SYNTHESIS AND CHARACTERIZATION OF COPPER NANOPARICLES

Project Report Submitted to

AYYA NADAR JANAKI AMMAL COLLEGE, SIVAKASI
(Autonomous, affiliated to Madurai Kamaraj University, Re-accredited (4th cycle) with ‘A$^+$’ grade (CGPA 3.48 out of 4) by NAAC and recognized as College of Excellence by UGC, STAR College by DBT and Ranked 58th at National Level in NIRF 2020)
SIVAKASI – 626 124.

In partial fulfillment of the requirements
for the award of the
Degree of
MASTER OF SCIENCE IN
PHYSICS
By
M. MATHUPRAKASH

(Register No: 19PP20)

Under the Guidance of
Dr. A. ARUL SANKAR M.Sc., M.Phil., Ph.D.

CENTRE FOR RESEARCH AND POST GRADUATE STUDIES IN PHYSICS
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AYYA NADAR JANAKI AMMAL COLLEGE
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MAY 2021

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CERTIFICATE

This is to certify that this project report entitled **“SYNTHESIS AND CHARACTERIZATION OF COPPER NANOPARTICLES”** being submitted by **M. MATHUPRAKASH** (**Reg.No.19PP20),** student of M.Sc., Degree programme in Physics, Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi, affiliated to Madurai Kamaraj University, Madurai, is a bonafide record of work carried out by him under the guidance and supervision of **Dr. A. ARULSANKAR, M.Sc.,M.Phil.,Ph.D.,** Assistant Professor of Physics, Department of Physics, Ayya Nadar Janaki Ammal College, Sivakasi..

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It is further certified that to the best of my knowledge, this project report or any part therefore has not been submitted in this University or elsewhere for any other Degree or Diploma.

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DECLARATION

I do hereby declare that the project report entitled, “SYNTHESIS AND CHARACTERIZATION OF COPPER NANOPARTICLES” has been carried out by me under the guidance and supervision of **Dr. A. ARULSANKAR, M.Sc., M.Phil., Ph.D.,** Assistants Professor and Head, Department of Physics (U.G) and has not been submitted elsewhere for the award of any other degree or diploma.

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ACKNOWLEDGEMENT

I express my heartfelt gratitude to the management, and the Principal, **Dr. C. Ashok, M.P.Ed., M.Phil., D.Y.Ed., Ph.D.,** and the staff of the Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi for providing all the necessary facilities to carry out this work.

I extend my sincere thanks to **Dr. B**. **SUNDARESAN, M.Sc., MPhil., B.Ed., Ph.D.,** Head and Associate Professor, Department of Physics (P.G), Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi, for his constant encouragement and valuable advice throughout the course.

I express my heartfelt and sincere gratitude to **Dr. A. ARULSANKAR, M.Sc., M.Phil., Ph.D.,** Assistant Professor and Head, Department of Physics (U.G), Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi, for his stimulating guidance, invaluable suggestions and persistent encouragement.

I would like to thank **God Almighty** for having showered blessings upon me to complete my project successfully.

I express my sincere thanks to the faculties of the Centre for Research and Post Graduate Studies in Physics. I wish to express my heartfelt thanks to P.G. And U.G. Laboratory Assistants, for their kindness and support throughout my project work.

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TABLE OF CONTENTS

CHAPTER – I

INTRODUCTION

1.1 Nano science

The word Nano science refers to the study, manipulation and engineering of matter, particles and structures on the nanometer scale (one millionth of a millimeter, the scale of atoms and molecules). Important properties of materials such as the electrical, optical, thermal, magnetic and mechanical properties were determined by the way molecules and atoms assemble on the nano scale into larger structures. In nanometer size structures these properties often different then on macroscale, because quantum mechanical effects become important.

1.2 Nanotechnology

Nanotechnology refers to any technology done on a nanoscale that has applications in the real world. It is defined as the control or restructuring of matter at the atomic and molecular levels in the size range of about 1–100 nm. Nanotechnology is the application of nanoscience leading to the use of new nanomaterials and nanosize components in useful products. Nanotechnology will eventually provide us with the ability to design custom made materials and products with new enhanced properties, new nanoelectronics components, new types of “smart” medicines and sensors.

1.2.1. History of Nanomaterials

The history of nanomaterials began immediately after the big bang when nanostructures were formed in the early meteorites. In nature, many other nanostructures like seashells, skeletons etc. were observed. Nanoscale smoke particles were formed during the use of fire by early humans. The scientific story of nanomaterials however began much later. One of the first scientific reports is the colloidal gold particles synthesized by Michael Faraday as early as in 1857. Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanostructured science and technology was a broad and interdisciplinary area of research and development activity. Now a day, nanomaterials are of great interest to the scientists because, at this size exclusive optical, magnetic, electrical, and other properties are emerged. These emergent properties have great influence in nanoelectronics, medicine, biological nano sensors, optoelectronics, nanodevices, information storage and catalysis which are significantly different from that of bulk material. Nanomaterials can be present in one dimension, two dimensions or three dimensions. They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. Nanomaterials have applications in the field of nano technology, and displays different physical chemical characteristics from normal chemicals (i.e., silver nano, carbon nano tube, fullerene, photocatalyst, carbon nano, silica).

1.2.2 Nanoparticles

Nanoparticles are of great interest as they were effectively a bridge between bulk materials and atomic or molecular structures. The properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of material become significant.

1.3. Preparation of nanomaterial

Synthesis of nanoparticles to have a better control over particles size distribution, morphology, purity, quantity and quality, by employing environment friendly economical processes has always been a challenge for the researchers. Nano particles can be prepared by using two different methods. They are

- Top down approach
- Bottom up approach

1.3.1 Top down approach

- The top-down approach is a process of miniaturizing or breaking down bulk materials (macro-crystalline) structures while retaining the original integrity.

- Top-down routes were included in the typical solid –state processing of the materials. This route was based with the bulk material and makes it smaller, thus breaking up larger particles by the use of physical processes like crushing, milling or grinding.

- Usually this route was not suitable for preparing uniformly shaped materials, and it was very difficult to realize very small particles even with high energy consumption.

- The biggest problem with top-down approach was the imperfection of the surface structure. Such imperfection would have a significant impact on physical properties and surface chemistry of nanostructures and nano materials.

- It was well known that the conventional top-down technique could cause significant crystallographic damage to the processed patterns.

- Top-down approach was also called as physical method.

1.3.2 Bottom up approach

- *The bottom-up approach* involves building of nanomaterials from the atomic scale (assembling materials from atoms/molecules): atom-by-atom, molecule-by-molecule or cluster-by-cluster.

- This route was more often used for preparing most of the nano-scale materials with the ability to generate a uniform size, shape and distribution.

- It effectively covers chemical synthesis and precisely controlled the reaction to inhibit further particle growth.

- Although the bottom-up approach was nothing new, it plays an important role in the fabrication and processing of nanostructures and nanomaterials.

- Bottom-up approach was also called as chemical method.

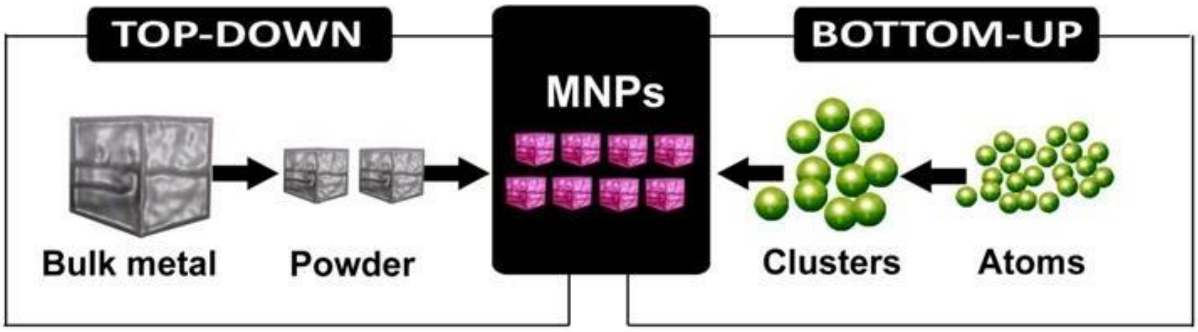


Fig.1.1. Top down and Bottom up approach

1.4. Chemical synthesis method

There were so many methods available to prepare nano materials. Some of them were listedbelow,

- Co-precipitation method.
- Sol gel method

1.4.1 Co precipitation method

Co-precipitation reactions involve the simultaneous occurrence of nucleation, growth, coarsening, and/or agglomeration processes.

Co-precipitation reactions exhibit the following characteristics

- The products were generally insoluble species formed under conditions of high super saturation.
- Nucleation was a key step, and a large number of small particles were formed.
- Secondary processes, such as Ostwald ripening and aggregation, dramatically affect thesize, morphology, and properties of the products.
- The super saturation conditions necessary to induce precipitation were usually the resultof a chemical reaction.

Typical co-precipitation synthetic methods were

- Metals formed from aqueous solutions, by reduction from nonaqueous solutions, electrochemical reduction, and decomposition of metallorganic precursors.
- Oxides formed from aqueous and nonaqueous solutions.
- Metal chalconides formed by reactions of molecular precursors.
- Microwave/sonication-assisted coprecipitation.

Advantages and disadvantages of coprecipitation method were as follows,Advantages

- Simple and rapid preparation.
- Easy control of particle size and composition.
- Various possibilities to modify the particle surface state and overall homogeneity.
- Low temperature.
- Energy efficient.
- Does not involve use of organic solvent.

Disadvantages

- Not applicable to uncharged species.
- Trace impurities may also get precipitated with the product.
- Time consuming. Batch-to-batch reproducibility problems.
- This method does not work well if the reactants have very different precipitation rates.

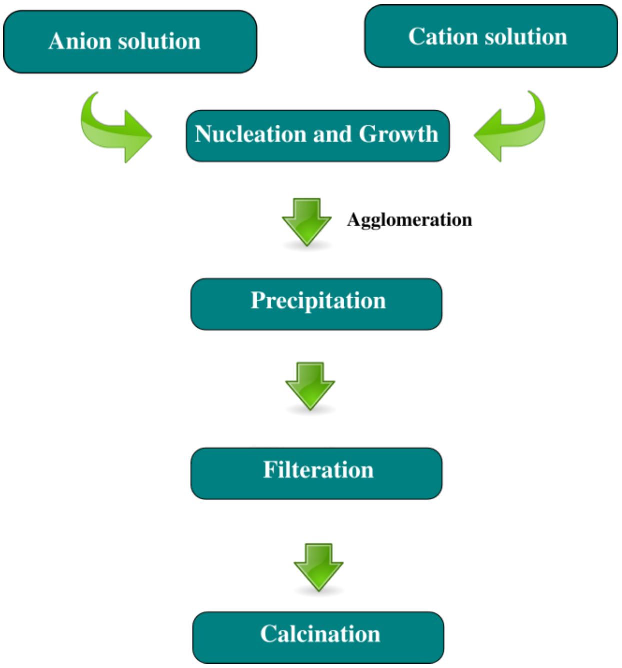


Fig.1.2. Flow chart of co – precipitation method

1.4.2. Sol gel method

Sol–gel method was one of the well-established synthetic approaches to prepare novel metal oxide NPs as well as mixed oxide composites. This method has potential control over the textural and surface properties of the materials.

Sol–gel method mainly undergoes in few steps to deliver the final metal oxide protocols and those were hydrolysis, condensation, and drying process. The formation of metal oxide involves different consecutive steps, initially the corresponding metal precursor undergoes rapid hydrolysis to produce the metal hydroxide solution, followed by immediate condensation which leads to the formation of three-dimensional gels. Afterward, obtained gel is subjected to drying process, and the resulting product is readily converted to Xerogel or Aerogel based on the mode of drying.

Sol–gel method can be classified into two routes, such as aqueous sol–gel and nonaqueous sol–gel method depending on the nature of the solvent utilized.

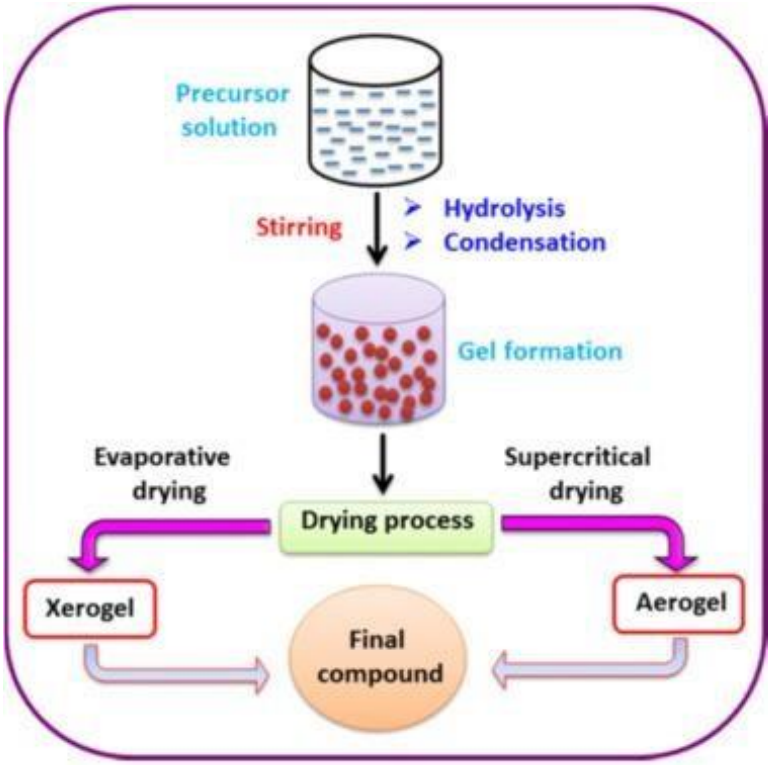


Fig.1.3. Schematic diagram of sol gel method

If water is used as reaction medium it is known as aqueous sol–gel method; and use of organic solvent as reaction medium for sol–gel process is termed as nonaqueous sol–gel route. In the sol–gel approach, nature of metal precursor and solvent plays a remarkable role in the synthesis of metal oxides NPs.

1.5 Literature Review

1. Copper nanoparticles have been synthesized by using chemical reduction method using de-ionized water as solvent. The surface morphology is observed by Atomic Force Microscope (AFM). The formation of copper nanoparticles was confirmed by UV-Visible spectrophotometer (UV-Vis), X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR). Copper nanoparticles fabricated by chemical reduction method have diameter in the range 14 nm to 55 nm. Structural analysis revealed the face centered cubic (fcc) crystal structure of copper nanoparticles.

2. Chemical methods such as chemical reduction, photochemical, electrochemical, and thermal decomposition are used to synthesize copper nanoparticles and among them chemical reduction is the most frequently applied method for the preparation of stable, colloidal dispersions in organic solvents. Copper nanoparticles can easily oxidize to form copper oxide. Therefore, the reduction methods are usually performed under an inert atmosphere, in organic solvents or in presence of surfactants such as poly (vinyl pyrrolidone).

3. The green copper nanoparticles (g-Cu NPs) were successfully synthesized by using medicinal plant *Hagenia abyssinica (Brace) JF. Gmel.* leaf extract. The presence of phytoconstituents such as polyphenols of tannins played roles in reducing and capping agents during the formation of g-Cu NPs. The UV-visible absorbance and reflectance spectra showing of 403 nm and of 2.19 eV, respectively, confirmed the formation of g-Cu NPs. FTIR spectra supported the presence of capping agents on the surface of g-Cu NPs. The crystalline nature and composition of g-Cu NPs were confirmed by XRD pattern and EDX spectrum, respectively. The SEM and TEM micrographs provided enough evidence towards the nanomorphology of g-Cu NPs with all possible shapes including spherical, triangular, hexagonal, and cylindrical shapes with an average particle size of 34.76 nm. HRTEM micrographs and SAED patterns confirmed the presence of Cu and surface

4. oxidized Cu_2O NPs. The wide zone of inhibition of g-Cu NPs against pathogens confirms their great potential as a remedy for infectious diseases caused by the tested bacterial pathogens. Finally, it can be concluded that the synergistic effect of bioactive compounds from medicinal plant coupled with Cu NPs has been proved to be beneficial against pathogens.

5. High dispersive copper nanoparticles were prepared by chemical reduction method using potassium borohydride as reducing agent. The effects of reactant ratio, concentration of $CuSO_4$, reaction temperature, and dispersant on the size of product and conversion rate were studied. The morphologies of copper nanoparticles were characterized by scanning

electron microscopy. The results show that the optimum process conditions are as follows: the molar ratio of KBH_4 to $CuSO_4$ is 0.75 (3:4), concentration of $CuSO_4$ is 0.4 mol/L, reaction temperature is 30 °C, and dispersant is *n*-butyl alcohol. The average particles size of copper powders with spherical shape gained is about 100 nm.

1.6. Objective of the work

The scope of this work is,

- To synthesize Copper nanoparticles by using co–precipitationmethod
- To characterize the nanoparticles using UV-Visible Spectroscopy, Fourier Transform Infrared Spectroscopy, X-Ray Diffractography and to estimate the size of the nanoparticles using Particle Size Analyzer.

CHAPTER – II

EXPERIMENTAL TECHNIQUES

2.1 Introduction

The fabrication of nano materials with solid control over size, shape, and crystalline has become very important for the applications of nanotechnology in various fields. The Bottom-up approach is widely popular for the synthesis of nanoparticles as it gives a homogeneous size distribution than the top down approach.

In the present work, copper nanoparticles are prepared by co-precipitation method.

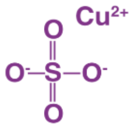
2.2 Materials used

- Copper sulphate
- Poly ethylene glychol
- L - ascorbic acid
- Sodium hydroxoide
- Sodium borohydride

2.2.1 Copper Sulphate

Copper sulfate is an inorganic compound that combines sulfur with copper. It can kill bacteria, algae, roots, plants, snails, and fungi. The toxicity of copper sulfate depends on the copper content. Copper is an essential mineral.

2.2.1.1. Structure



2.2.1.2. Properties of copper sulfate

Table 2.1 Properties of copper sulfate

Chemical formula	$CuSO_4$
Molar mass	249.685 g/mol
Appearance	Blue
Solubility	soluble in water
Density	2.26g/cm3
Melting point	110 °C
Boiling point	650 °C
pH	4.58

2.2.1.3 Uses of Copper Sulfate

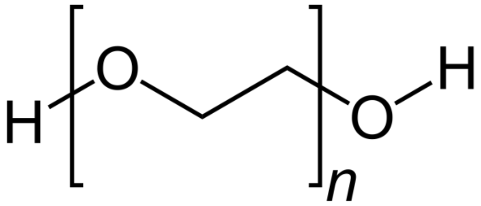
Basic chemistry sets that are used as educational tools generally include copper sulfate. The chemical compound $CuSO_4$ has a wide range of applications. Some of these uses are listed below.

- The pentahydrate of this compound, $CuSO_4.5H_2O$ is used as a fungicide due to its ability to kill several fungi.
- Copper sulfate is used in Benedict's solution and in Fehling's solution, which is used in testing for reducing sugars.
- It is also used to test blood samples for diseases like anaemia.
- $CuSO_4$ is mixed with $KMnO_4$ (potassium permanganate) to form an oxidant which can be used in the conversion of 1^o
- It is also used as a dye fixative in the process of vegetable dyeing.
- Solutions of copper sulfate in water can be used as a resistive element liquid resistors.
- It can also be used as a decorative since it can add colour to cement, ceramics, and other metals as well.
- Copper sulfate is also added to bookbinding glues in order to protect the printed paper from insects.

2.2.2. Poly ethylene glychol

PEG is soluble in water, methanol, ethanol, acetonitrile, benzene, and dichloromethane, and is insoluble in diethyl ether and hexane. It is coupled to hydrophobic molecules to produce non-ionic surfactants. PEGs potentially contain toxic impurities, such as ethylene oxide and 1,4-dioxane.

.2.2.2.1. Structure



Structure of Poly Enthlyene Glycol

2.2.2.2. Properties of poly ethylene glychol

Table 2.2 Properties of poly ethylene glychol

Chemical formula	HO–(CH_2CH_2O)$_n$–H,
Molar mass	18.02 g/mol
Appearance	White
Solubility	soluble in water
Density	1.12 g/cm³
Melting point	62.2 °C
Boiling point	Less than150 °C
pH	2-3

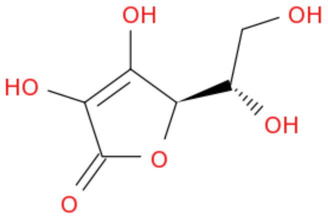
2.2.2.3. Uses of poly ethylene glychol

- PEG 4000 acts as an osmatic agent that increases fecal water content.
- A number of clinical studies have demonstrated that PEG 4000is effective in the treatment of constipation in adults and children (3-7)

2.2.3. L –Ascorbic acid

Pure vitamin is known as l-ascorbic acid. The “*L*” in front of is ascorbic reference to how the molecule itself rotates to light and refers to its source**.** L-ascorbic acidcomes from natural sources such as oranges. . l-ascorbic acid products penetrate the skin tissue and are more active in collagen production.

2.2.3.1. Structure



Structure of I – ascorbic acid

2.2.3.2. Uses of L-ascorbic acid

- It is used to prevent or treat low levels of vitamin c in people who do not get enough of the vitamin from their Diets.
- It is also functions as an antioxidant.

2.2.3.3. Proberties of L- ascorbic acid

Table 2.3 Properties of L-ascorbic acid

Chemical formula	$C_6H_8O_6$ or $HC_6H_7O_6$
Molar mass	176.13 g/mol
Appearance	White
Solubility	soluble in water
Density	1.65 g/cm^3
Melting point	190 °C
Boiling point	553°C
pH	1.0-2.5

2.2.4 Sodium Hydroxide

Sodium hydroxide is also known as lye or soda, or caustic soda. At room temperature, sodium hydroxide is a white crystalline odorless solid that absorbs moisture fromthe air. It is a synthetically manufactured substance. When dissolved in water or neutralized with acid it releases substantial amounts of heat, which may prove sufficient to ignite combustible materials. Sodium hydroxide is highly corrosive.

2.2.4.1. Structure

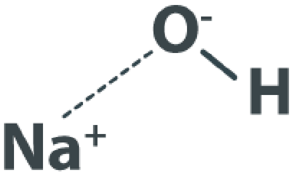


Fig.2.3. structure of sodium hydroxide

2.2.4.2. Properties of sodium hydroxide

Table 2.4 Properties of sodium hydroxide

Chemical formula	NaOH
Molar mass	39.997 g/mol
Appearance	colorless pellets
Solubility	soluble in water
Density	1.5 at 68 °F
Melting point	604 °F
Boiling point	greater than 266 °F
pH	greater than 14

2.2.4.3. Uses of Sodium hydroxide

- Sodium hydroxide is a popular strong base used in industry.
- It is used in many scenarios where it is desirable to increase the alkalinity of a mixture, or to neutralize acids.
- It is also used during water purification to raise the pH of water supplies. Increased pH

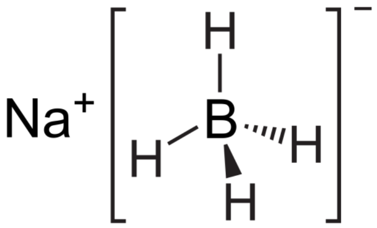
makes the water less corrosive to plumbing and reduces the amount of lead, copper and other toxic metals that can dissolve into drinking water.

- Sodium hydroxide is used as a precipitating agent.

2.2.5. Sodium borohydride

Sodium borohydride, also known as sodium tetrahydridoborate and sodium tetrahydroborate, is an inorganic compound with the formula $NaBH_4$. This white solid, usually encountered as a powder, is a reducing agent that finds application in chemistry, both in the laboratory and on an industrial scale.

2.2.5.1. Structure



Sodium boro hydrate

2.2.5.2. Properties of sodium borohydride

Table 2.5 Properties of sodium borohydride

Chemical formula	$NaBH_4$
Molar mass	37.83 g/mol
Appearance	White
Solubility	soluble in water
Density	1.07 g/cm³
Melting point	400 °C
Boiling point	500 °C
pH	greater than 10

2.2.5.3. Uses of sodium borohydride

- It is used for bleaching wood pulp, as a blowing agent for plastics, and as a reducing agent for aldehydes and ketones.

- Several antibiotics such as thiophenicol, dihydrostreptomycin are produced by employing sodium borohydride
- As a reducing agent.

2.2.6. EXPERIMENTAL METHODS

2.2.6.1. Synthesis of copper nanoparticles

Copper sulfate was dissolved in 100ml distilled water. Then 2g of polyethylene glycol was dissolved in 50ml distilled water and added to the aqueous solution of containing the copper salt while vigorously stirring in magnetic stirrer for some hours. 1.76g of L-ascorbic acid and 0.8 g of sodium hydroxide solution was added drop wise from two separate burettes into a reaction of synthesis solution. This solution is stirred continuously for few hours. Then sodium borohydride was added drop wise into synthesis solution. The reaction vessel was stirred for few minutes. After 48hrs the solution was precipitated. It was then filtered using whatmann filter paper and dried in hot plate stirrer. The resultant particles are collected and grained using mortar and pestle.

CHAPTER - III

CHARACTERIZATION STUDIES

3.1. Introduction

The following characterization studies are taken to understand the nature of the preparedsamples.

- Fourier Transform Infrared Spectroscopy (FTIR)
- Particle Size Analysis
- UV analysis
- XRD analysis

3.2. Fourier Transform Infrared Spectroscopy (FTIR)

FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

3.2.1. Why FTIR ?

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reducedto a matter of a few seconds rather than several minutes. Most interferometers employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beam splitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal whichexits the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source. This means that as the interferogram is measured, all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make an identification, the measured interferogram signal cannot be interpreted directly. A means of “decoding” the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.

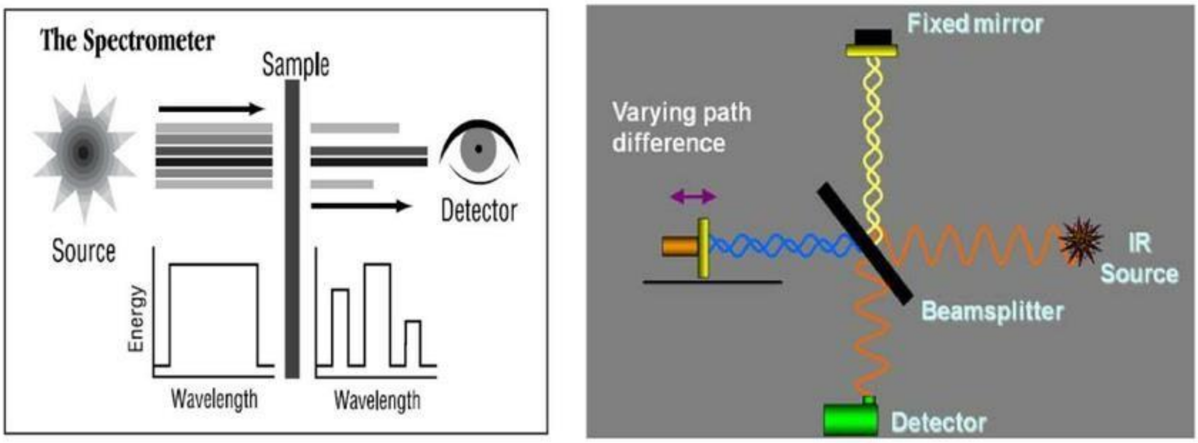


Fig.3.1. Working of FTIR

3.2.2. The Sample Analysis Process

The normal instrumental process is as follows:

1. **The Source:** Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).

2. **The Interferometer:** The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.

3. **The Sample:** The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending of the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, areabsorbed.

4. **The Detector:** The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

5. **The Computer:** The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation. Because there needs to be a relative scale for the absorption intensity, a background spectrum must also be measured. This is normally a measurement with no sample in the beam. This can be compared to the measurement with the sample in the beam to determine the “percent transmittance.” This technique results in a spectrum which has all of the instrumental characteristics removed. Thus, all spectral features which are present are strictly due to the sample. A single background measurement can be used for many sample measurements because this spectrum is characteristic of the instrument itself.

3.2.3. Advantages of FT-IR

Some of the major advantages of FT-IR over the dispersive technique include:

- **Speed:** Because all of the frequencies are measured simultaneously, most measurements by FT-IR are made in a matter of seconds rather than several minutes. This is sometimes referred to as the Felgett Advantage.

- **Sensitivity:** Sensitivity is dramatically improved with FT-IR for many reasons. The detectors employed are much more sensitive, the optical throughput is much higher (referred to as the Jacquinot Advantage) which results in much lower noise levels, and the fast scans enable the

Co addition of several scans in order to reduce the random measurement noise to any desired level(referred to as signal averaging).

- **Mechanical Simplicity:** The moving mirror in the interferometer is the only continuously moving part in the instrument. Thus, there is very little possibility of mechanical breakdown.

- **Internally Calibrated:** These instruments employ a HeNe laser as an internal wavelength calibration standard (referred to as the Connes Advantage). These instruments are self calibratingand never need to be calibrated by the user.

These advantages, along with several others, make measurements made by FT- IR extremely accurate and reproducible. Thus, it a very reliable technique for positive identification of virtually any sample. The sensitivity benefits enable identification of even the smallest of contaminants. This makes FT-IR an invaluable tool for quality control or quality assurance applications whether it be batch-to-batch comparisons to quality standards or analysis of an unknown contaminant. In addition, the sensitivity and accuracy of FT-IR detectors, along with a wide variety of software algorithms, have dramatically increased the practical use of infrared for quantitative analysis. Quantitative methods can be easily developed and calibrated and can be incorporated into simple procedures for routine analysis.

Thus, the Fourier Transform Infrared (FT-IR) technique has brought significant practical advantages to infrared spectroscopy. It has made possible the development of many new sampling techniques which were designed to tackle challenging problems which were impossible by older technology. It has made the use of infrared analysis virtually limitless.

3.3. Particle Size Analyzer

The particle size and size distribution of nanoparticles can be determined using numerouscommercially available instruments. Instruments can be used for the analysis of dry powders and powders dispersed in suspension. In general, there are two basic methods of defining particle size. The first method is to inspect the particles and make actual measurements of their dimensions. The second method utilizes the relationship between particle behavior and its size. This implies an assumption of equivalent spherical size developed using a size-dependent property of the particle relating it to a linear dimension.

The preparation of sample is the most important step when making a measurement. The accuracy for the measurement depends on sample preparation and extraction. One has to carefully define a method for extraction and sample preparation in order to obtain precise and reproducible results. For a measurement in dry mode, the sample should be first treated and then cone and quartered to represent an amount between 1mg and 100mg. in liquid mode representative of the powdered or liquid sample should be poured into the tanker.

3.3.1. Particle sizing by laser diffraction

Laser diffraction has become one of the most commonly used particle sizing methods, especially for particles in the range of 0.5 to 1000 microns. Laser diffraction has become very popular because it can be applied to many different sample types, including dry powders, suspensions, emulsions and even aerosols. It is also a very fast, reliable and reproducible technique and can measure over a very wide size range.

3.3.2. Principle

It works on the principle that when a beam of light (a laser) is scattered by a group of particles, the angle of light scattering is inversely proportional to particle size (ie. the smaller the particle size, the larger the angle of light scattering). Large particles scatter light at small angles relative to the laser beam and small particles scatter light at large angles. The angular scattering intensity data is then analyzed to calculate the size of the particles responsible for creating the scattering pattern, using the Mie theory of light scattering. The particle size is reported as a volume equivalent sphere diameter.

3.3.3. Instrument

A typical laser diffraction system is made up of three main elements,

1. Optical bench

A dispersed sample passes though the measurement area of the optical bench, where a laser beam illuminates the particles. A series of detectors then accurately measure the intensity of light scattered by the particles within the sample over a wide range of angles.

2. Sample dispersion units

Sample handling and dispersion are controlled by sample dispersion units designed to either measure the sample wet or dry. These ensure the particles are delivered to the measurement area of the optical bench at the correct concentration and in a suitable, stable state of dispersion. Wet sample dispersion units use a liquid dispersant, aqueous or solvent based, to disperse the sample. In order to keep the sample suspended and homogenized it is re circulated continuously through the measurement zone.

3. Sample Treatment

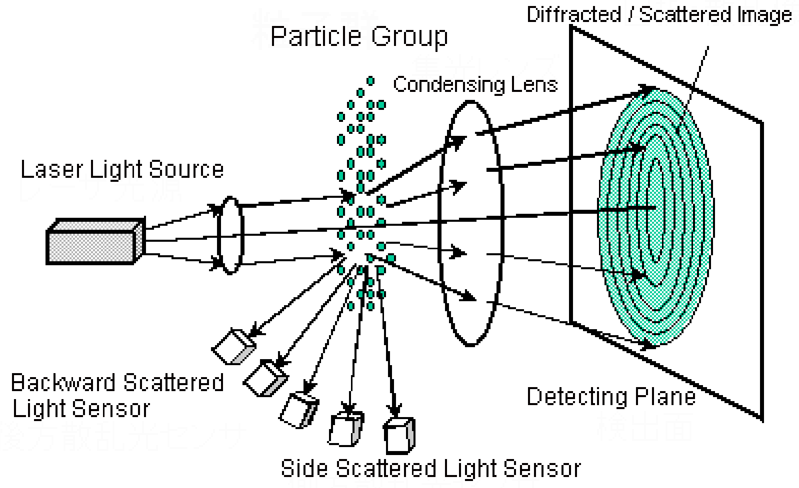
Dry powder sample dispersion units suspend the sample in a flowing gas stream, usually dry air. Normally the entire sample passes once only through the measuring zone, therefore it is desirable to capture data at rapid speeds, typically up to 10kHz, in order to ensure representative sample measurement.

4. Instrument software

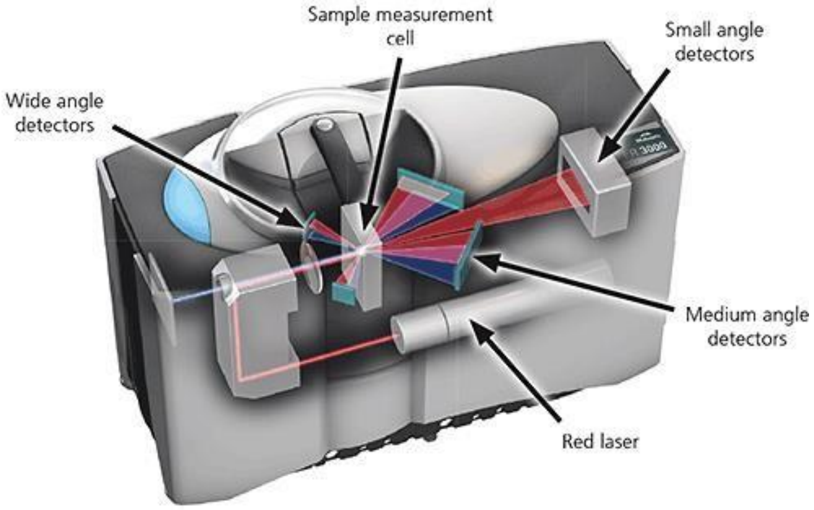
The instrument software controls the system during the measurement process and analyzes the scattering data to calculate a particle size distribution. In more advanced instrumentation it also provides both instant feedback during method development and expert advice on the quality of the results.

3.3.4. Other methods

There are many other methods for analysing particle size, other than laser diffraction. Sieving is one of the oldest particle sizing methods and is still widely used for relatively large particles (ie. > 1mm). When measuring very small particles (ie.< 0.5um), Dynamic Light Scattering is by far the easiest methods to use. And if you need to measure morphological properties of particles, (ie. shape as well as size), then image analysis methods are the only way to gain the extra information.



Working of Particle Size Analyzer



Particle Size analyzer Instrument

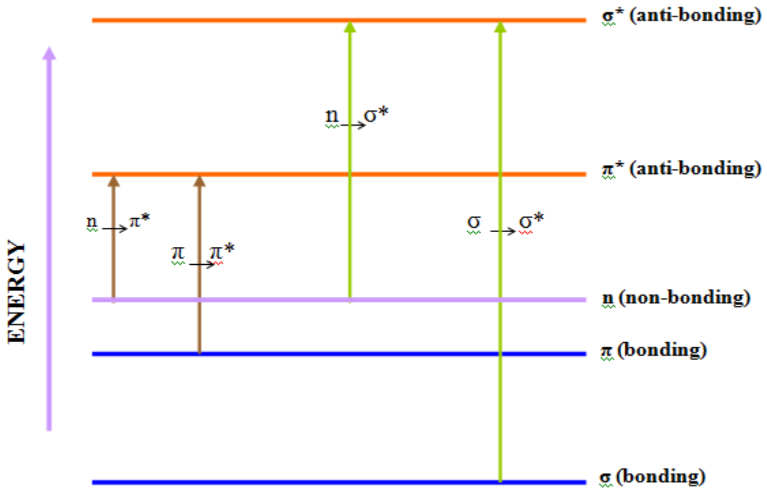
3.4. UV-VISIBLE SPECTRUM

Absorption of light in the UV-Visible part of the spectrum (210–900 nm). The transitions that result in the absorption of electromagnetic radiation in this region of the spectrum are transitions between electronic energy levels. Generally, the most probable transition is from highest occupied molecular orbital (HOMO) to lowest molecular orbital (LUMO). In the present work, an attempt has been made to analyze the optical absorption or transmittance data obtained on thei nano particle. This study helps to precisely identify the allowed direct and indirect transitions in the synthesized metal oxide.

The optical energy gap (E_g) can be calculated from the well-known quadratic equation (Tauc 1974) which is often called Tauc law:

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

Where, $h\nu$ –incident photon energy, E_g - band gap of the material, α – absorption coefficient



Energy level diagram with electronic transitions

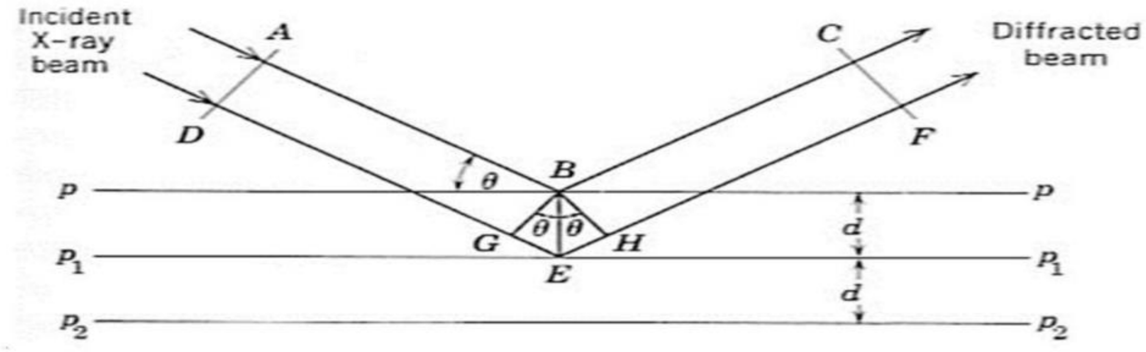
A - constant that depends on the electronic transition probability and ***n*** - an exponent that characterizes the type of electronic transition responsible for the optical absorption.

For direct allowed transition n = ½, indirect allowed transition n = 2 To determine the possible transitions, $(\alpha h\nu)$ versus$h\nu$ are plotted and corresponding band gap can be obtained from extrapolating the straight portion of the graph on $h\nu$axis at $\alpha = 0$. The absorption edge studies are important, especially in connection with the theory of electronic structure.

3.5. X-RAY DIFFRACTION MEASUREMENT

X-Ray diffraction (XRD) measurements of the bio reduced nickel solutions drop-coated into glass substrates were done for the determination of the formation of nanoparticles by an X'Pert Pro Analytical X-ray diffraction instrument with X' Pert high score plus software operating at a voltage of 45 kV and a current of 40 mA with Cu Kα radiation.

X-Ray Power diffraction is a rapid analytical techniques primarily used for phase identification of a crystalline material and can provide information on unit cell dimension. The analyzed material is finely ground, homogenized, average bulk composition is determine


Using the diagram, prove Bragg's Law.

Schematic diagram of X- ray diffraction

3.5.1. Fundamental Principles of X-ray Powder Diffraction (XRD

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law

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

'λ' is the wavelength of incident X-Ray and 'd' is the Spacing between the planes in the atomic lattice.

CHAPTER-IV

RESULTS AND DISCUSSION

4.1 INTRODUCTION

With the aim of understanding the copper nanoparticles which were synthesized successfully using co-precipitation method, several preliminary confirmations and the purity determination using different characterization techniques is undertaken. The synthesized materials were characterized using the techniques mentioned below and their results are discussed.

List of characterizations carried out in the present study are

- UV spectroscopy
- Fourier transform infrared spectroscopy
- Particle size analysis
- X ray diffraction

4.1 UV-VISIBLE SPECTROSCOPY STUDIES

UV-Visble absorption wavelength is sensitive to the size, shape and environment characteristics of nanoparticles. It can also leave a clue about the concentration of nanoparticles in the colloidal sample. The as prepared Copper Nanoparticles in colloidal form was investigated. The absorbance of copper nanoparticles was determined by UV–Visible spectroscopy at different wavelengths varying from 200 to 800 nm. The UV-Visible spectrograph of the sample is shown in figure 4.1.

The collective oscillations of surface dwelling electrons in the nanoparticles, absorb certain electromagnetic wavelength. When it encounters an appropriate electromagnetic radiation, they tend to oscillate because of the absorption of that particular wavelength in the interface between the nanoparticle and surrounding dielectric medium. This is known as surface plasmon resonance.

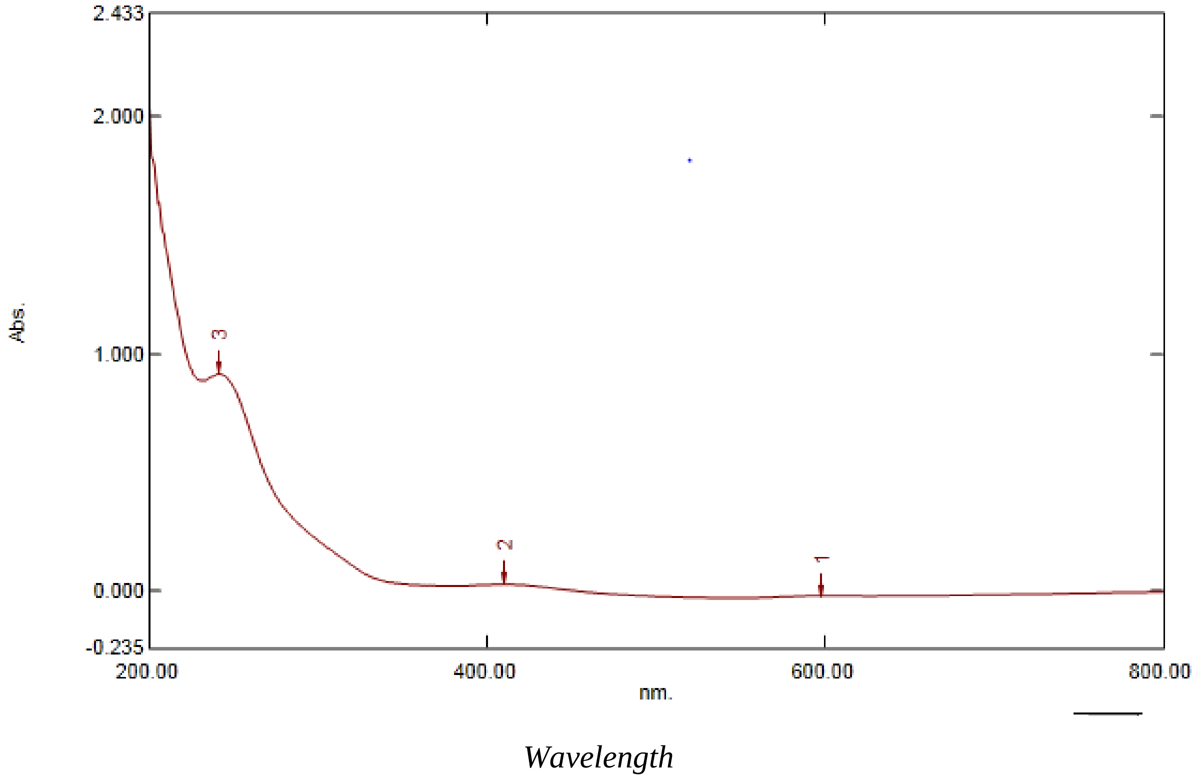


Fig. 4.1 UV-Visible spectrum of Copper Nanoparticles

The observed characteristic curve is comparable with that obtained for any metal nano colloids. The Surface Plasmon Resonance peak of copper nanoparticles is in the range of 500-600 nm [20]. From the figure, three peaks viz., 598 nm, 410 nm and 241 nm were observed. The peak observed at 598 nm is within the range of the characteristic range for the Copper nanoparticles.

The synthesized copper nanoparticles were not stable for an extended period of time. They settle at the bottom of the reaction vessel as days go by. The precipitate may be due to agglomeration and the inability of the dielectric medium to hold the surface charges in the nanoparticles. Also, it may be due to oxidation, because, copper readily oxidizes if not stabilized properly.

Hence, the synthesis was repeated over many times to ensure getting suitable samples for further characterizations. In that case, the formed copper nanoparticles were immediately separated by centrifuge.

Tauc Plot

The optical energy band gap can be calculated from the well-known quadratic equation (TAUC 1974) which is often called Tauc law

$$\alpha h\upsilon = A(h\upsilon - E_g)^{\frac{1}{2}}$$

The Tauc plot obtained from UV-Visible data can be used to determine the band gap associated with the nanoparticles by plotting nergy of photon on the X-axis and square of the energy multiplied by its absorbance on the Y-axis gives the plot as shown below.

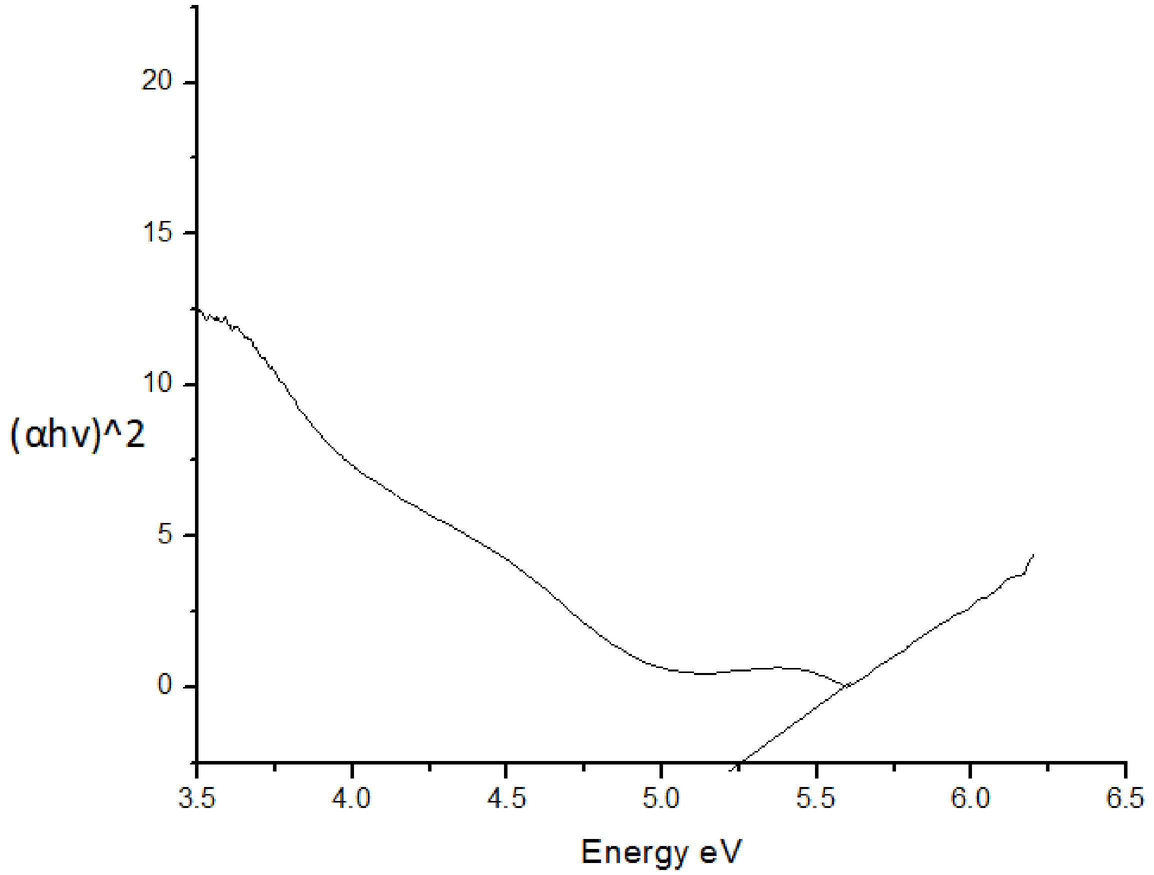


Fig. 4.2 band gap of Copper Nanoparticles

The band gap of synthesized Cu nanoparticles was found to be 5.25 eV [6], which is in good agreement with that reported in the existing literatures.

4.2 Fourier Transform Infrared Spectroscopy

FTIR spectrum of copper nanoparticles obtained by chemical co precipitation method is discussed. FTIR spectrograph plots percentage transmittance (%T) against wavenumber (1/λ). This analysis determines the functional organic groups present in the sample. The Fourier Transform Infrared Spectroscopy is studied in the spectrum range from 2000 cm^{-1} to 200 cm^{-1}. FTIR spectrum of the synthesized copper nanoparticles shown in the figure 4.3.

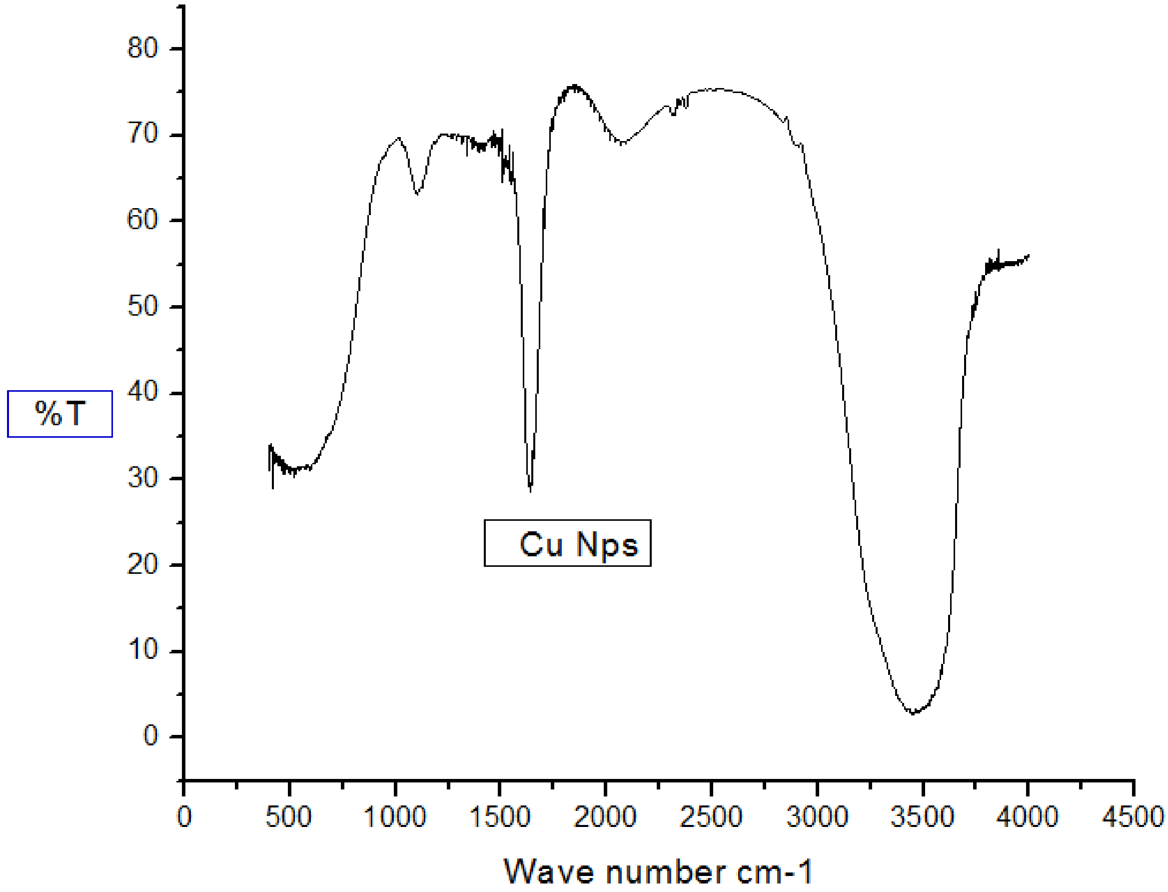


Fig 4.3 FTIR Spectrum of Cu Nanoparticles

The peak at 3447.52 cm^{-1} corresponds to O-H stretching. The peak at 1101.28 cm^{-1} is due to C-O stretching. The peak at 892.98 cm^{-1} is attributed to -CH bending. The transmittance peak at around 742.54 cm^{-1} denotes the presence of =CH bending.

The peak at 597.89 cm^{-1}corresponds to C-X bond. The strong absorption at around 1638.42 cm^{-1} corresponds to the bending vibration of copper nano particles [6].

The following table shows all the vibrational modes of the synthesized nanoparticles.

Table 1: Functional vibration of assignment of copper nano particles

Wavenumber (cm^{-1})	Modes of vibration
3447.52	O-H stretching
1101.28	C-O stretching
892.98	-CH bending
742.54	= CH bending
597.89	C-X bond
1638.42	Copper Characteristic Peak

All the absorption bands mentioned above are due to the surface adhered molecules of the reactant molecules involved in the synthesis of copper nanoparticles.

4.3 X RAY DIFFRACTION ANALYSIS

X-ray diffraction analysis is used as a tool to study the diffraction pattern of a particular material and thereby determining the following.

- Identifying the crystal structure
- Calculate lattice parameter
- Measure stresses in the crystal
- Measure crystallographic texture

The inter-planar distance between two successive planes of atoms can be calculated using the Braggs equation. The simplest and most widely used method for estimating the crystallite size of the diffraction peak using Scherrer equation, which can be expressed as

$$D = \frac{k\lambda}{\beta Cos\theta}$$

Where, ‘D’ is the crystalline size, ‘λ’ is the wavelength of the X Ray source, ‘β’ is the FWHM (Radians), ‘Ɵ’ is the diffraction angle and ‘k’ is the Scherrer constant (k= 0.94)

The crystal structure and phase composition of synthesized copper nanoparticles is analyzed by XRD. The obtained diffractogram is shown in figure 4.4. From the diffraction data it is confirmed that the copper nanoparticles have face centered cubic structure (FCC) with characteristic diffraction peaks in the planes represented by (111), (200) and (220) at 2θ value of 43.4º, 51.1º and 74.9º respectively. The XRD result is the clear evidence that the copper nano particle formed by the chemical co precipitation method were crystalline in nature and this is in good agreement of with earlier reports.

All the peaks obtained were well defined and sharp implying high crystalline nanoparticles in the sample.

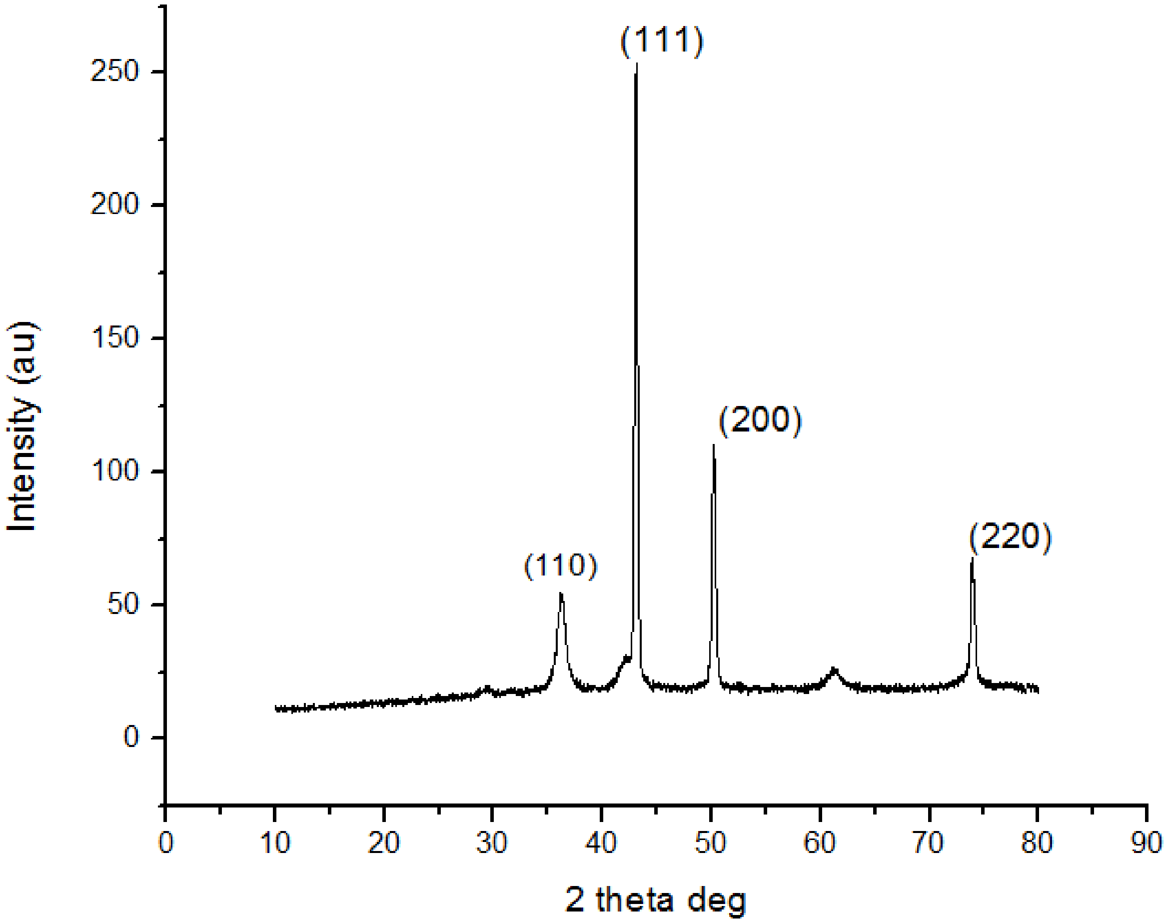


Fig 4.4 X-Ray Diffractogram of Cu Nanoparticles

Table 2: Determination of particle size

S.No.	FWHM	PARTICLE SIZE(nm)
1.	0.320	48.626
2.	0.363	44.013
3.	0.395	45.897
	Average Size:	46.179

The average particle size determined by debye – scherrer equations was found to be 46 nm [6].

4.4 Particle Size Analysis

The synthesized Copper nanoparticles were subjected to particle size analysis to ascertain, whether the size falls in the nano regime. ”X” axis denotes the particle diameter and “Y” axis denotes the normalized amount of particles. The results of the particle size analyzer is given below as a histogram.

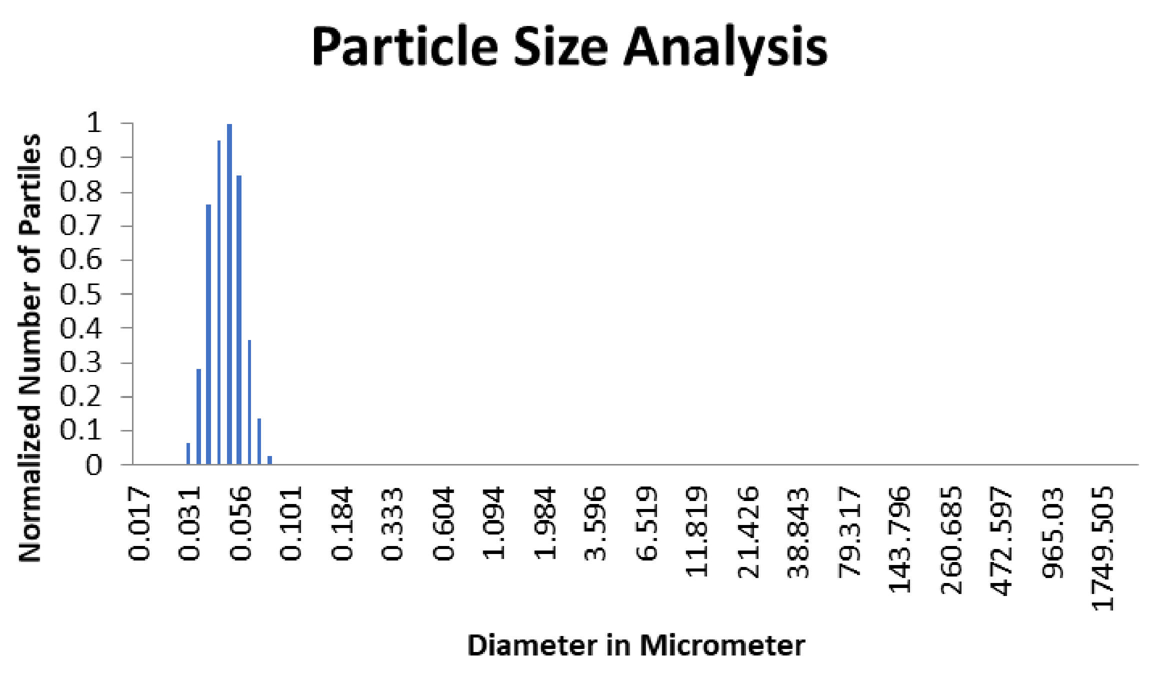


Fig 4.5 The graphical representation of grain size distribution of Cu Nanoparticles

The histogram shows the graphical representation of particle size distribution. The plot is Diameter of the Particles in micrometer against the Normalized Number of Particles [19]. From the histogram, it is observed that more number of particles was counted in the size range of 0.045 micrometer. Hence, the size of the Copper nanoparticles in this case is 45 nm. The value agrees with the crystallite size determined from the XRD analysis.

CHAPTER-V

SUMMARY AND CONCLUSION

- Copper nanoparticles were synthesized by using the standard chemical co-precipitation method.

- From the UV-Visible Spectroscopic studies, three peaks were identified. The peak at 598 nm lies between the values 500 nm and 600 nm [20] verified from existing literature and is in good agreement with the Surface Plasmon Resonance Peak values of Copper nanoparticles.

- From Tauc plot, the optical band gap of the synthesized Copper nanoparticles is estimated to be 5.25 eV. The high value, suggests that the size of the Copper nanoparticles were actually in the nano regime.

- From FTIR spectroscopic studies, the synthesized nanoparticles exhibited characteristic peaks of the functional groups like C−O, C−H,=CH and O−H that are present in the chemicals used to synthesize the same. The characteristic peak at 1638.42 cm^{-1} confirms the presence of Copper.

- X-Ray Diffractogram confirmed the high crystalline nature of the synthesized Copper nanoparticles following the FCC structure. Crystallite size was calculated using Scherrer formula using all the prominent peaks. The average crystallite size obtained was estimated to be 46 nm.

- Particle Size Analyzer results supports the results obtained from XRD Analysis. The average particle size of the prepared Copper Nanoparticles is in nanometer range at about 45 nm.

- The results of UV-Visible spectroscopy and Fourier Transform Infrared Spectroscopy are supported by the X-Ray Diffraction Analysis and Particle Size Analysis.

- It is concluded that that the chemical method for synthesis of copper nanoparticles is better than any other physical methods. The material can be used for biosensor and electrochemical sensor applications.

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