Chapter-1

Introduction
1.1. Introduction

The word “nano” means $10^{-9}$, so a nanometer is one-billionth of a meter. One definition of nanoscience is the study of atoms, molecules and objects, the size of which is in the range of about one to 100 nanometers. The term “nanotechnology” was defined by Professor Norio Taniguchi [1] as “Nano-technology mainly consists of the processing, separation, consolidation and deformation of materials by one atom or one molecule”. The real burst of nanotechnology didn’t come until the early 1990s. Because in the past decades, sophisticated instruments for characterization and manipulation such as Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Scanning Probe Microscopy (SPM) became more available for researchers to approach the nano world. Device miniaturization in semiconductor industry is also a significant factor for the development of nanotechnology.

The field of nanotechnology explores the materials and their properties [2-8], when at least one dimension of the nanostructure is in one hundred nanometer range; a regime is referred to as the nanoscale. Basically the materials in nanoscale have only few atoms or the clusters of atoms, and the properties of the materials have been found to be changed because of the quantum confinement effect. Nanomaterials have structural features in between to those of atoms and bulk materials. They exhibit a variety of properties that are different and often considerably improved in comparison with those of conventional materials because of the very fine grain sizes and consequent high density of interfaces. Some of the nanomaterials properties include increased strength, hardness, improved ductility, reduced elastic modulus, higher electrical resistivity and superior soft magnetic properties etc. Because of the change in the properties of the materials in nano range, nanomaterials have become important for the new research. According to literature, nanomaterials in different forms have gained interest because of their different applications such as nanosensors [9], nanomagnets [10], nanoparticles in drug delivery [11] etc.

Instead of variety of properties shown by nanomaterials still there is infancy, the fields of nanotechnology and the nanoscience are not fully developed; still we need to go deeper to understand the better ways of synthesis so as to use the nano products for device applications at an easy way. We need to fully understand and explore the basic phenomenon at the atomic level. In fact the research in this field aims to discover the unique structures properties and synthesis
mechanisms so that the nanostructures can be produced commercially. Even though the nanotechnology and the nanoscience have meaningful impact to the world of research at large, the fundamental characteristics and the rules governing the nanostructures still have to be uncovered. To understand the fundamental phenomenon in the nano range it is quite reasonable to know the synthesis processes as well as the structure of materials at the atomic level for the effective growth of nanostructures for commercial purpose. In the present work, we have synthesized zinc oxide (ZnO) nanostructures by facile solution route. The growth of synthesized nanostructures is investigated by varying the synthesis parameter. These synthesized ZnO nanostructures were used for environmental, optical and opto-electronics application.

The ZnO is an inorganic semiconductor material. In the old days, it was used as a salve for eyes and open wounds by humans around 500BC or before [12]. Naturally, it is a mineral found as zincite, however the ZnO is obtained by synthesis [13]. Normally, ZnO is white in color and it does not dissolve into the water. The ZnO has wide applications as an additive in rubbers, plastics, ceramics, cement, lubricants, paints, ointments, adhesives, pigments and first-aid tapes etc. As a history of the ZnO, in the period of twelfth to the sixtieth century, the Zn and ZnO were produced in India and in the seventieth century, Zn manufacture moved to China. In 1743, the first European Zn smelter was established in Bristol, United Kingdom (UK) and Antoine Lavoisier introduced Zn in the periodic table of elements in 1789 [14]. In earlier days; the main usage of ZnO was in paints and additive to ointments. Even up to 1834, ZnO did not mix well with oil, and was used as a watercolor. The problem of not mixing with oil was solved by finding optimized condition to synthesize ZnO, and in 1845 the first oil paint was produced by using ZnO in Paris. By 1850, Zn white was produced throughout Europe. The Zn white paint got success with respect to the traditional white lead because the Zn white is permanent in sunlight as it is not blackened, non-toxic and more economical. The Zn white being very clean was used for making tints with other colors and because of this it was used as a ground for oil paintings [15]. In electronics industry, the ZnO was started to use in 1920's. For making radio sets, a schottky barrier was created by contacting ZnO crystal with a copper wire, providing the rectification needed to convert the alternating current (AC) radio waves to direct current (DC) signals [16].
The semiconducting properties of ZnO were first studied in early nineteenth century [17]. After its semiconducting properties were found, the research was mainly on the growth of ZnO, characterizations and applications. Up to the end of the twentieth century, the ZnO was widely used in semiconductor industry for making the many elevated temperature devices [18] and ultrasonic transducers in high-frequency regions [19]. The ZnO was under the scientific spotlight after 1990s, because the scientists working in the field of ZnO wanted to develop high quality and closely lattice matched substrate materials for GaN. The GaN due to its promising wide band gap had been used for short wavelength photonic applications, such as UV and blue light emitting diode (LED) and lasers [20]. In the past decades, the ZnO is extensively studied and many interesting properties have been discussed. The very interesting aspect of ZnO is that it is relatively simple for ZnO to form various nanostructures including highly ordered nanowire arrays, tower-like structures, nanorods, nanobelts, nanosprings and nanorings [21] etc. Since the physical and chemical properties depends upon the type of nanostructures, the ZnO has been found to be promising in many applications, such as sensing [22-24], catalysis [25-27], photovoltaic [28] and nano-generators [29, 30] etc. Moreover, the ZnO has high refractive index, high thermal conductivity, binding, antibacterial and good UV-protection properties [31].

1.2. General properties of ZnO

The ZnO crystallizes in either of wurtzite, zinc blende or rock salt crystal structures. The crystal structures of ZnO are shown in Fig. 1.1. In these structures, each anion is surrounded by four cations in tetrahedral coordination, and vice-versa having sp³ covalent bonding. These compounds also have ionic nature which tends to enhance the band gap beyond the limit of covalent bonding. However, the large difference of the electro negativity of the two constituents of ZnO (Oxygen = 3.44 and Zinc = 1.65) is responsible for the strong ionic bonding between them. The ZnO is a wide direct band gap semiconductor whose ionicity lies at the boundary of ionic and covalent semiconductors. The most thermodynamically stable phase of ZnO is wurtzite under atmospheric conditions. In case of zinc blende, it is metastable phase and is stable only in case of hetero-epitaxial growth on cubic substrates (GaN) [32]. The rock salt is stable at relatively high pressures. ZnO also shows phase transition from the wurtzite (thermodynamically
stable) to the rocksalt phase in the range of 10 GPa high pressure. During this phase transition, there is reduction in volume by 17% [33]. This causes attenuation of lattice dimensions which leads to the interionic coulomb interaction to favor the ionicity. The wurtzite structure has hexagonal unit cell arrangement in 3 dimension with two lattice parameters \(a\) and \(c\) in the ratio of \(c/a = \sqrt{8/3} = 1.633\), with a density equal to 5.605 g cm\(^{-3}\) (for ideal wurtzite structure) [21]. The wurtzite structure deviates from the ideal arrangement in a real ZnO crystal by changing the \(c/a\) ratio. The lattice parameter ratio deviation from ideal one may be due to free charge, impurities, stress and temperature [34]. Since the \(c/a\) ratio also correlates with the difference of the electronegativities of the two constituents, and also components with the greatest differences show largest departure from the ideal \(c/a\) ratio [35].

![Figure 1.1: Crystal structure of ZnO (a) wurtzite (b) zinc blende and (c) rocksalt](image.png)
The lattice constants for the wurtzite ZnO structure mostly range from 3.2475 to 3.2501 Å for the a-parameter and from 5.2042 to 5.2075 Å for the c-parameter and c/a ratio varies from 1.593 to 1.6035 [17, 36-43]. The lattice stability and ionicity changes cause deviation in value of lattice parameters from that of the ideal wurtzite crystal. It has been reported that lattice expands due to free charge, proportional to deformation potential of conduction band minimum and inversely proportional to the carrier density and bulk modulus. The point defects such as zinc antisites, oxygen vacancies, and extended defects, such as threading dislocations are also responsible for the increment in lattice constants. The investigated lattice constant for zinc blende phase varies from 4.37 to 4.47 Å depending upon various techniques. These values are extremely different from wurtzite phase, indicating the formation of zinc blende ZnO structure. High-pressure phase transition from the wurtzite to the rocksalt structure of ZnO lead to the attenuation of lattice constant down to the range of 4.271–4.294 Å [44].

In case of electronic band structure of ZnO as suggested [45-51], the band structure calculations using the Local Density Approximation (LDA) results accurately for the Zn 3d electrons as shown in Fig. 1.2 [51]. The band structure along high symmetry lines is represented in the hexagonal brillouin zone. Both the upper limit of valence band and the lower limit of conduction band occur at the Γ point k = 0 indicate that ZnO is a semiconductor with direct band gap. The bottom 10 bands which occurs around −9 eV correspond to Zn 3d levels and the next 6 bands from −5 eV to 0 eV correspond to O 2p bonding states. The first two conduction band states are strongly Zn localized and correspond to empty Zn 3s levels. From this calculation, direct band gap of ZnO has been determined as 3.77 eV [51] which correlates with the experimental value of 3.4 eV, and is much closer than the value obtained from the standard LDA calculation [21].
Figure 1.2: The LDA band structure of bulk wurtzite ZnO calculated using dominant atomic SIC-PP [51].

The ZnO crystal exhibits crystallographic polarity, which gives the direction of the bonds, growth and structural arrangement of the crystal. The close-packed (111) planes indicate zinc blende and rocksalt structures and corresponding (0001) basal planes in the wurtzite structure differ from (i i i) and (000i) planes, respectively. When the bonds along the c-direction are from Zn$^{2+}$ to O$^{2-}$ or vice-versa, the polarity is referred to as Zn and O polarity, respectively. Several physical and chemical properties of the material depend on its polarity, growth and defect generation. In addition to the primary polar plane (0001) and corresponding growth direction <0001> of wurtzite phase, which is the most commonly used surface and direction for growth, many other secondary planes and directions exist in the crystal structure. Similar to other nanostructures, the ZnO structure grows in such a way that it tends to minimize the surface energy which leads to formation of diverse nanostructures [52].
1.3. Some ZnO nanostructures

The nanostructures of ZnO have all three forms i.e. 1D, 2D and 3D such as nanorods, nanowires, nanobelts, nanosheets, nanoflowers, nanocages and nanoparticles etc. The ZnO is probably the richest family of nanostructures both in structures and properties among all materials. It is nontoxic, inexpensive and chemical stable substance [53]. During the past several years, ZnO nanostructures due to its novel luminescent, electrical, mechanical, chemical, magnetic, biological and optical properties has been used extensive in many technological applications such as transducers, nanosensors, nanocantilevers, field effect transistors, transparent electrode in the solar cells, flat panel displays etc. The ZnO nanostructures have been used in nanosized sensors for the detection of different gases, chemical and biological molecules, and dependent on surface-mediated phenomena [54-56]. It is a promising material for photonic and optoelectronic applications. Different ZnO morphologies have also potential application in purification of water from organic dyes and microorganisms which are referred as photo-catalytic and antibacterial activity, respectively. Surface area, surface defects, doping, porosity of ZnO nanostructures are the factors responsible for these applications [57-65].

The ZnO is a wide band gap semiconductor with high excitonic binding energy 60 meV possesses higher density of free carriers trapping centers. Although, there are many types of ZnO nanostructures reported in the literature but here we review only some of the specific nanostructures such as flower-like structures, nanosheets and nanoparticles considering their relatively different geometries and potential use in different applications. We start our discussion with the ZnO flower-like (nanoflowers) structures and their properties with applications.

1.3.1. Flower-like structures and their applications

The flower-like are the structures which have interwoven nanosheets in the form of a flower. In other words, the nanosheets are interwoven in a way to form a flower-like structure. As the application is concerned, the ZnO nanoflowers were suggested to have pro-angiogenic properties in biological applications. This property is observed by in-vitro and in-vivo angiogenesis assays which led to significant formation of new capillaries from pre-existing blood vessels. The mechanism for angiogenesis property of flowers is the formation of reactive oxygen species
(ROS). This strategy gave rise to ZnO nanostructures as emerging material for alternative therapeutic treatment strategies for cardiovascular and ischemic diseases [66]. Shi et al. [67] report a self-catalyzed growth of ZnO nanoflowers via the formation of ZnO nanowires (NWs) by vapor deposition kinetics of ZnO nanomaterials under controlled atmosphere. They stated that the synthesized structures resulted in strongly luminescent material which was successfully applied for optical imaging applications and in-vitro tumor cell imaging. The ZnO nanoflowers synthesized by hydrothermal method show effective osteoblast growth with higher DNA content, alkaline phosphatase (ALP) activity and adhesion strength than those on ZnO film. The approach for fabricating nanoflower structures on biomaterial surfaces shows a potential application in bone tissue engineering as well [68].

Vinod et al. [69] demonstrated that ZnO shows room temperature photoluminescence properties exhibiting emission at 392 nm (UV emission) without a visible emission. They synthesized ZnO nanoflowers by hydrothermal process at 200 °C temperature and found defect free nanoflowers as observed by suppressed Raman bands at 541 and 583 cm\(^{-1}\), led to the application in UV light-emitting devices. Jun et al. [70] synthesized ZnO nanoflowers by low temperature solution-phase method, which was used as photoanodes on transparent conductive fluorine-doped tin oxide substrates by doctor-blade technique. They found that nanoflower structure enhances light harvesting and improves electron transport when used for fabrication photoanodes with a ZnO/TiO\(_2\) composite of dye-sensitized solar cell. Similarly, Ahmad et al. [71] in their work showed that the well-crystalline flower-shaped ZnO structures exhibit good photocatalytic property for the degradation of rhodamine B (RhB) and good photo-anode material for dye-sensitized solar cell applications. Kim et al. [72] in their work grown ZnO nanoflowers on a conducting glass substrate using a chemical solution deposition method. When used as synthesized ZnO nanoflowers in LED devices application, they demonstrated strong light emission as the micropixels for display application.

Guo et al. [73] synthesized ZnO flower-like by combining laser direct writing and hydrothermal growth. They demonstrated that the flower-like morphology shows excellent wettability and photocatalytic activity in the degradation of RhB dye. Lei et al. [74] synthesized ZnO nanoflowers with dextran ((C\(_6\)H\(_{10}\)O\(_5\))\(_n\)) assistance by a facile solution route. The flower-like
structure with dextran shows potential application for wastewater treatment by exhibits higher activity than ZnO fragments obtained without dextran. Umar et al. [75] investigated ZnO nanoflowers for their applications in an antimicrobial agent against escherichia coli (E.coli) and enzyme-free glucose sensor. They showed that ZnO nanoflowers are efficient as an antimicrobial agent and a highly sensitive non-enzymatic glucose sensor. ZnO nanoflowers as an efficient electron mediator also exhibit good sensitivity (∼411 μA M⁻¹cm⁻²) with detection limit of ∼1.25 mM and response time of ∼10 seconds (s) for non-enzymatic glucose sensor. Panwar et al. [76] used ZnO nanoflower structure for gas sensing purpose by growing them on glass substrates. They showed significant response (95%) for acetone gas at 325 °C. They observed that structure exhibits a fast response and recovery due to its surface morphology.

ZnO nanoflowers composed of needle-like nanorods synthesized by using aqueous chemical growth method at low-temperature were used for piezoelectric energy harvesting source by Khan et al. [77]. They synthesized ZnO nanoflowers uniformly on conductive flexible textile fabric substrate. They observed a significant output potential and current more than 600 mV and ∼650 nA, respectively and also good rectifying schottky behavior. Wang et al. [78] successfully synthesized ZnO nanoflowers by a simple low-temperature route and demonstrated that different ZnO morphology can be obtained simply by varying basicity in the solution and suggested ZnO nanoflowers growth mechanism in terms of the general theory of the crystal nucleation and crystal growth direction. The ZnO nanoflowers synthesized via surfactant free medium contains larger content of oxygen vacancy act as the active centers of the catalyst on the surface of 1D nanomaterials, responsible for good photocatalytic activity in degradation of 4-chlorophenol (4-CP) in aqueous solution under UV radiation.

1.3.2. **ZnO nanosheets and their applications**

The ZnO nanosheets is a two dimensional structure. The thickness of nanosheets is in tens of nanometer where as the width may be up to millimeters. Here we briefly discuss some important aspects of ZnO nanosheets.

Chen et al. [79] fabricated ZnO nanosheets by a physical vapor-transport technique and investigated by micro-photoluminescence spectroscopy. They observed that nanosheets resulted
in high-temperature (857 K) photon emission. The observed property could be used in high-temperature opto-electronic applications. Sesha et al. [80] synthesized nanosheets by wet-chemical method at low temperature (80°C) without substrate. ZnO nanosheets investigated by raman spectroscopy and photoluminescence measurements have shown intense green, blue and red emissions due to a variety of vacancy and interstitial defects, which attributed this material to act as blue-white fluorophore. The potential use of this blue-white fluorescent coating is in conjunction with ultraviolet emitting LEDs. Tan et al. [81] synthesized ZnO nanosheets on metallic Zn foils after hot-water treatment at 90 °C for 4, 8, 12 and 24 hours. They showed that the ZnO nanosheets exhibit near band edge UV and green emissions when observed by the photoluminescence spectra; indicating their good crystallinity with presence of oxygen related defects. Thus formed structure could be used for opto-electronic applications. Ahmad et al. [82] synthesized ZnO nanosheet networks on silicon substrate without any catalyst through thermal evaporation using ZnCl₂ and O₂ as source materials for zinc and oxygen, respectively. They observed that ZnO nanosheet networks showed a strong green band with a suppressed UV emission at room temperature. The UV emission at room temperature makes it applicable for opto-electronic and luminescence applications. The device made from two dimensional nanosheets and an anionic nanoclay layer heterojunction has potential to be the smallest size power package as observed by Kim et al. [83]. Further, this structure can be used to charge wireless nano/micro scale systems without the use of rectifier circuits to convert AC into DC to store the generated power. The combined effect of buckling behavior of the ZnO nanosheets, a self-formed anionic nanoclay layer, and coupled semiconducting and piezoelectric properties of ZnO nanosheets contributes an efficient DC power generation. The network of ZnO nanosheets proved a structurally stable system under huge external mechanical loads.

In wastewater treatment applications, the ZnO nanosheets show a good photocatalytic property for the degradation of methyl orange (MO), RhB and methylene blue (MB) dyes under UV light illumination and possess excellent super-hydrophilic ability. These properties demonstrate ZnO nansheets as promising nanomaterials for wastewater treatment [84]. The electrical contact between the ZnO nanosheets and brass substrate demonstrated potential applications of ZnO nanosheets in gas sensing and photocatalytic degradation [85]. As the
properties of nanosheets depends upon fabrication method, ZnO nanosheets film was fabricated by dip-coating and inkjet printing on glass plates by Hynek et al. [86]. The film morphology is highly influenced by the deposition method as in dip coating method; the film morphology is very smooth and nonporous, while the inkjet-printed films were rough and porous. However, in the photocatalytic degradation of 4-CP these films show two-fold efficiency than ZnO films prepared by the sol–gel technique. The obtained higher efficiency is due to the side-by-side alignment of ZnO nanosheets on the substrate resulted in thin, transparent, oriented ZnO surfaces with the high-energy {001} facets exposed. Therefore, the surface arrangement of ZnO nanosheet films makes them applicable for the construction of optical devices and dye-sensitized solar cells.

Recently, Wang et al. [87] reported the effect of synthesis parameters on the biological applications of ZnO nanosheets. They synthesized hexagonal ZnO nanosheets at nearly neutral pH (i.e., 7.3) and low temperature (i.e., 80°C) using structure-directing agent, tris(hydroxymethyl)aminomethane (tris). The tris molecule acts as the hydroxide anion generator and surface modification agent. The obtained ZnO nanosheets show strong fluorescence at wavelength 590 nm, which attributed to the defects on the surface of ZnO nanosheets, which makes their use for cell imaging, suggesting their promising clinic and biomedical applications. The ZnO nanosheets are also used as a sensing material. Zhang et al. [88] used sonochemical process to synthesize sheet-like ZnO nanostructure without any catalyst, template or seed layer, followed by an etching treatment in an alkali environment at room temperature. The as-prepared nanosheets were used to fabricate micro gas sensor for testing different concentration of volatile organic compounds (VOCs) gases. They observed that the nanosheet structures, due to large specific area, accessible surface and less agglomerated configuration, are responsible for excellent sensitivity to acetaldehyde and formaldehyde with response time less than 10 s and detection limit of 50 ppb. Amini et al. [89] fabricated UV detectors by using Zhang et al. [88] method. They observed that ZnO nanosheet photosensor shows faster response time in the UV region as compared with conventional ZnO nanoparticles based photosensors. The higher sensitivity of nanosheets is attributed to the low density of defect states on nanosheets surfaces.

1.3.3. ZnO nanoparticles and their applications
The nanoparticle is zero dimensional structure while considering the allowed direction. In this section, we discuss some of the important aspects of ZnO nanoparticles.

As an optical property, ZnO nanoparticles show high luminescent properties. Daniele et al. [90] prepared ZnO nanoparticles by co-precipitation method with variable amounts of aminopropyltriethoxy silane (APTS). They generate LED devices based on the organo-modified ZnO nanoparticles with the photoemission and observed their higher luminescent properties. In another study, Liu et al. [91] reported a photodetector based on flexible nanoparticle-assembled ZnO cloth, which was synthesized via a carbon cloth templated hydrothermal method. Under UV irradiation, the conductance of the device increased more than 600 times having response and decay time to be around 3.2 s and 2.8 s, respectively.

In environmental applications, the ZnO nanoparticles were suggested by Bagabas et al. [92], as they follows room temperature wet chemical route based on cyclohexylamine for synthesizing ZnO nanoparticles in aqueous and enthanolic media, and also tested for the photodegradation of cyanide ions. They conclude that the morphology was crucial in enhancing the cyanide ion photocatalytic degradation efficiency. Also ZnO nanoparticles were synthesized by calcination of precursor by the precipitation method with grafting polystyrene onto the surface of ZnO nanoparticles to improve the dispersion of the particles. They showed that ZnO nanoparticles possess high photocatalytic activity [93].

The nanoparticles with luminescent and magnetic properties show applications both in vitro and in vivo as detection probes and drug carriers etc. These nanoparticles, due to their good biocompatibility [94] and low cost, have shown promising potential in bioimaging and drug delivery [95]. Recently, Matsuyama et al. [96] suggested biological application of ZnO nanoparticles by the use of silica-coated ZnO-nanoparticle quantum dots (QDs) with biotin as fluorescent probe in cell-labeling applications and have suggested for selective destruction of tumor cells applications [97]. Also, ZnO nanoparticles have been appeared as a promising candidate for the realization of dye sensitized solar cells [98] and are used for sunscreens lotion as UV blockers [99]. Sun et al. [100] suggested a flexible nanogenerator made of ZnO nanoparticles which may bring out some important and interesting applications in energy harvesting.
In the present work, we have synthesized three morphologies of ZnO viz. flower-like structure, nanosheets and nanoparticles by facile solution method and have applied them for optical, opto-electronic and environmental applications. The synthesized ZnO structures exhibit near band edge UV emission as well as emissions in visible regime also (violet, blue, blue-green and green) as observed by photoluminescence spectra. This indicates good crystallinity of as synthesized ZnO nanostructures and presence of oxygen related defects. These defects with surface free bonds make ZnO nanostructures as a potential structure for environmental and opto-electronic applications. We have performed experiments related to the photocatalytic activity of ZnO nanostructures for the degradation of MB in presence of the sunlight and photodetector for detecting visible light (white, violet and green). Synthesized ZnO nanostructures were also applied in turbid lens imaging application in enhancing numerical aperture (NA) of objective lens. A comparative study of their performance indicated that the nanosheets show better light bending as compared with other nanostructures. When used in visible-light photodetector for detecting visible light (white, violet and green) at room temperature, again the nanosheets showed better performance as compared to other morphologies. Better performance of nanosheets is attributed to their higher effect of surface area and oxygen vacancies.

1.4. Synthesis methods for ZnO nanostructures

The controlled synthesis of the ZnO nanostructures has been one of the motivations for the researchers because the properties of nanostructures can be controlled by controlling the shape and size of the structure [101-105]. In literature, various techniques have been suggested for the growth of ZnO nanostructures [106-108]. The synthesis methods can be categorized as solid, liquid and vapor phase methods. The synthesis methods are summarized in Fig. 1.3.
Figure 1.3: Summary of synthesis methods for ZnO nanostructures.
Mainly there are three methods namely solid phase, liquid phase and gas phase. First of all, the solid phase method is a solid-state technique [109-111] for the synthesis of ZnO nanostructures. It involves grinding, mixing and subsequent heat treatment at high temperatures of precursor materials (metal oxides or carbonates) to facilitate diffusion of atoms or ions in the host material by chemical reaction. In this method, it is difficult to control the particle properties. This method have many disadvantages such as inhomogeneity, bigger crystallite, poor stoichiometry, phase impurity [112, 113] etc. Gases or vapor phase method is categorized as physical vapour deposition (PVD) and chemical vapour deposition (CVD), they are further divided as thermal evaporation, sputtering, pulse laser deposition (PLD) for PVD and CVD: thermal CVD, low pressure CVD (LPCVD), plasma-enhanced CVD (PECVD), metal-organic CVD (MOCVD), laser CVD (LCVD), atomic layer deposition (ALD) and molecular beam epitaxy (MBE). These methods are differentiated from each other based upon their source of bombardment, catalyst, precursor etc. These techniques have been used for the synthesis of ZnO nanostructures like nanocombs, nanoparticles, nanorods, nanowires etc. In PVD processes, material in a vapor form is physically released from a source and is transferred to a substrate at high temperature. It generally involves bombardment of the substrate to be coated with energetic positively charged ions during the coating process to promote high density in vacuum at pressure $10^{-2}$ to $10^{-4}$ mbar. Various compound compositions have been created during metal deposition by the introduction of reactive gases such as nitrogen, acetylene or oxygen into the vacuum chamber. In this process, the solidification of a vapor from source directly onto a surface takes place without a chemical reaction. In CVD process, the reaction of vapor phase chemical reactants containing the material occurs to form a non-volatile solid film or structures on a substrate. Hot furnace as reaction chamber is used for this process in which the reactant gases (H$_2$, O$_2$, CH$_4$, argon etc.) are introduced to decompose and react with the substrate to form the film or structures at high temperature. Generally, the gas phase approaches are relatively easy to control for the production of a variety of high quality, single crystal ZnO nanostructures and doping. However, they have requirement of the high temperature, costly gases and vacuum level [114].
The liquid phase/solution-based methods are divided in hydrothermal, chemical bath deposition (CBD), electrochemical deposition (ECD), sol-gel, co-Precipitation, spray pyrolysis, combustion, microwave assisted and polyol synthesis routes. All these methods have some merits as well demerits. In case of solution-based methodologies, there is an advantage of low growth temperature, potential for easy scaling up, and simplicity for fabrication of ZnO nanostructures as compared to vapor phase methods. From the commercialization point of view, the chemical waste treatments will also require to deal with the environment issues in the future. However, a low-cost chemical synthesis with high yield certainly is appropriate for commercialized production of nanostructure materials. Among all solution based methods, the co-precipitation methods results in atomic scale mixing. The calcining temperature required for the formation of final product is low, which lead to lower particle size [115]. Since, each synthesis requires its own special conditions, precursor reactions etc. Therefore in the co-precipitation process, it is required to control the concentration of solution, pH, temperature and stirring speed of the mixture in order to obtain the final product with required properties [116, 117]. All other solution based methods which are commonly used have some disadvantages such as sol-gel method has disadvantages of their products would contain high carbon content when organic reagents are used in preparative steps and this would inhibit densification during sintering, hydrothermal slurries are potentially corrosive and also may cause accidental explosion of the high pressure vessel and in polyol method, requirement and selectivity of large amount of polyhydroxy alcohol for individual processes, and collecting and purifying the intermediate particles are complicated [118-120]. In the present work, we have used a facile solution method for the synthesis of ZnO nanostructures at room temperature. The advantages of this method are:

1. Particle size and morphology control
2. Without use of template, directing agent, high temperature and high pressure vessel.
3. Easy and cost-effective route.
4. No use of harmful and explosive gases.
1.5. Synthesized ZnO nanostructures were characterized using the following techniques

(i) Field Emission Scanning Electron Microscopy (FESEM) installed with Energy Dispersive X-rays (EDAX): Using FESEM, we have observed the surface morphology. From EDX the information corresponding to the different elements present in the nanostructures has been obtained.

(ii) Transmission Electron Microscopy (TEM) installed with Energy Dispersive X-rays (EDAX): TEMs provide structural, compositional and crystalline information. High resolution imaging mode gives information regarding crystal lattice of a materials. This allows observing planar and lining defects, grain boundaries, interfaces, etc. The bright field/dark field imaging modes of the microscope, which operate at intermediate magnification, combined with electron diffraction, are also invaluable for giving information about the morphology, crystal phases, and defects in a material.

(iii) X-ray Diffraction (XRD): X-ray diffraction provides a convenient and a practical means for the qualitative structural identification of compounds because of the uniqueness of the pattern for each compound.

(iv) Fourier Transform Infrared Spectroscopy (FTIR): Infrared spectroscopy is quite useful to predict each functional group present in molecule absorbs a certain frequency of radiation and show corresponding peak. Hence the position of peak gives the information regarding the presence of certain functional group and the shift due to environment effect can be easily observed in spectrum.

(v) UV-Vis Spectroscopy: UV-Vis spectroscopy is used to study the optical properties of compounds. It is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules.
(vi) **Photoluminescence Spectroscopy (PL):** Photoluminescence spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials. Radiative transitions in semiconductors involve localized defect levels. The photoluminescence energy associated with these levels can be used to identify specific defects, and the amount of photoluminescence can be used to determine their concentration.

(vii) **Brunauer–Emmett–Teller (BET) surface area measurement:** The BET method is widely used in surface science for the calculation of surface areas of solids. The specific surface area of a powder is determined by physical adsorption of a gas on the surface of the powder and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. The determination is usually carried out at the temperature of liquid nitrogen. The amount of gas adsorbed can be measured by a volumetric or continuous flow procedure.

### 1.6. Thesis Outline

**Chapter 1** begins with the basic introduction of the nanotechnology. Also the nanostructures on the bases of the dimensionality have been classified. A brief explanation of the different synthesis methods is explained. Used characterization methods for synthesized nanostructures have been briefly explained. The reason of selecting the present system has been discussed in the last of this chapter.

**Chapter 2** explains the methodology, experimental procedure and morphology control used in this research work. In reference to the synthesis process the several processing parameters such as \(\text{OH}/\text{Zn}^{2+}\) ratio, reaction time, surfactant and solvent, which can be controlled and need to be selected properly before and/or during synthesis are also discussed. In the next section, the influence of synthesis conditions on the morphology of ZnO nanostructures is discussed. Then different characterizations for morphology, structural and optical properties of the grown nanostructures have been discussed.
Chapter 3 starts with a brief introduction of different types of nanostructures applied in environmental application and properties required for photocatalytic activity under sunlight. An experimental procedure for the photocatalytic activity is described in the second section of this chapter. In the next section, brief description of the mechanism of nanostructures formation and different aggregation tendencies of nanosheets is presented. Then photocatalytic performances of the grown nanostructures have been discussed. Further a brief description of the mechanism of photocatalytic activity of nanostructures is presented. Finally the chapter concludes with a brief summary.

Chapter 4 starts with an introduction of enhancing numerical aperture for turbid lens imaging is presented, and then the experimental process for enhancing numerical aperture and transmittance of turbid lens has been described. Characterizations of fabricated turbid film have been explained onwards in terms of their morphology and scattering. For a comparative study of the fabricated ZnO turbid film for enhancing numerical aperture and transmittance has been explained in brief. Next the principle behind this application is also given and in last a brief summary of the chapter is given.

Chapter 5 starts with an introduction of ZnO nanostructures based photodetectors. An experimental procedure for the formation of ZnO nanostructures film on glass substrate and fabrication of photodetector circuit has been described onwards. Next, for a comparative study of photodetector performance of the fabricated ZnO film has been explained in brief. Further the principle behind these performances is explained and in the end a brief summary is presented.

Chapter 6 includes summary conclusion and important suggestion towards the future work.