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Synthesis, Characterization and application of Copper Nano-Particles: A Review

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***Abstract*:- This review article presents a detailed report on the synthesis and characterization of copper nanoparticles (CuNPs). Different types of Nanoparticles, their importance in the present day, methods of synthesis, followed by characterization techniques are intensely reported. The synthesis of the Nanoparticles have been classified into physical, chemical and biological depending on their nature of origin and each of these syntheses has been explicitly reported. The characterization of the CuNPs by XRD, IR, TEM, DLS, UV-Visible, and HRTEM are clearly distinguished based on synthesis procedures. Many diagnostic studies to determine the physiochemical properties were reviewed which include TG-DTA, WAXD and EDAX. The XRD and electron diffraction technique confirms the formation of (FCC) copper nanoclusters. The applications in chemical, physical and biological fields and their importance in such fields have been presented exhaustively.**

Keywords: Nanoparticles; Copper; Antimicrobial; semi-conductors; Catalysis.

INTRODUCTION:

Nano particles acquire exclusive properties and find applications in various fields for which they are of great importance in the technological world.[1-3] The chemical surroundings, size and shape greatly influence the electronic, optical and catalytic properties of the nanoparticles.[4-5] Nanoparticles which are synthesized from plants are more beneficial in maintaining the cell culture rather than those prepared from biological methods.[6] Nano Particles are extremely small sized particles whose size range varies between 1 to 100 nanometers (nm) and these particles are enclosed by an interfacial layer. This interfacial layer incorporates organic molecules, inorganic molecules and ions. The coating of organic molecule over inorganic nanoparticles are normally referred to as capping agents or stabilizers.[7] Nano-sized particles are more beneficial when compared with biological macromolecules since they exert exclusive interactions with them and can be used in the treatment of cancer.[8] Nanoparticles are classified into three main types based on their structure they are single, two and three dimensional nanoparticles. Biological sensors, carbon nanotubes and Quantum dots are examples of the above three classification respectively.[9]

METAL NANOPARTICLES:

The size, shape and stability of the nanoparticles can be controlled by well-defined polymers such as dendrimers provided the size of the nanoparticles range between 1nm up to 4 or 5 nm.[10] Metal nanoparticles are primarily utilized for their distinctive properties in the field of catalytic, magnetic, magnetic and optical.[11-13]

MAGNETIC NANOPARTICLES:

The magnetic nanoparticles which are less than 5-500 nm in diameter can be used as an aid for the catalysts as they possess stunning properties. These can be used in the field of biomedicine, Magnetic Resonance Imaging, tissue-specific targeting, Nano-fluids, environmental remediation, and cation sensors and in optical fluids. These can be influenced by modifying the magnetic fields. These particles customarily accommodate two components: chemical and a magnetic component.[14]

ATTENTIVENESS TOWARDS COPPER NANOPARTICLES

The CuO nanoparticles are spherical in shape and they can engender apoptosis and they can curb the procreation of HeLa cells (cervical cancer cells). The CuO NPs have shown cytotoxic effects on HeLa cells.[8]The physical and chemical properties of the copper make it more suitable to be used for various applications. They are economical and hence they also play a key role in electronic circuits.[15] These Copper nanoparticles possess excessive surface to volume ratio and hence they interact well with other particles. They serve as sensors, catalysts, super strong materials and antibacterial materials over a long period of time.[13]The copper nanoparticles possess excellent antibacterial properties as they could inhibit the activity of bacteria like *E.coli* and *S. aureus* by penetrating through their dense cell walls.[16]

Copper nanoparticles revealed remarkable properties in the field of catalysts, lubricants, thermal transfer Nano-fluids and in optical devices.[17-21]The production of copper nanoparticles is quite easy as there are various methods which could yield them. Some of them are water- oil micro-emulsion, polyol reduction, supercritical CO_2 and through high-temperature decomposition of organometallic

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precursors.[22-25] Copper particles in the form as a catalyst could be employed in the fabrication of nanomaterials; e.g.; single-walled carbon nanotubes.[26] The copper nanoparticles exhibit tremendous antifungal and antibacterial properties.[27, 28] The absorption plasmon peak of the copper nanoparticles was found to be attained at Ca 570 nm.[29] Copper nanoparticles can be synthesized through various methods including photochemistry, electrode discharge, wet chemical reduction method and so on.[30-34] The morphology, size and the surface charge are the basis on which the nanoparticles are being characterized. This characterization is carried out using advanced microscopic techniques such as Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and Transmission Electron Microscopy (TEM). The distribution and the physical stability of the particle are influenced by the charge on the particle, the average diameter and the size distribution. Electron Microscope is employed in the determination of size, surface morphology and overall shape of the nanoparticles.[35] the copper nanoparticles are used for a number of applications like delivery of vaccines, delivery of genes, Nucleic acid transportation, Peptide transportation, specificity of cell, Silencing of Gene, mobilization of drug molecules, Internalization, efficacy improvisation and reduction in toxicity.[35]

ORIGIN:

Certain compounds possess antimicrobial properties, but their effect can be well seen only on Nano form and this lead to the origin of these compounds in Nano size. The copper nanoparticles are best known for their antimicrobial properties and this unique characteristic of these particles have been found out. It is due to Leaching action of these particles that make them an effective antimicrobial agent.[36] The nanoparticles could be generated when the compound is exposed water or humid air; for example, it is possible to obtain copper nanoparticles from copper wire upon oxidation and reduction under environmental conditions.[37] Even though a number of methods are employed in the fabrication of copper nanostructures, none of them are efficient enough in terms of large-scale production. This can be achieved at low temperature by following facile aqueous reduction technique.[38]

TYPES OF SYNTHESES:

Biological synthesis:

It is possible to synthesize the copper Nano-particles by ultrasonic treatment by copolymerizing and dispersing them with low volatile, good adhesive and widely applicable acrylic monomer. UVLED light source is used for irradiation and it is followed by the synthesis of acrylic functionalized copper Nano-particles, which are finally dried under vacuum.[39] Copper nanoparticles can be synthesized by microwave assisted one-pot method which uses the reducing agent hydrazine and the stabilizer *Psidiumguajava* leaf extract. Stock solution of $CuSO_4 \cdot 5H_2O$ is mixed with the leaf extract and hydrazine hydrate and the mixture is stirred well for 2mins and a pH of 5 is maintained. Color changes to deep yellow and after which the solution is exposed to microwave irradiation at a power of 720 W. The color change from orange to brick-red indicates the formation of CuNps.[40] Copper is not much effective in vivo delivery due to lack of suitable form. This can be overcome by synthesis of biocompatible copper Nano-particles from suitable microorganisms like copper resistant bacterial isolate obtained from copper mine. This microorganism was found exactly similar to *Bacillus cereus* and could resist copper ion up to a concentration range of 10mM. An SWSD1 isolate is grown and biomass is removed from it by centrifuging the culture and finally the supernatant is collected separately. The filtrate is adjusted for a particular pH, collected, incubated and then filtered to obtain copper Nano-particles.[41]The formation of fluorescent CuNPs template requires proper template that has to be designed and screened perfectly. We can synthesize fluorescent copper Nano-particles using the template of hairpin DNA along with poly T loop and random double-strand stem. This is achieved by diluting the stock solution of hairpin DNA to 0.5μM using a MOPS buffer and then blending it with 100 μm of $CuSO_4$. Ascorbic acid is added to the blended mixture and then incubated to obtain fluorescent CuNPs.[42]The copper Nano-particles can be synthesized in a single step by employing green methods of synthesis. This is achieved by incubating the leaf extract of *Impatiens balsamina* in a solution of copper sulfate and recording the absorption spectra at regular intervals. The appearance of light red colour indicates the generation of copper Nano-particles.[43]The copper Nano-particles can be synthesized by isolating the endophyticactinomycetes from the seaweeds. The synthesis involves isolation of colonies from the actinomycetes and centrifuging them. Supernatant is extracted and they are mixed with copper sulphate and this mixture is kept in a shaker and left overnight. They are further characterized and checked for antibacterial activity against pathogens.[44] The copper Nano-particles can be synthesized by mixing the copper chloride solution with the extract and refluxing the reactant mixture by using the reducing agent cyanide-O-3-glucoside, obtained from the skin of red plum at 65^0c and these synthesized particles can be used to inhibit the growth of Gram (+) and Gram (-).[45] Copper Nano-particles can be prepared by mixing 0.0001M of cupric acetate solution with 10 ml of the bud extract of *syngium aromaticum* in an eco-friendly manner. The color change form blue to pale bluish green indicates the formation of CuNPs. They are further purified by centrifuging at 10,000 rpm. The synthesized nanoparticles have zeta potential stability.[46]

CHEMICAL SYNTHESIS:

Under reflux condition, copper Nano-particles can be synthesized using hydrazine by reducing 2-ethoxyethanol and copper (II) acetate. This is carried out in an inert atmosphere. The similar procedure with water as a solvent is followed, to synthesize CuNPs from water.[47]Copper metallic Nano-particles can be synthesized from Copper Hydrazine Carboxylate (CHC) by two methods (i)

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Thermal process - in which thermal reduction occurs and the slurry obtained is centrifuged, washed and dried under vacuum. (ii) Sonochemical process- in which slurry of CHC is radiated and irradiated ultrasonically and then they are centrifuged washed and dried[48]. This process describes the method of hybrid Nano-composite production which consists of copper Nano-particles (3-10 nm) on a thin polyamide layer. The copper ions are doped over a polyamide matrix in the hydrogen atmosphere.[49]CuNps can be produced by following the synthesis of modified flame spray under reducing conditions. When soluble precursors of copper are introduced into a liquid fuel, fine black colored Nanopowders are obtained and these can be recovered from the flame top by using glass fibre filters.[50]The copper nanoparticles in an aqueous phase can be produced in a size controlled manner by sono-electrochemical method by using poly(N-vinylpyrrolidone) (PVP) as a stabilizer[51](Haas et al., 2006). Copper Nano-particles which are supported by alumina can be synthesized using aerogel protocol. Compounds like aluminiumisopropoxide and copper (II) acetylacetone are mixed, autoclaved at 10psi and then vented to yield aerogel material. This aerogel upon drying yields fine powder of nanoparticles.[52] The method of synthesis involves mixing up 20 mM copper (II) solution with 60 mM 1,2-hexadecandiol. The solution mixture is heated, stirred well and then mixed along with capping agents like oleylamine and oleic acid and they are allowed to cool and then precipitated. The precipitated Nano-particles were washed and dried thoroughly and the supernatant liquid was removed. The yield of the nanoparticles were examined for further analysis.[53]Precursor of Copper (II) acetylacetonate are decomposed thermally in the presence of a suitable surfactant to yield copper nanoparticles as well as Nanorods. These Nano-particles are found to have low dispersity and good stability and it increases with exchange of ligands.[54]Copper oxide-water Nano-fluid can be prepared in a spinning disk reactor (SDR) by synthesizing CuO nanoparticles. Reactants like sodium carbonate and copper (II) sulphatepentahydrate upon continuous liquid-liquid reaction leads to the formation of copper oxide precursors, which upon calcination up to 500 °C gives copper oxide Nano-particles.[55] Laser ablation can yield nanoparticles through laser pulses at 532 nm and 1064 nm. The NPs can be obtained in aqueous solutions of ligands, water or in pure acetone. The ligands include 1, 10-phenanthroline and 4,40-bipyridine and these can be adsorbed onto the metal surface through nitrogen lone pairs.[56] By reducing the $CuCl_2$ in the presence of the stabilizer like gelatin it is possible to synthesize copper nanoparticles. 10% of gelatin is mixed with 0.1 M solution of copper chloride solution. Later to the viscous solution of gelatin, Milli-Q water and copper chloride were added and the mixture is stirred well until the concentration of the copper salt attains 5.0 mM. Few drops of concentrated ammonia is added and the color change from green to blue is observed. This formation is reduced by addition of 5.0 M hydrazine, stirred, capped and left undisturbed which finally leads to the synthesis of CuNPs.[57]Colloidal copper nanoparticles can be synthesized by using gum acacia as capping agent, hydrazine hydrate as reducing agent and copper sulphate as copper precursor in aqueous solutions.[58] Copper is added to water to form an aqueous solution of copper sulfate. Ascorbic acid and PVP thus prepared are used as reducing agent and surfactant respectively. All the three solution thus prepared are mixed thoroughly and agitated with a magnetic stirrer. The reduction of copper sulfate by ascorbic acid leads to the formation of copper nanoparticles. Thus this study briefly describes the synthesis of water-based stable colloidal nanoparticles.[59] Copper nanoparticles can be synthesized by modified polyol process. The NPs thus obtained are highly pure, monodisperse and possess anti-oxidation properties. The precursor, reductant and the protector used are copper hydroxide, L-ascorbic acid and PEG-2000 respectively.[60] Copper Nano-particle scan be synthesized by mixing graphite along with methanol dissolved copper acetate monohydrate. The solution mixture is degassed in a hydrogen atmosphere and the produced solids were filtered and washed with acetone, water (deionized) and distilled methanol under vacuum conditions.[61] High concentration metallic CuNPs (300ppm) can be synthesized at room temperature in SDS solution by reducing the copper salt along with hydrazine. The change in color of the suspension from yellow to orange indicates the formation of CuNPs.[62] Copper nanoparticles can be obtained by following one-step synthesis which is described below. The copper chloride dehydrate is dissolved in a deionized water and to this mixture L-ascorbic acid is added in a drop-wise manner, stirred vigorously and allowed to stand for some time. The change in color of the solution from yellow to orange in the due course indicated the formation of Nanosized copper particles.[63]We can synthesize copper Nano-particles from supercritical water by using a flow type and a quartz tube batch type apparatus. The reducing agents are selected appropriately and their effects were determined. It has been found that very little quantity of formaldehyde is required for the method of supercritical hydrothermal synthesis to produce CuNPs.[64] Deionized water purified Bio choice Lignin, copper sulfate pentahydrate and nitric acid are used as he carbon source, metal catalyst and purification agent respectively. The mixture of copper sulfate and deionized water were dissolved in distilled water and they are heated, stirred, oven dried and sent to thermal treatment, where the particles in the furnace are cooled to argon atmosphere and then desiccated. Thus graphene encapsulated CuNPs were synthesized through Kraft lignin synthesis.[65] Chemical reduction methods are employed to synthesize copper Nano-particles in which surfactant like Aerosol-OT (AOT) are used. Strong reducing agents like NaBH4 are mixed with copper sulphate and water. This mixture on decomposition yields nanoparticles of copper.[66]The copper Nano-particles have found to exhibit property like high electrical conductivity. By photoreduction of a solution of copper acetate, we could get film of CuNP deposited over a substrate coated with TiO_2. Studies

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reveal that successive deposition of CuNP has led to high electrical conductivity and metallic luster. It has been found that, exposure of the film to fresh air will lead to decomposition of the film.[67]Capping agent Copper (II) acetate and the reducing agent tri-sodium citrate are taken in a beaker and mixed with thioacetamide. The obtained solution is mixed with double distilled water and allowed to stay at room temperature. The CuS nanoparticles will start to grow slowly and this suspension along with activated carbon is taken in an Erlenmeyer flask and they are kept for magnetic stirring. As a result CuS NPs are found to be deposited over the activated carbon thus Carbon supported CuSNPs are obtained.[68]Simple chemical reduction methods can yield copper nanoparticles in colloidal form by using octadecylsilane and octadecylamine as the reducing and stabilizing agent in toluene respectively. The copper (II) ions are reduced using suitable reducing agents like octadecylsilane and ODS is added to it in the presence of toluene at room temperature. The change in the color of the solution to black color indicates the formation of copper Nano-particles.[69]The CuO NPs can be synthesized by the following procedure. The colloidal copper oxide are hydrated and centrifuged at 1000rpm to get nanoparticles with small diameter.[70] Bimetallic nanocomposite (Ag-Cu) can be synthesized by the following method. Initially, a mixture of silver nitrate, hydrogen phosphate and $Cu(NO_3)_2 \cdot 2H_2O$ were mixed and stirred thoroughly. After sometime, the resulting precipitate is treated with ammonium hydroxide and is further taken in an electrolytic bath provided with three electrodes and finally the Ag-Cu nanoparticles gets deposited on glassy carbon electrode (GCE).[71] Copper Nano-particles can be produced by a simple and affordable method by stabilizing them in a polyvinyl alcohol-glycerol matrix. The produced Nano-particles occur in two forms (i) gel, (ii) moldable plastic.[72] L-His-Copper nanoparticles can be successfully synthesized by mixing Cu $(No_3)_2$ and L-histidine solution with Ascorbic Acid (AA) solution followed by magnetic stirring.[73] Fluorescence CuNPs can be synthesized at low cost by a simple method which employs ascorbic acid as a reducing and protective agent.[74]Reducing agents like carica papaya leaf extracts in aqueous form are mixed with silver nitrate and Cu $(NO_3)_2$.The mixture is heated and the conditions are optimized to yield small bimetallic (Ag-Cu) Nano-particles.[75]Copper nanoparticles can be synthesized in a fluoro-polymer matrix by annealing a thin film of metal with a thin fluoropolymer layer. This methods helps to retain the plasmonic properties by preventing their reduction due to the action of metal oxidation.[76] Polymeric matrix are used to synthesize CuNPs with narrow distribution of size and these particles can be stabilized under mild conditions. The film sample containing copper ions were dried, quantified by spectroscopic techniques and adjusted for required optical parameters. The soaked samples of the film are then stirred along with NaBH4, washed and oven dried.[77]Aqueous solutions of ascorbic acid, native cyclodextrin (NCD) and copper (II) sulfate are prepared separately. The aqueous copper solution thus prepared is heated in a round-bottomed flask and to this solution, the mixture of ascorbic acid and NCD are added in a dropwise manner. The change in color of the solution to dark yellow is noted and this is followed by formation of brown precipitate, which was then centrifuged at 4000 rpm for 10mins. The precipitate is washed and dried to obtain powdered copper nanoparticles.[78] Chemical co-precipitation method can yield Copper sulfide nanoparticles. pH of the solution is controlled from weakly acidic to basic pH (5.5-9.5) by using dilute HCl and ammonia solution. Copper acetate and sodium thiosulfate were dissolved in distilled water, stirred and cooled continuously. The product thus obtained is filtered, washed and dried to give Copper sulfide Nanopowders.[79]

PHYSICAL SYNTHESIS:

The production of copper Nano-particles with surfactants and polymers is influenced by several factors like pH, metal ion concentration, polymer or even by surfactant concentration. By optimizing these conditions, capped copper Nanoclusters can be produced by following the method of gamma radiolysis. It is possible to obtain small size up to 17nm by increasing the amount of capping agent. This radiolytic method is much better than the synthetic routes as it produces the nanoparticles in a highly pure and in a fully reduced state.[80] Spherical copper Nano-particles can be synthesized in a size controlled manner in an aqueous phase by following sono-electrochemical method. The stabilizer used for the copper cluster was Poly (N-vinylpyrrolidone) (PVP) and this PVP helps to increase the formation rate of copper particles and simultaneously reduces the deposition rate thus favoring the formation of mono-dispersed copper Nano-particles.[51] Micelle electrodeposition method produces a high yield of pyramidal copper Nano-particles on the gold substrate. Anisotropic Nanomaterials with unique structures can be fabricated by immersing the gold substrate in a copper ion containing the solution. Large quantities of Copper Nano-particles (up to 70%) are found to be synthesized on a gold substrate. The morphology of the Copper Nano-particles depends upon the concentration of the precursor, surfactant and the deposition time.[81] Copper Nano-particles can be synthesized in two hours by the method of direct thermal decomposition using the precursor brochantite at 750°c. This method is very efficient as it consumes less time, cheap raw materials and simple equipment to process. Owing to these advantages this method of synthesis is widely used in industries. [82] It is possible to produce copper Nano-particles in an Argon gas atmosphere by the method of wire-explosion in a controlled manner. The shape and yield of the Nano-particles can be modified by altering the application of the current density.[83] Spherical copper Nano-particles can be synthesized from gelled cellulose in an alkaline aqueous reaction condition. It is possible to obtain a hybrid material by following one-pot reaction and this hybrid material is capable of inhibiting the bacterial growth by 80%-95% after three days.[84]

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CHARACTERIZATION:

The morphology of the copper Nanoparticles has been studied manually and many types of equipment can be employed in the characterization of these particles. Various parameters like quantity of the stabilizing and reducing agent, pH, temperature, time of irradiation and power level were also investigated. Further, the degradation of the pollutants leads to the enhancement of the catalytic activity of the Nano-particles.[40]Several characteristics like zero potential, polydispersity index and particle size distribution have been found. The morphology of the particles was found to be uniform by conducting several microscopic techniques like SEM, TEM, and AFM.[41] Some sequences were found on the fluorescence of the CuNPs and upon the comparison of the sequences, it has been found that both the stem sequence and the circular poly T sequence play an adequate role in the enhancement of fluorescence.[42] Usual characterization techniques like XRD, UV-Vis and TEM were applied to verify the morphology, crystallinity and revealed the microstructure of the green synthesized Nano-particles. The mercury sensing ability and their photocatalytic ability are studied under empirical conditions.[43] The morphology of CuNPs synthesized from $CuCl_2$ is found to be quasi-spherical, they have a particles size of around 10 nm.[45]Size and shape of the Nano-particles are further known through morphological studies by using field emission scanning electron microscopy (FESEM), UV-Vis and TEM.[46] The copper nanoparticles thus synthesized are stable at room temperature.[80] The particle size is controlled by adjusting various parameters like temperature, sonic power, current density and deposition. Homogeneity of copper Nano-particles can be improved through size control. The synthesis of mono-dispersed copper Nano-particles depends mainly upon the transfer rate of PVP stabilized clusters between the cathodes and the bulk solution.[51]It has been observed that the surfactants in the electrolyte served with dual function (as a template and as a stabilizer). Several studies like Scanning Electron Microscopy, Fourier Transform Infra-Red test and HRTEM confirmed the Nano size of the produced particles and they are found to have a spherical shape with a particle size of 36.34 nm, which is confirmed by Scherrer's equation. The EDAX results show that the powder in the prepared sample has a major composition of copper and a very less composition of oxygen.[83]

Biological Characteristics:

The CuNPs synthesized from Marine endophyticactinomycetes are characterized to check their antibacterial action against various human pathogenic bacteria. The stabilization and capping were confirmed by FTIR analysis. Further analysis like EDX and TEM confirmed the presence and provided the size and shape of the synthesized particles.[44]

VARIOUS CHARACTERIZATION TECHNIQUES FOR COPPER NANOPARTICLES:

X-ray Diffraction (XRD):

Diffractometer is used to record the power XRD.[39] The Nano-particles were found to be spherical FCC structure with a size of about 15 nm according to the XRD studies.[40] The presence of the crystalline structure has been revealed by XRD spectral techniques.[41] The Seifert 3003TT XRD is used to analyze the structural properties of the synthesized CuNPs.[46] This diffraction confirms the phase formation and they also confirmed that the synthesized particles are in pure covellite phase.[79] The diffraction patterns were recorded on a Rigaku D/Max 250 with monochromated Cu Kα radiation (λ = 1.54 Å).[60] The XRD readings confirm the formation of CuNPs. Three peaks at 43 (111), 50 (200) and 74 (220) were observed. One of the major peaks obtained at 74° (at (311) plane) indicated the oxidation of CuNPs.[59] The results of XRD analysis confirmed that the synthesized product is metallic and possess an FCC structure.[78] The XRD pattern for the CuS powder has been attained in the range of 30-75^0 by scanning 2θ and the diffraction peaks for corresponding angles were obtained which shows that the CuS particles formed hexagonal covellite phase.[68] The estimated average size of copper crystallite was found to be 20nm. The compound contains 20% of Cu_2O as per the XRD data analysis.[84]

SCANNING ELECTRON MICROSCOPY (SEM):

This gives details about the structure morphology and they showed that the Nano-structures exhibited self-assembly due to agglomeration.[79] The SEM studies showed that the obtained particles exhibited a cubic and hexagonal morphology.[78] The SEM readings showed that the average size of the particles is 30 nm.[76] It has been found that the Copper oxide Nano-particles resemble the shape of a rod as shown by SEM image and has a length of 856 ± 5 nm and a diameter of 235 ± 5 nm. Tests were carried out to confirm the absence of Cu_2O in the synthesized copper Nano-particle.[82]

Raman spectroscopy:

Broad peak wavelength and excitation wavelength are obtained at 470 nm and 353 nm respectively.[79]

Field Emission Scanning Electron Microscope (FE-SEM):

It gives information regarding the size and morphology of the synthesized Copper Nano-particles.[60]This characterization showed that the surface morphology was homogeneous and relatively smooth. The size of the CuNPs was found to be in the range of 100-200 nm.[68]The distribution of polycrystalline Nano-particles (200-500nm) in a regenerated matrix of cellulose was confirmed by Field Emission scanning electron microscopy (FE-SEM) characterization.[84]

Laser Particle Analyzer:

Malvern ZetasizerNano ZS90 is used to analyze the size distribution of copper nanoparticles.[60]

X-ray Photoelectron Spectroscopy (XPS):

A multifunctional spectrometer PHI-5702 is used to record the spectra using an AI Kα X-ray excitation source.[60]

Fourier Transform Infrared Spectroscopy (FTIR):

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Thermo Nicolet IR200 spectrometer is used to record FTIR spectra.[39] The various functional groups of the copper Nano-particles have found to be involved in stabilizationaccording to the FTIR spectral studies.[40] The presence of protein structure has been revealed by FTIR spectral techniques.[41]For freeze-dried samples, FTIR spectroscopy is used.[46] The peaks were obtained in the range of 3549-3298 cm^{-1} with the characteristic peak at 1624cm^{-1}.[59] Since the Copper nanoparticles are in their pure form, the presence of their spectra does not occur in certain bands.[78] Spectra between 4000 and 1000 cm^{-1} were recorded using Vertex70 FT-IR-Spectrometer.[60] The scanning range obtained using an FT-IR was between 4000-400 cm^{-1} with an interval of three seconds.[65] The surface structure of the particles was observed using FT-IR and an absorption band was observed at 1633 cm^{-1}.[73] It confirms that the optical band gap of NPs varies with pH from 3.27 eV to 3.66 eV.[79]

UltraViolet Visible spectroscopy (UV-VIS):

Shimadzu MultiSpec-1501 spectrometer is used to record the UV-Vis spectra.[39] The UV-Vis spectra exhibit characteristics like surface plasmon resonance in the range of 561-572 nm.[40] The spectra of the sample were recorded with a wavelength range of 300-800 nm by using a Shimadzu UV-3600.[60] Particles showed spectra in the range of 200-700nm and an intense peak of 265 nm was observed in the absence of PVP and 600 nm in the presence of PVP with 0.53 as the maximum absorbance.[59] The changes in the resonance absorption peaks were monitored and examined by UV- visible spectrophotometry.

Surface Plasmon Resonance (SPR):

The Nano-particles thus produced in a cell-free filtrate has been characterized for morphology, surface plasmon resonance (SPR), spectroscopic properties and characteristics of the particle. The SPR peaks have been recorded and found to occur between 570–620 and 350–370 nm.[41]The SPR peaks for uncoated particles were obtained at a wavelength of 590 nm and for composite at 585 nm.[76]

TRANSMISSION ELECTRON MICROSCOPY (TEM):

The nanoparticles were found to be spherical FCC structure with a size of about 15 nm according to the TEM studies.[40] The TEM images reveal the uniform distribution of the obtained copper nanoparticles. Size of the copper nanoparticles can be determined using the Philips Tecnai 20 model electron microscope. It has a magnification capacity of 7,50,000× and has a resolution of 2Å.[59] The TEM studies showed that the particles are spherical in shape and the shell around them are not seen around the particle image as the particles are in their pure form. The size of the particles ranges from 2 to 33 nm.[78] The TEM results confirms the complete synthesis of the copper nanoparticles. It has also been reported that the particles are 2mm in diameter.[73]The copper particles thus produce have the size range between 17-18nm as revealed by transmission electron microscopy.[80]

HR-TEM:

HRTEM reports that the growth of CuNPs synthesized from $CuCl_2$ occurs in the (1 1 1) plane of the FCC crystal lattice.[45]The size distribution of the particles was analyzed by JEM 2100F HR-TEM device with the help of Image J software.[65]

Electron Spin Resonance:

The electron spin resonance confirms the purity of the produced copper particles.[60]

Wide Angle X-ray Diffraction (WAXD):

The Copper Nano-particles thus produced, when observed with a Wide Angle X-ray Diffraction is found to have (111), (200) and (220) crystalline orientation. They also possess a phase-pure FCC crystalline structure of the copper metal.[83]

APPLICATIONS:

Biological Applications:

The biologically synthesized copper Nano-particles can be used as a coating for domestic materials and in the development of anti-bacterial paints. They also help to reduce the possibility of fouling in marine environments. The synthesized copper Nano-particles can then be used as a biocide which offers better protection against the biofilm formation and due to their enhanced surface area they provide better control against leaching and thus are used in antifouling coatings.[39]CuNPs synthesized from micro-wave assisted one-pot synthesis exhibits antimicrobial activities against gram-negative *E.coli* and gram-positive *Staphylococcus aureus* when operated under specific dosage by the agar-well diffusion method. They also exhibit anti-oxidant potential by performing radical scavenging assays. Due to their enhanced thermal conductivity in water and ethylene glycol, they are used as heat transfer liquids. This method can be applied for synthesis of air-resistant CuNPs which in turn can be used for biological and industrial applications.[40]The biosynthesized copper Nano-particles are combined with the existing drugs and used to treat copper deficiency disorders like cardiovascular disorders, anemia, and osteoporosis. They also serve as a dietary supplement, biosensor, antimicrobial agent, cofactor for various enzymes and also used to in anticancer therapy.[41] The fluorescent copper Nano-particles synthesized from hairpin DNA template are used for the quantitative detection of NAD^+ and they have found to demonstrate very good sensitivity. The fluorescent CuNPs are also used in biochemical sensing.[42]The copper Nano-particles synthesized from *I. balsamina* through green technique can be used for the degradation of toxic organic dyes due to their enhanced photocatalytic property. They are also used in the detection on hazardous mercury ions up to a concentration of 1ppm. They are further employed in sewage treatment and in other wastewater management

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techniques due to their low toxicity.[43]It has been confirmed that the actinomycetes assisted synthesis of copper Nano-particles exhibited better control over human pathogenic bacteria[44], Since the copper Nano-particles act as a container for electron exchange with the microorganism they exhibit a better antimicrobial and inhibiting action against the pathogens like *Staphylococcus saprophyticus, Pseudomonas aeruginosa, and Staphylococcus epidermidis*.[45] The copper Nano-particles synthesized from *syzygiumaromaticum* bud extract exhibits antimicrobial activity against pathogens and they have shown zone of inhibition against *Bacillus*spp. and *Penicillium* spp. at 8mm and 6mm respectively.[46]

CHEMICAL APPLICATIONS:

The metallic copper nanoparticles thus synthesized have better catalytic activity than that of commercial powder and hence they are used to increase the rate of Ullmann's reaction, and are also employed in preparation of binary alloys of metallic clusters.[48] The copper nanoparticles thus synthesized are employed as intermediates for manufacture of variety of drugs.[52] The CuNPs thus synthesized in a size controlled manner can be used in the field of catalysis and for sensing chemicals.[53]The synthesized Nano-particles which are soluble in water are found to exhibit long-term stability and they possess excellent anti-fungal properties.[54]The CuNPs with high antibacterial potency exhibited antibacterial activity against gram-negative *E-coli*, by following the methods of flow cytometry, agar plating and phase contrast microscopy.[57]The CuNPs have proven to exhibit excellent antibacterial activity than silver NPs and other antibiotics. They also exhibited some anti-fungal properties.[62]The colloidal copper Nano-particles synthesized by the chemical reduction method can be effectively used as an active substrate for SERS and they also exhibit an SERS enhancement factors in the order of 10^3.[69]The CuO NP antibody conjugates thus synthesized can be used for application in sensitive areas of analysis like clinical and biological fields. They are also used in hybridization of DNA and in metalloimmunoassay of ETAAS.[70] Bimetallic Ag-Cu NPs find a wide application in the field of biosensor, optics and in electronics.[71]These copper Nano-particles find application as a catalyst in alkyne and azide. They also possess excellent antibacterial action against gram (+) and gram (-) bacteria.[72] The copper nanoparticles are employed to determine the presence of cyanide ions in aqueous solution by acting as a fluorescence probe.[74] The synthesized Bimetallic (Ag-Cu) NPs are efficiently used in purification of water and helps them from the contamination of pesticides.[75] Dispersion of Cu NP onto the mixture of polyol solution of copper hydroxide will lead to formulation of Copper based conductive ink. This ink can be further used for the manufacture of printing circuit board. Thus these can be considered as an economical material for printed electronics.[60]The heat transfer characteristics can be improved by adding the copper nanoparticles to a suitable base fluid. It has been observed that the values of Nusselt number and the heat transfer coefficient varies linearly with the concentration of the obtained CuNps.[59] Thus the Copper nanoparticles thus obtained can be used as a substitute in the place of silver NPs in plasmonic materials.[76]The synthesized CuNps by chemical reduction method acts as a sensor in detecting the Fe^{3+}ion in samples of water.[73]

Physical Applications:
Mono and Bimetallic Nano-particles have large surface area, and they help in enhancement of catalytic activity and hence are widely used in application of catalysis and semiconductors.[60] The size control of the synthesized copper Nano-particles yields several applications like hydrocarbon catalytic conversion, electron for sensor chemical application and for scanning probe applications.[81] The fingerprint identification of the copper nanoparticles is facilitated by Fourier Transform Infra-Red test (FTIR) in the wire explosion method.[83]Thus a wide range of hybrid materials of specific characteristics could be designed by following this synthesis and they could be employed in areas like the packaging of food, functional textiles, for electronic application as well as in catalysis.[84]

CONCLUSION:

Copper Nano-particles, which are the metallic based Nano-structured materials have established an alluring field in the overall science for their unremitting appraisals and in pursuit of their acceptable unique properties. Copper nanoparticles are a division of materials with properties which differ from their distinctiveness and find use in diverse areas such as Magnetic, Food, electronic, Biologocal and pharmaceutical, Drug, cosmetic, Energy, catalytic and materials applications. Copper nanoparticles are emerging as useful and exceptional green catalysts whose efficiency is recognized to their applications as the size is in nanoscale. Several new utilitarian attempts have been made and they have been in development by employing the application of these Nano-particles.

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NOMENCLATURE:

S.NO:	ABBREVATION	EXPANSION
1.	CuNPs	Copper Nano Particles
2.	XRD	X-Ray Diffraction
3.	IR	Infra-Red Spectroscopy
4.	TEM	Transmission Electron Microscopy
5.	DLS	Dynamic Light Scattering
6.	UV-VIS	Ultra-Violet Visible Spectroscopy
7.	HRTEM	High Resolution Transmission Electron Microscopy
8.	TG-DTA	Thermo-Gravimetry/ Differential thermal Analysis
9.	EDAX or EDX	Energy Dispersive X-Ray Analysis
10.	WAXD	Wide Angle X-Ray Diffraction
11.	FCC	Face Centered Cubic
12.	MRI	Magnetic Resonance Imaging
13.	SEM	Scanning Electron Microscopy
14.	AFM	Atomic Force Microscopy
15.	SPR	Surface Plasmon Resonance
16.	UVLED	Ultra-Violet Light Emitting Diode
17.	FESEM	Field Emission Scanning Electron Microscopy
18.	FTIR	Fourier Transform Infra-Red Spectroscopy
19.	XPS	X-Ray Photoelectron Spectroscopy
20.	SERS	Surface Enhanced Raman Scattering
21.	*S.aureus*	*Staphylococcus aureus*
22.	*E.coli*	*Escherichia Coli*
23.	CO_2	Carbon dioxide
24.	Ca	Calcium
25.	$CuSO_4.5H_{2O}$	Copper sulfate pentahydrate
26.	$CuCl_2$	Copper (II) chloride
27.	TiO_2	Titanium dioxide
28.	CuS NP	Copper (II) Sulfide Nanoparticle
29.	CuO NP	Copper (II) Oxide Nanoparticle
30.	Ag-Cu	Silver-Copper alloy
31.	HCl	Hydrochloric acid
32.	DNA	Deoxyribonucleic acid
33.	NAD^+	Nicotinamide adenine dinucleotide
34.	ETAAS	Electrothermal Atomic Absorption Spectrometry
35.	CHC	Copper Hydrazine Carboxylate
36.	PVP	poly (*N*-vinylpyrrolidone)
37.	SDR	Spinning Disk Reactor
38.	PEG	Poly Ethylene Glycol
39.	SDS	Sodium Dodecyl Sulfate
40.	AOT	Aerosol- OT
41.	GCE	Glassy Carbon Electrode
42.	AA	Ascorbic Acid
43.	NCD	Native Cyclo Dextrin
44.	eV	electron-Volt
45.	pH	Potential Hydrogen