

**Study of Zn Doping Induced Effects on Physical
Properties of CuO Nanostructures**



MS Thesis

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- X-rays diffraction
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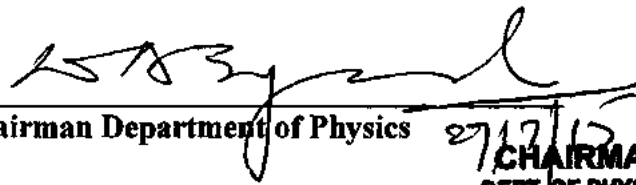
Study of Zn Doping Induced Effects on Physical Properties of CuO Nanostructures

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This Thesis submitted to Department of Physics
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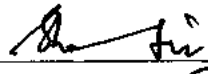
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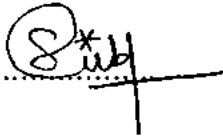


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Dedicated

to

Beloved Parents and Teachers

&

Uncle Prof. Maqsood Hussain

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Abstract

Metal oxides nanomaterials have attained a remarkable attention over few decades due to their potential applications in different fields. In comparison to all other metal oxides, CuO is one of the most common and widely used materials in nanoscience and technology. CuO is a p-type semiconductor having a direct band gap (1.22 - 1.55 eV). In present work, undoped and Zn doped CuO nanostructures have been successfully synthesized via chemical co-precipitation method at low temperature. All the prepared samples have been characterized using different techniques such as XRD, FTIR, SEM, EDS, BET and UV Spectroscopy. XRD results demonstrate the formation of single phase CuO structure for both cases of undoped and Zn doped CuO samples. The crystallite size of CuO is observed to increase with the increase in Zn dopant concentration. The morphology and particle size of the prepared samples have been analyzed using SEM. The prepared materials exhibit nanostructured morphology with average particle size of 26 nm. EDS spectra show that Cu and Zn are the major elements present in samples. The surface area of CuO decreases with increasing dopant concentration. The specific surface area of undoped CuO is 234 m²/g. The optical band gap of undoped CuO nanostructure is observed to be 2.39 eV.

Chapter No. 1

Introduction

1.1 What is Nanotechnology?

Nanotechnology is the study of very small-sized materials or structures. In nanotechnology, the dimension of these small size materials is in range from sub nanometer to several hundred nanometers. The physical properties of materials at nanometer scale are much different and their crystal structures are very stable at low temperature as compared to bulk. These nanomaterials have at least one dimension less than 100 nm.

A Greek word 'nano' which have meanings of dwarf is the base for word nanotechnology. In nanotechnology we study biology, chemistry, physics and engineering at nanolevel. The purpose of nanotechnology is to build new materials using the special properties arises at nanoscale. Most importantly surface to volume ratio of materials at nanoscale becomes large. This change in surface to volume ratio affects the properties of materials like optical, chemical, electrical etc [1].

Nanotechnology can be defined as;

- The study of synthesis, applications of materials and devices at nanometer scale is called nanotechnology.
- Nanotechnology deals the matter at atomic and molecular scale.
- Nanotechnology contains the idea of physics and chemistry of materials.

1.1.1 History of Nanotechnology

- (i) In 1914, Richard Adolf Zsigmondy was the person who used nanometer scale for characterizing particle size.
- (ii) Concept and idea of nanotechnology was first introduced by a physicist, Professor Richard Feynman in 1959 by saying "There is plenty of room at bottom".

- (iii) In 1976, Granqvist and Buhrmann published an article on synthesis of nanocrystals using inert-gas evaporation technique.
- (iv) In 1979, Late Norio Taniguchi was the 1st person who used the term nanotechnology.
- (v) 'Engines of creation, coming era of nanotechnology' is the 1st book on nanotechnology which was published in 1986.
- (vi) The first journal on nanotechnology was published by Chris Peterson in 1990 [2].

1.1.2 Importance of Nanotechnology

In recent years, nanotechnology has become very attractive among the researchers. It is very useful in our daily life for example in health and medical technology. It is also used for diagnostics and treatment of different diseases like cancer and tumors. This new technology has significantly enhanced the efficiency of treatment of different diseases. In textile industries, nanotechnology has brought exceptional change, for example, for the improvement of life time of clothes and to preserve them from harmful bacteria and viruses, nanoparticles are used. Therefore we can use these clothes for long period of time without any side effect [3, 4]. Nanotechnology is used to make sensitive chemical and gas sensors which can detect the gas at a very small concentration at room temperature. In the field of agriculture, scientists and experts are using nanoparticles to improve the production yield and to keep away the seeds and crops from the dangerous insects.

1.2 Applications of Nanotechnology

Nanotechnology has very wide range of possible applications in industries including biomedicine, energy, chemicals, agriculture and electronics etc. Carbon nanotubes are good conductors of electricity and heat as compared to copper and diamond. CNTs are much stronger than steel. Nanomaterials such as Bucky balls, single-walled Nanotubes (SWNTs) and microcapsules are known as smart materials.

Nanomaterials are in commercial use for several years or decades. There are so many commercial products available today. The most common commercial products are stain-resistant and wrinkle-free textiles, cosmetics, sunscreens, paints and varnishes. Some applications of nanotechnology are shown in figure 1.1.

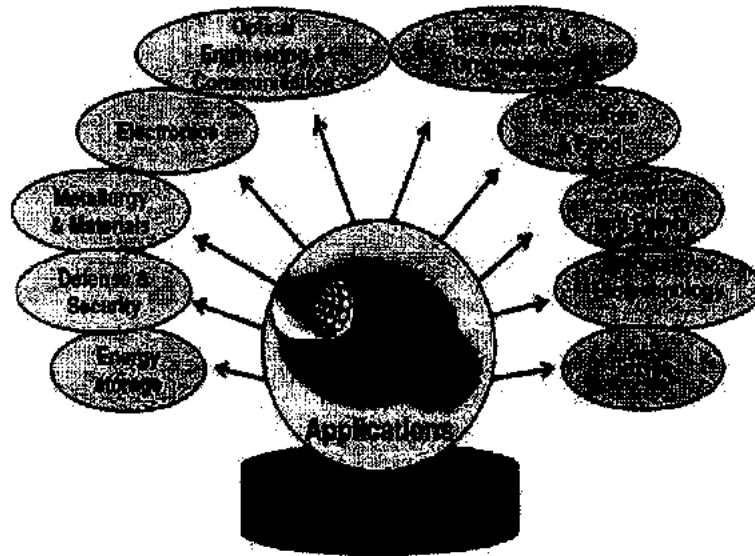


Figure: 1.1: Nanotechnology and its applications [5]

1.2.1 Electronics

Due to very rapid improvement of the electronic industry, it is very essential to fabricate such electronic devices which are more efficient, light in weight, having small size and more importantly these devices should consume less amount of power. With the help of nanotechnology, one can make display screens with less weight and thickness as a result, it consumes low power and memory devices having higher storage capacity can be designed. Cadmium selenide nanocrystals are being used to fabricate flexible electronic circuits. The examples of nanotechnology based electronics devices are small size memory chips, smart

phones, and light emitting diodes (LEDs), metal-oxide-semiconductor field - effect transistor, LASER etc.

1.2.2 Medical

Nanotechnology has brought a revolutionary development in the field of medicine. Drug delivery to diseased cells is possible by synthesizing the nanoparticles having size comparable to the molecular size. Nanocapsulations are used to inject the drugs in the human body. Gold nanoparticles are used to destroy the cancer cells in a human body. Cobalt nanoparticles show magnetic behavior which may find potential applications in medical engineering. The carbon allotrope such as graphene has nanostructure and can be used as hindrance against the HIV aids virus.

1.2.3 Food

Nanotechnology has a great impact in food technology because by nanoparticles, it is possible to preserve food for longer period and the growth of food can also be enhanced. In food science, there are so many applications regarding nanoparticles such as detection of bacteria, food shelf life, improvement in the food flavor and packing of food to keep it fresh for few days. This is all about the quality and safety of the food.

1.2.4 Industries

Nanotechnology has also applications in sports. It is used to make different materials used in sports. Carbon nanotubes are used in making hockey sticks, basket ball and sports shoes to make them lighter and harder to improve their performance and life time.

Nanotechnology is useful to make sensitive chemical and gas sensors which can detect very small concentration of gas at room temperature. Such chemical and gas sensors are made by using CNT'S, nanoparticles of Pd and nanowires of zinc oxide (ZnO). The

electrical characteristics of such sensing materials are changed either by a very little quantity of gas or by chemical particles [6].

1.3 Classification of Nanomaterials

Nanomaterials are classified into three types which are as follows [7];

- Zero Dimensional Nanomaterials
- One Dimensional Nanomaterials
- Two Dimensional Nanomaterials

1.3.1 Zero Dimensional Nanomaterials

When all the dimensions of materials are within the nanometer (no dimension else than nm) then they are called zero-dimensional nanomaterials. Examples of these materials are nanoparticles and quantum dots.

(i) Nanoparticles

Nanoparticles are the most common example of zero-dimensional nanomaterials. A material which has particle size less than or equal to 100 nm is known as nanoparticles. The properties of nanoparticles are very different from their bulk counterparts due to their small size. Nanoparticles are link between bulk materials and molecular or atomic structures. Nanoparticles can be,

- crystalline or amorphous
- metallic, polymeric, or ceramic
- have various shapes and forms

The typical morphology of nanoparticles is shown in figure 1.2.



Figure: 1.2: Overview of nanoparticles morphology [8]

(ii) Quantum Dots

Those zero-dimensional nanomaterials which are lesser than 10 nm in size are called quantum dots. Degree of freedom in case of quantum dots is zero because all three dimensions are confined. The quantum dot is comprised of few thousands of electrons. The number of electrons, shape and size can be controlled in quantum dots which are used in many useful purposes.

If one electron leaves or enters the structure, there is enormous variation in the characteristics of many quantum dots. Quantum dots are used in optoelectronic devices, optical and information storage. Color coded quantum dots (CCQD) are used in DNA testing.



Figure: 1.3: Quantum dots [9]

1.3.2 One Dimensional Nanomaterials

The materials in which two dimensions growth is at nanoscale but there are no restrictions on third dimension are known as one dimensional nanomaterial. Morphology of these one-dimensional nanomaterials includes nanowires, nanotubes, nanobelts and nanorods etc. Nanowires, nanobelts, nanotubes and nanorods are also known as quantum wires. One of the significant applications of one dimensional nanomaterial is in display technologies because due to change in direction of electric field cause the change in reflectivity of these materials.

One-dimensional nanomaterials can be,

- Crystalline or amorphous
- Metallic, polymeric, or ceramic
- Chemically pure or impure
- Single crystalline or polycrystalline

The typical morphology of nanowires, nanotubes and nanobelts is shown in figure 1.4(a, b, c).

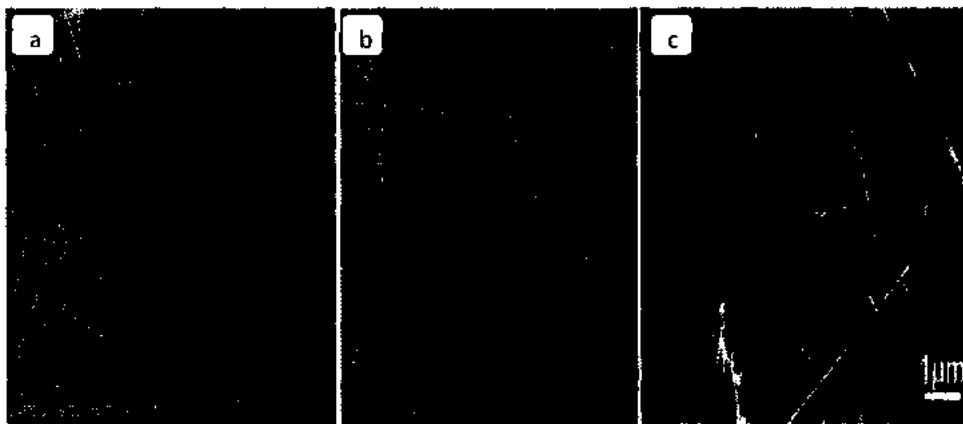


Figure: 1.4: Image of a) Nanowires, b) Nanotubes and c) Nanobelts morphology [10]

1.3.3 Two Dimensional Nanomaterials

Those materials which have one dimension at nanoscale and other two dimensions are not restricted are called two dimensional nanomaterials (electron or hole motion is bound in only one spatial direction) such as quantum well and thin film as shown in figure 1.5.

These two-dimensional nanomaterials are also known as quantum well. The quantum well can be defined as, “a structure where one dimension is comparable to exciton Bohr radius”. The energy of quantum well is given by,

$$E = n^2 \pi^2 \hbar^2 / 2mL^2 \dots\dots\dots 1.2$$

Where ‘m’ is mass of electron and ‘L’ is thickness of quantum well which is comparable to De-Broglie wavelength of the carriers (electron, hole).

Nano films, Nano layers, and Nano coatings are the main examples of two-dimensional nanomaterials. Two-dimensional nanomaterials can be,

- Crystalline or amorphous
- Metallic, ceramic, or polymeric
- Deposited on a substrate
- Hydrophobic (water repellent) and hydrophilic (water absorbent)

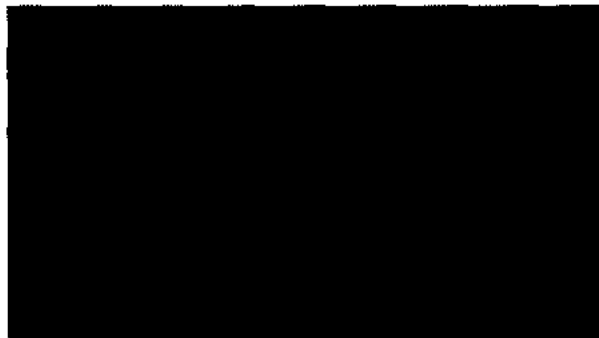


Figure: 1.5: Thin film [11]

1.4 Metal Oxides

The role of metal oxides in the field of natural sciences is very important. A large number of oxide compounds are formed by metal elements. Metal oxides behave as conductor, insulator and semiconductor depending upon the geometry and the arrangement of electrons in them. Metal oxides are used in the fabrication of electronic circuits, gas and chemical sensors and fuel cells. In nanotechnology, main goal is to compose metal oxide nanostructures having very special properties as compared to their bulk counterpart. Due to their limited size, metal oxide nanostructures show distinct physical and chemical properties.

In solid state chemistry, metal oxides are used due of their extremely diverse characteristics and structures [12]. They exhibit attractive magnetic and electronic properties. Metal oxide nanostructures are also used in catalysis, electroplating, pharmacy and in medical field. Metal oxides nanoparticles are also used as antibacterial agent because during interaction with water, metal oxides produce reactive oxygen species (ROS) which are known to kill bacteria.

1.5 Copper (II) Oxide (CuO)

Among metal oxides, copper oxide is of great interest. Copper (II) oxide in its pure form is a p-type semiconductor. In bulk CuO is metal oxide semiconductor which have narrow direct bandgap in the range of 1.2-1.55 eV. We choose CuO due to its easy availability and it is not very much costly to prepare by solution methods which are the key issues for many applications [13]. CuO is in the space group $2/m$ and have monoclinic structure as depicted in figure 1.6. In this structure, copper atom is surrounded by four oxygen atoms showing square planer configuration as shown in figure 1.6 [14].

Unit cell parameters of CuO are: $a= 4.682\text{\AA}$, $b= 3.424\text{\AA}$, $c = 5.127\text{\AA}$ and cell volume is 81.52\AA^3 [15]. As a mineral, it is called tenorite. The ionic and atomic radius of Cu is 0.72\AA and 1.28\AA respectively. The chemical composition of copper oxide is such that copper

is 79.87% and oxygen is 20.10%. There is ionic bonding between copper and oxygen atoms.

The bond length of CuO is 1.95 Å.

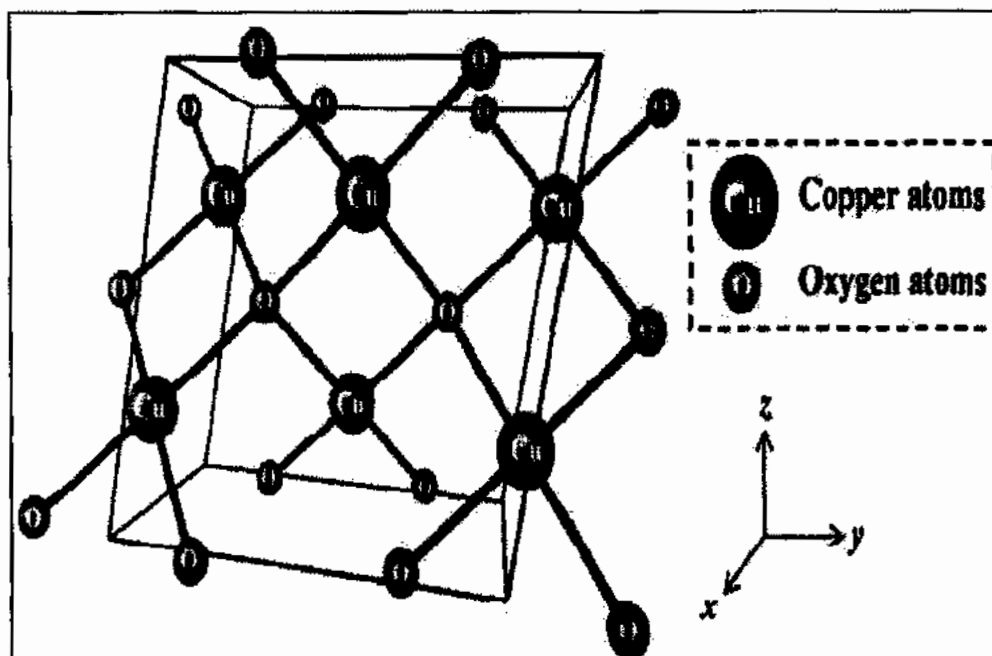


Figure: 1.6: Schematic representation of Copper oxide unit cell [16]

CuO nanostructures have a wide range of applications such as gas sensing, catalysis, lithium ion batteries, magnetic storage media, electrochemical capacitor electrodes, Solar cells technology, high temperature superconductors, field emission devices etc [17-20].

1.5.1 Fundamental Properties of CuO

Some basic fundamentals of CuO are given in table 1.1.

Table 1.1: Some fundamentals of CuO

Molecular Formula	CuO
Molar Mass	79.545 g/mol
Crystal Structure	Monoclinic
Appearance	Black powder

Density	6.32 g/cm ³
Melting Point	1134 °C
Boiling Point	2000 °C
Dielectric Constant	18.1
Band-gap	1.2-1.55 eV, direct
Refractive index	1.4

1.5.2 Significance and Applications of CuO

CuO draws much attention because starting growth material is inexpensive and easy to get and it can be prepared using low cost methods. CuO nanostructures have attracted the researchers due to their high surface area to volume ratio which make CuO a candidate for the sensing owing to its distinct electrochemical activity and the possibility of promoting electron transfer at low potentials [21].

CuO nanostructures are very important material for the fabrication of solar cells because of their photoconductive and photochemical properties. The use of CuO is very excellent in making sensors which are used for discovering the presence of dangerous gases. In lithium ion batteries, CuO is used as negative electrode [22].

CuO can also be used as a catalyst. It can be synthesized with various morphologies and as we know that morphology affects the catalyst activity so by using different morphologies of CuO we can enhance the properties of catalyst.

CuO nanosheets can be used as the electrode of electrochemical capacitors. These are electrochemical energy storage devices and also known as supercapacitors. Supercapacitors can be used as intermediates between conventional dielectric capacitors and batteries [23].

Recently, CuO has been used as an antimicrobial agent which can stop bacterial growth of different bacteria [24]. The antibacterial activity of CuO depends on the particle size and morphology.

1.6 Motivation of Thesis

CuO possesses very interesting physical properties such as narrow band gap which favors its use in photoconductive and photothermal applications. Due to distinct properties such as its large abundance in nature, having low cost, very stable and excellent electrical characteristics, CuO nanostructures are very suitable for their use in many applications. These are widely used in high temperature superconductors, solar cells, catalysts, antibacterial agent, gas and chemical sensors. Due to size confinement and surface effect, CuO nanostructures have shown improved chemical and physical properties comparing to their bulk counterpart. Zn is known as an interesting dopant for enhancement in magnetic properties, band gap tuning and structural modification for different oxides. In this thesis, a complete study will be performed to understand the influences of Zn doping on the morphological, structural and optical properties CuO host matrix.

Chapter No. 2

Synthesis of Nanostructures

2.1 Different Synthesis Approaches for Nanostructures

Nanotechnology deals with very small structures: a nanometer is a billionth of a meter. The aim of nanotechnology could be achieved by synthesizing the materials whose one dimension is at least less than 100 nm. Nanomaterials are found in variety of different structures like nanowires, nanorods, nanoparticles, nanotubes and nanolayers. In this chapter, different routes of synthesizing nanomaterials will be discussed. There are two main following approaches to synthesize nanostructures.

- i) Top-Down Approach
- ii) Bottom-Up Approach

2.1.1 Top-Down Approach

The top-down is an approach of breaking down bulk material into nano sized structure. Several top down fabrication techniques are used to fabricate useful nanostructures such as ball milling, lithography, molding, embossing and skiving. In semiconductor industry lithography technique is used to fabricate various elements like integrated circuits for computer chips. In ceramic industry top down method used to make alloys which are very difficult by ordinary methods.

Top-down approach is an efficient technique but the main problem with this approach is the imperfection of surface structure. Synthesizing nanostructures using Top-down approaches requires dirt free room environment which makes this approach very costly, that's why this approach is not used in commercial applications. There is lot of chances of

impurities in final product during top down process. Schematic diagram of top down approach is shown in figure 2.1.

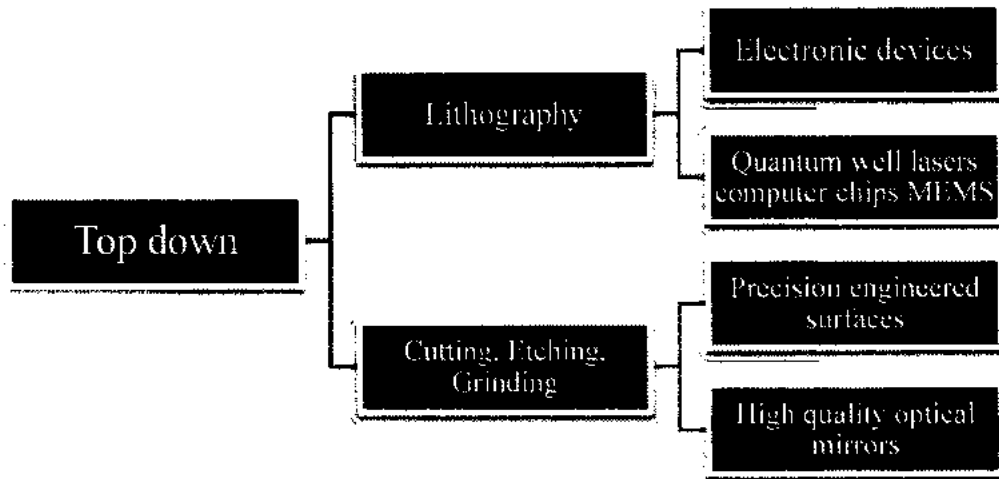


Figure: 2.1: Schematic diagram of top-down approach

2.1.2 Bottom-Up Approach

This is reverse approach of top-down approach. In bottom-up technique, atom, molecules or ions are assembled to form complex nanostructures which are stable at room temperature. The concept of this approach comes from nature, as nature creates the cells, crystals and human being using bottom up technique. Colloidal dispersion is most common examples of bottom up approach [25]. This technique is divided into liquid phase and gas phase methods. In both of these techniques, nanomaterials are synthesized through controlled synthetic routes starting from single atom or molecule. It allows smaller geometries to form nanostructures. Different nanostructures such as nanoparticles, nanotubes, nanowires and nanosheets can be grown through bottom up process very easily.

Bottom up technique is the most widely used method in nanostructures fabrication because it is less expensive and easy to handle than top down approach. As we have

synthesized our samples through co-precipitation technique which is bottom up hence this technique is discussed in detail. Schematic diagram of bottom up approach is shown in figure 2.2.

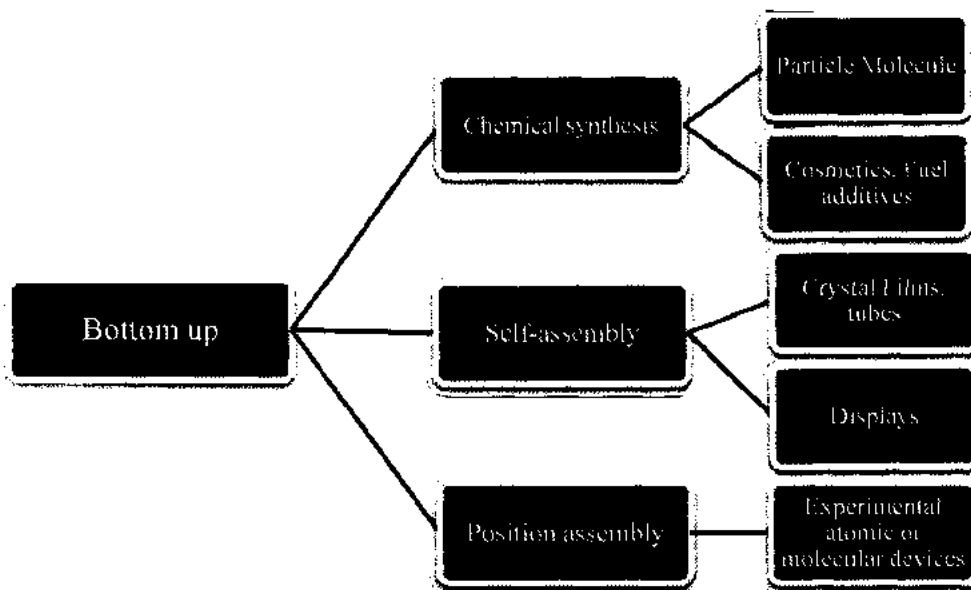


Figure: 2.2: Schematic diagram of bottom-up approach

2.2 Chemical Co-precipitation Method

Chemical co-precipitation method is based on the process of precipitation of metal ions. When chemical reaction takes place in a solution some of the solute remain insoluble which is taken out of the solution, this process is known as precipitation. Precipitation of any element takes place when its concentration is very high in the solution that is when solution is supersaturated. Such a solution is unstable which leads nucleation to form large clusters. In order to synthesize monodispersed nanoparticles reaction parameters should be controlled accurately. This might be achieved by adjusting the reaction parameters such as changing the mixing ratio of reactants, using different solvents and adding surfactants. During the slow growth mode, nanoparticles follow Ostwald ripening process in which energetic small particles assemble to give rise to a more stable particles [26].

2.2.1 Significance

Chemical co-precipitation method is a very efficient, cost effective, easy and environment friendly method for the synthesis of nanostructures. It is a bottom up approach for synthesizing nanostructures. Using this method, the nanostructures of 40-80 nm size or even less can be synthesized. The most important thing about this method is that it can be carried out both in aqueous and non-aqueous medium. In co-precipitation method, a large quantity of product having high purity can be obtained. This method is less expensive and very easy to synthesize nanostructures as it operates on low temperature. The chemical co-precipitation has been employed for the synthesis of undoped and Zn doped CuO nanostructures.

2.3 Experimental Procedure

Undoped and Zn doped CuO has been synthesized in Laboratory of Nanoscience and Technology using co-precipitation method. For this purpose, molar ratio method is used to control the concentration of reactants. Copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and zinc chloride (ZnCl_2) are used as precursors. A strong base, sodium hydroxide (NaOH) is used to maintain the required pH value of solution. The acetic acid (CH_3COOH) is used as a surfactant to control the particle size. Distilled water is used as solvent in the solution. The reaction is carried out under constant heating and vigorous stirring.

A 0.1M solution of copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) is prepared in distilled water. The solution was put for 10 min into fume hood on hot plate for magnetic stirring at 100°C per 550 rotations per minute (rpm). 2ml Acetic acid (CH_3COOH) was added to solution to control particle size. The pH of the solution was enhanced by pouring NaOH drop by drop in the solution. Precipitates starts appearing when pH reaches 8. Furthermore addition of NaOH was stopped as the pH reaches to 10. Then the solution is left for stirring for 1 hour at 100°C

and 650 rpm. After this leave the solution so precipitates settle down and the extra water is removed. Then the rest of solution is centrifuged for 3 minutes at 3000 rpm for three times. Impurities were separated from the solution as the precipitates settle down which is collected in a beaker and kept in the oven for drying overnight at 100°C. Next day the dried sample was grinded to powder form and put in oven for annealing at 300 C° for 2 hours. The synthesis parameters used in fabrication were first optimized to get final products.

For doped solution, the same procedure was repeated and for Zn doping different concentration of zinc chloride ($ZnCl_2 \cdot 2H_2O$) was added. Different doping concentrations (1 %, 3 %, 5%, 7 % and 10 %) of Zn are used in CuO host matrix. The flow chart of whole synthesis process is given in figure 2.3.

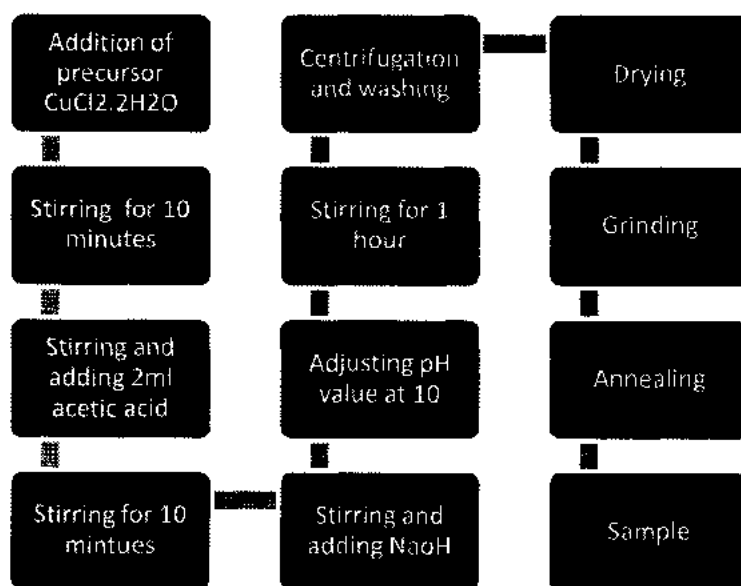


Figure: 2.3: Flow chart of experimental procedure

Chapter No. 3

Characterization Techniques

There are different characterization techniques which provide information about sample. These techniques give details about structure, morphology, physical and chemical properties of the sample. Some characterization techniques are briefly described below.

1. X-ray diffraction (XRD)
2. Scanning electron microscopy (SEM)
3. Energy disperse X-ray spectroscopy (EDS)
4. Fourier transform infrared spectroscopy (FTIR)
5. UV spectroscopy

3.1 X-ray Diffraction (XRD)

XRD stands for X-ray diffraction because the basic principle of XRD machine is based on x-rays. X-rays were first time termed by William Roentgen in 1895. He described that when an electron beam strikes on a solid target material, some of the radiations come out of the target. He named these unknown radiations as x-rays.

Using XRD technique, the different structural data such as lattice parameters, stress and porosity can easily be calculated. It gives us information about that whether the material under study is crystalline, polycrystalline or amorphous. It also helps us to find the crystal shape, size and orientation.

3.1.1 Working

We know that there is a regular arrangement of atoms, ions and molecules in a crystal. These atoms or ions are regularly arranged in all three dimensions in different patterns such

as cubic, orthorhombic, tetragonal etc. There are series of planes in a crystal which are separated by a distance 'd' called inter planer distance.

X-rays are electromagnetic waves (EMWs) having wave length ($\lambda = 0.5\text{\AA}$ to 2.5\AA). The wavelength of these (EMWs) is compare able to inter atomic distance d of the solid material. There are two types of x-rays one having shorter wavelength known as soft x-rays and others having longer wavelength are called as hard. Hard x-rays can't explain the crystal structure and radiations of small wavelengths are diffracted at small angles. X-rays are scattered by crystal atoms. These scattered x-rays interfere with each other. When these rays are in phase, they produce constructive interference to form a diffraction pattern in specific direction.

3.1.2 Bragg's Law

Bragg's Law helps us to understand the diffraction pattern of the x-rays and the spacing between the atomic planes. When monochromatic x-rays having wavelength (0.7\AA to 2\AA) are bombarded on the surface of sample then reflection take place as shown in figure 3.1. It is observed that only reflection at some selective planes (depends upon wavelength and lattice constant) take place. So using the interference effects, these selective reflections can be easily explained. The incident x-rays falls on the crystal planes just like a mirror reflects. After reflection from planes, the behavior of these x-rays can be observed as shown in fig 3.1.

When constructive interference occurs, the path difference is $n\lambda$. Where n shows the order of reflection and λ is wavelength of X-rays. Mathematically Bragg's law can be expressed as

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

Where, λ = wavelength of radiation,

d = inter planer distance

θ = angle of diffraction

$$n = 1, 2, 3, \dots$$

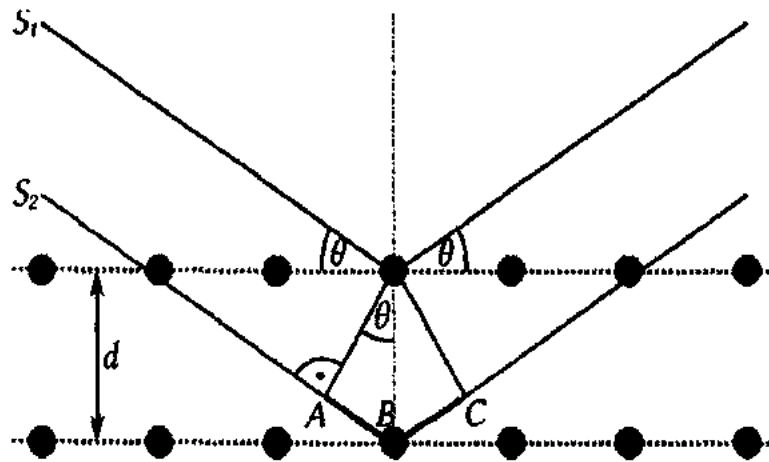


Figure: 3.1: Schematic diagram of Bragg's law [27]

3.1.3 Advantages of XRD

- Most commonly used for the characterization of a crystalline material.
- The main advantage of this technique is that we can use it for both nano and bulk materials [28].

3.2 Scanning Electron Microscopy (SEM)

SEM stands for scanning electron microscopy. In this type of microscopy, a focused beam of electrons is used to create the image of a sample. It is very useful technique to study the surface morphology of materials. A focused electron beam is used to create image in SEM. The resolution of image of SEM is very high. The images of the surface are taken using back scattered electrons.

3.2.1 Working Principle of SEM

In SEM, high energy (0.5-30keV) electrons beam is made to fall on the specimen. An electron gun is used to generate beam of electrons by means of a heating filament. This

electron beam is known as primary electron beam. The filament is heated by applying high voltage about 0.1 kV to 40 kV.

The electron gun emits the high energy electrons which are directed toward the sample. These ejected electrons strike with the samples surface and transfer their energy to surface electrons. As results of this interaction, various types of electronic signals are produced such as back scattered electrons, characteristic x-rays, sample current and transmission electrons etc. When incident primary electrons reflect back from the surface electrons are called back scattered electrons. These electrons are used to determine the contrasts in composite sample to detect the back scattered electrons at detector used in a SEM. When incident electron beam strikes the sample the secondary electrons is produced. One can use these electrons to find morphology and topography of the samples. Secondary electron detector is used to detect these electrons. The electrons from inner shells of the atoms of samples are kicked out by incident electron so higher energy electrons come in to fill lower shells as a result x-rays are emitted known as characteristic x-rays. The compositions and number of elements can be measured by studying x-rays at x-ray detector. The electrons transmitted through the sample are known as transmission electrons. These all types of signals can be detected with the help of different detectors. These signals are used for the image formation of a sample. This image gives complete information about sample like morphology, orientation and structure of sample. The schematic diagram of SEM is shown in figure 3.2.

There are some special requirements for the working of SEM. A 10^{-4} torr pressure vacuum or more is required to operate. As the pressure is low, there is better vacuum and SEM works better in high vacuum. The surface of the sample which is under testing must be dry and clean. The sample must be place inside the vacuum chamber.

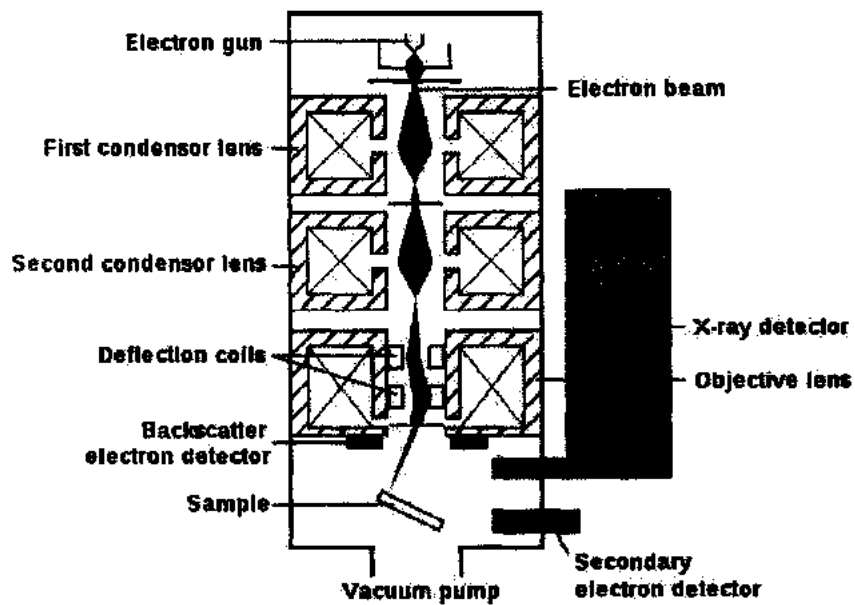


Figure: 3.2: Schematic diagram and setup of SEM [29]

3.2.2 Some Important Applications of SEM

- SEM is used to get high resolution images of surface of materials.
- SEM is used to find the chemical compositions and constituents of a sample with the help of EDS.
- SEM is used to identify the crystalline phases of different samples.
- SEM is used to examine the crystallographic orientations through back scattered electron images.
- SEM is used for examination of surface morphology and size of particles. It is also used for corrosion and oxidization problems identification [30].

3.3 Energy Dispersive X-ray Spectroscopy (EDS)

EDS is used to examine the composition of different elements present in the sample. This technique is based on the interaction between the material and high energetic electron

beam which ejects the electrons of atom from their bound inner shell. Due to the ejection of electrons from their inner shell, a vacancy (hole) is created. In order to fulfill this vacancy, the higher shell electrons jump into the lower shell as a result characteristic x-rays are emitted. These x-rays are detected with x-ray detector. This whole process actually occurs in the SEM. The working principle of EDS is shown in figure 3.3.

X-rays which are produced due to electron transitions are used to identify the elements. There are several signals of x-rays which are produced due to the different elements in the composition. EDX spectroscopy allows us to identify the presence of particular elements and their relative proportions (atomic % for example).

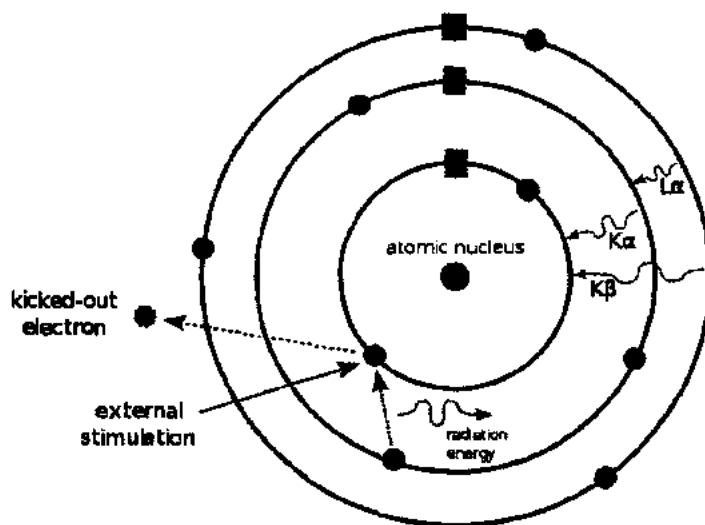


Figure: 3.3: Working principle of EDS [31]

3.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR stands for Fourier Transform Infrared and consider being most preferred infrared spectroscopy. It is an analytical instrument used to differentiate organic as well as inorganic materials. The basic principle of FTIR is Michelson interferometer and schematic is shown in

figure 3.4. It is easier to use and less expensive than other interferometers. It is used as to measure the chemical purity and different stretching modes of the elements of the sample.

3.4.1 Working Principle of FTIR

In this spectroscopy, IR radiations are made to pass from the sample. When radiation falls on the sample some of its part is absorbed and some of the radiations are transmitted through the sample. The final FTIR spectra show the absorption and transmission by molecules. This spectrum is similar to a fingerprint of the sample. Like a fingerprint, no two molecules have the same infrared spectrum that is why it is very useful for many applications.

In FTIR, black body is used to produce infrared radiations. This infrared radiation falls on the splitters. One part of the light is refracted to the mirror which is fixed and one part is transmitted through the mirror which is moving. The transmitted radiation passes through the sample. Infrared radiations interact with the sample and give useful information about the structure, bonding and molecular components of the sample. Figure 3.4 depicts the working of FTIR.

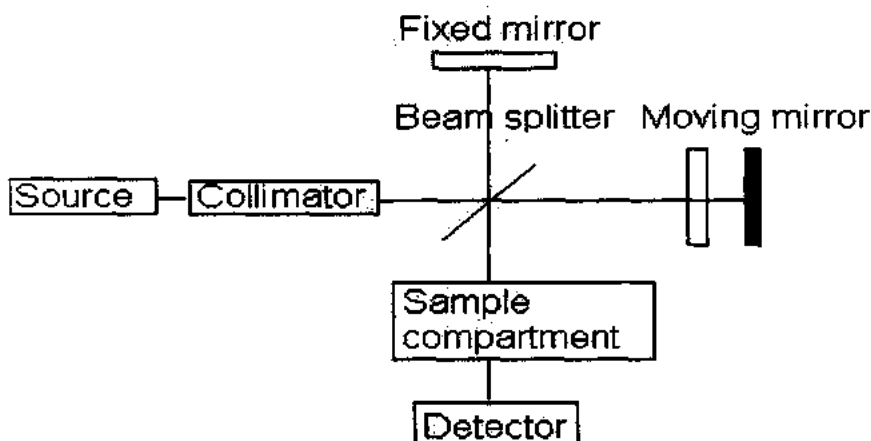


Figure: 3.4: Schematic diagram and working principle of FTIR [32]

3.4.2 Uses of FTIR

- FTIR is used to distinguish the components of a mixture gas.
- FTIR is used for the analysis of liquid chromatography fraction.
- FTIR can be used to identify the unknown materials.
- FTIR can be used to check the quality and consistency of the sample.

3.5 UV Spectroscopy

Spectrophotometry is a technique which measures the electromagnetic spectrum quantitatively. A device called spectrometer measures the quantity of reflected and absorbed light by the specimen. UV spectroscopy is very useful technique to find the energy band gap of different materials. In this technique, light is allowed to fall on the sample. The light which is absorbed, reflected or transmitted is measured. This measured light is used to find the energy band gap of semiconductors and impurities in organic materials [33]. The absorption of light in visible and ultra violet region affects the color of the sample. Due to absorption and reflections of ultraviolet and visible light, electrons can excite from lower shell to higher shell. This absorption of ultraviolet radiations measures the transition from the lower energy state to the higher energy state.

3.5.1 Working Principle of UV Spectroscopy

Ultraviolet radiations are made to fall on the sample. These radiations are either reflected or transmitted by the sample. When this light passes through the sample, the intensity of remaining light and light transmitted through the sample are measured with the help of a photo detector. The reflected and absorbed light intensity also noted. There are single beam spectrophotometers and double spectrometer for this purpose. A single spectrometer measures the beam light intensity of the test specimen. Double beam photo

spectrometer measures the wavelengths of light passing between two different slits. Both spectrophotometers measure the transmitted light as well as reflected light by the specimen.

3.5.2 Uses of UV Spectroscopy

- It is used to find the energy band gap of the semiconductors.
- It is used to study electronic transitions in molecules.
- It can be used to study the kinetics of reaction.
- It is helpful in structure clarification of organic molecules as well as for the presence and absence of un-saturation.

Chapter No. 4

RESULTS AND DISCUSSIONS

4.1 Overview

Various Characterization techniques are used which give analysis about the sample structure, morphology, compositional constituents and bonding which are the most necessary results required for a sample

4.2 Structural Analysis

In order to check the crystal structure and phase purity of undoped CuO and Zn-doped CuO nanostructures synthesized by chemical co-precipitation method is characterized by XRD using X-ray of wavelength ($\lambda = 1.5405 \text{ \AA}$). The XRD patterns of undoped CuO and 1%, 3%, 5%, 7%, 10% Zn doped CuO nanostructures annealed at 300 °C show that all diffraction peaks can be readily indexed (JCPDS card no. 00-041-0254) to standard monoclinic CuO nanostructures as shown in figure 4.1. All the diffraction peaks in figure 4.1 could be well indexed to the typical monoclinic structure of CuO with no other crystallographic phases related to Zn or other impurities. Moreover, the diffraction peak intensities are observed to increase with Zn doping which suggests improvement in the crystalline quality of the synthesized samples. Zn ions can be successfully doped into CuO due to similarity in the ionic radii of Cu (0.72 Å) and Zn (0.74 Å) ions. The absence of peaks other than that of CuO in the XRD patterns of the synthesized samples confirms the successful substitution of Zn ion on the sites of Cu ions in CuO lattice. The micro-structural parameters such as crystallite size (D) and microstrain (ϵ) for the synthesized samples have been calculated using the following relations [34, 35];

$$D = k\lambda / \beta \cos\theta \dots\dots\dots (4.1)$$

$$\epsilon = \beta \cos \theta / 4 \dots \dots \dots (4.2)$$

Where, λ is the wavelength of the X- rays which is 1.54 \AA , k is a shape constant whose value is 0.89 and β is full width at half maximum (FWHM).

The average crystallite size of CuO has been observed to increase with the increasing concentration of Zn while ϵ is found to increase as shown in figure 4.2. This behavior may be attributed to the slightly larger ionic radii of dopant as compared to host ions.

The lattice parameters 'a' and 'c' are increased while b decreases with Zn doping as compared to the undoped CuO [36]. The values of lattice parameters, crystallite size, microstrain and volume of unit cell for each sample are given in the table 4.1.

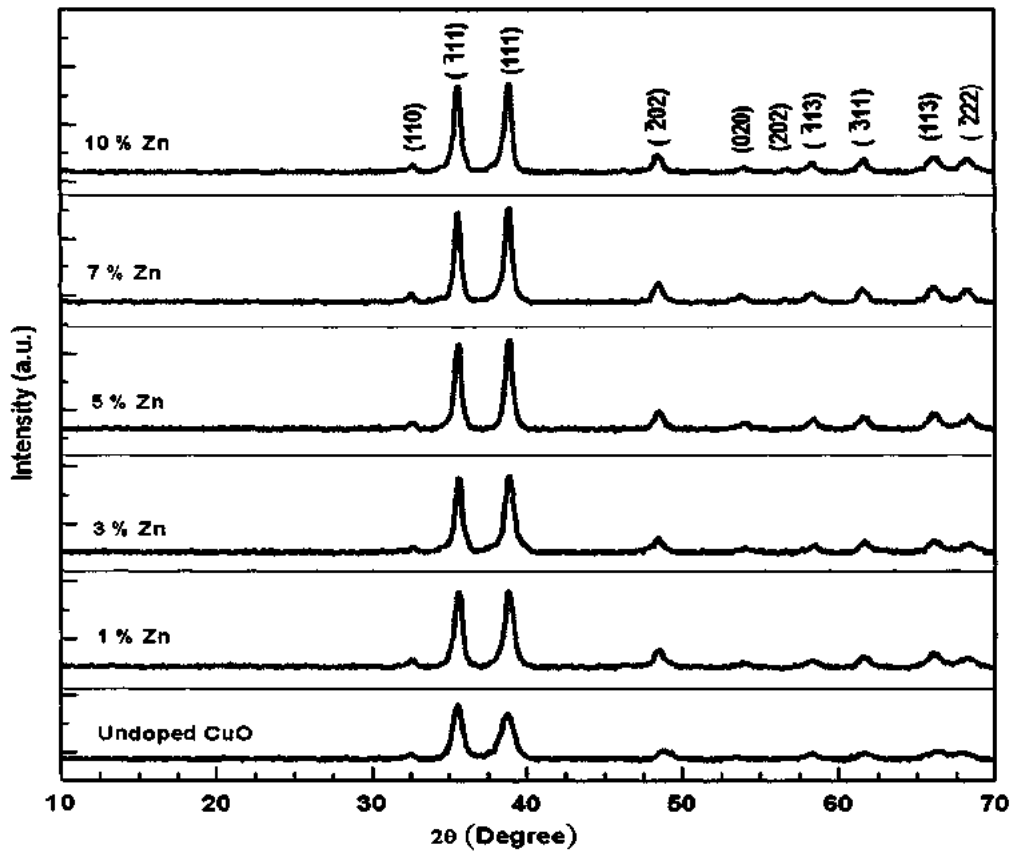


Figure 4.1: Combine XRD patterns for undoped and Zn doped CuO nanostructures

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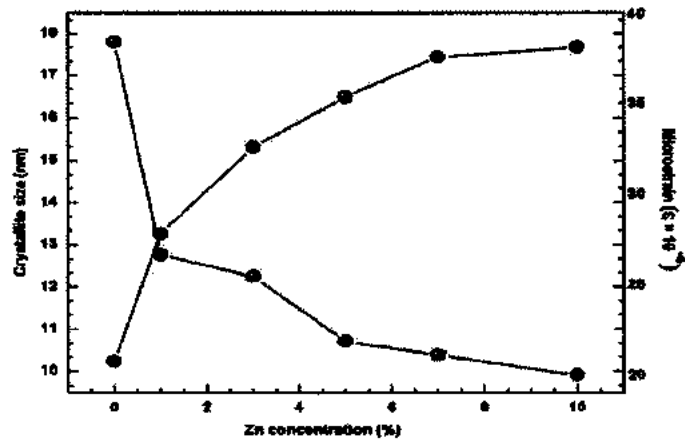


Figure 4.2: Plot of crystallite size and microstrain against Zn concentration

Table 4.1: Values of Lattice Parameters, crystallite size, microstrain and volume of unit cell for undoped and Zn doped CuO nanostructures.

Zn Doping (%)	a (Å)	b (Å)	c (Å)	Crystallite size D(nm)	Microstrain $\epsilon \times 10^{-4}$	Volume (Å ³)
0 %						
1 %	4.6851	3.4228	5.1322	13.27	26.62	82.29
5 %	4.6858	3.4221	5.1329	16.48	21.81	82.26
10 %	4.6867	3.4215	5.1337	17.67	19.95	82.24

4.3 FTIR Analysis

FTIR is a very useful technique to find out the information about the surface chemistry and vibrational properties of nanostructures. The FTIR spectra recorded in solid phase using KBr pallet technique in the wave number region $4000-400\text{cm}^{-1}$ for undoped and Zn doped

CuO is shown in figure 4.5. Several stretching modes involving metal oxide bonds and carbon to oxygen are obtained in this region [37].

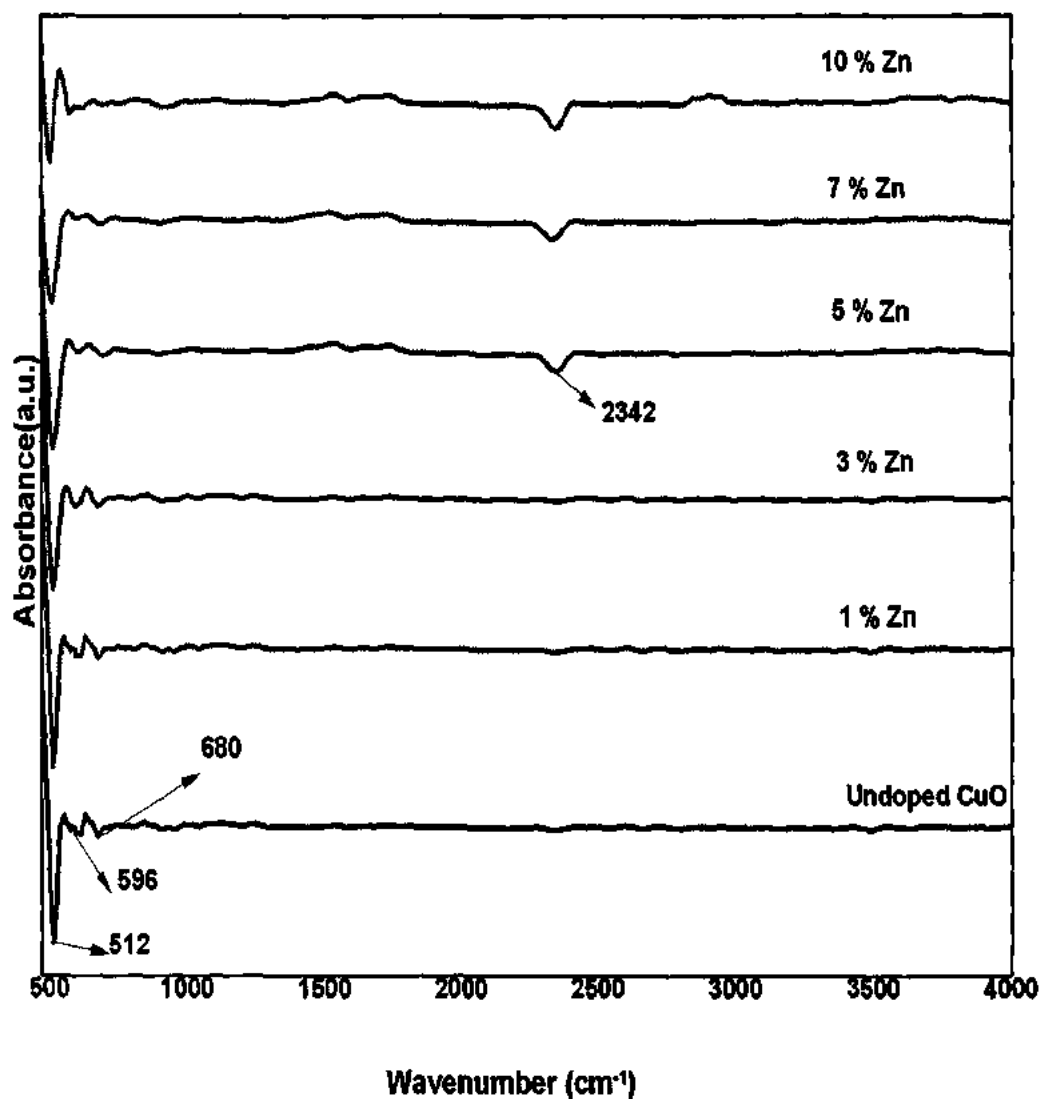


Figure 4.3: Combined FTIR spectra of undoped CuO and Zn doped CuO nanostructures

FTIR spectra of undoped and Zn doped CuO nanostructures have shown absorption peaks at around 512, 598 and 680 cm^{-1} , associated with Cu–O stretching vibrations of monoclinic CuO, which is also previously reported in literature for CuO nanostructures [38,

39]. The absorption band at about 2342 cm^{-1} corresponds to the existence of CO_2 , which may be adsorbed on the samples from the atmosphere [40]. It can see from the FTIR spectra that there is no vibration modes related to Cu_2O , ZnO or other impurities which depicts that all the prepared nanostructures are of the purely monoclinic CuO phase. These FTIR results are in good agreement with the XRD results.

4.4 Morphological Analysis

SEM has been used for the analyzing the morphology and grain sizes of the prepared samples. The SEM images of the synthesized Zn doped CuO samples which clearly indicate the formation of hierarchical nanostructures as shown in figure 4.4 (a, b, c, d, e).

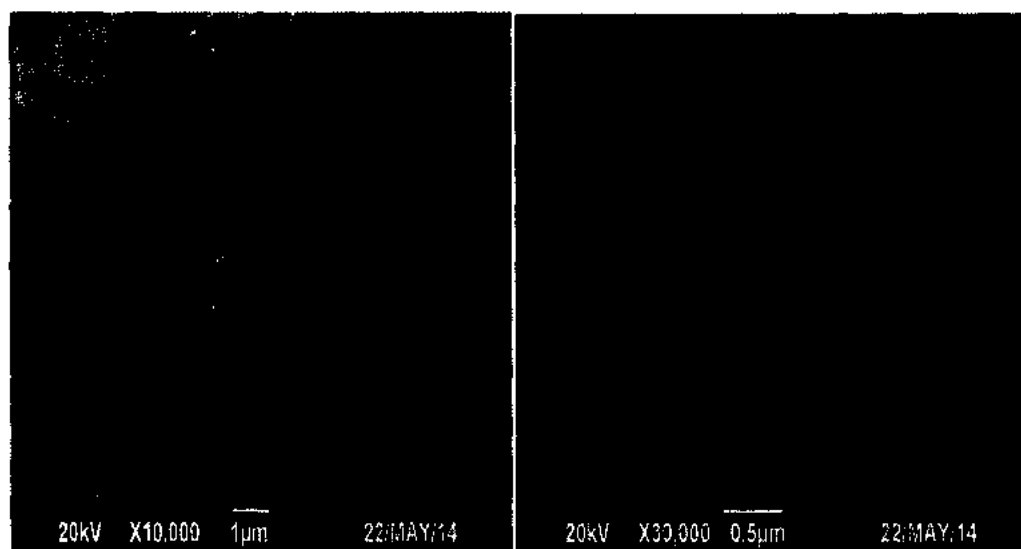


Figure 4.4 (a): SEM images of 1 % Zn doped CuO nanostructures

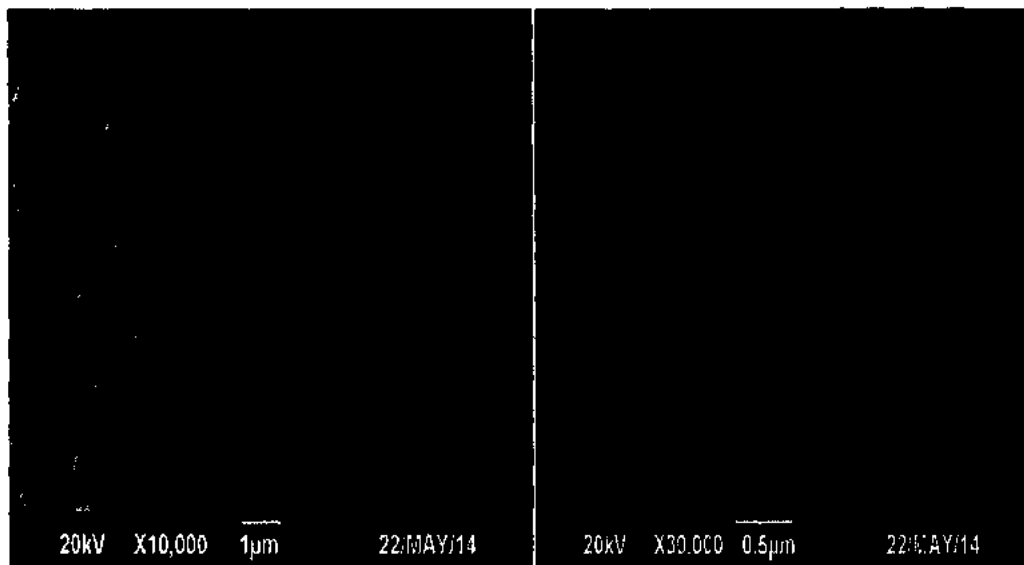


Figure 4.4 (b): SEM images of 3 % Zn doped CuO nanostructures

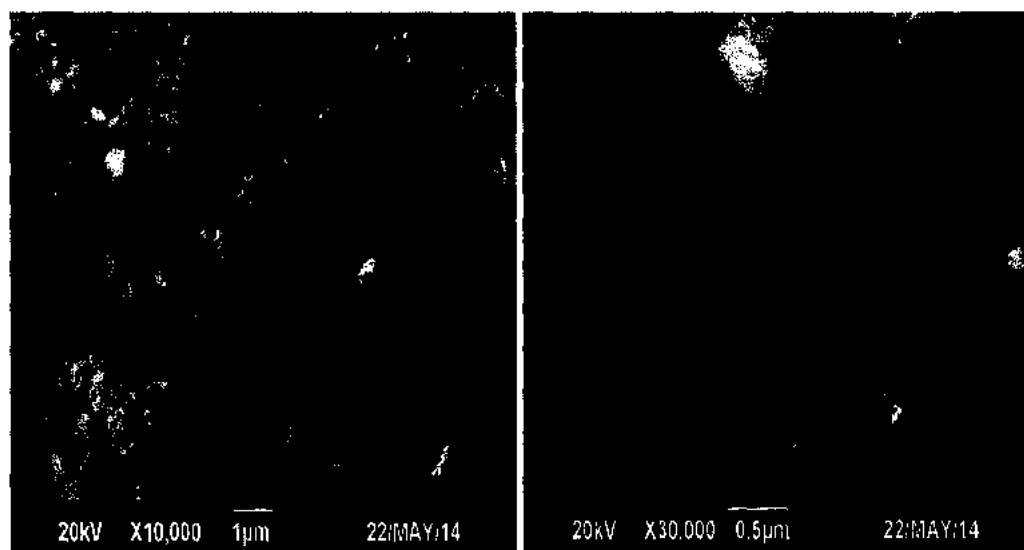


Figure 4.4 (c): SEM images of 5 % Zn doped CuO nanostructures

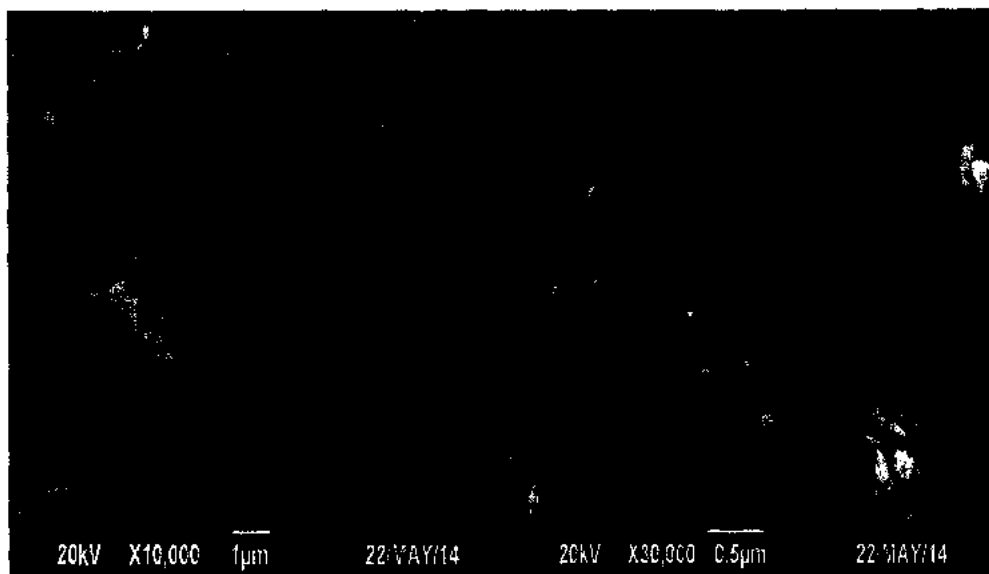


Figure 4.4 (d): SEM images of 7 % Zn doped CuO nanostructures

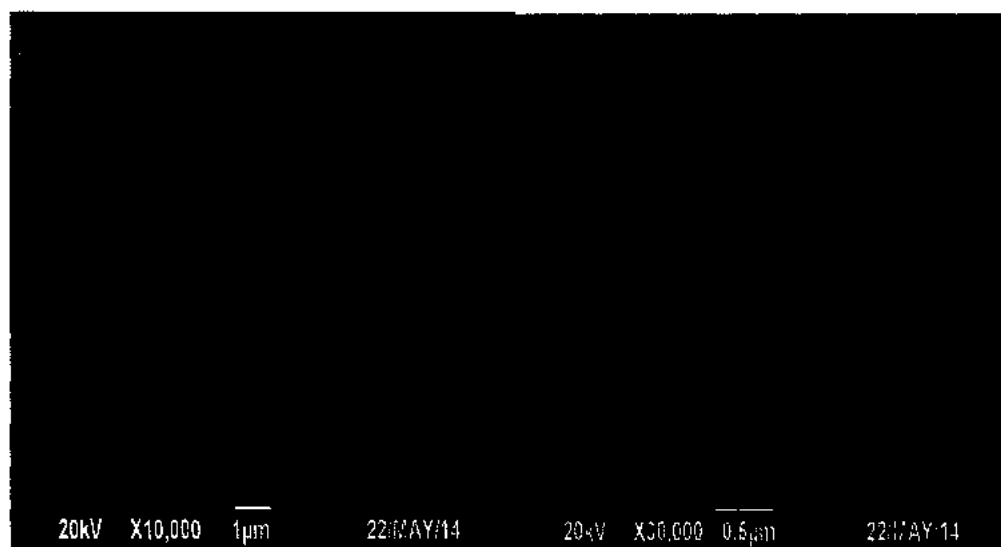


Figure 4.4 (e): SEM images of 10 % Zn doped CuO nanostructures

The average particle size has been found to be 26 nm for 1 % Zn doped CuO which is increased up to 43 nm with Zn doping of 10 %. It has been observed from SEM micrographs that the shape and grain size of the synthesized nanostructures is significantly influenced by Zn concentration. This phenomenon may be linked with the variation in structural disorder and microstrain induced by Zn doping into CuO host matrix.

Table 4.2: Particle size measurements by SEM investigation

Sr. No.	Samples	Average particle size (nm)
2	$Zn_{0.03}Cu_{0.97}O$	29.82 ± 5.267
4	$Zn_{0.07}Cu_{0.93}O$	41.21 ± 8.615

4.5 Compositional Analysis

The quantitative compositional analyses of the synthesized Zn doped CuO nanostructures were carried out by Energy Dispersive x-ray Analysis (EDX). Figures 4.5 shows the EDS spectra of Zn doped CuO nanostructures. This confirms the presence of Cu, Zn and O elements in the samples and their compositions are given in Tables 4.3-4.7.

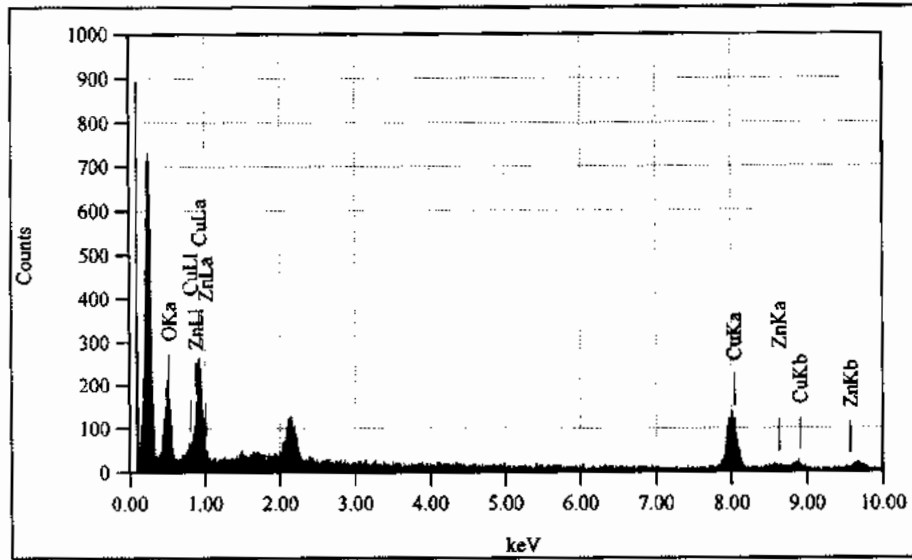


Figure 4.5 (a): EDS spectrum of 1 % Zn doped CuO nanostructures

Table 4.3: Concentrations of constituent in 1% Zn doped CuO nanostructures

Element	KeV	Mass %	Atoms %
Cu	8.040	69.84	37.17
Zn			
Total	-	100	100

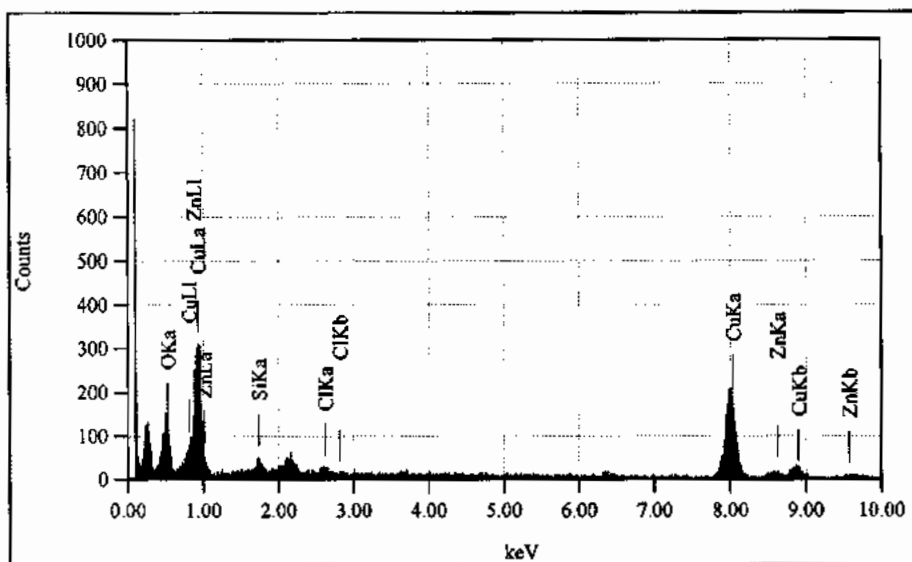


Figure 4.5 (b): EDS spectrum of 3 % Zn doped CuO nanostructures

Table 4.4: Concentrations of constituent in 3% Zn doped CuO nanostructures

Element	KeV	Mass %	Atoms %
O			
Si	1.739	2.58	3.91
Cu	8.040	77.65	51.91
Zn			
Total	-	100	100

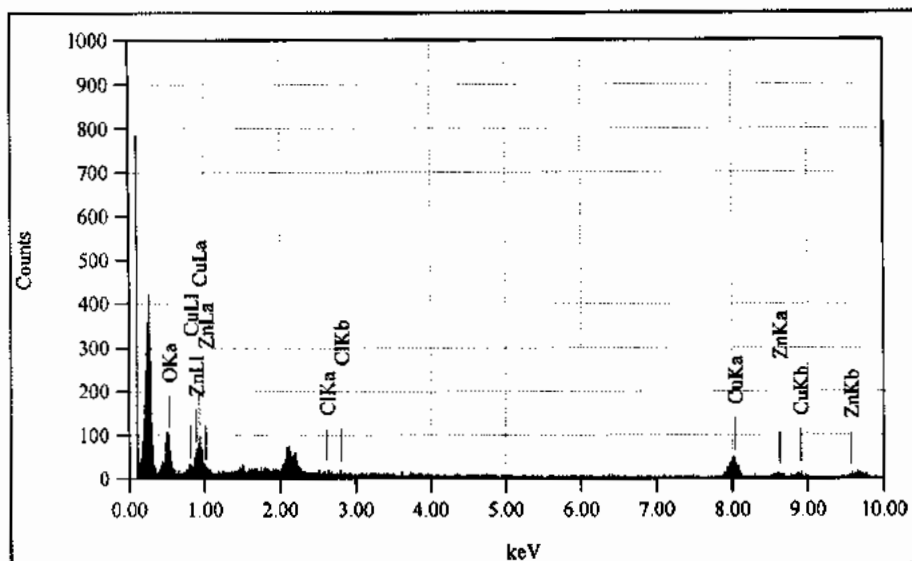


Figure 4.5 (c): EDS spectrum of 5 % Zn doped CuO nanostructures

Table 4.5: Concentrations of constituent in 5% Zn doped CuO nanostructures

Element	KeV	Mass %	Atoms %
Cu	8.040	59.69	30.39
Zn			
Total	-	100	100

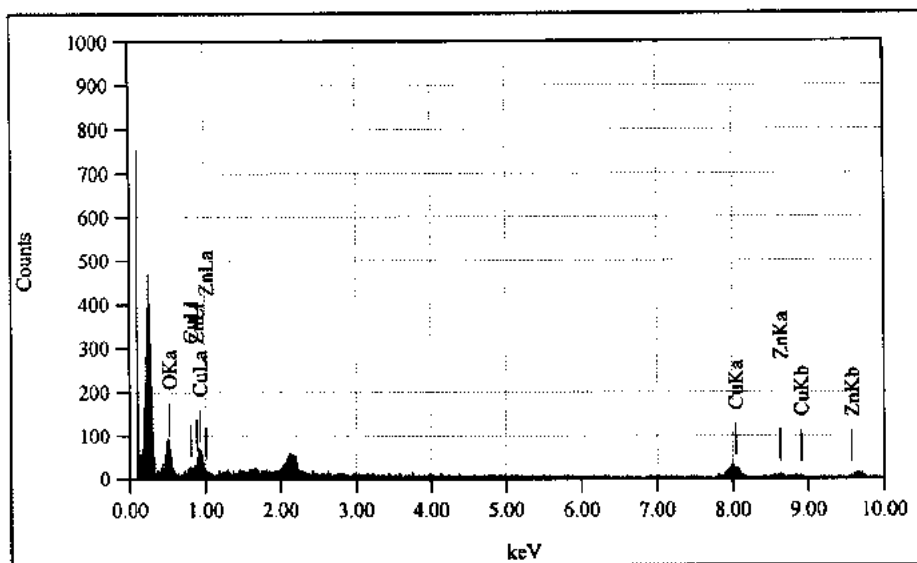


Figure 4.5 (d): EDS spectrum of 7 % Zn doped CuO nanostructures

Table 4.6: Concentrations of constituent in 7% Zn doped CuO nanostructures

Element	KeV	Mass %	Atoms %
O			
Cl	2.621	0.35	0.21
Cu			
Zn	8.630	8.25	3.94

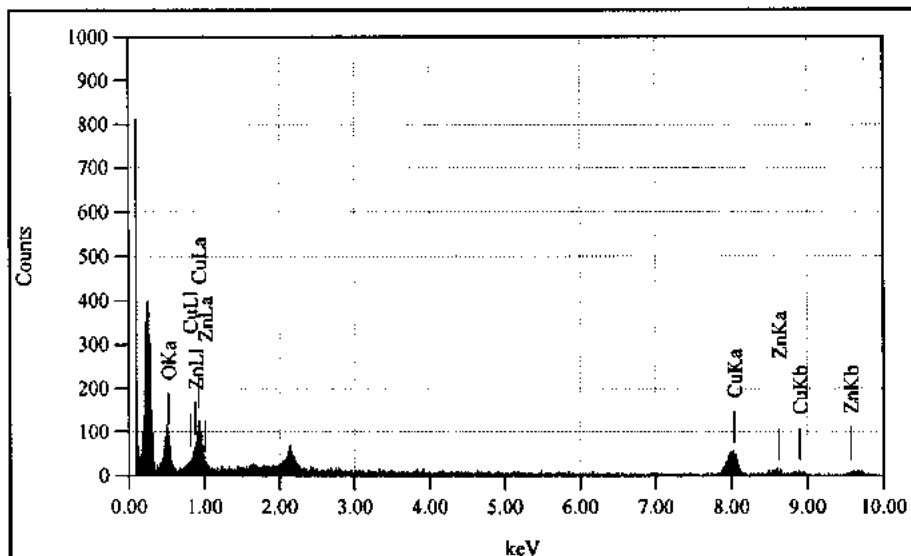


Figure 4.5 (c): EDS spectrum of 10 % Zn doped CuO nanostructures

Table 4.7: Concentrations of constituent in 10 % Zn doped CuO nanostructures

Element	KeV	Mass %	Atoms %
O			
Cu	8.040	48.99	2.230
Zn			
Total	-	100	100

All of these tables and spectra show the presence of all constituents in all the samples. The strong peaks of copper, zinc and oxygen in the spectra show that the concentrations of these elements are higher as compared to other elements. The concentration of Zn dopant is

consistent with the stoichiometric ratio used at the time of synthesis and; can be removed by annealing and washing. There are Cl peaks in the EDS spectra of 3 % and 7 % Zn doped CuO samples which may be due to the precursor used in synthesis. Also there is a signal of Si in 3 % Zn doped CuO sample which is due to EDS setup.

4.6 Surface Area Analysis

Nanostructures have gained enormous attention due to their high surface area (i.e. surface to volume ratio). Numbers of physiochemical properties of nanostructures are strongly dependent on their surface area such as chemical reactivity, adsorption, biological activity and electrical properties [41]. Therefore, knowing the surface area of the synthesized CuO nanostructures and Zn dopant concentration induced effects on it is very important for number of applications. In this study, the BET method has been used to measure the surface area of undoped and Zn doped CuO nanostructures. In this method nitrogen gas molecules are adsorbed on a solid surface, which allows measurement of the surface area of a material. BET multipoint adsorption method is used to calculate the surface area.

The BET equation is given by,

$$\left[\frac{1}{w} \left\{ \frac{P}{P_0} - 1 \right\} \right] = \left[\frac{1}{W_m} C + \frac{C - 1}{W_m} \frac{P}{P_0} \right] \dots \dots \dots 4.5$$

Where W is weight of adsorbed gas, P/P₀ is relative pressure, W_m is amount of gas adsorbed in a monolayer and C is BET constant.

For the solution of BET equation a liner plot of 1/[W (P/P₀)-1] against P/P₀ is required.

Formula for W_m is given,

$$W_m = 1/(s + i) \dots \dots \dots 4.6$$

Where s is slope and i is y-intercept of BET plot.

Total surface area is,

$$S_t = (W_m N A_{cs}) / M \dots\dots\dots 4.7$$

Where N is Avogadro's number (6.023×10^{23}), M is molecular weight of adsorbate and A_{cs} is adsorbate cross sectional area (16.2 \AA^2 for nitrogen).

Specific surface area is then calculated by total surface area by sample weight,

$$S = S_t / W \dots\dots\dots 4.8$$

Figure 4.6 shows BET plot for undoped and Zn doped CuO nanostructures.

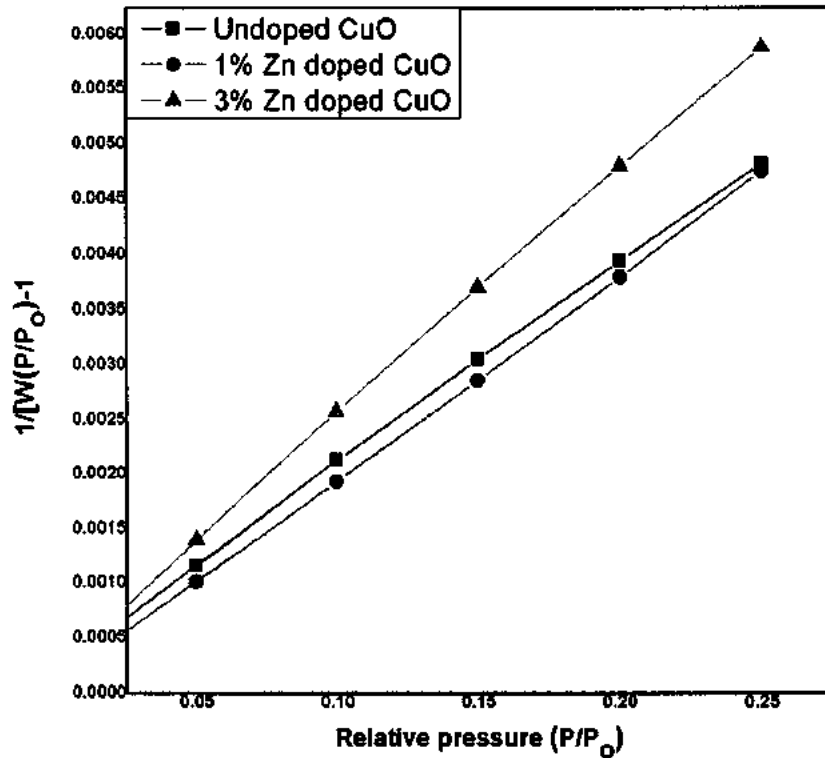


Figure 4.6(a): BET plot for undoped and 1%, 3% Zn doped CuO nanostructures

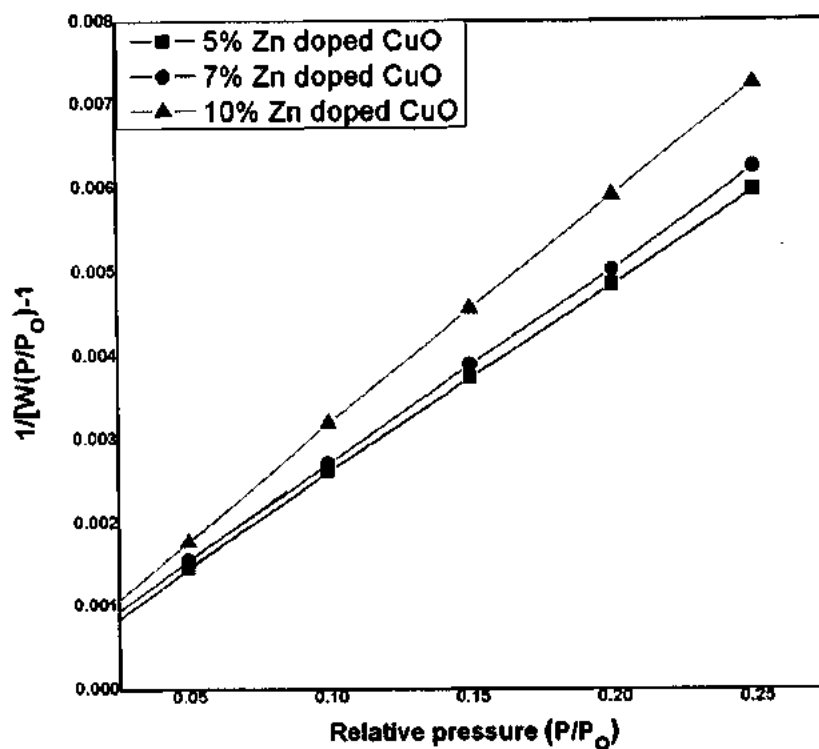


Figure 4.6 (b): BET plot of 5%, 7%, 10% Zn doped CuO nanostructures

Table 4.8: BET analysis results of slope, y-intercept, and surface area.

Sample	Slope	Y-intercept	BET Surface area m^2/g
Undoped			
Zn_{0.01}Cu_{0.99}O	0.18701	0.000584	232 ± 0.99
Zn_{0.03}Cu_{0.97}O			
Zn_{0.05}Cu_{0.95}O	0.022458	0.000852	190 ± 1.1
Zn_{0.07}Cu_{0.93}O			
Zn_{0.10}Cu_{0.90}O	0.27262	0.001115	156 ± 1.44

Figure 4.7 depicts the SSA of the synthesized CuO nanostructures as a function of Zn dopant concentration. It can be clearly seen from this figure that the SSA of CuO nanostructures decreases as concentration of Zn increases. SSA of 234 m²/g has been calculated for undoped CuO nanostructures which are decreased significantly down to 156 m²/g. The SSA of nanostructures is strongly dependent on grain size [42]. In our case, the grain size has been observed to increase significantly with Zn doping. The grain size of CuO nanostructures has been increased from 26 nm undoped CuO to 41 nm for 10% Zn doped CuO as observed from SEM analysis. Hence, this reduction in SSA may be associated with the increase in grain size.

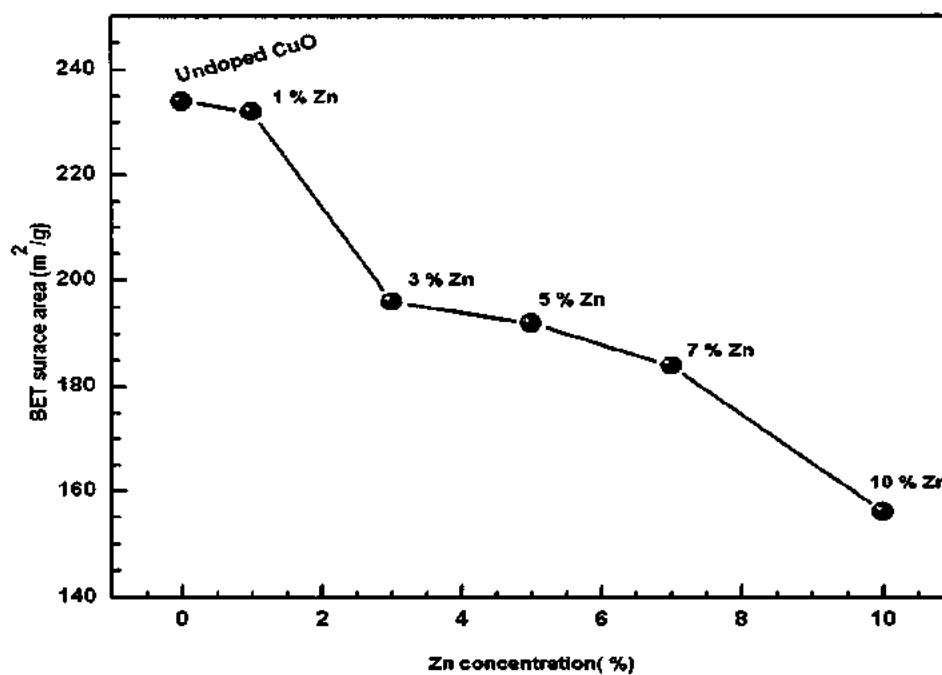


Figure 4.7: Plot of BET surface area against Zn concentration

4.7 Optical Properties

UV-visible absorption spectroscopy has been used to study the Zn doping induced effects on the optical properties of CuO nanostructures. Figure 6 shows the absorption spectra

of the synthesized undoped and Zn doped CuO nanostructures. Undoped CuO nanostructures exhibit band edge absorption peak at 390 nm which is red shifted with Zn doping. Furthermore, Zn doping results in the widening of the absorption peak towards visible region. It is observed from figure 4.8 that Zn doping has effectively enhanced the visible light absorption capability of CuO nanostructures which might be potential for visible light photocatalysis. This enhancement in absorption of light in visible region with Zn doping may attributed to d-d transition between closely spaced Zn²⁺ and Cu²⁺ ions [43]. The optical band gaps (E_g) of the undoped and Zn doped CuO nanostructures have been determined using the following relation [44];

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

Where $h\nu$ is photon energy, α is absorption coefficient, B is constant whose value depends on material and n is 2 for direct transition and 1/2 for indirect transition. Here for direct band gap calculations n is taken to be 2.

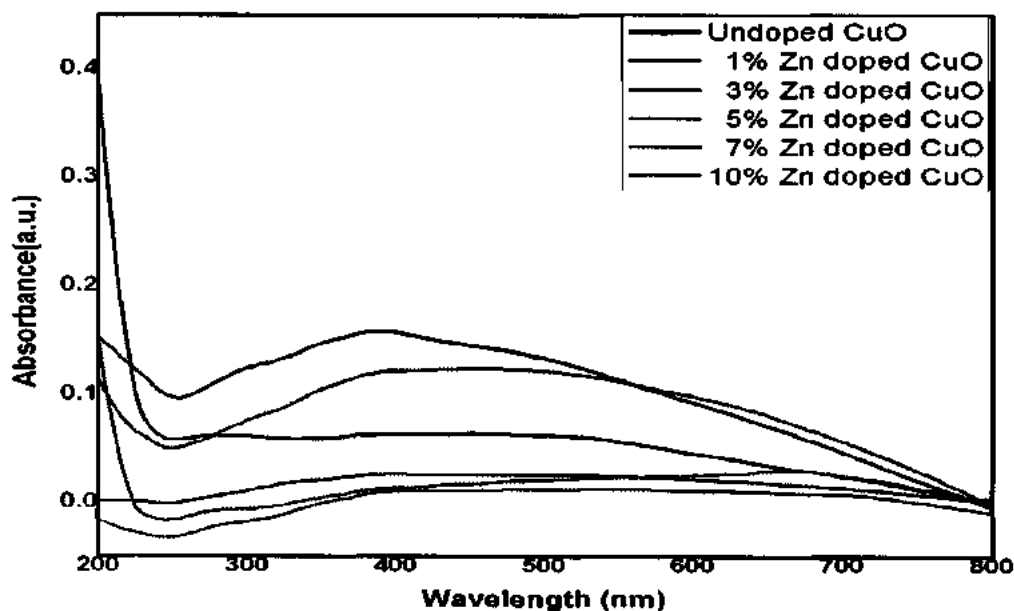


Figure 4.8: UV spectra of undoped and Zn doped CuO nanostructures

The direct band gap energy of all samples have been calculated by plotting $(\alpha h\nu)^2$ against energy of incident photons (i.e. $E = h\nu$) and extrapolating the curves to energy axis as shown in figure 4.9.

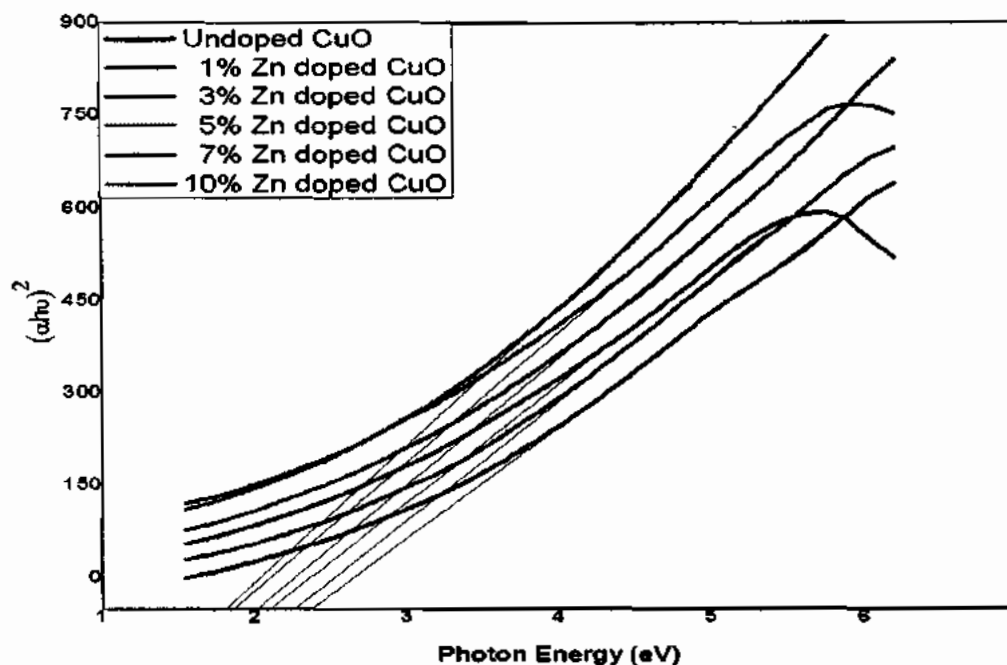


Figure 4.9: Band gap of undoped and Zn doped CuO nanostructures

The value of direct band gap energy of undoped CuO nanostructures is observed to be 2.39 eV, which is large as compared to the bang gap value for bulk CuO (1.55 eV) [45]. This reduction of E_g may be linked with quantum confine effects. Similar value of E_g is also reported for CuO nanostructures previously [46]. Zn doping into CuO nanostructures have led to further reduction of E_g down to 1.82 eV for 10% Zn doped CuO nanostructures. Zn doping into CuO host matrix may lead to the formation of shallow levels inside the band gap of CuO nanostructures causing reduction in E_g [47]. Moreover, the reduction of E_g may be also regarded as the consequence of combined transition from oxygen 2p states to d sates of Cu and Zn [43]. Values of band gap for all samples are given in table 4.9.

Table 4.9: Values of band gap of undoped and Zn doped CuO nanostructures

Sr. No.	Samples	Energy Band Gap (eV)
2	$Zn_{0.01}Cu_{0.99}O$	2.26
4	$Zn_{0.05}Cu_{0.95}O$	2.02
6	$Zn_{0.10}Cu_{0.90}O$	1.82

CONCLUSIONS

Undoped CuO and Zn doped CuO nanostructures have been successfully prepared using Co-precipitation solution method. The prepared nanostructures have been studied using XRD, SEM, FTIR, EDS, BET and UV Spectroscopy. The following conclusions are drawn by the use of these techniques;

- Undoped CuO and Zn doped CuO nanostructures have single phase monoclinic crystal structure without forming any extra impurities phase. The crystallite size increases from 10.23 nm to 17.67 nm with the increase of Zn concentration which may be due to difference in the ionic radii of host cation (Cu) and dopant cation (Zn).
- FTIR results further validated the successful doping of Zn into CuO host matrix.
- SEM results depict the formation of hierarchical nanostructures in the grain size range of 26 nm to 43 nm.
- From EDS spectra it is noted that copper, zinc, oxygen and chlorine are the major elements present in samples.
- The SSA surface area has been observed to decrease with Zn doping which is assigned to decreasing in the particle size.
- The optical band gap energy of the CuO hierarchical nanostructures has been found to decrease significantly upon Zn doping. The band gap of undoped CuO nanostructure is 2.39 eV which is found to decrease to 1.82 eV with Zn doping. The tuned band gap is potential for sun light activated photocatalyst and solar cell applications.

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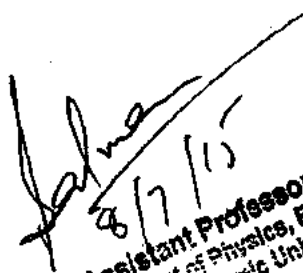
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2CuO is a p- type semiconductor having a direct band gap

(1.22—1.55 eV).

1Undoped and Zn doped CuO nanostructures have been successfully synthesized via chemical co-precipitation method

at low temperature. All the prepared samples have been characterized

1using different techniques such as XRD,