

# **ANALYSIS ON PHOTOCATALYTIC DYE DEGRADATION OF COPPER DOPED ZINC OXIDE NANOPARTICLES**

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# ABSTRACT

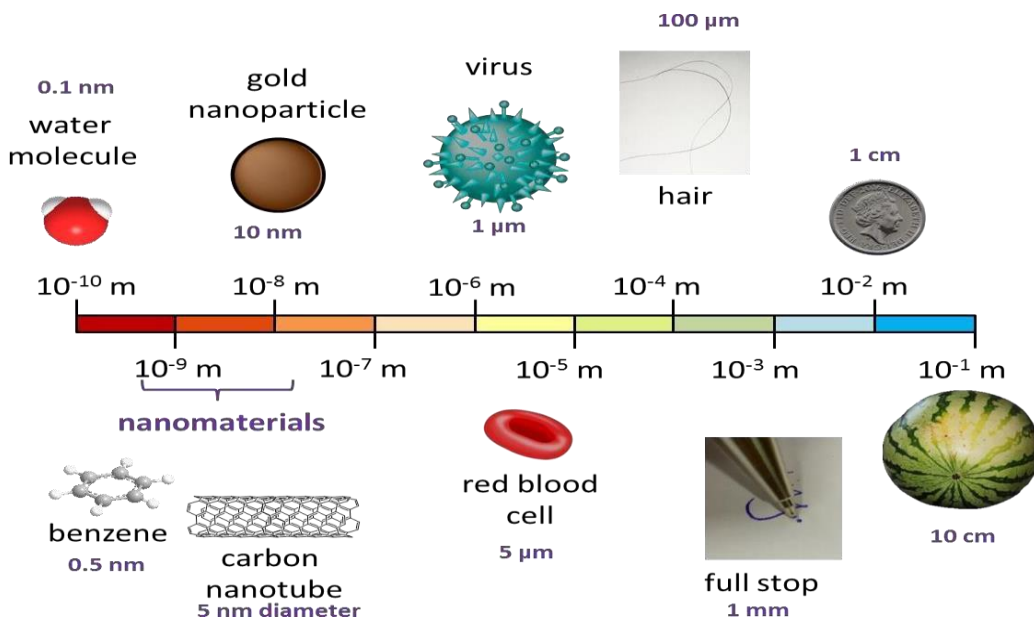
Copper-doped Zinc Oxide nanoparticles were synthesized by viable hydrothermal method. Structural, morphological, and optical studies were done to characterize the material's properties. X-ray Diffraction analysis showed that the nanoparticles have a hexagonal wurtzite structure without having any other impurity peaks. Surface morphology of prepared samples characterized using Field Emission Scanning Electron microscopy showed nanorod morphology. The UV- Visible spectra showed variation in bandgap energy of the prepared samples by doping low composition Cu on ZnO nanostructure. It is found that the optical properties of nanorods can be simply tuned by changing the doping concentration. The prepared samples were tested as adsorbents to study the dye degradation potential of ZnO and Cu doped samples by taking Methylene Blue (MB) as a model dye. The highest degradation efficiency was observed for 2.5% Cu doped ZnO nano catalyst with a small crystalline size. The results thus reveal the practical applicability of prepared samples in photodegradation applications.

# Chapter 1

## INTRODUCTION

### 1.1 Nanoscience and Nanotechnology

The word ‘Nano’ is derived from the Greek word for dwarf means  $10^{-9}$  and hence a nanometer is one billionth of a meter,  $10^{-9}$  m. Nanometer objects are too small to be seen with our eye. In fact, if we wanted to see a 10nm sized marble, our eye would have to be smaller than a human hair which is approximately 80,000nm wide.



**Figure 1.1: Size Comparison of Nanoparticles**

Nanoscience is an emerging area of science which concerns itself with the study of materials that have very small dimensions and it involves chemistry, physics, biology, mathematics, cognitive science and life science. It is referred as “The study of phenomena, performance and manipulation of ultra – small structures or materials at atomic, molecular and macro molecular scales, where properties differ significantly from those at a larger scale”.

The special properties or characteristics imparted by the nano-dimension are:

- 1) The large ratio of surface area to volume

- 2) The large fraction of surface atom to that in its bulk.
- 3) The smallness of size which makes many barriers transparent.
- 4) The size dependent properties such as absorption of light of a certain frequency due to onset of quantum effect at the nanometer scale. Nanoparticles are also called quantum dots due to quantum effect.

Nanotechnology is considered as the one of the most promising technologies of the 21<sup>st</sup> century. Since it converts the Nano science theory to useful applications by observing, measuring, manipulating, assembling, controlling and manufacturing matters that are at the nanometer scale. Nanotechnology is a blanket term and its principle and products are relevant to a wide range of fields including medical, electronics, robotics, etc. Currently the developments in nanotechnology are exhibiting a certain potential , that is aiding humanity and changing the world which we live in . The nanoworld of Nanoscience and Nanotechnology provides scientists with a rich set of materials useful for probing the fundamental nature.

## **1.2 Nanomaterials and Nanoparticles**

Nano materials (NMs) are materials that have structural components smaller than 1 micrometer in at least one dimension. These materials exhibit many unique properties and are classified on the basis of its size, morphology and dimensions.

Nanoparticles (NPs) are particles with at least one dimension smaller than 1 micron and is potentially as small as atomic and molecular length scales. Nanoparticles can have amorphous or crystalline form, but their surfaces can act as carriers for different liquid droplets or gases.

## **1.3 Historical Aspect**

The history of nanomaterial began immediately after the big bang when the nanostructures were formed in the early meteorites. The nature later evolved to have many other nanostructures like seashells ,skeletons etc. The use of fires by early humans lead to the formation of nano scale smoke particles. The scientific story of nanomaterial began much later. The Nanoparticles and their structures were used by humans in fourth century AD. The Romans were the first once to

demonstrate the most interesting examples of nanotechnology to the ancient world. During the 9th–17th centuries, the Islamic world used glowing, glittering “luster” ceramic glazes and later in Europe contained Ag or copper (Cu) or other nanoparticles. The Italians also made as well as used nanoparticles in creating Renaissance pottery during 16th century. They were influenced by Ottoman techniques: during the 13th–18th centuries, to produce “Damascus” saber blades, cementite nanowires and carbon nanotubes were used to provide strength, resilience, and the ability to hold a keen edge.[12]

One of the first scientific reports is the colloidal gold particles synthesized by Michael Faraday as early as 1857. Richard Adolf Zsigmondy was the first to use nanometer for characterizing particle size in 1914. The conceptual underpinnings of nanotechnologies were first laid out in 1959 by well-known physicist Richard Feynman in his lecture “There is plenty of room at the bottom”. Feynman explored the possibility of manipulating material materials at the scale of individual atoms and molecules, foreseeing the increasing ability to examine and control matter at the nano scale.

The term “nanotechnology” was not used until 1974 when *Norio Taniuchi*, a researcher at the university of Tokyo, Japan used it to refer, the ability to engineer materials precisely at the nanometer level. In 1980’s the concept of nanotechnology to engineering through the concept of molecular manufacturing was done, for the first time and it was applied by Eric Drexler. He presented nanotechnology as a scientific field that exclusively revolved around molecule manufacturing and his vision is often called “Molecular Nanotechnology”. Nanotechnology and Nanoscience got boosted in the early 1980s with two major developments: The birth of cluster science and the invention of SEM. This development led to the discovery of fullerenes in 1985 and the structural assignment of carbon nanotubes a few years later. In 1986, Binnig and Rohrer received the Nobel Prize in Physics “for their design of the STM”. This invention led to the development of the atomic force microscope (AFM) and scanning probe microscopes (SPM).[12]

In the early 1990’s Huffman and Kretschmar discovered how to synthesis and purify large quantities of fullerenes. Using the same or similar tools as those used by Huffman and Kraetschmer, hundreds of researchers further developed the field of nano-based nanotechnology. In 2004, a new class of carbon nanomaterials called carbon dots (C-dots) with size below 10 nm was discovered accidentally by Xu et al. Today Nano phase engineering expands in a rapidly growing number of

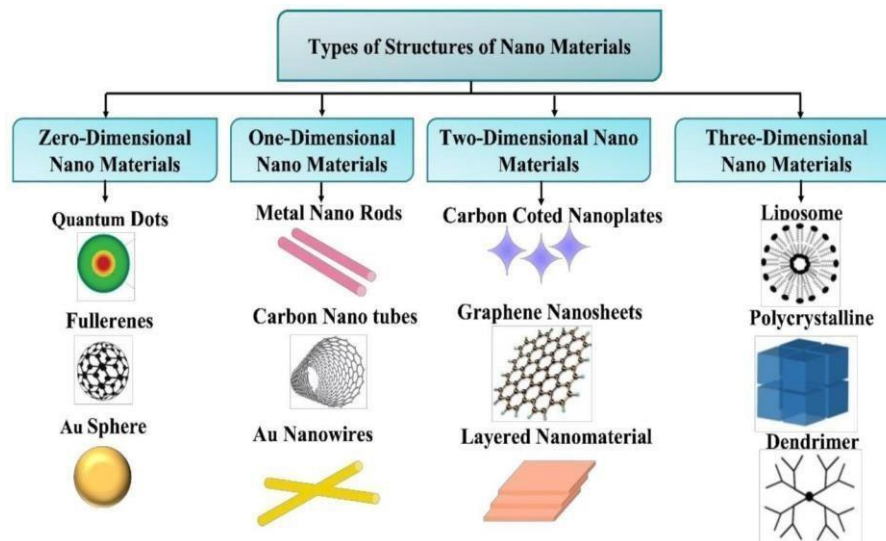


structural and functional materials, both inorganic and organic, allowing to manipulate mechanical, catalytic, electric, magnetic, optical and electronic functions. The production of Nano phase or cluster-assembled materials were usually based on the creation of separated small clusters which are then fused into a bulk-like materials. For example , the Nano phase silicon, which differs from normal silicon in physical and electronic properties, could be applied to macroscopic semiconductor processes to create new devices. In case of ordinary glass, which is doped with quantized semiconductor "colloids" , becomes a high- performance optical medium with a potential applications in optical computing.

## 1.4 Classification of Nanomaterials

On the basis of morphology, size and forms nanomaterials are divided into various categories

### 1.4.1 Classification based on dimension



**Figure 1.2: Types of Structures of Nano Materials based on dimension**

- Zero dimensional nanomaterials
- One dimensional nanomaterial (1D NMs)
- Two dimensional nanomaterials (2D NMs)
- Three dimensional nanomaterials (3D NMs)

(1) **Zero-dimensional nanomaterials:** Here the dimensions (x, y, z) are at nano scale which means that there is no dimensions are greater than 100 nm. It comprises of nanospheres and nanoclusters.

(2) **One-dimensional nanomaterials:** Here the two dimensions (x, y) are at nanoscale and the other one is outside the nanoscale. These nanomaterials exhibit needle like shape nanomaterials. It comprises of nanofibers, nanotubes, nanorods, and nanowires.

(3) **Two-dimensional nanomaterials:** Here, one of the dimensions (x) is at nanoscale and the other two are outside the nanoscale. These nanomaterials exhibit plate-like shapes. It includes nanofilms, nanolayers and nano-coatings with nanometer thickness.

(4) **Three-dimensional nanomaterials:** These are the nanomaterials that are not confined to the nanoscale in any dimension. These materials have three arbitrary dimensions above 100 nm and are composed of a multiple arrangement of nano size crystals in different orientations. It includes dispersions of nanoparticles, bundles of nanowires and nanotubes as well as multi-nanolayers (polycrystals) in which the 0D, 1D and 2D structural elements are in close contact with each other and form interface.

## **1.4.2 Classification based on the materials**

### **1.4.2.1 Carbon-based material**

The Carbon-based materials are made of carbon content and has a variety of morphologies. Fullerenes, Carbon Nanotubes (CNTs), Graphene (GR), carbon nanofibers, and carbon black are some of the different types of carbon nanomaterials.

#### (a) Fullerenes

Fullerenes (C<sub>60</sub>) are carbon atoms bound together by sp<sup>2</sup> hybridization and are spherical (hollow sphere) in shape. Due to its electrical conductivity, strength, structure, electron affinity and versatility it attracts economic interest.

#### (b) Graphene (GR)

Graphene is an allotrope of carbon. It is planar and layered structure in which every layer has atoms of carbon arranged in honeycomb-like network.

(c) Carbon nanofiber

Graphene nano foil is transferred into carbon nanofiber as carbon nanotubes. But here instead of cylindrical tubes, nano foil is twisted into a cone or cup.

(d) Carbon black

A carbon-based amorphous material with diameters ranging from 20 to 70 nm with a usually spherical form. There is a lot of interaction between particles, therefore they are stuck together in a clump.

(e) Carbon nanotubes (CNTs)

Carbon nanotubes were earlier known as buckytubes. These are elongated cylindrical fullerenes having diameters of  $<1$  nm and 50 lengths in micrometer or millimeters. They exhibit a unique combination of stiffness, strength, and tenacity compared to other conductive materials. The Carbon nanotubes are categorized into Single wall nanotubes (SWAT) and Multi wall nanotubes. The single wall nanotubes may be zigzag, armchair and chiral depending on the manner in which the graphene sheets are rolled. The Multi-walled nanotubes (MWNT) consist of several single walled nanotubes with different diameters.

### **1.4.2.2 Metal-based material**

Metal-based nanomaterials, are synthesized from metals to nm sizes using destructive or constructive methods. Divalent and trivalent metal ions are the beginning ingredients for metal nanostructures. Metal ions are converted to metal nanoparticle using reducing agents. These have a large surface area and a good ability to adsorb small molecules. Commonly employed in a variety of scientific, environmental, and other fields.

### **1.4.2.3 Semiconductor-based material**

Semiconductor nanostructures possess both metallic and non-metallic characteristics. By changing it they shows diverse properties with broadband gaps. They are mainly used in photocatalysis and electronic gadgets.

## **1.5. Properties of Nanomaterials**

Properties of nanomaterials can be classified into:

### **1.5.1 Chemical properties**

The nanomaterial composition and chemical structure have a salient role to provide the desired function. Chemical properties such as surface energy, chemical potential, oxidation process, and catalysis have great impact on the composition of nanomaterials.

### **1.5.2 Physical properties**

The physical properties of nanomaterial depend upon the size, shape, colour, and morphology of particles. Size effect, crystalline structure, lattice parameter, and morphology of nanomaterials. The morphology of nanomaterials are due to the combined effects of size, shape, and arrangement of particles.

### **1.5.3 Optical properties**

Optical properties of nanomaterials include reflection, light emission, absorption, and transmission. These factors depends on their electronic structure since the electronic structure depends upon surface atoms. Optical properties are used to observe the size effect when particle size reduces to ~10 nm.

### **1.5.4 Mechanical properties**

The mechanical behaviour of nanomaterials leads to high strength conditions and high-speed plasticity. Mechanical properties of nanomaterials significantly deal with the influence of grain size, material structure, hardness, elastic modulus, adhesion, and friction.

### **1.5.5 Electrical properties**

The electrical resistivity of nanocrystalline materials is observed to be stronger than that in the coarse-grained substance of the same chemical components which is due to the higher volume fraction of atoms lying at the grain boundaries. The electrical resistivity decreases at a specific temperature with a decrease in grain size and for constant grain size, the electrical resistivity increases with temperature, and all of these results are consistent with the theoretical study of grain boundary scattering of electrons. The configuration of the band gap energy and the density of the charging carrier in the materials are being adjusted very significantly from its bulk and in effect, the electronic properties of a substance will be modified.

### **1.5.6 Magnetic properties**

The magnetic properties of nanomaterials differ usually in two points from that of bulk. Unlike bulk magnetic fields which appear in multiple magnetic domains, many ferromagnetic nano particles would contain a single magnetic domain. The super-paramagnetism occurs in cases of a single system, in which the magnetic moment of the particles is distributed evenly and aligned only under an external magnetic field. The nano particle's magnetic flux is found to be much less when compared to its bulk size. Besides, the large surface-by-volume ratio offers a dynamic local environment, leading to mixed volume and magnetic features for the surfactant molecules in their magnetic coupling or impact with the physical atoms.

## **1.6 Synthesis Of Nanomaterials**

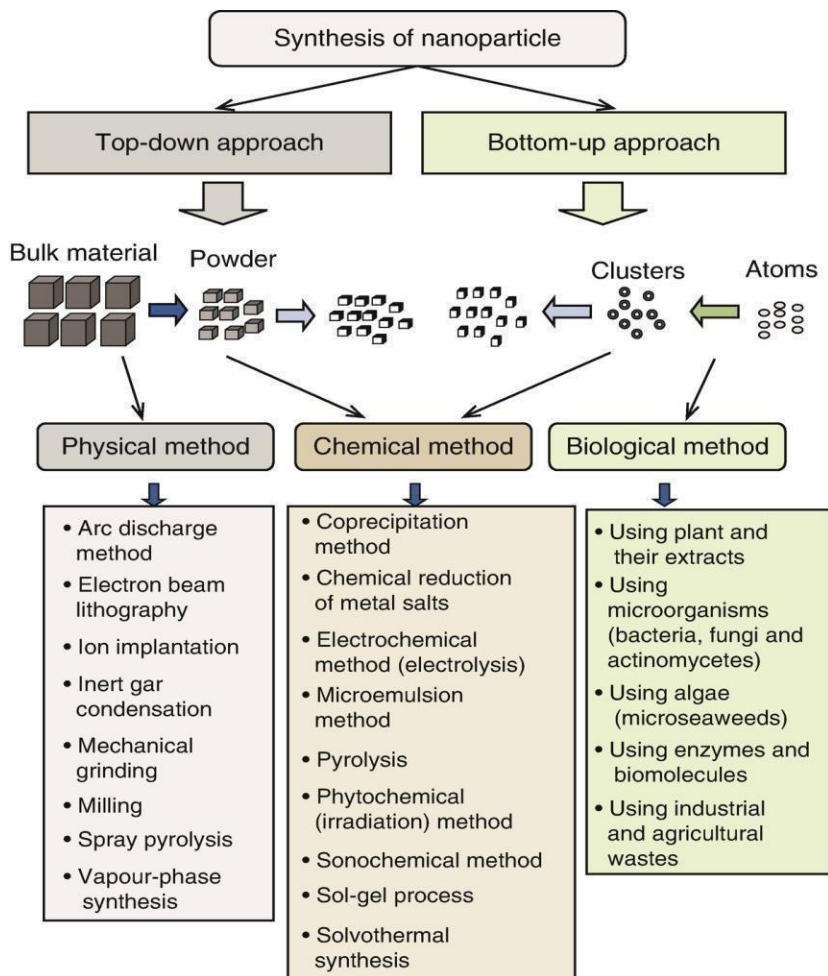
Methods for synthesizing nanomaterial are classified into:

### **1.6.1 Top-down approach**

This approach involves the breaking down of the bulk material into nano sized of particles. Top-down synthesis techniques are extensions of those that have been used for producing micro sized particle. Top-down approach is inherently simpler and depend either on removal or division of bulk material or miniaturization of bulk fabrication process to produce desired structures with appropriate properties. It is ineffective in manufacturing irregularly shaped and extremely small particle. There is a difficulty in acquiring proper particle size and shape.

### **1.6.2 Bottom- up approach**

The alternative approach which has the potential of creating less waste and hence the more economical is the 'bottom –up'. This approach refers to the building up of a material from the bottom that means atom by atom, molecule by molecule or cluster by cluster. Limitation of this approach is that large scale production is difficult and chemical purification of nanoparticle are required.



**Figure 1.3 : Synthesis of Nanoparticles**

## **1.7. Application of nanotechnology**

### **(a) Gas sensing applications**

Developments of nanomaterials with controlled morphology, size, and architecture have attracted intensive interest for the development of sensors. This is because they offer acceptable sensing concert in terms of sensitivity, good reversibility and without the need for complex measurement techniques as compared to other classes of materials. So far, a variety of nanostructured metal oxides has been used as semiconductor sensors for the finding of toxic and tense gases in the air. For example, the surface effective nanomaterials show good sensor act for carbon monoxide, methane, methanol, and ethanol towards diverse gases such as ethanol, methane, nitric oxide, acetone, ammonia, hydrogen, and hydrogen sulfide.

### **(b) Food processing**

Nanotechnology could be also applied in the processing, production, safety, as well as packaging of food. A nanocomposite coating process progresses food packaging by placing anti-microbial agents that are flexibly on the surface of the coated film. Nanocomposites can increase or decrease the gas porousness of different fillers as it is needed for diverse goods. And also, nanocomposites can expand the mechanical and heat-resistance assets and lower the oxygen transmission rate. Now a days researches are being done to apply nanotechnology for the detection of chemical and biological substances for sensing biochemical changes in foods.

### **(c) Textiles**

The use of engineered nanofibers are used for making clothes which are water- and stain-repellent or wrinkle-free. In textile industries nanotechnology has been used to integrate tiny carbon particles membrane and guarantee full-surface protection from electrostatic charges for the wearer.

### **(d) Nano medicine**

The unique properties of nanomaterials is widely used in biological and medical research communities for various applications. The terms such as bio-nanotechnology, biomedical nanotechnology, and nanomedicine are used to describe this hybrid field. Functionalities could be added to nanomaterials by interfacing them with biological molecules or structures. The size of nanomaterials is similar to that of most biological molecules as well as there structures. As a result nanomaterials could be useful for both in vitro and in vivo biomedical research and their applications. Up until now the integration of nanomaterials with biology has led to the development of various diagnostic devices, analytical tools, contrast agents. And also used in physical therapy applications.

### **(e) Energy storage applications**

Transition metal oxides, such as  $\text{MnO}_2$ ,  $\text{SnO}_2$ ,  $\text{CO}_2\text{O}_4$ ,  $\text{ZnO}$ , and  $\text{MoO}_3$  have been widely studied for application as electrodes in high energy density redox super-capacitor, by taking the advantages of their fast kinetics and quasi-reversible redox processes. Moreover, it has been revealed that a mixture of transition metallic oxides could exhibit a coactive behaviour paying to their high

electrochemical performance as well as surface area and morphology of the materials. These are the key parameters for improved specific capacitance.

#### **(f) Catalysis for various fields**

Nanotechnologies approaches to catalysts gives new opportunities in the development of advanced heterogeneous catalysts. It is distinguished that the metal oxide catalysts have a vast importance in the heterogeneous catalysis, especially the chemical processes in various industries. The performance of metal-oxide catalysts depends on the nature, size, shape, and, surface area as well as their relationship is a critical factor in determining both catalytic activity and selectivity. According to the synthetic approaches towards the metal-oxide-based catalysts, their activity could be changed due to thermal treatments. Suitable nanomaterial-based photocatalyst would be categorized by (a) photoactive, (b) visible or near UV light, (c) chemically and biologically inert (d) cost-effective and (e) unharmed. Besides, the redox potential in hydroxyl radical it could be located in the bandgap of the semiconductor, the catalyst photochemically active as a sensitizer. Photocatalysis a method that uses bandgap radiation to create electron-hole pairs that could lead to redox reactions to the surface adsorbed material. The high degree has though by photocatalytic efficiency decreased by the recombination of photo-induced power supply and holes in semiconductors, and obstructing the practical application in water and air pollutants degradation.

#### **(g) Antibacterial applications**

The nanomaterials were effectively exploited in the nano-chemistry to develop the action of catalysts and their immobilization, in their active semiconductor engineering and the area of pharmaceutical and medical sciences. The metal-oxide nanomaterials illustrate that noticeable antimicrobial possession. Metals such as zinc, gold, cadmium and silver were used for existing periods as bactericidal and bacteriostatic agents for each by diverse assets and varieties of activity. There are numerous more metal-oxide-based nanomaterials and nanocomposites that reveal better antimicrobial belongings.

## **1.8. Introduction of Transition Metals Oxides**



Transition metal oxides are widely known for their large variety of physical and chemical properties. Transition metal oxides (TMOs) are the oxides of d-block elements in the periodic table with partially filled d-sub-shell. Due to its unique and fabulous properties such as they are well recognised by the research communities. Transition metal oxides manifest a number of properties that are helpful to catalytic applications, including thermal and mechanical stability needed to survive severe reaction conditions.

## **1.9 Zinc Oxide (ZnO)**

Zinc oxide (ZnO) is an inorganic compound and exists in earth crust in the form of zincite, which occurs rarely in nature. It generally becomes visible as white powder and almost unsolvable in water. ZnO a direct and wide band gap semiconductor, is one of the members of II-VI compounds. ZnO is self-activated n-type semiconductor and has hexagonal. Due to its low cost, good chemical stability, easy accessibility, large exciton binding energy, direct and wide band gap, high melting temperature (2248K), large cohesive energy, near UV-emission, high transparency in the visible spectral range, low electrical resistivity and resistant to high temperature electronic degradation. ZnO doped with the transition metals such as Cu, Fe, Ni, Co, Mn, Cr etc. have attracted much interested due to multifunctional device applications.

ZnO has become most suitable material for device applications. It has extensive history of being treated for shielding coatings on metals, pigments and in facial powder and reveals many industrial applications such as electro-luminous phosphorous, high power and high frequency electronic devices, piezo-electronic transducers, chemical gas sensors, surface acoustic wave devices, antibacterial treatment and photocatalysis. In recent times, manufacturing of ZnO nanostructures have encouraged concentrated research interests as these created applications in field emission flat panel displays, nano-particle dye synthesized solar cells, due to their prospective relevance in spintronics. The intrinsic defects, for instance the O-vacancies as well as Zn- interstitials act as donor.

### **1.9.1 Crystal structure of ZnO**

Zinc oxide has the wurtzite hexagonal crystal structure. In case of commercial zinc oxides, they show this crystal structure only under electron microscope examination. The precise shape of the crystal depends on the method of formation. In regular size zinc oxide vary between a circular needles and plate shaped crystals. Zinc oxide can be induced to a very large variety of crystalline shapes using specialized deposition methods, which is presently a very active area of research. Zinc oxides usually crystallizes in three different forms such as hexagonal wurtzite, cubic zinc blende and cubic rock salt. The cubic rock salt is rarely found. The wurtzite structure is most stable at certain ambient conditions.

### **1.9.2 Electrical properties of ZnO**

The fundamental study of electrical properties of ZnO nanostructures led a crucial path for developing their future applications in nano electronics. ZnO has quite large band gap of 3.3 keV at room temperature. The main advantages of such a large band gap include higher values of breakdown voltages, sustaining large electric fields, high-temperature and high-power operations. In the absence of doping the ZnO has n-type character.

### **1.9.3 Optical properties of ZnO**

ZnO generally have a transparent to visible light .But it strongly absorbs ultra violet light below 3655 Å. The absorption is typically stronger than other white pigments. When we consider the region of visible wavelengths, regular ZnO appears to be white but rutile. The band gap energy (between valence and Conducting bands) is 3.2 keV. Under ultra Violet light ZnO is photoconductive. The combination of optical and semiconductor properties makes doped ZnO a nominee for new generations of devices. The Solar cells require a transparent conductive coating, for that ZnO (doped) is the best materials. Intrinsic optical properties of ZnO nanostructures are being intensively studied for implementing it in the photonic devices. Photoluminescence (PL) spectra of ZnO nanostructure have been extensively reported in various fields. The excitonic emissions have been observed from the photoluminescence spectra of ZnO nanorods. It is revealed that quantum size confinement can considerably enhance the exciton binding energy.

### **1.9.4 Applications of ZnO**

- 1) ZnO nanoparticle is used in industrial sectors including synthesis of textile, food packaging, medical care, healthcare as well as construction and decoration
- 2) Rubber Manufacturing: ZnO is used for vulcanization of rubber and it also shields rubber from fungi and ultra violet light.
- 3) Ceramic Industry: In ceramic industry, considerable amount of zinc oxide is used for the enhancement in development of lustrous and shining surfaces.
- 4) Medicine: ZnO is used in creams, ointments, sunscreen lotions to protect skin damage caused by UV radiations. ZnO nanoparticles increase the antibacterial action of Ciprofloxacin. Also used as a drug carrier. It is widely used to treat leukemia and carcinoma cancer cell.
- 5) UV Absorber: Nano sized ZnO gives strong protection against UV radiations and is used for making ultra violet blocking sunglasses.

## Chapter 2

### LITERATURE REVIEW

Muthukumaran *et al* [1] formulated Co precipitation method to synthesized Cu doped ZnO and annealed it at 500°C in the presence of Ar. The synthesized sample have been determined by powered X-ray diffraction (XRD), UV-visible spectroscopy, Fourier transform infrared spectroscopy (FTIR). The hexagonal wurtzite structure was divulged from XRD analysis. It was found that sample does not have any impurities. The average crystalline size is been calculated and analysed. From this analysis it was found that there is a reduction in the average crystalline size. The reduction of average crystalline size was due to the distortion in the ZnO lattice by Cu<sup>2+</sup>. As a result there is a decrease in the nucleation as well as in subsequent growth rate due to the addition of Cu concentration. In the UV visible spectroscopy data, the bandgap values indicates that in the ZnO lattice the Cu is been doped. .

Shukla *et al* [2] investigated the outcomes of pure ZnO and copper (Cu) doped ZnO depending upon the properties of ZnO thin films which was developed by chemical bath deposition (CBD) dip coating method. For comparing the powder samples of pure ZnO and Cu-doped ZnO were developed at room temperature. UV-vis-NIR transmission spectroscopy were used to determined the optical properties. From the UV-visible spectroscopy data, it was discovered that the band gap for copper-doped ZnO samples decreases when it was compared to the undoped samples. This indicates that the copper doping can degenerates the impurity band and valence band of the ZnO system and the bottom of the conduction band moves toward the lower energy.

Thomas *et al* [3] synthesised ZnO nanoparticles by hydrothermal method. By X- ray diffraction method, studied structural properties of sample. The peaks were exactly fitted using Rietveld Refinement which revealed that ZnO nanostructures has a hexagonal wurtzite structure. W-H plot method was utilized for the determination of the lattice strain values and crystalline size. UV visible Spectroscopy was used to find the optical properties and value of bandgap of the ZnO nanoparticles which revealed that there is a reduction in the bandgap of ZnO from 3.18eV to 3.09eV due to sp-d

spin exchange interactions. Morphological properties of pristine and Mn doped ZnO nanoparticles were determined by FESEM which showed that the nanoparticles possess rod like structure. Rod like structure was found to be distorted due to doping. Both adsorption capacity and photocatalytic degradation of malachite green dye using ZnO and ZnO: Mn nanostructures as photocatalyst were verified. Pure ZnO nanostructures has lower photocatalytic activity than Mn doped ZnO nanostructures. The effects of Mn doping on the adsorption and photocatalytic behaviour is studied.

Mohan *et al* [4] synthesized ZnO nanoparticles by hydrothermal method under different conditions and studied various properties using different tools of nanomaterials. FTIR studies showed the presence of ZnO bonding and also the purity of the samples. The grain size was found to decrease with the rise in reaction temperature and to increase with reaction time. The formation of nanorods under same reaction temperature, also nanoflowers and nanospheres for different temperatures were revealed from TEM images. Due to variation in interplanar spacing the intensity of luminescence peaks is found to be changed. The UV-visible spectra helped to identify the rise in photon absorption in particles which are bigger in size and the change in bandgap value is also observed, which was due to the difference in size of nanoparticles.

Saad *et al* [5] prepared pure and Cu doped zinc oxide nanoparticles using hydrothermal synthesis with a solution of Zinc sulphate as precursor with phenylenediamine structure act as a directing agent in the appearance of different amounts of CuSO<sub>4</sub> and NaOH. Their structural properties were determined using XRD, UV-Visible spectroscopy, Raman spectroscopy and Photo Luminescence methods. The obtained data from these methods disclosed that the Cu doping does not change the ZnO wurtzite structure and the average crystalline size of pure ZnO was nm 13.05. Whereas in case of Cu doped ZnO there was a decrease in the average crystalline size (12-11nm). The UV - Visible spectroscopy data showed that the bandgap decreased from 3.18-3.11eV as the amount of Cu increased. The reason for decrease in bandgap was explained by spin swap p-d interactions between the band electrons and localized d one of the transition metal ions replacing the Cu<sup>+</sup>.

Kadam *et al* [6] studied the absorption kinetics and photocatalytic dye degradation efficiency of hydrothermally synthesized ZnO and ZnO doped with Manganese nanostructures. The structural studies from X-Ray diffraction data showed that ZnO, ZnO: Mn has hexagonal wurtzite structure.

Using UV visible Spectroscopy, it is found that the bandgap of ZnO decreases from 3.19eV to 3.14 eV which was due to sp-d spin exchange interactions. The photoluminescence studies revealed that the green emission is present in ZnO nanostructures and ZnO: Mn shows yellow emissions with small green components. The morphology and internal structure of synthesized ZnO and ZnO doped with Mn nanostructures were studied using FESEM which disclosed that the ZnO particle possess rod like structure. But due to doping rod like structure is distorted and shows a tendency of agglomeration. It was revealed from the photocatalytic dye degradation efficiency that Mn doped ZnO possess higher photocatalytic activity than pure ZnO nanostructures for Malachite Green dye.

Maleki *et al* [7] studied the ZnO:Cu nanoparticles by investing it as efficient synthesized catalyst for photodegradation of humic substance in aqueous solution under the sunlight. By using mild hydrothermal method ZnO doped with Cu was prepared. This method was characterized by using FTIR, powder XRD and SEM technique. The analysis of XRD revealed the crystalline hexagonal wurtzite structure of Cu-doped ZnO. The SEM data disclosed that the nanoparticles fabricated have heterogeneous morphology which is dominated by rod-shaped tetragonal crystals. Due to higher sunlight illuminance, the photocatalytic degradation of humic substance results in the increase of UV irradiation content of sunlight. Subsequently, the Cu-doped ZnO nanoparticles can be used as a well promising and efficient catalyst for degradation of humic substance under sunlight irradiation.

Singal *et al* [8] synthesized pure Cu doped ZnO nanoparticles using co precipitation method the morphological studies were done using Transmission Electron Microscopic analysis [TEM] which revealed that the genesis of quasi-spherical nanoparticles. The XRD analysis indicated that ZnO have hexagonal wurtzite nanostructures. These nanostructures were formed does not have any impurities, this is due to the proper substitution of Cu ions in the Zn sites. This substitution is done without affecting the crystal structure of ZnO. The effect of Cu doping on the structural and electrical properties of ZnO lattice has been studied and presented by proper systematization. For Cu doped samples decrease in lattice parameters as well as crystallite size. As Cu doping decreases DC resistivity as well as the activation energy also decreases.

Jose *et al* [9] synthesized biogenic ZnO nanostructures from Aloe vera leaf extract and degradation of an organic dye -Malachite Green from aqueous medium using the same catalyst. The adsorption mechanism was evaluated using Lagergren's pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetics models. The X-ray diffraction analysis confirmed the formation of hexagonal wurtzite ZnO. The crystalline size estimated from Scherrer equation (12.62nm) and Williamson Hall plot (19.27nm) had small variations. This difference was due to the difference in averaging the particle size. The FESEM micrograph showed the formation of randomly distributed ZnO nanosheets with well-defined. UV visible Spectroscopy revealed the optical bandgap energy of the synthesized ZnO. Using Tauc plot it was found as 3.19eV. With the aid of FTIR spectrophotometer the Zn-O stretching vibrations were recorded. Results on analysis disclosed that for the degradation of MG dye, biosynthesized ZnO nanosheets are very effective.

Joshi *et al* [10] synthesized Cu -doped ZnO thin films using Sol gel spin coating technique. For understanding the materials properties of thin film, various methods such as X-ray diffraction, scanning electron microscopy, Atomic Force Microscopy, Raman Spectroscopy and UV visible Spectroscopy methods were used. XRD results showed the polycrystalline nature with hexagonal wurtzite structure of ZnO. The polycrystalline nature of Cu-ZnO thin films is confirmed from by structural analysis. From structural analysis it is found that there is an increase in crystallite size upon increasing the doping concentration of thin films. In the optical studies addition, widening and narrowing of band gap for the Cu-ZnO thin films were discussed. This anomalous behaviour in band gap tuning that is widening and narrowing under different doping concentrations and annealing temperature is understood by the influence of induced stress effects. The induced stress effect is due to creation of intrinsic defects with band gap renormalization and Secondary phase formation.

Fu *et al* [11] reported the synthesis of Cu doped ZnO nanoparticles using Sol gel method. For the characterization of Cu doped ZnO samples XRD, XPS, UV visible Spectroscopy technique were used. Under UV irradiation the photocatalytic activity was tested for methyl orange degradation. XRD result indicated that ZnO nanoparticles are hexagonal wurtzite structure and the crystal growth of ZnO was inhibited by its Cu-doping. The doped Cu element existed as  $\text{Cu}^{2+}$  and its optimal doping concentration in ZnO is revealed to be 0.5 wt.%. The increased charge carrier

separation as well as enhanced surface hydroxyl groups were mainly due to Cu-doping which resulted in the enhancement of photocatalytic activity. The photocatalytic degradation of MO kinetics followed the first order reaction efficiently.



## Chapter 3

# CHARACTERIZATION TECHNIQUES

The measurement and characterization of nanoscale objects have always been a technical and metrological challenge. The developments in nanotechnology analysis and metrology over the last few years however, allowed for continuously smaller nanoscale dimensions to be measured and controlled. In order to determine the nanoparticles specific properties, we apply different characterization and analytical method depending on the physical or chemical quantity to be determined. Following are the different techniques used for determining the specific properties of nanoparticles based on the physical and chemical quantity which is to be determined.

### **3.1 Powder X-Ray Diffraction (XRD)**

X-ray diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material as well as providing information about its structure, size, chemical composition and physical properties. It is mainly based on constructive interference of monochromatic X-rays and a crystalline sample. The X- rays are generated from a cathode ray tube which is filtered to produce a monochromatic radiation which collimated to concentrate and is finally directed toward the sample.

#### **3.1.1 Principle**

Bragg's Law states that when the X-ray is incident onto a crystal surface, its angle of incidence,  $\theta$ , will reflect with the same angle of scattering,  $\theta$ . And, when the path difference,  $d$  is equal to a whole number,  $n$ , of wavelength,  $\lambda$ , constructive interference will occur.

It explains the relationship between an x-ray light shooting into, and it is reflected off from the crystal surface.

Bragg's Law is given by:

$$n\lambda = 2d \sin\theta$$

Where,  $\lambda$  = wavelength of the x-ray.

$d$  = spacing of the crystal layers (path difference).

$\theta$  = incident angle.

$n$  = an integer.

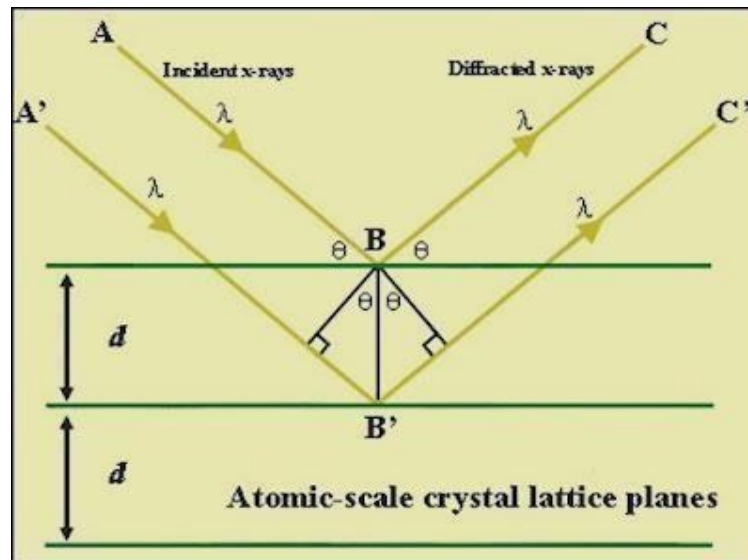


Figure 3.1: Bragg's law

### 3.1.2. Instrumentation

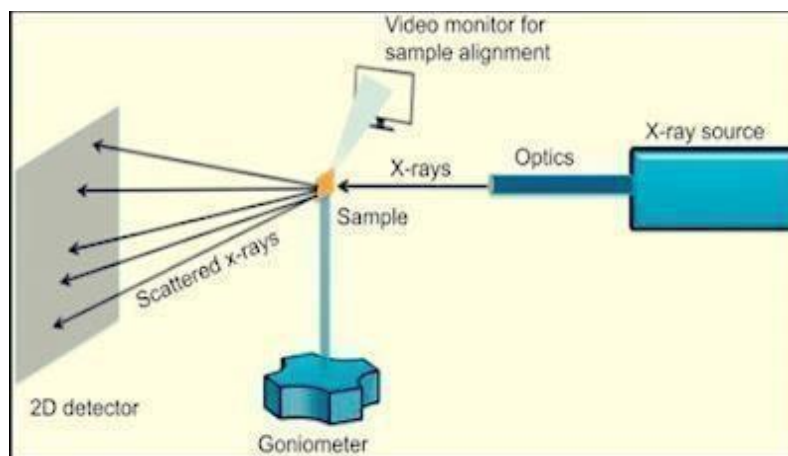


Figure 3.2: Instrumentation of Powdered X-Ray spectrometer.

X-ray spectrometer consist of three basic elements: a X-ray tube, a sample holder, and an X-ray detector. The X-rays are generated in a cathode ray tube by heating a filament to produce electrons. The electrons that are accelerated moves towards a target by applying a voltage that leads to the bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, a characteristic X-ray spectra is been produced. These spectra consist of several components in which the most common is  $K\alpha$  and  $K\beta$ . The specific wavelengths are the characteristics of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochromators is required to produce monochromatic X-rays. These monochromatic rays are needed for diffraction. Copper is the most common target material for single-crystal diffraction, with  $CuK\alpha$  radiation ( $1.5418\text{\AA}$ ). These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor..

### **3.1.3. Applications**

- Structure of crystals is determined.
- Measurement of sample purity
- Polymer characterization is done.
- Identification of unknown materials such as (minerals, inorganic compounds)
- Particle size determination:
  1. Spot counting method.
  2. Broadening of diffraction lines.
  3. Low angle scattering.

### **Advantages**

- It is a rapid and powerful technique for identifying unknown minerals and materials.
- It only requires preparation of a minimal sample for analysis

- Interpreting the resulting data is relatively straightforward.
- XRD measurement instruments are widely available.

### **Disadvantages**

- To best identify an unknown powder material, the sample should be homogeneous.
- Typically XRD analysis requires access to standard reference data .
- Preparation of samples often requires grinding them down to a powder.

## **3.2. UV-Visible Spectroscopy**

Spectroscopy is the measurement and interpretation of electromagnetic radiation absorbed or emitted when the molecules or atoms or ions of a sample move from one energy state to another energy state. And it is related to the interaction of light with matter. UV spectroscopy is a type of absorption spectroscopy in which light of the ultra- violet region (200-400 nm) is absorbed by the molecule which results in the excitation of the electrons.

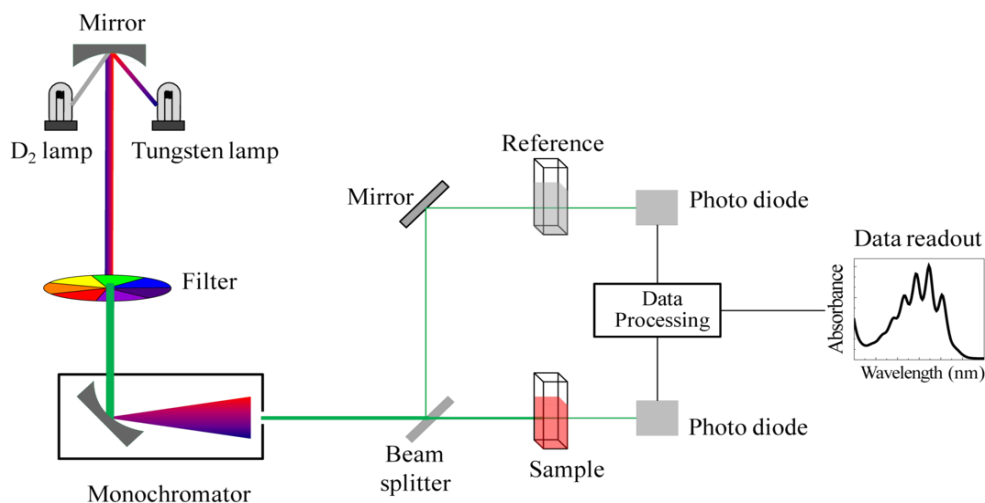
### **3.2.1 Principle**

Beer-Lambert law states that the quantity of light absorbed by a substance dissolved in a fully transmitting solvent is directly proportional to the concentration of the substance and the path length of the light through the solution.  $A = \epsilon bc$ , where  $\epsilon$  is the molar absorptivity of the absorbing species,  $b$  is the path length, and  $c$  is the concentration of the absorbing species.

### **3.2.2 Instrumentation**

The UV-Visible spectrophotometer consists of two parts a spectrometer and a photometer. The spectrometer consists of a light source, monochromator, sample and reference cells and the photometer consist of photodiode (detector), amplifier, recording device. The light source used here is Tungsten filament lamps and Hydrogen-Deuterium lamps which are the most widely used and are the suitable light sources as they cover the whole UV region. Tungsten filament lamps are rich in red radiations that they emit the radiations of 375 nm, while the intensity of Hydrogen-

Deuterium lamps falls below 375 nm. The monochromators generally are composed of prisms and slits. Most of the spectrophotometers are double beam spectrophotometers. The various wavelengths of the light source are separated by the prism and are then selected by the slits such that the rotation of the prism results in a series of continuously increasing wavelengths to pass through the slits for recording purposes. The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism. There is a sample cell and reference cell in which contains the sample and reference solutions. Then one of the two divided beams are passed through the sample solution and the second beam passes through the reference solution. There are two photodiode which serve the purpose of the detector in UV spectroscopy. One of the photodiodes receives the beam from the sample cell and the second photodiode receives the beam from the reference cell. This results in the generation of pulsating or alternating currents in the photocells. The alternating current generated in the photocells is transferred to the amplifier. The amplifier is coupled to a small servo meter and the current generated in the photodiode is of very low intensity. The main purpose of the amplifier is to amplify the signals many times so we can get clear and recordable signal. Most of the time amplifier is coupled to a pen recorder which is connected to the computer. The computer stores all the data generated and produces the spectrum of the desired compound.



**Figure 3.3: Instrumentation of UV-Visible Spectrophotometer**

### **3.2.3 Applications**

1. Detection of impurities.
2. Structure of elucidation of organic compound.
3. Quantitative analysis.
4. Molecular weight determination.
5. Distinction between cis & trans isomerism.
6. Effect of conjugation.

### **3.3. FESEM**

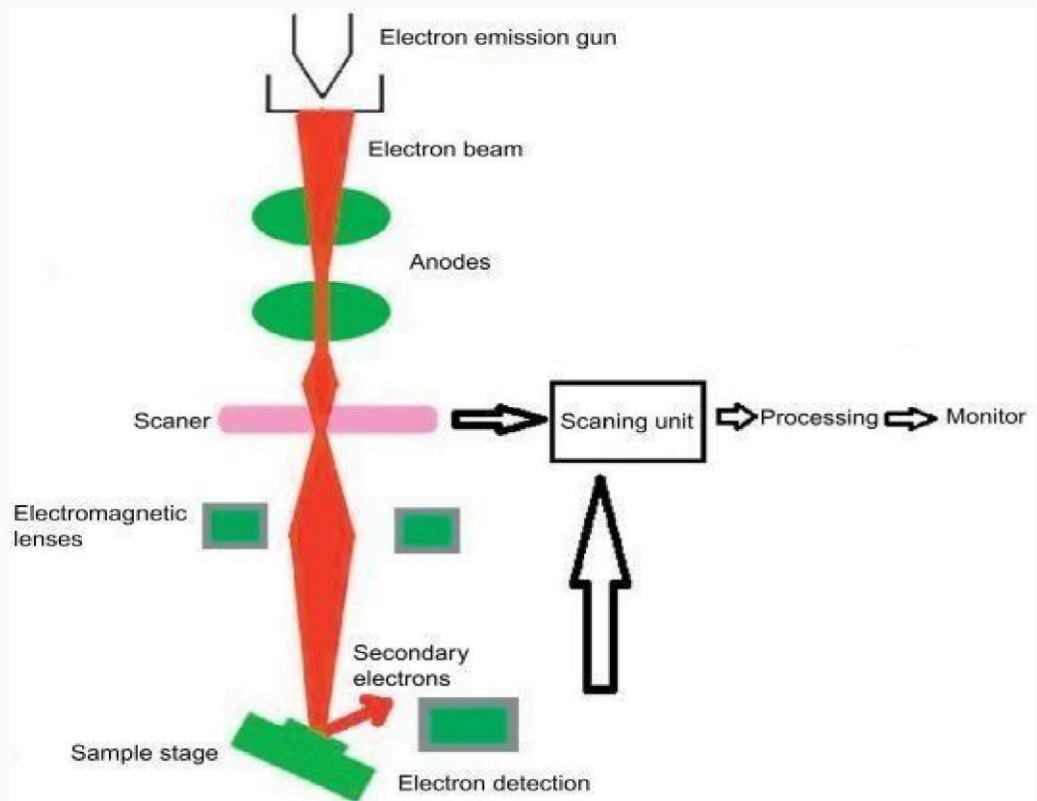
Field emission scanning electron microscopy (FESEM) provides topographical and elemental information at magnifications with virtually unlimited depth of field. FESEM produces clearer, less electrostatically distorted images with spatial resolution.

#### **3.3.1. Principle**

A field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage.

#### **3.3.2. Working**

Electrons are liberated from a field emission source and accelerated in a high electrical field gradient. Within the high vacuum column these so-called primary electrons are focused and deflected by electronic lenses to produce a narrow scan beam that bombards the object. As a result secondary electrons are emitted from each spot on the object. The angle and velocity of these secondary electrons relates to the surface structure of the object. A detector catches the secondary electrons and produces an electronic signal. This signal is amplified and transformed to a video scan-image that can be seen on a monitor or to a digital image that can be saved and processed further.



**Figure 3.4: Instrumentation of FESEM**

### **3.3.3 Applications**

- Semiconductor device cross section analyses for gate widths, gate oxides, film thicknesses, and construction details.
- Advanced coating thickness and structure uniformity determination.
- Small contamination feature geometry and elemental composition measurement.
- Characterization of very fine specimen features

### **Advantages**

- The ability to examine smaller-area contamination spots at electron accelerating voltages compatible with energy depressive spectroscopy.

- Reduced penetration of low-kinetic-energy electrons probes closer to the immediate material surface.
- High-quality, low-voltage images with negligible electrical charging of samples (accelerating voltages ranging from 0.5 to 30 kilovolts).
- Essentially no need for placing conducting coatings on insulating materials.
- For ultra-high-magnification imaging



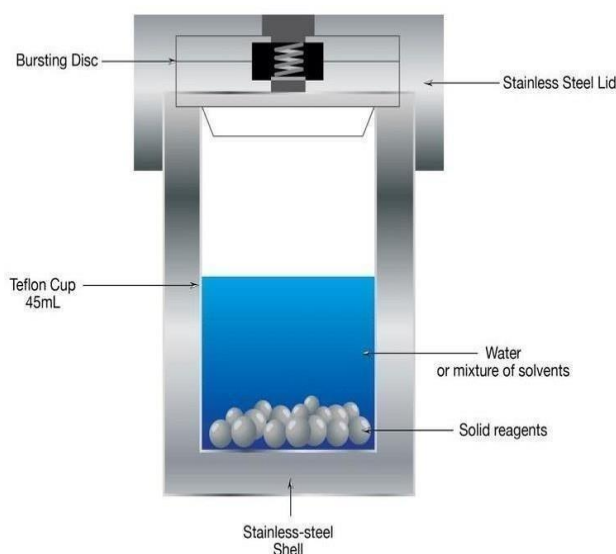
# Chapter 4

## SYNTHESIS AND CHARACTERIZATION

### 4.1. Hydrothermal Method

Hydrothermal synthesis is defined by reaction of solid material with aqueous solution in a reaction vessel at high temperature and pressure and leads towards small particles deposition. Hydrothermal is a solution reaction –based approach. The process is referred to as hydrothermal because water is used as a solvent in this method. The hydrothermal process is performed in a autoclave where processing conditions are controlled by adjusting temperatures. The pressure attained are in the range of 10 to 150 kilobars which depends on the chosen temperature of water. Temperature is increased beyond the boiling temperature of the water, attaining vapor saturation. The powders are either crystalline or amorphous depending on the applied temperature.

The hydrothermal method has a great contribution to modern science and technology due to homogeneous precipitation, low cost, friendly environment, easy scaling up, and pure final product. And also the hydrothermal method can be divided into hydrothermal synthesis, treatment, and crystal growth, treatment of organic wastes and prepare functional ceramic powder.



**Figure 4.1: Autoclave Reactor**

## **Advantages**

- Precise control of size in nanoparticles.
- Low melting point
- High vapor pressure
- Produce nanocrystal with crystallinity.

## **Disadvantages**

- Crystal growth information cannot observe directly
- Expensive autoclave
- Difficult to control
- Accidental explosion of the high pressure vessel cannot be ruled.

## **4.2. Synthesis of nanoparticles by Hydrothermal method**

Cu doped ZnO nanostructures (0,2.5,5%) were synthesized by simple hydrothermal method using zinc acetate dihydrate and copper acetate monohydrate as metal precursor. For the synthesis of undoped ZnO nanoparticles, 1M Zinc acetate dissolved in 50 ml distilled water stirred well. The solution is then placed in Teflon lined autoclave and placed in the oven for about 150°C for 2 hours. Then the filtered solution is washed, dried and packed for further characterization and application studies. For Cu doped ZnO nanoparticles, copper acetate was added to Zinc acetate solution with respect to the concentration (2.5,5%) and followed the same procedure as above after adjusting the pH (9-11) using ammonium hydroxide. Pure ZnO, 2.5, and 5 % Cu doped ZnO samples were respectively named Zn, CZ2.5, and CZ5 for convenience.

## **4.3. Photocatalytic dye degradation using Cu doped ZnO nanostructures**

Photocatalytic degradation of methylene blue dye under sunlight carried out in which 10ppm dye in 200mL initial concentration used. For evaluating the photocatalytic efficiency of the sample prepared, 200mL of methylene blue solution with initial concentration of 10ppm is used. 10mg of prepared nanoparticle added to the above dye solution and kept it in dark for half an hour with continues stirring so as to attain the adsorption- desorption equilibrium. It is then irradiated under

sunlight. Photocatalytic dye degradation of samples was evaluated using UV Visible spectroscopy by taking known number of samples at regular intervals into the UV Visible spectrometer.

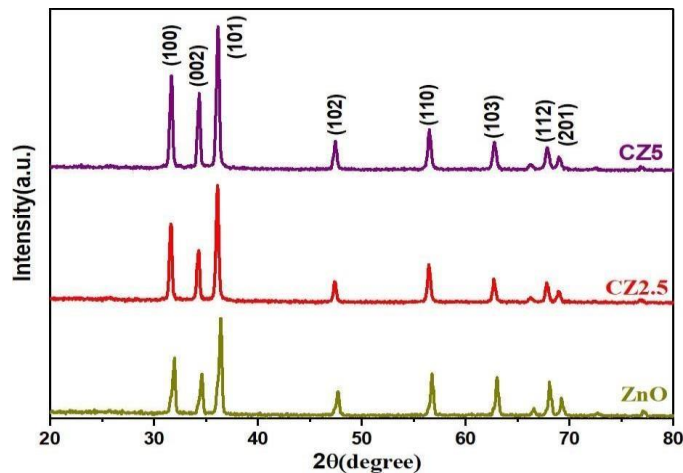
# Chapter 5

## RESULT AND DISCUSSION

### 5.1. XRD analysis

The crystal structure of the sample was analysed using XRD spectrometer. The figure 5.1 shows X-ray diffraction patterns of ZnO and Cu doped samples. From the XRD spectra analysis, we can determine the crystalline size as well as the sample purity. The peaks have been found to be quite sharp and intense which implies high crystallinity of sample. Peaks were observed at  $2\theta$  values of  $31.52^\circ$ ,  $34.15^\circ$ ,  $35.95^\circ$ ,  $47.28^\circ$ ,  $56.28^\circ$ ,  $62.52^\circ$ ,  $66.11^\circ$ ,  $67.68^\circ$ ,  $68.83^\circ$ ,  $72.22^\circ$  and  $76.84^\circ$  corresponds to the ZnO crystal planes. Major diffraction peaks of (100), (002), and (101) planes are in good agreement with the hexagonal wurtzite ZnO crystal structure (JCPDS No. 36-1451) which is the most stable ZnO phase. From the figure 5.1 we can find that there are no peaks other than ZnO and in addition to that there was no diffraction peak of CuO were observed, confirming the proper substitution of Cu over the Zn sites

[8,14].



**Figure 5.1: XRD Spectra of ZnO and Cu doped ZnO nanorods synthesized by hydrothermal method at  $150^\circ\text{C}$  for 2hr**

The average crystalline size can be calculated using the Debye Scherrer formula by estimating the full –width at half maximum of the most intense diffraction peak (101).

The Debye-Scherrer formula is given by

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

Where D is the average crystalline size in nm, K is the Scherrer constant,  $\lambda$  is wavelength of X-ray(1.514),  $\theta$  is the Braggs angle in degree and  $\beta$  is the full width half maximum in radians [2]. Scherrer constant denotes the shape of the particle and its value is most commonly taken as 0.9.

The average crystalline size and the corresponding micro strain is calculated and shown in table 1. From the table it is clear that CZ2.5 shows crystalline size which is smaller than pure ZnO. The decrease in crystalline size may due to the  $\text{Cu}^{2+}$  addition which decreases the nucleation and growth rate [1,8]. The existence of  $\text{Cu}^{2+}$  ions in the ZnO lattice restricted the crystal grain size increment.

Sl. No	Sample ID	FWHM( $\beta$ ) (degree)	2 $\theta$ (degree )	Debye Scherrer method D(nm)	Strain( $\epsilon$ ) ( $10^{-3}$ )
1.	ZnO	0.236	35.45	35.21	0.00098
2.	CZ2.5	0.320	35.39	26.08	0.00133
3.	CZ5	0.293	36.09	28.49	0.00121

**Table 1: Crystalline size and strain calculated using Debye-Scherrer formula**

## **5.2. Optical studies**

The UV visible absorption spectra of the synthesized undoped and doped ZnO nanoparticles which is carried out to study the effect of Cu doping on the ZnO lattice, are shown in figure 5.2[2]. Using Tauc relation, band gap energy can be calculated as,

$$\alpha h\nu = A (h\nu - E_g)^n$$

Where A is the proportionality constant, h is Planck's constant,  $\nu$  is the frequency of incident photon in Hz,  $E_g$  is the bandgap energy in eV and n is the power factor which has values  $\frac{1}{2}$  for direct

allowed transitions, 3/2 for direct forbidden and 2 or 3 for indirect allowed or indirect forbidden transitions.  $n=1/2$  is taken here because ZnO is a direct band gap material [3].

By plotting incident photon energy ( $h\nu$ ) versus  $(\alpha h\nu)^2$  and extrapolating the curve, the band gap energies of the samples can be calculated. The energy was calculated as 3.18eV, 3.15eV and 3.22 eV for Zn, CZ2.5 and CZ5 respectively. From the analysis of band gap, it is observed that bandgap of CZ5 is higher than the pure ZnO. It is observed that the bandgap of the material firstly decreased at low composition Cu doping and then increased as the concentration increased implies that the bandgap of prepared nanorod can be tuned while doping with transition metals. Variation in bandgap energy can be explained based on quantum size effect and modified electronic structure [14,15]. The variation in band gap energy with the addition of Cu doping may also arise as a result of decrease in strain which is due to the increase in the number of unit cells per particle [16].

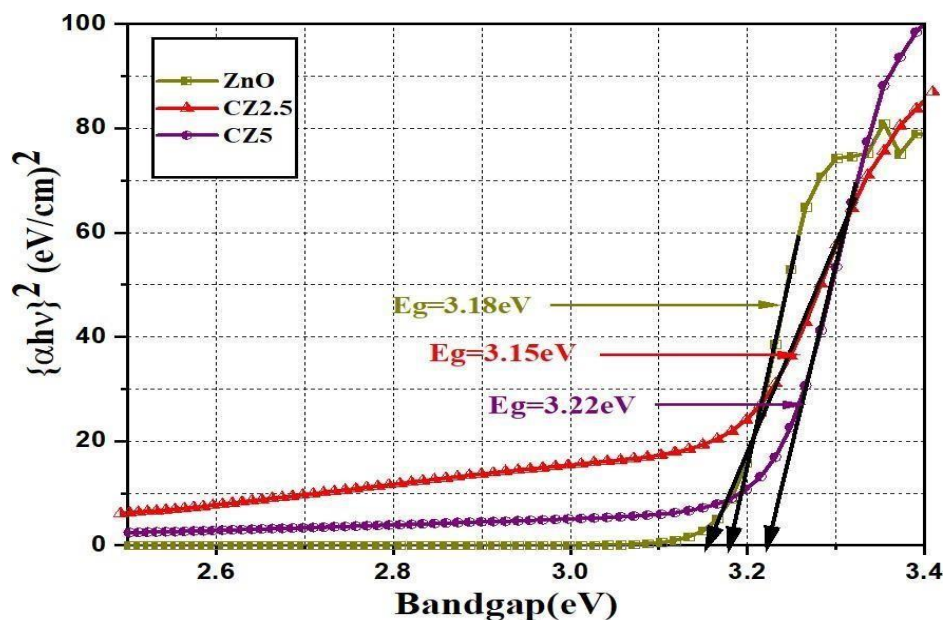
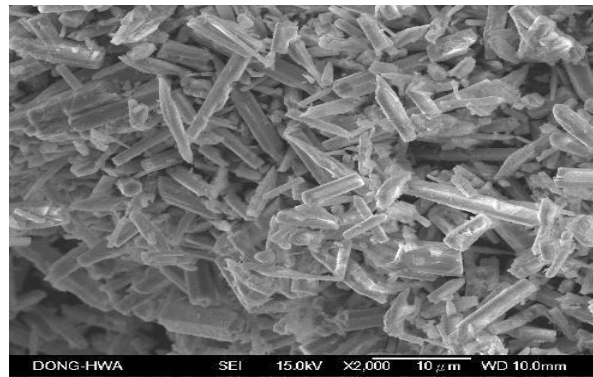


Figure 5.2: Tauc plot corresponding to ZnO and Cu doped ZnO nanorod synthesized by hydrothermal method at 150°C for 2hr

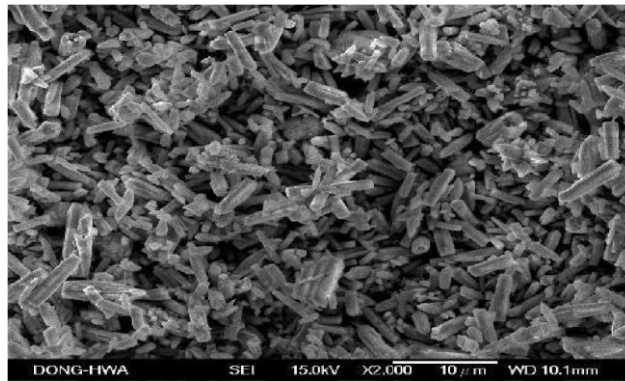
### 5.3. FESEM analysis

The surface morphology of nanoparticles can be determined using FESEM. The FESEM images of pure and doped ZnO are shown in figure 5.3. From all these images it is observed that the sample shows nano rod-shaped morphology for doped as well as undoped ZnO. These images also indicate

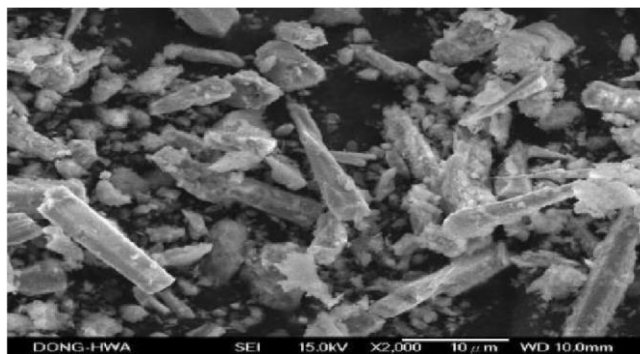
that the shape as well as morphology of ZnO nanoparticle changes with the increasing concentration of copper concentration. Due to this in the Cu-doped ZnO samples, the particles seem to be agglomerated [3].



(a)



(b)

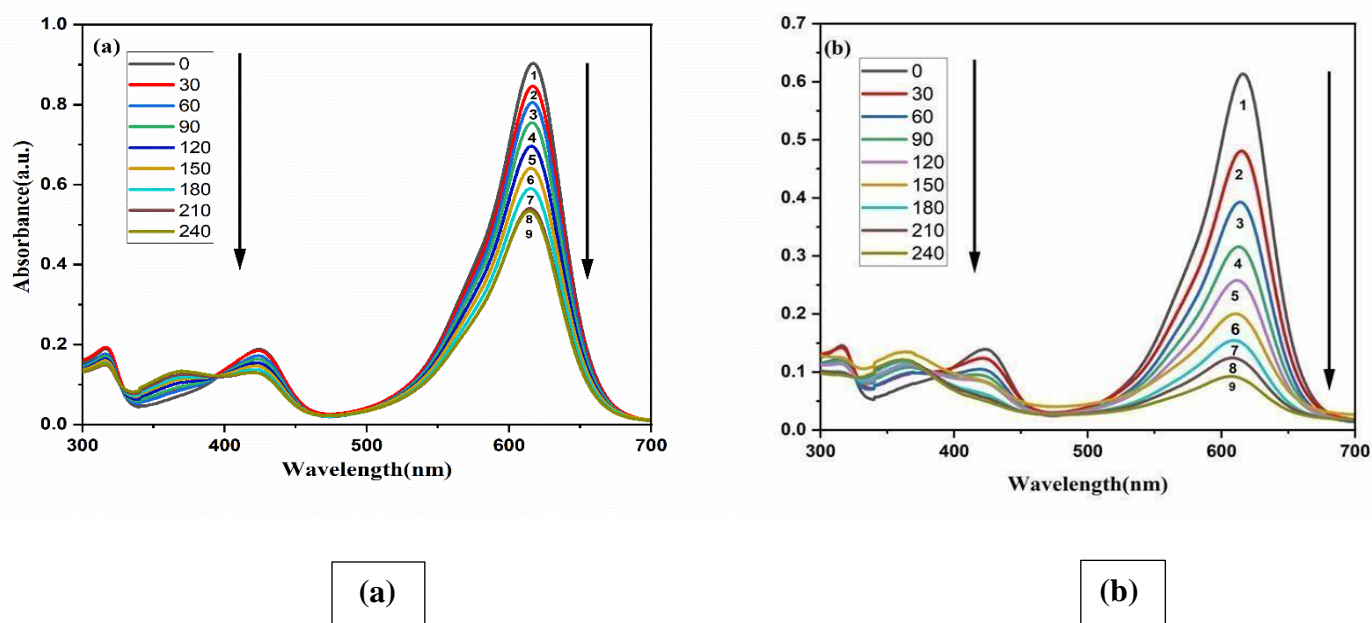


(c)

**Figure 5.3: FESEM images of (a) ZnO (b) CZ2.5 and (c) CZ5 samples hydrothermally synthesized at 150°C for 2hr**

## 5.4. Photocatalytic measurements

The photocatalytic dye degradation potential of synthesized samples was investigated by using MB as a model dye. The absorption spectra corresponding to MB dye with Pure and Cu doped nano catalyst were evaluated for different time intervals. UV- Visible absorption spectra of MB dye solution shows maximum absorption band around 663nm. The dye degradation study was done with pure ZnO and CZ1 samples. The reason behind choosing CZ1 is that, it has smaller crystalline size as compared to other samples, thus the higher surface-to-volume ratio of CZ1 increases the adsorption of dye over the catalyst surface [10]. Figure 5.4 shows the variation in absorbance spectra of MB dye in presence of nano catalyst. The intensity of absorption spectra decrease with an increase in irradiation time shows the degradation of MB dye under sunlight [16].



**Figure 5.4: Absorbance spectra of MB dye using ZnO nanostructure(a) degradation of MB with ZnO and (b) CZ2.5 samples hydrothermally synthesized at 150 C for 2hr**



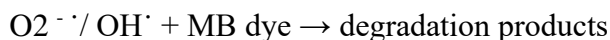
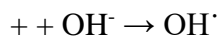
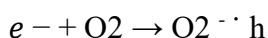
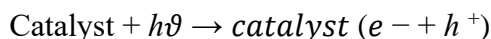
The photocatalytic efficiency of the sample can be calculated as:

$$\text{Degradation rate } \eta (\%) = \frac{C_0 - C}{C_0} \times 100\% = \frac{A_0 - A}{A_0} \times 100\%$$

$C_0$  is the initial concentration of dye solution and  $C$  is the final concentration,  $A_0$  denotes the initial absorbance of MB dye solution and  $A$  is the final absorbance. About 40% of the dye is degraded from the water with ZnO nano catalyst. For CZ2.5-containing dye solution, degradation of dye increased above 81% within 3 hours. Thus it can be concluded that CZ1 is a better candidate for photocatalytic dye degradation of MB dye as compared to pure ZnO nanoparticles.

### **Mechanism of photocatalysis**

MB dye solution with nano catalyst is irradiated under sunlight where electron-hole pair generation happens. These induced charge carriers move to the surface of catalyst and cause redox reaction. The positively charged holes react with the  $H_2O$  producing OH radical and negatively charged electrons react with  $O_2$  generating superoxide oxygen radicals. Under sunlight irradiation, it is observed that the absorption peak corresponds to Methylene blue which is at 663nm get decreases.



The photocatalytic activity shown by ZnO nanorod is due to the presence of various defect states including oxygen vacancies, interstitial zinc atom, zinc vacancies, etc. Here the cationic MB dye receives an electron from the excited donor energy level and results in degradation. Degradation of dye can be observed by adding CZ1 to the dye solution. CZ1 possesses low crystalline size as observed in XRD chosen for achieving enhanced photocatalytic activity compared to other samples. The addition of Cu ions onto the ZnO lattice may alter the physical and chemical properties of pristine ZnO. The mechanism behind this can be explained as that the presence of Cu and defect states acts as a better pathway for the electrons and holes generated by the ZnO catalyst. This

decreases the recombination of electron-hole pairs, results in the production of highly oxidizing and reducing agents. Here generation of OH radicals enhance the rate of degradation of dye with the CZ1 catalyst. Also, it can clarify with the introduction of surface defects due to Cu doping and the production of space charge at the surface which suppresses the electron-hole recombination and contributed to the enhancement of photocatalysis [17][11] .

## Chapter 6

### CONCLUSION

Cu doped ZnO nanorod with crystalline size ranging between 35-28nm synthesized by viable hydrothermal method. Cu doping on ZnO lattice resulted in variation in its crystalline size with CZ1 showing less crystalline size as compared to Zn and CZ2 samples. UV Visible absorbance spectra data revealed that the bandgap undergoes a redshift for the CZ1 sample and undergoes an increase in bandgap for the CZ2 sample. The photocatalytic dye degradation efficiency of pure and Cu-doped ZnO samples was investigated by the degradation of MB dye. The results demonstrated better photocatalytic activity for dye solution with CZ1 catalyst. CZ1 having a less crystalline size and possessing a bigger surface-to-volume ratio in nanorod morphology increased the surface activity. Photocatalytic properties of ZnO nanoparticles were enriched upon Cu doping and the enhancement is due to the combined effect of ZnO and Cu doped particles. Cu doped ZnO nanoparticles reported in this paper are thus stated as an effective material for photocatalytic application.

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