

SYNTHESIS AND CHARACTERISATION OF CORE-SHELL NANO PARTICLES

Submitted in partial fulfillment of the requirements for the award of
Master of Science Degree in Physics

By

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DEPARTMENT OF PHYSICS
SCHOOL OF SCIENCE AND HUMANITIES

SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of M R YOGAJOTHIESHWARAN (Reg No. 41590027) who carried out the project entitled "SYNTHESIS AND CHARACTERISATION OF CORE-SHELL NANO PARTICLES" under my supervision from November 2022 to May 2023.

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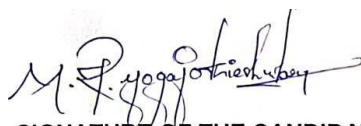
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DECLARATION

I M R YOGAJOTHIESHWARAN (Reg No. 41590027) hereby declare the project report entitled “SYNTHESIS AND CHARACTERISATION OF CORE-SHELL NANO PARTICLES” done by me under the guidance of DR.S.ANANDHI Ph.D., at SATHYABAMA INSTITUTE OF SCIENCE AND TECHNOLOGY, is submitted in the partial fulfilment of the requirements for the award of MASTER OF SCIENCE in PHYSICS.

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ABSTRACT

The paper focuses on bimetallic nanoparticles made of a core made of inexpensive metal with excellent electrical conductivity, like CuSO_4 and $[\text{Ag}(\text{NH}_3)_2]^+$, and a shell made of noble metal that is stable to oxidation, like Ag or Au. We discuss the physical and chemical methods for creating these particles, as well as the combination of the two, the development of conductive compositions and their use in printed electronics and conductive coatings, and the stability of core-shell nanoparticles against oxidation under varied conditions. The synthesised nanoparticles were characterized by X-ray powder diffraction (XRD), Ultraviolet visible (UV) and Fourier transform infrared spectroscopy (FTIR). Hence, the synthesized Core-Shell NPs could be used as biomedical application.

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LIST OF SYMBOLS AND ABBREVIATIONS

NP- Nano Particles

nm - nanometre

μm - micrometre

$\text{\AA}$ - Angstrom θ

- Theta

α - Alpha

β - Beta

γ - Gamma g

- Gram

a, b, c - Unit cell parameters

λ - Wavelength

ϵ_0 - Permittivity of free space

ϵ_r - Dielectric constant

AgNO_3 - Silver Nitrate

CNP- Core-Shell Nanoparticle

SEM- Scanning Electron Microscope

FT-IR - Fourier Transform Infrared

SHG - Second Harmonic Generation

UV - ultraviolet

XRD - X-Ray Diffraction

CHAPTER 1

INTRODUCTION TO NANO PARTICLES

INTRODUCTION TO NANOSCIENCE AND NANOTECHNOLOGY

Nanostructured materials, and more precisely nanoparticles, have been a constant presence in human daily life for the duration of the history of the species. The link began with the creation of the first tools, which were particles, and most likely, the unintentional inhalation of nanoparticles. Together with other benefits like a tremendous increase in food, the invention of fire also brought with it the potential for unintentional inhalation of carbon nanoparticles from burning wood. In the attrition process used to create their pigments, prehistoric artists were exposed to iron oxide, manganese dioxide, charcoal, kaolin, or mica nanoparticles. Ancient Egyptians were exposed to lead nanoparticles from cosmetics much later. Ancient Greeks and Romans had already written about silicosis, which affects miners and stone workers, and it is now understood to be a result of prolonged exposure. Recently, bimetallic catalysts with a core/shell nanostructure have attracted a lot of attention as a particular type. These nanostructures have a core consisting of inorganic substances like metal, metal oxide, silica, or organic substances, which is encased in an inorganic or organic substance.

WHAT IS NANOSCIENCE

The study, manipulation, and engineering of substances, particles, and structures with dimensions smaller than a nanometer is referred to as nanoscience (one millionth of a millimeter, the scale of atoms and molecules). The manner in which molecules and atoms come together on the nanoscale to form bigger structures affects important features of materials, such as the electrical, optical, thermal, and mechanical

properties. Furthermore, because to the importance of quantum mechanical phenomena, these features in nanometer-sized structures are frequently different from those on the macroscale.

WHAT IS NANOTECHNOLOGY

The word "Nano," which means "dwarf" in Greek, is used to describe extremely microscopic features. Nanotechnology is the understanding and control of matter at dimensions between approximately 1 and 100 nanometres, where unique phenomena enable novel applications. It is the application of nanoscience leading to the use of new nanomaterials and nanosized components in useful products.

The ideas that gave rise to nanotechnology were initially introduced in 1959 by renowned physicist Richard Feynman in his lecture There's plenty of room at the bottom, in which he highlighted the potential for synthesis through direct atom manipulation. The phrase was first used by Norio Taniguchi of Tokyo Science University in 1974 to refer to semiconductor technologies like thin film deposition that deal with control on the order of nanometres. He stated that "Nanotechnology primarily consists of the processing of separation, consolidation, and deformation of materials by one atom or one molecule," and that description is still the fundamental one used today.

NUCLEATION AND PARTICLE SIZE

The mechanisms of precipitation of a solid phase from solution are involved in the chemical growth of materials that are smaller than a nanometre. Homogeneous nucleation, heterogeneous nucleation, and secondary nucleation are the three different types of nucleation processes. In the absence of a solid contact, homogenous nucleation happens when solute molecules combine to form nuclei. There is a limit to how much of a solute may be dissolved in a given solvent without causing the

development and precipitation of nanoparticles. The solution needs to be supersaturated for nucleation to happen.

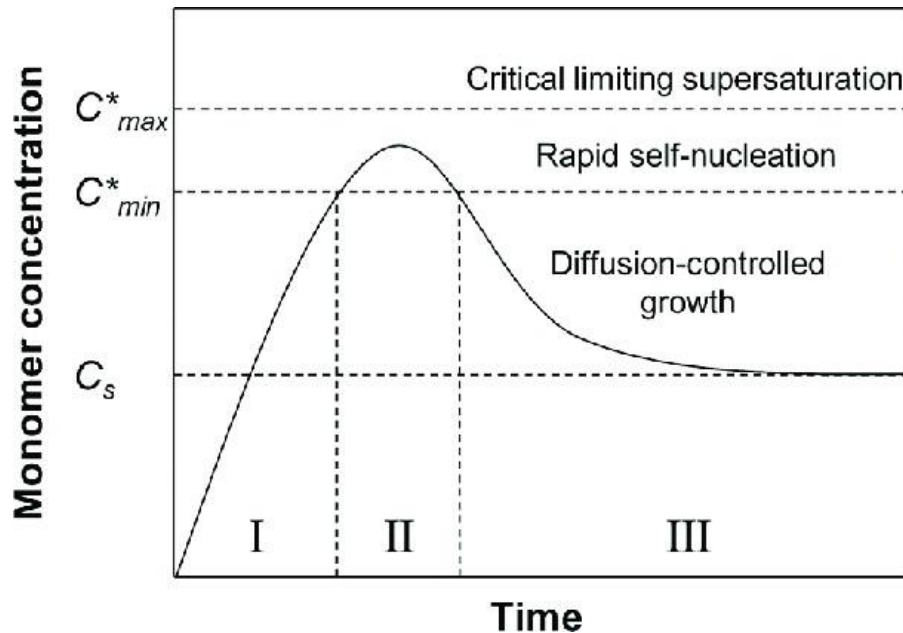


Fig.1.4 I. Pre-nucleation period; II. Nucleation; III. Growth.

Victor Kuhn Lamer hypothesised that diffusion-driven crystallisation was a process in 1952. Also, he produced a very helpful graph that enables visual evaluation of homogeneous nucleation-based crystal development. There are three steps in the model. The concentration of the reactive material in solution initially rises until it reaches a critical level, known as supersaturation. The materials then start to clash and form clusters beyond this point. The first stable nuclei are produced via nucleation when the clusters become more stable and permit it to happen. When the concentration of free material stops rising and finally starts to fall, a critical supersaturation has been reached. The term "critical supersaturation point" refers to this location. When unbound material and stable nuclei are no longer present, the supersaturation is suppressed.

APPROACHES OF SYNTHESIS

There are two methods for synthesising nanomaterials: "Top Down" and "Bottom-up." The "Top Down" approach frequently employs conventional workshop or microfabrication techniques, in which materials are cut, milled, and shaped using tools under external control. Contrarily, "Bottom-up" techniques leverage the chemical characteristics of individual molecules to trigger the automated arrangement of individual molecule components into a functional shape. These methods make use of molecular self-assembly principles. Understanding the chemical and physical characteristics of nanoparticles and directing them to self-assemble are key to bottom-up manufacturing. Neither the top-down nor the bottom-up strategy is currently preferable; each has benefits and drawbacks. The inherent size limit of the bottom-up strategy, however, is substantially lower than that of the top-down approach. Additionally, bottom-up approaches have the potential to be more cost-effective in the future due to their absolute precision, total process control, and minimal energy loss as compared to top-down approaches.

SYNTHESIS OF CuSO_4 NANOPARTICLES

The first step in the preparation process is to add 120 mL of starch (1.2%) solution to a 0.1 M copper (II) sulphate pentahydrate solution while vigorously stirring for 30 minutes. The second stage involves adding 50 mL of 0.2 M ascorbic acid solution while continuously and quickly stirring the synthesis solution. Chemical, and physical techniques can all be used to create metal nanoparticles. Three components are required in order to produce nanoparticles, particularly copper nanoparticles. Ions of copper are first provided by a precursor. Second, a reducing agent is necessary to provide electrons in order to produce copper atoms. The third component, the surfactant, aggregates the copper atoms produced by the reducing agent into copper nanoparticles when the appropriate temperature and pH conditions are met.

We can divide the synthesis processes into three categories based on the source of the electrons: green, which is when the reducing agent is a biological organism

(bacteria, moulds, algae, or plants); chemical, which is when the reducing agent is a chemical compound; and physical, which is when the source is physical, like electricity.

SYNTHESIS OF AgNO₃ NANOPARTICLES

The two most significant physical methods are laser ablation and evaporation-condensation. The benefits of physical synthesis techniques over chemical processes are the absence of solvent contamination in the generated thin films and the uniformity of NPs distribution. Atmospheric pressure physical synthesis of silver NPs has some drawbacks. For instance, the tube boiler takes up a lot of room, uses a lot of energy when raising the temperature around the source material, and takes a long time to reach thermal stability. Also, a typical tube boiler needs to be preheated for several tens of minutes and use more than a few kilowatts of power to attain a steady operating temperature.

The most common approach for synthesis of silver NPs is chemical reduction by organic and inorganic reducing agents. In general, different reducing agents such as sodium citrate, ascorbate, sodium borohydride (NaBH₄), elemental hydrogen, polyol process, Tollens reagent, N, N-dimethylformamide (DMF), and poly (ethylene glycol)-block copolymers are used for reduction of silver ions (Ag⁺) in aqueous or non-aqueous solutions. These reducing agents reduce Ag⁺ and lead to the formation of metallic silver (Ag⁰), which is followed by agglomeration into oligomeric clusters. These clusters eventually lead to the formation of metallic colloidal silver particles. It is important to use protective agents to stabilize dispersive NPs during the course of metal nanoparticle preparation, and protect the NPs that can be absorbed on or bind onto nanoparticle surfaces, avoiding their agglomeration. The presence of surfactants comprising functionalities (*e.g.*, thiols, amines, acids, and alcohols) for interactions with particle surfaces can stabilize particle growth, and protect particles from sedimentation, agglomeration, or losing their surface properties.

BIOMEDICAL APPLICATION

Nanoscience and nanotechnology are widely regarded as having enormous potential to advance many fields of study and application, including medicine, agriculture, and energy. The use of nanoparticles in biomedicine is highlighted in the section that follows.

Nano medicine is the field of medicine that uses nanoparticles.

Drug and gene transport, protein detection, diabetes treatment, tissue engineering, DNA structure analysis, tumour eradication, and cancer therapy are all aspects of Nano medicine.

As they are the same size as biological structures and are well integrated into the system, nanomaterials of various kinds have important applications in the biomedical field, particularly in diagnosis, imaging, drug delivery, and biomaterials as prostheses and implants (Ramos).

The sources of the nanomaterials include metals, non-metals, chemicals, microbes, and plants (Makarov et al., 2014). Although liposomes and micelles made of lipids and proteins are increasingly preferred as Nano carriers for drug delivery, metallic and non-metallic NPs have been the most widely used in biomedicine (Allen and Collis, 2013). There are already 175 distinct nonmedicinal compounds, the majority of which (more than 100) are at the stage of recyclable plastics polymers for agriculture Microbial \s origin Chemical \synthesis.

CHAPTER 2

LITERATURE SURVEY

S.NO	RESEARCH ARTICLE	AUTHOR	PUBLICATION DETAILS
1	Core/Shell Nanoparticles: Classes, Properties, Synthesis Mechanisms, Characterization, and Applications	Rajib Ghosh Chaudhuri and Santanu Paria	ACS PUBLICATIONS ,2011 American Chemical Society
2	Core-Shell Nanoparticles: Synthesis, Design, and Characterization	Kyler Carroll Virginia Commonwealth University	Virginia Commonwealth University VCU Scholars Compass
3	CORE-SHELL NANOPARTICLES: SYNTHESIS, CHARACTERIZATION AND BIOCOMPATIBILITY STUDIES	Carmen Mihaela Vogt	CARMEN VOGT, Muhammet S. Toprak, Sophie Laurent, Jean-Luc Bridot, Robert N. Müller, Mamoun Muhammed, High quality and tuneable silica shell - magnetic core nanoparticles, Journal of Nanoparticle Research, 2010, 12, 1137-1147

4	Synthesis of Cu@Ag core-shell nanoparticles for characterization of thermal stability and electric resistivity	Shengyan Shang 1 _ Anil Kunwar2 _ Yanfeng Wang1 _ Xiao Qi 1 _ Haitao Ma1;_ _ Yunpeng Wang1;__	Acta Mater., 144:314{324, 2018
5	Biological synthesis of copper nanoparticles using plant extract	Hyo-Jeoung Lee, Geummi Lee, Na Ri Jang, Jung Hyun Yun, Jae Yong Song and Beom Soo Kim	NSTI-Nanotech 2011, www.nsti.org, ISBN 978-1-4398-7142-3 Vol. 1, 2011

CHAPTER -3

AIM AND SCOPE

AIM OF THE PRESENT INVESTIGATION

- Silver (I) diamine cation, copper(II) sulphate by using the sol-gel process, core/shell nanoparticles were created.
- Using UV-Vis, XRD, and SEM investigation, Cu@ Ag (CoZ) was described.
- We examined Cu@Ag (CoZ) Core/shell NPs against Gram-negative and Gram-positive microorganisms.
- Rhodamine B's photocatalytic degradation was also used to the synthesised CoZ NPs.

SCOPE

The present investigation mainly deals with the green synthesis and characterization of core shell application of 2D and 3D coating and printing technologies for the fabrication of various 2D and 3D electronic devices, has acquired great interest and is a successfully growing field of materials science and technology [1–8]. The applications span from electrical circuits, transparent conductive films, thin-film transistors, solar cells, RFID tags, flexible touch panels and light-emitting displays, electrochemical storage devices, super capacitors, to electrical actuators.

CHAPTER 4

EXPERIMENTAL PROCEDURE AND MEASUREMENTS

EXPERIMENTAL TECHNIQUES

The experimental techniques involved in the synthesis, characterization and structural studies of the present compound is discussed in this chapter. According to the literature survey, various methods have been used for synthesis of compounds such as solid-state method, chemical precipitation method, microwave method, ball milling method, combustion method etc. The present compound has been synthesized using materials have been used.

SYNTHESIS OF CORE-SHELL NANOPARTICLES

Cuso₄ and [Ag (NH₃)₂]⁺, and absolute Ascorbic-Acid were used as received without additional purification. All aqueous solutions were prepared using high purity deionized water. The Cu NPs were prepared by a modified procedure according to the recently reported literature [16] wherein PVP and ASCORPIC are used as reducing agent and surfactant respectively. In a typical synthesis route, 5 mL of 2.5 mM PVP was added to a 5 mL of 0.02 M CuSO₄ solution and the resultant solution was stirred for 10 min to ensure they wholly dissolved. Then, when 1% of 0.02 M NaBH₄ was poured into the prepared solution, the colour of the solution changed from colourless into a transparent yellow due to the formation of copper NPs. Subsequently, 5 mL of freshly prepared 0.02 M AgNO₃ was slowly injected into the mixed solution and allowed to complete the reaction for several minutes. When the first drop of the silver salt was added to the solution, redox-trans metalation process commenced and the silver ions are reduced by the copper atoms directly and deposited on its surface. This was confirmed by the colour changing from the transparent yellow into deep green, green and ended with yellowish–green. Finally the resultant Ag coated Cu products were washed several times with ethanol and deionized water to remove the excess

residues and harvested by centrifugation–dispersion process (10,000 rpm for 20 min) and stored in ethanol for further analysis

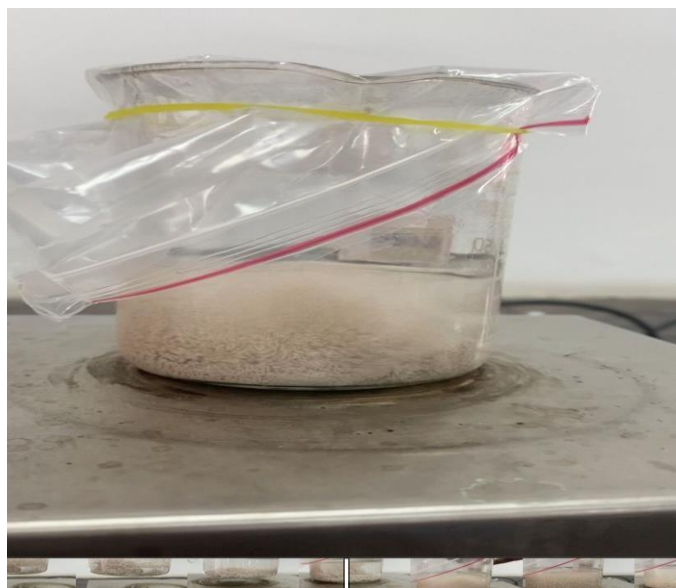


fig.4.2 SYNTHESIS WORK



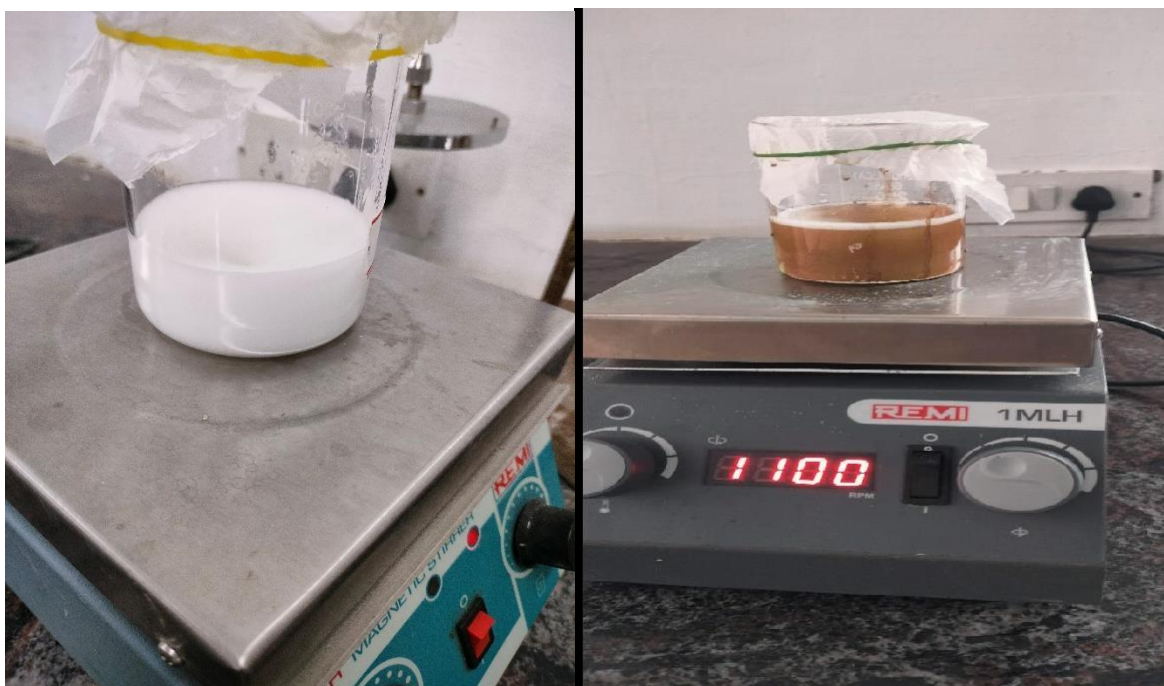


Fig.4.2.1 SYNTHESIS WORK

CHARACTERIZATION AND STRUCTURAL STUDIES

X-RAY POWDER DIFFRACTION (XRD)

In 1912, Max von Laue made the discovery that crystalline materials behave for X-Ray wavelengths like the spacing of planes in a crystal lattice, acting as three-dimensional diffraction gratings. Nowadays, X-ray diffraction is a widely used method for examining crystal structures and atomic distances.

The adaptable and non-destructive method of X-ray powder diffraction (XRD) provides comprehensive details concerning the identification of phases, identifying the purity of samples, and figuring out the crystallinity of goods. The unidentified phases present in each sample were determined by comparing the locations of the diffracted beam's peaks to benchmarks offered by the Joint Committee on Powder Diffraction Standards (JCPDS) and the International Centre for Diffraction Data (ICDD).

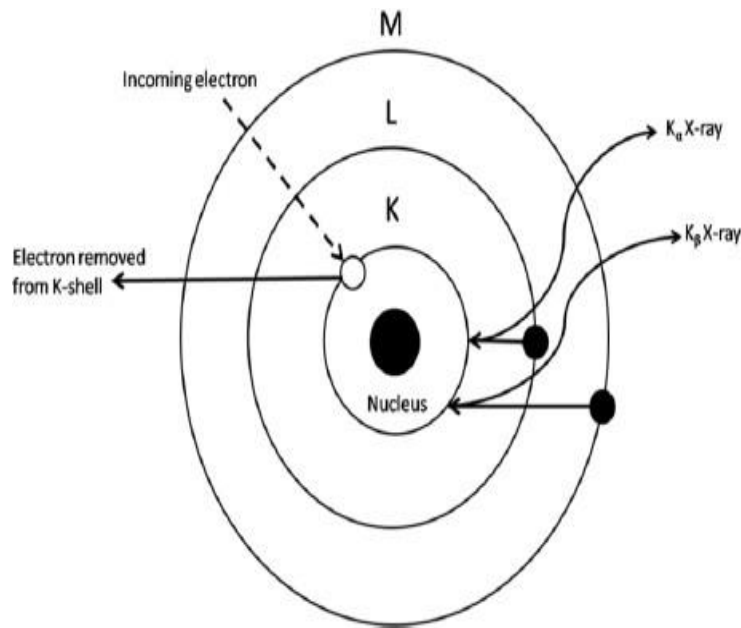


Fig.4.3.1 Ejection of a core electron

Schematic illustrating the process of an ejection of a core electron and the resulting x-ray emissions by electrons filling the ejected electron hole.

X-rays are produced by a beam of fast electrons bombarding a metal target in an evacuated tube. The energetic electrons excite the target atoms, which subsequently emit high frequency electromagnetic radiation as they decay back to their ground states.

Bragg's law:

The fundamental principle of X-ray diffraction is the constructive interference of monochromatic X-rays with crystalline material. These X-rays are produced by a cathode ray tube, filtered to create monochromatic radiation, concentrated by collimation, and then directed at the sample. When the situation satisfies Bragg's law, the interaction between the incident rays and the sample creates constructive interference. This rule connects the diffraction angle and lattice spacing in a crystalline sample to the wavelength of electromagnetic radiation. Afterwards, these diffracted X-rays are identified, handled, and tallied. Due to the powdered material's random orientation, it should be feasible to obtain all potential lattice diffraction directions by scanning the sample across a variety of 2θ angles. Each mineral has a unique set of d-spacing, hence converting the diffraction peaks to d-spacing enables the

identification of the mineral. This is often accomplished by comparing the d-spacing with accepted reference patterns.

For that particular wavelength, crystal lattice planar spacing, and angle of incidence (θ), constructive interference will happen. In a crystal, each rational plane of atoms will experience refraction at a single, distinct angle (for X-rays of a fixed wavelength). Bragg's Law describes the overall relationship between the incident X-ray wavelengths, angle of incidence, and distances between atoms' crystal lattice planes.

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

Where,

n (an integer) is the "order" of reflection,

λ is the wavelength of the incident X-rays,

d is the interplanar spacing of the sample,

θ is the angle of incidence.

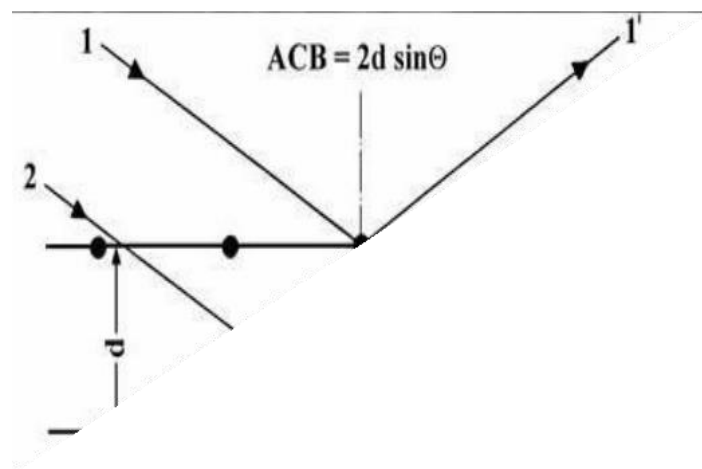


Fig. 4.3.2 Bragg's law of diffraction

To recognise and describe unidentified crystalline minerals, X-Ray Powder Diffraction (XRD) is an effective analytical technique. The interplanar spacing of the ambiguous materials is calculated using monochromatic X-rays. To ensure that the beam "samples" all crystallographic directions, samples are analysed as grains in powder

form with random orientations. The relative peak height of the "reflection" produced when the Bragg criteria for constructive interference are met is typically proportional to the number of grains in a preferred orientation.

Hence, the X-ray spectra produced by this method offer a structural fingerprint of the unidentified. Analysis of crystalline mixtures is another option, and semi-quantitative estimations of abundances can be obtained by comparing the peak heights of various materials. You might also utilise a glancing X-ray beam to learn more about the structural characteristics of thin layers on surfaces. Moreover, it is simple to identify shifts in peak position that correspond to compositional variation (solid solution) or structure-state information (such as order-disorder transitions, resolution, etc.). Peak sites are found where the crystal structure has caused the X-ray beam to diffract. This pattern's distinctive set of d-spacing can be used to "fingerprint" the material. An X-ray diffractometer's geometry is such that the sample spins at an angle in the direction of the collimated X-ray beam, and the X-ray detector rotates at an angle of 2θ to capture the diffracted X-rays. A goniometer is the device used to hold the angle and rotate the sample. Data is gathered at 2θ from 10° to 80° , angles that are present in the X-ray scan, for typical particle patterns. Shimadzu's X-ray powder diffractometer was used in the current investigations to record the XRD patterns of the produced powder samples at a scanning rate of 3.0000 deg/min in the range of 20° to 80° .

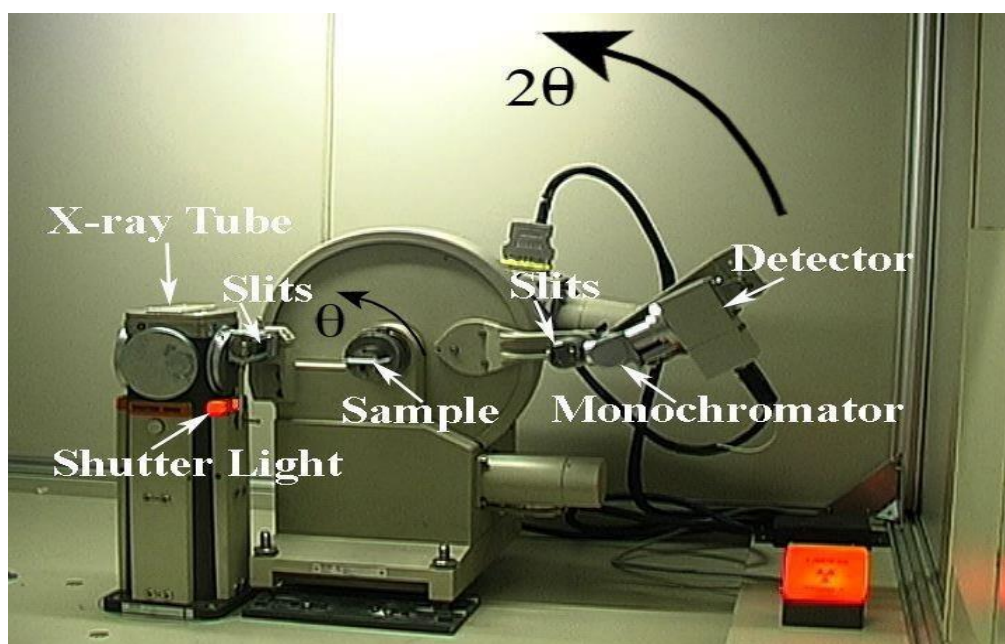


Fig.4.3.3 X-Ray Powder Diffraction

X-Ray powder diffractometer

An X-ray generator emits its distinctive X-rays, which are collimated and aimed at the sample. The intensity of the reflected X-rays is measured while the sample and detector spin. The X-ray radiation is captured, processed, and converted by a detector into a count rate, which is then transmitted to a machine like a printer or computer monitor. The term "goniometer" refers to the device used to maintain the angle and rotate the sample.

The benefits are as follows:

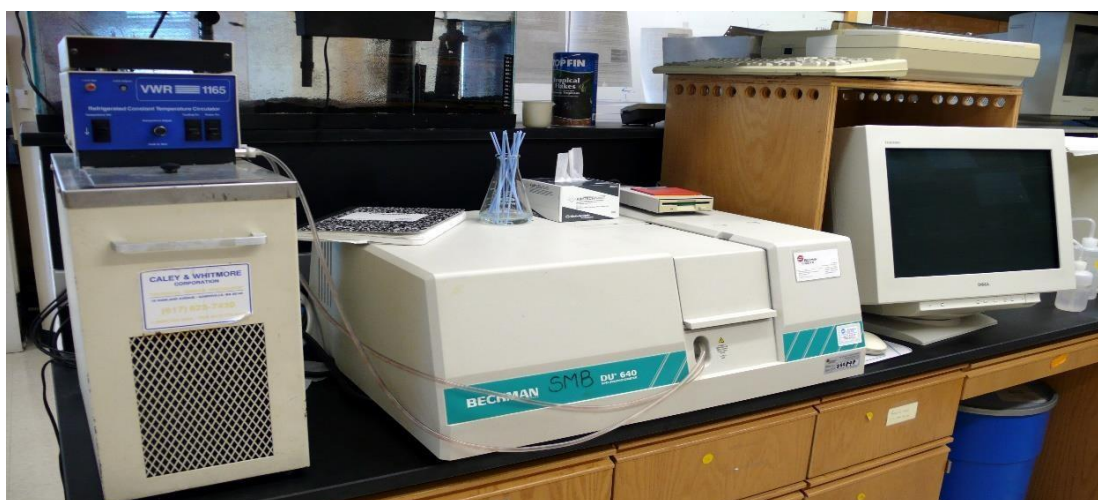
- It produces an unambiguous mineral determination in most circumstances and is a powerful and quick technique for identifying an unknown substance.
- The sample only has to be lightly prepared.
- XRD equipment is generally accessible.
- Data interpretation is a rather simple process.

The following restrictions apply.

- Material that is homogeneous and single-phase works best for identifying unknown materials.
- Must have access to an inorganic compound standard reference file (d-spaced Hkl's).
- Needs tenths of a gram of material that must be ground into a powder.
- The detection threshold for mixed components is up to 2% of the sample.
- Indexing of patterns for non-isometric crystal systems is difficult when determining unit cells.
- Peak overlay is a possibility and gets worse for high-angle reflections.

UV-Visible (UV-Vis) Spectroscopy

The spectroscopy of photons in the UV-visible region is a part of UV-visible absorption spectroscopy. This indicates that it makes use of light in the visible, near ultraviolet (UV), and near infrared (NIR) bands. The colour of the compounds involved is directly impacted by absorption in the visible spectrum.



4.3.4 UV-Visible (UV-Vis) Spectroscopy

Molecules go through electronic transitions in this part of the electromagnetic spectrum. Fluorescence spectroscopy deals with transitions from the excited state to the ground state, whereas absorption measures transitions from the ground state to the excited state, making this approach complementary to fluorescence spectroscopy.

One of the earliest and most effective instrumental techniques is light absorption by a solution. A compound's chemical structure determines the wavelength of light that it will absorb. By energising particular forms of molecular and atomic motion to greater energy levels, certain areas of the electromagnetic spectrum are absorbed. The excitation of molecule rotational motion is the primary mechanism by which microwave radiation is absorbed. The vibrational movements of molecules are linked to infrared absorption. The excitation of electrons to higher energy states in both atoms and molecules is correlated with the absorption of visible and ultraviolet (UV) radiation. All

molecules will experience electronic excitation after absorbing light, although the majority of molecules need extremely high energy radiation (UV in the vacuum, about 200 nm).

Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm. In the present investigations, the UV-Vis absorption spectra of the samples dispersed in isopropyl alcohol medium were recorded using UV-1800 Shimadzu UV-Visible spectrophotometer at room temperature.

FOURIER TRANSFORM INFRARED SPECTROSCOPY

By producing an infrared absorption spectrum, which is similar to a molecular "fingerprint," Fourier Transform Infrared (FTIR) spectroscopy is a powerful method for detecting the many types of chemical interactions in a molecule. It can be applied to quantify some combination components. Analysis of solids, liquids, and gases can be done with it. [Willard and associates 1986]. As observed from the spectrum, the chemical bond's wavelength is a property of the light that is absorbed.

A molecule's chemical bonds can be identified by reading the infrared absorption spectra. As neither nitrogen nor oxygen absorb infrared light, FTIR spectroscopy does not require a vacuum.

Depending on the elements and the type of bonding, molecular bonds vibrate at different frequencies. There are a number of distinct frequencies at which a particular bond can vibrate. These frequencies correspond to the ground state (lowest frequency) and numerous excited states in quantum mechanics (higher frequencies). The bond can be excited by having it absorb light energy, which raises the frequency of the molecular vibration. The energy difference between the two states—typically the ground state (E) and the first excited state—must be exactly equal for each given transition between two states, as dictated by the light's wavelength (E).



Fig 4.3.5 Ftir Spectrometer

The shortcomings of dispersive devices were addressed with the creation of FTIR spectroscopy. The lengthy scanning procedure was the biggest challenge. It was necessary to develop a technique for sensing all infrared wavelengths simultaneously as opposed to separately. An interferometer, a very basic optical tool, was used to create a solution. All of the infrared frequencies are "encoded" into a special kind of signal that the interferometer generates. The measurement time for the signal is typically on the order of one second or less. As a result, the time element per sample is decreased from several minutes to a few seconds. The beam splitter used by the majority of interferometers separates the incoming infrared beam into two optical beams. One beam reflects off of a flat mirror which is fixed in place. A flat mirror that is permanently fixed reflects one beam. The other beam bounces off a flat mirror that is mounted on a mechanism and may be moved a very small distance away from the beam splitter. The two beams meet again at the beam splitter after each beam bounces off its corresponding mirror. The signal that emerges from the interferometer is the consequence of these two beams "interfering" with one another since one beam has a fixed route and the other's path is dynamic due to the movement of its mirror. The resulting signal, known as an interferogram, has the special characteristic that each data point (a function of the changing mirror position) that makes up the signal

contains details about each infrared frequency that originates from the source. As a result, all frequencies are monitored simultaneously while the interferogram is being measured.

The measured interferogram signal cannot be easily evaluated since the analyst needs a frequency spectrum (a depiction of the intensity at each specific frequency) to make identification. The distinct frequencies must be "decoded" somehow. A well-known mathematical method called the Fourier transformation can be used to do this. The computer does this change, after which it gives the user the desired spectral data for analysis. In the present investigations, prepared zirconia nanostructures was examined by recording their FTIR spectra using Perkin ElmerRX1 Model FTIR spectrophotometer in the range of 4000 cm^{-1} to 400 cm^{-1} .

Scanning Electron Microscopy (SEM)

The surface of the sample is imaged by the scanning electron microscope (SEM), which scans it using a high-energy electron beam in a raster scan pattern. The sample's atoms and electrons interact to produce signals that provide details about the sample's surface topography, chemical composition, and other attributes like electrical conductivity.

Secondary electrons, backscattered electrons (BSE), distinctive X-rays, light cathodoluminescence, specimen current, and transmitted electrons are some of the signs that a SEM can produce. All SEMs feature secondary electron detectors, however it is uncommon for a single instrument to have detectors for every potential signal. The signals are the consequence of interactions between the electron beam and atoms on or near the sample surface. The SEM can provide extremely high-resolution images of a sample surface in the most popular or standard detection mode, secondary electron imaging of SEI, revealing features as small as 1 to 5 nm in size. SEM micrographs have a significant depth of field because of the extremely narrow electron beam, giving them a distinctive three-dimensional appearance that is helpful for comprehending the surface structure of a sample. Magnifications that are 250 times greater than those of the greatest light microscopes are attainable, ranging from

roughly 10 times to more than 500,000 times. Elastic scattering causes beam electrons to be reflected off the sample and become back-scattered electrons (BS). BSE are frequently utilised in analytical SEM together with spectra created from the distinctive X-rays, and because the intensity of the BSE signal is strongly correlated with the atomic number (Z) of the specimen, BSE images can reveal information about the distribution of various elements in the sample. Similarly, BSE imaging can scan colloidal gold immuno-labels with a diameter of 5 or 10 nm that would otherwise be challenging or impossible to see in secondary electron pictures of biological samples. When an inner shell electron from the sample is removed by the electron beam, a higher energy electron fills the empty shell and emits characteristic X-rays. The composition and elemental abundance of the sample are determined using these distinctive X-rays.

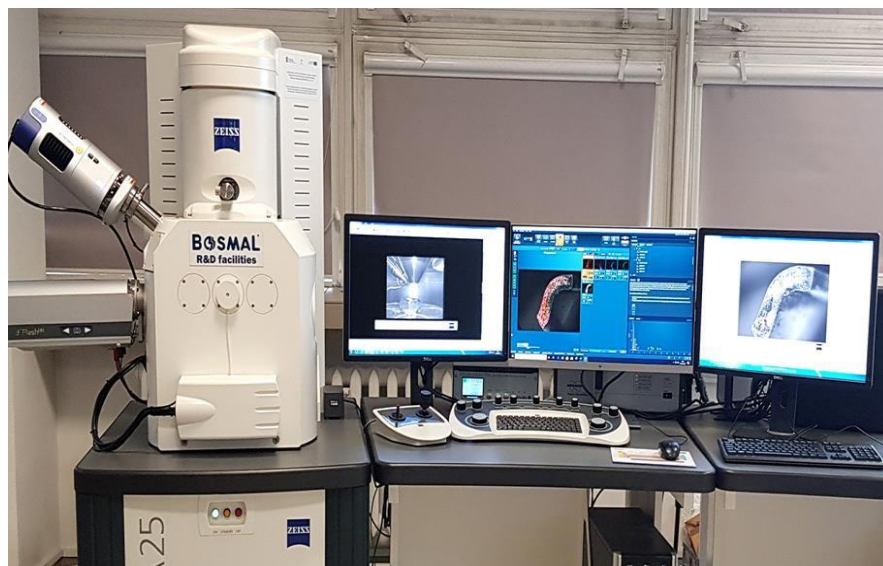


Fig 4.3.6 SEM EDAX machine

A tungsten filament cathode-equipped electron gun emits an electron beam thermionically in a conventional SEM. Due to its inexpensive price, high melting point, and low vapour pressure among all metals, tungsten is typically employed in thermionic electron cannons since it can be heated for electron emission. One or two condenser lenses focus the electron beam, which has an energy range of 0.5 keV to 40 keV, to a point with a diameter of between 0.4 μ m and 5 μ m. In the electron column, usually in the last lens, the beam goes via a pair of scanning coils or a pair of deflector plates that deflect it in the x and y axes. Hence, the laser scans in raster fashion over

a rectangular area of the sample surface. A distribution map of the intensity of the signal, which is being emitted from the scanned area of the specimen, is obtained as a result of synchronising the raster scanning of the CRT display with that of the beam on the specimen in the microscope. A high resolution cathode ray tube can be used to take a picture of the image. Yet, with the aid of modern technology, the image can be digitally recorded, seen on a computer monitor, and saved to the hard drive.

A SEM's controllable range of magnification extends up to six orders of magnitude, from roughly 10 to 500,000 times. In contrast to optical and transmission electron microscopes, the SEM's picture magnification is independent of the objective lens's power. Although condenser and objective lenses are used in SEMs, their primary purpose is to focus the beam on a specific area rather than to image the specimen. While this is conceivable, the SEM's resolution is insufficient to photograph individual atoms. A scanning electron microscope (SEM) research was carried out in the current investigation. The morphology and dispersion of the ready samples were described using the SUPRA JSM-6390 SEM.

As a result, only a transmission electron microscope can see individual atoms because the resolution of the SEM is insufficient (TEM). To evaluate the morphology and distribution of the generated samples in the current examination, a scanning electron microscopy (SEM) analysis was carried out using SMARTLAB Rigaku Japan, SEM with EDX-WDS.

CHAPTER 5

RESULTS AND DISCUSSION

STRUCTURE ANALYSIS XRD

The XRD pattern of as synthesized and calcined nanocomposites are shown in the figure.

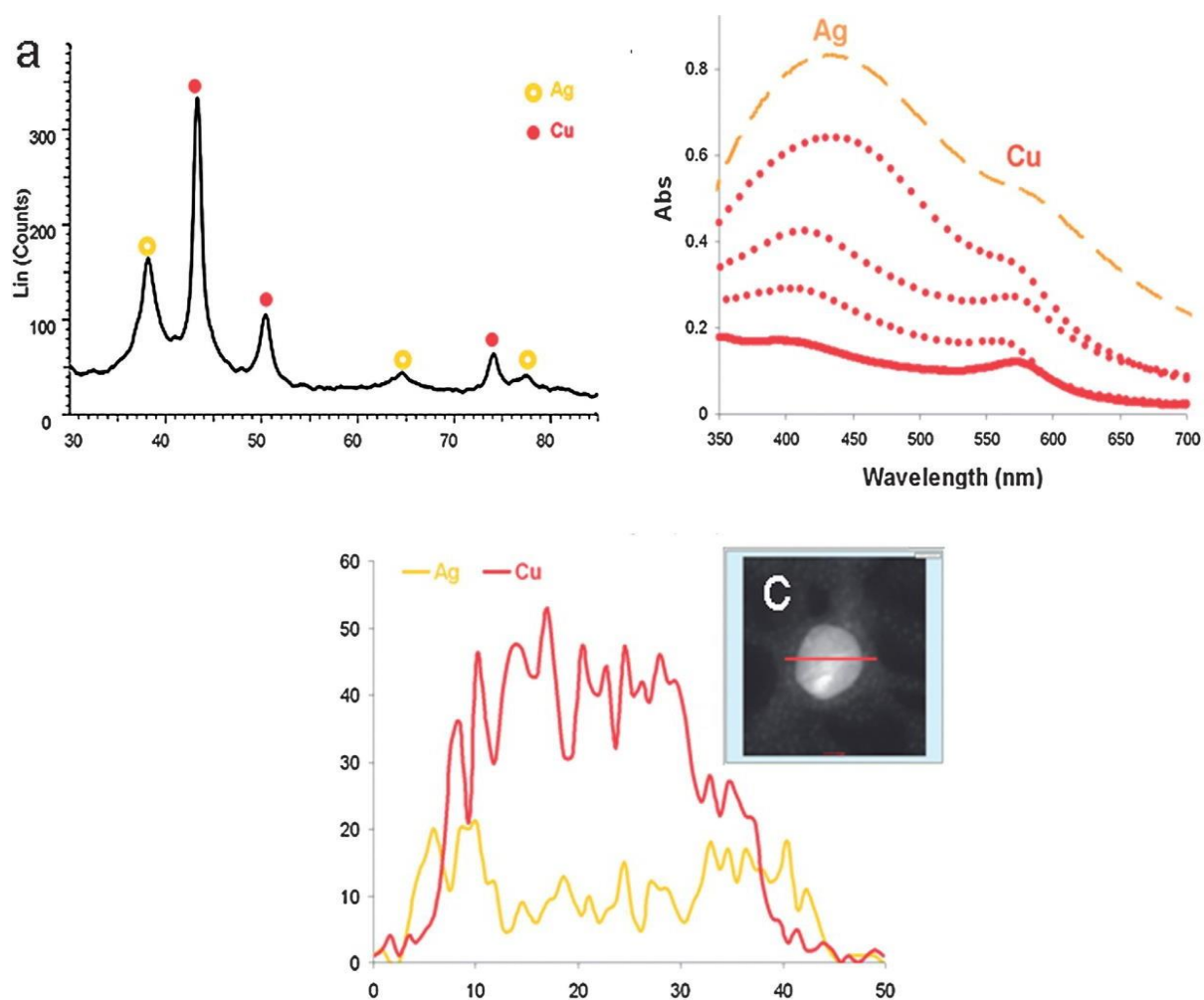


Fig 5.1 .X-Ray Diffraction Graph

XRD pattern of a dried Cu@[Ag(NH₃)₂]⁺ NPs dispersion at room temperature with distinctive copper (2.089, 1.809, and 1.279) and silver (2.355, 1.444, and 1.231) d-spacing.

Bombarded with 0.3 MeV of e-beam energy) [126]. The use of a combination of physical and chemical techniques led to greater success. Cu@Ag NPs, for instance, were successfully created by heating a mixture of

In a microwave reactor, copper nitrate and sodium acrylate were heated to 160 °C before being transmetalated with silver diamine [95]. Cu@[Ag(NH₃)₂]⁺ NPs were synthesised in glycerol using an identical method. Silver acetate [93] or silver nitrate [94] solutions were added to the copper salt solution after microwave irradiation in order to coat the NPs with a layer of silver [93, 94]. Another method involved sono electrolysis of copper sulphate to produce copper nanoparticles, which were then thoroughly washed, dried, and trans metalized to create Cu@[Ag(NH₃)₂]⁺ NPs.

UV-VIS SPECTROSCOPY

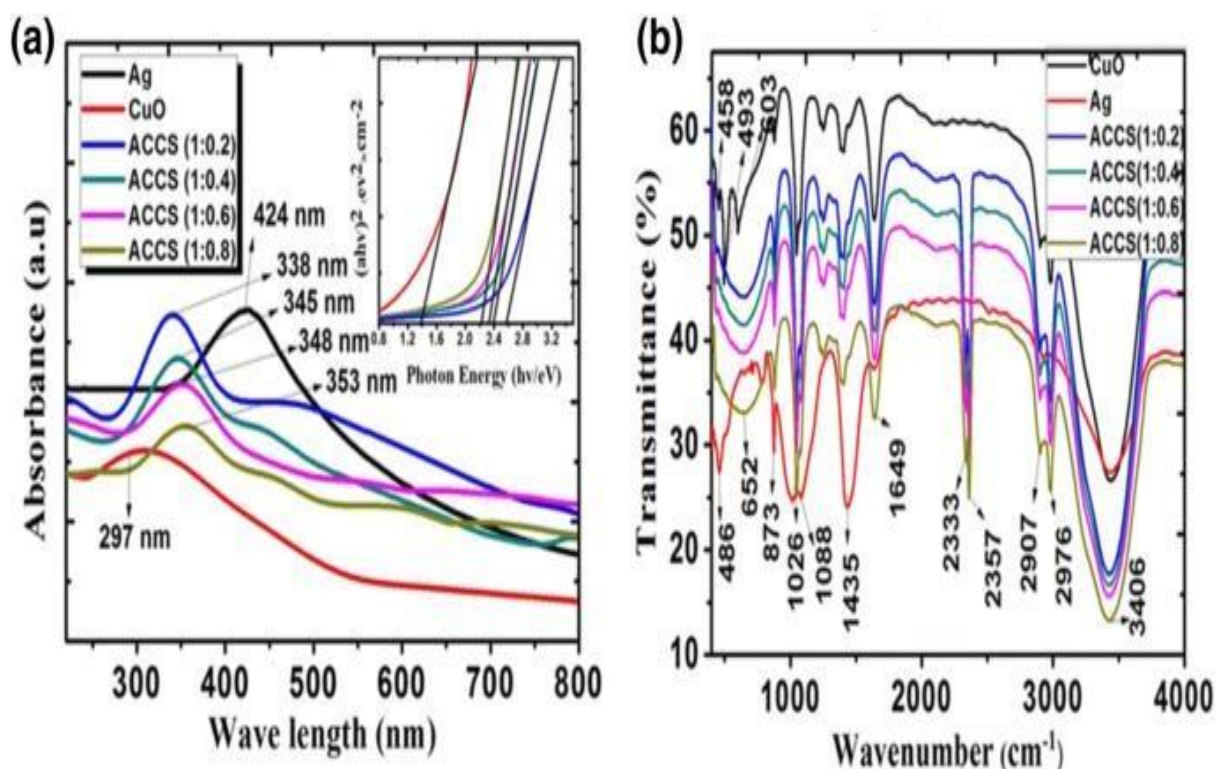


Fig.5.2 UV-Vis Spectroscopy

Properties, solubility, and colloidal stability characters of the as-prepared samples were probed by UV-Vis spectroscopy. Fig. 6 illustrates the absorption spectra of core, core/shell and core/shell/shell NPs in distilled water over the range of 200-600 nm. As seen in Fig. 6, a significant enhancement and redshift in absorption edge was observed due to optically active silica that has been grafted to the surface of core/shell NPs. We observed a similar trend in the absorption spectra measured in absolute ethanol. It was also confirmed by FTIR spectroscopy that the surface of prepared samples is covered by a large number of hydroxyl groups which render them aqueous-soluble.

FUNCTIONAL GROUP ANALYSIS-FTIR

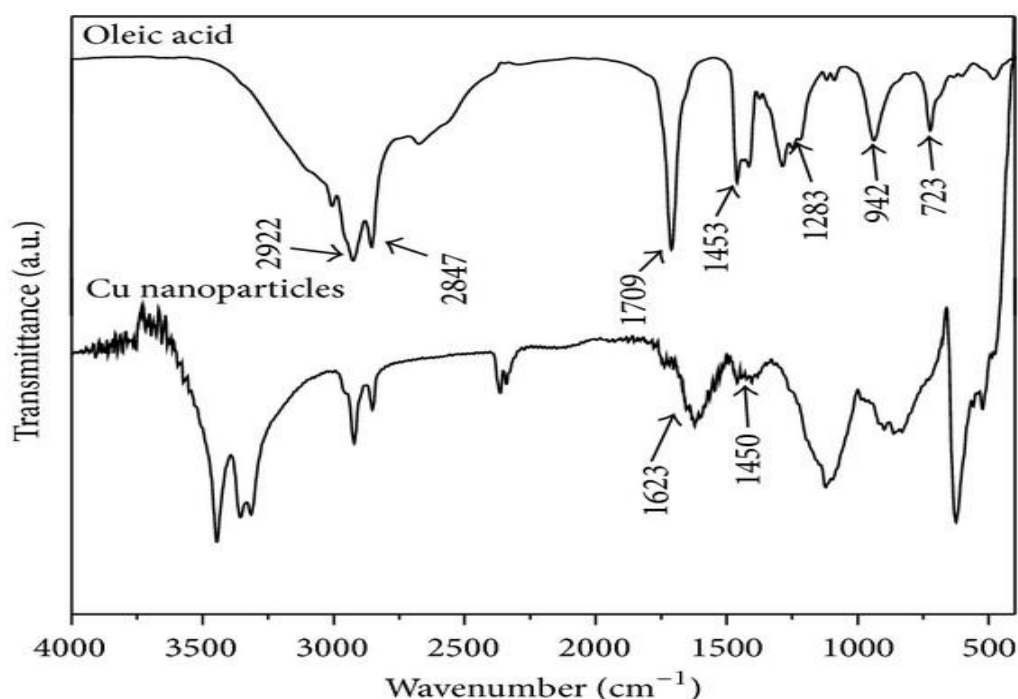


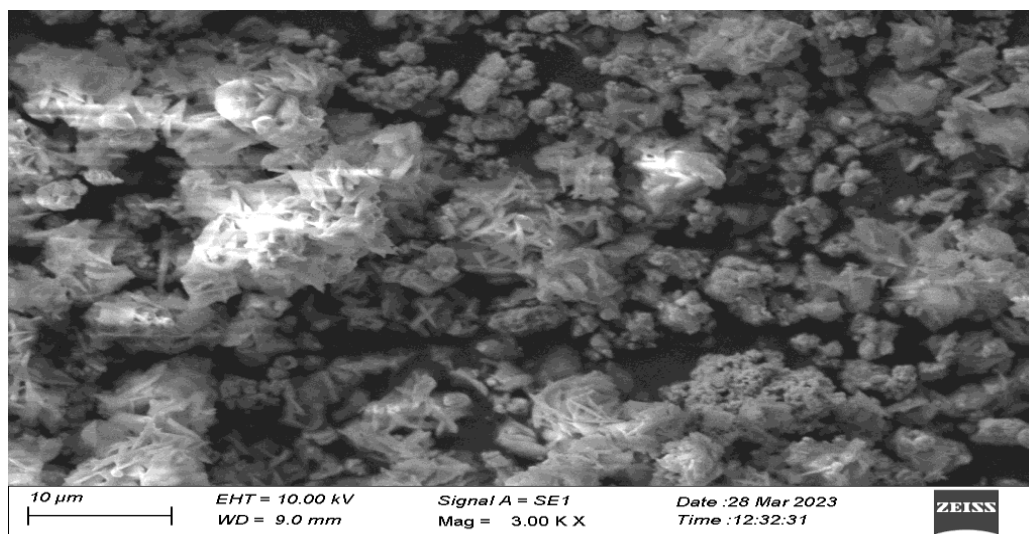
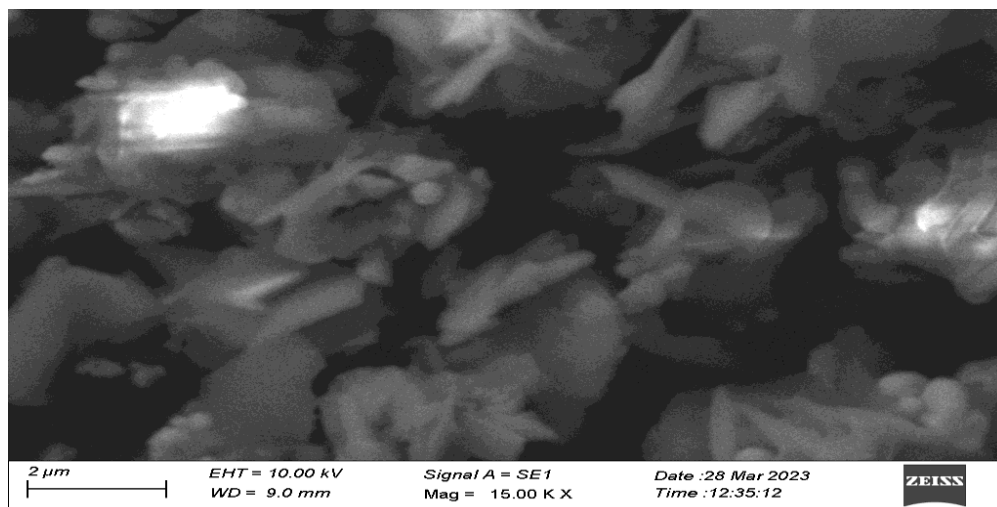
Fig.5.3 FTIR Graph

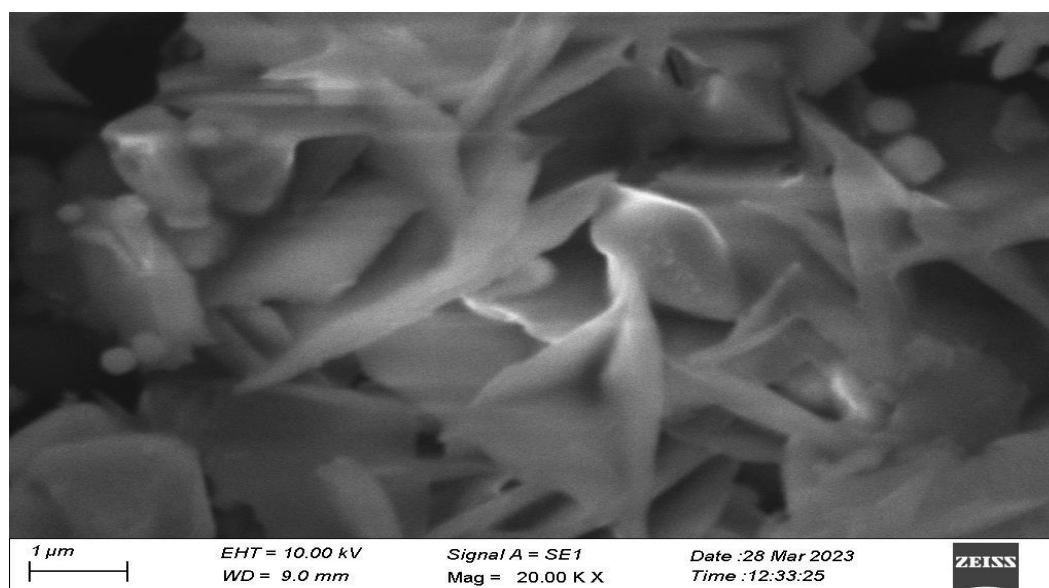
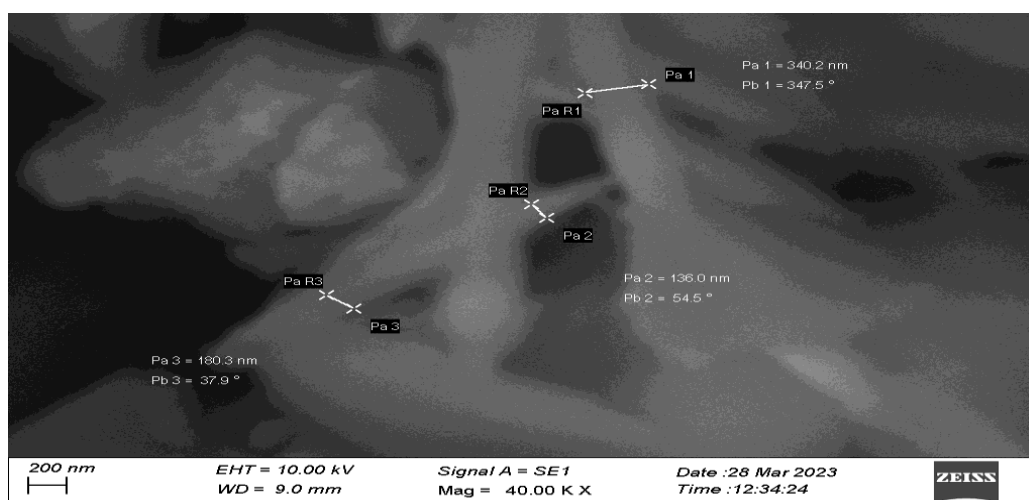
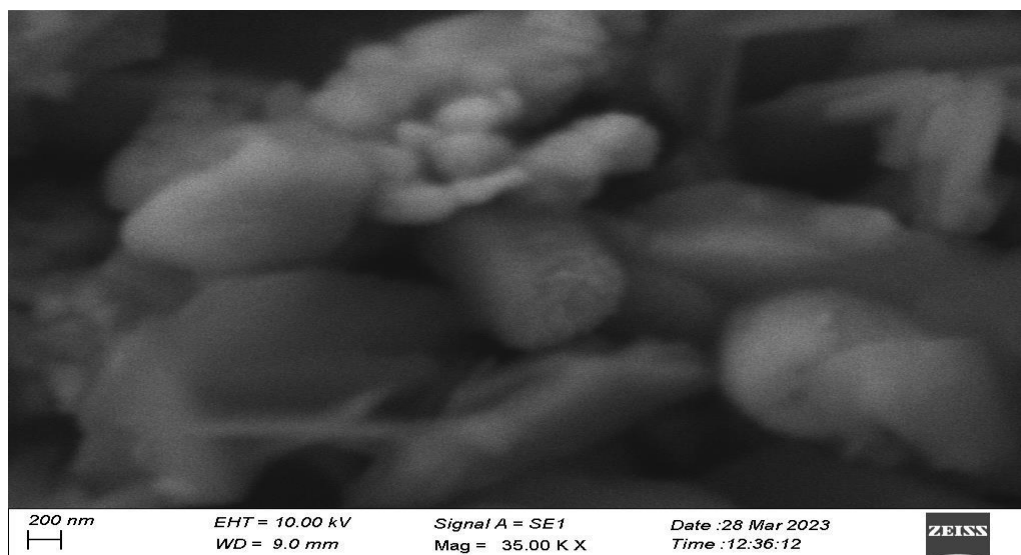
FTIR spectra in the range of 500-4000 cm^{-1} of core-shell structures

SURFACE ANALYSIS-SEM

SEM is used to thoroughly analyse the shape and particle sizes of the individual and linked oxides. The sample CuSO_4 's SEM picture reveals the dispersion of tiny rod-shaped CuO particles on the surface of $[\text{Ag}(\text{NH}_3)_2]^+$.

It may be assumed that the extra CuO that is deposited on the surface of the nanocomposites, as seen in earlier work, is what causes the decrease in surface area.





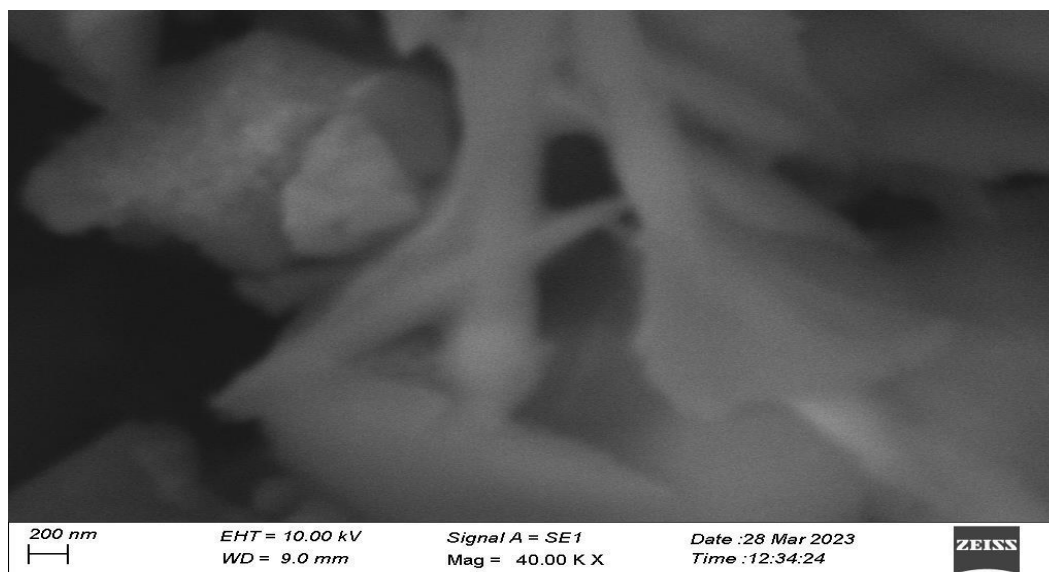


Fig.5.4 SEM

A) Field Emission–SEM image of Cu@Ag NPs obtained by sequential reduction of ammonia complexes of copper and silver [110] (Reprinted with permission of Elsevier) by reduction of AgNO₃ in the dispersion of Ni powder.

CHAPTER 6

SUMMARY AND CONCLUSION

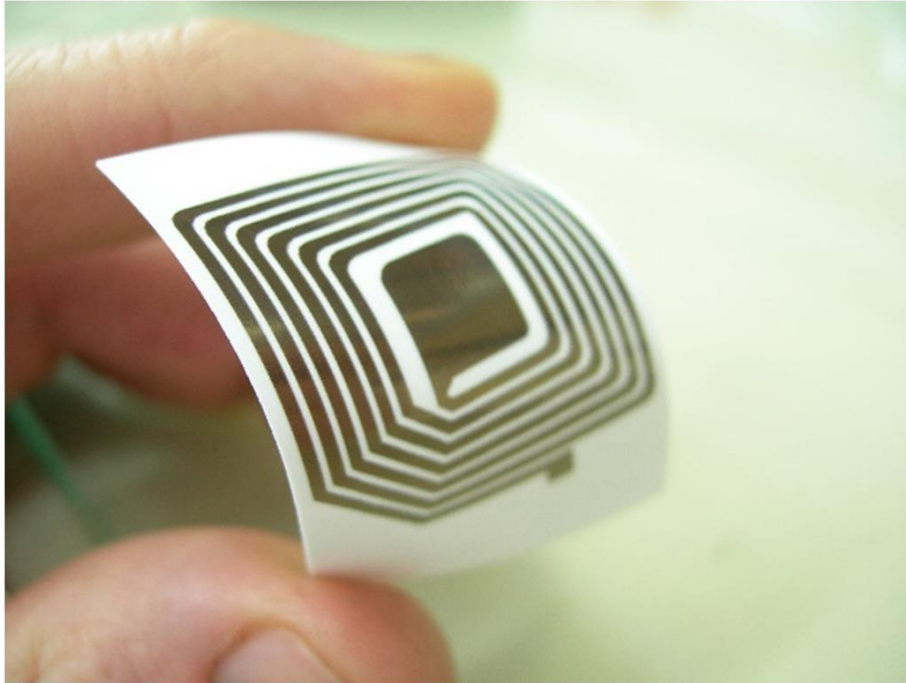
SUMMARY AND CONCLUSION

In this research, air-stable Cu@ [Ag(NH₃)₂]⁺, core-shell nanoparticles were synthesized by two-step synthetic method, and based upon the molar proportion of Cu and Ag in the core-shell nanostructures, they have been characterized for morphology, thermal stability and electrical resistivity properties. The following conclusions can be drawn from the study:

1. The molar composition of Cu and Ag during the procedure of nanoparticles synthesis greatly influences the morphology of the resultant core shell nanoparticles. At excess supply of Ag reagent (e.g. [Cu]: [Ag(NH₃)₂]⁺, = 1:1), agglomeration of bulk Ag interferes with the formation of individual core-shell nanostructure. At limited supply of Ag (e.g. [Cu]:[Ag(NH₃)₂]⁺, = 6:1), most of the Cu cores are not completely enveloped by Ag shell, thus rendering the Cu susceptible to thermal oxidation. An optimized molar composition (intermediate supply of Ag), needs to be employed to solve the oppositely faced agglomeration and oxidation phenomena.

2. The Cu@Ag core-shell diameter increases with an increase in the initial molar proportion of Ag reagent. 3. From XRD results, considering the samples held for 3 months at room temperature and subjected to same magnitude of heating speed, the Cu@Ag nanoparticles with [Cu]/[Ag] molar ratio at 4:1, were observed with the slowest oxidation rate and thus are considered the one with the highest thermal stability. 4. The electrical resistivity of Cu@Ag nanoparticles, in general, has been observed to increase with the increment in the content of Cu. The increment rate of resistivity is quite small upto the sample [Cu]: [Ag (NH₃)₂]⁺, = 4:1, and for samples with Cu content higher than this limit, the increment rate is quite larger. For equal molar fraction of Cu and Ag in the nanostructures ([Cu]: [Ag(NH₃)₂]⁺, = 1:1, the mean value of measured electrical resistivity Cu@Ag core-shell nanoparticles is 61.74 μΩ·cm. This value is just 64.24 μΩ·cm for sample [Cu]:[Ag] = 4:1, whereas it is around 83.7 μΩ·cm for test

specimen $[\text{Cu}]:[\text{Ag}(\text{NH}_3)_2]^+]$ = 6:1. 5. In practical applications requiring enhanced electrical conductivity properties, higher thermal stability, reduced agglomeration effects, lowered material cost; the test specimen $[\text{Cu}]: [\text{Ag}(\text{NH}_3)_2]^+]$ = 4:1, can be selected as the sample characterized with optimum properties.



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