ISSN: 0973-3469, Vol.15, No.(3) 2018, Pg. 279-295

Material Science Research India

www.materialsciencejournal.org

A Review on Green Synthesis and Applications of Cu and CuO Nanoparticles

H C ANANDA MURTHY[1]*, BUZUAYEHU ABEBE[1], TEGENE DESALEGN Z[1], PRAKASH C H[2] and KUMAR SHANTAVEERAYYA[3]

[1]Department of Applied Chemistry, School of Applied Natural Science, Adama Science and Technology University, P O Box 1888, Adama, Ethiopia.
[2]School of Mechanical, Chemical and Materials Engineering, Adama Science and Technology University, P O Box 1888, Adama, Ethiopia.
[3]School of Civil Engineering and Architecture,Adama Science and Technology University, P O Box 1888, Adama, Ethiopia.

Abstract

Green method for the synthesis of metallic and metallic oxide nanoparticles has been known to play a significant role in the advancement of nanomaterial applications in various sectors since last few decades. Green synthesis of copper and copper oxide nanoparticles (Cu and CuO NPs) was more economical and an alternative method to many existing physical and chemical methods. Green fabricated Cu and CuO NPs finds applications in catalysis, photocatalysis, electrocatalysis, organic dye degradation, biomedicine, pharmaceutics, cosmetics and energy. The morphology and topography of biogenic NPs widely depend on the bioactive components of the plant extracts and preparative conditions. The present review aims to bring awareness about various plants applied in the biogenic synthesis of Cu and its oxide NPs for multifunctional applications in antimicrobial activity evaluation and catalysis. The characterization of biogenic Cu NPs by number of analytical tools for their compositional, morphological and topographical features has also been discussed.

Article History

Received: 28 November 2018
Accepted:16 December 2018

Keywords

Antimicrobial Activity,
Copper Nanoparticles,
Green Synthesis,
Morphology,
Catalysis

CONTACT H C Ananda Murthy anandkps7@yahoo.com Department of Applied Chemistry, School of Applied Natural Science, Adama Science and Technology University, P O Box 1888, Adama, Ethiopia.

Doi: http://dx.doi.org/10.13005/msri/150311

Introduction

The research on synthesis and characterization of metallic nanomaterials is an emerging field of nanotechnology due to applications of nanoparticles for scientific, technological, pharmacological and biomedical sectors. Various physical and chemical routes have been employed to synthesize nanoparticles.[1] The chemical method of synthesizing nano particles is extremely costly affair with additional environmental and biological risk. But biogenic synthesis which involves plants for the production of nanoparticles, is a cheap, less costly and environment-friendly method.

Metallic nanoparticles are multifunctional in nature and hence finds huge number of applications in various sectors for environmental, biomedical and antimicrobial, solar power generation and catalytic causes.[2] Application of plant extracts to synthesize copper and its oxide nanoparticles is a green chemistry methodology which establishes strong relationship between natural plant material and nanosynthesis.[3]

It has been reported in the past study that copper, gold and silver nanoparticles exhibited excellent antimicrobial activity against various disease causing pathogens. In recent years, copper nano particles (Cu NPs) have gained significance due to their multifunctional uses in industries and medicine. However, other nanoparticles, such as platinum, gold, iron oxide, silicon oxides and nickel have not shown bactericidal effects in studies with Escherichia coli.[5] The antibacterial study on E. coli and Bacillus subtilis using Cu and Ag NPs, revealed the fact that Cu exhibited superiority over Ag.[6] Cu NPs have wide applications as heat transfer systems[7] antimicrobial materials[8], sensors[9], and catalysts.[10] In addition, copper and its compound have been applied as antifungal, antiviral, and molluscicidal agents. The synthesis of Cu NPs by using extracts of various plants found all over the globe have been reported by many researchers in the past.[11,12]

It is essential to develop clean, reliable, biocompatible, cheap, and nontoxic green method of nanoparticle's synthesis. Many plants parts or whole plants have been used for the green synthesis of Cu NPs[13] due to the presence of large number of bioactive compounds in plants. The extracts of plants Nerium oleander[14], Punica granatum[15], Aegle marmelos[16] & Ocimum sanctum,[17] Zingiber officinale[18] have been efficiently applied for this purpose.

The present review concentrates on biogenic synthetic processes for Cu NPs using extracts of diverse range of plant species including medicinal plants found across the globe and their applications in electronic, magnetic, optoelectronic, biomedical, pharmaceutical, cosmetic, energy and catalysis.

Green Synthesis of Cu and CuO NPs

Plants consists of large number of biologically active compounds and hence, most of the plants have proven record for their anthelmintic, antitumor, antimutagenic, antibacterial and fungicidal properties. The synthesis of metallic NPs involves simple mixing of metal solution with extract of plant. Nanoparticles are produced in the medium due to reduction of metal ions. The scheme of synthesis of metallic NPs is as shown in Figure 1.

Many earlier investigations revealed that Cu NPs can be synthesised by the application of most common precursor copper salts namely, cupric acetate (monohydrate) (($(CH_3COO)_2Cu{\cdot}H_2O$)[19], Copper chloride di-hydrate ($CuCl_2$. $2H_2O$)[20] and Copper sulfate pentahydrate ($CuSO_4.5H_2O$).[21] Various factors such as concentration, pH, temperature, influence the nature and properties of synthetic Cu NPs as well as CuO NPs.

The reduction of copper ions to get stable copper nanoparticles can be attributed to the presence of biologically active compounds present in the leaf broth of Azadirachta indica.[22] It was found in this study that the rate of production varied linearly with percentage of leaf broth. The other optimum conditions for the synthesis are; $[CuCl_2]$ = 7.5×10^{-3} M, pH =6.6 and temperature = 85°C.

Formation of greenly synthesized copper nano particles capped with T. cordifolia (Cu NPs@Tc) was also reported.[23] Synthesis of Cu nanoparticles has been successful with extracts of various parts of plant species that include, Citrus medica Linn. (Idilimbu) juice,[24] Ziziphus spina-christi (L.) Willd,[25] Asparagus adscendens Roxb. Root and Leaf,[26] Eclipta prostrata leaves,[27] Ginkgo biloba Linn,[28] Plantago asiatica leaf,[29] Thymus vulgaris L,[30] black tea leaves[31], Terminalia catappa leaf[32] and many more[33-77] presented in Table 1.

The organic hydrocarbon part of citron[24] facilitates the protection of copper. The antioxidant nature and acidic property of citron also prevents oxidation of copper as the protons present in the medium influence electro-deposition of copper at low pH range. Cu colloid formation of non-oxidized Cu NPs was observed with uv-absorption peak at 565 nm during the green synthesis of Cu NPs by Eclipta prostrata leaves extract.[27]

The reduction of Cu^{2+} ions to Cu NPs by the phenolics and other chemicals of Thymus vulgaris L. leaf extract was reported.[30] These biomolecules cogently reduce copper salts but also avoid agglomeration. The hydroxyl and ketonic groups of phenolic compounds bind to metals and show chelate effect. Flavonoids can directly scavenge molecular species of active oxygen. Antioxidant action of flavonoids resides mainly in their ability to donate electrons or hydrogen atoms.

The reduction of copper ions to give Cu NPs was attributed to the phenolic compounds present in the Rheum palmatum L. root extract.[51] The extract constituents believed to function both as reducing and capping agents in the stabilization of prepared Cu NPs.

The bioactive molecules present in the Carica papaya leaves extract[61] also found to reduce precursor copper sulphate to form copper oxide nanoparticles.

In the similar way CuO NPs were also synthesised by using plant extracts of Aloe vera[33], Oak fruit hull (Jaft),[34] Ixoro coccinea leaf,[35] Syzygium alternifolium (Wt.) Walp,[36] Ferulago angulata (schlecht) boiss,[37] Rosa canina fruit,[38] Azadirachta indica,[39] Olea europaea leaf extract,[40] Malus Domestica leaf extract,[41] Bauhinia tomentosa leaves extract,[42] Moringa oleifera leaves Extract,[44] Abutilon indicum leaf extract,[47] Eclipta prostrata leaves extract,[48] Euphorbia Chamaesyce leaf extract[50] and many more as given in Table 1.

Characterization of Cu and CuO NPs

The Characterization of biogenically synthesized Cu and CuO nanoparticles has been carried out by using analytical tools namely, uv-visible spectroscopy (uv-vis), x-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDS), dynamic light scattering (DLS), scanning electron microscopy (SEM), tunneling electron microscopy (TEM), Fourier transform infra-red spectroscopy (FTIR), particle analyzer, Surface Plasmon resonance etc. The uv–vis absorption spectroscopy was applied to detect color change in Cu nanoparticle synthesised by using Ziziphus spina-christi leaves[25] which is possibly due to the surface plasmon vibrations. The surface plasmon vibration bands for Cu-NPs synthesised by many plant extracts was found to be between 191 nm and 721 nm as given in Table 1.

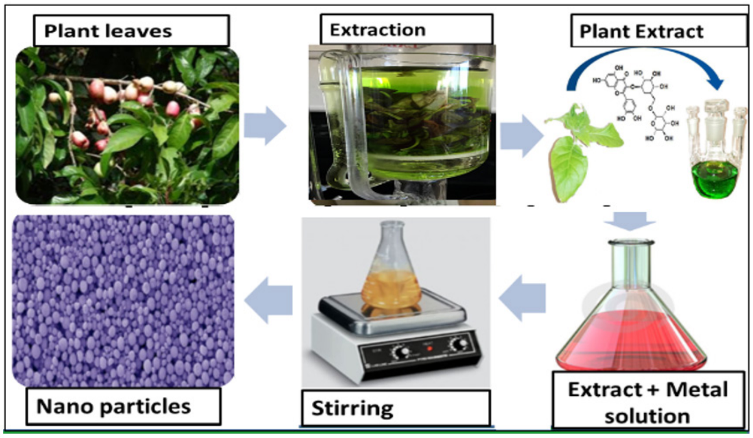
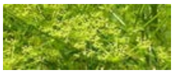


Fig. 1: A schematic diagram of green synthesis of metal nanoparticles from plant extracts

Table 1: Various plants extracts used in the synthesis of Cu and CuO NPs and their applications

Plant	Image	Precursor	Size, morphology, surface plasmon vibration (SPV)	Applications	Ref.
Syzygium aromaticum bud		Cupric acetate (monohydrate) ($(CH_3COO)_2Cu{\cdot}H_2O$)	~12 nm, spherical, SPV@ ~580 nm	Antimicrobial properties	19
Stachys lavandulifolia		Copper chloride di-hydrate ($CuCl_2$. $_2H_2O$)	80 ± 8 nm, near-spherical, SPV@ ~ 590 nm	antibacterial activity	20
black bean		Copper sulfate pentahydrate ($CuSO_4.5H_2O$)	~ 26.6 nm, spherical, hexagonal and uneven shapes,	anticancer activity	21
Azadirachta indica leaves		Cupric chloride di-hydrate ($CuCl_2$. $2H_2O$)	48nm, cubical,SPV @ ~ 506 nm	-	22
Tinospora cordifolia		Copper chloride ($CuCl_2$(II))	50–130 nm, spherical, SPV@ ~ 250 nm	Catalytic Degradation	23
Citrus medica Linn. (Idilimbu) juice		Copper sulphate ($CuSO_4$)	33 nm, SPV@ ~ 631 nm nm	antimicrobial activity	24
Ziziphus spina-christi (L.) Willd		Copper sulphate ($CuSO_4$)	8–15 nm, spherical, SPV@ ~ 551 nm	triphenylmethane dye and anti bacterial assay	25
Asparagus adscendens Roxb. Root and Leaf		Copper sulphate ($CuSO_4$)	10– 15 nm, Spherical, SPV@ ~ 500 to 700 nm	Antimicrobial Activities	26
Eclipta prostrata leaves		Copper acetate ($Cu(OAc)_2$)	31±1.2 nm, spherical, hexagonal and cubical, SPV@ ~ 565 nm	antioxidant and cytotoxic activities	27
Ginkgo biloba Linn		Copper chloride (CuCl2)	15-20 nm, spherical, SPV@ 560 to 580 nm	catalytic activity	28
Plantago asiatica leaf		Cupric chloride di-hydrate, ($CuCl_2{\cdot}$ $2H_2O$)	7–35 nm, spherical, SPV@ 565 nm	catalytic activity	29

Thymus vulgaris L.		Copper sulphate ($CuSO_4$)	various sizes, sheeted,SPV @ ~ 520 nm	catalytic activity (MB)	30
black tea leaves		Copper sulphate ($CuSO_4$)	26–40nm, Spherical,	antibacterial, antifungal and aflatoxin B1 adsorption activity	31
Terminalia catappa leaf		Copper sulphate pentahydrate ($CuSO_4$.5H2O)	21–30 nm, Spherical,	Antibacterial test	32
Aloe vera extract		$CuSO_4$	15 and 30 nm, dispersed, versatile and spherical, SPV@ ~ 265 and 285 nm	-	33
Oak Fruit Hull (Jaft)		Copper acetate ($Cu(CH_3COO)_2$)	34nm, quasi-s pherical, SPV@ ~ 590 nm	Photocatalytic Degradation (Violet 3)	34
Ixoro coccinea leaf		Copper sulphate ($CuSO_4$)	80–110 nm, Spherical, SPV@ ~ 191 nm	-	35
Syzygium alternifolium (Wt.) Walp.		Copper sulfate pentahydrate ($CuSO_4.5H_2O$)	17.5 nm, spherical, SPV@ ~ 285 nm	Antiviral Activity	36
Ferulago angulata (schlecht) boiss		Copper acetate ($Cu(CH_3COO)_2$)	~ 44 nmSPV@ ~ 554 nm	photocatalytic degradationof Rhodamine B (RhB)	37
Rosa canina fruit		Cupric acetate, $Cu(OAc)_2$	Spherical15-25 SPV@ ~ 262 nm	C-N Ullmann couplingreactions	38
Azadirachta indica		Copper nitrate trihydrate ($Cu(NO_3)_2$.3H=O)	28-35 nm, spherical, SPV@ ~ 262 nm	antibacterial activity(E. coli)	39
Olea europaealeaf		Copper sulphate ($CuSO_4$)	20–50 nm, Spherical, SPV@ ~ 289 nmtheir	toxicity activities	40
Malus Domestica leaf		Copper sulphate ($CuSO_4$)	18 - 20 nm, spherical and crystalline, SPV	antibacterial, antioxidant, DNA	41

			@ ~ 335 nm	cleavage activities	
Bauhinia tomentosa leaf		$CuSO_4$	22-40nm, Clustered & spherical, SPV@ ~ 384 nm	antibacterial	42
E. camaldulensis		copper nitrate $Cu(NO_3)_2$	89.24 nm	Biofilm Formation	43
Moringa oleifera Leaves		Copper sulfate pentahydrate ($CuSO_4.5H_2O$)	6 and 61 nm	Nitrates Removal	44
tragacanth gel		Copper nitratetri hydrate ($Cu(NO^3)_2$ $3H_2O$)	18-33 nm, uniform spherical & narrow size distributions, SPV@ ~ 262 nm	-	45
turmeric, etc leafs		$Cu(NO_3)_2$ and $Fe(NO_3)_3$	30 - 80 nm,	Photo-catalytic degradation	46
Abutilon indicum leaf		Copper (II) nitratetri hydrate ($Cu(NO_3)_2$. $3H_2O$)	nanometer range (not homogenous) agglomerated, hexagonal wurtzite, SPV@ ~ 725nm	Antimicrobial, antioxidant and photocatalytic dye degradation activities	47
Eclipta prostrata leaves		Cupric acetate $Cu(OAc)_2$	31±1.2nm, face-centered cubic structure, SPV@ ~ 565 nm	antioxidant and cytotoxic activities	48
Calotropis procera		Copper sulfate pentahydrate ($CuSO_4.5H_2O$)	15–20 nm, quasi-spherical, SPV@ ~ 565 nm	adsorptive of Cr(VI)	49
Euphorbia Chamaesyce leaf		Copper chloride ($CuCl_2$)	~36–40 nm, Spherical, face-centered cubic (fcc), SPV@ ~ 325 nm	catalytic activity (4-nitrophenol)	50
Rheum palmatum L.		Copper chloride ($CuCl_2$)	10–20 nm, Spherical, SPV@ ~ 250–300 nm	catalytic activity	51
Leucaena leucocephala L.		Copper acetate monohydrate(Cu ($CH_3COO)_2.H_sO$)	10-25 nm, Spherical,	upshot against human pathogens	52
Drypetes sepiaria		Cupper nitrate tri-h ydrate ($Cu(NO^3)_2$. $3H_{ss}O$)	spherical, 25 nm,SPV @ ~ 298 nm	catalytic activity	53

Cavendish banana peel		Copper nitrate tri hydrate (Cu $(NO_3)_2$. $3H_2O$)	50-85nm, spherical, SPV@ ~ 495 nm	photocatalytic activities	54
Gloriosa superba L.		Copper nitrate (Cu $(NO_3)_2$)	5-10nm, Spherical, SPV@ ~ 380 nm	antibacterial activity	55
Coffee Powder		Copper nitrate nonahydrate ($Cu(NO_3)_3$ $9H_2O$)	20-60 nm, monoclinic, SPV@ ~ 262 nm	-	56
Thymbra spicata		Cupric acetate $Cu(OAc)_2$	10–20 nm, spherical	catalyst	57
Aglaia elaeagnoidea		Copper nitrate nonahydrate ($Cu(NO_3)_3.9H_2O$)	20–45 nm, spherical, SPV@ ~ 250–350 nm	Catalyst	58
Azadirachta, etc		Cupric acetate ($Cu(OAc)_2$)	9.8 - 10.77 nm, Spherical SPV@ ~ 220–235 nm	antioxidant and anticancer activity	59
Caloropis procera leaf		Cupric acetate $Cu(OAc)_2$	40 nm, monoclinic structure (cylindrical), SPV@ ~ 291 and 355 nm	-	60
Carica papaya		Copper sulfate pentahydrate ($CuSO_4.5H_2O$)	140 nm, rod,SPV@ ~ 250–300 nm	photo catalysis (dyedegradation)	61
Anthemis nobilis flower		Copper chloride ($CuCl_2$)	18-60nm, face-centered cubic (fcc),SPV@ 250 nm	catalytic activity (A3 coupling-reaction)	62
Thymus vulgaris L. leaves		Copper chloride di-hydrate ($CuCl_2$. $2H_2O$)	30 nm, face-centered cubic (fcc), SPV@ ~ 250 nm	catalytic activity	63
Saraca indica Leaves		Copper chloride monotahydrate ($CuCl_2.H_2O$)	13–15 nm, spherical, SPV@ ~ 213 and 339 nm	Photolumine scence Studies	64
Aloe vera Leaf		Copper nitrate (Cu $(NO_3)_2$)	20 to 30 nm, aggregated spherical,SPV @ ~ 670 nm	Antibacterial Activity (Fish Bacterial Pathogens)	65
Euphorbia esula L		Copper chloride di-hydrate ($CuCl_2$. $2H_2O$)	20–110 nm, facecentered cubic (fcc), SPV	catalytic activity	66

			@ ~580 nm		
Henna leaves		Copper sulfate Pentahydrate ($CuSO_4.5H_2O$)	as-synthesized (27 nm) and calcined (45 nm), agglomerated spherical, SPV@ activity 570 nm	Electrical conductivity	67
Punica granatum		copper sulfate ($CuSO_4$)	15 to 20 nm, spherical,SPV@ ~ 585 nm	antimicrobial activity (opportunistic pathogens)	68
Stereum hirsutum		$CuCl_2$,$Cu(NO_3)_2$,and $CuSO_4$	5 to 20 nm, Spherical, SPV @ cu (~580 and 590) & CuO (~590 and 800nm)	-	69
Capparis Zeylanica leaf		copper sulfate ($CuSO_4$)	50-100 nm, cubical, SPV@ ~560- 640 nm	-	70
Vitis vinifera Leaf		Cupric acetate $Cu(OAc)_2$	3 – 6 nm, SPV@ ~337 nm	Antimicrobial Activity(Escherichia coli and Bacillus subtili)	71
Zingiber Officinale stem		copper sulfate ($CuSO_{4.}2H_2O$)	3nm, Spherical, SPV@ ~ 208nm	-	72
Tabernaemontana divaricate leaf		copper sulfate ($CuSO_4.2H_2O$)	48 ± 4 nm, spherical, SPV@ ~ 220–225 nm	antibacterial activity (urinary tract)	73
Morinda morindoides leaf		Copper chloride di-hydrated ($CuCl_2$. $2H_2O$)	16–21 nm, Spherical, -	catalyst (organic dyes)	74
Tinospora cordifolia		Copper nitrate trihydrate $Cu(NO_3)_3$. $3H_2O$	6–8 nm, Sponge, SPV @ ~ 275 and 372 nm	photocatalytic, antioxidant and antibacterial properties	75
P. granatum seeds		Copper chloride ($CuCl_2$)	40–80 nm, semi spherical,SPV@ ~ 553 nm	photo-catalytic activity	76
Centella asiatica L. leaf		Copper chloride di-hydrated ($CuCl_2.2H_sO$)	Spherical, SPV@ ~ 570 nm,	catalytic (organicdyes and nitroarenes)	77

XRD patterns (Figure 2) obtained for the Cu NPs synthesized using citron juice and Aloe vera extract showed intense peak confirming crystalline copper[24] and crystalline CuO NPs[33,50] (Figure 3) respectively.

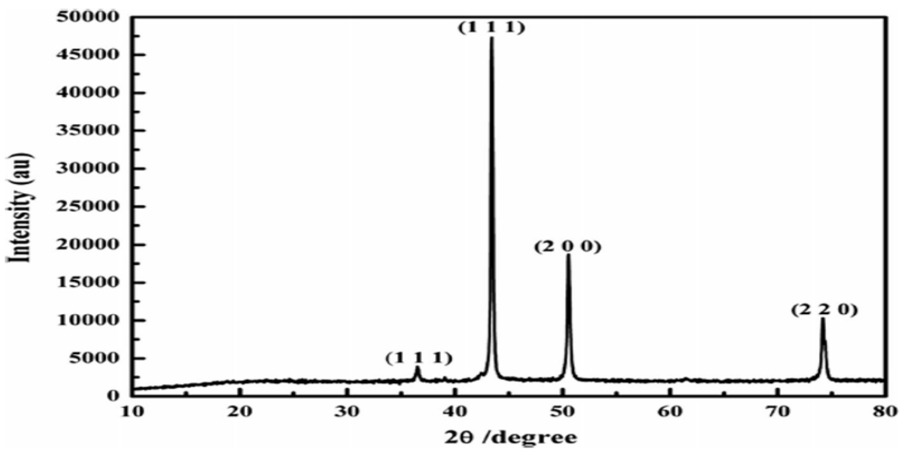


Fig. 2: XRD pattern of Cu NPs showing the FCC structure of crystallite

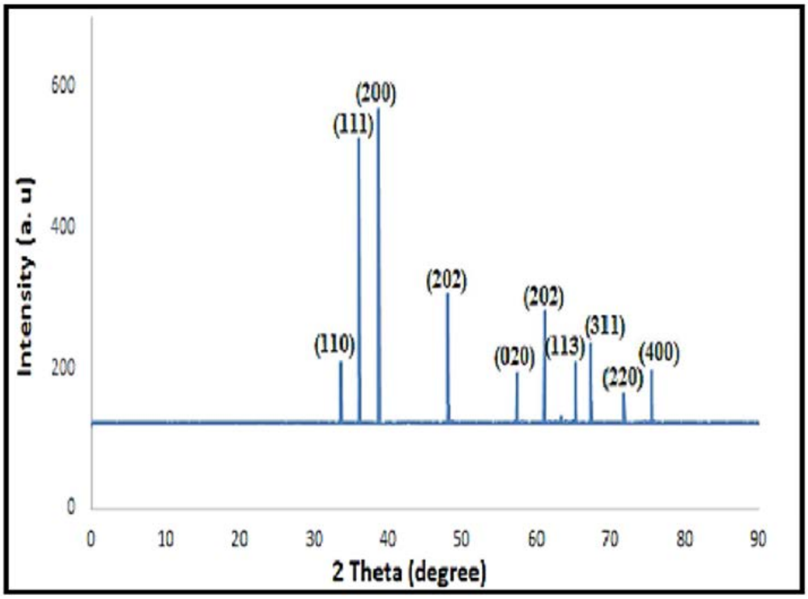


Fig. 3: XRD pattern of green synthesised CuO NPs

The analysis of FTIR spectra provides information about functional groups of biomolecules present in plant extracts. IR peaks were observed at 3,333 cm^{-1} for the hydroxyl group (H-bonded OH stretch); 2,917 cm^{-1} for methylene C-H asym. / sym. stretch; 1,615 cm^{-1} for aromatic ring stretch.[27] The peaks at about 3400, 1650, 1595, 1400 and 1100 cm^{-1} corresponds to -OH, C=O, C=C, C-OH and C-H vibrations.[28] The common IR bands[32] for cellulose were usually found at 3304 cm^{-1}, 2891 cm^{-1}, 1664 cm^{-1}, 1011 cm^{-1} corresponds to vibrations of -OH, CH_2, H_2O, and C-OH groups. Peaks at 610, 499 and 415 cm^{-1} confirmed Cu–O bond vibrations that support the presence of monoclinic phases of CuO synthesised by Aloe barbadensis Miller extract.[33] The IR band recorded at about 800 cm-1 corresponds to C–H out of plane bending vibrations due to adsorbed phenolic compound on to the CuO NPs.[34]

Electron microscopy is used for morphological characterization and internal composition of biogenic copper and silver nanoparticles.

Homogeneous and spherical morphology of biogenic Cu NPs were revealed by FESEM image[25] as shown in Figure 4.

The average particle size varied from 20 nm to 500 nm. TEM micrographs also revealed spherical nature for NPs with least tendency towards agglomeration. DLS studies reveal size distribution of Cu NPs. The average particle size of NPs synthesised by using Azadirachta indica leaves was found to be around 50 nm.[22]

The spherical morphology and narrow diameter distributions[25,28] of Cu NPs were also confirmed by TEM image (Figure 5). Biomolecules present in Aloe vera extract[33] believed to act as stabilizing and capping agent for copper caused a raise in the size of NP up to 30 nm but without change in shape.

FESEM images of CuO NPs too confirmed their spherical nature (20 nm to 300 nm). CuO NPs synthesised by Oak fruit extract exhibited average diameter of 34 nm.[34] CuO NPs were found to exhibit agglomeration tendency thus enhancing average particle size to as high as 300 nm.[35] HRTEM studies

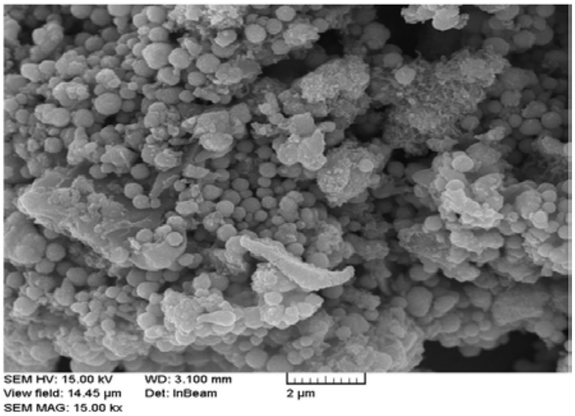


Fig. 4: FESEM image of biosynthesized Cu-NPs

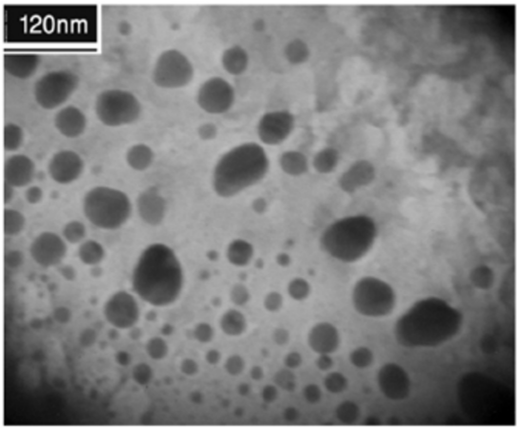


Fig. 5: TEM image of biosynthesized Cu-NPs

involving in-depth analysis of CuO NPs synthesised by using fruit extract of Syzygium alternifolium[36] recorded particle size of 2 nm. HRTEM image of CuO NPs[48] is shown in Figure 6 given below,

CuO NPs synthesised by ferulago angulata (schlecht) boiss extract[37] revealed shell like sheet structure. CuO NPs with relatively good monodispersed and virtually spherical structures were obtained with size range of 15 to 25 nm without agglomeration.[38] TEM analysis of CuO NPs synthesized using B. tomentosa leaf extract[42] also showed spherical morphology (size of 22 to 40 nm). EDS will reveal the elemental composition of the particles. EDS spectrum of green synthesised CuO NPs is as shown in Figure 7.

Applications of Cu and CuO NPs

Cu and CuO nanoparticles are multifunctional in nature and hence finds significant role in applications that include antimicrobial activities, catalytic degradation, anticancer activity, photocatalytic degradation, antiviral activity, Biofilm formation, nitrates removal, upshot against human pathogens, photoluminescent activities, organic dye degradation catalysis, etc.,

Cu NPs demonstrated good antimicrobial influence on Bacillus spp. and prominent fungicidal influence on Penicillium spp. microorganisms.[19] Cu NPs exhibited greater inhibition on Escherichia coli in comparison with Klebsiella pneumoniae, Pseudomonas aeruginosa, Propionibacterium acnes and Salmonella typhi. Fusarium culmorum was found to establish more sensitive plant pathogenic fungi, [26]. Cu NPs were also used for antioxidant and cytotoxic activities.[27]

Cu NPs were found to be excellent antibacterial agent against the wide range of bacterial species

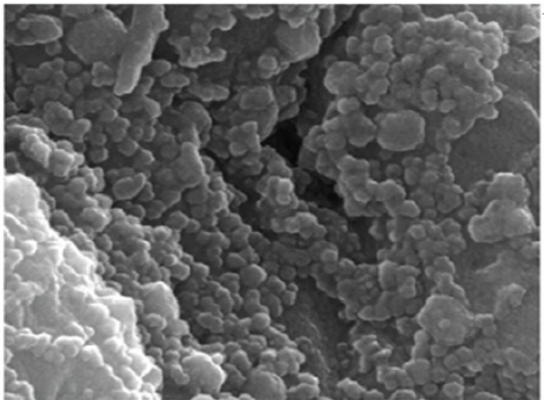


Fig. 6: HRTEM image of biosynthesized CuO-NPs

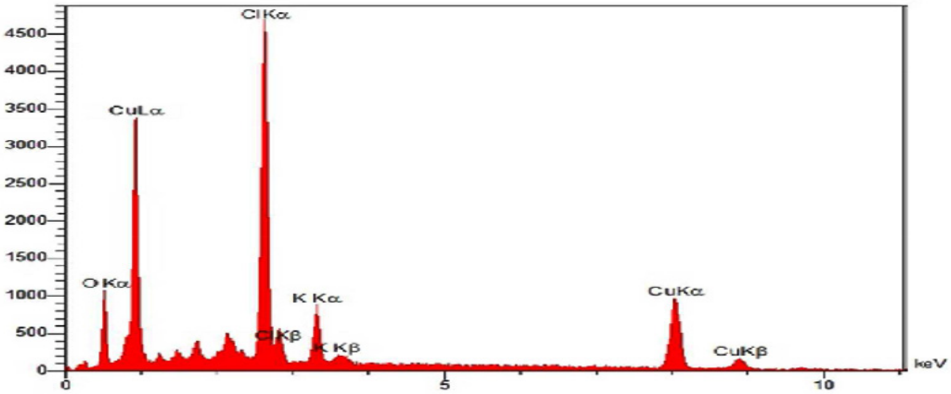


Fig. 7: XRD pattern of green synthesised CuO NPs

which could be attributed to interactions of NPs with -SH groups leading to protein denaturation.[78] Cu NPs were believed to exert effect on cell membrane due to their strong affinity towards amines and carboxyl groups present on the cell surface of organisms like B. subtilis.[79,80] Cu NPs bind with DNA molecules and disturb the helical structure by cross-linking within and between the nucleic acid strands.[81]

CuO NPs adsorbed on cell surface of E.coli interact with the cell wall and later cause damage to the cell membrane, increasing its permeability and leading to a decrease in the viability of bacteria in copper oxide solution. The exact mechanism concerning antimicrobial effect of copper nanoparticles is not understood fully and needs to be elucidated.

Cu NPs green engineered by Ginkgo biloba L. leaf extract[28] found catalytic application for Huisgen [3 + 2] reaction. Cu- NPs synthesized with Z. spina-christi fruits extract proved to be excellent nanoadsorbent for Crystal Violet removal from aqueous solution.[25]

Catalytic degradation of basic violet 3 dye in water was successful with CuO NPs obtained by using extract of Oak fruit hull.[34] The extract of Rheum palmatum L was also used to synthesize CuO nanoparticles which proved to be efficient catalyst for degradation of 4-nitrophenol, methylene blue rhodamine B and Congo red.[53] Effective catalytic application The role of CuO as catalyst can be attributed to high surface to volume ratio associate with large number of active sites. On the same line these particles were found to be photocatalyst,[54,61] for Congo red degradation and nanocatalyst for arylation recation.[57,58]

CuO NPs synthesised by aqueous extracts of Anthemis nobilis flowers[62], Thymus vulgaris L. leaves[63] and Euphorbia esula L[66] were reported to be catalytically active for the synthesis of propargylamines via aldehyde–amine–alkyne (A3) coupling reaction, and Ullmann- coupling reaction respectively. CuO particles synthesized by Saraca indica Leaves exhibited photoluminescence properties.[64]

Aloe vera leaf extract mediated biogenic CuO NPs exhibited the capability to serve as antimicrobial agents against fish bacterial pathogens.[65]

Cu nanoparticles and nanobiocomposites synthesised using plants animal sources found to have potential electronic device applications.[67] Cu NPs synthesized by using peel extract of Punica granatum[68] have demonstrated significant antibacterial inhibition against pathogens. In general, large number of plant extracts have been applied towards the green synthesis of Cu and CuO nanoparticles for applications[71-77] such as catalytic, antimicrobial activity (urinary tract), photocatalytic, antioxidant and organic dye degradation.

Conclusions

Green synthesis of copper and copper oxide nanoparticles has gained great significance in the recent past due to its simplicity, cost effectiveness and environment friendly nature. Large number of plant extracts have been successfully applied for the biogenic synthesis of Cu and CuO NPs. The bioactive compounds in the plant extracts were found to play dual role of reduction of the copper ions and also stabilization of copper NPs. UV-Visible spectroscopy, XRD, EDS, DLS, SEM, TEM, FTIR, HRTEM, Particle analyzer and Surface Plasmon Resonance are the most applied analytical tools for the characterization of copper and its oxide nanoparticles. Cu and CuO NPs were found to exhibit spherical morphology with size range of 2 - 500 nm depending on concentration of extracts as well as on preparative conditions. Cu and CuO nanoparticles proved to be multifunctional in nature with significant applications with great future implications in the fields of catalysis, photocatalysis, organic dye degradation, cosmetics, biomedicine and pharmaceutics.

Acknowledgements

Authors are great full to the management of Adama Science and Technology University for providing support towards this work.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

References

1. Cao G. Nanostructures and nanomaterials: synthesis, properties and applications. 576 London: Imperial College Press; 2004.
2. Akhtar, M. S., Panwar, J., Pilani, S. & Yun, Y. Biogenic synthesis of metallic nanoparticles by plant extracts. ACS Sustain. Chem. Eng. 591–602 (2013).
3. Mubarakali, D., Thajuddin, N., Jeganathan, K. & Gunasekaran, M. Plant extract mediated synthesis of silver and gold nanoparticles and its antibacterial activity against clinically isolated pathogens. Colloids Surfaces B Biointerfaces 85, 360–365 (2011).
4. Ravindra, S., Mohan, Y. M., Reddy, N. N. & Raju, K. M. Fabrication of antibacterial cotton fibres loaded with silver nanoparticles via " Green Approach ". Colloids Surfaces A Physicochem. Eng. Asp. 367, 31–40 (2010).
5. Williams, D. N., Ehrman, S. H. & Holoman, T. R. P. Evaluation of the microbial growth response to inorganic nanoparticles. J. Nanobiotechnology 4, 1–8 (2006).
6. Yoon, K., Byeon, J. H., Park, J. & Hwang, J. Susceptibility constants of Escherichia coli and Bacillus subtilis to silver and copper nanoparticles. Sci. of the Total Environ. 373, 572–575 (2007).
7. Eastman, J. A., Choi, S. U. S., Li, S., Yu, W. & Thompson, L. J. Anomalously increased effective thermal conductivities of ethylene glycol- based nanofluids containing copper nanoparticles. Appl. Phys. Lett. 718, 4–7 (2012).
8. Guduru, R. K., Murty, K. L., Youssef, K. M., Scattergood, R. O. & Koch, C. C. Mechanical behavior of nanocrystalline copper. Mater. Sci. Eng. 463, 14–21 (2007).
9. Xu, Q., Zhao, Y., Xu, J. Z. & Zhu, J. Preparation of functionalized copper nanoparticles and fabrication of a glucose sensor. Sensors Actuators B 114, 379–386 (2006).
10. Rodriguez, J. A., Liu, P., Hrbek, J., Evans, J. & Pørez, M. Water Gas Shift Reaction on Cu and Au Nanoparticles Supported on CeO_2(111) and ZnO(0001): Intrinsic Activity and Importance of Support Interactions. Heterog. Catal. 2, 1329–1332 (2007).
11. Kumar, A., Chisti, Y. & Chand, U. Synthesis of metallic nanoparticles using plant extracts. Biotechnol. Adv. 31, 346–356 (2013).
12. Borkow, G. & Gabbay, J. Copper , An Ancient Remedy Returning to Fight Microbial , Fungal and Viral Infections. Curr. Chem. Biol. 3, 272–278 (2009).
13. Mondal, A. K., Parui, S. M., Samanta, S. & Mallick, S. Synthesis of Ecofriendly Silver Nanoparticle from Plant Latex used as an Important Taxonomic Tool for Phylogenetic Inter- relationship. Adv. Biores. 2, 122–133 (2011).
14. Gopinath, M., Subbaiya, R., Selvam, M. M. & Suresh, D. Synthesis of Copper Nanoparticles from Nerium oleander Leaf aqueous extract and its Antibacterial Activity. Orig. Res. Artic. 3, 814–818 (2014).
15. Kaur, P., Thakur, R. & Chaudhury, A. Biogenesis of copper nanoparticles using peel extract of Punica granatum and their antimicrobial activity against opportunistic pathogens. Green Chem. Lett. Rev. 9, 33–38 (2016).
16. Science, N., Technology, N. & Paper, F. Synthesis of copper nanoparticles with aegle marmelos leaf extract. NNano Sci. Nano Technol. An Indian J. 8, 401–404 (2014).
17. Kulkarni, V., Rajguru, H., Rajgurunagar, M. & Kulkarni, P. Green Synthesis of Copper Nanoparticles Using Ocimum. Int. J. Chem. Stud. 1, 1–4 (2014).
18. Subhankari, I. Antimicrobial Activity of Copper Nanoparticles Synthesised by Ginger (Zingiber officinale) Extract. World J. Nano Sci. Technol. 2, 10–13 (2013).
19. Rajesh, K. M., Ajitha, B., Kumar, Y. A., Suneetha, Y. & Reddy, P. S. Assisted green synthesis of copper nanoparticles using Syzygium aromaticum bud extract : Physical , optical and antimicrobial properties. Opt. - Int. J. Light Electron Opt. 154, 593–600 (2018).
20. Khatami, M., Heli, H., Jahani, P. M., Azizi, H. & Nobre, A. L. Copper / copper oxide nanoparticles synthesis using Stachys lavandulifolia and its antibacterial activity. IET Nanobiotechnology Res. 11, 709–713 (2017).

21. Nagajyothi, P. C., Muthuraman, P., Sreekanth, T. V. M., Hwan, D. & Shim, J. Green synthesis : In-vitro anticancer activity of copper oxide nanoparticles against human cervical carcinoma cells. Arab. J. Chem. 10, 215–225 (2017).
22. Nagar, N. & Devra, V. Green synthesis and characterization of copper nanoparticles using Azadirachta indica leaves. Mater. Chem. Phys. 213, 44–51 (2018).
23. Sharma, P. et al. Green Synthesis of Colloidal Copper Nanoparticles Capped with Tinospora cordifolia and Its Application in Catalytic Degradation in Textile Dye : An Ecologically Sound Approach. J. Inorg. Organomet. Polym. Mater. 0, 0 (2018).
24. Shende, S., Ingle, A. P., Gade, A. & Rai, M. Green synthesis of copper nanoparticles by Citrus medica Linn . (Idilimbu) juice and its antimicrobial activity. (2015). doi:10.1007/s11274-015-1840-3
25. Khani, R., Roostaei, B., Bagherzade, G. & Moudi, M. Green synthesis of copper nanoparticles by fruit extract of Ziziphus spina-christi (L .) Willd .: Application for adsorption of triphenylmethane dye and antibacterial assay. J. Mol. Liq. 255, 541–549 (2018).
26. Thakur, S., Sharma, S., Thakur, S. & Rai, R. Green Synthesis of Copper Nano-Particles Using Asparagus adscendens Roxb . Root and Leaf Extract and Their Antimicrobial Activities. Int. J. Curr. Microbiol. Appl. Sci. 7, 683–694 (2018).
27. Chung, I. L. L. M. I. N. et al., Green synthesis of copper nanoparticles using Eclipta prostrata leaves extract and their antioxidant and cytotoxic activities. Exp. Ther. Med. 14, 18–24 (2017).
28. Nasrollahzadeh, M. & Sajadi, S. M. Green synthesis of copper nanoparticles using Ginkgo biloba L . leaf extract and their catalytic activity for the Huisgen [3 + 2] cycloaddition of azides. J. Colloid Interface Sci. (2015). doi:10.1016/j.jcis.2015.07.004
29. Cn, K. F., Nasrollahzadeh, M., Samaneh, S. & Sajadi, S. M. Green synthesis of copper nanoparticles using Plantago asiatica leaf extract and their application for the cyanation of aldehydes using. J. Colloid Interface Sci. 506, 471–477 (2017).
30. Issaabadi, Z., Nasrollahzadeh, M. & Sajadi, S. M. Green synthesis of the copper nanoparticles supported on bentonite and investigation of its catalytic activity. J. Clean. Prod. 142, 3584–3591 (2017).
31. Asif, M. et al., Iron , copper and silver nanoparticles : Green synthesis using green and black tea leaves extracts and evaluation of antibacterial , antifungal and a fl atoxin B 1 adsorption activity. LWT - Food Sci. Technol. 90, 98–107 (2018).
32. Muthulakshmi, L., Rajini, N., Nellaiah, H., Kathiresan, T. & Jawaid, M. Preparation and properties of cellulose nanocomposite films with in situ generated copper nanoparticles using Terminalia catappa leaf extract. Int. J. Biol. Macromol. 95, 1064–1071 (2017).
33. Gunalan, S., Sivaraj, R. & Venckatesh, R. Aloe barbadensis Miller mediated green synthesis of mono-disperse copper oxide nanoparticles: Optical properties. Spectrochim. ACTA PART A Mol. Biomol. Spectrosc. 97, 1140–1144 (2012).
34. Sorbiun, M., Shayegan, E. & Ali, M. Green Synthesis of Zinc Oxide and Copper Oxide Nanoparticles Using Aqueous Extract of Oak Fruit Hull (Jaft) and Comparing Their Photocatalytic Degradation of Basic Violet 3. Int. J. Environ. Res. 4, (2018).
35. Vishveshvar, K., Krishnan, M. V. A., Haribabu, K. & Vishnuprasad, S. Green Synthesis of Copper Oxide Nanoparticles Using Ixiro coccinea Plant Leaves and its Characterization. Bionanoscience (2018).
36. Yugandhar, P., Vasavi, T., Jayavardhana, Y., Palempalli, R. & Maheswari, U. Cost Effective , Green Synthesis of Copper Oxide Nanoparticles Using Fruit Extract of Syzygium alternifolium (Wt .) Walp ., Characterization and Evaluation of Antiviral Activity. J. Clust. Sci. 1, (2018).
37. Shayegan, E., Mina, M., Ali, S., Saeid, R. & Fardood, T. Plant-mediated synthesis of zinc oxide and copper oxide nanoparticles by using ferulago angulata (schlecht) boiss extract and comparison of their photocatalytic degradation of Rhodamine B (RhB) under visible light irradiation. J. Mater. Sci. Mater. Electron. 0, 0 (2017).

38. Hemmati, S., Mehrazin, L., Hekmati, M., Izadi, M. & Veisi, H. Biosynthesis of CuO nanoparticles using Rosa canina fruit extract as a recyclable and heterogeneous nanocatalyst for C-N Ullmann coupling reactions. Mater. Chem. Phys. 214, 527–532 (2018).
39. Green synthesis of CuO nanoparticles using Azadirachta indica and its antibacterial activity for medicinal applications. Mater. Res. Express (2018). doi:MRX-109160.R1
40. Sulaiman, G. M., Tawfeeq, A. T. & Jaaffer, M. D. Biogenic synthesis of copper oxide nanoparticles using Olea europaea leaf extract and evaluation of their toxicity activities : An in vivo and in vitro study. Formul. Eng. Biomater. (2017). doi:10.1002/btpr.
41. M. S. Jadhav, S. Kulkarni, P. Raikar, D. A. Barretto, S. K. V. and U. S. R. Green Biosynthesis of CuO & Ag-CuO nanoparticles from Malus Domestica leaf extract and evaluation of antibacterial, antioxidant, DNA cleavage activities. New J. Chem. (2017). doi:10.1039/C7NJ02977B
42. Sharmila, G. et al. Biogenic synthesis of CuO nanoparticles using Bauhinia tomentosa leaves extract : Characterization and its antibacterial application. J. Mol. Struct. 1165, 288–292 (2018).
43. Shanan, Z. J., Hadi, S. M. & Shanshool, S. K. Structural Analysis of Chemical and Green Synthesis of CuO Nanoparticles and their Effect on Biofilm Formation. Baghdad Sci. J. Vol.15(2)2018 15, 211–216 (2018).
44. Galan, C. R., Silva, M. F. & Mantovani, D. Green Synthesis of Copper Oxide Nanoparticles Impregnated on Activated Carbon Using Moringa oleifera Leaves Extract for the Removal of Nitrates from Water. Can. J. Chem. Eng. 9999, 1–9 (2018).
45. Fardood, S. T. & Ramazani, A. Green Chemistry Approach For The Synthesis Of Copper Oxide Nanoparticles Using Tragacanth Gel And Their Structural Characterization. J. Struct. Chem. 59, 494–498 (2018).
46. Naghikhani, R., Nabiyouni, G. & Ghanbari, D. Simple and green synthesis of $CuFe_2O_4$ – CuO nanocomposite using some natural extracts : photo-degradation and magnetic study of nanoparticles. J. Mater. Sci. Mater. Electron. (2017). doi:10.1007/s10854-017-8421-1
47. Ijaz, F., Shahid, S., Khan, S. A. & Ahmad, W. Green synthesis of copper oxide nanoparticles using Abutilon indicum leaf extract : Antimicrobial , antioxidant and photocatalytic dye degradation activities. Trop. J. Pharm. Res. April 16, 743–753 (2017).
48. Chung, I. L. L. M. I. N. et al. Green synthesis of copper nanoparticles using Eclipta prostrata leaves extract and their antioxidant and cytotoxic activities. 18 Exp. Ther. Med. 14 14, 18–24 (2017).
49. Dubey, S. & Chandra, Y. Calotropis procera mediated one pot green synthesis of Cupric oxide nanoparticles (CuO - NPs) for adsorptive removal of Cr (VI) from aqueous solutions. Appl. organometalic Chem. 1–15 (2017). doi:10.1002/aoc.3849
50. Maham, M., Sajadi, S. M., Kharimkhani, M. M. & Nasrollahzadeh, M. Biosynthesis of the CuO nanoparticles using Euphorbia Chamaesyce leaf extract and investigation of their catalytic activity for the reduction of 4-nitrophenol. IET Nanobiotechnology 11, 766–772 (2017).
51. Bordbar, M. & Shari, Z. Green synthesis of copper oxide nanoparticles / clinoptilolite using Rheum palmatum L . root extract : high catalytic activity for reduction of 4-nitro phenol , rhodamine B , and methylene blue. (2016). doi:10.1007/s10971-016-4239-1
52. Aher, Y. B. et al. Biosynthesis of copper oxide nanoparticles using leaves extract of Leucaena leucocephala L . and their promising upshot against the selected human pathogens. Int. J. Mol. Clin. Microbiol. 7, 776–786 (2017).
53. Herrera, A. & Reyes, A. Biosynthesis of Copper Oxide nanoparticles from Drypetes sepiaria Leaf extract and their catalytic activity to dye degradation Biosynthesis of Copper Oxide nanoparticles from Drypetes sepiaria Leaf extract and their catalytic activity to dye degradation. Mater. Sci. Eng. 263, (2017).
54. Aminuzzaman, M., Kei, L. M. & Liang, W. H. Green Synthesis of Copper Oxide (CuO) Nanoparticles using Banana Peel Extract and Their Photocatalytic Activities. Am. Inst. Phys. 1828, (2017).

55. Naika, H. R. et al. Green synthesis of CuO nanoparticles using Gloriosa superba L. extract and their antibacterial activity. J. of Taibah Univ. Sci. (2014). doi:10.1016/j.jtusci.2014.04.006
56. Fardood, S. T. & Ramazani, A. Green Synthesis and Characterization of Copper Oxide Nanoparticles Using Coffee Powder Extract. J. Nanostruct. 6, 167–171 (2016).
57. Veisi, H., Hemmati, S. & Javaheri, H. N -Arylation of indole and aniline by a green synthesized CuO nanoparticles mediated by Thymbra spicata leaves extract as a recyclable and heterogeneous nanocatalyst. Tetrahedron Lett. 58, 3155–3159 (2017).
58. Manjari, G., Saran, S., Arun, T., Bhaskara, A. V. & Devipriya, S. P. Catalytic and recyclability properties of phytogenic copper oxide nanoparticles derived from Aglaia elaeagnoidea flower extract. J. Saudi Chem. Soc. 21, 610–618 (2017).
59. Rehana, D., Mahendiran, D., Kumar, R. S. & Rahiman, A. K. Evaluation of antioxidant and anticancer activity of copper oxide nanoparticles synthesized using medicinally important plant extracts. Biomed. Pharmacother. 89, 1067–1077 (2017).
60. Reddy, K. R. Green synthesis , morphological and optical studies of CuO nanoparticles. J. Mol. Struct. 1150, 553–557 (2017).
61. Sankar, R., Manikandan, P., Malarvizhi, V. & Fathima, T. Green synthesis of colloidal copper oxide nanoparticles using Carica papaya and its application in photocatalytic dye degradation. Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 121, 746–750 (2014).
62. Nasrollahzadeh, M., Sajadi, S. M. & Rostami-vartooni, A. Green synthesis of CuO nanoparticles by aqueous extract of Anthemis nobilis flowers and their catalytic activity for the A 3 coupling reaction. J. Colloid Interface Sci. 459, 183–188 (2015).
63. Nasrollahzadeh, M., Sajadi, S. M., Rostami-vartooni, A., Mamand, S. & Rnh, A. Green synthesis of CuO nanoparticles using aqueous extract of Thymus vulgaris L . leaves and their catalytic performance for N -arylation of indoles and amines. J. Colloid Interface Sci. 466, 113–119 (2016).
64. Prasad, K. S., Patra, A., Shruthi, G. & Chandan, S. Aqueous Extract of Saraca indica Leaves in the Synthesis of Copper Oxide Nanoparticles : Finding a Way towards Going Green. J. Nanotechnol. 2017, (2017).
65. Kumar, P. P. N. V., Shameem, U. & Kollu, P. Green Synthesis of Copper Oxide Nanoparticles Using Aloe vera Leaf Extract and Its Antibacterial Activity Against Fish Bacterial Pathogens. BioNanoSci. 5, 135–139 (2015).
66. Nasrollahzadeh, M., Sajadi, S. M. & Khalaj, M. Green synthesis of copper nanoparticles using aqueous extract of the leaves of Euphorbia esula L and their catalytic activity for ligand-free Ullmann-. RSC Adv. 4, 47313–47318 (2014).
67. Cheirmadurai, K., Biswas, S., Murali, R. & Thanikaivelan, P. Green synthesis of copper nanoparticles and conducting nanobiocomposites using plant and animal sources. Electron. Suppl. Mater. RSC Adv. 1–11 (2016).
68. Kaur, P., Thakur, R. & Chaudhury, A. Green Chemistry Letters and Reviews Biogenesis of copper nanoparticles using peel extract of Punica granatum and their antimicrobial activity against opportunistic pathogens. Green Chem. Lett. Rev. 9, 33–38 (2016).
69. Cuevas, R., Durán, N., Diez, M. C., Tortella, G. R. & Rubilar, O. Extracellular Biosynthesis of Copper and Copper Oxide Nanoparticles by Stereum hirsutum, a Native White-Rot Fungus from Chilean Forests. J. Nanomater. 2015, (2015).
70. Saranyaadevi, K., Subha, V., Ravindran, R. S. E. & Renganathan, S. Synthesis and Characterization of Copper Nanoparticle using Capparis Zeylanica leaf Extract. Int. J. ChemTech Res. 6, 4533–4541 (2014).
71. Shaikh, R. R. & Lettre, D. P. Biosynthesis of Copper Nanoparticles using Vitis vinifera Leaf Extract and Its Antimicrobial Activity. Sch. Res. Libr. 8, 265–272 (2016).
72. Delma, M. B. T., Vijila, M. B. & Rajan, M. J. Green Synthesis of Copper and Lead Nanoparticles using Zingiber Officinale stemextract. Int. J. Sci. Res. Publ. 6, 134–137 (2016).
73. Sivaraj, R., Rahman, P. K. S. M., Rajiv, P., Abdul, H. & Venckatesh, R. Biogenic

copper oxide nanoparticles synthesis using Tabernaemontana divaricate leaf extract and its antibacterial activity against urinary tract pathogen. Spectrochim. ACTA PART A Mol. Biomol. Spectrosc. 133, 178–181 (2014).

74. Nasrollahzadeh, M., Atarod, M. & Sajadi, S. M. Green synthesis of the Cu / Fe 3 O 4 nanoparticles using Morinda morindoides leaf aqueous extract : A highly efficient magnetically separable catalyst for the reduction of organic dyes in aqueous medium at room temperature. Appl. Surf. Sci. 364, 636–644 (2016).
75. Nethravathi, P. C., Kumar, M. A. P., Suresh, D. & Lingaraju, K. Tinospora cordifolia mediated facile green synthesis of cupric oxide nanoparticles and their photocatalyti, antioxidant and antibacterial properties. Mater. Sci. Semicond. Process. 33, 81–88 (2015).
76. Nazar, N. et al. Cu nanoparticles synthesis using biological molecule of P . granatum seeds extract as reducing and capping agent : Growth mechanism and photo-catalytic activity. Int. J. Biol. Macromol. 106, 1203–1210 (2018).
77. Nasrollahzadeh, M., Sajjadi, M. & Sajadi, S. M. Biosynthesis of copper nanoparticles supported on manganese dioxide nanoparticles using Centella asiatica L . leaf extract for the efficient catalytic reduction of organic dyes and nitroarenes. h, 109–117 (2018).
78. Schrand AM, Rahman MF, Hussain SM, Schlager JJ, Smith DA, Syed AF. Metal-based nanoparticles and their toxicity assessment. WIREs Nanomed Nanobiotechnol 2:554–568 (2010).
79. Beveridge TJ, Murray. RGE Sites of metal deposition in the cell wall of bacillus subtilis. J Bacteriol 141:876–877 (1980).
80. Ren G, Hu D, Cheng EWC, Vargas-ReusMA, Reip P, Allaker RP. Characterization of copper oxide nanoparticles for antimicrobial applications. Int J Antimicrob Agents 33:587–590 (2009).
81. Avinash P. Ingle, Nelson Duran, Mahendra Rai. Bioactivity, mechanism of action, and cytotoxicity of copper-based nanoparticles: A review, Appl Microbiol Biotechnol, (2013).
82. Gopalakrishnan K, Ramesh C, Ragunathan V, Thamilselvan M. Antibacterial activity of Cu_2O nanoparticles on E. coli synthesized from tridax procumbens leaf extract and surface coating with polyaniline. Dig J Nanomater Bio 7(2):833–839 (2012).