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Review article

Cu Nanoparticle: Synthesis, Characterization and Application

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ABSTRACT

The applications of copper nanoparticle are gradually increased because of Cu is inexpensiveness and high abundance in nature. However, synthesis of copper nanoparticles is very challenging because of transformation from Cu nanoparticles into copper oxide in presence of air, though colloidal Cu NPs have significantly catalytic activity and biological applications. This review article exploring the synthesis of copper nanoparticles by different methods such as wet chemical, microemulsion, micro-oven assisted and thermal decomposition, moreover, explains about green and biological modes of synthesis. Some of the characterization methods for copper nanoparticle have discussed seem, electron microscopes and X-ray spectroscopy. Furthermore, applications of degrading treatment of textile effluents containing methylene blue dye and expose the mechanism of degradation. The copper nanoparticles show a catalytic activity in organic transformation, while have mentioned the biological application for anti-microbial and wound healing of copper NPs.

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Graphical Abstract

Introduction

The metal nanoparticle has varieties of application such as catalytically activity, energy storage and biological application [1]. However, the copper nanoparticle having a problem for stability. From the few decades, the scientists have been working on this nanoparticles, because copper has the affinity towards oxidation. Suppose comparing the copper nanoparticles and copper oxide nanoparticle having immense potential catalytical activity with the copper nanoparticles. Once copper gets oxidize than the catalytical activity of nanoparticles will reduce. Moreover the problem of agglomeration of nanoparticles. According to the periodic table, the copper resembles the properties of gold and silver. Therefore suppose we found some synthesis methods to a synthesis of this copper nanoparticle than we possibly use this kind of immense potential nanoparticle for some industrial application wherever we are using the expensive metal nanoparticle we can switch with this cheapest metal nanoparticles. However, the important is the synthesis methods that we will be discussing throughout the review article to get an idea what are chance to improve the methods and to get more stable nanoparticles [2].

Noble metal nanoparticles (NMN) have been utilized in various different fields such as catalysis, photonics, and electronics due to its unique optical, electronic, mechanical, magnetic, and chemical properties [3]. The metals contain a free electron which shows the Plasmon resonances in the visible spectrum and gives an appearance of such intense color. These characteristics mainly
observed in Au, Ag, and Cu metal due to a presence of the free conduction electrons. The nanoparticles are fabricated by physical and chemical methods experiencing impediments like an expensive reagent, hazardous reaction condition, longer time, slow process to divide nanoparticles. Therefore, it is essential to generate new approaches for the synthesis of nanoparticles; moreover, it is imperative to find the suitable and eco-friendly methods. Copper is profoundly conductive and also inexpensive than that of silver and gold. Notwithstanding, the aggregation of nanoparticle and oxidation to form copper oxide are the prominent problems involving the synthesis of copper nanoparticles. In contemporary decades, the researchers have been extensively interested in Cu NP due to its application in wound dressings, biocidal properties, and potential industrial for gas sensors, catalytic process, high-temperature superconductors and solar cells.

Cu nanoparticles also have been using for antibacterial pharmaceuticals, textiles photocatalysis, electrical conductors, biochemical sensors, oxidative capacity. The Cu NP possesses potentially appropriated in cooling fluids for electronic systems and conductive inks due to the Plasmon surface resonance properties. Though, in a proximity of encompassing atmospheric pressure and temperature synthesized particles converts into surface oxide layers due to its more stability in oxides rather than pure Cu [4]. To evade the aggregation several protecting agents are generally used i.e., polymer, organic ligand, biological chelating agent etc. It has been some methods for synthesized of Cu NP such as chemical reduction, thermal decomposition, laser ablation, electron beam irradiation. Among these methods, the chemical reduction method is superior because it is easy, economical and cheap. Too, it can help to achieve the better-presumed size by changing the molar ratio of reagent and concentration of the capping reagent. It is working as the antioxidant and chelating agent. Green synthesis gives the pure Cu NP by the anti-oxidant agent like ascorbic acid. Ascorbic acid is the driving force of anti-oxidant due to the scavenging the free radical and reactive oxygen molecules following the benefaction of the electron to form semi-dehydroascorbate radical and dehydroascorbic acid [5].

The necessary for cost-effective and environmental favorable bactericide materials increases steadily for numerous industries as well as conventional life, such as sterilization of medical instruments devices, water purification, and food industry. In multiple biological processes due to its inexpensiveness and congeniality in an environment, copper compounds (Cu) have more trends to substituted silver and composites of different precious metals [6]. Synthesis of copper nanoparticles by biological and eco-friendly ways is limited toxic, employ low energy, and lower the costs of synthesis and the conspicuous alternative of chemical and physical synthesis. Many researchers have been augmenting more interest in the synthesis of nanoparticles by green or
biological methods. In green or biological synthesis, living organisms like bacteria, fungi, and plants are employing for nanoparticles synthesis rather than hazardous chemical materials [7]. Copper nanoparticles show lower toxicity than gold, silver, and cobalt nanoparticles have been synthesizing by laser ablation method in biocompatible aqueous solvents for isolation of pure nanoparticles. According to Kim’s data, half Minimal Inhibitory concentration (IC50) of gold, silver, and copper in Hela and PC3 cell lines is 66.4 and 82.9 μg/mL, 78.9 and 88.6 μg/mL and 85.5 and 91.7 μg/mL respectively, suggesting lower cytotoxicity of copper NP [8].

Cu nanoparticles have a distinguished tendency towards bacterial filamentation and cell killing by a generation of reactive oxygen species, lipid peroxidation, protein oxidation and also DNA degradation in bacterial cells [9]. Reactive oxygen species are generated via electron transfer to the molecular oxygen which is stimulated by membrane integrated copper nanoparticles and cytoplasmic respiratory chains in E.coli strain [10]. The study shows copper nanoparticles have more inhibitory activity in bacteria rather than in fungi [11]. Use of copper nanoparticles in a manufacturing of bactericidal plasters, bandages, and medicines displays great potential in the biomedical field. Copper nanoparticles are notably toxic to microorganism though this antimicrobial activity exceedingly depends on the factors like synthesis conditions, size, aggregation status, polymers present on its surface and charge of nanoparticles in aqueous solutions as well as the type of microorganisms [12, 13].

**Growth and synthesis of Cu NP**

The synthesis of Cu NP is very challenging because it is sensitive to air oxidation. Its prevention from oxidation, capping agents like the organic ligand, biological ligand, and polymers are commonly it has to use. The study of the growth mechanism on Cu nanoparticles is essential to understand a synthetic method. The size and shape of nanoparticles could be controlled by the concentration of precursor and reaction condition. Predestinate, research has done computational and experimental learning but what is the exact procedure or mechanisms for synthesis is still not completely understood. The most common synthetic approach is “seed-mediated growth,” it could be conceivable by the reducing reagent [3]. Liu et.al have reported the preparation of Cu nanorods through seed-mediated growth by PVP as a surface stabilizer. The different growth mechanism observed by in Cu vapour formed by the one-step synthetic method and re-deposit on a substrate under a vacuum condition such as very low pressure to formed Cu nanostructure. Cu could be developed into rods like structure at low temperature on the supported amorphous carbon film. The Cu nucleation is the rough edge of the holes in the carbon film [14].
Synthesis and characterization of Cu nanoparticles

Cu nanoparticle has been challenging since immediate transfiguration of Cu oxide and precautionary steps of this conversion using the capping or protecting reagent. Currently so many methods for the fabrication of Cu nanoparticle are available, such as a) wet chemical synthesis, b) reverse micelles, c) microwave assisted, d) bio-synthesis, e) ionic liquid, e) sonochemical method, f) electrochemical, g) photochemical, h) thermal treatment, i) atomic layer deposition, k) supercritical condition, l) sputtering etc. Among these methods, a most noticeable method is a wet chemical synthesis; nevertheless, a more modern method is available for selectivity and control the size. Wet chemical synthesis using reducing and capping reagents for reducing Cu$^{2+}$ to CuO and avoids the oxidation respectively. It has been some of the reducing agents such as sodium borohydride, hydrazine hydrate etc. and capping reagent like ascorbic acid, glucose, and organic ligand was being used during this synthesis. In this review article reconnoitre some of the synthesis methods of Cu nanoparticle i.e. wet chemical, physical and biological.

Synthesis of Cu nanoparticle by wet chemical

The surfactants have the unique class of the surface-active group help to control the growth of nanoparticles with the craved shape, size, surfactant architecture while they have individual property resembling self-assembly [17]. Wu et al., have synthesized Cu nanoparticle by reduction of cupric chloride with hydrazine. Furthermore, using a capping reagent as surfactant i.e., CTAB (Cetyltrimethylammonium bromide). The pH value 10 has adjusted by the ammonium solution [18]. Lisiecki et al., have prepared in SDS (sodium dodecyl sulphate), it was published that copper oxide was formed when SDS was below critical micellar concentration (CMC). The synthesis of Cu nanoparticles in an aqueous medium at a high cupric ion concentration including an inadequacy of any external inert gases was studied using the cationic surfactant cetyltrimethylammonium bromide (CTAB) as a capping agent [19]. Yu et al., have reported the chemical reduction method for fabricating monodisperse Cu nanoparticles utilizing water and glycol. The reduction rate of copper was higher in the glycol than water furthermore the amount of reducing agent reduced more. Ascorbic acid has novel properties i.e., scavenge free radical and reactive oxygen molecules, this quality plays a particularly important role in reducing reagent and antioxidation i.e., capping agent. Moreover, they were observed the stability of Cu nanoparticle by thermo-gravimetrically analysis and they started oxidized above 210 °C, the change in color of solution within water and glycol completely out the synthesis of Cu nanoparticles [20, 21]. Han-Xuan Zhang et al., stated the synthesis of facile of ultrafine Cu nanoparticles in an organic solvent, the nanoparticles in 1.4 to 3.5
has observed, further particles size reducing with respect to the accumulative the ratio of PVP and Cu precursor. The organic solvents used as ethylene glycol and pH co-effect have shown for formation of desired particle size [20].

**Figure 1.** Change of colour during synthesis of copper nanoparticles in A) Water B) Glycol. Reprinted with the permission from copyright 2009 Nanoscale Res Lett

**Microwave (MW) assisted synthesis**

The synthesis of metal oxide nanoparticle by employing microwave due to its capability of significant heating in chemical synthesis. Microwave heating is not only responsible for the reduction of metal oxide and formations of a nanoparticle; but at the same time reducing reaction is significant. Moreover, rapid heating is established by a microwave because the nanoparticles are readily aggregated when heating time held a long time. MW heating has been triumphantly appropriated to achieve smaller particles resembled these fabricated with normal heating. T. Nakamura et al., has reported monodispersed Cu nanoparticle managing the microwave and reducing reagent as alcohol. They have reported selective Cu nanoparticles *i.e.*, with or without surface Plasmon absorbance. Besides, no copper oxide observed in the electron diffraction pattern of Cu nanoparticle. Furthermore, they have used organic ligand as the longest alkyl chain for controlling the particle size. The reduction rate has depended upon the alkyl chain length attached to the precursor as well as the temperature of microwave [18, 19]. M.I. Dar et al., has studied microwave assisted reaction with the rapid reductive decomposition of copper acetylacetonate within reducing solvent as benzyl alcohol play an important role as capping and the managing the size of copper nanoparticles. The benzyl alcohol has been non-using aqueous solvent for the synthesis of nanomaterials [21].

**Synthesis of Cu nanoparticles by microemulsion method**

Q. Chen et al., have synthesized copper nanoparticle by copper chloride as a precursor and sodium borohydride as reducing reagent within the water in oil *i.e.*, reverse micelles. The microemulsion
has produced by Triton X-100, n-hexanol, cyclohexane and water. This microemulsion has nano-sized water droplets as separated in oil media and stabilized by surfactant molecules assembled at oil and water interface. The highly dispersed water pools have given to be ideal nanostructured reaction media or microreactors, that entity responsible for a formation of ultrafine and monodisperse nanoparticles [22]. J.N. Solanki et al., has synthesized the copper nanoparticles through microemulsion methods. The microemulsion has adapted from the Triton X 100, cyclohexane and water through the ratio of water and surfactant perform a key role in the synthesis. The size of core composition depends upon the ratio of water to surfactant. The microemulsion has thermodynamically enduring associations of amphiphilic surfactants which embed a nano-sized water core in contact with the hydrophilic head groups of the surfactants. The hydrophobic tails of the surfactant have solvated by a bulk consecutive phase solvent. Meanwhile, water-soluble polar and ionic substances have dissolved within the microemulsion water core, the coherent phase of the solvent has left substantially unaltered. The purpose of nanomaterial synthesis has effected by control the reactions in the water core. The size of the micelle core could characterize by an important parameter [23].

Synthesis of Cu nanoparticle by using the thermal decomposition
The synthesis of Cu nanoparticles through the wet chemical method possesses a chance of agglomeration of nanoparticles, to circumvent such problem then researcher motility towards the physical synthesis. In this review article, examine some physical methods such as thermal decomposition. R. Betancourt-Galindo et al., held deliberate fabrications of nanoparticles using the thermal decomposition method in the appearance of organic surfactant at high temperature. This method was utilized due to the formation of crystalline nanoparticles with size distribution control. It results that the Cu nanoparticle is reactive than Cu oxide. The fabrications of nanoparticles have used the thermal decomposition method in the port of organic surfactant at high temperature. The precursor copper chloride and sodium oleate was dissolved in a mixture of hexane, ethanol, and distilled the water. The solution was heated and refluxed for 4 h and transformed into a separation funnel for excreting the aqueous sediments. The organic phases with copper-oleate complex and hexane were immersed three times with the distilled water then it was shifted to the petri dish for evaporation and finally seize the residue. The residues were negotiated with oleic acid and phenyl ether and the reaction mixture was kept for 30 min at 250 °C [24].

Preparation of Cu nanoparticles plays the key role of pH
Liu Qingming et al., has analysed an effect of pH through a synthesis of Cu nanoparticle affecting
with size. The Cu nanoparticle synthesis by using PVP and ascorbic acid, besides the change of pH 3, 5, 7, 9 and 11. The pH has kept 5 or 7 then the formation of Cu(OH)$_2$ as precursor moreover 9 or 11 embodiments of Cu$_2$O, afterwards, stir for 10 min, however only pH 3 generation of Cu nanoparticles within 10 min. Furthermore, pH at 5 to 11 appeared copper oxide as intermediate and lengthened stir for 4 h then obtained as Cu nanoparticles. It was scrutinised with XRD pattern at pH 3 nanoparticles developed within 10 min, however the size of a particle was increased in pH 5 to 7, size was decreased and at pH 9 to 11, the copper nanoparticle could not obtain, therefore resolved that copper nanoparticle generally raised in pH reduction in average size. Cu$_2$O was created after stirring with 4 h outgrowths of possibility formation CuO. It is extremely challenging for reducing to form the Cu nanoparticle at pH 5 to 7 [25].

**Green and biological synthesis**

Somewhat, copper nanoparticles have generally used in accomplishing numerous medical expectations due to its immense toxicity towards microorganisms and its strength to cover up wound healing. The consequence of that the need for limited toxic nanoparticles rises and this can achieve by utilization of hazardous chemical obligation reduced while the synthesis. The living organism like microorganism and plant extract are immeasurable dilemmas for hazardous chemicals. Metal nanoparticles have been synthesizing by biological or green methods and organised into two divisions. The first division is bioreduction, in which metal nanoparticles have reduced by oxidation of certain enzymes already in the organisms [26], and a different category is a biosorption. In which several microbial organisms like bacteria, fungi, and also plant express peptides or customized cell walls, possess the ability to bind with metal ions for the establishment of stable complexes [27]. Several plants have been using for the synthesis of nanoparticles for green synthesis methods. Furthermore, for the green synthesis of nanoparticles, different parts of plants such as seed, stem, flower, and leaf are used exclusively amidst these plant extract are principally used for reduction of nanoparticles due to the bearing of fatty acids, alkaloids and flavonoids. Numerous researchers amalgamate copper nanoparticles by plant extract as a reducing agent as well as a capping agent. Extract of *Gloriosa Superba* L. [28], bark extract of *Punicagranatum* [29], 23 nm sized particles synthesized by T. Arjuna bark [30]. Reduction by an extract of *Ocimum sanctum* leaf extract protects the formation of copper nanoparticles within 8 to 10 minutes [31]. *Datura innoxia* (Solanaceae) extract, *Magnolia* leaf extract, *Artabotrys Odoratissimus* (Nag Champa), rebate by *Magnolia* leaf extract can produce copper nanoparticles ranging from 40 to 100 nm [32]. *Nerium Oleander* extract and L. ascorbic acid become an application in the reduction and stabilization of
copper nanoparticles [33]. Copper nanoparticles could likewise be integrated with a port of curd, milk, butter, soap nut, lime juice, and tamarind juice as capping agents in acidic solution while using CuSO₄ as a precursor in aluminium lined reaction vessel [34].

Facile use of green tea in the synthesis of nanoparticles improves constantly on account of its employment as a reducing agent, capping agent as well as a stabilizing agent in nanoparticle synthesis. Green, white, black and oolong teas these all teas originate from the same source of plant, which are the leaves of the *Camellia* sinensis plant. Green tea includes the chemicals such that, polyphenols [35], caffeine (approximately 3.5% of the total dry weight), theobromine (0.15–0.2%), theophylline (0.02–0.04%) and other methylxanthines, lignin (6.5%), organic acids (1.5%), chlorophyll (0.5%), theanine (4%), free amino acids (1–5.5%), numerous flavour-rich compounds, flavones, phenolic acids, depsides, carbohydrates, alkaloids, minerals, vitamins and enzymes [36, 37]. Copper particles synthesized at 100 °C are 20 nm in size and intimates tremendous growth interference efficiency toward gram-positive bacteria rather than gram-negative bacteria [38]. L-ascorbic acid, a ketolactone with two ionizable hydroxyl groups which provides two electrons for reducing the Cu²⁺ ion to CuO by preparing itself oxidized into dehydroascorbic acid. The study suggests, reduction of copper sulphate (CuSO₄. 5H₂O) starch mixtures by ascorbic acid at a higher temperature following mechanical stirring [39]. Nanoparticles synthesized by the greenway can be stabilized by various polymers similar Native cyclodextrin (NCD) [40], and chitosan because of its solubility, biocompatibility, few toxicities, associate in the reduction of nanoparticles as well as used capping agent is for stabilization of copper nanoparticles [41]. Reduction of copper sulphate pentahydrate by fruit juice of C. medical Linn and heat a mixture at higher temperature is optimising a time for copper particles synthesis within 15-20 minutes [42].

**Synthesized by microorganism**

Amid scant microorganisms, a researcher dispenses prominent interest in prokaryotes for synthesizing metallic nanoparticles due to multiple properties such as omnipresent in the environment, accommodation ability in various environment, fleet developing, cost-effective to encourage and the principal matter is that its growth condition like temperature, oxygenation and incubation time can readily be measured. The study explains alteration in the pH of the growth medium of microorganism during incubation leads to the generation of different sizes and shape of nanoparticles [7-43]. Microorganisms likewise play a significant role in the synthesis of copper nanoparticles. *Pseudomonas stutzeri* practised for the creation of spherical nanoparticles and if this bacteria isolated from wastewater is used for formation of a cubic nanoparticle by electroplating.
Morganella utilizes for the synthesis of polydisperity nanoparticles supporting aqueous physical environment [45]. Copper nanoparticles synthesized by fungi growing into a CuSO₄ solution for 96 h, at pH 5 [46]. *Penicillium* species such as *Penicillium Vaksmanii*, *Penicillium Aurantiogriseum* and *Penicillium citrinum*, isolated from soil, have been using for the synthesis of copper nanoparticles, where the monodispersity, pH, and concentration affected their morphology [47].

**Characterization of Cu nanoparticles**

The characterization of copper nanoparticle concludes size, shape, morphology, structure, and coating of nanoparticles. The electron microscopes are using the conclusion of all mentions aspects exceptional of coating it can be possible by the IR spectroscopy. In this review article, we are exploring some technique *i.e.*, TEM, SEM, moreover XRD and XPS also explain.

**Scanning electron microscopy (SEM)**

Electron microscopy source of light is electrons for higher resolution. The source of electrons begetting energy varying from several hundred eV to 50 KeV, concentrated into a beam with a spot size of ~5 nm. Collision and penetration of electrons from the surface leads to a number of synergies, because of emission of electrons and photons, images are produced on cathode ray tube (CRT). SEM technique is categorised into versatile assortments on the evidence of the factors such as disclosure and imaging capacity. Based on the preceding circumstances SEM technique separates into 3 types: 1) secondary electron image, 2) backscattered electron image, 3) elemental X-ray maps. Interaction of primary electron with atoms represents to elastic and inelastic scattering with an atomic nucleus and atomic electrons respectively. The inelastic collision, electrons transfer its energy to other electrons and the ejected electrons have lower energy than the primary electrons is held to as a secondary electron whereas backscatter is an elastic scattering of electrons having the same energy as a primary electron. The third type of the SEM, primary electrons collides with the core electrons emanating from excited atoms which regain its ground state by emitting characteristic X-ray photons or an Auger electron both are used for chemical characterization [85]. SEM has an ability to contribute morphology and microstructure of bulk as well as nanostructures and also renders chemical composition and distribution. Energy-dispersive X-ray spectroscopy (EDS, EDX, EDXS or XEDS) also called an energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA) is widely used for the elemental analysis or chemical composition of a sample. EDX works on the principle of an interaction of some source of X-ray excitation and a sample. Due to a variance in their atomic structures, every single element proffers
the individual assortment of peaks on its electromagnetic emission spectrum. Bombardment of high energy particles on an atom which contains ground state electrons results in the formation of electron-hole by releasing an excited electron from the inner shell. An electron from the outer shell and higher energy shell try to fill the empty shell and this energy disparity between the high-energy shell and the lower energy shell may be dispensed under the form of an X-ray. This could be covered by an energy-dispersive spectrometer. Emitting X-rays helps to identify specific elements and its proportion. For SEM sample analysis samples are exhausted within a powder and positioned on a sample holder and subsequent coating by a conductive metal like gold by using a sputter coater [48, 49]. H.M. Hossein et al., have formed a copper nanoparticle with the help of non-ionic surfactant i.e., triton X 100, tween 80, dodecylamine, the non-ionic surfactant used as capping agents. The copper nanoparticles have produced by the decomposition of copper oxalate in the presence of triphenylphosphine. Moreover, inquired by the different characterisation methods and recorded the SEM images for surface morphology (Figure 2). The three types of surfactants have used and record the size of nanoparticles in between 8 to 20 nm. Dodecylamine has built approx. 8 nm, although largest particles in Triton X 100, however, highest yield and uniform particles size [50].

![Figure 2. SEM images of copper nanoparticles. Reprinted with the permission from copyright 2010 microchim acta](image)

**Transmission electron microscopy (TEM)**

A transmission electron microscopy is an indispensable instrument for material science. A high energy electron beam is used as a light source and those electrons are relinquished through a very rare sample and the interactions between the electrons and the atoms can be used for various meanings like to perceive crystal structure, dislocations, grain boundaries, study the growth of layers, their composition, defects in semi conductors and due to its high resolution, it can be used
for analyzing the quality, shape, size, density of quantum wells, wires, nanoparticles, and dots. The typical TEM thin films of a specimen are irradiated by the uniform electron beam which catches through a column containing two or three stage condenser system under vacuum pressure and magnifies by that and noticed on the fluorescent screen and also digitally recorded. Electromagnetic lenses in condenser have the ability to focus the electrons into a very thin beam. The based on the density of the materials remarkable electrons are scattered and eliminate from the beam and the unscattered electrons hit a fluorescent screen at a bottom. Preparation of sample for TEM analysis is simple, a material which requires to be crammed put for drying on the carbon coated copper grid containing meshes and then after studied under the TEM for analysis [85]. W. Yu et al., has reported a synthesis of monodispersed Cu nanoparticles in water and ethylene glycol further characterized under TEM moreover characterisation of transmission electron microscope. The poly (N-vinyl-2-pyrrolidone) (PVP) has dispersant medium formed in water with different concentration than a size of copper nanoparticle exhibit 7 and 4 nm (Figure 3a), instead of water used as ethylene glycol so a size of a particle formed 6 and 3 nm (Figure 3b). The foregoing analysis we can conclude that increasing the concentration of PVP consequence of that decrease in the size of copper nanoparticles [19].

**Figure 3a.** TEM images of Cu NP synthesis in PVP within water

**Figure 3b.** TEM images of Cu NP synthesis in PVP within ethylene glycol. Reprinted with the permission of copyright 2009 Nanoscale Res Lett
X-ray diffraction spectroscopy (XRD)

Emre Aslan et al., has observed XRD characterization used for observing crystallinity structure and average particles size. XRD patterns show the peak i.e., (111), (200), (220), moreover the copper is highly reactive towards oxidation so, in presence of oxygen copper forms copper oxides and XRD peaks also suggest this. The average particle size can be calculated by using the Scherer’s equation,

\[ D_c = \frac{0.9 \times \lambda}{L \cos \theta} \]

Whereas \( D_c \) is a crystalline diameter, \( L \) is the half-intensity the width of the diffraction peak, \( \lambda \) is the X-ray wavelength and \( \theta \) is the angle of diffraction. The using above equation calculated the particle size it corresponding to 30 nm (approx.). Moreover, we can also calculate the average size of copper nanoparticles using mean value, according to above data mean size of nanoparticles are 28 nm (approx.) as shown in Figure 4 [51-86].

![Figure 4. XRD pattern of Copper Nanoparticles. Reprinted with the permission from copyright 2015 Chem. Eur. J.](image)

X-ray photoelectron spectroscopy (XPS)

For XPS relatively low energy, X-ray is used to eject the electron from an atom via the photoelectric effect. The energy of ejected electrons (\( E_a \)) is determined by both the energy of the incident photons \( h\nu \) and the bound electron state (\( E_b \)) shows \( E_a = h\nu - E_b \).

The earlier time XPS has used for the surface technique, however, it has been used as chemical and elemental composition analysis. In some cases, during XPS analysis like aggregation of particles or improper coating of surfactant may lead to complication.
Huang et al., were studied XPS spectra of the samples 25.0 wt% Cu@h-BN and 30.7 wt% Cu@h-BN. As explained in Figure 3a, the main peak at 189.9 eV with a shoulder at 190.8 eV in B 1s spectra can be attributed to B-N bonds and B-O bonds sequentially. The N 1S core-level XPS spectrum (Figure 5a) shows a strong photoelectron signal at 397.6 eV, which can be assigned to the B-N bonds, uniform with record values for N3- in BN layers (Figure 5b). In the case of the Cu 2p core-level spectrum (Figure 5c & 5d), two intense peaks found at 933.9 and 952.5 eV are recognized, which can be assigned as Cu 2p3/2 and Cu 2p1/2 spin-orbital elements sequentially. Importantly, no satellite peaks resembling Cu2+ species are recognized, ordering out the CuO in our samples. Moreover, the Cu LMM Auger peak is recognized at a kinetic energy of 918 eV (Figure 5b), related to that found for pure copper metal. Consequently, the XPS results in combination with the above XRD, analyses confirm that Cu nanoparticles can be stabilized in the air and not be oxidized by the protection of h-BN wrapping [53, 54].

**Figure 5.** (5a) B 1s, (5b) N 1s, and (5c) Cu 2p core-level spectra of the 25.0 wt% Cu@h-BN sample, (5d) Cu 2p core-level spectrum of the 30.7 wt% Cu@h-BN sample. Reprinted with permission from copyright 2015 Scientific Report

**Application of copper nanoparticles**

The application of copper nanoparticles has been gradually increased because it shows properties like Au and Ag nanoparticles. Au and Ag show a catalytic and biological activity, but these are
expensive. Therefore, researchers have been attracted towards the copper metals which exhibit excellent biological as well as catalytic activity. This review article explores some application of catalytic activity and biological moreover, Cu Np has been used for catalytically activity in organic transformation \textit{i.e.}, enhancing the yield as well as optimization of time.

**Degradation of methylene blue**

India has been progressing in the textile industries consequently; the predicament of wastewater which receives harmful chemicals is one of the main sources of water pollution. The dyes effluents are delivering into the water then anaerobic degradation, causing additional toxicity caused by mutagenic end products, so it wants to treatment upon the wastewater through any materials \textit{i.e.}, inexpensive and high catalytically active. It is possible by using the nanoparticles that manifest improving the degradation properties combined with any reducing reagents decrease the energy activation barrier completely the reaction with reducing reagents and degrade the dye indoors a several minutes. T. Sinha et al., have crammed about a degradation of methylene blue in wastewater utilising the photocatalytic properties, \textit{i.e.}, the copper nanoparticles dispersed in methylene blue dye, adsorption and desorption process of the dye on the surface of nanoparticles was carried out in dark area. Furthermore, the entire reaction solution treated with sunlight then the degradation process was observed by UV-spectroscopy subsequently perform degradation perceived after 135 min. Moreover, catalytic activity was seen externally sunlight the reaction progress like the absence of a catalyst; nevertheless the appearance of sunlight than the reaction completed within minutes [55].

**The feasible mechanism for photocatalytically activity of Cu nanoparticles**

The reaction material is interacting with light material which is correlating with photon absorption, charge formation, dynamics, and surface trapping. Furthermore, correlate with surface reactivity and surface radical creation that is associating with H$_2$O, O$_2$, and organic pollutants. If copper NPs are co-operating with a solar light then shows the surface Plasmon resonance, Cu NPs photoexcited, therefore Cu nanoparticles undergo plasmonic decay by following three mechanisms.

1. An elastic radiative re-emission of photons, wherever the absorbed molecules absorb a photon and gain energy from the plasmonic structure of Cu NPs.
2. Abruptly, the photon energy endures a non-radiative Landau damping and converts to a single electrons-holes pair excitation; consequently excited primary electrons then generate several other electrons via columbic inelastic scattering.
3. Eventually, the induction of a direct electron injection into adsorbate appears due to the interaction between the adsorbate and excited surface plasmons. Further, the electrons and holes fabricated by plasmonic decay can respond with O₂ and H₂O molecules to provide active molecules; anionic superoxide radical (O²⁻) and hydroxyl radical (OH), sequentially. While the subsequent step, hydroperoxyl radical (HO₂) is created by the protonation of the superoxide ion (O²⁻). Here hydroperoxyl radical then moulds to H₂O₂ that eventually dissociates into highly reactive hydroxyl radicals (OH). Sequentially both oxidation, as well as reduction, occurs on the surface of the photocatalyst. Henceforward, the complete degradation process can be drawn in following reaction and picturesque representation (Figure 6) [55].

**Figure 6.** Pictorial representation process of methylene blue degradation. Reprinted with permission from copyright 2015 Environ SciPollut Res

**Reaction:**

1) \( \text{Cu} + h_\text{v}^+ \rightarrow h^+(\text{Cu}) + e^-(\text{Cu}) \)

2) \( \text{H}_2\text{O(ads)} + h^+ \rightarrow \text{HO}^\bullet \)

3) \( \text{O}_2 + e^- \rightarrow \text{O}_2(\text{ads}) \)

4) \( \text{O}_2^- (\text{ads}) + \text{H}^+ \leftrightarrow \text{HO}^\bullet \) (Free radical)

5) \( 2\text{HO}^\bullet (\text{ads}) \rightarrow \text{H}_2\text{O}_2(\text{ads}) + \text{O}_2 \)

6) \( \text{H}_2\text{O}_2(\text{ads}) \rightarrow 2\text{OH}^\bullet \)

\[ \text{Dye} + \text{HO}^\bullet \rightarrow \text{CO}_2 + \text{H}_2\text{O} \text{ (dye intermediate)} \]

\[ \text{Dye} + h^+ \rightarrow \text{Oxidation product} \]

\[ \text{Dye} + h^+ \rightarrow \text{Oxidation product} \]
Catalytically activity in organic transformation

Copper nanoparticles have been using as catalysts for a very extensive extent of organic transformations. This is engaging chiefly for this purpose because they constantly enable reactions to be conducted under green or sustainable reaction conditions that would reduce the activity of conventional catalysts. The Cu-NP negotiated catalysis of click chemistry, reduction and oxidation reactions, A3 coupling, cross-coupling, single and multicomponent reactions, C−H functionalization, clock reactions, borylation, oxidative coupling, and other distinct reactions. Accordingly, there is a feasibility of enhancing the organic transformation rate. In this review article, explore the azide cycloaddition reaction via click chemistry. Huisgen et al., was studied about 1,3-dipolar cycloaddition reaction in between azides and terminal alkynes is probably the enormously well-known “click” reaction and has composed a surviving indention on industrial, biological, and synthetic chemistry. This reaction gives synthetically and biologically helpful 1, 2, 3-triazole-type products with high regioselectivity under ambient conditions. It proceeds placidly in the propinquity of air and water and allows a wide the range of functional groups. Cu NPs have been widely using to catalyse 1,3-dipolar cycloaddition reactions of azides, containing a one-pot hydrazinolysis dimroth rearrangement catalysed by ligand-free Cu NPs [3-56].

Enhancing the thermal conductivity of ethylene glycol with Cu nanoparticle

A thermal conductivity of fluid has adopted in complex industrial utilisation seem to food, textile, and chemical. Consequently, intensifying the thermal conductivity of fluid which effective for industrial application. In 1995 Eastman et al., illustrated enhances the thermal conductivity of fluid with an addition of nanoparticles in fluid. The nanoparticles hold a large surface area; since improving the thermal conductivity of fluid which has been called a nanofluid. Seok Pil Jang found the Brownian motion has played a very significant role in molecular level and nanoparticle fluid suspension [55]. The Eastman proclaimed on ethylene glycol addition of Cu nanoparticles it helps to significantly enhance the thermal conductivity. Advanced study it has dispensed that metal nanoparticles suspension in the fluid then it could be possible to develop the thermal conductivity [56, 57, 58], Nevertheless, the conductivity has independent of the size and shape of nanoparticle but dependent upon the volume fraction of nanoparticles in fluid. However, B.A. Suleimanov et al., has described the effect of agglomerations and volume portion of nanoparticle in a fluid, in their study addition of 0.2% wt Cu nanoparticle in glycerol and water the followed become of thermal conductivity 25% and 35% respectively [61].
Glucose sensor
The apprehension of glucose it is vital for diagnostic the diabetics. However, it is not that much efficiently try out by the normal photometrical analysis because in glucose there are absent of the chromophoric and fluorophoric ligand. The surmounted this problem Cu nanoparticle-based nanosensor will be a remedy. The Qin Xu et al., have originated Cu based sensor with help of functionalization of nanoparticle with dimethylglyoxime (DMG) in microwave synthesis. The DMG has practised for a chelating reagent which plays role in establishing a size of nanoparticle and generation of a positive scan in an electrochemical experiment. This nanosensor it has discerned high selectivity and sensitivity [62]. Jing Luo et al., have developed a non-enzymatic glucose sensor through transformed the graphene sheet with the help of potentiostatically electrodepositing metallic Cu nanoparticles. The electrochemical reaction of graphene-Cu has observed at the hand of cyclic voltammetry and chronoamperometry. Moreover, Cu-graphene bestows the synergetic effect towards oxidation of glucose in an alkaline medium as higher oxidation and negative shift peak potential. This kind of nano-sensor avoid from some poisoning elements seem chloride as well as some of the interfering reagent likewise ascorbic acid, dopamine and uric acid etc. In addition exhibit the fast amperometric of detection of glucose, which is possible to a fabrication of non-enzymatic glucose sensor [63].

Anti-microbial activity
The nanoparticles like Au [64], Si [65], Ag [66] and Cu [67] have been using as anti-bacterial agents due to its crystalline structure, larger surface area, and smaller size which improve its synergy with microorganisms [11]. Copper nanoparticles manifest tremendous activity towards bacteria than the fungi. The bacteria, copper particles expose a higher proclivity towards gram-positive bacteria than the gram-negative bacteria and less affection towards spore-forming gram-positive bacteria [4-68]. Anti-bacterial activity of copper nanoparticles customarily depends on the size as well as the shape of the particles. Particles, whose size lies between 1-10 nm. Triangular nanoplates truncated with a plane (111) have immeasurable activity than spherical and rod-shaped nanoparticles [56]. The three-hypothetical mode of action is possible for copper nanoparticles of antibacterial activity are widely accepting, 1) presence of copper nanoparticles in bacterial cell membrane extend its permeability by issuing its ingredients such as lipopolysaccharides, membrane proteins, and intracellular biomolecules. This results in the reduction of the proton motive force across the plasma membrane [69, 70], 2) Increasing ROS engendering for imparting succeeding oxidative damage to cellular structures [71, 72, 73], and 3) exhaustion of intracellular ATP and DNA synthesis
by uptake of metallic ions derived from NPs or NPs itself into bacterial cells [74]. Ruparelia et al., have recommended that interaction of Cu ions from its NPs with phosphorus and sulphur containing biomolecules like DNA and protein may lead to misshape their structures and thus obstruct its role in various biochemical processes [75]. S.H. Wu et al., outline the excellent role of Cu nanoparticles in mesoporous copper-doped silica aerogels for anti-microbial activity, which confers 5% concentration of copper nanoparticles in gels can have the ability to kill microorganisms up to 99% in 1 h. Figure 7. Show the antimicrobial mechanism of copper nanoparticles by agitating DNA in which log phase E. coli K12 strains were nurtured for 37° C in 7.5 μg/mL CuCl₂ and Cu nanoparticles individually. Cu NP managed cells eliminated after 30, 60 and 120 min, on the other hand, CuCl₂ treated cells were withdrawn after 120 min of incubation and their DNA was isolated for electrophoresis. Cells treated by CuCl₂ did not show DNA fragmentation while cells treated with Cu NPs shows continuous DNA fragmentation with time [9, 76]. Raffi et al., studied the minimal inhibitory concentration of copper nanoparticles for E. coli bacteria. Results show that there is no growth colony formed after treated with samples having 60 μg of copper nanoparticles [77]. Cu/cellulose nanocomposite film is highly effective to obliterating of gram positive and gram negative bacteria within a 1 h by releasing copper ions and this anti-bacterial activity was long permanent due to the slow deliverance of copper ions [78]. Copper nanoparticles synthesized by hydrazine reduction and stabilized by silica gel showed a higher effect on gram-negative bacteria than gram-positive bacteria [79], and also copper encapsulated polyurethane and silicon have greater bactericidal activity than the pure polyurethane and silicon [80].

![Figure 7](image)

**Figure 7.** It shows four lanes, which suggest DNA of cells treated with CuCl₂ for 2 hrs, Cu nanoparticles for 30 min, 1 hr, and 2 hr respectively. Reprinted with permission from copyright 2014 IOP science
Wound healing

The various microorganisms get collected at a site of wounds and make their path to the body's inland part to expand infection so, relocation of microorganism from the site of the infection or wound must be necessary for wound healing [81]. Associated silver nanoparticles, copper nanoparticles have been extensively using anti-bacterial as well as an anti-inflammatory agent. These properties of copper particles help to reduce bacterial load from the site of the wound and also copper is the co-factors for such enzymes related superoxide dismutase and cytochrome oxidase. Copper provokes the angiogenesis at the site of a wound by animating vascular endothelial growth factor (VEGF) which is necessary for the nutrient and the biomolecules transport. Copper can also enhance the immunity against various microorganisms by stimulating IL-2 production. Copper has the manhood to moderated oxidative damage in tissue and initiates tissue remodelling by expression integrin, stabilisation of fibrinogen, and up-regulation of copper-dependent enzymes like lysyl oxidase. Due to remodelling and anti-inflammatory property of copper nanoparticles it has been using to halt severe phosphorus burns [82]. Tiwari et al., studied wound healing property of copper nanoparticles in which they anaesthetized animal and placed a cut of 500 mm². The classified animals into four different categories like control, control gel, copper native gel and biosynthesized copper nanoparticles (BNCPs) and studies the area of wound systematically which showed BNCPs have a substantial role in wound healing process. Wound healing property in the BNCPs gel-treated animals was twice that in the control group of animals and significantly higher than the control gel and the copper native gel-treated animals. Eventually the 10th day of the sectioning, animals handled by BNCPs reduced 92% of the wound size [54]. BNCPs have the ability to enhance cell proliferation and increase cell migration from scar within 24 hours. COX₂ (cyclooxygenase -2) is an enzyme responsible for pain and inflammation. Study of COX₂ expression by RT-PCR suggested that BNCPs have great potency for anti-inflammatory activity rather than copper itself by suppressing the expression of the COX₂ enzyme [84].

Conclusion

Aforementioned survey report investigates the various synthesis methods before mentioned as chemical, physical and green synthesis. Cu Np syntheses are quite challenging and to achieve stability for long-term, since, evading the oxidation of copper nanoparticle different surfactant, capping reagents and plant extract have used by researchers. Conversion of copper nanoparticles into copper oxide nanoparticles lessen the antimicrobial activity, furthermore, the applicability of Cu NP is the degradation of dyes in textile effluents and including for organic transformation.
Eventuality, synthesis of colloidal copper nanoparticles amidst immense stability sway be more convenient, too capability to create radical species, copper nanoparticles might be widely used in cancer therapy. Moreover, throughout organic transformation, it is used as a catalyst for time optimisation and improves the yield.

References
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