CHAPTER 2

LITERATURE REVIEW

2.1 Zinc Oxide Synthesis

Among nanomaterials, ZnO is the most significant metal oxides as far as its application perspectives are concerned. So their fabrication procedures and the rules governing their synthesis are also significant. The various parameters used (viz. temperature $^{1-43}$, stirring $^{1-44}$, concentration, time, etc) plays an imperative function in the development of different types of fabrication techniques. A large number of varied methods were reported worldwide for the synthesis of ZnO nano-powder, nano-composites, nano-films, etc. These varied methods upto some extent either evolved or pre-decided to give some sort of useful applications viz. photo-catalytic activities of different dyes, drugs, pesticides, etc; anti-microbial activities against harmful bacterias, protozoans, etc; polymer nanocomposites with characteristic optical, mechanical behaviours, etc; growth on different substrates like thin films finds their uses in devices, solar cells, sensors, electronics/ photonics, semi-conductors, etc; in anti-oxidant studies and so on. The details of more will be discussed in next section $^{45}$.

The well known techniques for the syntheses of different ZnO
Nanoparticles, growths of ZnO on various substrates and the development of ZnO complexes/ composites/ doped structures are generally performed through sol-gel process, hydrothermal process, microwave technique, wet-chemical method, a number of facile / complex novel processes, etc.\(^{46}\)

Considering the growths of ZnO on various substrates, there are different protocols\(^{47}\) of Nanoscaled ZnO growth in the arrangement of Nanostructures or in the arrangement of thin films. The basic criterion for this purpose is the availability of a suitable substrate viz. glass, ITO, Si, p-Si, In, Al, Ga, steel, alumina, CNTs, graphite, quartz, sapphire, (solitary or in combination and so on. In some cases, different catalysts (Au, Ni, Cu, others) and surfactants (CTAB, SDS, etc) are also used to ease the deposition process with some attributed morphology. The various method in the ZnO growth process are differentiated on the basis of different process parameters, reactants, experimental setup, all leading to a set of characteristic morphological growth of Nanoscaled ZnO structures. Some of the prominent techniques for the ZnO Growths are through Chemical Vapor Deposition (CVD,) Chemical Solution Depostion (CSD), Metal-organic Chemical Vapour Deposition (MOCVD), Physical Vapor Depostion (PVD), Pulsed Laser Deposition (PLD), Magnetron Sputtering (MS), Sol-Gel Process, Spray Pyrolysis, etc.

As far as the development of ZnO complexes/ composites/ doped structures are concerned; in common, several fabricated ZnO products are associated with different organic/inorganic elements or their compounds or alloys; with various biological/inorganic polymers and different metals or its compounds are used as dopants. For this purpose, the techniques used to fabricate the ZnO complexes/ composites/ doped structures are almost same, as used in the development of ZnO Nanoparticles and in the growth
techniques of ZnO on various substrates. The different elements/polymers used are Li, Al (AZO), Au, Ag, Cu, Pt, Fe, In, Ni; TiO$_2$, CaCO$_3$, Fe$_2$O$_3$; Polymethyl methacrylate (PMMA), Polyaniline (PANI), Polystyrene (PS), Polypropylene (PP), Poly(butanediolmonoacrylate) (PBDMA), Poly(styrene butylacrylate), Poly(vinyl pyrrolidone) (PVP), poly(3-hexylthiophene) (P3HT), nylon-6, etc. The outcome of these developments of ZnO complexes/composites/doped structures results into the improvements in properties and application perspectives.$^{48,49}$

In this section, the various techniques accountable for giving rise to diverse forms of 1D, 2D, 3D morphologies; growths; assemblies; properties and applications are concise reviewed in terms of synthesis of ZnO Nanoparticles.

The syntheses of ZnO crystallites of different morphologies, orientations, shapes, sizes, etc are further decided by the basic parameter (viz. reaction temperature, type of solvent, temperature, etc) opted to fabricate them. This may further leads to their different efficiencies in various applications. The huge diversity of ZnO Nanoparticle syntheses could be divided into significant categories, as mentioned below:

2.1.1 ZnO Nanoparticles synthesis by Sol-Gel route

It is a well known route used by scientists worldwide for syntheses, as far as ZnO Nanoparticles are concerned.$^{8,20,50-56}$ In the characteristic sol-gel method, the development of colloidal solution in the form of ‘SOL’ and their transformation into aqueous alkaline/acidic phase as ‘GEL’ takes place. This transformation is an important step in the development of particle formation, which is responsible for its vast tendency of various properties metamorphosized at nano-
level. The different types of precursors, capping agents are used along with the presence of acidic or basic ion-carriers following with hydrolysis, stirring, condensation, etc during the process.

Figure 2.1  Sol - Gel Process

Nipane et al. obtained the ZnO-Nps of size about 50-100 nm. The spherical-flower shaped ZnO-Nps also exhibited admirable UV shielding and transparency properties \(^5\). Chen et al. produced blue-emitting ZnO Nanoparticles by sol-gel process at the optimal annealing temperature and time of about 100 °C and 0.5 h, respectively.
Figure 2.2  ZnO Nanostructures (ZnO-Ns) synthesized through Sol - Gel route
They claimed the hexagonal wurtzite structure with diameter range from 17.42 to 25.8 nm\textsuperscript{52}.

A. Sharma et al. synthesized the ZnO Nanoparticle via sol-gel route and also reported the effect of surface groups on the luminescence property of the synthesized ZnO-Nps\textsuperscript{8}. Liu et al. developed the size controlled ZnO quantum dots (QD) using sol-gel technique by means of photo-induced desorption\textsuperscript{55}. A. Erol et al. synthesized ZnO-Nps of diameter 10 nm and investigated the humidity adsorption and desorption kinetics by quartz crystal microbalance technique (QCMT)\textsuperscript{20}. Tokumoto et al. studied the chemical and structural behaviour of ZnO powders synthesized from ZAD via sol-gel route and highlighted the dependency of temperature and nature of catalyst used in the hydrolysis step of the process\textsuperscript{50}. Cheetham et al. reviewed the use of the in-situ methods for studying the materials syntheses from sol-gel precursors and he emphasized on the formation of the crystalline phases from solid gel precursors\textsuperscript{53}.

2.1.2 ZnO Nanoparticles synthesis by Hydrothermal route

In the characteristic hydrothermal method, the growth of crystallites occurs at high temperatures and at high pressures, performed in the presence of autoclaves\textsuperscript{11,39,57-65}. The different works related to ZnO Nanoparticles syntheses via hydrothermal route, performed by different groups worldwide are reviewed in brief as:
Figure 2.3  ZnO Nanostructures (ZnO-Ns) synthesized through Hydrothermal route
L. Sun et al. reported the facile hydrothermal synthesis of ZnO structures with diverse morphologies viz. flower-like, hexagonal sphere-like, oblate-like, and hexagonal bipyramid-like. They found this as a result of the change in molar ratios of the reactants and the surfactant, TEA used in an alkaline environment of reactions. They have also reported an enhancement in the photocatalytic behaviour to the synthesized ZnO structures against the dye, methylene blue (MB) \(^{11}\). Y. Sun et al. presented the series of ZnO three-dimensional (3D) structures with star-like, sphere-like, flower-like and sea urchin-like morphologies via hydrothermal route, in the absence of catalyst/template. They reported the ZnO 3D structures with strong emission peak at 405 nm and also a high sensitivity and selectivity for ethanol \(^{57}\). R. Yi et al. also synthesized flower-like ZnO microstructures with an average diameter of 1µm via hydrothermal route. They investigated the effect of hydrothermal temperature, reaction time, concentration of NaOH and TEA on morphology and size of the final products \(^{65}\).

### 2.1.3 ZnO Nanoparticles synthesis by Microwave assisted route

Since three decades, the microwave-assisted techniques have gained a significant interest in the field of Nanotechnology as far as Inorganic compounds including oxide syntheses are concerned. Without any sophistication, along with minimum power consumption, the desired products at good rates and at enhanced proportions. This all leads to a superior impact over different characteristic qualities of the developed nanostructures \(^{66-75}\).
Figure 2.4  ZnO Nanostructures synthesized through Microwave Technique
The different works related to ZnO Nanoparticles syntheses by microwave route, performed by different groups worldwide are presented as: Bilecka et al. presented the microwave-assisted synthesis of ZnO Nanoparticles from zinc acetate and benzoyl alcohol. They also presented the kinetics and thermodynamical aspects of ZnO synthesis along with the comparison of microwave route and the conventional heating and reported the performance level of prior one accelerated 69.

Zhu et al. reported various hierarchical nanostructures of ZnO via microwave-assisted route. The various ZnO nanostructures accounted were straw-bundle-like, wide chrysanthemum-like, and oat-arista-like morphologies and microspheres 73. Cho et al. exhibited the morphology-controlled growth of ZnO nano- and microstructures via microwave irradiation. The structures including nano-rods, nano-candles, nano-needles, nano-disks, nano-nuts, micro-stars, micro-UFOs, and micro-balls of Zinc oxide were synthesized at 90°C and about 50 W microwave heating along with subsequent aging process 66.

2.1.4 ZnO Nanoparticles synthesis by Sonochemical method

The Sonochemical technology has gained significant attention in the syntheses of different compounds in material sciences. It involves the extreme/varying temperature and pressure ranges of ~5000 K and ~1000 atm respectively.
Its peculiarity is due to its characteristic mechanism related to effects of acoustic cavitation (formation, growth and implosive collapse of liquid bubbles) leading to a featured growth in nanostructures. The different works related to ZnO Nanoparticles syntheses via sonochemical technology, performed by some groups as:

Zak et al. fabricated ZnO Nanostructures via sonochemical method by applying the ultra-sonication duration from 5 – 6 minutes. They reported the ZnO nanorods of diameter 50 nm (ultra-sonication duration – 15 minutes) and flowerlike ZnO Nanostructures (ultra-sonication duration - 30 minutes). Wahab et al. synthesized nano-
needles of ZnO via sonochemical technique and reported ‘sonication time’ as an important parameter for the shape determination \(^{82}\).
2.1.5 ZnO Nanoparticles synthesis by Different routes

Besides, some of the significant techniques reviewed before; there are still a number of different processes. Wahab et al. presented the fabrication of ZnO micro-flowers processed via solution method and investigated their anti-bacterial activity. Wen et al. investigated the growth of ZnO Nanostructures by solvothermal process and with different morphologies viz. nano-wires, nano-rods, nano-corns, nano-shuttles, nano-worms and nano-flowers is presented. They presented the dependence of growth process for the change in morphology of the Nanostructures. Wahab et al. prepared the ZnO Nanoparticles (ZnO-NPs) via non-hydrolytic solution route using ZAD and Aniline under refluxing for 6 hours and at ~65 °C. They have also investigated the anti-bacterial activity of the fabricated ZnO-NPs against four pathogens namely Staphylococcus aureus, Escherichia coli, Salmonella typhimurium, and Klebsiella pneumonia. Zhu et al. employed the ionothermal process to synthesize the ZnO hierarchical Nanostructures with different morphologies. The characteristic feature for this synthesis was the utilization of metal-containing ionic liquids that performed as solvent as well as metal precursors. They presented the dependency of ZnO morphologies over the nature of corresponding ionic-liquid precursors. Damonte et al. presented the structural & optical characterization of ZnO Nanocrystalline powders (with grain size less than 20 nm) obtained via mechanical milling process. In addition to all these procedures, there are plentiful studies by different labs, various collaborators of divergent fields and many individual scientists, all in common,
Figure 2.7  ZnO Nanostructures (ZnO-Ns) synthesized through Different routes
presented a large range of tailored ZnO Nanostructure morphologies, properties and application. The extensive efforts are the outcomes of ZnO Nanostructures growing demand in many new domains for its usages. Furthermore, there is still room with abundant space for thinking out of the box, down the line as far as ZnO robustness is concerned.

2.2 ZINC OXIDE PROPERTIES

Since more than a decade, the need to explore novel applications of ZnO at nanoscale have emerged into acquiring new trends of its properties resulting on behalf of diverse techniques used to fabricate ZnO Nanostructures, Thin films, Composites, etc, as these fabrications are further accountable for the development of devices (based on opto-electronics, piezoelectrics, spintronics, biological, chemical, others); sensors; displays; Blue/UV-emitters; switches; detectors; solar cells; etc.

The numerous facile trends of Nanoscaled ZnO properties covers Zinc oxide chemical\textsuperscript{97}, dielectric \textsuperscript{7,98-100}, electrical \textsuperscript{9,97,101-115}, magnetic \textsuperscript{97,107}, mechanical \textsuperscript{97,116-131}, optical \textsuperscript{3,8,99,59,132-163}, piezoelectric \textsuperscript{164-173}, structural \textsuperscript{7,9,174-180}, thermal properties \textsuperscript{107}, etc. Only some of the basic properties of Zinc Oxide have been reviewed as:

2.2.1 Optical Property

The inherent optical properties of bulk Zinc oxide and its counterpart, the nano-scaled ZnO produced as a result of quantum sized confinement, has been reported by various groups worldwide \textsuperscript{3,132-163}.

The facile studies have been utilized for different optical or photonic applications. S. Xu and Z. L. Wang \textsuperscript{156} reviewed various
aspects of 1D ZnO nanostructures prepared by wet chemical approach, as they are environmentally friendly and with sound optical properties with various applications in novel devices.

Figure 2.8 FE-SEM, PL and Optical Transmittance of ZnO films with thicknesses: (a) 14.2 nm, (b) 20.7 nm, (c) 42.7 nm, (d) 51.4 nm and (e) 62.7 nm

S. S. Shariffudin et al. reported optical properties dependency on different thicknesses of fabricated ZnO films. They found that the UV emission intensity of photoluminescence spectra decreases on increasing the film thickness. A. Sharma et al. recorded the photoluminescence spectra of ZnO nanoparticles synthesized via sol-gel route at normal room temperature. They showed that some chemical entities (plausibly hydroxyl groups), adsorbed physically on nanoparticles surfaces, are liable for green luminescence peaks blue shift towards 2.35 eV under vacuum conditions as compared to
atmospheric conditions. S. Kant et al. prepared Ni doped ZnO as Zn1-xNixO (x=0, 0.5), which reported the shifting of absorption from UV region, hence claiming the increase in absorption towards visible region, on doping.

W. Bousslama et al. reported the formation of single phase ZnO nanoparticles through sol-gel route with superior UV emission and quenched green emission, hence conforming the nanoparticles with has been observed which confirms that the synthesized ZnO nanoparticles have fine optical properties with few defects.

2.2.2 Mechanical Property

From previous studies, it has been proved that the materials like Zinc oxide has a bulk hardness (H) of about 5.0±0.1 GPa and a bulk Young’s modulus (E) of about 111.2±4.7 GPa. Some others characteristics of ZnO are found to be as good heat capacity and heat conductivity, poor thermal expansion with high melting points. S. O. Kucheyev et. al. studied that on using a 4.2μm indenter tip, a c-axis oriented ZnO has been created where the maximum load was 15mN and extensive damage was reported in the region directly under the indent. This study was of importance when designing and fabrication of ZnO-based nano-devices were carried out.

Bradby et al. studied Nano-indentation of ZnO with a spherical indenter of radius about 4.2μm. This study was meant for probing the mechanical properties of materials used for fabrication of devices as indentation leads in the quenching of the excitonic luminescence. One of the useful concept as far as the mechanically utilized semi-conductor ZnO is concerned is piezoelectricity, where the
mechanical energy is converted to the electrical energy with the help of the fabricated devices.

However, in case of nano-devices, the measurement of mechanical performance was not same as that for bulk samples. Bai et al. performed the experiment where they characterized the bending modulus of ZnO nanobelts using TEM holder, which was responsible for an electric field between ZnO belt and an electrode. This field in turn vibrated the nanobelt and with the help of classical elasticity theory, bending modulus was calculated. Based on this study, ZnO nanobelts became an important material as nano-resonator and nano-cantilever\textsuperscript{116}.

H. D. Espinosa et al.\textsuperscript{130} reviewed the piezoelectric Nanowires (viz. ZnO and GaN) with respect of mechanical and electrochemical properties. The different methods used in mechanical characterizations of 1D ZnO Nanostructures are MEMS in situ SEM/TEM, AFM cantilever in-situ SEM/TEM, etc. They have studied that the size influence on ZnO Nanowires modulus of elasticity, in direction of [0001] as increases with decrease in diameter (below 100 nanometers). They concluded that the rate-dependent mechanical properties of nano-ZnO are potential areas where further research holds good scope.

K. Eom et al.\textsuperscript{128} reviewed that many groups worldwide worked out Nanomaterial base NEMS (nano electro-mechanical systems) leading to structures like Nanowires, Nanotubes, etc through which experimental validation is possible by various modeling and simulation techniques.
2.2.3 Piezoelectric Property

The piezoelectricity is a unique property of ZnO which has been widely used in applications like surface and bulk acoustic wave devices, optic modulators, force-sensors, etc. Many works exploited this concept of configuration of bonding between Zn and O atoms, which is responsible for this unique property.\textsuperscript{161}
By executing external force on ZnO materials, the displacement of their crystal charges results into the development of a huge Dipole moment, throughout the material (Figure 2.10).

Different groups exploited this concept in the development of various novel nano-devices. Wang et al.\textsuperscript{162} presented the fabrication of 1D ZnO nanowire arrays, with an attempt at building of nano-generators for getting electrical energy from mechanical efforts. Y.-Y. Cheng et al.\textsuperscript{167} developed a piezolelectric nano-generator constituted of ZnO nanorod array electrode with an Au coated films, behaving as another electrode. By executing rolling efforts on upper electrode of the nano-device, an optimal current density of 11nA/cm\textsuperscript{2} has been generated.
Figure 2.11 (a) Schematic diagram of Piezoelectric nano-device with ZnO nanorods; Output parameter generated by piezoelectric nanogenerators with ZnO nanorods: (b) Current density of piezoelectric nano-device; (c) Output voltage \( (V \propto) \) of piezoelectric nano-device 167

2.2.4 Electrical Property

The concept of electrical properties of semi-conductor like ZnO can be utilized in the phenomenon and applications of nanoelectronics and opto-electronics. The different morphologies of ZnO Nanostructures are responsible for a charge flow, with the help of proper design and fabrication of the Nanostructures and these ZnO Nanostructures with the arrangement of FET (Field Electron Transistor) are made to behave as electrodes, in order to measure the values 97,106.
The defects of ZnO produced due to oxygen and zinc, are accountable for the n-type behaviour of ZnO Nanostructures like nano-rods and nano-wires. Though ZnO already has a large band gap of about 3.3 eV (at room temperature), and further development of p-type ZnO leads to the applications of p-n junction diodes and LEDs’, etc.

K. Eom et al. reviewed that many groups and labs worldwide worked out Nanomaterial base NEMS (nano electro-mechanical systems) leading to structures like Nanowires, Nanotubes, etc through which experimental validation is possible by various modeling and simulation techniques. M. Girtan et al. produced In-doped ZnO thin films for their applications in solar cells. They investigated that the electrical conductivity stability of developed films at different heating and cooling cycles were influenced by the presence of oxygen and the oxygen absorption/desorption processes are of reversible nature.

S. S. Shariffudin et al. reported electrical properties dependency on different thicknesses of fabricated ZnO films. The I-V curve of the thin films in ambient light and voltage supply from -10V to 10V was measured where resistivity is plotted as function of films’ thickness. They found two deviations. For films >50 nm thickness, the increased grain sizes contributed to the enhancement of carrier mobility resulting into the decrease in resistivity and for films <50 nm thickness, due to porous thin films, an enhancement of trapped carriers in grain boundary resulted increase in thin films resistivity.
Figure 2.12 I-V values of ZnO films with thicknesses: (a) 14.2 nm, (b) 20.7 nm, (c) 42.7 nm, (d) 51.4 nm, and (e) 62.7 nm.

F Li et al. produced transparent CNT/Ag/AZO conductive films and reported that these multilayer AZO films have potential usage in optoelectronic devices. L. P. Shen et al. fabricated ZnO-insulated oil nanofluid. They reported that electrical conductivity have increased approximately thousand times when 0.75% volumetric portion of ZnO nanoparticles (synthesized by solvothermal technique) was added into the insulated oil.

K. Maejima et al. developed AZO layer by controlling c-axis orientation with the help of ZnO (undoped) buffer layer. The c-axis orientation alignment was controlled in achieving the improvement in electrical properties of the developed AZO layers.
2.3 **Nanoscaled Zinc Oxide Characterization**

One of most essential measure after the fabrication of ZnO Nanostructures, is their correlation, with the help of prominent techniques and instrumentations used for characterization of these structures followed by their analysis based on the robust literature review performed before. The general characterization techniques which have been employed in this study to investigate the crystallite sizes, morphologies, structures and optical, thermal properties, etc of the ZnO nanostructures mentioned in subsequent chapters are as:
2.3.1 X-Ray Diffractometer (XRD)

The X-ray diffraction\textsuperscript{177,178} of prepared ZnO nanostructures were done with the help of an X-ray diffractometer (Figure 2.14), BRUKER AXS D8 ADVANCE (Germany) using X-ray beam with nickel filtered CuK\textalpha radiations of wavelength equal to 1.54 Å and with a step dimension of 0.01° and scanning speed of 0.02 steps/second. A fixed power generation of 40 kV and 40 mA was used.

The nanoparticulate sizes were further calculated with the help of spectral peaks by Debye-Scherer formula\textsuperscript{253,254}:

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

where,

- \(D\) = Crystallite size
- \(k\) = proportionality constant (0.9)
- \(\lambda\) = X-ray wavelength (1.54178 Å)
- \(\beta\) = FWHM of XRD peaks
- \(\theta\) = Braggs’ angle

The calculation further become simple by the integrated software, Diffrac\textsuperscript{plus}.
2.3.2 Scanning Electron Microscope with Energy Dispersive Spectroscopy (SEM with EDS)

The investigation of the surface morphology, dimensional characteristics of Zinc Oxide nanostructures have been done with the help of non-destructive instrument called Scanning electron Microscope. It also provides the details of crystal structures of the developed Nanostructures. Here the scanning of samples is performed in the presence of high-energy electron beam and magnification power (upto 5 lakhs times) is monitored by variation of V-I supply. We can also study the different parameters of the sample overheaded on the sample holder viz. lengths, widths, forms, orientations, etc of the single crystals or of the colonies. The samples were made more viable when coated with gold sputtering. The different morphological aspects were recorded with the help of Scanning electron microscopy, JEOL JSM-6510 LV (Japan) shown in (Figure 2.15).

The chemical stoichiometries of the ZnO nanostructures have been investigated with the help of Energy dispersive X-ray spectroscopy. The EDS of Oxford was working in an inbuilt attachment with SEM. The samples were made more viable when coated with gold sputtering. The SEM images of the sample as well as the EDS graphs were exposed in the Chapter 3 and 4 respectively.
2.3.3 Transmission Electron Microscope (TEM)

The morphological characteristics and the size of the particle of the fabricated Zinc oxide nanostructure were studied with the help of Transmission Electron Microscope (TEM) with model no. JEOL JEM-2100 (Japan), featuring ultra high resolution and rapid data acquisition (Figure 2.16). The instrument was well operational with high energy electrons of 200kV class analytical TEM with a probe size under 0.5 nm. The goniometer stage gives ease of use in tilting, rotating, heating and cooling. This analytical machine has also been equipped with STEM, MDS, EELS and CCD cameras, magnetic lenses which could provide better magnification of images at nano-levels. The scattered electrons give a characteristic diffraction pattern of the Nanostructure samples, which helps in analysing their crystal structure.\(^3\)

2.3.4 Fourier Transform Infrared spectrometer (FT-IR)

The Fourier transform infrared spectra were taken with the help of model Thermo Scientific Nicolet iS 10 spectrometer as shown in (Figure 2.17). The FT-IR spectra are collected after the absorption of electromagnetic waves with the frequency range from 400 to 4000 cm\(^{-1}\). The FT-IR spectrometer gathers the spectral information of a broad spectral region.\(^{180}\)

The identification of various functional groups and chemical structures in the nanoscaled ZnO is made possible by absorption of electromagnetic waves at distinctive frequencies & intensities. Hence the different groups and structures show a typical characteristic band arrangement and geometry for ZnO nanostructures.
2.3.5 Photoluminescence Spectrofluorophotometer (PL)

The non-destructive, room temperature photoluminescence (PL) spectral study of nanoscaled Zinc oxide is performed with the help of SHIMADZU Photoluminescence spectrofluoro photometer having model no. RF 5301pc (Figure 2.18) \(^{181}\).

The photoluminescence (PL) study is carried out by using a light source 150W Xenon lamp with the operation temperature range of 15-35°C, humidity range of 40-80% (below 70% with temperature higher than 30°C) and the wavelength range of 220-900nm. The PL spectral study is extensively employed for the determination of different materials properties viz. material bandgap, defects, etc. Here, the study performed to get the PL details of Zinc oxide nanostructure synthesized at different parametric conditions.

2.3.6 UV-VIS spectrophotometer (UV-vis)

The UV-visible absorption spectroscopy was performed by double beam PERKIN-ELMER SPECTOPHOTOMETER and SHIMADZU (UV-3600) shown in (Figure 2.19).

In the basic principle, a beam of visible/UV light source, segregated into its constituent ‘wavelengths’ by diffraction grating. Further, each single beam splits into two equivalent intensity beams. The intensity of prior beam passes through the sample placed in cuvette (I) and latter beam passes through the reference solvent in another cuvette for background correction (I\(_0\)), are monitored and evaluated. The DD water was used as a reference for background correction \(^{182}\).
The *ultra-violet (UV)* and *visible* comprises the regions ‘200 to 400 nm’ & ‘400 to 800 nm’ respectively.

### 2.7 Thermogravimetric, Differential Scanning Calorimetry analyzer (TG-DTA & DSC)

The thermogravimetric & differential scanning calorimetry analyzer (SDT Q-600 TA Instruments) as shown in (Figure 2.20), was used to study the thermal stability of nanoscaled Zinc oxide structures, prepared at different parametric conditions.

The SDT Q600 provides concurrent calculation of weight change (TG-DTA) and differential heat flow (DSC) on the same sample with the heating rate of 0.1 to 25°C/min from ambient upto 1,500 °C and DTA sensitivity of about 0.001°C.

Around 5 mg of the samples were heated. The heating was carried out at the rate of 20°C/min upto 900°C. In the thermogravimetric & differential scanning calorimetry (TG-DTA & DSC) analysis, different exothermic peaks have been reported. Based upon the resulting thermogram the conclusions have been drawn over the presence of amorphous oxide compounds.
Figure 2.14  XRD
Figure 2.15 SEM with EDS

Figure 2.16 TEM
Figure 2.17  FT-IR

Figure 2.18  PL Spectrophotometer
Figure 2.19  UV-Vis Spectrophotometer

Figure 2.20  TG-DTA & DSC
2.4 Applications of Zinc Oxide Nanostructures

Among nanomaterials, ZnO is the most significant metal oxides as far as its application perspectives are concerned. So their fabrication procedures and the rules governing their synthesis are also significant. The various parameters used (viz. temperature, concentration, time, etc) plays an imperative function in the development of different types of fabrication techniques. A large number of varied methods were reported worldwide for the synthesis of ZnO nano-powder, nano-composites, nano-films, etc. These varied methods upto some extent either evolved or pre-decided to give some sort of useful applications viz. photo-catalytic activities of different dyes, drugs, surfactants, pesticides, herbicides, etc; anti-microbial activities against harmful bacterias, protozoans, etc; polymer nanocomposites with characteristic optical, mechanical behaviours, etc; growth on different substrates like thin films finds their uses in devices, solar cells, sensors, electronics/ photonics, semi-conductors, etc; in anti-oxidant studies and so on. The details of few have been presented below as:

2.4.1 ZnO for Photocatalytic Activity

With the emergence of industrialization, technological advancements and different techniques used for agricultural productivity may directly or indirectly leading to cause harmful results in the environment. The different types of dangerous compounds eluting from the drugs, dyes, surfactants (used in shampoos, insects, etc.), pharmaceutical and many other chemical/gas industries; insecticide, fungicides, herbicides, etc from agri-practices; all may resulting into the huge contamination of water bodies, soil, air, etc.

Hence, for the sake of mankind, flora and fauna, it is necessary
that all the harmful and poisonous contaminants going into different water bodies (viz. surface water, underground water, etc), could be checked and sound initiatives should be taken to purify the different water resources, used for the betterment of life.

To check the growing percentage of these pollutants in water is a crucial measure to safeguard the environmental wellbeing. For this purpose, suitable techniques for the degradation of contamination of various water bodies, especially water necessary for drinking and household use and also to maintain the large aquatic life; are essential. For the same purpose, the researchers are attempted to present a cheap and facile technique, since decades and the demand is growing time to time to develop an efficient treatment facility. And many countries have gained a good success in this direction.

The treatment of these contaminated water bodies could be achieved through Phocatalytic Degradation technique as it is performed at ambient temperature and pressure conditions and is also cost effective. For this purpose, the metallic semi-conductor oxides (viz. ZnO, TiO₂, their composites, etc) are in use since decades. However, the various materials used for the purpose of heterogeneous photocatalysis are GaP, SiC, Fe₂O₃, WO₃, SnO₂, etc. Moreover, due to many reasons like cost, availability, enhanced results; ZnO Nanostructures and their composites are gaining a wide attention and has been proved to be a good photocatalyst for various dyes, drugs, chemicals, heavy metal ions, etc.

‘Photocatalysis’ means the use of photon energy in the catalytic reactions (like photosynthesis in plants). Since few years,
photocatalytic processes involving semiconductor ZnO Nanostructures under UV light illumination have been shown to be potentially beneficial and helpful in the treatment of various hazardous pollutants. Different studies have proved this with different pollutants like dyes, drugs, surfactants, pesticides, herbicides, insecticides and fungicides that can be completely mineralized in the presence of ZnO Nanostructures 16,18,67,92,185-203.

Figure 2.21 Photocatalytic Degradation from ZnO Nanostructures

As far as the mechanism of photo-catalytic degradation is concerned, it is comparable with the mechanism of chlorophyll in photosynthesis. On the exposure of light/photon energy (where $h\nu > 3.2$ eV) on the ZnO Nanostructures; free electrons ($e^-$) find its position at Conduction state, leaving behind holes ($h^+$) at the Valence state, as shown in the (Figure 2.21). These further leads to the
oxidation-reduction reactions between the pollutants and ZnO Nanostructures, both present in the water solution and hence the photo-catalysis of pollutants (viz. drug, dye, surfactant, etc) occurs.

Figure 2.22  Experimental setup diagram of Photo-catalytic Degradation

\[
\text{ZnO}_{(N_4)} + \text{hv} \rightarrow e^- + h^+ \quad \text{Eq. (2.2)}
\]

\[
\text{O}_2 + e^- \rightarrow \text{O}_2^- \quad \text{Eq. (2.3)}
\]

\[
\text{H}_2\text{O} + h^+ \rightarrow \text{OH} + \text{H}^+ \quad \text{Eq. (2.4)}
\]

It is the oxidation reactions which are responsible for the photo-catalytic degradation of harmful drugs, dyes, etc. Both the free electrons (e^-) as well as the free holes (h^+), interact with Oxygen and Water molecules, to form radicals of superoxides’ and hydroxyl groups respectively.
2.4.2 ZnO for Anti-Microbial Activity

Due to diversified uses of Metal Oxide Nanoparticles (MONPs) in research, industrial and health related applications, metal oxide nanoparticles are increasingly being developed through inexpensive and user friendly approaches. Hence, in other words, the effect of MONPs with the pathogenic microbes is an evolving field of research. Out of these, Zinc oxide Nanoparticles (ZnO-Nps) are useful as antimicrobial agents against microbes of therapeutic significance when blended with medicines, ointments and personal care products. Due to specific compatibility towards both aqueous and organic solvents, ZnO-Nps are allowing for incorporation into most material processes, therefore, ZnO-Nps are also considered as bacteriostatic and fungistatic against microbes of industrial importance when included into materials, such as surface coatings (paints), wallpapers, textile fibers, plastics and ceramics. The advertisements seen by us for antibacterial refrigerators and bathroom tiles are some of the best examples. There are several examples of highly significant antimicrobial activity of ZnO-Nps against medically and industrially important Gram-positive and Gram-negative bacteria, ascomycetes and protozoans.

The antimicrobial potentiality of ZnO-Nps against different disease causing pathogenic microbial strains has been already evaluated using qualitative and quantitative assays. The applications of ZnO-Nps for *Staphylococcus aureus* (cellulitis), *Salmonella typhimurium* (typhoid fever), *Candida albicans* (candidiasis), *Listeria monocytogenes* (septicaemia), *Campylobacter jejuni* (Guillain-Barré syndrome) and *Pseudomonas aeruginosa*
(bacteremia) are well documented. Besides, ZnO-Nps could potentially be used as an effective antimicrobial agent to protect agricultural and food safety from foodborne pathogens especially Bacillus subtilis, Escherichia coli, Pseudomonas fluorescens, Salmonella enteritidis and Botrytis cinerea, Penicillium expansum by disintegrating the cell membrane and increasing the membrane permeability and oxidative stress to lyse these food-borne bacteria. These points suggested that the application of ZnO-Nps as antimicrobial agents in medicine and food systems may be effective for microbial growth inhibition.

Plausibly, the antibacterial activity of ZnO-Nps is dependent on its size, morphology and architecture of nanoparticulate. The enhanced surface area of ZnO-Nps allows for increased interaction with microbes which permits using a smaller amount of ZnO-Nps for the same or improved biostatic behavior. Moreover, the microbicidal property of these nanoparticles suggested that these particles were more diffusible in the growth medium which in turn allowed greater interaction between microbial cells and nanoparticle. From the previous reports, it is considered that ZnO-Nps cell surface interaction affects the cell morphology as well as cell membrane permeability, consequently the entry of ZnO-Nps induces oxidative stress in bacterial cells resulting in the inhibition of cell growth and eventually cell death.
All of the above information regarding ZnO-Nps suggests that these nanoparticulates have a potential application as a pathogen growth inhibitor and may have future applications in the development of derivative agents to control the spread and infection of a variety of microbial strains.

2.4.3 ZnO as Sensors

There are diversified range of shapes and morphologies of ZnO Nanostructures tailored by optimizing different reaction parameters. These nanostructures could be exploited in various applications. The different properties and morphologies could further be enhanced by the effect of doping on these ZnO nanostructures eg. doped ZnO nano-belts, etc.
As sensors, various forms of fabricated ZnO are used i.e. ZnO single crystals, ZnO pellets, ZnO ThF & TF, etc \(^{230,231}\).

In the field of BS, the various ZnO sensors concerned with living systems have come into existence viz. pH sensors, cholesterol sensors, glucose sensors, etc \(^{232-234}\). With the help of dopants, the efficiency of ZnO-Ns have been increased \(^{235-236}\).

Few applications based on ZnO Nanostructures working as bio-sensors (BS) and chemo-sensors (CS) has been put forth as:

### 2.4.3.1 Bio-Sensors (BS)

A biosensor is a device which converts the physio-chemical properties of enzymes, receptors, micro-organisms, etc; into different kinds of signals \(^{237}\).

Biosensors are of different types viz. electro-chemical, thermal, piezoelectric, optical, etc. The Glucose Biosensors based on ZnO are used in different applications for clinical, biological and chemical examinations. In the majority of glucose biosensors, the concentration of Glucose is determined with the help of Glucose Oxidase, GOD (an enzyme), where ZnO is grown by various techniques like Vapor phase transport, Vapor - liquid solid, Thermal evaporation, Hydrothermal Decomposition, Wet Chemical route, etc. The different techniques results in various types of ZnO-Ns viz. Nc, Nr, Nps, etc \(^{238,239}\).
The biosensors based of ZnO Nr with biotin have found to be highly sensitive for detection of biological molecules \(^{240}\). An alternative for ZnO nanowires was developed as ZnO nano-flakes; which were grown on the tip of Al-coated glass capillary and applied as intracellular glucose biosensor (Figure 2.24) \(^{242}\).

The ZnO biosensors are used to detect the DNA sequence of the harmful agent, *Bacillus anthracis* by successfully selecting its DNA sequence from other genetically related species \(^{241}\).
2.4.3.1 Chemo-Sensors (CS)

A Chemical sensor is a transducer which provides direct information about the chemical composition of its environment. It consists of a physical transducer and a chemically selective layer \(^{244}\).

Like GS, the ZnO based CS were also use in applications concerned with chemical and environmental origins. The electrical and chemical sensing properties of single ZnO Nr revealed that their electrical transport system was depended on adsorption or desorption nature of chemical groups \(^{245}\).

The chemical sensitivity of ZnO Nw FET CS, for the detection of NO\(_2\) & NH\(_3\) (at room temperature), were found to be very high. This was due to the experimental observations that by applying a large –ve gate voltage, the adsorbed molecules could be desorbed electrically \(^{246}\).

The ZnO CS are prepared by coating a paste of ZnO Nr with polyvinyl alcohol solution on Al\(_2\)O\(_3\) tube, fitted with two gold leads. This CS was used for the detection of C\(_2\)H\(_5\)OH and H\(_2\)S \(^{247,248}\). The ZnO Nw CS, fabricated with MEMS technology showed the good sensitivity for C\(_2\)H\(_5\)OH \(^{248}\). The ZnO CS, fabricated with MEMS technology and doped with Cd, were used for the detection of humidity \(^{249}\). The similar detection was also shown by ZnO Nw films \(^{250}\). Later, ZnO Nw FET CS were reported for their sensitivity for NO\(_2\) and NH\(_3\) \(^{251}\). The single ZnO Nw CS, coated with Pt clusters by sputtering method, detected Hydrogen at room temperature \(^{252}\). The nano-sensor technology based on Zinc oxide Nanostructures,
single crystals, hetero-junctions, thick & thin films of different sizes and shapes viz. Nanodots, nanocombs, nanobelts, nanorods, nanopillars, nanowires, nanoparticles, etc; all of which find their sensitivity based on their surface to volume ratio. These nano-sensors are one of the major developments in today’s world for the detection of various entities (chemical, biological, optical, etc). Some of them are bio-sensors, chemo-sensors, optical sensors, gas sensors, thermal sensors, electrochemical sensors, etc.

However, the sensitivity of all these sensors varies with temperature along with other factors. The sensor technology comprises of various interdisciplinary fields. So, the one who is working over the sensor technology, should be well aware of the properties of material used and the properties of target chemicals, biological materials, etc, for these sensors.

The versatile nature of ZnO Nanostructures leads to its explorations in different applications. Whether it may be antimicrobial activity shown by nano-scaled ZnO or it may be the functions of sensing various biological molecules, chemicals, gaseous, etc; whether it may be photo-catalytic activity by ZnO against different pollutants or it may be anti-cancerous activity or the functioning as solar cells; so on and so forth. Its huge applications perspective proved its vast requirement worldwide. Furthermore, enhancement of its quality characteristic with improvement in its properties further leads to its better usage. Since few decades, with the advent of nanotechnology, the applications of nano-scaled ZnO have been mounting rapidly. But still there is a big room left for
various scientific groups worldwide, in order to present more efficient and innovative technologies based on ZnO Nanostructures.

2.5 References


5. Shao Y. F. and Yan B., (2012), ‘Photofunctional hybrids of rare earth complexes covalently bonded to ZnO core–shell nanoparticle
substrate through polymer linkage’, *Dalton Trans.*, vol. 41, pp. 7423-7430.


27. Goswami N. and Sharma D. K., (2010), ‘Structural and optical properties of unannealed and annealed ZnO nanoparticles prepared
by a chemical precipitation technique’, *Physica E*, vol. 42, pp. 1675-1682.


nanoparticles via a simple solution-combusting method’, 


100. Feng Y. J., Yong Z. Z., Gui Y. T., Wu Z. and Ni Y. J., (2009), ‘Hydrothermal synthesis and dielectric properties of
chrysanthemum-like ZnO particles’, *Chinese Physics B*, vol. 18, pp. 1674-1056.


158. Xiong H. M., Ma R. Z., Wang S. F. and Xia Y. Y., (2011), ‘Photoluminescent ZnO nanoparticles synthesized at the interface
between air and triethylene glycol’, *J. Mater. Chem.*, vol. 21, pp. 3178-3182.


ZnO nanowire arrays via a simple solution-phase approach’, 


photocatalytic and antibacterial activities of Ag-doped ZnO powders modified with a diblock copolymer’, *Powder Technology*, vol. 219, pp. 158-164.


Antibacterial Behaviour of Suspensions of ZnO Nanoparticles Against E. Coli.’, Springer Netherlands, 2010.


