2024-10

Optical Properties of Copper Nanoparticles: A Systematic Review

Muhabaw, Assefa

OPTICAL PROPERTIES OF COPPER NANOPARTICLES: A SYSTEMATIC REVIEW

BAHIR DAR UNIVERSITY

COLLEGE OF SCIENCE

DEPARTMENT OF PHYSICS

A PROJECT SUBMITTED TO THE DEPARTMENT OF PHYSICS PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN PHYSICS

BY:

MUHABAW ASSEFA

ADVISOR: AMARE BINOR (PhD)

OCTOBER, 2024

BAHIR DAR ETHIOPIA

DECLARATION OF ORIGINALITY

I hereby declare that except where specific reference is made to the work of others, the content of this Project work is original and has not been submitted in whole consideration for any other degree or qualification at any other university. This project work is my own work and contains nothing that is the outcome of work done, except as specified in the text and acknowledgments.

Muhabaw Asefae	_____	_____
Student name	Signature	Date
Amare Binor (PhD)	 _____	_____
Advisor name	Signature	Date
Tamiru Nigusse (PhD)	_____	_____
Head of physics Department	Signature	Date

ADVISOR'S APPROVAL PAGE

To the best of my knowledge and as understood by the student in the research integrity and copyright disclaimer, this project work entitled "Optical Properties Of Copper Nanoparticles" submitted in partial fulfillment of the requirement for the degree of master of science in physics adheres to the provision of guidelines, policies, and legislation during his project work and use of copyright material. The project work is completed and can be presented to the project work evaluation committee.

Amare Binor (PhD)	_____	_____
Name of Advisor	Signature	Date (D/M/Y)G.C

BAHIR DAR UNIVERSITY

COLLEGE OF SCIENCE

DEPARTMENT OF PHYSICS

The undersigned at this moment certify that they have read and recommend to the College of Science for acceptance a project work titled "**Optical Properties of Copper Nanoparticles"** by **MUHABAW ASSEFA** in partial fulfillment of the requirements for the degree of Master of Science in Physics.

APPROVED BY THE EXAMINING COMMITTEE

Amare Binor (PhD)	_____	_____
Advisor Name	Signature	Date
Tamiru Nigusse (PhD)	_____	_____
Internal Examiner	Signature	Date
_____	_____	_____
External Examiner	Signature	Date
_____	_____	_____
Chair Person	Signature	Date

BAHIR DAR UNIVERSITY

COLLEGE OF SCIENCE

DEPARTMENT OF PHYSICS

Author: **Muhabaw Assefa**

Title: OPTICAL PROPERTIES OF COPPER NANOPARTICLES

Department: **Physics**

Degree: **M.Sc.** Convocation: **October** Year: 2024

Dedication

This project is dedicated to the almighty God who has been my strength and source of knowledge throughout my period of studies. To my family and loved ones, God bless you all.

List of acronyms and abbreviations

Cu – Copper

NPs- Nanoparticles

CNPs- Copper Nanoparticles

SEM -Scanning electron microscopy

TEM - Transmission Electron microscopy

AFM - Atomic force microscopy

MNPs-Metallic Nanoparticles

XEDS- X-ray energy dispersive spectra

DLS- Dynamic light scattering

PR- Plasmon resonance

SPR- Surface Plasmon resonance

LPR- Local Plasmon resonance

SERS- Surface Enhanced Raman Scattering

QDs- Quantum dots

0D, 1D, 2D, 3D-Zero, One, Two, Three dimensional

CMAR-Carcinogenic Mutagenic Asthmagenic Reproductive toxin

XRD-X-ray diffraction

HAADF-High-angle annular dark-field

FTIR-Fourier-transform infrared spectroscopy

UV-Vis-Ultra-visible spectroscopy

SQUID-Superconducting quantum interference device

ESR-Electron spins resonance spectroscopy

THW-Transient hot wire

TGA –Thermo gravimetric analysis

SAED- Selected area electron diffraction

Table of contents

Contents page

List of Figure

List of Table

Acknowledgments

First of all, I would like to thank God, who is always beside me all the time. Secondly, I am happy to express my respect and gratitude to my advisor Dr. AmareBenor,who helped me from the beginning to the final how to do my project by giving constructive ideas, suggestions, and comments throughout my work. Secondly, and most importantly, I would like to express my utmost gratitude to Mr.Assaye, Ph.D candidate of the physics department, who helped me how to do my project by giving constructive ideas and comments. Finally, I would like to thanks my loving and wonderful families for their financial, moral support and encouragement and also their efforts to overcome various challenges which affect the work.

ABSTRACT

Scientific interest in nanoparticles of various shapes and morphologies is growing proportionally. Besides the distinct size characteristic, properties of nanoparticles vary widely with alteration of structural and morphological features. Metallic nanoparticles' characteristics are mostly determined by their shapes and sizes. These shape-dependent nanoparticles hold an impressive potential for to be used in numerous scientific technologies with promising applications. Due to their small size, metallic nanoparticles have special optical, magnetic, and electrical, strength, surface area, sensitivity, and stability features. Surprisingly, the phase change occurs when bulk materials are converted into nanoparticles, which means that materials that were previously non-magnetic become magnetic at the nanoscale. Because of their unique features, nanoscale matter is a separate form of matter from the solid, liquid, gaseous, and plasma states.Copper nanoparticles have drawn tremendous attention over other metals due to their unique and fascinating property known as Localized Surface Plasmon Resonance (LSPR). Mie theory can describe the optical properties of copper nanoparticles when the size of the nanoparticle is not too small.In this study, a critical overview the optical properties of copper nanoparticles from a theoretical approach (Mie scattering theory) and experimental investigations were intensively reviewed.Additionally, classifications, synthesis techniques, characterization methods of nanoparticles, and applications of copper nanoparticles in various fields are offered.

CHAPTER ONE

1. INTRODUCTION

1.1Background of the study

Nanotechnology is an emerging scientific discipline focused on the manipulation of matter at the atomic and molecular scale. This realm, often referred to as the nanoscale, encompasses structures with at least one dimension measuring between 1 and 100 nanometers (nm) as presented in Figure 1.[1] Within this infinitesimal domain, materials exhibit unique properties that differ significantly from their bulk counterparts. By harnessing these properties, nanotechnology enables the manufacture of novel materials, devices, and systems with a wide range of applications.[2] A key component of nanotechnology is the production and utilization of nanoparticles, which are ultrafine particles with diameters ranging from 1 to 100 nanometers and lengths up to 1000 nanometers. The dimensions of these nanoparticles are influenced by both the synthesis method and the surrounding environment.[3] Nanoparticles have emerged as versatile building blocks with transformative potential across diverse scientific and technological domains, including chemistry, materials science, pharmaceuticals, and biotechnology.[4] Their unique properties at the nanoscale have encouraged extensive research and development efforts to harness their capabilities. These unique properties vary based on their material composition, shape, and origin making them extraordinary properties that diverge significantly from their bulk counterparts.[5]For instance, based on material and composition: (i) carbon-based nanomaterials such as carbon nanotubes and fullerenes, exhibit exceptional mechanical and electrical characteristics[6] (ii) Inorganic nanomaterials, including metallic and metal oxide nanoparticles like silver, gold, titanium dioxide, copper-based nanoparticles, and zinc oxide, possess catalytic, antimicrobial, and electronic properties that have enabled their integration into diverse applications.[7] (iii) Organic nanomaterials, derived from biological or synthetic organic molecules, often demonstrate biocompatibility and self-assembly capabilities.[8](iv) Lastly, the incorporation of components from various categories into composite nanomaterials results in intricate structures with tailored functionalities.[9] Among these, metal nanoparticles have exceptional electrical conductivity, and these properties position them as promising candidates for fabricating intricate wiring patterns in advanced electronic components. Moreover, the remarkable thermal conductivity exhibited by these nanoparticles offers paths for creating highly

efficient heat-dissipating materials. Finally, their substantial surface area-to-volume ratio makes them priceless for the development of catalystswithenhancedreactivity.

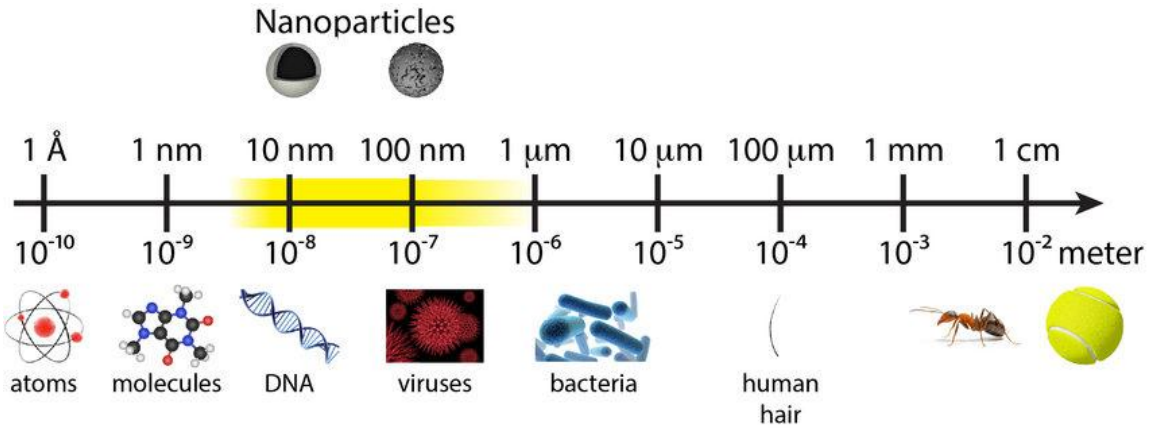

Figure 1.1: The size of nanoparticles ranges from 1-100nm, compared to other typical sizes of everyday objects and organisms.[1]

Besides, copper nanoparticles (Cu NPs) have emerged as a promising material due to their distinct properties. Copper (Cu) is the eighth most abundant metallic element within the Earth's crust. Once released from its mineral form into the environment, copper is neither created nor destroyed, necessitating precise regulation of its levels to maintain homeostasis.[10] As a transition metal with atomic number 29 and an atomic mass of 63.546, copper exhibits a characteristic reddish-orange type and metallic shine. Its density exceeds 5 grams per cubic centimeter (g/cm^3). Notably, copper possesses exceptional ductility, malleability, and thermal and electrical conductivity, coupled with high corrosion resistance and low chemical reactivity. Furthermore, its conduction electrons, or free-moving electrons, can interact strongly with visible light when the nanoparticle's plasmonic mode aligns with the energy of incoming photons. This unique characteristic makes Cu NPs a subject of increasing interest across various fields.[11]

The enormous diversity of the copper nanoparticles arising from their wide chemical nature, shape and morphology, the medium in which the particles are present, the state of dispersion of the particles and most importantly the possible surface modifications the copper nanoparticles can be subjected to make this an important active field of science now-a-days. Currently copper nanoparticles have received considerable attention because copper is a versatile material which finds various applications in different fields of research.[12] Nowadays optical properties of nanoparticles are intensively investigated because they are widely used for

technical applications. Their capability to interact intensively with light is used for amplification of stimulated Raman scattering and fluorescence.[13]

Copper is the most abundantly used metal in electronics applications due to its high conductivity and owing to fairly low costs, copper plays a significant role in modern electronic circuits. The development of minimized to nano devices that integrate electronic, photonic, chemical, and/or biological features is important for future electronic and sensing devices. The large extinction cross section and photosensitivity of noble metal nanostructures make them promising platforms as highly sensitive optical nano sensors, photonic components, and in surface-enhanced spectroscopy.[14] The signature optical response of interest is known as the localized surface Plasmon resonance (LSPR). The LSPR is excited when light (electromagnetic radiation) interacts with the free (conduction) electrons of a metallic nanostructure, which results in the collective excitations (oscillations) that lead to strong enhancements of the local electromagnetic fields surrounding the nano-particles.[15]

Copper nanoparticles are generally characterized by their size, morphology and surface charge, using microscopic techniques such as scanning electron microscopy (SEM), transmission Electron microscopy (TEM) and atomic force microscopy (AFM) and UV-Visible spectroscopy. This review focuses on the optical properties of copper nanoparticles.

1.2 Statement of the problem

The field of study known as nanotechnology includes the synthesis, engineering, and application of nanomaterials. Due to the innovative and intriguing applications of nanomaterials, nanotechnology has attracted a lot of interest over time. Among the noble metallic nanoparticles,copper nanoparticles are increasingly used in various fields, including medical, health care, consumer,agriculture, biomedicine, electronics, energy, pollution, food engineering, transportation, telecommunication, cosmetics, coatings, materials, and mechanical engineering are just a few of the industries that use nanomaterials. It has been confirmed that the technology that uses copper nanoparticles is more effective than the technology that uses bulk materials. Secondly, copper nanoparticles are used to develop tools to diagnose and control the epidemic diseases. But due to their unique physical and chemical properties such as optical, electrical, mechanical, chemical and thermal as well as high electrical conductivity, and biological

properties and their diverse applications we are interested to deal the optical properties of copper nanoparticles.

1.3 Objectives of the study

1.3.1 General objective of the study

The general objective of this project work is to review the optical properties of copper nanoparticles.

1.3.2 Specific objectives of the study

The specific objectives of this project work are the following:

- To review relationship between plasma resonance of copper nanoparticles and size of the nanoparticle.
- To review the characterization technique of used in the study of copper nanoparticles.
- To review the application of copper nanoparticles.

1.4 Significance of the project Work

Nanoparticles are usually characterized by their size distribution, morphology, surface properties, stability and interactions. The characterization of the copper nanoparticles is a fundamental process to evaluate their properties and to obtain information on composition, structure and morphology. It has been found that the copper particles that are synthesized as a stabilizer activity which depends on the size. As the project work I aimed at the study of the optical properties of copper NPs. It will have a significant contribution for the solid state Physics and the scientific community in the field. The finding may also initiate other researchers to conduct similar studies in the field. Besides .the finding of this project will serve a reference to similar studies in other compounds exhibiting/manifesting similar features..

1.5 Outline of the Project

The project work is organized in to five chapters. The first chapter focuses on the introductory part of the project work in which background of the study, statement of the problem, objectives of the study, significance and outline of the project work. The second

chapter focuses on the literature review project in which nanoparticles, classifications of nanoparticles, synthesis methods of nanoparticles, characterization methods of nanoparticles, and properties of nanoparticles. Chapter three focuses on the methodology of the project work. Chapter four focuses on the results and discussions of the project work in which plasma resonance of copper nanoparticles and size of nanoparticles, characterization techniques of copper nanoparticles, optical properties of copper nanoparticles and applications of copper nanoparticles. Chapter five is about summery and outlooks of the project work.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Nanoparticles

Nanoscience is the study of properties of matter at the nanoscale that focuses on the unique, size-dependent properties of solid-state materials.[16]Nanotechnology deals with the synthesis, engineering, and utilization of materials whose size ranges from 1 to100 nm, known as nanoparticles.[17]Nowadays, nanomaterials are used in a wide range of applications because of their unique properties.[18]The two main factors that cause why nanomaterialsare significantly different physically and chemically than the same materials at larger dimensions are surface effects and quantum effects.[19]The two factors contribute nanoparticles exhibiting enhanced mechanical, thermal, magnetic, electronic, optical, and catalytic properties.[20]

The three main reasons why nanoparticles have different surface effects compared to bulk materials are: (a) dispersed nanoparticles have a very large surface area and high particle number per mass unit,(b) the fraction of atoms at the surface in nanoparticles is increased, and (c) the atoms located at the surface in nanoparticles have fewer direct neighbors. Larger surface areas and larger surface-to-volume ratios generally increases the reactivity of nanomaterials due to the larger reaction surface, and resulting changes of surface properties on their structure. [21] The strong attractive interactions between particles can bring in the agglomeration and aggregation of nanoparticles, which negatively affects their surface area and their nanoscale properties. [22]Agglomeration can be prevented by increasing the zeta potential of nanoparticles, [23] and by optimizing the pH and the ionic strength of the suspension medium.[24]By shrinking the size of the material, quantum effects become more pronounced, and nanoarticles become quantal.[25]As a result of quantum confinement affects some non-magnetic materials in bulk (palladium, platinum, and gold) become magnetic in the nanoscale.[19]NPs can be of different shapes, sizes, and structures. They can be spherical, cylindrical, conical, tubular, hollow core, spiral, etc., or irregular.[26]Nanoparticles can be crystalline with single or multi-crystal solids, or amorphous. Nanoparticles can be either loose or agglomerated.[27]NPs can be uniform, or can be composed of several layers. The layers of NPs often are: (a) the surface layer that consists of a variety of small molecules, metal ions, surfactants, or polymers, (b) the shell layer that is made of a

chemically different material from the core layer and (c) the core layer, which is the central portion of the NP.[28]

The noble metals nanoparticles(Cu, Au, and Ag) have unique optical properties due to their large cross-section.[29]These noble metal nanoparticles express the unique absorption peak in the visible region known as the surface Plasmon resonance (SPR) peak. This is because of mutual oscillations of the cloud of conduction electrons on metal nanoparticles. When the frequency of vibration matches that of the electromagnetic field, a huge amount of energy is shifted from the field to metal nanoparticles. The Ag and Au nanoparticles used for plasmonic applications and biocompatibility etc because of their intense SPR peak.[30] Copper is a non-expensive metal and is easily available. The optical characteristics of copper nanoparticles are impressive due to the fact of are phenomenon of harmonicity of energy of SPR with inter-bandshift, although for silver and gold nanoparticles, the Plasmon response energy remains comparatively lower to the inter-band shift. The dependence of the inter-band shift edge on particle size is occurring mainly by the surface stress-induced alterations in lattice constant and correlated alterations in electronic band structure[31,] Sheen et al.[32]have reported high-performance polymer solar cells improved by merging of copper nanoparticles. They defined a drop in device resistance and enhancement of sharp current density and power conversion efficacy due to copper nanoparticles.

Another interesting feature to study is to have a control on the SPR wavelength of noble metal nanoparticles, for which one has to understand the basics of Mie scattering[33]and the parameters on which SPR wavelength is dependent. The position SPR peak can be characterized by the Mie theory in which all particles are considered to be spherical that there is absolutely no particle-particle interaction term in the effective potential of the system .The parameters which can be played on the SPR wavelength are the size/shape of nanoparticles, and the dielectric constant of metal. Nano particulate matter is a distinct state of matter from the solid state, liquid state, gaseous state, and plasma state. They have distinctive optical, magnetic, and electrical properties.[34]

Nanoscience is concerned with the characteristics of matter at the nanoscale, with a focus on the special, size-dependent characteristics of solid-state materials.[35] Nanotechnology includes the synthesis, engineering, and application of nanomaterials. Due to the innovative and intriguing

applications of nanomaterials, nanotechnology has attracted a lot of interest over time.Agriculture, biomedicine, electronics, energy, pollution abatement, food engineering, transportation, telecommunication, cosmetics, coatings, materials, and mechanical engineering are just a few of the industries that use nanomaterials.[36] It has been confirmed that the technology that uses nanomaterials is more effective than the technology that use sbulk materials.[37]Secondly, nanomaterials are used to develop tools to diagnose and control epidemic diseases. In 2019, COVID-19, a disease that was killing many people in the world, was able to be diagnosed and controlled using nanomaterials.[38]To diagnose and treat the monkeypox disease that is currently happening in the world by using nanomaterials.[39]

2.2 Classifications of Nanoparticles

Nano materials, nano science and nano technology will play a significant role in the development of the world.[40]So we have adequate knowledge and understanding about nanoparticles. Nowadays researchers show that they focus on the classification, preparation method, properties, and applications of nanoparticles.[41] Nanoparticles can be classified in to five major groups based on their size, origin, structural configuration, pore diameters, and potential toxicity.[42]

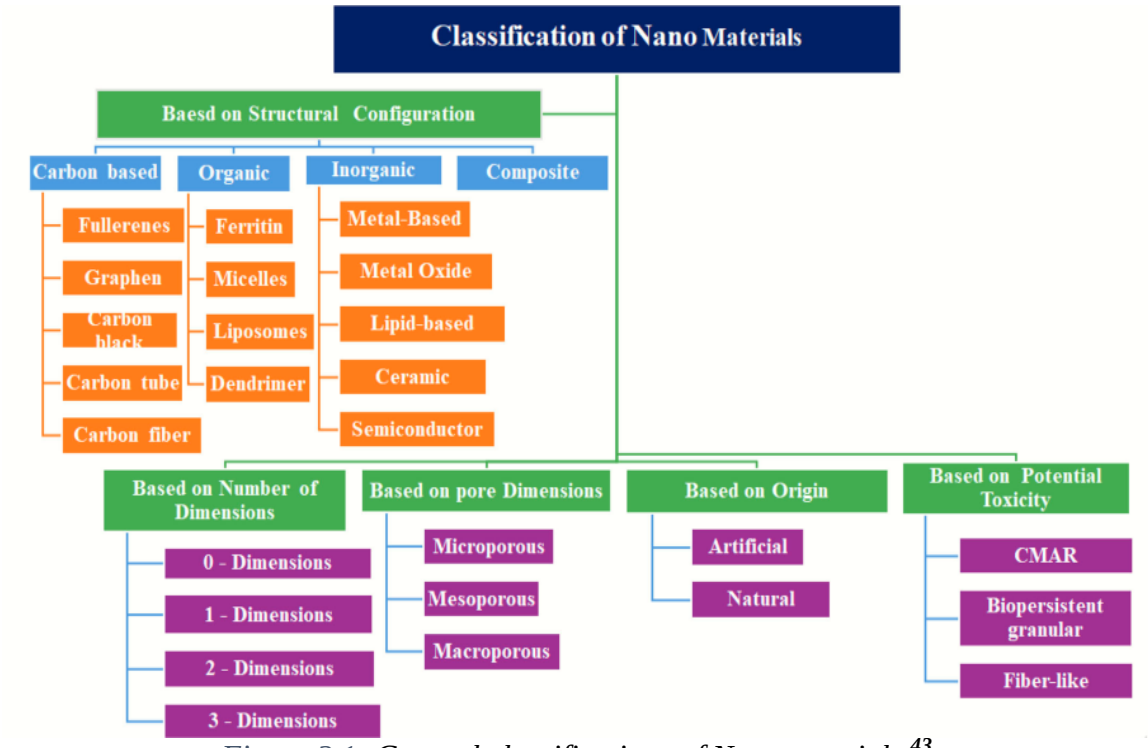

Figure 2.1: General classifications of Nanomaterials.[43]

2.2.1Based on origin

Depending on their origin, nanoparticles grouped as natural and artificial nanoparticles.[44]

a) Natural Nanoparticles

Natural nanoparticles can be found in nature, including viruses, protein molecules, minerals like clay, natural colloids (milk and blood, or liquid colloids), fog, gelatine, mineralized natural materials like shells, and bones, insect wings and opals, spider silk, volcanic ash, and ocean spray.

b) Artificial Nanoparticles

Examples of artificial nanoparticles are carbon nanotubes and semiconductor nanoparticles like quantum dots (QDs).

2.2.2Based on Dimensions

Nano patricles are grouped in to four groups depending on their dimensions.

a) Zero-dimensional (0D) Nanoparticles:

0D NPs have all three dimensions (x, y, and z) within the nanoscale range or are not dimensional outside the nano metric range (>10 nm) and they can be amorphous or crystalline, single crystalline or polycrystalline, exhibit various shapes and forms, and be metallic or ceramic. Quantum dots, fullerenes, and nanoparticles are examples of 0D nanomaterials.

b) One-dimensional(1D) Nanoparticles:

1D NPs have two of their three dimensions (x, y) in the nanoscale range, but one dimension of the nanostructure is outside the non-metric range (>10 nm). 1D nanoparticles (nanofibers, nanotubes, nano horns, nano rods, thin films, and nanowires) are needle-shaped nanoparticles. They can be amorphous or crystalline, single crystalline or polycrystalline, chemically pure or impure, sandal one materials, or embedded within another medium, such as metallic, ceramic, or polymeric. 1D nanoparticles can be metallic, ceramic, or polymeric.

c) Two-dimensional (2D) Nanoparticles:

2D nanoparticles have plate-like shapes with two dimensions outside the nanometer range, but 1D (x) is at the nanoscale (between 1 and 100 nm) coatings and thin film multilayer, nano sheets or nano walls, free particles, tubes, fibers, ultrafine-grained over layers, wires, and

platelets are examples of 2D nanomaterials. 2D nanomaterials can be amorphous or crystalline, made of various chemical compositions, deposited on a substrate, or integrated into a surrounding material, ormetallic.[45]

d) Three-dimensional (3D) Nanoparticles:

The 3D arenanomaterials that are not confined to the nanoscale in any dimension range. All dimensions of a 3D material are outside the nano meter range or greater than 100 nm, but the bulk material is made up of individual blocks that are in the nano meter scale (1–100 nm), so 3D nanomaterials have three arbitrary dimensions above 100 nm. It includes nanoparticle dispersion, bundles of nanowires and nanotubes, and multi-nano layers in which the 0D, 1D, and2D structural elements are in close contact and form interfaces. Thin films with atomic-scale porosity, colloids, and free nanoparticles with various morphologies are examples of 3D nanomaterials.

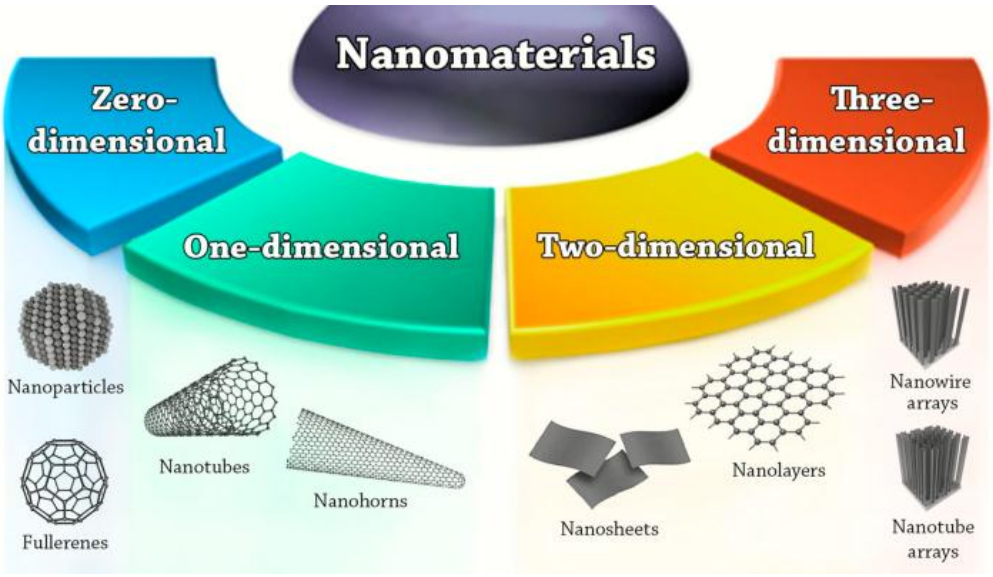

Figure 2.2: Classification of nanomaterials according to dimension.[45]

2.2.3 Based on the structural configurations

Nanoparticles can be classified into four groups based on their structural configurations named as organic/dendrimers, inorganic, carbon-based, and composite.

a) Organic nanoparticles:

Some examples of organic nanoparticles or polymers are liposomes, dendrimers, micelles, and ferritin, and they may be useful for drugadministration.[46]

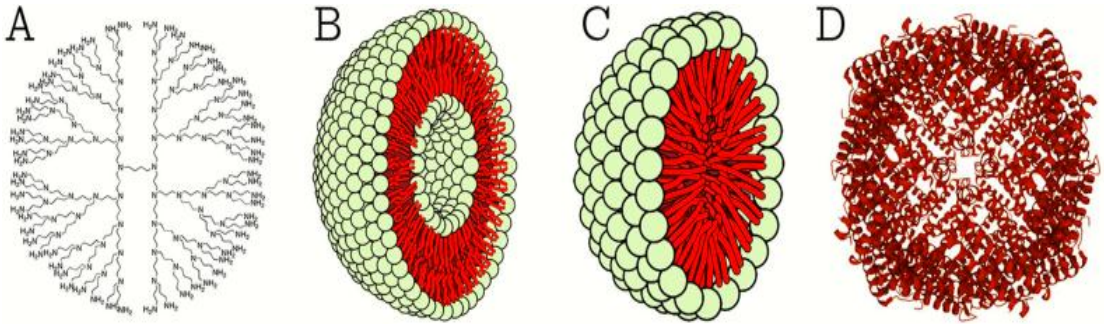

Figure 2.3: Types of Organic NPs: A dendrimers; B Liposome; Cmicelles; and D ferritin.[44]

b) Inorganic nanoparticles:

Inorganic nanoparticles are nanoparticles that lack carbon atoms and they are typically classified in to five: metal-based, metal oxide-based, Semiconductor-based, Ceramic-based and Lipid-based nanoparticles. Aluminium, cadmium, cobalt, copper, gold, iron, lead, silver, and zinc are metal materials that are frequently used in nanoparticle synthesis. Because of their quantum effects and huge surface-to-volume ratio. Metal oxide nanoparticles are contains positive metallic ions and negative oxygen ions such as silicon dioxide (SiO2), titanium oxide (TiO2), zinc oxide (ZnO), and aluminium oxide (Al2O3).

Semiconductor nanoparticles exhibit the same properties as metals and insulators.[47] Ceramic nanomaterials are solids made up of carbides, carbonates, oxides, carbides, carbonates, and phosphates and they can be formulated in drug delivery systems, especially in targeting tumors, glaucoma, and some bacterial infections. Lipid-based nanoparticles are spherical, with diameters ranging between 10 and 100 nm. It consists of a solid core made of lipids and a matrix containing soluble lipophilic molecules. They are applicable in the biomedical field as a drug carrier and RNA release therapy in cancer therapy.

c) Carbon based nano materials

Carbon-based nanomaterials contain carbon include five main materials, namely, carbon nanotubes, Graphene, fullerenes, Carbon Nano fiber and Carbonblack as shown in Figure 2.4.

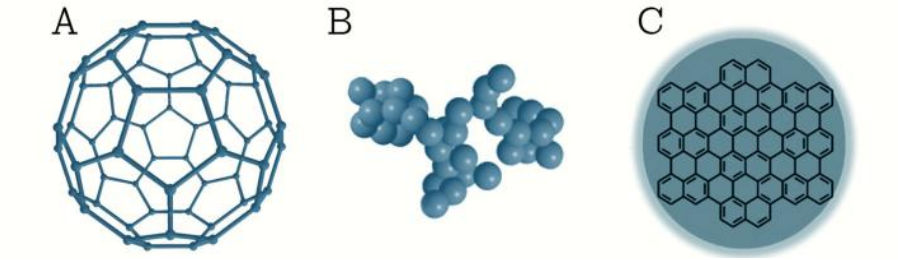

Figure 2.4: Different types of carbon-based NPs A C60 Fullerene; B carbon black NPs; and C carbon quantum dots.[36]

d) Composites Nanoparticles:

Composites Nanoparticles are made up of nanoparticles combined with other nanoparticles, nanoparticles combined with larger-scale materials, and nanomaterials combined with bulk-type materials.

2.2.4 Based on pore dimensions

Depending on their length of diameter dimensions nanoparticles are classified into three groups, which are micro porous materials, mesoporous materials, and macroporous materials. The diameter of the pores determines the size of molecules and gives information about the diffusion and interaction properties.[48]

a) Micro porous Nanoparticles:

They include gases or linear molecules that have very narrow pores with diameters less than 2 nm and they have slow diffusion kinetics and high interaction properties.

b) Mesoporous Nanoparticles: They have pores with a diameter larger than 2 nm but smaller than 50 nm.

c) Macro porous Nanoparticles: They include Carbon micro tubes, porous gels, and porous glasses with pores with enough diameters (greater than 50 nm) to host very large molecules and typically used as matrices to store functional molecules.

2.2.5 Based on potential toxicity

Based on their potential toxicity, nanoparticles are divided into three categories namely fiber-like nanoparticles, Bio persistent granular nanoparticles, and Carcinogenic, Mutagenic, Asthmgenic, and Reproductive toxin (CMAR) nanoparticles.Fiber-like nanoparticles are rigid, bio-permanent carbon nanotubes, fiber-like metal oxides, and carbon nanotubes.[49]The proposed

exposure limits for bio-persistent granular nanoparticles are 2 × 107 particles/m^3.Nickel, cadmium-containing QDs, chromium VI, beryllium, arsenic, and zinc chromate are examples ofCMARNanomaterials. The proposed work exposure limits from CMAR nanoparticles are 2 × 107 - 4 × 107 particles/m^3.

2.3 Synthesis Methods of Nanoparticles

Metal nanoparticles can be produced using green, chemical and physical methods. To obtain nanoparticles, especially copper nanoparticles, three elements are needed. First, a precursor that provides copper ions. Second, to obtain copper atoms are reducing agent is required to supply electrons. Given the correct temperature and pH conditions, the third component, the surfactant, aggregates the copper atoms resultingfrom the reducing agent into copper nanoparticles.Nanoparticles are synthesized by using a variety of methods, which are classified into two main categories: bottom-up and top-down methods, as shown in Figure 2.5

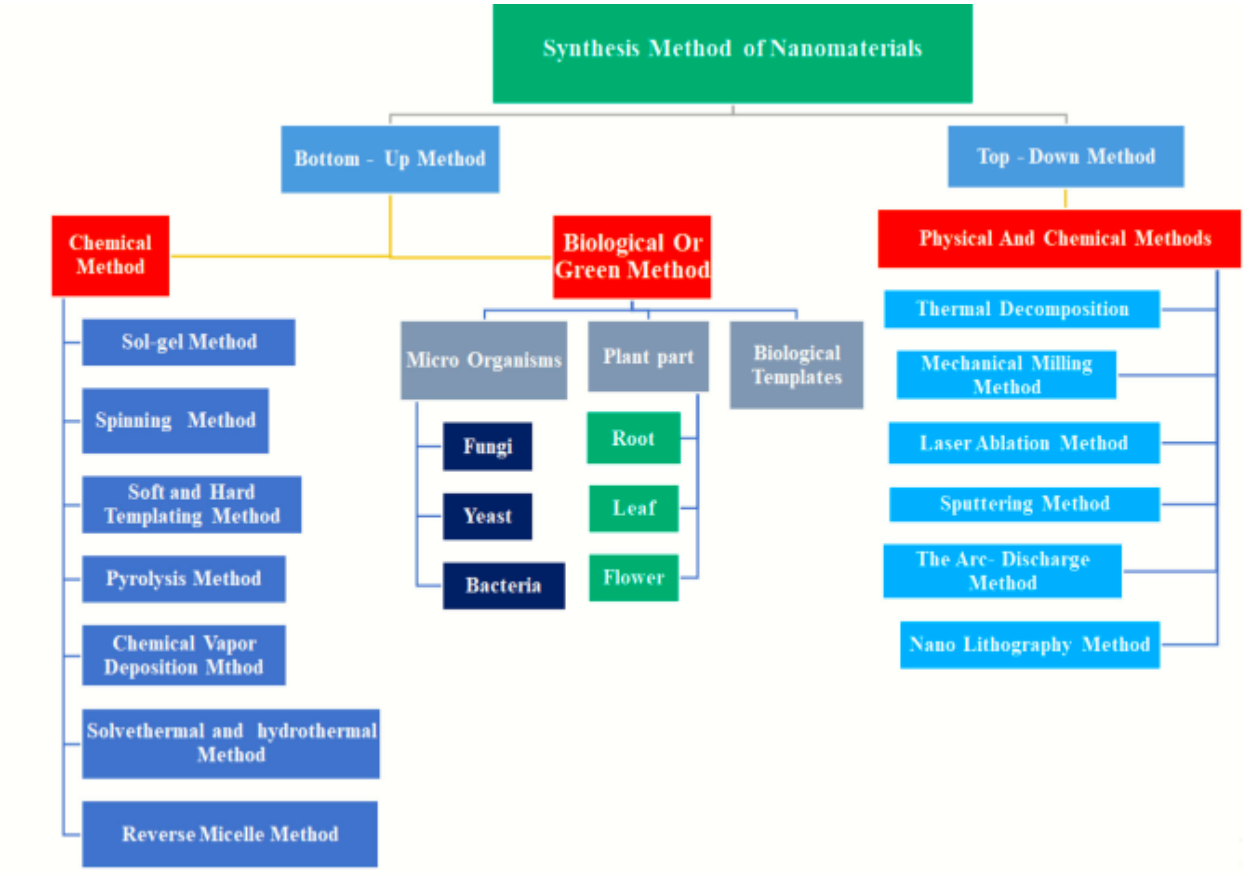

Figure 2.5: Different nanoparticle synthesis methods of nanomaterials.[43]

2.3.1 Top-down or Destructive Method

The top-down method decomposes bulk materials into smaller materials and finally changesthem into nanoparticles. The basic known top-down synthesis methods of nanoparticles are mechanical milling or ball milling nanolithography, laser ablation, thermal decomposition, sputtering, and, arc discharge methods.[50]

a) Mechanical milling method: This method is used in the production of oxide- and carbide-strengthenedaluminium alloys, wear-resistant spray coatings, aluminium or nickel or magnesium or copper-based nanoalloys, and a variety of other nanocomposite materials.

b) Nanolithography method: This synthesis technique is the process of printing a required shape or structure on a light-sensitive material and selectively removing a portion of the material to create the desired shape and structure. It is used for creating nanoarchitectures with a concentrated electron or light beam. Its purpose is to create a cluster with the required shape and size but requires complex tools and related costs or expenditures.

c) Laser Ablation method: This synthesis method produces nanoparticles by striking the target material with a powerful laser beam. Metal atoms vaporize in laser ablation and are immediately solvated by surfactant molecules to form nanoparticles in the solution.

d) Sputtering method: Sputtering is the phenomenon of nanoparticle deposition using ejected particles colliding with ions. Sputtering is the method of deposition of a thin layer of nanomaterials followed by annealing.

e) Thermal decomposition method: This method is endothermic. The chemical bonds are broken and changed into smaller ones by heat. The metal is broken down at specific temperatures to produce the nanoparticles.

f) The arc discharge method: This process is used to create different nanostructured materials. Fullerenes, carbon nano-horns, carbon nanotubes, few-layer graphene, and amorphous spherical carbon nanoparticles are some of the carbon-based materials produced by nanomaterials.

2.3.2 Bottom-up or Constructive Method

The bottom-up method involves the building of material from atoms to clusters to nanoparticles. The common bottom-up synthesis methods of NPs are sol-gel, spinning, chemical

vapor deposition, pyrolysis, solvothermal and hydrothermal, Soft and hard templating, reverse micelle, and Biosynthesis/biological methods.[51]

a) Sol-gel method: It is the method by which an appropriate chemical solution serves as a precursor. Metal oxide and chloride are common sol-gel method precursors.[45]

b) Spinning method: Spinning is a process carried out by a spinning disc reactor which comprises of a rotating disc contained within a chamber or reactor where physical parameters such as temperature can be controlled. It is determined by several factors, including disc surface, liquid/precursor ratio, disc rotation speed, liquid flow rate, and feed location. Magnetic nanoparticles were created using spinning disc processing.[52]

c) Chemical vapour deposition (CVD) method: CVD is the deposition of a thin film of gaseous reactants onto a substrate. When a heated substrate comes into contact with a combined gas, a chemical reaction occurs.This reaction forms a thin film of product on the substrate surface, which is recovered and reused. The disadvantages of CVD are the requirement of special equipment and the fact that the gaseous by-products are highly toxic.

d) Pyrolysis method: Pyrolysis is the most commonly used process in industries for the large-scale production of nanoparticles. It is simple, efficient, cost-effective and a continuous process with high yield.

e) Solvethermal and hydrothermal methods: This process produces nanostructured materials through a heterogeneous reaction carried out in an aqueous hydrothermal method and used in closed systems. Hydrothermal and solve thermal methods are useful for producing various nano geometries of materials such as nanowires,nanorods, nanosheets, and nanospheres.

f) Soft and hard templating methods: Soft and hard template methods are extensively used to synthesize nanoporous materials. The soft template method is a simple conventional method for the production and nano-porous materials are produced using plenty of soft templates, such as block copolymers, flexible organic molecules, and anionic, cationic, and non-ionic surfactants.

g) Reverse micelle method: This process is useful for the synthesis nanomaterials with the desired shapes and sizes. It is formed in a water-in-oil emulsion.

h) Biosynthesis/biological method: It is an environmentally friendly and green approach to the formation of non-toxic and biological nanoparticles. Green synthesis nanoparticles have distinct and enhanced properties that make them suitable for biomedical applications. Microorganisms, biological templates, and various plant parts are used in the biosynthesis of nanoparticles. It includes the biosynthesis method using microorganisms, the biosynthesis method using biological templates, and the biosynthesis method using different plant parts.[53]

2.4 Characterizations Methods of Nanoparticles

Different methods are used for the analysis and characterization of the properties of NPs. The physicochemical properties and features that can be resolved by each characterization methods are the morphological and topographical, structural and chemical, optical, electronic and electrical, magnetic, thermal, and mechanical characterizations.

2.4.1Morphologicaland Topographical Characterization

The morphological and topographical features of NPs include the size, shape, dispersity, localization, agglomeration/aggregation, surface morphology, surface area, and porosity of the NPs. The methods which are used for the characterization of morphological and topographical features of NPs are Scanning electron microscopy (SEM), scanning tunneling microscopy (STM), transmission electron microscopy (TEM), Dynamic light scattering (DLS), Nanoparticle tracking analysis (NTA), Brunauer–Emmett–Teller (BET), and Barrett–Joyner–Halenda (BJH) methods. The SEM, STM, and TEM methods are frequently used for the analysis of morphological and topographical features of NPs such as size, shape, and surface.

a) Scanning electron microscopy (SEM): In SEM, an electron gun is used to produce a beam of electrons that is controlled by a set of lenses to follow a vertical path through the microscope until it hits the samples. Once the sample is hit by the beam, electrons and X-rays are ejected from the sample. Detectors are then used to collect the X-rays and scattered electrons to create a 3D image of the sample. SEM provides different information about the NPs such as size, shape, aggregation, and dispersion. [54]

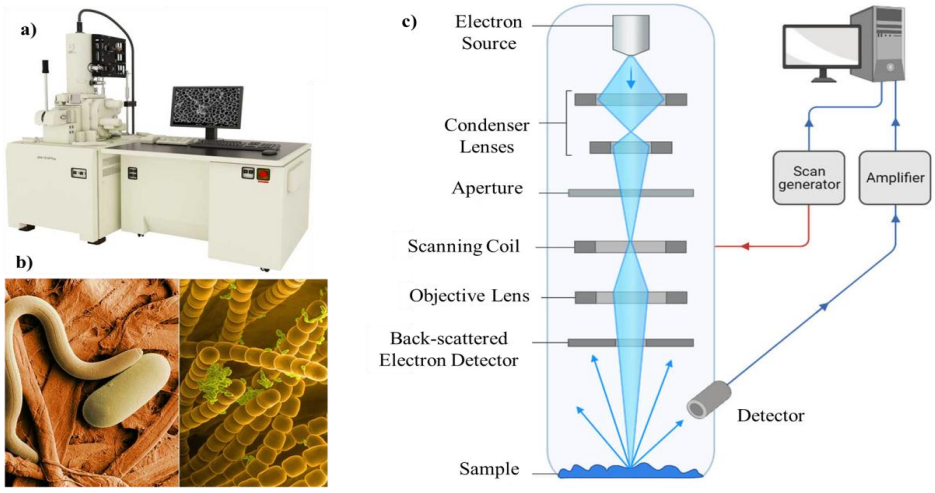

Figure 2.6: Scanning Electron Microscopy; device (a), image (b), working principle (c).[55]

b) Transmission electron microscopy (TEM): TEM provides information about the size, shape, localization, disparity, and aggregation of NPs in two-dimensional images. TEM employs an electromagnetic lens that focuses a very fine beam of electrons into an ultrathin section of the sample. This beam passes through the specimen where the electrons either scatter or penetrate the sample and hit a fluorescent screen at the bottom of the microscope. The difference in electron densities is used for the contrast to create an image of the specimen. TEM can be also used for the characterization of NP crystal structure through the use of selected area electron diffraction (SAED), where the electron beam is focused on a selected area in the sample, and the scattered electrons are used to obtain a diffraction pattern.

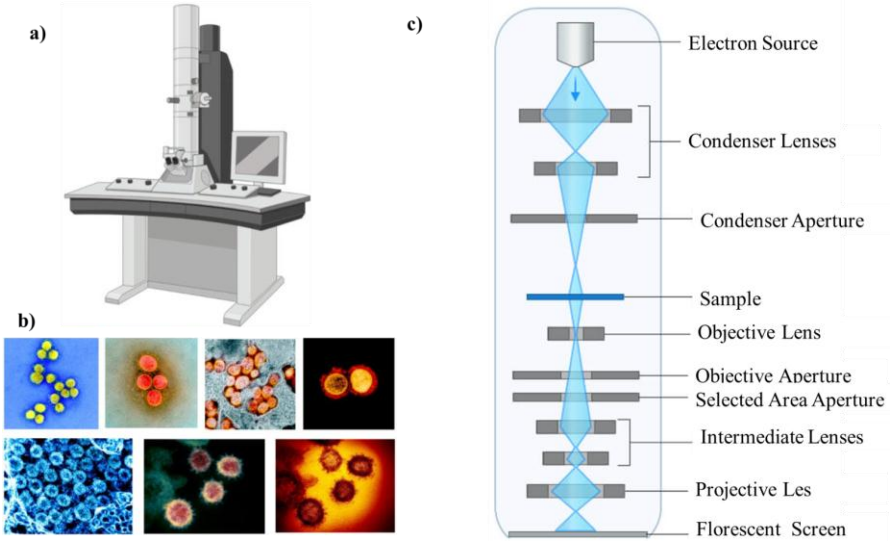

Figure 2.7: Transmission Electron Microscopy; device (a), image (b), working principle (c).[56]

c) Scanning tunneling microscopy (STM): STM is based on the phenomenon of quantum tunneling, where a metallic tip is brought very close to the sample surface and used to apply voltage. When voltage is applied, electrons from the sample surface are extracted creating an electrical current that is used to reconstruct an image of the surface with atomic resolution.[57]STM is mainly used to characterize the topography of NPs.[58]TEM was used for the characterization of Ag NPs produced by *Arbutus unedo*leaf extract.The NPs have a spherical morphology with a uniform size of 30 nm. The NPs were found to agglomerate into small aggregates, each including 5–6 NPs. At the same time, the SAED approach was used to determine the crystal structure of the NPs. The majority of the NPs were found to be single crystalline cubic materials.[59] For the characterization of Ag NPs produced by *Diospyros kaki*leaf extract, SEM helped to show that the NPs were also spherical and the size was 32 nm with some deviations.[60] STM is less frequently used for the characterization of biogenic NPs.[61]

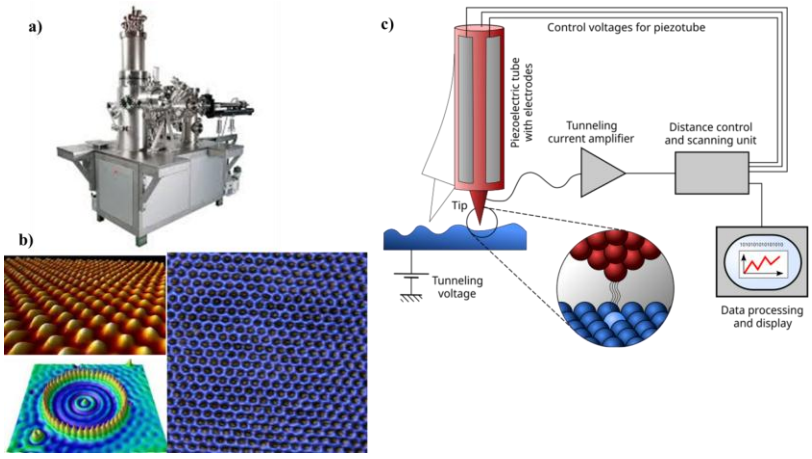

Figure 2.8: Scanning Tunneling Microscopy; device (a), image (b), working principle (c).[62]

d) Dynamic light scattering (DLS): The DLS technique is used for the analysis of NPs size and size distribution which involves the measurement of light interference based on the Brownian motion of NPs in suspension.[63] The size distribution range of NPs is shown as the polydispersity index, which is the output of an autocorrelation function.The polydispersity index values lies between 0 and 1, where 0 represents a completely homogenous population and 1 represents a highly heterogeneous population. DLS also allows the analysis of non-spherical NPs. DLS was used to measure the size and the size distribution profile of a wide range of biogenic NPs. The average size of Ag NPs produced by *Trichodermakoningii*fungi was found to

be around 25 nm and the size distribution profile was between 14 and 34 nm. The polydispersity index for those NPs was 0.681, which indicates that they are polydisperse.[64]The average size of Ag NPs produced by potato (*Solanumtuberosum*) was found to be around 10–12 nm with a wider distribution profile between 3–65 nm.[65]

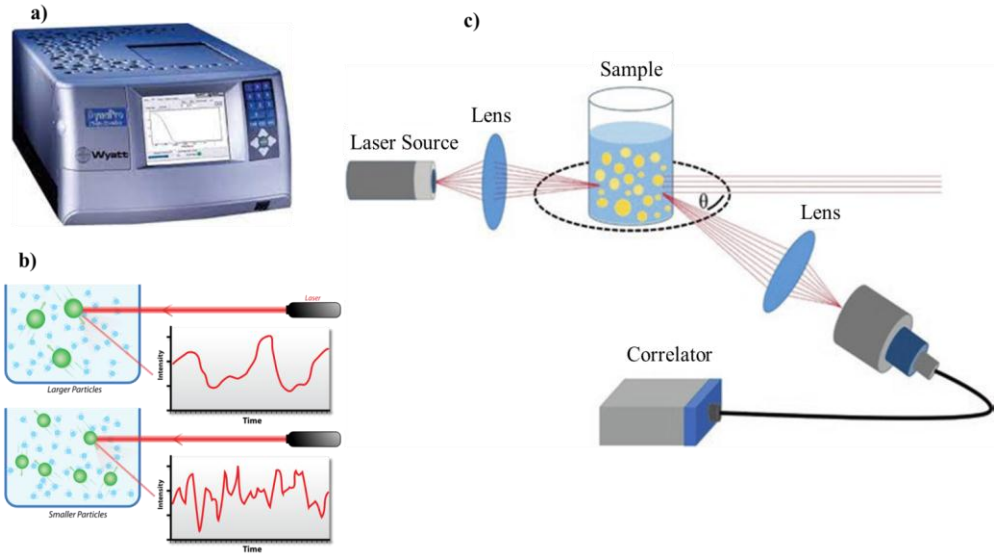

Figure 2.9: Dynamic light scattering; device (a), image (b), working principle (c).[66]

e) Nanoparticle tracking analysis (NTA):NTAmethod is used for the analysis of NP size in suspensions based on their Brownian motion. Like in DLS, the rate of NP movement is correlated with their size, allowing the measurement of size distribution profiles for NPs with 10–100 nm diameters. Its advantage over DLS is that NP motion is analyzed by video. Individual positional changes of NPs are tracked in two dimensions, which are used to determine NP diffusion rates, and by knowing the diffusion coefficient, the hydrodynamic diameter of the particles can be calculated. In DLS, individual NPs are not visualized, but instead, the time-dependent intensity fluctuations caused by Brownian motion are used to calculate the polydispersity index.[67] NTA was found to be more precise for sizing mono disperse as well as poly disperse organic NPs compared to DLS.[68]NTA was used to measure the size and dispersity of Ag NPs produced by *Camellia sinensis*(green tea) powder, the NPs were found to be well dispersed in an aqueous medium with an average size of 45±12 nm.[69]

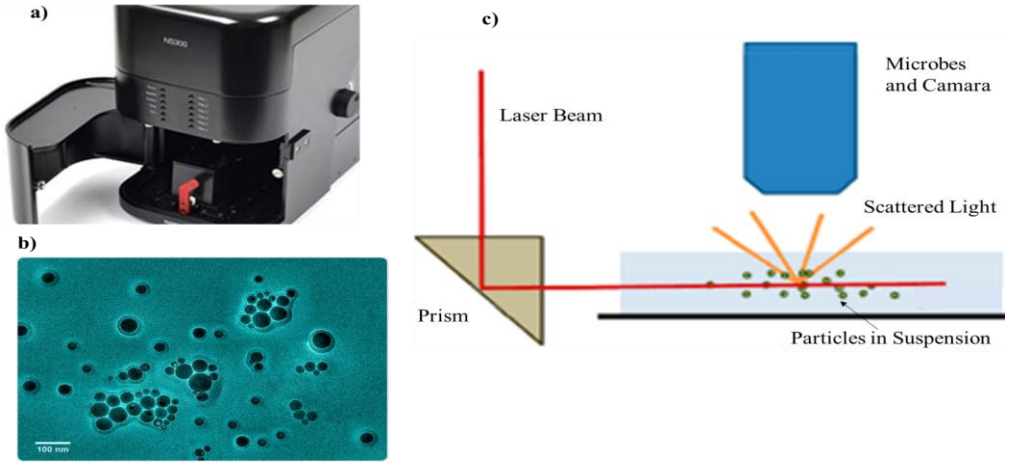

Figure 2.10: Nanoparticle tracking analysis; device (a), image (b), working principle (c).[70]

f) Brunauer–Emmett–Teller (BET) method: BET is considered one of the best methods for the analysis of NP surface area. BET method was employed to measure the surface area of CeO_2 NPs produced by *Eucalyp-tusglobulus*leaf extract. The surface area was found to be 40.96 m^2/g of biogenic CeO2 NPs, much higher than the commercial CeO2 NPs (8.5m^2/g).[71] BET was also used to measure the surface area of SiO2 NPs produced by rice husk, CuO NPs produced by *Leucaenaleucocephala*leaf extract, and Ag NPs produced by *Acan-thospermumhispidum*leaf extract. The surface area was 7.15m2/g, 47.54 m^2/g, and 9.91 m^2/g, respectively.[72]This method is used for the determination of porosity.

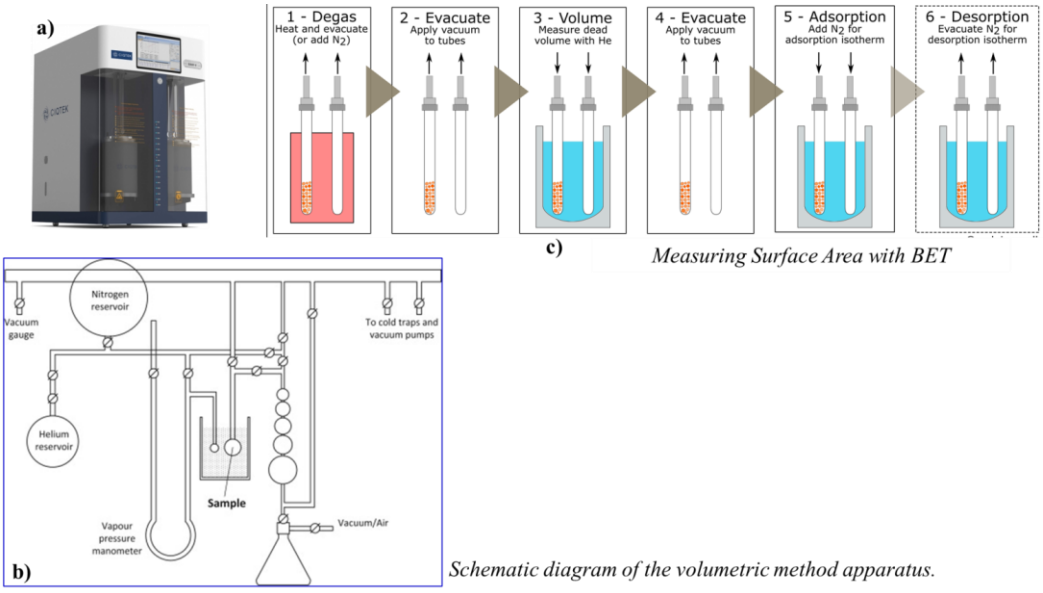

Figure 2.11: Brunauer–Emmett–Teller (BET); device (a), image (b), working principle (c).[73]

g) Barrett–Joyner–Halenda (BJH) method: The BJH method was employed to study the pore size of a wide range of biogenic NPs. The pore size of CeO2 NPs produced by *Eucalyptus globulus*leaf extract was found to be 7.8 nm, the pore size of CuO NPs produced by *Leucaenaleucocephala*leaf extract was 2.13 nm,the pore size of SiO2 NPsproduced by rice husk and Ag NPs produced by *Acan-thospermumhispidum*leaf extract was much larger,being 29.63 nm and 36.34 nm, respectively.[74]

2.4.2 Structural and Chemical Characterization

The structural and chemical features of NPs include composition, phase, crystallinity, functionalization, chemical state (oxidation), surface charge, polarity, bonding, and electrochemical properties. The methods which are used for the characterization of *Structural and chemical properties of* NPs are X-ray diffraction analysis (XRD) Energy-dispersive X-ray spectroscopy (EDX), High-angle annular dark-field imaging (HAADF) X-ray photoelectron spectroscopy (XPS),Cyclic voltammetry (CV),Fourier-transforms infrared spectroscopy (FTIR),andZeta potential analysis methods.

a) X-ray diffraction (XRD): The XRD technique is based on irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material.[75] It is used for the analysis of NP phase and crystallinity. The resolution and accuracy of XRD can be affected in cases where the samples have highly amorphous characteristics with varied inter atomic distances or when the NPs are smaller than several hundreds of atoms.For the characterization of biogenic Ag NPs, the XRD results of Ag NPs produced by *Tricho-derma koningii*,*Solanumtuberosum*, and *Acanthospermumhispidum*leaf extract displayed characteristic peaks occurring at roughly $2\theta=38^{o}$, 44°,and 64^{o} corresponding to (111), (200), and (220) planes, respectively. These results are in good agreement with the reference to the face-centered cubic structure of crystalline silver. The XRD results of Ag NP sproduced by *Solanumtuberosum*were not as clear as the other biogenic Ag NPs and had several impurities.[76]

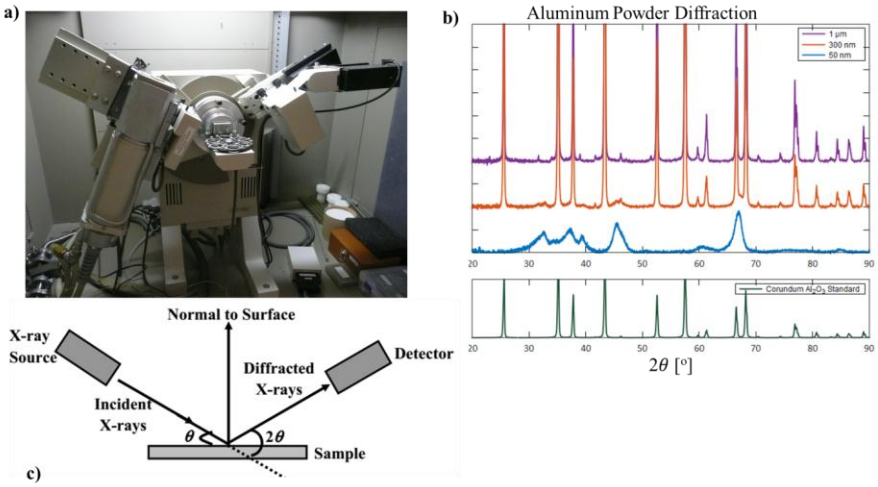

Figure 2.12: X-ray diffraction analysis; device (a), image (b), working principle (c).[77]

b) Energy-dispersive X-ray spectroscopy (EDX): EDX technique is based on the irradiation of the sample with an electron beam. Electrons of the electron beam when incident on the sample surface eject inner shell electrons; the transition of outer shell electrons to fill up the vacancy in the inner shell produces X-rays. Each element produces a characteristic X-ray emission pattern due to its unique atomic structure, and therefore can be used to perform chemical compositional analysis.[78] The shortfall of EDX is that the resulting spectra give only qualitative compositional information. This technique does not require sophisticated additional infrastructures; usually, it is a small device that is connected to an existing SEM or TEM. This allows the use of SEM or TEM for the morphological characterization and EDX is used simultaneously for the analysis of chemical composition.[79]

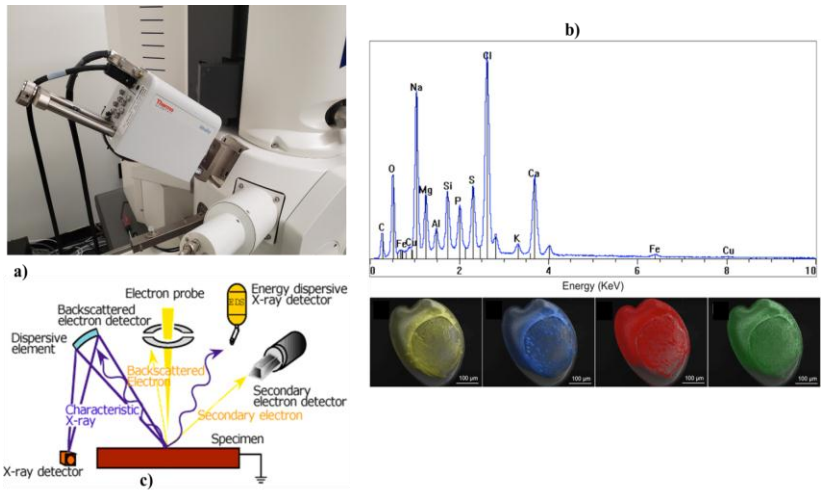

Figure 2.13: Energy dispersive X ray spectroscopy; device (a), image (b), working principle (c)[80]

c) High-angle annular dark-field imaging (HAADF): HAADF method is used for the elemental mapping of a sample using a scanning transmission electron microscope (STEM). The images are formed by the collection of incoherently scattering electrons with an annular dark-field detector.[81]This method is used for elemental composition analysis usually when the NPs of interest consist of relatively heavy elements. The contrast of the images is strongly correlated with atomic number and specimen thickness. [82]The employment of this approach in the characterization of Cu NPs produced by *Shewanellaoneidensis*revealed that Cu NPs remained stable against oxidization under anaerobic conditions, but when they were exposed to air a thin shell of Cu2Odeveloped around the NPs.[83]

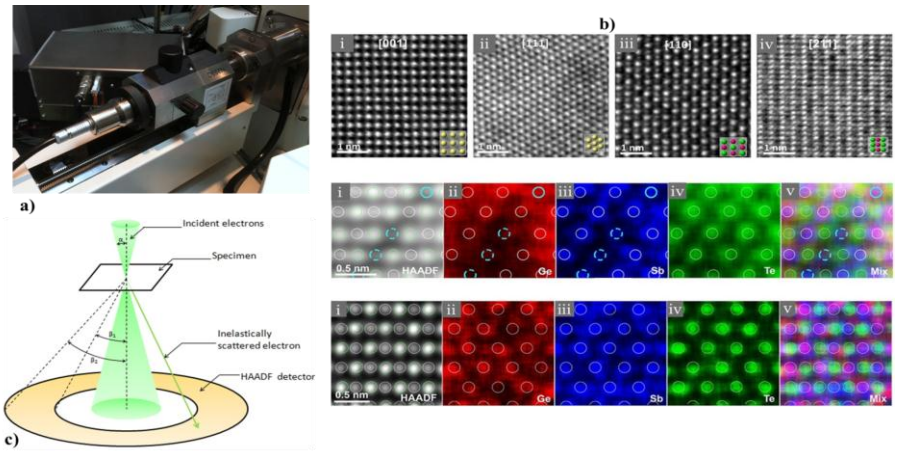

Figure 2.14: Energy dispersive X-ray spectroscopy; device (a), image (b), working principle(c)[84]

d) X-ray photoelectron spectroscopy (XPS): TheXPStechnique is considered as the most sensitive approach for the determination of NP exact elemental ratios, chemical state, and exact bonding nature of NP materials. XPS is based on the photoelectric effect that can identify the elements within a material, or covering a material, as well as their chemical state with high precision. XPS can also be used to provide in-depth information on electron transfer.XPS was used for measuring the purity of Au NPs produced by cumin seed powder.[85] XPS was used for the determination of the oxidation states of Ag NPs produced by *Rosa canina*. The two oxidation states for Ag NPs (Ag (0) and Ag (I)). In both cases, the zero-oxidation state was the abundant one, the presence of a small amount of the other oxidation states suggests that some of the NPs were oxidized or had unreduced species. XPS was used for the determination of the exact elemental ratios and the bonding nature of NPs.[86]

e) Fourier transforms infrared spectroscopy (FTIR): TheFTIR technique is based on irradiating a material with infrared light, where the absorbed or transmitted radiation is recorded. The resulting spectrum represents a unique fingerprint of samples, and it provides the nature of the sample such as the bonds involved, polarity, and oxidation state of the sample.[87] FTIR is mainly used for the characterization of organic materials such as the surface chemical composition or functionalization of NPs. It is also used for the identification of contaminants when high purity is sought.[88] For biogenic NPs, FTIR is usually used for the identification of probable functional groups present on the surface of NPs that are responsible for the reduction and stabilization of the NPs. For plant-mediated NP synthesis, for instance for Ag NPs produced by *Camel-liasinensis*, the FTIR results indicate the presence of *Camellia sinensis*phyto compounds, such as caffeine and catechin, on the surface of Ag NPs that could be responsible for the reduction of Ag or act as stabilizing agents.[69] For microbe-mediated NP synthesis, FTIR results show the presence of protein residues on the surface of NPs confirming the involvement of different proteins in the reduction/stabilization process, such as in Ag NPs produced by *Streptomyces sp.* NH28.[89]

f) Zeta potential analysis Method: Zeta potential measurements are used for the determination of NP surface charge in colloidal solutions. The surface charge of NPs attracts counter-ions that form a thin layer on the surface of the NPs (called the Stern layer). This layer travels with the NPs as they diffuse through the solution. The electric potential at the boundary of this layer is known as NP zeta potential.The instruments used to measure this potential are called zeta potential analyzers. [90] Zeta potential values are indicative for NP stability, where higher absolute values of zeta potential indicate more stable NPs.[58]The zeta potential is a good indicator of the stability of NPs, where NPs with zeta potentials of more than 30 mV or less than - 30 mV are considered stable. Zeta potentials have been measured for a wide range of biogenic NPs. The zeta potential for Ag NPs produced by *Ziziphusjujuba*leaf extract of - 26.4 mV.[91] Ag NPs produced by other organisms have different zeta potential values, for example, Ag NPs produced by *Punicagra-natum*peel extract have a zeta potential of - 40.6 mV indicating their higher stability,[92] while Ag NPs produced by *Aspergillustubingensis*have a zeta potentialof+8.48 indicating their relative instability. [93]The pH of the sample is another important parameter for zeta potential values, the higher the pH the lower the zeta potential value.[94]

g) Cyclic voltammetry (CV): CV is an electrochemical technique for measuring the current response of redox-activesolutions to a linearly cycled potential sweep between two or more set values. It is used for determining information about the reduction potential of materials, the kinetics of electron transfer reactions, and the thermodynamics of redox processes.[95]It can be employed for two different purposes in the context of biogenic NP characterization. Firstly, CV can be used for measuring the stability of NPs in electrocatalysis. For this purpose, the biogenic NPs are assembled on an electrode of the electrolysis cell and are tested for their electro catalytic behavior against a redox reaction over different cycles. As an example, Ag NPs produced by *Citrus sinensis*were found to be stable in phenolic compound redox reactions over multiple cycles.[96]Secondly, CV can be used for monitoring the progress of reduction of metallic NPs or for the determination of the reducing agent involved in the reduction.[97]

2.4.3 Characterization of optical, electronic, and electrical properties

The optical, electronic, and electrical features of NPs include absorption, reflectance, fluorescence, luminescence, electronic state, band gap, photo activity, and electrical conductance properties of NPs. The methods that are used for the characterization of optical properties of NPs are Raman spectroscopy, Ultraviolet-visible spectroscopy (UV–vis),photoluminescence spectroscopy (PL), and UV–vis diffuse reflectance spectroscopy (DRS).

a) Raman spectroscopy: This technique is based on irradiating a sample with monochromatic light emitted by a laser, in which the interactions between the laser light and molecular vibrations (photons and phonons) are recorded. It records the elastically scattered photons, known as Raman scattering (named after the Indian physician C. V. Raman).[98]The output Raman spectroscopy is a unique fingerprint for each sample. It is used to characterize the chemical and intermolecular bonding of the sample. It can also be used to characterize the crystallographic orientation of the sample and it is used for the characterization of optical properties nanoparticles.[99]Raman spectroscopy was used to characterize Fe3O4 NPs produced by *Pisumsativum*peel; the researchers found that the NPs were Fe3O4 NPs with a face-centered cubic phase which was in agreement with their XRD measurements. [100]Surface-enhanced Raman spectroscopy (SERS) provides a more sensitive, specific, and selective technique for identifying molecular structures.[101] It is also used for the characterization of the optical

properties of NPs, where the recorded photons and phonons are used to understand the plasmonic resonance of NPs.The SERS technique was used to study Au NP surface-associated bimoleculartо narrow down the list of bimolecular involved in the bio-production process. The researchers found that several bimolecular such as, glutathione, β-carotene, chlorophyll, and hydroxyquinoline were associated with Au NPs surface, thus, ruling out other molecules such as, glutaraldehyde fixing agent, saccharides, lipids, and DNA from the list.[102]

b) Ultraviolet–visible spectroscopy (UVS) and photoluminescence spectroscopy (PL): In absorption spectroscopy such as UV–vis, the transition of electrons from the ground state to an excited state is measured, while in photoluminescence spectroscopy, the transition of electrons from the excited state to the ground state is measured. [103]UV– vis spectroscopy uses visible and UV light to measure the absorption or reflectance of a sample. In photoluminescence spectroscopy, usually UV light is used to excite the electron and then measure the luminescence or fluorescence properties of a sample. UV–vis spectroscopy is used for the characterization of the optical properties of NPs. For instance, for the characterization of the optical properties of Ag NPs produced by*Trichodermaviride*, the UV–vis spectrum showed that a Ag surface Plasmon band occurs at 405 nm, which is a characteristic band for Ag NPs. The intensity of this band over the reaction time increased as a result of increasing Ag NP concentration in the solution. The photoluminescence properties of these NPs were recorded, with an emission in the range between 320–520 nm, which falls in the blue-orange region.[104] For biogenic Cu NPs, the common absorption peaks are located between 530–590 nm. The difference in NP size and the bio-active molecules used for the reduction process is believed to be the reasons behind the differences in the absorption peaks.[105] For instance, 15 nm spherical Cu NPs produced by *Calotropisprocera*have an absorption peak of 570 nm,[106] while 76 nm spherical Cu NPs produced by *Durantaerecta*have an absorption peak of 588 nm. [107]The same applies to photoluminescence effects, where 27 nm spherical Cu NPs produced by *Tilia*extract emit light of 563 nm (dark brown),[108] while 19 nm spherical Cu NPs emit light of 430 nm (green).[109]

c) UV–vis diffuse reflectance spectroscopy (DRS):DRSuse UV and visible light to measure the diffuse reflectance of material (the reflection of light in manyangles, as opposed to specular reflection). The resultingdiffuse reflectance spectra are used to determine the electronic state of a sample, which is then used to calculatethe band gap.Bandgap determination

is crucial for determining conductance and photocatalytic properties especially for semiconductor NPs.[110]

The DRS technique was used to calculate thebandgap for a wide range of biogenic NPs. For instance,TiO2 NPs produced by *Andrographispaniculate*exhibitanoptical energy bandgap of 3.27 eV.[111]Interestingly, biogenic ZnO NPs produced by different organism showdifferent bandgaps, for example, ZnO NPs produced by *Pseudomonasputida*have a bandgap of 4 eV[112]whileZnO NPs produced by *Calotropisprocera*leaf extracthave a bandgap of 3.1 eV.[113]

2.4.4 Characterization of magnetic properties

The magnetic features of NPs include magnetization, Ramanan magnetization coercivity, magnetic field intensity, magnetic force, and magnetic susceptibility. The magnetic properties of NPs are potentially giving NPs great advantages in catalysis, electronics, and medical applications. Several techniques were developed for the detection and quantification of small magnetic moments in NPs. The common ones are Magnetic force microscopy (MFM), Vibrating sample magnetometer (VSM), Superconducting quantum interference device (SQUID) magnetometer, and Electron spin resonance spectroscopy (ESR), and spectroscopic ellipsometry.

a) Magnetic force microscopy (MFM): MFMtechnique is a variety of atomic force microscopy (AFM), in which a magnetic tip is used to scan the sample. The magnetic tip is approached very close to the sample, where the magnetic interactions between the tip and the sample are recorded.[114] At closer distances to the sample (0–20 nm), other forces such as van der Waals forces also interact with the tip. Therefore, MFM measurements are often operated with two-pass scanning method. The tip is firstly used to measure the topography of the sample including the molecular forces as van der Waals. Afterwards, the tip is lifted and a second scan is operated following the same. The first scan is done very close to the surface to obtain the topography of the sample. Then, the tip is lifted and a second scan is performed following the topography outline obtained in the first scan topography outline. In the second scan, the short-ranged van der Waals forces disappear and the long-range magnetic forces are almost exclusively recorded. Researchers found that 22 nm was the optimal scanning height for the second scan, at which van derWaals forces are very weak while the distance is still small enough to measure the magnetic interactions for Pd-Fe bimetallic NPs.[115]In a different study, MFM was

used to characterize the magnetic properties and to estimate the size of the magnetic kernel of the magnetisms produced by the same strain, and it was determined that the NPs behaved like single mono domain nanomagnets.[116] The magnetic properties of NPs made from materials such as Pd that only exhibit significant magnetism on the nanoscale can also be studied by MFM, however, the magnetic moment of these NPs is much lower than for ferromagnetic NPs. The magnetic decoration of Pd NP samples with Fe2O3 NPs strongly enhances the weak magnetic signal of Pd NPs up to 15times.[117] This approach could make the MFM technique useful for the characterization of weak magneticNPs.

b) Vibrating sample magnetometry (VSM): VSM technique measures the magnetic properties of materials based on Faraday's law of induction. In VSM, the sample is placed in a constant magnetic field in a special holder that vibrates vertically. As the holder starts vibrating, the magnetic moment of the sample creates a magnetic field that changes as function of time. The alternating magnetic field created in the sample induces an electric current that is recorded and used to calculate the magnetic properties of the sample.VSM was used to compare the magnetic properties of iron oxide NPs produced *Moringaoleifera*with the magnetic properties of the same NPs but coated with chitosan. The researchers found that saturation magnetization, remnant magnetization, and coercively have lower values when the NPs are coated with chitosan.[118]

c) Superconducting quantum interference device (SQUID) magnetometer: SQUID technique measures the magnetic properties of materials based on the Josephson effect. Niobium or other metal alloys are used in the device which needs to be operated at temperatures very close to the absolute zero to main superconductivity, where liquid helium is used to maintain the cold environment.[119]However, other kinds of SQUID also exist where high-temperature superconductors are used. After reaching superconducting environments, the Josephson junctions contained in the device help to create a super current, which is recorded and used to calculate the magnetic properties of the sample [120] for the characterization of iron oxide NPs produced by *Cnidiummonnieri*seed extract, SQUID magnetometer revealed the saturation magnetization, remnant magnetization, a coercively, and a magnetic susceptibility at room temperatures, indicating the super paramagnetic behavior of these NPs. SQUID magnetometer was also used for the characterization of the magnetic properties of zinc incorporated magnetite

NPs produced by *Geobactersulfurreducens*, showing that the loading of only 5% zinc results in the enhancement of saturation magnetization of the NPs by more than 50%.[121]

d) Electron spin resonance spectroscopy (ESR): ESR technique measures the magnetic properties of materials by characterizing and quantifying the unpaired electrons in the sample when the sample is placed in strong magnetic field. The unpaired electrons can change their spins by absorbing or emitting photons, in ESR the sample is irradiated with microwave pulses to excite electron spins until a resonance state is reached.[122] It can be used to measure the ferromagnetic and anti-ferromagnetic properties of NPs. ESR was used to characterize the magnetic properties of iron oxide NPs produced by *Ficuscarica*.The trees naturally produce iron oxide NPs as a defense mechanism when they are subjected to stress. The researchers found that the magnetic properties of iron oxide NPs produced by the same tree but grown in different environmental conditions have different magnetic properties. In addition, the magnetic anisotropy of the signal was visible as the magnetic properties of these NPs varied strongly at different temperatures.[123] ESR was also used to characterize the magnetic properties of Se nanomaterials produced by anaerobic granular sludge.The ESR results revealed the presence of Fe (III) atoms incorporated in the Se nanomaterial, which enhanced their overall magnetic properties, giving it ferro-magnetic behaviour.

e) Spectroscopic ellipsometry:This technique is based on irradiating a sample with polarized light to measures changes in polarization. It is widely used to calculate the optical constants of a material (refractive index and extinction coefficient).[124] This technique is also used to characterize the electrical conductivity and dielectric properties of materials.[125]Spectroscopic ellipsometry is not a common technique for the characterization of biogenic NPs. For chemically produced NPs, the optical properties for different-sized Au NPs partially embedded in glass substrate were measured by spectroscopic ellipsometry. In this example, a clear transition from LSPR to SPR mode was found as the thickness increases. The partially embedded Au NPs had much higher refractive index sensitivity compared to Au NPs fully immobilized in a glass substrate.[126] Spectroscopic ellipsometry was also used to measure the changes in the optical constants of a layer of 5 nm ZnO NPs induced by UV illumination.It was found that the UV illumination of ZnO NPs in inert atmospheres resulted in a clear blue shift in the absorption. The UV illumination of ZnO NPs results in the desorption of O_2 from the NPs surface leading to the population of the lowest levels in conduction band with mobile electrons. This phenomenon is

reversible, in which the exposure to O_2 from air results in the scavenging of these mobile electrons.[127]

2.4.5 Characterization of Thermal Properties

Thethermal features of NPs include melting points, crystallization and structural-phase transition points, heat capacity, thermal conductivity, and thermal and oxidative stability. Several techniques can be used for the characterization of the thermal features of NPs. The common ones are Differential scanning calorimetry (DSC), Differential thermal analysis (DTA), Thermogravimetric analysis (TGA), and Transient hot wire (THW) methods.

a) Differential scanning calorimetry (DSC):DSC technique is widely used to measure melting points, crystallization points, structural-phase transitionpoints, latent heat capacity, heat of fusion, and oxidative stability. For the characterization of Ag NPs produced by Rhodomyrtustomentose leaf extract, DSC showed three exothermic peaks at 44°***c***, 159***c***°, 243°***c***, and an endothermic peak at 441 °C. The first peak (at 44 °C) indicates that this temperature the NPs face a gradual loss of water from their surface. The second peak (at 159 °C) shows that the thermal decomposition of the sample happens at this temperature. The last temperature (441 °C) indicates the melting temperature for those NPs. [128] For Ag NPs produced by Partheniumhysterophorus leaf extract, DSC showed that their melting temperature was at 750 °C. The researchers also found that these NPs had completely thermally decomposed and crystallized simultaneously.

b) Differential thermal analysis (DTA):DTA technique is based on heating or cooling a sample and an inert reference under identical conditions, where any temperature difference between the sample and the reference is recorded. DTA is primarily used for the study of phase diagrams and transition temperatures. DTA is also used to measure the melting points, thermal, and oxidative stability.[129]

c) Thermogravimetric analysis (TGA):TGA technique measures the change in the mass of a sample as a function of temperature and/or time in a controlled atmosphere. TGA technique is mainly used to study the thermal stability of materials, and it is used to measure structural-phase transition points, thermal activation energies, and oxidative stability. The resulting thermo gram is unique for each compound and therefore can also be used for the determination of

material composition.[130] TGA and DTA are usually combined in the same thermal analyzing instrument, called thermogravimetry/differential thermal analysis (TG/DTA). TG/DTA is a common technique for the characterization of thermal properties of biogenic NPs. For instance, the thermal properties of Ag NPs produced by Daphne mucronate leaf extract were studied in the range between 0–1000 °C where the sample was heated at rate of 10 °C/min. The researchers found that between400–500 °C the NPs faced a dominant weight loss, while the weight loss below 400 °C and above 500 °C was negligible and showed an intense exothermic peak in the range between 400–500 °C, this indicates that the crystallization of NPs happens in this temperature interval.[131]

d) Transient hot wire method (THW):THW method is used for the determination of thermal conductivity based on increasing the temperature of a material by a thin hot wire as a function of time, where the heating wire is located directly in the test sample. The advantage of THW method over other thermal conductivity measurement methods is the very short measuring time; this gives high accuracy of thermal conductivity due to the negligible values of convection in such short times.[132] THW methods, the NPs are added to a solution (usually water or ethylene glycol) forming a colloidal dispersion called a nanofluid. Then thermal conductivity of the nanofluid is measured and compared to the thermal conductivity of the base fluid, giving a thermal conductivity ratio which is used to evaluate the thermal conductivity of different NPs. The thermal conductivity ratios of three different concentrations (0.12, 0.18, and 0.24%) of biogenic SnO_2 NPs produced by Punicagranatum seed extract were measured in ethylene glycol at 303 K. The researchers found a linear relationship between NPs concentration and the thermal conductivity. The thermal conductivity enhancement of nanofluid to base fluid was between 6 and 24%.[133]

2.4.6 Characterization of mechanical properties

The mechanical features of NPs include toughness, tensile and compressive strengths, elasticity, viscoelasticity, hardness,and stiffness. The known methods that can be used for the characterization of the mechanical properties of NPs are Tensometery Instrumented indentation testing, Dynamic mechanical analysis (DMA), and Dynamic mechanical analysis (DMA).

a) Tensometery: It is used to measure the elasticity (elastic modulus), tensile and compressive strengths (Young's modulus) of materials. The machine used for this method is

called a universal testing machine (UTM) or a tensometer.The sample is placed between grips and an extensometer, where changes in gauge length are recorded as a function of load.[134] Other mechanical changes in addition to the change in gauge length are also recorded in this machine, such as the elasticity. The mechanical properties of different biogenic NP-containing composites can be measured by this machine. For example, the mechanical properties of orthodontic elastic ligatures containing Ag NPs produced by *Heterothecainuloides*were studied by comparing the maximum strength, tension, and displacement of the composite with and without the biogenic NPs. The researchers found that maximum strength, tension, and displacement have improved after the addition of Ag NPs. Interestingly, the addition of biogenic Ag NPs produced by *Diospyros lotus* fruit extract to starch and polyvinyl alcohol hydro gel membranes resulted in an adverse effect. The researchers attributed this adverse effect to the possibility that the addition of Ag NPs could have resulted in blocking the cross linking between starch and polyvinyl alcohol, or to the possibility of the formation of break age points in the polymer matrix due to NPs agglomeration.[135]

b) Instrumented indentation testing: This method is used to characterize the hardness features of materials by using a well-defined hard indenter tip typically made of diamond. The indenter tip is used to make an indentation in the sample by placing incremental loads on the tip, after which the area of indentation in the sample is measured and used to calculate the hardness features.[136]The method is also called micro- or nano-indentation testing. This method was used to characterize the mechanical properties of calcite NPs produced by *Ophi-ocomawendtii*brittle star. The arm plates of this brittle star are covered by hundreds of nanoscale calcite lenses that focus light onto photoreceptor nerve bundles positioned beneath the brittle star. The researchers used the nanoindentation method to compare Young's modulus, hardness and fracture toughness of biogenic calcite with geo-calcite. The results showed that the biogenic calcite lenses have higher hardness and fracture toughness compared to geo-calcite (more than twofold). The mechanical properties of silica cells compared to other types of cells of Moso bamboo (*Phyllostachyspubescens*) were studied by instrumented indentation testing. The researchers found that the cell wall of silica cells display higher hardness and elastic recovery compared to fiber and epidermal cells, which is attributed to the presence of biogenicSiO2 NPs in the silica cells.[137]

c) Dynamic mechanical analysis (DMA): DMA method is used to study the mechanical properties of materials by measuring the strain of a material after applying a stress.DMA method helps to obtain three different values: storage modulus, loss modulus, and loss tangent. These values are important to give an overview about the stiffness and visco-elasticity behavior of materials.[138]The DMA method was used to characterize the mechanical properties of polymethyl methacrylate denture base polymer filled with Ag NPs produced by *Boesenbergia rotunda*. In this study frequency sweep test was used to determine the viscoelastic behavior of this nano composite where the temperature was constant at 37°C and the frequency was increasing from 0.5to 100 Hz in tension mode. The researchers found frequency dependence for storage modulus, loss modulus, and loss tangent for the nanocomposite with various Ag NPs loading concentrations. The frequency dependence of storage modulus, loss modulus, and loss tangent indicates the visco-elastic response of this polymer. The results showed that the storage modulus for the nanocomposite is much higher than the loss modulus over the range of frequencies, indicating the elastic dominance of the nanocomposite. The researchers found that storage and loss moduli increase with increasing Ag NPs loading concentrations, which is due to the interaction between polymethyl methacrylate and Ag NPs.[139]The behaviour of storge modulus and loss tangent was studied as a function of temperature for different cellulose nanocrystals loading concentrations. The results showed that the unloaded polymer behaves like an amorphous polymer, the storage modulus remains constant until the temperature reaches 25 °C then it starts to sharply decrease due to glass–rubber transition. A relaxation process was also evident for the unloaded polymer, where the loss tangent reaches its maximum at 35 °C then it starts to fall. The addition of cellulose nanocrystals to the polymer positively enhanced both effects. The dramatic drop of storage modulus at25 °C was less for the nanocomposite, where the drop for the polymer loaded with 15% cellulose nanocrystals was almost cancelled. Similar positive enhancement was found for loss tangent. These enhancements could be attributed to the mechanical coupling effect, in which the NPs connect and form stiff continuous network linked through hydrogen bonding.[140]

2.5 Properties of Nanoparticles

The properties of nanometer-scale materials differ significantly from those of atoms and bulk materials due to surface charge/interaction, crystallography, composition, surface area, and nanoscale size effects, which can be seen in the magnetic, optical, electrical, mechanical,

chemical, and physical properties ofnanomaterials.The purity and performance of the nanoparticles are determined by its chemical or elemental composition. Particle size is one of the most fundamental and important measurements for nanoparticle characterization. Electron microscopy is the most commonly used technique to measure the size and its distribution. The surface area-to-volume ratio of a nanoparticle has a significant impact on its performance and properties. The surface area is most commonly measured using Brunauer–Emmett–Teller (BET) analysis. A nanoparticle's interactions with a target are determined by either its surface charge or its overall charge. One of the most common applications for a zeta potentiometer is to measure the surface charges and dispersion stability of a substance in a solution.The scientific study of the arrangement of atoms and molecules within crystals and othermaterials is known as crystallography. Crystallography can be used to determine the structural organization of nanoparticles using powder x-ray diffraction, electron diffraction, or neutron diffraction. Nanomaterial's concentration is needed to quantify the number of nanomaterials dispersed throughout the gaseous phase in order to calculate the concentration of air or gas required for the operation. Generally, the common properties of nanoparticles are physical, magnetic, electrical, chemical,mechanical and optical properties.

2.5.1 Physical Properties of Nanoparticles

The melting point of a bulk material is not dependent on its size, but the melting point of nanomaterial depends on its size. Because as the particle size of the nanoparticles decreases, the melting point decreases due to the unbounded surface atoms. The total volume of a bulk material remains unchanged when it is subdivided into nanoscale materials, but the collective surface area increases. In comparison to bulk materials, this results in an increase in the surface-to volume ratio at the nanoscale. The surface molecules or atoms have a high surface energy and a proclivity to agglomerate.[141]The physical properties of elements can change at the nanoscale.

Figure 2.15: The colors of gold and silver nanomaterials are size-dependent, as are their effects on the coloring of stained glass.[142]

2.5.2 Magnetic Properties of Nanoparticles

The magnetic behavior of elements can change at the nanoscale because of the size of magnetic nanoparticles. The nano structuring of bulk magnetic materials alters the curves, resulting in soft or hard magnets with improved properties at the nanoscale. The size has the ability to increase coactivity and super-paramagnetic behavior at critical grain sizes. Nonmagnetic bulk materials can become magnetic at the nanoscale. Metallic and semiconductor NPs possess interesting linear absorption, photoluminescence emission, and nonlinear optical properties due to the quantum confinement and localized surface plasmon resonance (LSPR) effect.[143]

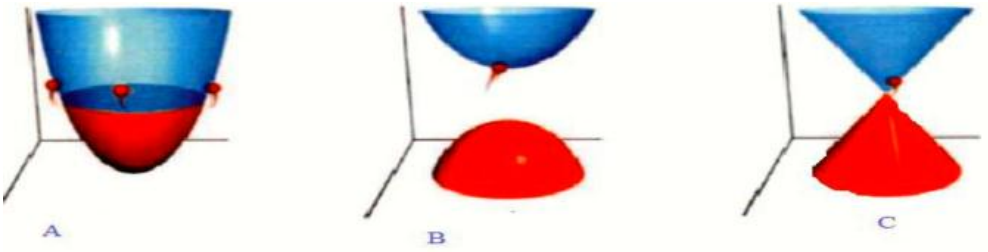

Figure 2.16: Electrical behavior of nanotubes: A, metal; B, semiconductor; C, graphite.[144]

2.5.3 Electrical Properties of Nanoparticles

Nanomaterials can increase conductivity in ceramics, but increase electric resistance in metal. Electron conduction is delocalized in bulk materials, which means electrons can move freely in all directions. When the scale is reduced to the nanoscale, the quantum effect takes over; electron delocalization occurs along the axis of nanotubes, nanorods, and nanowires. Due to electron confinement, the energy bands are replaced by discrete energy states, causing conducting materials to behave as either semiconductors or insulators. This result indicates that the metal is becoming a semiconductor. Carbon nanotubes, for example, can be either conductors or semiconductors depending on their nanostructure. To reduce the diameter of the wire, the number of electron wave modes contributing to electrical conductivity is reduced in well-defined quantized steps.

2.5.4 Chemical Properties of Nanoparticles

The applications of this substance are determined by its chemical properties, which include the reactivity of the nanoparticles with the target and their stability and sensitivity to elements such as moisture, environment, heat, and light. The flammability, corrosiveness, anti-

corrosiveness, oxidative potential, and reduction potential of the nanoparticles all play a role in determining their applications. Nanomaterials have significantly improved or novel catalytic properties such as reactivity, selectivity, and catalysts compared to their bulkanalogues.

2.5.5 Mechanical Properties Nanoparticles

Materials mechanical properties of the materials, such as elasticity, ductility, tensile strength, and flexibility, play an important role in their application. Influence on mechanical properties in nanomaterials, such as increased hardness, yield strength, elastic modulus, and toughness compared to bulk materials. The strength and hardness of nanostructured materials increase with decreasing grain size and grain boundary deformation.The increase in mechanical strength is simply due to a lower probability of defects and an increase in imperfection. It improved alloy hardness and toughness as well as ceramic superplasticity.

2.5.6 Optical Properties of Nanoparticles

Metallic and semiconductor nanoparticles possess interesting linear absorption, photoluminescence emission, and nonlinear optical properties due to the quantum confinement and localized surface plasmon resonance (LSPR) effect. The efficiency of system operation was determined by the optical properties of nanoparticles that depended on their structure, size, shape, and radiation wavelength. [145]LSPR phenomena arise when the incident photon frequency is constant with the collective excitation of the conductive electrons.[28]Due to this phenomenon, noble metal nanoparticles exhibit a strong size-dependent UV–visible extinction band that is not present in the spectra of bulk metals. Generally, the optical properties of nanoparticles depend on the size, shape, and the dielectric environment of the NPs. The collective excitations of conductive electrons in metals are called plasmons.[146] Depending on theboundary conditions, bulk plasmons, surface-propagating plasmons, and surface-localized plasmons are distinguished (Fig 18A–C). Because of their longitudinal nature, the bulk plasmons cannot be excited by visible light. The surface-propagating plasmons propagate along metal surfaces in a waveguide-like fashion.[147]

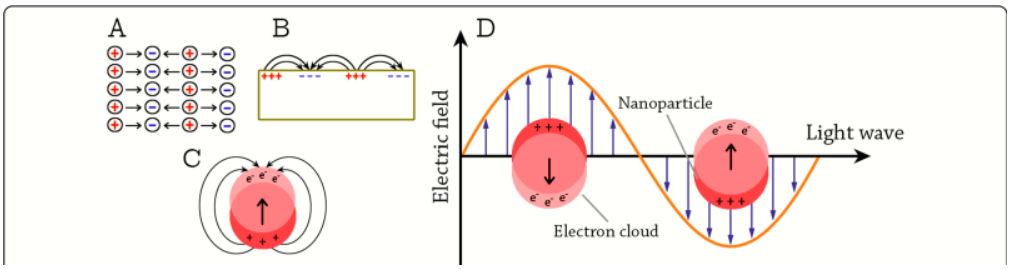

Figure 2.17: Graphical illustrations of The Types of Plasmon's. A Bulk; B surface Propagating; C Surface Plasmon's; And D Graphical Illustration of Local Surface Plasmon Resonance.[148]

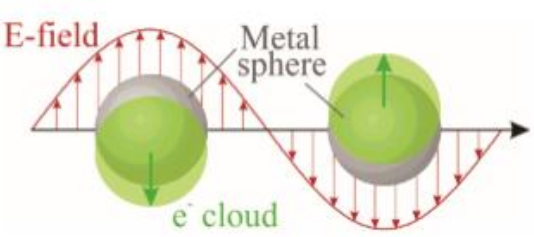

Figure 2.18: Schematic of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei.[148]

In the case of nanoparticles, when they are irradiated by visible light, the oscillating electric field causes the conductive electrons to oscillate coherently. When the electron cloud is displaced relative to the nuclei, a restoring force raises from Coulomb attraction between electrons and nuclei that result in oscillation of the electron cloud relative to the nuclear framework.[149]This creates uncompensated charges at the nanoparticle surface. As the main effect producing the restoring force is the polarization of the nanoparticle surface, these oscillations are called surface plasmons and have a well-defined resonance frequency.The significant differences in their optical properties based on the size of particles.Researchers found that the shape of the NPs also is critical for the optical properties, the plasmon resonance wavelength shifts to the red as the NPs become more oblate,Plasmon resonance strongly depend on NPs shape. With respect to the dielectric environment of the NPs, both the surrounding solvent and the support (substrate) were found to be critical for the optical properties. The Plasmon wavelength linearly depends on the refractive index of the solvent.

Localized surface plasmon resonance (LSPR) is an optical property of nanoparticles. Studies have shown that the line width is influenced by the size of nanoparticles. Due to their very small size, nanoparticles can lose their LSPR and becomephotoluminescent.[150]As a result of quantum confinement in nanomaterials, visible light emission can be tuned by varying the nanoscale dimensions. It has been discovered that as the size of the nanomaterials decreases, the

peak emission shifts toward shorter wavelengths. Matter can change color at the nanoscale; for example, gold nanospheres can turn to yellow at 100 nm, greenish yellow at 50 nm, and red at 25 nm, while silver can also turn orange at 200 nm, light blue at 90 nm, and blue at 40 nm spherical thin film length.The optical properties of nanoparticles are intensively investigated because they are widely used fortechnical applications. Their capability to interact intensively with light is used for amplification of stimulated Raman scattering and fluorescence. Metal (including copper) nanoparticles are widely used in nonlinear optics devices.[151]The noble metals nanoparticles of Cu, Au, and Ag have interesting optical properties due to their large cross-section. These noble metal nanoparticles express the unique absorption peak in the visible region known as the surface plasmon resonance (SPR) peak. This is because of mutual oscillations of the cloud of conduction electrons on metal nanoparticles. When the frequency of vibration matches that of the electromagnetic field, a huge amount of energy is shifted from the field to metal nanoparticles. The Ag and Au nanoparticles have been used for plasmonic applications due to their intense SPR peak and multipurpose performance such as biocompatibility etc.[152]Many researchers have effectively used Au and Ag nanoparticles and their alloy nanoparticles into the buffer layer of polymer solar cells to enhance their light-harvesting power. They improvement in photocurrent is reported due to the SPR and enhancement in backscattering. All these surveys have revealed an enhanced absorption of light and increased power conversion efficiency. But the high cost of Au and Ag nanoparticles hinders the development of a cost-effective photovoltaic device.[153]

The copper nanoparticles are interesting in point of view as copper is a non-expensive metal and is easily available also. The suitable and most commonly used technique for developing the outstanding optical properties of metals nanoparticles including copper nanoparticles is to integrate them in an appropriate matrix and will also prevent the oxidation probability of metal and stabilize them in the matrix.[154]

The opticalcharacteristics of copper nanoparticles are impressive due to the fact of a rare phenomenon of harmonicity of energy of SPR with inter-band shift, although for silver and gold nanoparticles, the plasmon response energy remains comparatively lower to the inter-band shift. The dependence of the inter-band shift edge on particle size is occurring mainly by the surface stress-induced alterations in lattice constant and correlated alterations in electronic band structure.[155]Shen et al.[156]have reported high-performance polymer solar cells improved by

merging of copper nanoparticles. They defined a drop in device resistance and enhancement of sharp current density and power conversion efficacy due to copper nanoparticles.

Another interesting feature to study is to have a control on the SPR wavelength of noble metal nanoparticles, for which one has to understand the basics of Mie scattering[157]and the parameters on which SPR wavelength is dependent. The position of SPR peak can be characterized by the Mie theory in the easiest case in which all particles are considered to be spherical and isolated to one another so that there is absolutely no particle-particle interaction term in the effective potential of the system. The parameters which can be played are the size/shape of nanoparticles, the dielectric constant of metal, and the matrix. The post-deposition techniques which can be used to alter these parameters are mainly thermal annealing and a thermal annealing by ion irradiation.

A widely applied thermal annealing is a method where the entire film is provided with high-temperature treatment in an inert atmosphere. An additional essential method is ion irradiation where the selective area of the thin film can be irradiated and altered consequently. Ion irradiation is not merely a substitute for heat treatment, but an improved method that produces a better control at the discharge of a particular species. The impact of ion irradiation is not only restricted to the composition changes but could also be involved to alter the atomic structure of specific phases. It was also reported that ion irradiation can represent the impacts on the atomic structure of applied pressure and vibration states. [158]The process of damage depends upon the energy and mass of ions. At high energies, electronic excitation causes changes by the electron-phonon coupling providing a thermal spike, although, at low energies, objective atoms are knocked off by their lattice sites introducing collision cascades. Although both nuclear energy and electronic energy losses are considerable, competitive processes may overshadow the mechanism of energy conversion. The modifications of structural, optical, and electrical properties of metal-fullerene nanocomposites caused by swift heavy ion irradiation and thermal annealing.[159]These studies were concentrated mainly on the dominance of electronic energy loss in the objective materials and the modification caused by this electronic energy loss. The result of collision cascades on Cu-fullerene nanocomposite is also a significant characteristic to inspects the microstructure of carbon prepared by high energy ions and low energy ions will be different and it will alter the optical properties of copper-fullerene nanocomposite.[160]

CHAPTER THREE

3. METHODOLOGY

3.1 Method

The methodologies used in the review of the optical properties of copper nanoparticles are above 193 different books, reviews and single articles were selected by the search methodology. Among these 15 are related to the background of the study,145 are related to the literature review and 33 are related to their analysis or results and discussions.. The most important key ideas were included in this review. These books, reviews and single articles which are used in the methodologies contain data about the nanoparticles, classifications of nanoparticles, characterization methods of nanoparticles, synthesis methods of nanoparticles, properties of nanoparticles, optical properties of copper nanoparticles, and the applications of copper nanoparticles. The period reviewed they allowed an assessment of the topic, including research and publications supported by recent findings. The selected papers were organized with their respective bibliographic information. The methodology for calculating the optical properties of the Cu nanoparticles is based on Mie theory. The theory consists of solving the classical electromagnetic equations for the interaction of an incident light with a metallic sphere surrounded by any medium. The interaction of light with metallic spheres produces scattering, extinction and absorption of the incident plane wave. According to the Drude-Summerfeld free electron model, the quantum behavior of an electron gas is determined by its frequency dependent complex dielectric function that can be expressed as

$$\varepsilon_m = 1 - \frac{\omega_p^2}{(\omega^2 + i\gamma\omega)} \quad \text{..... (3.1)}$$

Where $\gamma \ll \omega_p$, is the screening and the Plasmon frequency is defined as

$$\omega_p^2 = \frac{ne^2}{m\varepsilon_o} \quad \text{..... (3.2)}$$

Where m and e are the mass and charge of the electron,ε_o is the permittivity of vacuum and ω is the frequency of the incident light.The spatial and temporal dependence for the electric field of this surface wave can be expressed in terms of plane waves,

$$E(r,w) = \overrightarrow{Eo} exp\left(i\left[\acute{k}.\acute{r} - \omega t\right]\right) \quad \text{..... (3.3)}$$

Where E is the intensity of the electric field and k is the wave vector.The calculations of the optical characteristics of nanoparticles can correctly be performed in the context of the Mie

theory. The extinction (Q_{ext}), scattering (Q_{sca}), and absorption efficiency factors (Q_{abs}) of light with wavelength λ were calculated for spherical nanoparticles of radius *R* within the framework of the Mie theory. These parameters are equal to the ratios of the extinction, scattering, and absorption cross sections to the geometrical cross sections of the sphere (πR^2). To calculate the light extinction and scattering efficiency factors, the following formula

$$Q_{ext}=\sum_{i=1}^{\infty}(F_1^C ext + F_1^b ext) \quad \text{(3.4)}$$

$$Q_{sca} = \sum_{i=1}^{\infty}(F_1^C sca + F_1^b sca) \quad \text{(3.5)}$$

The light absorption efficiency factor was calculated as a difference between the extinction and scattering efficiency factors ($Q_{abs} = Q_{ext} - Q_{sca}$). [161]The quantities in brackets that specify contributions of electric and magnetic oscillations to each efficiency factor have the form

$$F_1^C ext = \frac{2}{\rho^2}(2i+1)\,|c1|^2 \quad \text{(3.6)}$$

$$F_1^b ext = \frac{2}{\rho^2}(2i+1)\,|b1|^2 \quad \text{(3.7)}$$

$$F_1^C sca = \frac{2}{\rho^2}(2i+1)\,Imc1 \quad \text{(3.8)}$$

$$F_1^b sca = \frac{2}{\rho^2}(2i+1)\,Imb1 \quad \text{(3.9)}$$

Where $\rho = 2\square Rm0/\lambda$ is the dimensionless nanoparticle radius and *m*o is the refractive index of the medium

CHAPTER FOUR

4. RESULTS AND DISCUSSIONS

4.1Plasma resonance of Copper Nanoparticles and Size of Nanoparticles

An interesting aspect of nanostructures of noble metals, such as gold (Au), silver (Ag) and copper (Cu), is that their optical properties depend strongly on the particle size, surrounding medium and shape because of their ability to exhibit LSPRs. Therefore, they are potential candidates in many applications. LSPRs are well known to have certain properties of collective electronic excitations within metal nanostructures that tend to trap optical waves near their interface between the metal and a dielectric medium under an excited electromagnetic field. LSPRs were also observed with Cu nanoparticles in the visible wavelength region. They were weaker than those induced by Au and Ag NPs. Therefore, up to now much work has concentrated only on the LSPRs given by Au and Ag NPs, which have mainly been utilized in highly conductive elements in electronic devices. However, considering the cost of these metals, it is important to develop many application devices, and Cu has a relatively low cost. For this reason, this work focuses on the optical properties of Cu NPs. In addition, it has excellent electrical and thermal conductivities, resulting in a wide range of applications in the field of nano-devices, such as organic bulk-heterojunction solar.

Metal nanostructures are among the most studied nanomaterials due to their outstanding size-dependent properties. In particular, copper nanoparticles show an interesting optical behavior known as size-dependent surface Plasmon resonance (SPR) as the nanoparticle diameter becomes comparable with, or smaller than the wavelength of incident light. Plasmon resonance is the collective oscillation of conduction electrons and occurs when the frequency of incident light matches the resonance frequency of a gas of free electrons. It is more easily observed in certain noble metals (such as Cu) because of the relative oxide-free surfaces of these which form a favorable environment for their observation, at a low nanoparticle's dielectric constant.

The change in wavelength that is observed when a photon undergoes Raman scattering is attributed to the excitation (or relaxation) of the vibration modes of a molecule. Because different functional groups have different characteristic vibration energies, every molecule has a unique Raman spectrum. By the Raman selection rule, the molecular polarizability changes as

the molecular vibrations displace the constituent atoms from their equilibrium positions. The intensity of Raman scattering is proportional to the magnitude of the change in molecular polarizability. Raman scattering cross sections are typically orders of magnitude smaller than those of fluorescence; therefore, the Raman signal is still several orders of magnitude weaker than the fluorescence emission in most cases. Because of the inherently small intensity of the Raman signal, the sensitivity limits of available detectors, and the intensity of the excitation sources, the applicability of Raman scattering was restricted for many years. However, its utility as an analytical technique improved with the advent of the laser and the evolution of photon detection technology. In 1977, Jeanmaire and Van Duyne demonstrated that the magnitude of the Raman scattering signal can be greatly enhanced when the scattered is placed on or near a rough noble-metal substrate.[162] Strong electromagnetic fields are generated when the localized surface Plasmon resonance (LSPR) of nanoscale roughness features on a silver, gold, or copper substrate is excited by visible light. When the Raman scattered is subjected to these intensified electromagnetic fields, the magnitude of the induced dipole increases, and accordingly, the intensity of the inelastic scattering increases. This enhanced scattering process is known as surface-enhanced Raman (SER) scattering.

Plasmon effects are the most dominate of the optical properties of the metallic copper nanoparticles. The plasmatic effects include two main components: The Surface Plasmon (SP) polaritons that is the charge density wave propagation on the interface of metal and dielectric, and the localized Surface Plasmon (LSP) resonance, which is the non-propagating collective oscillation of electrons coupled to electromagnetic field. SP represents the charge density wave propagation on the interface of metal and dielectric, while LSP describes the collective oscillation of the conduction electrons in metal nanomaterials associated to electromagnetic field. Here, energy is confined within the interface of the metal and the dielectric and propagating in the other two dimensions (Fig.4.1. (a)). It requires necessary phase-matching between the modes from the two sides of the interface. In comparison, the condition to generate LSP is looser, where Plasmon resonances can be excited by direct light illumination. Due to the size restriction of the nanostructure (nanoparticle), electrons are oscillating collectively against the restoring force of the nuclei, along the direction of the electric field of the electromagnetic wave to which they are coupled, rendering the nanoparticle a dipole-like oscillation source (Fig. 4.1.(b)).

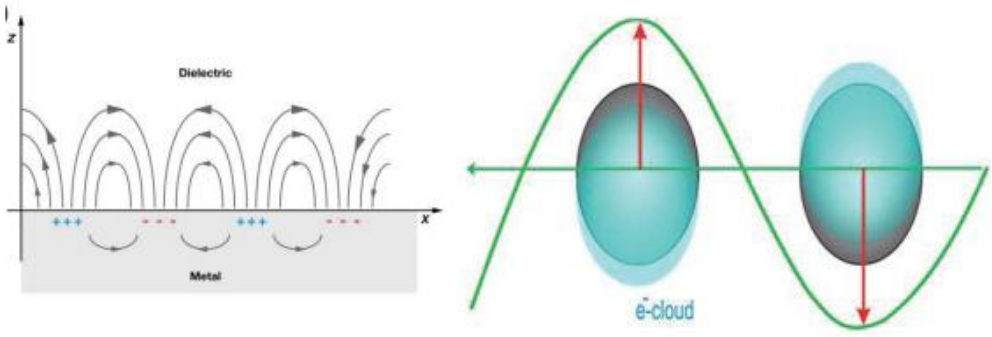

Figure 4. 1: Schematic diagrams illustrating (a) surface Plasmon (SP) Polaritons and (b) localized surface Plasmon (LSP) resonance showing Plasmon oscillations in metal spheres induced by an electromagnetic wave.'[163]

4.1.1 Dipole Plasmon Resonances

When a small spherical metallic nanoparticle is irradiated by light, the oscillating electric field causes the conduction electrons to oscillate coherently. This is schematically pictured in Fig.4.2.

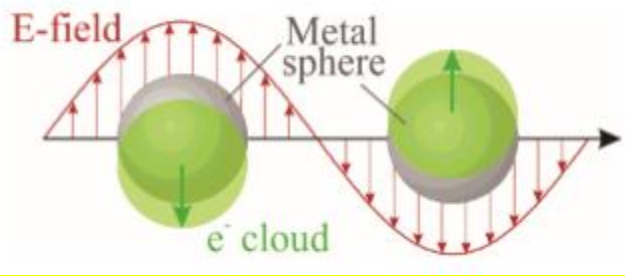

Figure 4. 2: Schematic of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei'[164]

When the electron cloud is displaced relative to the nuclei, a restoring force arises from Coulomb attraction between electrons and nuclei that results in oscillation of the electron cloud relative to the nuclear framework. The oscillation frequency is determined by four factors: the density of electrons, the effective electron mass, and the shape and size of the charge distribution. The collective oscillation of the electrons is called the dipole plasmon resonance of the particle (sometimes denoted "dipole particle plasmon resonance" to distinguish from plasmon excitation that can occur in bulk metal or metal surfaces). Higher modes of plasmon excitation can occur, such as the quadruple mode where half of the electron cloud moves parallel to the applied field and half moves antiparallel. For a metal like copper, the plasmon frequency is also influenced by other electrons. However, it is not hard to relate the plasmon frequency to the metal dielectric constant, which is a property that can be measured as a function of wavelength

for bulk metal. To relate the dipole plasmon frequency of a metal nanoparticle to the dielectric constant, consider the interaction of light with a spherical particle that is much smaller than the wavelength of light. Under these circumstances, the electric field of the light can be taken to be constant, and the interaction is governed by electrostatics rather than electrodynamics. Plasmon can exist in bulk metals, on thin metallic surfaces or they can be localized inside, or on the surface of metallic nanoparticles. Depending on the specific situation, we may have bulk plasmons (BP), surface Plasmons (SP) or localized plasmons (LP). This classification is due to the different boundary conditions associated with different structures.

Absorption of electromagnetic radiation is the way by which the energy of a photon is taken up by matter, typically the electrons of an atom. UV-visible spectroscopy is used when involving the absorptionof these high energy lights by atoms or molecules, which causes electronic excitation. Bulkplasmons refer to collective modes of oscillation of the free electron gas inside a sufficiently large volume of bulk metal. The excitation of bulk plasmons leads to the collective motion of a very large number of free electrons, resulting in small density fluctuations around the average density n, of the unperturbed electron gas.[165] According to the Drude-Sommerfeld free electron model, the quantum behavior of an electron gas is determined by its frequency dependent complex dielectric function that can be expressed as

$$\varepsilon_m = 1 - \frac{\omega_p^2}{(\omega^2 + i\gamma\omega)} \quad \text{..... (4.1)}$$

Where$\gamma \ll \omega_p$, is the screening and the Plasmon frequency is defined as

$$\omega_p^2 = \frac{ne^2}{m\varepsilon_o} \quad \text{..... (4.2)}$$

Where m and e are the mass and charge of the electron,ε_o is the permittivity of vacuum and ω is the frequency of the incident light. The presence of an imaginary part in ε_m is a consequence of the fact that metals can absorb light. Surface Plasmons(SP) are associated with coherent electron oscillations which occur at the interface of a sufficiently thin metallic film and a dielectric medium. Plasmons are in this case confined in the proximity of the metallic surface so that plasmonic waves propagate along the interface of the two media. The spatial and temporal dependence for the electric field of this surface wave can be expressed in terms of plane waves,

$$E(r, w) = \overrightarrow{Eo} exp\left(i\left[\acute{k}.\acute{r} - \omega t\right]\right) \quad \text{..... (4.3)}$$

Where E is the intensity of the electric field and k is the wave vector. The planar geometry of the boundary conditions allows writing eq. (4.3) in a way that separates the spatial components of the wave in directions parallel and orthogonal to the surface with wave vectors,

Localized surface Plasmon unlike the case of a SP, in which an electromagnetic wave coupled to a free electron gas results in a propagating field along a metallic surface, localized plasmons (LP) involve a non-propagating collective excitation of electrons confined in small metallic structures. A sub wavelength metallic particle can be treated as a spherical region in which electrons are allowed to move freely as shown in Fig 22. Drift of conduction electrons upon excitation by an external electric field results in the formation of polarization charges of opposite sign on the two hemispheres forming the surface of the particle.

There is some relationship between the absorption spectrum of copper nanoparticles caused by surface plasmon absorption and their sizes. For nanoparticles, the excitation of the surface resonance absorption can occur in visible light region. Such absorption spectra can be analyzed using Mie theory. In particular, according to this theory, for nanoparticles smaller than the mean free path of the conduction electrons there is a relationship between the resonance broadening and the sizes of nanoparticles.

The actual part of the dielectric constant of the metal determines the SPR position and the imagery part determines the bandwidth. Decreasing particle size leads to the blue shifts in the SPR wavelength. [166]The expression for the frequency of the surface Plasmon resonance localized on a spherical particle can be determined. If the spherical nanoparticles are not much smaller than a wavelength the dipole surface plasmon approximation is not satisfied. In this case, the scattered electric field is not purely dipolar in nature, but is formed by an infinite superposition of multi poles. The multi-polar nature of the scattered field manifests itself with the fact that the field intensity undergoes several oscillations, with maxima and minima at specific distances r from the surface of the particles, while the dipolar field follows a much simpler trend and exponentially decays away from the metal surface.

$$\omega_{LP} = \frac{\omega_P}{\sqrt{(1+2\varepsilon_d)}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.4)$$

where W_{LP}- frequency of plasma resonance, W_P-plasma frequency, and ε_d- dielectrics constant of the medium in which the nanoparticle is embedded

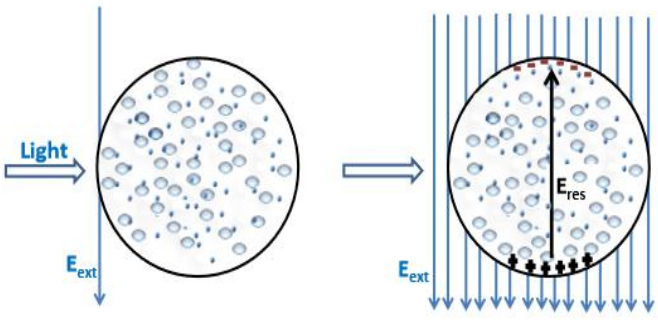

Figure 4.3: Schematic depiction of the influence of external light field on randomly oriented charges in a metallic nanoparticle. The incident electromagnetic wave excites charge separation to create an electric dipole.[166]

4.2 Characterization Techniques of Copper Nanoparticles

Copper Nanoparticles can be characterized through various techniques. Each of them is useful to determine a property of the obtained copper nanoparticles. The chemical composition and concentration are not enough. Physical properties (size, shape, and surface properties) need to be measured to be able to successfully reproduce experiments. The synthesized nanoparticles can be characterized using different tools as shown in Table4.1. In this category UV–visible spectroscopy is used to confirm the bio reduction of the nanoparticle through the obtained surface plasmon resonance (SPR) peak as well as to determine the shape, size, bandwidth, and possible aggregation state of nanoparticles.TEM, SEM, STM, and AFM analysis are conducted to study the size, shape, morphology, topography, roughness of the surface, and texture of the nanoparticle. XRD analysis is used to find the crystalline structure of the nanoparticle.DLS (referred to as quasi-elastic light scattering) helps in size determination and aggregation of NPs. Biomolecules and a functional group involved in the reduction and stabilization of nanoparticles are identified by Fourier transform infrared spectroscopy (FTIR).The functional groups present on the surface of the nanoparticle and the presence of protein, carbonyl groups, and CH bonds in amines, which is the source for the biosynthesis can also be determined by FTIR. EDAX analysis could be used to determine the elemental composition and purity of synthesized nanoparticles.

Table 4.1: Common characterization techniques and parameters obtained.[167]

Characterization Techniques	Parameters Assessed
Scanning Electron Microscopy Transmission Electron Microscopy	Topology, Size, Morphology, Crystallography and structure[168]
Atomic Force Microscopy	Topology, Size, Morphology, Crystallography[169]
Scanning Tunneling Microscopy	Size, morphology, surface roughness and texture[170]
Dynamic Light Scanning	Topology, surface modifications, chemical analysis[171]
UV spectroscopy	Size distribution[172]
Fourier Transform Infrared Spectroscopy	Transmission, shape, size, composition and concentration[173] Functional group and chemical bonding[174]
X-ray Diffraction	Structure type and crystallinity[175]
Differential Scanning Calorimetry	Polymorphism and amorphous content[176]
Thermo Gravimetric Analysis	Kinetic, chemical and physical properties[177]
X-Ray Photoelectron Microscopy	Chemical analysis, uniforming of composition and binding energy[178]

4.3 Optical Properties of Copper Nanoparticles

The calculations of the optical characteristics of nanoparticles can correctly be performed in the context of the Mie theory. The extinction (Q_{ext}), scattering (Q_{sca}), and absorption efficiency factors (Q_{abs}) of light with wavelength λ were calculated for spherical nanoparticles of radius *R* within the framework of the Mie theory. These parameters are equal to the ratios of the extinction, scattering, and absorption cross sections to the geometrical cross sections of the sphere (πR^2). To calculate the light extinction and scattering efficiency factors, the following formula

$$Q_{ext}=\sum_{i=1}^{\infty}(F_1^C ext + F_1^b ext) \quad \text{.....(4.5)}$$

$$Q_{sca} = \sum_{i=1}^{\infty}(F_1^C sca + F_1^b sca) \quad \text{..... (4.6)}$$

The light absorption efficiency factor was calculated as a difference between the extinction and scattering efficiency factors ($Q_{abs} = Q_{ext} - Q_{sca}$). [179]The quantities in brackets that specify contributions of electric and magnetic oscillations to each efficiency factor have the form

$$F_1^C ext = \frac{2}{\rho^2} (2i+1) |c1|^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.7)$$

$$F_1^b ext = \frac{2}{\rho^2} (2i+1) |b1|^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.8)$$

$$F_1^C sca = \frac{2}{\rho^2} (2i+1) \text{Im} c1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.9)$$

$$F_1^b sca = \frac{2}{\rho^2} (2i+1) \text{Im} b1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.10)$$

Where $\rho = 2\pi Rm0/\lambda$ is the dimensionless nanoparticle radius and *m*o is the refractive index of the medium .The coefficients *c*1 and *b*1 in Eq. (4.7) and (4.8) were determined from the boundary conditions on the nanoparticle surfaces. The main parameter in calculations was the complex metal refractive index whose values for some wavelengths are given.[180]The calculated dependences of the light extinction, scattering, and absorption efficiency factors on the copper nanoparticle radius at the indicated wavelengths are shown in Fig. 4.4 *a–c*, respectively. Each dependence$Q_{ext}(R)$ has a maximum whose position is determined by the light wavelength. For smaller radii, the curve decays to zero; for larger radii, it reaches a plateau with damped oscillations.

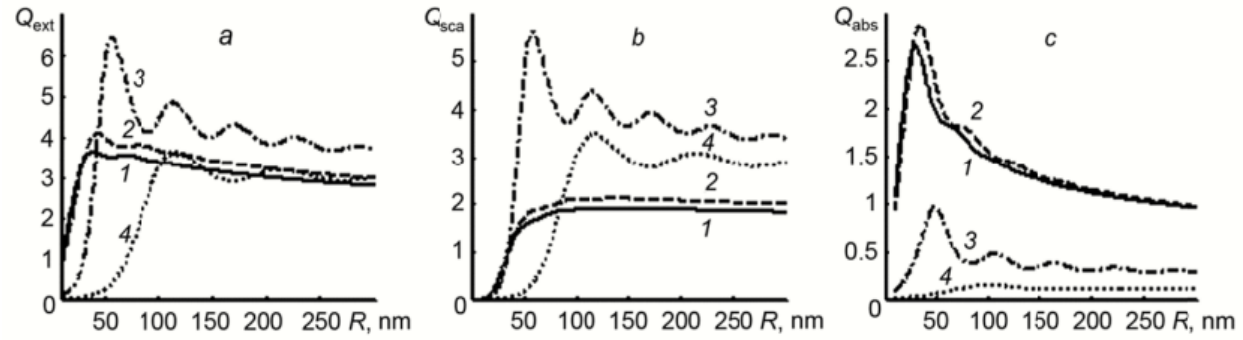

Figure 4.4:Dependences of the light extinction(a),scattering (b), and absorption efficiency factor(c) on the radii of the copper nanoparticles calculated for wavelengths of 450(curve 1),532 (curve 2) ,650(curve 3), and 1064nm (curve 4).[180]

The results of calculations of the maximal values of the absorptions (Q_1), scattering (Q_2), and extinction efficiency factors (Q_3) in the spectral range 400-1100nm and the corresponding nanoparticle radii (R_1, R_2, and R_3) together with the complex copper refractive indices and the linear absorption coefficient of the bulk metal. Attention is attracted to the monotonic dependences of positions (R_1 and R_3) of the maximal absorption and the extinction efficiency factors on the wavelength.In the dependence Q_2 (R_2) on the wavelength, a minimum is observed at wavelength 600nm. The reason for this is that in the blue region of the spectra, the maxima of

the extinction and absorption coefficients are mainly caused by the dipole electric oscillations c1. The extinction efficiency factor in the blue region of the spectrum is determined by a superposition of the electric dipole, quadrupole, and octopole oscillations as well as the magnetic dipole and quadrupole oscillations with comparable contributions. The resonance of scattering on the electric dipole oscillation at a wavelength of 450nm is observed for copper nanoparticles with a radius of 53nm, which is much closer to the abscissas of the maxima on the dependences of the absorption and extinction efficiency factors. The greatest value of the maximum absorption efficiency factor is observed at the wave length close to the minimum of the absorption coefficient of the bulk metal. The calculated spectra dependences of the extinction (Q_{ext}), scattering (Q_{sca}), and absorption efficiency factor (Q_{abs}) of copper nanoparticles are shown in figure4.4. Calculations were performed for nanoparticle radii of 10, 20, 30, and 60nm. The character of the spectral dependences Q_{ext} and Q_{abs} changes with increasing nanoparticle radii. A weakly expressed local maximum on the dependences Q_{ext} and Q_{abs} is observed at the wave length 572nm for R=10nm. Two local maxima in the blue region of the spectrum are observed on the dependences Q_{ext} for nanoparticle radii of 20nm and 30nm. With increasing wavelength, Q_{ext} and Q_{abs} values decrease and tend to zero as the wavelength approaches to infinity. The relationship between the amplitudes of the maxima increases with copper nanoparticle radius so that the local maximum in the blue region of the spectrum disappeared for a nanoparticle radius of 60nm.An increase in the half-width of the first local maximum at half maximum on the dependence Qext toward greater wavelengths should be noted with increasing nanoparticle radii. This half-width is equal to 20nm for copper nanoparticles with radius R =10nm. it is equal to 95nm for nanoparticles with radius R =60nm. From comparisons of the dependences the ratio of Q_{sca}/ Q_{ext} increases with the nanoparticle radius, that is, small nanoparticles mainly absorb light, whereas large nanoparticles scatter it.

The spectrum of copper nanoparticles in the silicate glass was presented on which a weak Plasmon resonance band was seen at a wavelength of 570nm against the background of the extinction increasing in the blue region of the spectrum. Its weakness was due to a wide nanoparticle size distribution with a maximum for a nanoparticle radius of 5.6nm.[181]The spectral dependences of light extinction coefficient of copper nanoparticles were presented demonstrating local maxima at wavelengths of 564 and 579 nm. A clearly pronounced shoulder was observed for the dependencies in the blue region of the spectrum. The spectral dependence of the light

extinction coefficient of copper nanoparticles in lithium niobate was presented with the local extinction maximum in the range 560–680 nm followed by a shoulder in the blue region of the spectrum. This shoulder is reproduced by the results of our calculations (Fig.4.5*a*) and is typical for the spectral dependencies of the optical properties of copper nanoparticles. We now compare the observed spectral dependences of the optical constants of copper nanoparticles with the dependence of the complex refractive index on the wavelength. The real component of the refractive index in the region 450–530 nm remains almost constant, then in the wavelength region 530–625 nm a sharp decrease of the real component is observed with further slow increase in the region 625–1000 nm. The modulus of the imaginary component remains almost unchanged in the region 450–575 nm and then grows nearly linearly.Narrow bands of Plasmon resonance of nanoparticles are observed mainly in the range 550-600nm; they broadened considerably at large wavelengths.

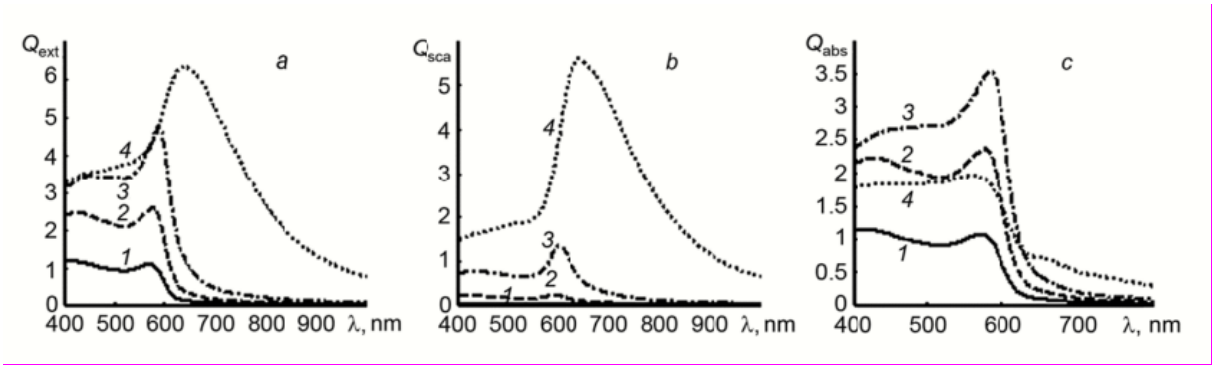

Figure 4.5: Spectral dependences of the light extinction(a) ,scattering (b), and absorption efficiency factor(c) copper nanoparticles with radii 10(curve 1), 20 (curve 2) ,30(curve 3), and 60nm (curve 4).[181]

From the above expression it follows that the position of the maximum on the spectral dependence is primarily determined by the influence of the wavelength on the coefficient of the dipole electric oscillations through the spectral dependence of the complex refractive index. For $\lambda > 600$ nm, the real component of the refractive index is practically independent of the wavelength, and the modulus of the imaginary component almost linearly increases with λ.Therefore, the position of the maximum turns out to be proportional to the nanoparticle radius.The observed change in the characteristic bandwidth of the plasmon resonance with increasing copper nanoparticle radius (Fig.4.5) is caused by the change of contributions. As the plasmon maximum is shifted toward $\lambda > 600$ nm, the contribution of the given terms decreases, which leads to a decrease in the modulus of the second derivative at the point of maximum and

to an increase in the characteristic extinction bandwidth. The calculations allow us to predict the influence and to estimate the optimal radii of copper nanoparticles in various functional devices that require increased local absorption of radiation energy. For all nanoparticle radii, the absorption efficiency factor increases with decreasing wavelength. Therefore, copper nanoparticles demonstrating a stronger change of the optical properties with decreasing wavelength can be used to obtain photosensitive composites. The high value of the light absorption efficiency factor of copper nanoparticles at the wavelength of the second harmonic of the neodymium laser allows us to predict the efficiency of their application as light-absorbing additives in the matrix of a secondary explosive for optical detonator capsules.[182]

4.4 Applications of Copper Nanoparticles

The two fields where copper nanoparticles can be used to prevent infections and diseases are hospitals—as seen below in Figure4.6—and transportation.

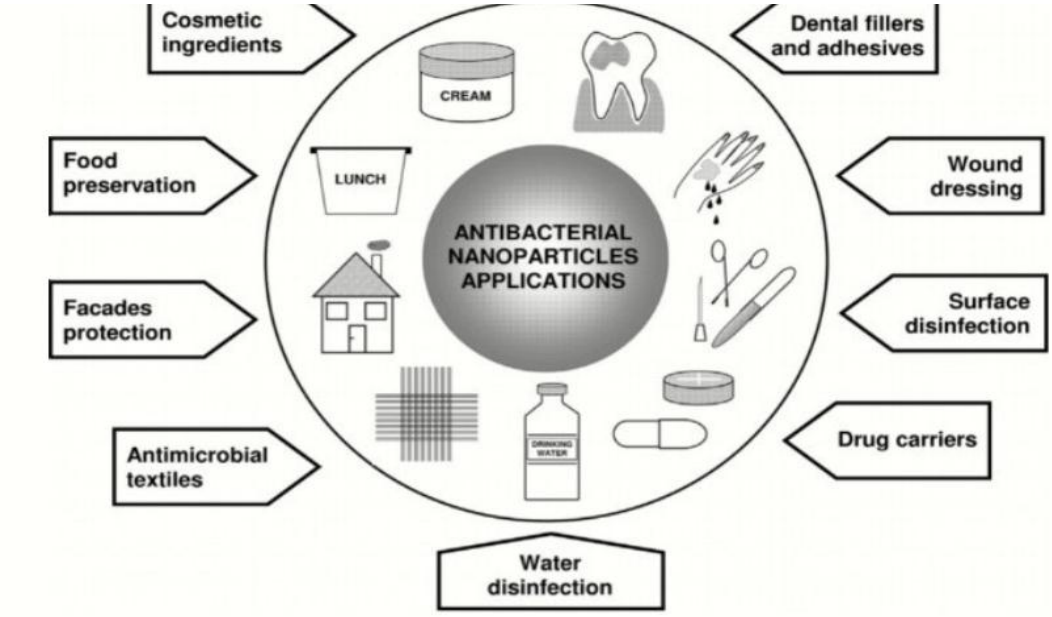

Figure 4.6: Antibacterial nanoparticles applications.[183]

Nanoparticles are used in many fields of application, which are nanomedicine fields such as nano drugs, medical devices, and tissue engineering, and chemical and cosmetic fields such as nanoscale chemicals and compounds, paints, and coatings, in materials science Nanoparticles fields such as carbon nanotubes, biopolymers, paints, and coatings, in the Food Sciences field such as processing, nutraceutical food, nano-capsules,in Environment and Energy field such as water and air purification filters, fuel cells, photovoltaic, Military and Energy field such as

biosensors, weapons, sensory enhancement, in Electronics Semiconductors field such as chips, memory storage, photonic, optoelectronics, and in Scientific tools fields, atomic force fields such as a microscopic and scanning tunneling microscope, and agriculture field atomic force, microscopic and scanning tunneling microscope. Generally, the major fields of sciencethatbenefitfrom Cu NPs are covered below.

4.4.1 Biological Applications

Nanoparticles have potential applications in biomedical and pharmaceutical fields due to nano-size and high surface area. Copper NPs show antimicrobial activity towards Bacillus subtilis, E. coli, S. aureus, Micrococcus luteus,Pseudomonasaeruginosa, Salmonella enterica, and Enterobacteraerogenes[184] and also antifungal activity against Fusariumoxysporum and Phytophthoracapsici.[185]The copper ions are capable of damaging cell membrane, DNA, RNA and other molecules, thus Cu NPs have shown profound effect against viruses such as human influenza A (H1N1), avian influenza (H9N2),and many more including COVID-19 virus reducing its viability.[186]Nanoparticles tend to elicit intrinsic and extrinsic apoptotic pathway for death of cancerous cells, and copper has found promising against cancer. Copper and copper oxide nanoparticles exhibit anticancerous activity against HeLa cells, MD A-MB-231 (human breast cancer cell lines), Caco-2 (human colon cancer cells), and HepG2cells (Hepatic cancer cells) and Mcf-7 breast cancer cells.[187]

4.4.2 Therapeutics

Nanoparticles provide a site-specific drug-delivery system, due to their small size, large absorptive surface for drugs to carry and also show improved therapeutic efficiency with less toxicity. Breast Cancer was targeted using chitosan-coated copper nanoparticles at different pH for the drug doxorubicin, on MCF-7 cell line by studying the apoptotic activity of cells.[188] Antimicrobial activity using biopolymer chitosan microparticles conjugated with copper NPs which showsa greater synergic effect for antibacterial activity of tetracycline against Gram-positive and Gram-negative bacteria[189] also core-shell nanocarriers were used to enhance the activity of tetracycline where copper oxide NPs was used as core and hyper-branched polyglycerol as shell.[190]

4.4.3 Bioremediation

Copper being low cost metal, less toxicity and copper based catalyst can be recycled and reused again. Bioremediation of pollutant such as dyes has become important to treat the polluted water which can lead to alterations in aquatic life and can lead to dangerous outcome. So the properties of CuNPs are discussed for remediating polluted water bodies due to textile effluents, industrial disposal etc.[191]

4.4.4 Textile

UK manufacturer Promethane Particles along with textile companies and research institutes are developing Personal Protective Equipment (PPE) and are designing fabrics having Nano-copper into polymer fibers such as nylon, by melt extrusion process and developing antimicrobial fabrics which are under examination.[192] Copper nanoparticles are incorporated in cotton fibers and antimicrobial evaluation is done against *E. coli*, *S. aureus*, *Proteus vulgaris*,and*K. pneumoniae*[193]which can be used in textiles to produce PPE.

4.4.5 Other Applications

Copper NPs have also shown profound applications in food packaging and agriculture for crop improvement. The use of copper nanoparticles in agriculture is cost effective and their small size facilitates easy absorption by plants. It has proved its antagonism against fungi, insects, pests of crop plants, etc. Therefore, it has the potential to be explored as nano herbicides,nano pesticides, and nano fertilizers with several cost benefits. Using copper nanoparticles alone serves as fungicide, pesticide, micronutrient, and fertilizer thereby solving the extra cost incurred by the separate use of fungicide, pesticide, fertilizers in conventional agriculture.

Copper nanoparticles being economical and eco-friendly, it is used as an antimicrobial agent in food packaging as well. It forms an impermeable food packaging material protecting from UV radiation increasing their shelf life for a longer time Copper nanoparticles have also been reported to suppress diseases during stress and drought conditions, thus increasing the drought tolerance and production efficacy. It is also reported to enhance anthocyanin, chlorophyll, and carotenoid content responsible for increasing seed number, grain yield under stressfulenvironments, and wastewatermanagement.Thus Copper nanoparticle shows a wide range of applications in the field of biological, physical, and chemical sciences.

In Conclusion, nanoparticle production from natural extracts is emerging widely in the field of nanotechnology as the greener the process better the outcome without any toxic effects. The main reason to use natural extracts is it becomes eco-friendly and free of chemical contaminants which has applications in major fields of science. A proper method, time, precursor, pH, temperature, incubation time must be taken into consideration to optimize the synthesis process. These methods are scalable, safer, and stable then produced through physical and chemical procedures.

CHAPTER FIVE

5. SUMMARY AND OUTLOOKS

5.1 Summary

In summary, we presented in this paper nanoparticles and their classifications, synthesis methods, characterization methods and the optical properties of copper nanopatricles and their applications. The dimensions of nanoparticles are influenced by both the synthesis method and the surrounding environment. Copper is neither created nor destroyed, necessitating precise regulation of its levels to maintain homeostasis. *The* two main factors that cause why nanoparticles significantly different physically and chemically than the same materials at larger dimensions are surface effects and quantum effects. Copper exhibits a characteristic reddish-orange type and metallic shine. Copper possesses exceptional ductility, malleability, and thermal and electrical conductivity, coupled with high corrosion resistance and low chemical reactivity. Furthermore, its conduction electrons, or free-moving electrons, can interact strongly with visible light when the nanoparticle's plasmonic mode aligns with the energy of incoming photons. Nanoparticles can be classified into five major groups based on their size, origin, structural configuration, pore diameters, and potential toxicity. Nanoparticles are synthesized by using a variety of methods, which are classified into two main categories: bottom-up and top-down methods. The top-down method decomposes bulk materials into smaller materials and finally changed into nanoparticles while the bottom-up method involves the building of material from atoms to clusters to nanoparticles.The physicochemical properties and features of Nanoparticles that can be resolved by each characterization method are the m*orphological and topographical, structural and chemical, optical, electronic and electrical, magnetic, thermal, and mechanical characterizations.* An interesting aspect of copper nanoparticles is that their optical properties depend strongly on the particle size, surrounding medium, and shape because of their ability to exhibit LSPRs. Plasmon resonance is the collective oscillation of conduction electrons and occurs when the frequency of incident light matches the resonance frequency of free electrons.

The morphological and topographical features of Nanoparticles include the size, shape, dispersity, localization, agglomeration/aggregation, surface morphology, surface area, and porosity of the NPs. The SEM, STM, and TEM methods are frequently used for the analysis of morphological and topographical features of NPs such as size, shape, and surface. Dynamic

Light Scattering (DLS) can be used to determine the size of the nanoparticles. The elemental composition of copper Nanoparticles can be analyzed by Energy Dispersive X-ray spectrum.

The optical characteristics of copper nanoparticles can correctly be performed in the context of the Mie theory. That are the extinction (Q_{ext}), scattering (Q_{sca}), and absorption efficiency factors (Q_{abs}) of light with wavelength λ were calculated for spherical copper nanoparticles of radius *R* within the framework of the Mie theory. Mie theory can describe the optical properties of copper nanoparticles when the size of the nanoparticle is not too small. It has been the Plasmon extinction band on the spectral dependence is shifted with increasing nananoparticle radius, which is followed by the band broadening. Copper nanoparticles have a big role for societies due to their fantastic and power-full applications in many fields like biological, therapeutics, bioremediations, textile and other applications such as agriculture, electrical engineering, medicine etc in the real world.

5.2 Outlooks

Copper and copper-based Nanoparticles have a promising role in various applications, owing to their excellent physicochemical properties, and high electrical conduction. Besides their applications, there is still a need to understand the fate, exposure, and toxicity of the copper nanoparticles. Therefore, large trials in forwarding and developing futuristic investigations based on perceived gaps of knowledge are required to be executed as well as various support from researchers and funding from the government and non-government to utilize the benefits of copper nanoparticles in sustainable production in industries is also needed. The research areas covered by or related to the topic of optical properties of copper nanoparticles are huge. Multiple disciplines are involved in the study and development of various types of nanoparticles, aiming at the eventual utilization of the nanoparticles for different applications. Although similar studies are carried out actively and intensively by others, there are still a variety of open questions to be addressed related to the topic. These questions have been, to a certain extent, solved or givensuggestions for potential solutions, with experiment-based studies. Therefore, it is necessary to further study the optical properties of copper nanoparticles and their interaction, applications, and toxicity.

References

[1].Bloemen, M., 2015.Immunomagnetic separation of bacteria by iron oxide nanoparticles.

[2]. Pokropivny, V., Lohmus, R., Hussainova, I., Pokropivny, A. and Vlassov, S., 2007. Introduction to nonmaterial and nanotechnology (pp. 45-100). Tartu: Tartu University Press.

[3].Khan, I., Saeed, K. and Khan, I., 2019. Nanoparticles: Properties, applications and toxicities. Arabian journal of chemistry, 12(7), pp.908-931.

[4].Harishchandra, B.D., Pappuswamy, M., Antony, P.U., Shama, G., Pragatheesh, A., Arumugam, V.A., Periyaswamy, T. and Sundaram, R., 2020. Copper nanoparticles: a review on synthesis, characterization and applications. Asian Pacific journal of cancer biology, 5(4), pp.201-210.

[5].Ealia, S.A.M. and Saravanakumar, M.P., 2017, November.A review on the classification, characterisation, synthesis of nanoparticles and their application. In IOP conference series: materials science and engineering (Vol. 263, No. 3, p. 032019). IOP Publishing.

[6]. Din, M.I. and Rehan, R., 2017. Synthesis, characterization, and applications of copper nanoparticles. Analytical Letters, 50(1), pp.50-62.

[7].Scida, K., Stege, P.W., Haby, G., Messina, G.A. and García, C.D., 2011. Recent applications of carbon-based nanomaterials in analytical chemistry: critical review. AnalyticaChimicaActa, 691(1-2), pp.6-17.

[8].Wu, W., 2017. Inorganic nanomaterials for printed electronics: a review. Nanoscale, 9(22), pp.7342-7372.

[9]. Grimsdale, A.C. and Müllen, K., 2005. The chemistry of organic nanomaterials. AngewandteChemie International Edition, 44(35), pp.5592-5629.

10. Gawande, M.B., Goswami, A., Felpin, F.X., Asefa, T., Huang, X., Silva, R., Zou, X., Zboril, R. and Varma, R.S., 2016. Cu and Cu-based nanoparticles: synthesis and applications in catalysis. Chemical reviews, 116(6), pp.3722-3811.

[11.] Wei, C. and Liu, Q., 2017. Shape-, size-, and density-tunable synthesis and opticalproperties of copper nanoparticles. CrystEngComm, 19(24), pp.3254-3262.

[12].Sulekh Chandra, Avdhesh Kumar, Praveen Kumar T (2014) Synthesis and characterization of copper nanoparticles by reducing agent. Journal of Saudi Chemical Society 18(2): 149-153.

[13]. V. A. Kharenkov, V. A. Donchenko, A. A. Zemlyanov, and I. A. Edriev, Izv. Vyssh.Uchebn.Zaved.Fiz.56, No.8/3, 239–241 (2013).

[14].Haes, A. J.; Hall, W. P.; Chang, L.; Klein, W. L.; Van Duyne, R. P. Nano Lett. 2004, 4, 1029-1034

[15].Bohren, C. F.; Huffman, D. R. Absorption and Scattering of Light by Small Particles; Jo Wiley & Sons: New York, 1983.

[16].Mulvaney P. Nanosciencevs nanotechnology—defining the field.ACSNano.2015. https://doi.org/10.1021/acsnano.5b01418.

[17]. Hasan S. A review on nanoparticles: their synthesis and types. Res JRecent Sci. 2015;2277:2502

[18]. Bratovcic A. Different applications of nanomaterials and their impact onthe environment.Int J Mater Sci Eng. 2019;5:1–7.

[19]. Roduner E. Size matters: why nanomaterials are different. ChemSocRev. 2006;35(7):583–92.

[20]. Buzea C, Pacheco II, Robbie K. Nanomaterials and nanoparticles:sources and toxicity. Biointerphases. 2007;2(4):MR17–71

[21]. Ikhmayies SJ. Characterization of nanomaterials.JOM. 2014;66(1):28–9.

[22]. Ashraf MA, Peng W, Zare Y, Rhee KY. Effects of size and aggregation/agglomeration of nanoparticles on the interfacial/interphase propertiesand tensile strength of polymer nanocomposites.Nanoscale Res Lett.2018;13(1):1–7.

[23]. Suttiponparnit K, Jiang J, Sahu M, Suvachittanont S, CharinpanitkulT,Biswas P. Role of surface area, primary particle size, and crystal phaseon titanium dioxide nanoparticle dispersion properties. NanoscaleResLett. 2011;6(1):1–8.

[24]. Fubini B, Ghiazza M, Fenoglio I. Physico-chemical features ofengineered nanoparticles relevant to their toxicity. Nanotoxicology.2010;4(4):347–63.

[25] .Geoffrion LD, Guisbiers G. Quantum confinement: size on the grill! JPhysChem Solids. 2020;140: 109320.

[26]Ealia SAM, Saravanakumar MP. A review on the classification, characterisation, synthesis of nanoparticles and their application. In: IOP Conference Series: Materials Science and Engineering. IOP Publishing; 2017.p.

[27]. Machado S, Pacheco JG, Nouws HPA, Albergaria JT, Delerue-Matos C.Characterization of green zero-valent iron nanoparticles produced with tree leaf extracts. Sci Total Environ. 2015;533:76–81.

[28]. Khan I, Saeed K, Khan I. Nanoparticles: properties, applications and toxicities. Arab J Chem. 2019;12(7):908–31.

[29]. I. Khan, K. Saeed, I. Khan, Nanoparticles: properties, applications, and toxicities, Arab. J. Chem. 12 (7) (2019) 908–931. Nov 1.

[30]. M. Lismont, L. Dreesen, Comparative study of Ag and Au nanoparticles biosensors based on surface plasmon resonance phenomenon, Mater. Sci. Eng. C 32 (6) (2012) 1437–1442. Aug 1.

[31] .B. Karmakar, T. Som, S.P. Singh, M. Nath, Nanometal-glass hybrid nanocomposites: synthesis, properties, and applications, Trans. Indian Ceram. Soc. 69 (3) (2010) 171–186. Jul 1.

[32]. P. Shen, Y. Liu, Y. Long, L. Shen, B. Kang, High-performance polymer solar cells enabled by copper nanoparticles-induced plasmon resonance enhancement, J.Phys. Chem. C 120 (16) (2016) 8900–8906. Apr 28.

[33] .S.K. Ghosh, T. Pal, Interparticle coupling effect on the surface plasmon resonance of gold nanoparticles: from theory to applications, Chem. Rev. 107 (11) (2007) 4797–4862. Nov 14.

[34]. A. M. Ealias, M. P. S, I. O. P. Conf. IOP Conf. Ser.: Mater. Sci. Eng. **2017**, 263, 032019. https://doi.org/10.1088/1757-899X/263/3/032019

[35]. C. Buzea, I. I. Pacheco, K. Robbie, Biointerphases2 **2007**, MR17. https://doi.org/10.1116/1.2815690

[36] E. Gaffet, (preprint) arXiv1106.2206. **2011**. https://doi.org/10.1016/j.crhy.2011.06.002

[37]. National Research Council.Advancing risk assessment, **2009**.

[38]. S. Talebian, G. G. Wallace, F. S A. Schroeder, J. Conde, Nat. Nanotechnol. **2020**, 15, 618, 21. https://doi.org/10.1038/s41565-020-0751-0

[39]. N. A. Mohamed, L. Zupin, S. I. Mazi, H. A. Al-Khatib,S. Crovella, Mdpi**2023**, 11, 428. https://doi.org/10.3390/vaccines11020428

[40]. A. Barhoum, A. S. H. Makhlouf. Emerging Applications of Nanoparticles and Architecture **Nanostructures**.Elsevier, Amsterdam, the Netherlands; **2018**. https://doi.org/10.1016/B978-0-323-51254-1.00012-9

[41]. D. Mrinmoy, P. S. Ghosh, V. M. Rotello. Adv. Mater. **2008**, 20,4225. https://doi.org/10.1002/adma.200703183

[42]. F. Findik, Period. Eng. Nat. Sci. **2021**, 62, 75. https://doi.org/10. 21533/pen.v9i3.1837

[43] .B. Mekuye, B. Abera, Nano Select. **2023**, 4, 486.https://doi.org/10.1002/nano.202300038

[44].S. Khan, M. K. Hossain, In Nanoparticle-Based Polymer Composites.Woodhead, London; **2022**, 15.

[45].Joudeh and LinkeJournal of Nanobiotechnology (2022) 20:262 https://doi.org/10.1186/s12951-022-01477-8

[46]. J. Lv, Q. Gu, X. Mo, X. Jiang, Sens. Actuators A **2022**, 113376. https://doi.org/10.1016/j.sna.2022.113376

[47]. G. Tadesse, Master Thesis, Addis Ababa University, **2006**. http://thesisbank.jhia.ac.ke/id/eprint/7376

[48]. M. Rai, T. A. Nguyen, editors. Nanomaterials Recycling.Elsevier,Amsterdam, Netherland; **2021**.

[49]. P. Dolez, editor. Nanoengineering: Global Approaches to Health and Safety Issues. Elsevier, Amsterdam, Netherland; **2015**

[50].A. B. Albeladi.Synthesis of silver nanoparticles and their sensing applications.

[51]. A. Nouailhat. John Wiley & Sons.**2010**.

[52]. I. Ijaz, E. Gilani, A. Nazir, A. Bukhari. Green Chem. Lett.Rev.**2020**, 13, 223, 45. https://doi.org/10.1080/17518253.2020.1802517

[53]. L. A. Kolahalam, I. K. Viswanath, B. S. Diwakar, B. Govindh, V.Reddy, Y. L. Murthy. Mater. Today: Proc. **2019**, 18, 2182. https://doi.org/10.1016/j.matpr.2019.07.371

[54]. Vladár AE, Hodoroaba V-D. Characterization of nanoparticles by scanning electron microscopy. In: Characterization of nanoparticles. Elsevier;2020. p. 7–27.

[55] .Wikipedia, JEOL USA, Inc.

[56]*Wikipedia*, *Microbe Notes*..

[57]. Kano S, Tada T, Majima Y. Nanoparticle characterization based on STM and STS. ChemSoc Rev. 2015;44(4):970–87.

[58].Kumar A, Dixit CK. Methods for characterization of nanoparticles. In: Advances in nanomedicine for the delivery of therapeutic nucleic acids.Elsevier; 2017. p. 43–58.

[59]. Kouvaris P, Delimitis A, Zaspalis V, Papadopoulos D, Tsipas SA, Michailidis N. Green synthesis and characterization of silver nanoparticles produced using Arbutus unedo leaf extract. Mater Lett. 2012;76:18–20.

[60].Song JY, Kim BS. Rapid biological synthesis of silver nanoparticles using plant leaf extracts. Bioprocess Biosyst Eng. 2009;32(1):79–84.

[61]. Hungund BS, Dhulappanavar GR, Ayachit NH. Comparative evaluation of antibacterial activity of silver nanoparticles biosynthesized using fruit juices.J NanomedNanotechnol. 2015;6(2):1.

[62] .*Wikipedia, Nano-Instrument .*

[63]. Li Z, Wang Y, Shen J, Liu W, Sun X. The measurement system of nanoparticle size distribution from dynamic light scattering data. Opt Lasers Eng. 2014;56:94–8.

[64]. Tripathi RM, Gupta RK, Shrivastav A, Singh MP, Shrivastav BR, Singh P. Trichodermakoningii assisted biogenic synthesis of silver nanoparticles and evaluation of their antibacterial activity. Adv Nat SciNanosciNanotechnol. 2013;4(3):35005.

[65] .Roy K, Sarkar CK, Ghosh CK. Photocatalytic activity of biogenic silver nanoparticles synthesized using potato (Solanumtuberosum) infusion.SpectrochimActa Part AMolBiomolSpectrosc. 2015;146:286–91.

[66] .*Wikipedia, Institut Pasteur.*

[67]. Filipe V, Hawe A, Jiskoot W. Critical evaluation of nanoparticle tracking analysis (NTA) by NanoSight for the measurement of nanoparticles and protein aggregates. Pharm Res. 2010;27(5):796–810.

[68]. Gross J, Sayle S, Karow AR, Bakowsky U, Garidel P. Nanoparticle tracking analysis of particle size and concentration detection in suspensions of polymer and protein samples: influence of experimental and data evaluation parameters.Eur J Pharm Biopharm. 2016;104:30–41.

[69]. Rodrigues MC, Rolim WR, Viana MM, Souza TR, Gonçalves F, Tanaka CJ,et al. Biogenic synthesis and antimicrobial activity of silica-coated silver nanoparticles for esthetic dental applications. J Dent. 2020;96: 103327.

[70] .*Wikipedia, GeorgyShafeev/Shutterstock.*

[71]. Balaji S, Mandal BK, Vinod Kumar Reddy L, Sen D. Biogenic ceria nanoparticles (CeO2 NPs) for effective photocatalytic and cytotoxic activity.Bioengineering. 2020;7(1):26.

[72]. Sankar S, Sharma SK, Kim DY. Synthesis and characterization of mesoporous SiO2 nanoparticles synthesized from biogenic rice huskash for optoelectronic applications. Int J Eng Sci. 2016;17(1):353–8.

[73]. Naderi, M., 2015. Surface area: brunauer–emmett–teller (BET). In *Progress in filtration and separation* (pp. 585-608).Academic Press.

[74]. Ghotekar S, Pansambal S, Pawar SP, Pagar T, Oza R, Bangale S. Biological activities of biogenically synthesized fluorescent silver nanoparticles using Acanthospermumhispidumleaves extract. SN Appl Sci.2019;1(11):1–12.

[75]. Epp J. X-ray diffraction (XRD) techniques for materials characterization.In: Materials characterization using nondestructive evaluation (NDE)methods. Elsevier; 2016. p. 81–124.

[76]. Hazarika M, Borah D, Bora P, Silva AR, Das P. Biogenic synthesis of palladium nanoparticles and their applications as catalyst and antimicrobial agent. PLoS ONE. 2017;12(9): e0184936.

[77] .*https://www.ebatco.com/laboratory-services/x-ray-diffraction/*

[78] .Groarke R, Vijayaraghavan RK, Powell D, Rennie A, Brabazon D. Powder characterization—methods, standards, and state of the art. In:Fundamentals of laser powder bed fusion of metals. Elsevier; 2021.p.491–527.

[79]. Goldstein JI, Newbury DE, Michael JR, Ritchie NWM, Scott JHJ, Joy DC.Scanning electron microscopy and X-ray microanalysis. Cham: Springer;2017.

[80] .*infinitalab.com, and Wikipedia.*

[81]. Otten MT. High-Angle annular dark-field imaging on a tem/stem system. J Electron Microsc Tech. 1991;17(2):221–30.

[82].Utsunomiya S, Ewing RC.Application of high-angle annular dark field scanning transmission electron microscopy, scanning transmission electron microscopy-energy dispersive X-ray spectrometry, and energyfiltered transmission electron microscopy to the characterization of nanopar. Environ Sci Technol. 2003;37(4):786–91.

[83]. Kimber RL, Lewis EA, Parmeggiani F, Smith K, Bagshaw H, Starborg T, et al. Biosynthesis and characterization of copper nanoparticles using Shewanellaoneidensis: application for click chemistry. Small. 2018;14(10):1703145.

[84] .*JEOL Ltd., and Vrogue.co*

[85]. Sneha K, Sathishkumar M, Lee SY, Bae MA, Yun Y-S. Biosynthesis of Au nanoparticles using cumin seed powder extract.J NanosciNanotechnol. 2011;11(2):1811–4.

[86]. Huo Y-C, Li W-W, Chen C-B, Li C-X, Zeng R, Lau T-C, et al. Biogenic FeS accelerates reductive dechlorination of carbon tetrachloride by ShewanellaputrefaciensCN32. Enzyme Microb Technol. 2016;95:236–41.

[87].Manor J, Feldblum ES, Zanni MT, Arkin IT. Environment polarity in proteins mapped noninvasively by FTIR spectroscopy. J PhysChemLett. 2012;3(7):939–44.

[88]. Chevali V, Kandare E. Rigid biofoam composites as eco-efficient construction materials. In: Biopolymers and biotech admixtures for ecoefficient construction materials. Elsevier; 2016. p. 275–304.

[89]. Składanowski M, Golinska P, Rudnicka K, Dahm H, Rai M. Evaluation of cytotoxicity, immune compatibility and antibacterial activity of biogenic silver nanoparticles. Med MicrobiolImmunol. 2016;205(6):603–13.

[90]Sikora A, Bartczak D, Geißler D, Kestens V, Roebben G, Ramaye Y, et al. A systematic comparison of different techniques to determine the zeta potential of silica nanoparticles in biological medium.Anal methods. 2015;7(23):9835–43.

[91]. Gavade NL, Kadam AN, Suwarnkar MB, Ghodake VP, Garadkar KM.Biogenic synthesis of multi-applicative silver nanoparticles by using Ziziphusjujubaleaf extract.SpectrochimActa Part A MolBiomolSpectrosc. 2015;136:953–60.

[92]. Edison TJI, Sethuraman MG. Biogenic robust synthesis of silver nanoparticles using Punicagranatumpeel and its application as a green catalyst for the reduction of an anthropogenic pollutant 4-nitrophenol.SpectrochimActa Part A MolBiomolSpectrosc. 2013;104:262–4.

[93]. Ballottin D, Fulaz S, Souza ML, Corio P, Rodrigues AG, Souza AO, et al. Elucidating protein involvement in the stabilization of the biogenic silver nanoparticles. Nanoscale Res Lett. 2016;11(1):1–9.

[94]. Fayaz AM, Balaji K, Girilal M, Yadav R, Kalaichelvan PT, Venketesan R. Biogenic synthesis of silver nanoparticles and their synergistic effect with antibiotics: a study against gram-positive and gram-negative bacteria. NanomedNanotechnolBiol Med. 2010;6(1):103–9.

[95]. Chooto P. Cyclic voltammetry and its applications. In: Voltammetry. IntechOpen; 2019.p. 1.

[96]. Khan AU, Wei Y, Khan ZUH, Tahir K, Khan SU, Ahmad A, et al. Electrochemical and antioxidant properties of biogenic silver nanoparticles.Int J Electrochem Sci. 2015;10(10):7905–16.

[97]. Roy N, Mondal S, Laskar RA, Basu S, Mandal D, Begum NA. Biogenic synthesis of Au and Ag nanoparticles by Indian propolis and its constituents.Colloids Surf B Biointerfaces. 2010;76(1):317–25.

[98].Long DA.Raman spectroscopy. New York. 1977;1.

[99]. Huang M, Yan H, Chen C, Song D, Heinz TF, Hone J. Phonon softening and crystallographic orientation of strained graphene studied byRaman spectroscopy. ProcNatlAcad Sci. 2009;106(18):7304–8.

[100]. Prasad C, Yuvaraja G, Venkateswarlu P. Biogenic synthesis of Fe3O4 magnetic nanoparticles using Pisumsativumpeels extract and its effect on magnetic and methyl orange dye degradation studies. J MagnMagnMater. 2017;424:376–81.

[101]. Lin T, Song Y-L, Liao J, Liu F, Zeng T-T.Applications of surfaceenhanced Raman spectroscopy in detection fields. Nanomedicine.2020;15(30):2971–89.

[102]. Lahr RH, Vikesland PJ. Surface-enhanced Raman spectroscopy (SERS)cellular imaging of intracellulary biosynthesized gold nanoparticles.ACS Sustain Chem Eng. 2014;2(7):1599–608.

[103]. Skoog DA, Holler FJ, Crouch SR, editors.Principles of instrumental analysis (7th edn). Boston, USA: Cengage learning; 2017. ISBN 978-1-305-57721-3

[104].Fayaz M, Tiwary CS, Kalaichelvan PT, Venkatesan R. Blue orange light emission from biogenic synthesized silver nanoparticles using Trichodermaviride.Colloids Surf B Biointerfaces. 2010;75(1):175–8.

[105]. Al-Hakkani MF. Biogenic copper nanoparticles and their applications: a review. SN Appl Sci. 2020;2(3):1–20.

[106]. Harne S, Sharma A, Dhaygude M, Joglekar S, Kodam K, Hudlikar M. Novel route for rapid biosynthesis of copper nanoparticles using aqueous extract of CalotropisproceraL. latex and their cytotoxicity on tumor cells. Colloids Surf B Biointerfaces. 2012;95:284–8

[107]. Ismail M, Gul S, Khan MI, Khan MA, Asiri AM, Khan SB. Green synthesis of zerovalent copper nanoparticles for efficient reduction of toxic azo dyes congo red and methyl orange.

Green Process Synth.
2019;8(1):135–43.
[108]. Hassanien R, Husein DZ, Al-Hakkani MF. Biosynthesis of copper nanoparticles using aqueous Tilia extract: antimicrobial and anticancer activities. Heliyon. 2018;4(12): e01077.
[109]. Suresh Y, Annapurna S, Bhikshamaiah G, Singh AK. Green luminescent copper nanoparticles. In: IOP Conference Series: Materials Science and Engineering. IOP Publishing; 2016.p. 12187.
[110]Zhang P, Hong RY, Chen Q, Feng WG. On the electrical conductivity and photocatalytic activity of aluminum-doped zinc oxide. Powder Technol. 2014;253:360–7.
[111]. Karthik K, Vijayalakshmi S, Phuruangrat A, Revathi V, Verma U. Multifunctional applications of microwave-assisted biogenic TiO2 nanoparticles. J Clust Sci. 2019;30(4):965–72.
[112]Jayabalan J, Mani G, Krishnan N, Pernabas J, Devadoss JM, Jang HT.
Green biogenic synthesis of zinc oxide nanoparticles using Pseudomonas putidaculture and its In vitro antibacterial and anti-biofilm
activity. BiocatalAgricBiotechnol. 2019;21: 101327.
[113]. Gawade VV, Gavade NL, Shinde HM, Babar SB, Kadam AN, GaradkarKM.Green synthesis of ZnO nanoparticles by using Calotropisproceraleaves for the photodegradation of methyl orange. J Mater Sci Mater Electron.2017;28(18):14033–9.
[114]. Claxton J, Joudeh N, Røyne A, Linke D, Mikheenko P. Sequential magnetic mapping of bacteria loaded with Pd-Fe nanoparticles. In: 2020 IEEE 10th International conference nanomaterials: applications &properties (NAP). IEEE; 2020. p. 1–5.
[115]. Campaña AL, Joudeh N, Høyer H, Røyne A, Linke D, Mikheenko P. Probing van der Waals and magnetic forces in bacteria with magnetic nanoparticles. In: 2020 IEEE 10th International conference nanomaterials: applications & properties (NAP). IEEE; 2020.p. 01NSSA03-1.
[116]. Albrecht M, Janke V, Sievers S, Siegner U, Schüler D, Heyen U. Scanning force microspy study of biogenic nanoparticles for medical applications. J MagnMagn Mater. 2005;290:269–71.
[117]. Campaña AL, Joudeh N, Mikheenko P, Linke D. Magnetic decoration of Escherichia coli loaded with Palladium nanoparticles. In: 2021 IEEE 11th International conference nanomaterials: applications and properties (NAP). IEEE; 2021. p. 1–5.

[118]Tovar GI, Briceño S, Suarez J, Flores S, González G. Biogenic synthesis of iron oxide nanoparticles using Moringaoleiferaand chitosan and its evaluation on corn germination. Environ NanotechnolMonit Manag.2020;14: 100350.

[119]. Sawicki M, Stefanowicz W, Ney A. Sensitive SQUID magnetometry for studying nanomagnetism. SemicondSci Technol. 2011;26(6):64006.

[120]. Enpuku K, Minotani T, Gima T, Kuroki Y, Itoh Y, Yamashita M, et al.Detection of magnetic nanoparticles with superconducting quantum interference device (SQUID) magnetometer and application to immunoassays. Jpn J Appl Phys. 1999;38(10A):L1102.

[121]Byrne JM, Coker VS, Cespedes E, Wincott PL, Vaughan DJ, PattrickRAD,et al. Biosynthesis of zinc substituted magnetite nanoparticles with enhanced magnetic properties. AdvFunct Mater. 2014;24(17):2518–29.

[122]. Atherton NM, Davies MJ, Gilbert BC.Electron spin resonance. Vol. 14.Royal Society of Chemistry; 1994.

[123]. Nasibova A, Khalilov R, Abiyev H, Trubitsin B, Eftekhari A. Identification of the EPR signals of fig leaves (Ficuscarica L.). Eurasian ChemCommun. 2021;3(3):193–9.

[124].Tompkins H, Irene EA. Handbook of ellipsometry.William Andrew; 2005.

[125]. Losurdo M, Bergmair M, Bruno G, Cattelan D, Cobet C, de Martino A, et al. Spectroscopic ellipsometry and polarimetry for materials and systems analysis at the nanometer scale: state-of-the-art, potential, and perspectives. J Nanoparticle Res. 2009;11(7):1521–54.

[126]. Moirangthem RS, Yaseen MT, Wei P-K, Cheng J-Y, Chang Y-C.Enhanced localized plasmonic detections using partially-embedded gold nanoparticles and ellipsometric measurements. Biomed Opt Express.2012;3(5):899–910.

[127]. Lakhwani G, Roijmans RFH, Kronemeijer AJ, Gilot J, Janssen RAJ, Meskers SCJ. Probing charge carrier density in a layer of photodopedZnO nanoparticles by spectroscopic ellipsometry. J PhysChem C.
2010;114(35):14804–10.

[128]. Ontong JC, Singh S, Nwabor OF, Chusri S, Voravuthikunchai SP. Potential of antimicrobial topical gel with synthesized biogenic silver nanoparticle using Rhodomyrtustomentosa leaf extract and silk sericin.BiotechnolLett. 2020;42(12):2653–64.

[129] .Thomas S, Thomas R, Zachariah AK, Kumar R. Thermal and rheological measurement techniques for nanomaterials characterization, vol. 3.Amsterdam: Elsevier; 2017.

[130] .Saadatkhah N, Carillo Garcia A, Ackermann S, Leclerc P, Latifi M, SamihS,et al. Experimental methods in chemical engineering: thermogravimetric analysis—TGA. Can J Chem Eng. 2020;98(1):34–43.

[131]. Shah A, Lutfullah G, Ahmad K, Khalil AT, Maaza M. Daphne mucronatamediatedphytosynthesis of silver nanoparticles and their novel biological applications, compatibility and toxicity studies. Green ChemLett Rev. 2018;11(3):318–33.

[132].Healy JJ, De Groot JJ, Kestin J.The theory of the transient hotwire method for measuring thermal conductivity.Physica B + c.1976;82(2):392–408.

[133]. Kumari MM, Philip D. Synthesis of biogenic SnO2 nanoparticles and evaluation of thermal, rheological, antibacterial and antioxidant activities. Powder Technol. 2015;270:312–9. .

[134]. Davis JR. Tensile testing.ASM international; 2004.

[135]. Batool S, Hussain Z, Niazi MBK, Liaqat U, Afzal M. Biogenic synthesis of silver nanoparticles and evaluation of physical and antimicrobial properties of Ag/PVA/starch nanocomposites hydrogel membranes for wound dressing application. J Drug DelivSci Technol. 2019;52:403–14. .

[136].Schuh CA. Nanoindentation studies of materials. Mater Today. 2006;9(5):32–40.

[137]. Xuexia Z. Mechanical properties of silica cells in bamboo measured using in situ imaging nanoindentation. Wood Fiber Sci. 2016;48(4):1–6..

[138]. Franck A, Germany TI.Viscoelasticity and dynamic mechanical testing. TA Instruments, New Castle, DE, USA AN004. 1993; .

[139]. Siripanth J, Wongwitthayakool P. Flexural strength and viscoelastic properties of acrylic resin denture base material containing silver nanoparticle synthesized from fingerroot aqueous extract. In: Key engineering materials. Trans Tech Publ; 2018. p. 178–82. .

[140]. Bettaieb F, Khiari R, Dufresne A, Mhenni MF, Belgacem MN. Mechanical and thermal properties of Posidoniaoceanica cellulose nanocrystal reinforced polymer. CarbohydrPolym. 2015;123:99–104. .

[141]. D. Bokov, A. TurkiJalil, S. Chupradit, W. Suksatan, M. Javed Ansari, I. H. Shewael, G. H. Valiev, E. Kianfar, Adv. In Mater.Sci.Engi.**2021**, 1, 21.https://doi.org/10.1155/2021/5102014.

[142]S. Horikoshi, N. Serpone, editors. Microwaves in Nanoparticle Synthesis: Fundamentals and Applications. John Wiley &Sons,Germany; **2013**. https://doi.org/10.1002/9783527648122.ch1 .

[143].Kumbhakar P, Ray SS, Stepanov AL. Optical properties of nanoparticles and nanocomposites.Hindawi; 2014

[144]. P. Peng, A. Hu, A. P. Gerlich, G. Zou, L. Liu, Y. N. Zhou, ACS Appl. Mater. Interfaces **2015**.https://doi.org/10.1021/acsami. 5b02134

[145]. A. V. Kalenski, A. A. Zvekov, M. V. Anan'eva, et al., Fiz.GoreniyaVzryva, **50**, No. 3, 98–104 (2014)

[146]. V. G. Kriger, A. V. Kalenskii, A. A. Zvekov, et al., Fiz. GoreniyaVzryva, **48**, No. 6, 54–58 (2012).

[147].. B. P. Aduev, M. V. Anan'eva, A. A. Zvekov, et al., Fiz.GoreniyaVzryva, **50**, No. 6, 92–99 (2014).

[148].E. M. Perassi, L. R. Canali and E. A.Coronado, J. Phys. Chem. C 113, 6315–6319 (2009).

[149]. I. I. Obraztsova, G. Yu. Simenyuk, and N. K. Eremenko, Zh. Prikl. Khim.,**84**, No. 6, 887–891 (2011).

[150]. A. A. Zvekov, A. V. Kalenskii, A. P. Nikitin, and B. P. Aduev, Komp. Opt., **38**, No. 4, 749–756 (2014).

[151]. K. Kolwa, A. Derkachova, and M. Shopa, J. Quant. Spectrosc. Rad. Transfer, **110**, Nos. 14–16, 1490–1501(2009). .

[152].M. Lismont, L. Dreesen, Comparative study of Ag and Au nanoparticles biosensors based on surface plasmon resonance phenomenon, Mater. Sci. Eng. C 32 (6) (2012) 1437–1442. Aug 1.

[153].S. Saravanan, R. Kato, M. Balamurugan, S. Kaushik, T. Soga, Efficiency improvement in dye-sensitized solar cells by the plasmonic effect of green synthesized silver nanoparticles, J. Sci. Adv. Mater. Devices 2 (4) (2017) 418–424.Dec 1..

[154]. N. Jardon-Maximino, ´ M. P´ erez-Alvarez, R. Sierra-Avila, ´ C.A. Avila-Orta, ´ E. Jim´enez-Regalado, A.M. Bello, P. Gonz´ alez-Morones, G. Cadenas-Pliego, Oxidation of copper nanoparticles protected with different coatings and stored under ambient conditions, J. Nanomater. 2018 (2018), 9512768, https://doi.org/ 10.1155/2018/9512768. Jan 1.

[155].B. Karmakar, T. Som, S.P. Singh, M. Nath, Nanometal-glass hybrid nanocomposites:synthesis, properties, and applications, Trans. Indian Ceram. Soc. 69 (3) (2010) 171–186. Jul 1.

[156].P. Shen, Y. Liu, Y. Long, L. Shen, B. Kang, High-performance polymer solar cells enabled by copper nanoparticles-induced plasmon resonance enhancement, J.Phys.Chem. C 120 (16) (2016) 8900–8906. Apr 28.

[157].S.K. Ghosh, T. Pal, Interparticle coupling effect on the surface plasmon resonance of gold nanoparticles: from theory to applications, Chem. Rev. 107 (11) (2007)4797–4862. Nov 14.

[158]. S.A. Shojaee, Y. Qi, Y.Q. Wang, A. Mehner, D.A. Lucca, Ion irradiation induced structural modifications and increase in elastic modulus of silica based thin films, Sci. Rep. 7 (1) (2017) 1–3. Jan 10.

[159].R. Singhal, D. Kabiraj, P.K. Kulriya, J.C. Pivin, R. Chandra, D.K. Avasthi, Blueshifted SPR of Au nanoparticles with ordering of carbon by dense ionization and thermal treatment, Plasmonics 8 (2) (2013) 295–305. Jun.

[160].R. Singhal, S. Gupta, R. Vishnoi, S. Aggarwal, G.D. Sharma, A. Sharma, S. Ojha, Optical properties of Cu-C70 nanocomposite under low energy ion irradiation, Mater. Res. Express 5 (3) (2018), 035044. Mar 28.

[161]. K. Kolwa, A. Derkachova, and M. Shopa, J. Quant. Spectrosc. Rad. Transfer, **110**, Nos. 14–16, 1490–1501(2009).

[162]. Jeanmaire, D. L; Van Duyne, R. P. J. Electroanal. Chem. 1977, 84, 1–20.

[163] . S. Asano and G. Yamamoto, Appl. Opt. 14(1), 29–49(1975).

[164]. K. Lance Kelly, Eduardo Coronado, Lin Lin Zhao, and George C. Schatz 2002, 60208-3113.

[165].Sagadevan S, Koteeswari P. Analysis of structure, surface morphology, optical and electrical properties of copper nanoparticles.J Nanomed Res. 2015;2(5):133–136. DOI: 10.15406/jnmr.2015.02.00040

[166].A. Henglein, P. Mulvaney, T. Linnert, Chemistry of Agn aggregates in aqueous solution: non-metallicoligmeric clusters and metallic particles. J. Faraday Discuss. 92 (1991) 31, DOI: 10.1039/
FD9919200031.

[167] .K. Kolwa, A. Derkachova, and M. Shopa, J. Quant. Spectrosc. Rad. Transfer, 110, Nos. 14– 16, 1490–1501(2009

[168]. U. Burkhardt, H. Borrmann, P. Moll, M. Schmidt, Y. Grin, and A. Winkelmann,Sci. Rep., 10, 1 (2020).

[169]. A. Venkateshaiah, V. V. Padil, M. Nagalakshmaiah, S. Waclawek, M. Černík, and R. S. Varma, Polymers, 12, 512 (2020).

[170]. D. Barceló and M. Farré, Analysis and Risk of Nanomaterials in Environmental and Food Samples (Oxford, Newnes) 59 (2012).

[171]. M. H. Nayfeh, Applications of Nano Silicon in Plasmonics and Fullerenes:Current and Future Trends (Elsevier, Amsterdam) (2018).

[172]. N. Raval, R. Maheshwari, D. Kalyane, S. R. Youngren-Ortiz, M. B. Chougule, and R. K. Tekade, (Academic, New York) 369 (2019).

[173]. E. Tomaszewska, K. Soliwoda, K. Kadziola, B. Tkacz-Szczesna, G. Celichowski, M. Cichomski, and J. Grobelny, J. Nanomater., 2013, 1-10 (2013).

[174].A. Dutta, Spectroscopic methods for nanomaterials characterization (Elsevier,Jaipur, India) 73 (2017).

[175].L. M. Moreau, D. H. Ha, H. Zhang, R. Hovden, D. A. Muller, and R. D. Robinson,Chem. Mater., 25, 2394 (2013).

[176].E. J. Munson, Analytical techniques in solid-state characterization (Academic press, New York) 61 (2009).

[177]. S. Loganathan, R. B. Valapa, R. K. Mishra, G. Pugazhenthi, and S. Thomas,Thermal and Rheological Measurement Techniques for Nanomaterials Characterization (Elsevier, Amsterdam) 67 (2017).

[178]. G. Greczynski and L. Hultman, Prog. Mater.Sci., 107, 100591 (2020).

[179]. K. Kolwa, A. Derkachova, and M. Shopa, J. Quant. Spectrosc. Rad. Transfer, **110**, Nos. 14–16, 1490–1501(2009).

[180]. P. B. Johnson and R. W. Christy, Phys. Rev., **B6**, No. 12, 4370–4379 (1972)

[181].S. Mohapatra, Y. K. Mishra, A. M. Warrier, et al., Plasmonics, **7**, No. 1, 25–31 (2012).

[182].B. P. Aduev, M. V. Anan'eva, A. A. Zvekov, et al., Fiz.GoreniyaVzryva, **50**, No. 6, 92–99 (2014).

[183]. Moritz, M.; Geszke-Moritz, M.The newest achievements in synthesis, immobilization and practical applications of antibacterial nanoparticles.Chem. Eng. J. **2013**, 228, 596–613.

[184].Jayarambabu N, Akshaykranth A, VenkatappaRaoT,VenkateswaraRao K, Rakesh Kumar R. "Green synthesis of Cu nanoparticles using Curcuma longa extract and their application in antimicrobial activity,". Mater.Lett. 2020;259:126813.

[185]. Pham ND, Duong MM, Le MV, Hoang HA, Pham LKO. "Preparation and characterization of antifungal colloidal copper nanoparticles and their antifungal activity against Fusariumoxysporum and Phytophthoracapsici,".ComptesRendusChim. 2019;22(11-12):786-93.

[186]. Zuniga JM, Cortes A. The role of additive manufacturing and antimicrobial polymers in the COVID-19 pandemic.Expert Review of Medical Devices. 2020 04 30;17(6):477-481. https://doi.org/10.1080/17434440.2020.1756771

[187]. Yugandhar P, Vasavi T, Uma Maheswari Devi P, Savithramma N. Bioinspired green synthesis of copper oxide nanoparticles from Syzygiumalternifolium (Wt.) Walp: characterization and evaluation of its synergistic antimicrobial and anticancer activity. Applied Nanoscience. 2017 08 23;7(7):417-427. https://doi.org/10.1007/s13204-017-0584-9

[188]. Varukattu NB, Vivek R, Rejeeth C, ThangamR,Ponraj T, Sharma A, Kannan S. Nanostructured pHresponsive biocompatible chitosan coated copper oxide nanoparticles: A polymeric smart intracellular delivery system for doxorubicin in breast cancer cells. Arabian Journal of Chemistry. 2020 01;13(1):2276-2286. https://doi. org/10.1016/j.arabjc.2018.04.012.

[189]. Assadi Z, Emtiazi G, Zarrabi A. Novel synergistic activities of tetracycline copper oxide nanoparticles integrated into chitosan micro particles for delivery against multiple drug resistant strains: Generation of reactive oxygen species (ROS) and cell death. Journal of Drug Delivery Science and Technology. 2018 04;44:65-70. https://doi.org/10.1016/j. jddst.2017.11.017

[190].Assadi Z, Emtiazi G, Zarrabi A. Hyperbranchedpolyglycerol coated on copper oxide nanoparticles as a novel core-shell nano-carrier hydrophilic drug delivery model. Journal of Molecular Liquids. 2018 01;250:375-380. https://doi.org/10.1016/j.molliq.2017.12.031

[191].M. Rafique, et al. "l P of," Opt. - Int. J. Light Electron Opt.2020;:p. 165138.

[192]. "Promethean Testing Copper Nanoparticles Gainst Viruses," 2020.[Online]. Available: Https://Www.Technicaltextile.Net/News/Promethean-Testing-Coppernanoparticles-Against-Viruses-266670.Html. [Accessed: 20-Jun-2020].

[193]. Vasantharaj S, et al. "Synthesis of ecofriendly copper oxide nanoparticles for fabrication over textile fabrics: Characterization of antibacterial activity and dye degradation potential,". J. Photochem. Photobiol. B Biol. 2019; 191(November 2018):143-9.