterization. An X-ray generator operates at a voltage of 40kV and applied current of

30mA at room temperature. Intensities were measured at room temperature in steps of $0.05s^{-1}$, over the range of $10^{o} \leq 2\theta \leq 80^{0}$,the diffractometer is connected to a computer for data collection and characterization displays. Then, the peaks of the X- ray diffraction pattern can be compared with the standard available data for the confirmation of the structure.

3.3.2 Scanning Electron Microscopy (SEM)

The synthesized ZnO NPs were grinded to fine powders and measured by beam balance and taken to metal plate. Then, the morphology of the resulting nanoparticles was studied by using scanning electron microscope (JEOL JSM 6510), operates under high vacuum and the magnification ranging from 20X to 30,000Xapproximately, spatial resolution of 50 to 100 nm. The fixed sizes, higher magnification of ZnO NPs were obtained by reducing the raster size of the specimen, and vice versa.

3.3.3 Fourier Transform Infrared Spectroscopy (FT-IR)

The vibrational spectra of ZnO NPs were measured by FT-IR (Perkin Elmer 65) in the range of wave number from 400-4000cm^{-1} by adjusting scan parameters like measurement mode (transmittance), Apodization, number of scan and resolution. Then, Small amount of ZnO nanopowders were taken into bore cylinder of potassium bromide plate. After this, the instrument is allowed to warm for 30min and the vibrational spectra of ZnO NPs were recorded.

3.3.4 Ultraviolet-Visible (UV-Vis) Spectroscopy

Absorbance spectra of ZnO NPs were measured using UV-Vis Spectroscopy (Perkin Elmer, Lambda 950), using 1 cmquartz cuvette over 300-800nm range of wavelength. About 0.3 gm of ZnO NPs dissolved in double distilled water and its solution was poured into quartz cuvette. Then, the cuvette is taken in to Ultraviolet visible spectrophotometerand the absorbance spectra of ZnO NPs were measured.

3.3.5 Fluorescence spectroscopy

The emission spectra of ZnO NPs were measured by Fluorescence spectroscopy (Fluoromax-4 Spectrofluorometer) using 5 nm slit widths, 264 excitation wavelengths and 380-520 ranges of wavelength. In additional, accessories, variation of signal with time, temperature, concentration, polarization, or other variables were monitored. Then, amount of ZnO NPs solution were taken into Fluorescence Spectroscope by 1cmquartz cuvette. Fluorescence spectrometers use laser sources, which contains wavelength selectors, sample illumination, detectors and corrected spectra. Then absorption spectra of ZnO NPs were measured.

4. Result and Discussions

4.1 X-Ray Diffraction Analysis of ZnONPs

Figure 4.1 shows the XRD patterns of the zinc oxide nanoparticles prepared by chemical precipitation methods at different annealing temperature of 400℃, 500℃ and 600℃. The characteristic peaks were observed at 31.802°, 34.468°, 36.306°, 47.600°, 56.592°, 62.951°, 68.952° and their corresponding reflection from (100), (002), (101), (102), (110), (103), (112) of crystal plane.The average particles size of ZnO NPs were calculated by Debye Scherrer formula of Eq. (4)and tabulated in the table 4.1below. The average particle sizes of ZnONPs annealed at 400℃, 500℃ and 600℃ are 22nm, 24.1nm and 28.9nm respectively. This result shows that, the averageparticle sizes of ZnO NPs increase as the annealing temperature increase which is in good agreement with the result reported by [44].

The increment of ZnO NPs size as the temperature increase is due tosupply of sufficient thermal energy[44]. Similarly, the diffraction peaks increases with increasing annealing temperatures, indicate the increase crystalline of ZnO NPs [45]. On other hand, the Full-Width at Half Maxima (FWHM) ofZnO NPs decreases as the annealing temperatures increases as shown in Table 4.1 below.

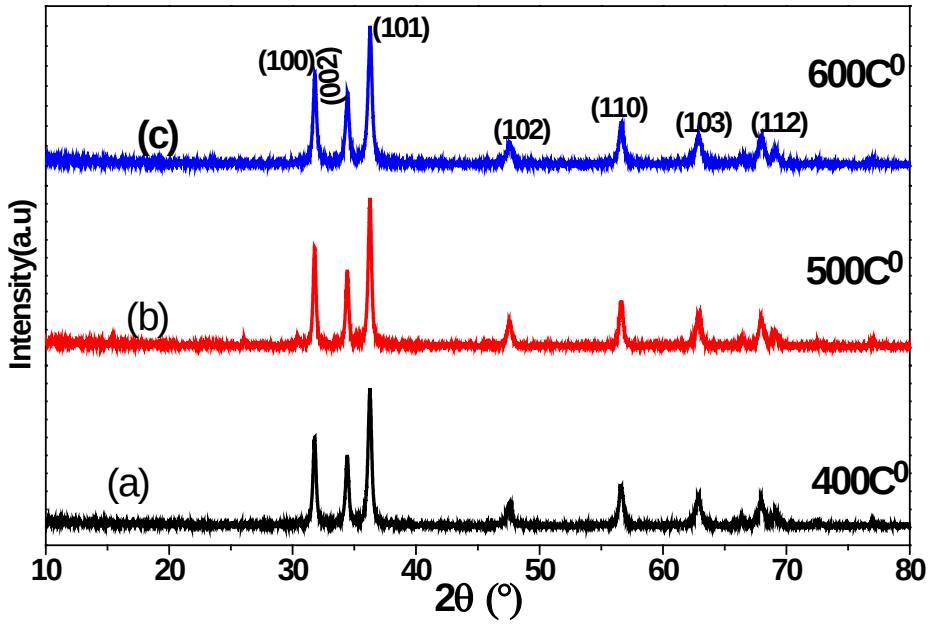

Figure 4.1:XRD patterns of ZnO NPs synthesized by annealing temperatures of a) 400℃, b) 500℃and c) 600℃

Annealing Temperature (T = 400℃)					
2θ	***θ***	(hkl)	FWHM	Particle size (D)	D (av.)
31.802	15.901	100	0.31834	25nm	22 nm
34.4680	17.23	002	0.30711	27nm	
36.3067	18.1534	101	0.37743	22nm	
47.6009	23.800	110	0.45807	18nm	
56.5912	28.2956	120	0.4806	17nm	
62.9523	31.4762	103	0.42914	21nm	
68.3522	34.1761	112	0.39039	24nm	
Annealing Temperature (T = 500℃)					
31.8225	15.9113	100	0.2669	28nm	24.1nm
34.5684	17.2842	002	0.2998	29nm	
36.1581	18.079	101	0.31345	26nm	
47.5752	23.7876	110	0.3473	21nm	
56.6077	28.3038	120	0.39675	22.74nm	
62.2918	31.146	103	0.29619	20nm	

68.2178	34.6089	112	0.22985	22nm	
Annealing Temperature (T= 600℃)					
31.3102	10.6551	100	0.20371	40nm	28.9 nm
34.2310	12.1155	002	0.28315	29nm	
36.6531	13.3265	101	0.25087	33nm	
47.1983	18.0991	110	0.25318	30.59nm	
56.6635	23.832	120	0.323897	23nm	
62.7525	28.3762	103	0.38897	23.21nm	
68.9666	31.4833	112	0.27824	23.46nm	

Table 4.1:Angle of diffraction, full width at half maxima and average particle size of synthesizedZnO NPS at the temperature of 400℃, 500℃ and 600℃.

The effect of annealing temperature on the lattice parameter of ZnONPs were calculated by Eq. (2) and tabulated in table 4.2 below. The lattice parameters of prepared ZnONPs are temperature dependent i.e. an increase in temperature leads to expansion of latticeparameters. From this table, one can understand the prepared ZnO NPs arewurtzite structurewith two lattice parameter ‘a’ and ‘c’which is almost related to the result reported by [45].

Temperatures	hkl	lattice parameter			d_{hkl}
		a(nm)	c(nm)	c/a	
400℃	101	0.2846	0.3124	1.0976	0.1925
500℃	101	0.3239	0.5609	1.7317	0.3871
600℃	101	0.4719	0.8172	1.8371	0.4087

Table 4.2:Lattice parameterand spacing distance of synthesized ZnONPs

Atdifferent annealing temperatures

Figure 4.2 shows, intensity versus angle diffractions of powder XRD patterns of ZnO NPs synthesized by changing concentration of PVA solution (1.89, 2.27 and 3.34M) at 400℃ respectively. The X-ray diffraction peaks of ZnO NPs with different concentrations have seven main broad band’s at 2θ values of 31.99°, 34.45°, 36.32°, 47.60°, 56.86°, 62.93° and

67.86°toreflection from (100), (002), (101), (110),(120),(103) and (112) of crystal plane respectively. The calculated average particle sizes of ZnO NPs are 19.23nm, 21.82nm and 23.84nm for the PVAconcentration (1.89, 2.27 and 3.34M) respectively as shown in table 4.2.The particle sizes of ZnO NPs were increased as the PVA concentrations increase due to an increase the number of molecules that required the minimum energy [46].

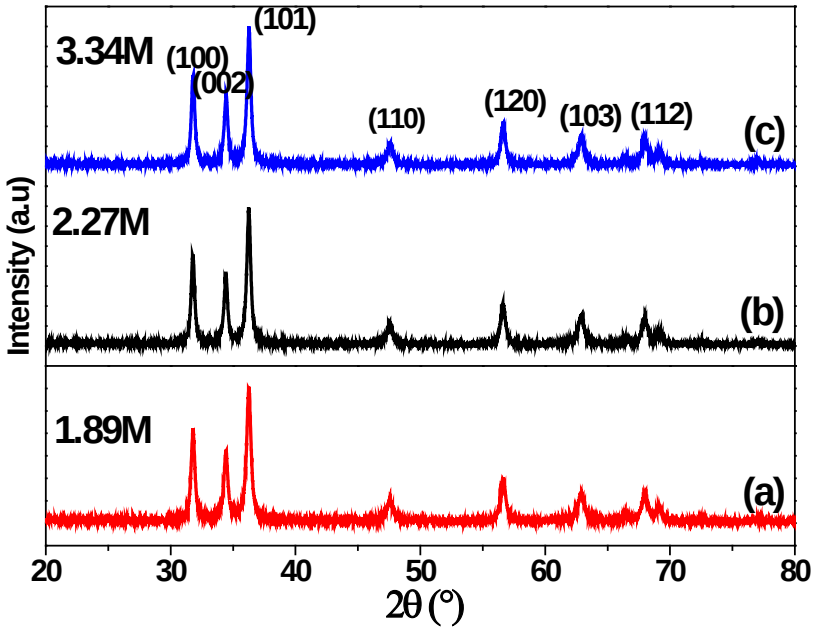

Figure 4.2:XRD patterns of ZnO NPs synthesized by changing concentration at a) 1.89M, b) 2.27M and c) 3.34M

Concentration (1.89M)					
2θ	Θ	hkl	FWHM	Particle size(D)	D (av.)
31.9958	15.9979	100	0.3804	21.72nm	19.23nm
34.4565	17.2282	002	0.3671	22.65nm	
36.3226	18.1613	101	0.4254	19.65nm	
47.6008	23.8004	110	0.5151	16.85nm	
56.8694	28.4347	120	0.4766	18.95nm	
62.939	31.4695	103	0.5762	16.16nm	

68.8605	33.93025	112	0.5139	18.63nm	
Concentration(2.27M)					
31.7088	15.8544	100	0.3284	28.43nm	21.82nm
34.4565	17.2282	002	0.3098	26.84nm	
36.3226	18.1613	101	0.3562	23.47nm	
47.7443	23.8721	110	0.5077	17.11nm	
56.5823	28.2911	120	0.4673	19.30	
62.7956	31.3978	103	0.5421	17.17nm	
68.004	34.002	112	0.4688	20.43nm	
Concentration (3.34M)					
31.8523	15.9261	100	0.3098	26.66nm	23.84nm
34.6001	17.3005	002	0.2825	29.44nm	
36.1790	18.0895	101	0.3451	24.21nm	
47.6008	23.8004	110	0.4337	20.02nm	
56.7259	28.9362	120	0.4156	21.72nm	
62.6520	31.3260	103	0.4805	19.35nm	
68.004	34.002	120	0.4538	25.47nm	

Table 2.3:Angle of diffraction, full width at half maxima and average particle size of Synthesized ZnO NPS by changing concentrations

Concentrations	hkl	Lattice constant			d_{hkl}
		a(nm)	c (nm)	c/a	
1.89 M	101	0.2976	0.4236	1.4233	0.2346
2.27 M	101	0.3159	0.5272	1.795	0.3042
3.34M	101	0.3412	0.6225	1.8244	0.3835

Table 4.4:Lattice parameter and spacing distance of synthesized ZnONPs at different PVA concentrations

Our results are almost similar with the result reported by [43].From this one can conclude the synthesized ZnONPs has hexagonal wurtzite structures.

4.2 SEM Analysis of ZnO NPs

Figure 4.3 (a) & (b) shows the SEM morphology of the synthesized ZnONPs at annealing temperatures of 400℃ and 500℃. It clearly demonstrates that,flower like shapeZnONPs, and the change in the morphology of the nanoparticles were observed annealing temperatures increase. As it is shown in figure, the particle size and size distribution of ZnONPs are increasing with increasing annealing temperature and larger particle sizes with small surface area of NPs are produced[44].

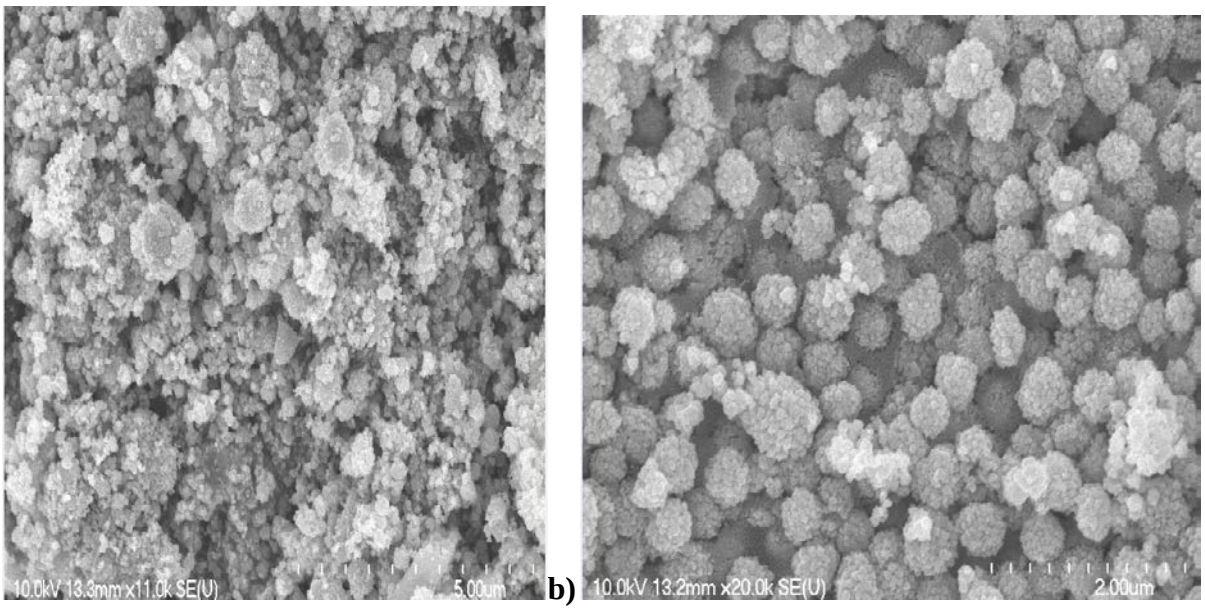

Figure 4.3:Flower shape of Scanning Electron Microscope imagesat a) 400℃ and b) 500℃ of annealing temperatures

4.3 FT-IR Analysis of ZnO NPs

Figure 4.4, shows that the FT-IR spectra of samples measured in the wave number regions of 400-4000cm^{-1}. The sharp peak observed from the wave number regions of 400-600cm^{-1}were attributed to the stretching vibration modes of ZnONPs. The FT-IR peaks observed in the

wavefrom 1200-1600 cm^{-1}regions were corresponding lattice vibrationC = O[45].Similar, the characteristic peaks observed of 2800- 3200cm^{-1}were corresponding to CH_2stretching vibration due to the PVA structure. In addition this, the peaks observed 0f 3200-3600cm^{-1}wereOH stretching vibrations dueto bending modes of water absorber [46].

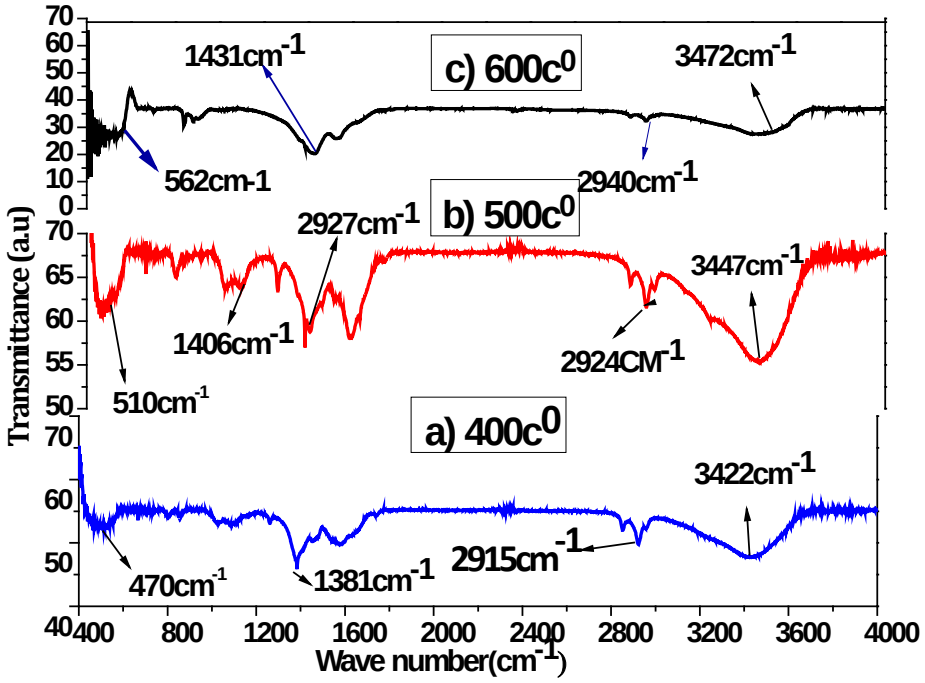

Figure 4.4:FT-IR spectra of synthesized ZnO NPs at different annealing temperatures

Similarly, the FT-IR spectra of measuredZnO NPs by varying the concentrations are shown in figure 4.5 below. From the graph the broad band observed in the region of 3200-3600cm^{-1} are due topresence of hydrogen bond (O–H) vibration. Presence of O-H group represents the presence of water molecules on the surface of ZnO nanoparticles [47].Similarly,the transmission peaks observedin the region of 2800- 3200cm^{-1} are due to C-Hstretching frequency of alkyl groups.The presence of benzene rings in polyvinyl structures was also confirmed with an intense

C–H in the region of 1200-1600cm^{-1}.The peak positioned in the range of 517-553 cm^{-1}were attributed to wurtziteZnO NPs [45]

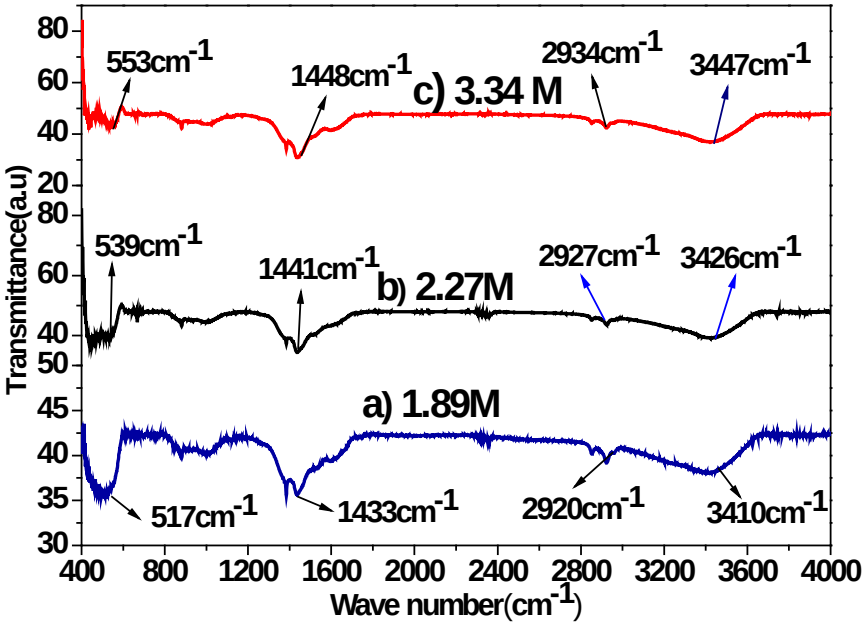

Figure 4.5:FT-IR spectra of synthesized ZnO NPs at 1.89, 2.27 and 3.34M ofConcentration

4.4 UV-Vis Spectroscopy Analysis of ZnONPs

Figure 4.6 shows UV-Vis absorption spectra of preparedZnO NPs at different annealing temperature (400-600℃).The absorption peak was observed in each spectrum at 370nm,377nmand 382nmfor annealing temperatures of 400, 500 and 600℃ respectively. These peaks are optical characteristic bands for the pure ZnONPs [47].The red shift in absorption spectra was observed for the product annealed at different temperatures due to changes in morphologies and particles size.The absorption peaks shifts towards higher wavelength with

increasing temperature. This is due to increase particle size [48]. The band gap energy of ZnO NPs was calculated using Eq. (6) were 3.314 eV, 3.251 eV and 3.176 eV) for 400℃, 500℃ and 600℃respectively. Thus, the bang gaps energy of ZnO NPs weredecrease as increasing temperature [49].

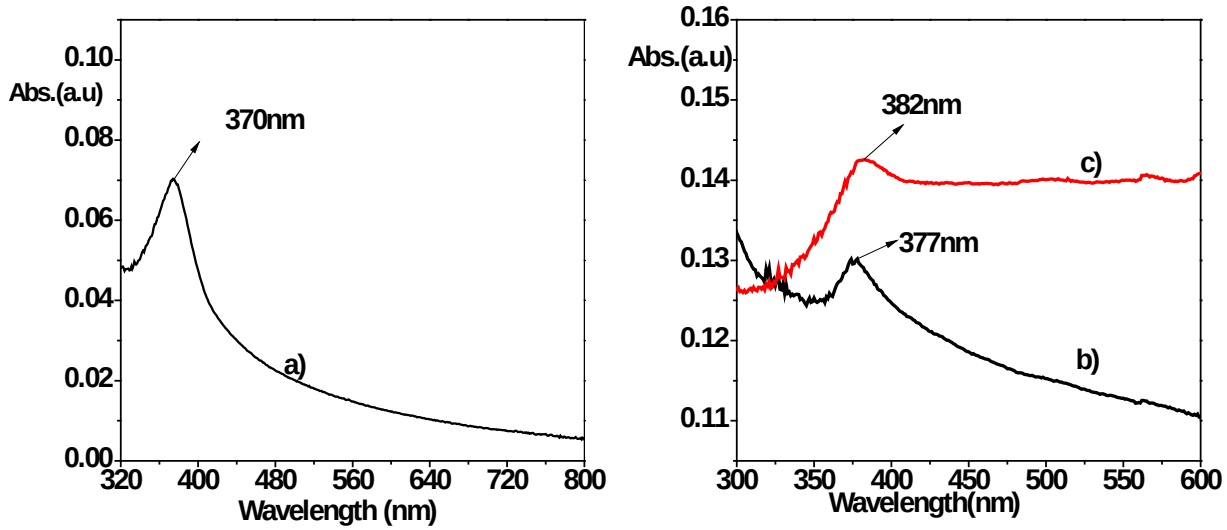

Figure 4.6:UV/vis Spectra of synthesized ZnO NPs at a)**400**℃b)**500**℃and c)**600**℃

Similarly, the absorption spectra of ZnONPs synthesized at different PVA concentrations were shown in the figure 4.7 below. The absorption peak spectra of ZnONPswere observed at 372nm,377nmand 380nmof PVAconcentrations at 1.89 M, 2.27 M and 3.34 M respectively which is attributed to excitonic absorption peak of ZnO NPs. The calculated energy band gaps of ZnO NPs were 3.334eV, 3.322 eV, and 3.214eV for 1.89 M, 2.27 M and 3.34 M respectively. The energy band gaps of ZnO NPs weredecreased as the PVA concentrations increases. The absorption peaks (maximum wavelength) also increase as the concentration increase. Thus,the

red shift spectra of ZnO NPs were observed with in increasingPVA concentrations,were a good agreement with a literature reported by [46].

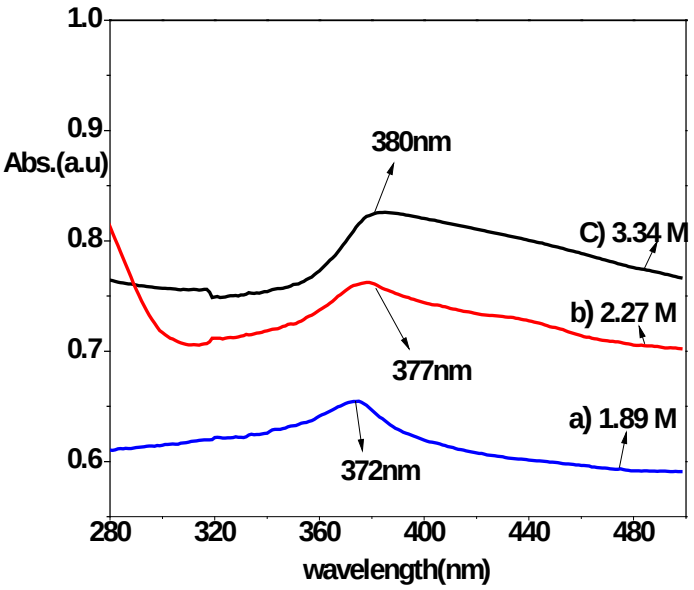

Figure 4.7:UV-Vis Spectra of synthesized ZnO NPs at different concentration

4.5 Emission Spectral Analysis ofZnO NPs

Figure 4.8 shows the emission spectra of synthesized ZnO NPs at annealing temperatures of 400℃, 500℃ and 600℃respectively. The emission spectra of ZnONPs have emission band in the UV and Visible region. The UV peaks are usually considered as characteristic peak emission of ZnO NPs and attributed to band transition.The emission peaks observed at 386 nm, 395 nm and 398 nm for 400℃, 500℃ and 600℃respectively aredue to the transition of electron from conduction band to valance[50]. On the other hand, the emission peaks observed at 465 nm and

467 nm for 400℃ and 500℃ of annealing temperatures respectively were attributed to oxygen vacancy [51].

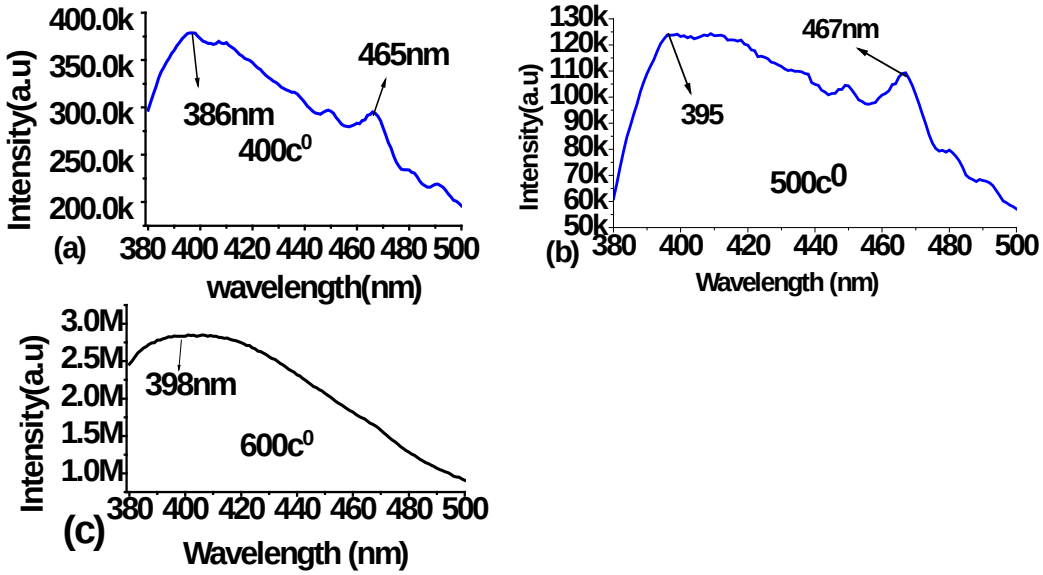

Figure 4.8:Emission spectra of synthesized ZnO NPs ata) 400℃b) 500℃and c) 600℃

Similarly, the fluorescence emission spectra of synthesized ZnO NPs by changing the PVA concentration are shown in the figure 4.9 below. The emission peaks observed at 357 nm, 376 nm and 398 nm for 1.89 M, 2.27 M and 3.37 M in the UV-region respectively were due excitonic emission of ZnO NPs which is the transition from conduction band to valance band [52].Also the emission peaks observed in the visible regions are 412 nm and 467 nm for 2.27 M and 3.34 M respectively was due ionized oxygen vacancies [53].

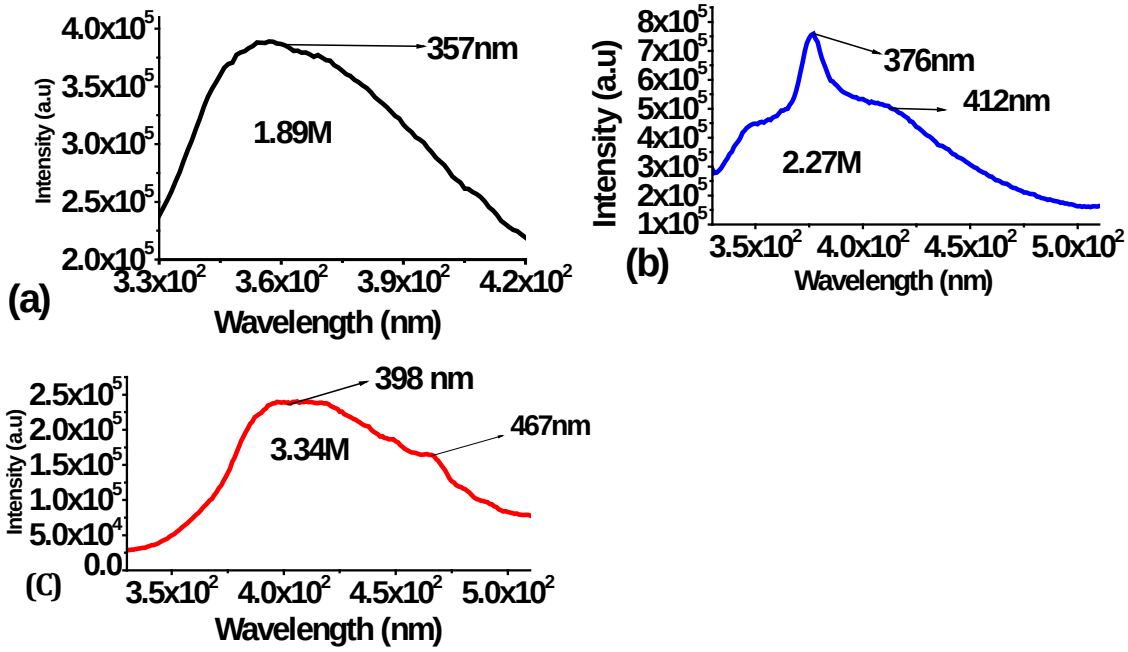

Figure 4.9:Emission spectra of ZnONPs at a) 1.89M, b) 2.27M and c) 3.34M of concentrations

5. Conclusions

Zinc oxide nanoparticles were synthesized via precipitation methods by annealing temperature at 400℃, 500℃ and 600℃and PVA concentrationsfrom 1.89M to 3.34M. The prepared ZnO NPs were characterized by XRD, SEM, FT-IR, UV-Visand Fluorescence Spectroscopy. The XRD and SEM image of ZnO NPs result indicate that, the particle size of ZnO NPs increase as the temperature and PVA concentration increases.Also, the hexagonal wurtzite structure of ZnO NPs was resulted from X-ray diffraction. The FT-IR data showsthe presence of certain functional groups attached to ZnO NPs. The band gaps energy ofZnO NPs were estimate from UV-vis absorption and the absorption peaks shifts towards higher wavelength (red shift) as the temperatures and PVA concentration increases. From emission spectra of ZnO NPs two peaks were observed in ultra-violet and visible region. The transmission of electron from conduction band to valance band results in the peak foundof ultraviolet region and oxygen vacancy in visible region.

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Declaration

I declare that, this thesis is my original work and has not been presented for degree in any other Universities, and that all sources of materials used for thesis work have been dually acknowledged.

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