DEPARTMENT OF CHEMISTRY
BHARATA MATA COLLEGE, THRIKKAKARA
(Affiliated to Mahatma Gandhi University, Kottayam)

CERTIFICATE

This is to certify that the Project entitled **"*SYTHESIS AND CHARACTERISATION OF COPPER SULFIDE NANOPARTICLES*"** submitted in partial fulfilment of the requirements for the award of the degree of Bachelor of Science in Chemistry to Mahatma Gandhi University, Kottayam is authentic record of work carried out by **Ms**. **ANJANA C S** (**Reg. No:170021025600)** under my supervision and guidance.

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DECLARATION

I, **ANJANA C S**, hereby affirm that the project report entitled **"*SYTHESIS AND CHARACTERISATION OF COPPER SULFIDE NANOPARTICLES*"** submitted to Mahatma Gandhi University, Kottayam, in partial fulfilment for the award of the degree of BSc Chemistry, is an authentic record of original work done by me, under the guidance of Prof. Baiju K.P, Department of Chemistry, Bharata Mata College, Thrikkakara and no part of this has been previously formed on the basis for the award of any degree or assistantship of any other institution.

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CHAPTER 1
INTRODUCTION

Objectives of the work

Synthesis of CuS nanoparticles using microwave and its characterizations using X-Ray Diffraction Analysis and Transmission electron microscopy etc.. Check its ant cancerous properties.

Nano Science

Nano science implies a scale of measurement that exists at the level of the nanometer approximately 1-100nanometer range. Nanoscience is the study of materials and structures in nanometer scale. Nanoscience is the study of structures and materials on an ultra-small scale, and the unique and interesting properties these materials demonstrate. Nanoscience is cross disciplinary, meaning scientists from a range of fields including chemistry, physics, biology, medicine, computing, materials science and engineering are studying it and using it to better understand our world.

Nanotechnology (also sometimes called molecular manufacturing), on the other hand, is the design, production and application of structures, devices and systems at the nanoscale. So essentially one is studying nanomaterials and their properties and the other is using those materials and properties to create something new or different. Regarding the word nanotechnology, it is derived from the words nano and technology. Nano, typically employed as a prefix, is defined as one billionth of a quantity or term that is represented mathematically as $1x10^{-9}$ or simply as 10^{-9}. The new technology thus allows the engineering of matter by systems and processes that deal with atoms; or as Drexler-the father of nanotechnology, put it: “entails the ability to build molecular systems with atom-by-atom precision yielding a variety of nanomachines”.

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed. Thus, the properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. For bulk

materials larger than one micrometer (or micron), the percentage of atoms at the surface is insignificant in relation to the number of atoms in the bulk of the material. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material.. Their increasing importance in the detection and treatment of cancer and other diseases, drug delivery, and in vitro biosensing applications can be partly attributed to their favorable and easily tunable physical, chemical, magnetic, and/or optical properties. Copper sulfide (CuS), a p type semiconductor with excellent optical and electrical properties, has been extensively studied for various applications.

Synthesis Methods

There are various synthesis methods adopted for preparing nano dimensional materials. These methods have been developed to enhance the performance of nanomaterials displaying improved properties with the aim to have a better control over the particle size and distribution. In general, top down and bottom up are the two main approaches for synthesis.

TOP-DOWN APPROACH: Bulk material is made smaller with the help of various physical process which includes crushing and milling. These physical processes are not suitable for preparing uniformly shaped materials. The surface imperfection is one of the main defects. The top –down approach can cause significant crystallographic damage to the processed patterns.

BOTTOM-UP APPROACH: A bottom-up synthesis method implies that the nanostructures are synthesized onto the substrate by stacking atoms onto each other, which give rise to crystal planes. Bottom up approach is more often used for preparing most of the nanoscale materials with the ability to generate a uniform shape, size and distributions. This technique effectively covers chemical synthesis and precisely control the reaction to prevent further particle growth. The main bottom – up approaches are hydrothermal synthesis, combustion, co-precipitation method, sol-gel technique, etc.

Microwave synthesis

A microwave oven is a kitchen appliance that heats food by bombarding it with electromagnetic radiation in the microwave spectrum causing polarized molecules in the food to rotate and build up thermal energy in a process known as dielectric heating. Microwave ovens heat foods quickly and efficiently

because excitation is fairly uniform in the outer 25–38 mm of a dense (high water content) food item; food is more evenly heated throughout (except in thick, dense objects) than generally occurs in other cooking techniques. The basic principle behind microwave heating is rotation of water molecules causes the water molecules to heat. A microwave oven converts only part of its electrical input into microwave energy.

A microwave oven consists of a high voltage power source, commonly a simple transformer or an electronic power converter- which passes energy to the magnetron, a high voltage capacitor connected to the magnetron, transformer and via a diode to the chassis, a cavity magnetron, which converts high-voltage electric energy to microwave radiation, a magnetron control circuit (usually with a microcontroller),a waveguide (to control the direction of the microwaves),a metal cooking chamber.

The cooking chamber is similar to a Faraday cage (but there is no continuous metal-to-metal contact around the rim of the door), and prevents the waves from coming out of the oven. The oven door usually has a window for easy viewing, but the window has a layer of conductive mesh some distance from the outer panel to maintain the shielding. Because the size of the perforations in the mesh is much less than the microwaves' wavelength (12.2 cm), most of the microwave radiation cannot pass through the door, while visible light (with a much shorter wavelength) can.

PROPERTIES AND APPLICATIONS

The classic laws of science are different at the nanoscale. Nanoparticles possess large surface areas and essentially no inner mass, i.e., their surface-to-mass ratio is extremely high. This new science is based on the knowledge that particles in the nanometre range, and nanostructures or nanomachines that are developed from these nanoparticles possess special properties and exhibit unique behaviour. These special properties, in conjunction with their unique behaviour, can significantly impact physical, chemical, electrical, biological, mechanical, and functional qualities.

Present-day and future applications include chemical products, including plastics, specialty meals, powders, computer chips, computer systems, and miscellaneous Parts pollution prevention areas that can include energy conservation, environmental control, and health/safety issues, plus addressing crime and terrorism concerns . Some of the properties of nanoparticles that are often exploited in various sectors are:

- The properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. For bulk materials larger than one micrometre the percentage of atoms at the surface is minuscule relative to the total number of atoms of the material. The interesting and sometimes unexpected properties of nanoparticles are partly due to the aspects of the surface of the material dominating the properties in lieu of the bulk properties. Nanoparticles often have unexpected visible properties because they are small enough to confine their electrons and produce quantum effects. For example gold nanoparticles appear deep red to black in solution.
- Nanoparticles have a very high surface area to volume ratio. This provides a tremendous driving force for diffusion, especially at elevated temperatures. Sintering can take place at lower temperatures, over shorter time scales than for larger particles. This theoretically does not affect the density of the final product, though flow difficulties and the tendency of nanoparticles to agglomerate complicates matters. The large surface area to volume ratio also reduces the incipient melting temperature of nanoparticles.
- Nanoparticles have been found to impart some extra properties to various day to day products.
- A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface Plasmon resonance in some metal particles and superparamagnetism in magnetic materials.

1 X-Ray Diffraction

X-Ray Powder Diffractometry is one of the most powerful and established technique for material structural analysis, capable of providing information about the structure of a material at the atomic level. Low and High temperature measurement facilities are available. Here we used Bruker AXS D8 Advance X-Ray Diffractometer. It yields complete information about the crystal structures, orientation, lattice constants, crystallite size and composition. It requires no elaborate sample preparation and is essentially non destructive. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern therefore allows us to deduce the distribution of atoms in a material. The peaks in a x-

ray diffraction pattern are directly related to the atomic distances. For a given set of lattice plane with an inter -plane distance of d, the conduction for a diffraction (peak) to occur can be simply written as

$$2d\sin\theta = n\lambda \quad (1)$$

This is known as the Bragg's law, named after W.L. Bragg, who first proposed it .In the equation, λ is the wavelength of the x-ray, θ the glancing angle and n is an integer representing the order of diffraction peak. The Bragg's Law is one of most important laws used for interpreting x-ray diffraction data.

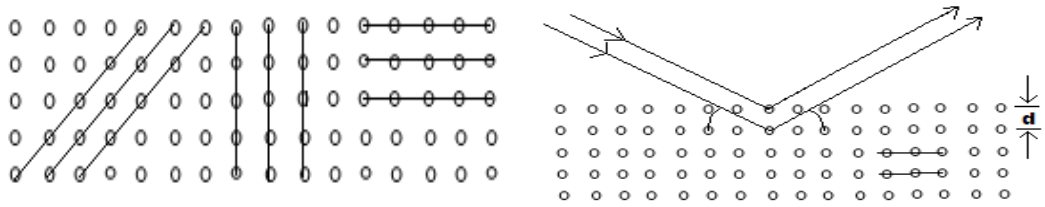

Fig2.2 lattice plane in a crystal structure

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

It is important to point out that although we have used atoms as scattering points in this example, Bragg's Law applies to scattering centers consisting of any periodic distribution of electron density. In other words, the law holds true if the atoms are replaced by molecules or collections of molecules, such as colloids, polymers, proteins and virus particles. A graph with 2θ on the X axis and intensity on the Y axis is plotted. The d value is calculated from the above equation by applying the corresponding θ value.The peak positions, intensities, widths and shapes all give important information about the structure of the material. From the width of diffraction lines, the average grain size can be calculated using Debye-Scherrer's formula.

$$L=K\lambda/(\beta\cos\theta) \quad (2)$$

Where K is a constant which is nearly equal to 0.9 and β is the full width half maximum usually measured in radians got by Gaussian fit of the peak corresponding to a 2θ value. In the present study, XRD analysis was done using Bruker AXS D8 Advance X-ray Diffractometer, with CuKα (λ =1.5406Å) radiation, operated at 40kV and 35mA.

Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a versatile technique to analyse the size, morphology, crystallographic structure, and chemical composition of a wide range of nanomaterials (NM).

It can be considered as a golden standard for the characterization of NM for several reasons [1]: (i) TEM analysis is one of the few methods that can provide a spatial resolution reliably covering the complete nanometre size range from 1 to 100 nm. (ii) TEM readily produces projected 2D images of NM. (iii) The combination of TEM imaging with image analysis allows determining the physical properties (size, shape, and surface morphology) of individual nano-objects quantitatively, based on the characteristics of their 2D projections. Multiple properties can be measured simultaneously for each individual particle, from which descriptive statistics and corresponding number-based distributions can be determined, as requested in regulations and guidelines [2–4]. (iv) TEM allows assessing the agglomeration and/or aggregation state of a material, and to some extent constituent, primary particles can be identified in agglomerates/aggregates. (v) Spectroscopic methods (EDS and EELS) can be incorporated in the TEM for elemental analysis of nano-objects and examination of chemical bonding allowing characterization of subpopulations of nano-objects in mixtures and nano-objects in the context of a complex matrix. (vi) Selected area electron diffraction (SAED) allows studying the crystallographic structure of nano-objects.

covellite (CuS)

Chalcogenides are materials containing one or more chalcogen elements (e.g. S, Se or Te) as a substantial constituent. They are covalently bonded materials and, although they may be amorphous or crystalline, they are fundamentally semiconductors with a band gap typically of 1–3 eV, depending on composition.

CHAPTER 2
EXPERIMENTAL

Materials

1. Coppersulfate
2. Thiourea
3. Ammonia Solution
4. Distilled Water

Equipments

1. Microwave Oven
2. Magnetic Stirrer
3. Hot Air Oven

Characterisations

1. XRD
2. TEM

PREPARATION OF SAMPLE

For the preparation of CuS nanoparticles, we used copper sulfate and thiourea as the sources of copper and sulfur respectively. We took distilled water as solvent for the nanoparticles synthesis. First we prepare 0.2 M Copper Sulfate solution by weighing accurately 1.596 gm and make up into 50mL. Stirred well in two minutes. In another 50ml standard flask we prepare 0.4 M Thiourea solution by weighing 1.5224 gm. Approximately 3mLAmmonia is added to Copper Sulfate solution to maintain the pH of the solution at 10. Subsequently thiourea solution is added slowly to the above solution with constant stirring. Then the solution is turned in to a blue coloured homogeneous one.

Preparation of 0.2 M Copper Sulfate solution

Molecular Weight = 159.60g

Weight = (molarity * molecular mass * volume) / 1000

= 0.2*159.6*50/1000

=1.596 gm

Weight 1.596gm coppersulfate and transfer into 50ml standard flask and makeup using distilled water up to the mark and stir well in two minutes.

Preparation of 0.4 M Thiourea Sulfate solution

Molecular Weight = 76.12 g

Weight = (molarity * molecular mass * volume) / 1000

= 0.4*76.12*50/1000

=1.5224 gm

Weight 1.5224gm thiourea and transfer into 50ml standard flask and makeup using distilled water up to the mark and stir well in two minutes.

Microwave Synthesis

The prepared precursor solution is treated in microwave oven. It is kept in microwave power level mode for two minutes at 600 Watts Power. The solution obtained after microwave heating turns in to black colour. The microwave treated solution is filtered, washed with distilled water and acetone. The precipitate is dried in the hot air oven at 100^0 C for 1 hour. The powder is grinded in the agate mortar. The prepared material is taken for analysis.

Here we used microwave IFB microwave oven model number 30SC3 for the nanoparticle synthesis. Rated microwave output is 900 W and the operation frequency is 2450MHz. It can be used in convection mode, microwave heating,

microwave + convection mode etc. according to our necessity. The microwave power can be adjusted to high, medium or low.

CHAPTER 3
RESULT AND DISCUSSION

Introduction

Copper sulphide nanoparticles have been prepared by employing microwave assisted synthesis. We could obtain copper sulphide nanoparticles using the copper to sulphur ratio 1:2.

X-Ray Diffraction Analysis

The XRD pattern matches well with the JCPDScard number 06-0464. The planes corresponding to the main peaks are indexed. The peaks are indexed with hexagonal symmetry with lattice constants of a = 3.7903 Å and c = 16.3601Å which are in good agreement with those reported in the literature

Sl.No.	**Angle (2θ)**	**Plane**
1	29.35	**(102)**
2	32.07	**(103)**
3	32.40	**(006)**
4	48.11	**(110)**
5	52.60	**(108)**

The crystallite size is determined from the plane (102) at **2θ=** 29.35^{o}.

Crystallite Size is calculated using Debye Scherrer formula

$$D = 0.9\lambda/\beta\cos\theta$$

λ =1.5414Å

β=Full Width at Half Maximum (FWHM)

θ= Bragg's diffraction angle

28.71-29.50

$$D = 0.9 \text{ x}1.5414 / 0.79 \text{ x } \cos(14.675)$$

Transmission Electron Microscopy

The morphology of the material is determined from bright field Transmission Electron microscopy images (Fig.3.2). The spherical nature of particles is observed in the image. The

Very minute nanosized particles are clearer from the scale fitted in the image.

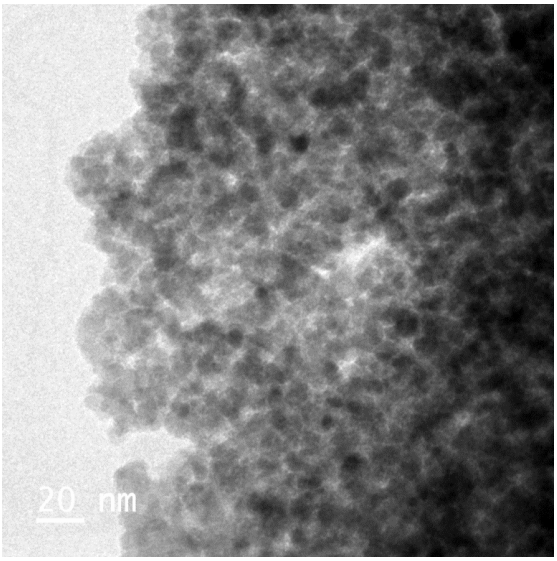

Figure. 3.2. Bright field image of copper sulfide nanoparticles

The HRTEM images in Figure 3.3 demonstrates the different planes of the copper sulfide nanoparticles.

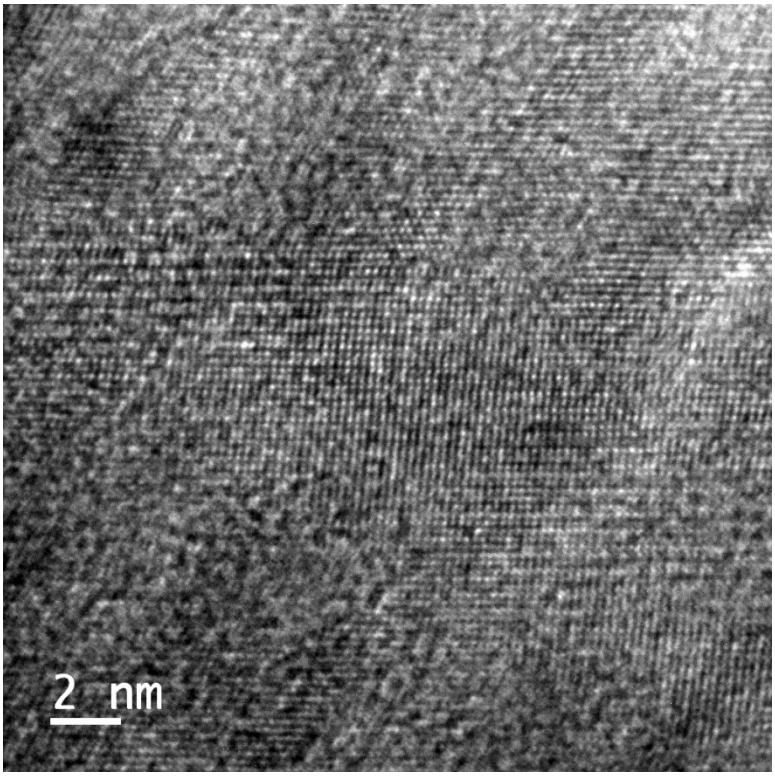

Fig.3.3. HRTEM image of copper sulfide nanoparticles

Conclusion

CuS nanoparticles have been prepared successfully by microwave method. The XRD pattern confirmed the hexagonal symmetry of the material. The crystallite size is found to be nm. The spherical morphology of the CuS nanoparticles is confirmed from transmission electron microscopy.

CHAPTER 4
CONCLUSION

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