

REVIEW

Open Access



Current status of plant metabolite-based fabrication of copper/copper oxide nanoparticles and their applications: a review

Khwaja Salahuddin Siddiqi¹ and Azamal Husen^{2*} 

Abstract

Since green mode of nanoparticles (NPs) synthesis is simple, advantageous and environment friendly relative to chemical and physical procedures, various plant species have been used to fabricate copper and copper oxide nanoparticles (Cu/CuO-NPs) owing to the presence of phytochemicals which often act as capping as well as stabilizing agent. These Cu/CuO-NPs are highly stable and used in the degradation of organic dyes like methylene blue and reduction of organic compounds such as phenols. They are also used as antibacterial, antioxidant and antifungal agent due to their cytotoxicity. They are also examined for agricultural crops growth and productivity. Cu-NPs increased the root and shoot growth of mung bean. In wheat plants, these particles reduced shoot growth; and enhanced the grain yield and stress tolerance through starch degradation. Similarly, CuO-NPs treated seedlings have shown reduced chlorophyll, carotenoid and sugar content, whereas proline and anthocyanins were increased in *Brassica rapa* seedlings. Overall, this review presents the recent understanding of plant-mediated Cu and CuO-NPs fabrication and their application in biomedicine, environmental remediation and agricultural practices. A comparison of the traditional/conventional method of fabrication of NPs with those of green protocols has also been made. Some misconception of copper chemistry has also been critically discussed in terms of oxidation and reduction reactions.

Keywords: Cu/CuO NPs, Biogenic synthesis, Biomedical, Crop growth, Applications

Introduction

Recent advancement in nanotechnology has accelerated our interest in designing nano sized particles of desired shape and size. Since their property changes with morphology they have been used in various areas of medicine, agriculture and environmental remediation [1–4]. The ‘green synthesis’ of nanoparticles (NPs) using plant is advantageous over chemical, physical and or microbial synthesis as it removes the complicated protocol; and can also meet the large-scale production requirement. Further,

the deliberate synthesis of NPs by chemical/physical methods require fairly large amount of toxic chemicals which also leave undesirable materials that pollute the environment. Disposal of such by products is also hazardous to human beings. Besides the use of expensive chemicals, the NPs thus fabricated are not capped/coated, and therefore they are not protected and are relatively less stable than those produced by plant-based materials. In order to protect these nanomaterials (NMs) they are coated with polyethylene glycol like polymers. Methods using lower and higher plant materials and their products; fungi and sometimes microorganisms for NPs fabrication are eco-friendly (Figs. 1 and 2) [2–5]. Since these materials are

* Correspondence: adroot92@yahoo.co.in

²Wolaita Sodo University, P.O. Box: 138, Wolaita, Ethiopia

Full list of author information is available at the end of the article



© The Author(s). 2020 **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>. The Creative Commons Public Domain Dedication waiver (<http://creativecommons.org/publicdomain/zero/1.0/>) applies to the data made available in this article, unless otherwise stated in a credit line to the data.

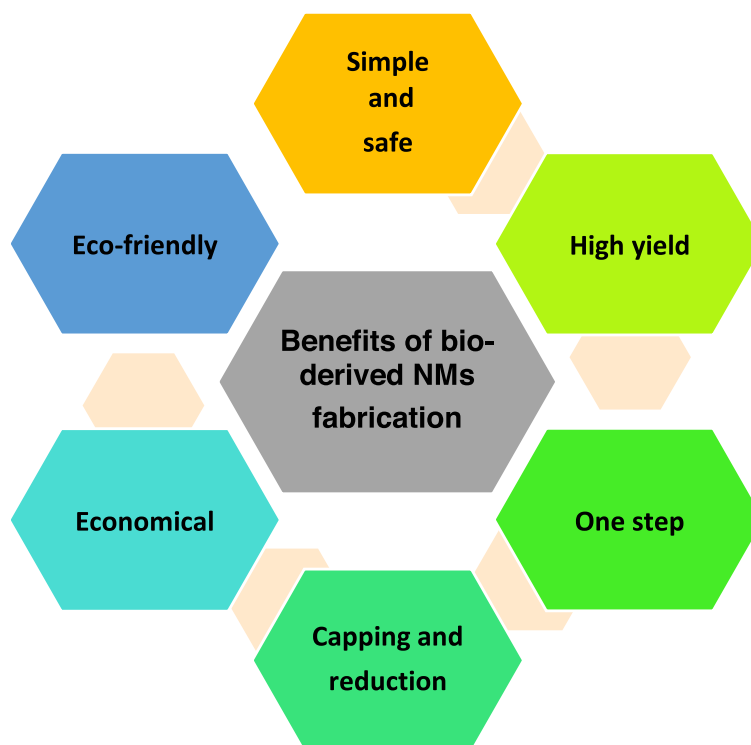


Fig. 1 Benefits of bio-derived fabrication/green synthesis of nanoparticles over chemical and physical procedures

easily available and do not require organic solvent as reaction medium, they are easy to handle and economical. In major cases the NMs thus synthesized are capped by biomolecules like phenols, tannin, flavonoids and ascorbate present in the plant materials. They enhance stability of NPs and also prevent their interaction with atmospheric oxygen. These NMs are thus not oxidized and can be kept for long period of time without undergoing any change in their properties. Green synthetic methods make use of many waste materials like banana peels, lemon rind, dried leaves of medicinal plants and algae etc. The precursor even in crude form may react with these materials to produce NPs. The noble metal NPs for example silver, gold, platinum and their alloys have been frequently biosynthesized by various workers [6–12]. Among the coinage metal NPs, copper nanoparticles (Cu-NPs) are of great interest due to their low cost, easy availability and high electrical conductivity [13–15]. Borkow and Gabbay [16] and Zheng et al. [17] have reported that the copper ions are used as pesticides, fungicides and fertilizers. Copper oxide (CuO) is also a cheaper material in comparison to silver/gold and can easily be mixed with polymers due to their stability [18]. Recently, Din et al. [19] have discussed the synthesis and characterization of cupric-oxide nanoparticles (CuO-NPs) together with their application as antioxidant, antibacterial and antifungal agent.

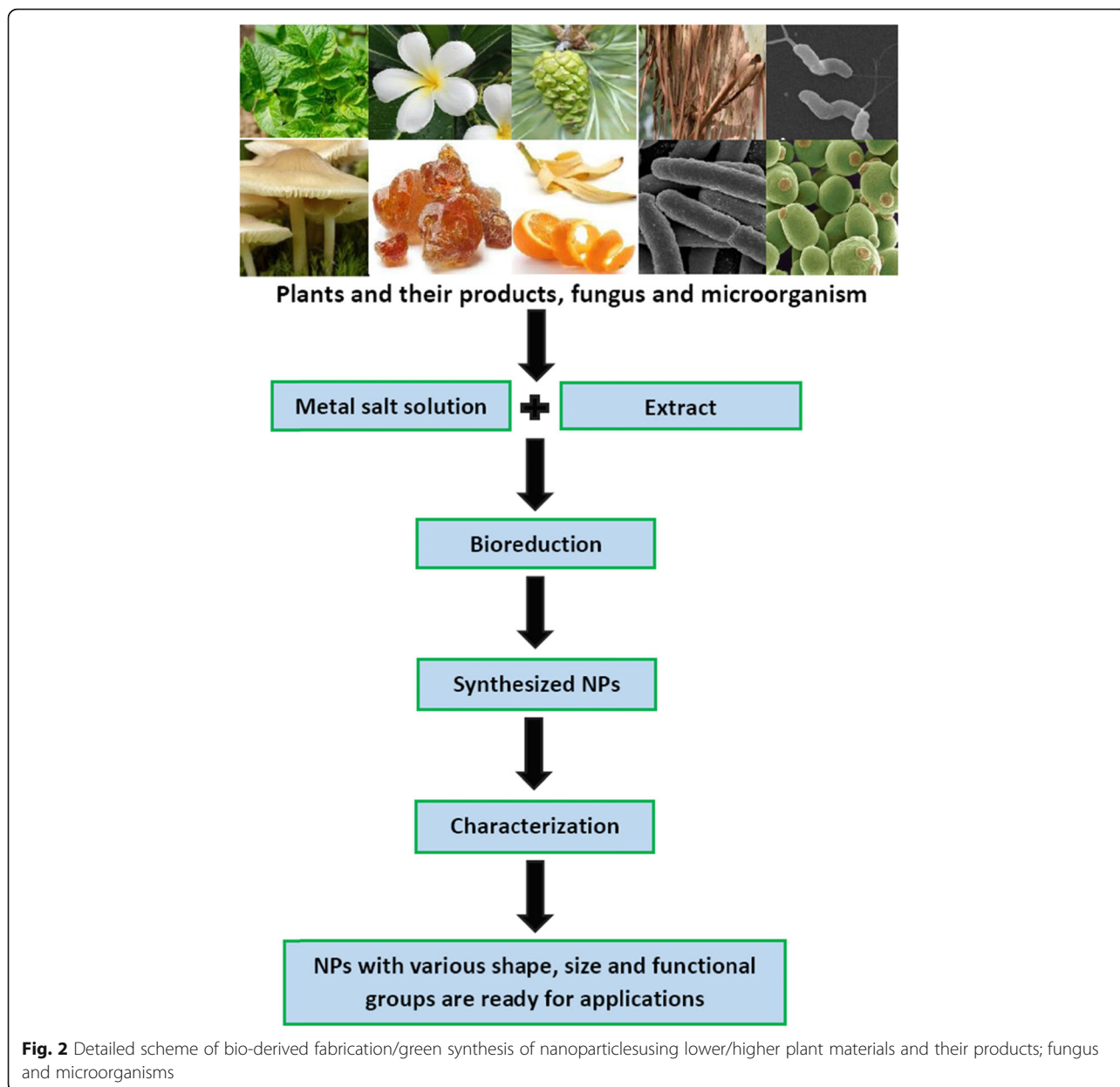
In general, Cu-NPs are used as an antimicrobial, antioxidant, antidiabetic, anti-inflammatory and antifouling agent when integrated in coatings, plastics and textiles [20–23]. They also find application in heat transfer fluids, sensors, e-sensitized solar cells, lithium ion batteries, gas -sensing, heterogeneous catalysis and as anticancer agent [24–28].

Based on the current information, the present review unfolds the protocol of plant-mediated bio-fabrication of Cu-NPs/CuO-NPs followed by their characterization and application in different areas. Attempt has also been made to enlist the impact of NPs on crops as growth promoter and the effect of size of NPs on their efficiency as catalyst and antibacterial agent.

Fabrication of cu-NPs/CuO-NPs

Cu-NPs

Synthesis of spherical Cu-NPs of 23 ± 1.10 nm from aqueous flower extract of *Millettia pinnata* and their characterization by ultraviolet–visible spectroscopy (UV-Vis), scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and selected area electron diffraction (SAED) has been reported by Thiruvengadam et al. [21]. UV-Vis study has confirmed the reduction of copper acetate to Cu-NPs. The maximum absorption was recorded at 384 nm which confirmed the



surface plasmon resonance (SPR) of the NPs. Their FTIR spectrum indicated the presence of proteins, acids, flavonoids, polyphenols, carboxylic acid and alkaloids which reduced the copper ions into Cu-NPs.

Cu-NPs of 50–250 nm diameters have been fabricated from *Magnolia kobus* leaf extract at room temperature [29]. Most of these NPs were spherical in shape and their formation was confirmed from UV-Vis spectrum exhibiting a peak at 560 nm. As the concentration of Cu-NPs increases the intensity of absorption peak measured at 560 nm also increases. It has also been observed that with increase in temperature yield of the Cu-NPs increases. However, complete conversion was achieved at about 90–95 °C. It was observed that when

concentration of *Magnolia* leaf extract was increased up to 20%, smaller and spherical NPs were formed [30]. It is suggested that organic molecules/metabolites acting as capping agents also cause aggregation of NPs but it takes long time. Energy-dispersive x-ray (EDX) spectra showed signals for copper along with oxygen and carbon. Signals for other elements may not be due to biomolecules adhering to the surface of Cu-NPs but they may be due to impurity present in the colloidal mixture of NPs and leaf extract. It has been noted that chemically fabricated NPs were air oxidized while those synthesized by *Magnolia* leaf extract were stable for more than 30 days [30]. It is because the biomolecules acting as capping agent protect the Cu-NPs from oxidation by air.

Kulkarni et al. [31] have examined the fabrication of Cu-NPs from copper sulfate and *Eucalyptus* sp. leaf extract at room temperature. A slight change in pH of the copper sulfate solution from 2.16 to 2.83 was observed when leaf extract at pH 6.96 was added followed by a change in colour of the resulting mixture which showed absorption at 572 nm in its UV-Vis spectrum. FTIR spectrum of the Cu-NPs showed the presence of phenol, amine, amino acid and flavonoids. It has been suggested that the biomolecules present in the eucalyptus leaf extract act both as reducing and capping agent. The NPs were highly crystalline with face centred cubic (FCC) structure. Their average size was found to be 38.62 nm. It is worth observing that the concentration and pH of the reducing agent is mainly responsible for the production of NPs.

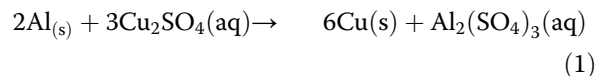
Biosynthesis of Cu-NPs from leaf broth of *Azadirachta indica* and the influence of concentration of precursor salt, concentration of leaf broth, temperature and pH of the medium were reported on the conversion rate of Cu-NPs [32] which are similar to those found above [31].

Ultrasmall Cu-NPs of 2.90 ± 0.64 nm diameter have been synthesized from lemongrass tea by one pot method [33]. Although, colour of the mixture containing both the Cu-NPs and lemongrass was yellow it did not exhibit any absorption in the UV-Vis region (350-950 nm). It has been ascribed to extremely small size of Cu-NPs which are devoid of surface plasmon resonance [34, 35]. It is strange and unusual for NPs to exhibit colour but no absorption. Generally, a sharp peak is observed in 560 to 570 nm region for Cu-NPs if they are larger than 5 nm [34–36]. Their IR spectra showed the presence of polyphenols, proteins and carbohydrate [37, 38] as reducing agents. SEM and TEM images showed the presence of finely divided and dispersed Cu-NPs. However, they were not found to be oxidized either to cuprous oxide or cupric oxide which is quite obvious because in presence of reducing agents oxidation cannot occur. It has been observed that polyethyleneglycol or polyvinyl pyr olidone can also prevent the NPs from oxidation and aggregation [39–41].

Cu-NPs synthesized using aqueous leaf extract of henna (*Lawsonia inermis*) showed an absorption peak at 570 nm which is the signature peak of CuO-NPs [42]. Blue copper sulfate absorbs at 810 nm but Cu-NPs are reddish brown if all copper ions have been reduced to NPs. It has been reported that Cu-NPs are surrounded by a thin film of copper oxide (CuO and Cu₂O) which is characterized by absorption at 800 nm [43]. It may be due to the presence of already oxidized copper sulfate present as impurity because in solution it cannot be oxidized unless it is heated in open at about 900 °C. Cu-NPs are efficiently formed at pH 11. Perhaps reduction of copper ions is facilitated in highly alkaline medium as the lawsones are stabilized at higher pH. Electrical

conductivity of calcined Cu-NPs was enhanced because all particles come closer as a result of which the mobility of electrons increases [44]. Authors have found that the absorption of Cu-NPs at 570 nm was lost and a new peak appeared at 285 nm when Cu-NPs were calcined. It is highly improbable for a calcined material to absorb in UV region of spectrum. It may be quite likely that the spectrum was not carefully run otherwise any transition metal or its oxide will not show any absorption in UV range. Their interpretation of electronic transition from inner to the outermost shell of copper [45] is highly unlikely because such situation occurs only when copper ion forms a coordination compound with a very strong ligand and forces one of the 3d⁹ electrons to be transferred to the outer 4d orbital. Since there are no copper ions this peak at 284 nm is most likely to be due to some impurity. SEM and EDAX showed agglomerated spherical Cu-NPs. The suggestion that Cu-NPs are oxidized to CuO on exposure to air is author's lack of knowledge of copper chemistry. If the Cu-NPs are exposed to air they will form CuSO₄ which is evidenced by a distinct blue colour on its surface but it is not oxidized to copper oxides.

Biogenic synthesis and characterization of Cu-NPs from *Citrus medica* juice has been reported [46]. UV-Vis spectrum showed absorption peak at 631 nm which has been taken as an evidence for the formation of Cu-NPs. Since the reduction reaction was carried out in an aluminum vessel instead of a glass vessel some fraction of aluminum would have dissolved in the citron juice. Blue CuSO₄ solution turned reddish brown due to formation of Cu₂SO₄ after the addition of citron juice, followed by deposition of shiny brown precipitate on the wall of aluminum vessel. It is suggested that a more reactive metal displaces a less reactive metal from its compound in aqueous medium [47] according to the following reaction.



Also, it has been stated that usually, copper cannot be obtained through the reduction of CuSO₄ in water [48]. The reduction stops at Cu₂O stage due to aggregation of water molecules around copper core [49]. However, reduction of CuSO₄ to Cu₂O is highly improbable because it is unstable and quickly oxidized to CuSO₄ again. Addition of a surfactant at this stage yields Cu-NPs. Size of Cu-NPs ranged between 10 and 60 nm although average size was found to be 33 nm.

Fabrication of Cu-NPs from aqueous leaf extract of *Euphorbia esula* has been reported [50]. Catalytic activity of the NPs for the reduction of 4-nitrophenol and ligand free Ullmann-coupling reaction has also been

investigated. Phenols and flavonoids in the leaf extract of *E. esula* act as reducing and capping agent for Cu-NPs. It has been shown from TEM images and size distribution studies that Cu-NPs are of 20–110 nm diameter. However, particles with 40 nm diameter are in abundance with FCC structure. Catalytic activity of Cu-NPs for the reduction of 4-nitrophenol to 4-aminophenol has been studied in presence NaBH₄. The reduction of nitrophenol to aminophenol was ascertained from a change in colour from light yellow to deep yellow followed by shift of absorption from 317 to 403 nm due to the formation of nitrophenolate ions. When Cu-NPs were added, the solution became colourless after 580 s with the appearance of a new peak at 300 nm, as a result of the formation of 4-amino phenol.

Fabrication of Cu-NPs of 15–20 nm from aqueous peel extract of *Punica granatum* has been achieved which also acts as reducing as well as capping agent [51]. The UV-Vis spectrum of Cu-NPs practically shows a flat line without any absorption in the vicinity of 500–700 nm. Although there is a very faint elevation at 585 it cannot be considered as an absorption corresponding to Cu-NPs [52]. The other absorptions below 400 nm have been assigned to the presence of proteins, enzymes and flavonoids. Since the mixture containing extract and CuSO₄ was heated at 80 °C, the enzymes would have certainly denatured and therefore the absorption in the above region may be only due to other stable phytochemicals present in the extract.

Activated carbon microfibers (ACF) coated with copper and stabilized with sodium dodecyl sulphate have been used as carrier for copper transport [53]. It was calcined at 350 °C to CuO-ACF and finally reduced in a current of hydrogen to generate Cu-ACF carbon nanofibers (CNF). They were then grown on Cu-ACF to produce Cu-CNF/ACF [53]. The *Cicer arietinum* plant treated with Cu-CNF grew well relative to the untreated plant. Shoots of the plant showed the presence of Cu-CNF. Presence of copper and carbon fibers was seen in the shoot of plant. It is supposed to be translocated via xylem of the plant. This material is a source of transport of copper as a micronutrient. Cu-NP released is thought to be converted to Cu²⁺ ions and Cu-CNF is considered as growth stimulant to plants. Further details of various plant species and their parts used in Cu-NPs synthesis and other associated activities are presented in Table 1.

CuO-NPs

Biosynthesis of CuO-NPs from gum karaya has been reported [54]. A mixture of CuCl₂ and gum in aqueous solution was made alkaline and heated at 75 °C with continuous stirring. Blue copper chloride turned black after 1 h which was separated as black powder. CuO-NPs were deposited on the surface of gum karaya perhaps due to their affinity for gum. XRD analysis showed the presence of crystalline CuO-NPs scattered all over the gum matrix which is identical to those reported earlier [55]. FTIR spectrum showed peaks in the lower region of the spectrum corresponding to Cu-O stretching

Table 1 Recent studies (during 2018–19) on plant-mediated synthesis of Cu-NPs, their morphology, and various applications

Plant	Part of plant used	Active compounds	Shape and size	Various applications	Key references
<i>Azadirachta indica</i>	Leaf	Flavonoids, terpenoids and polyphenols	Crystalline, cubical; ~ 48 nm	–	[32]
<i>Cissus arnotiana</i>	Leaf	Biomolecules	Spherical; 60–90 nm	Antibacterial and antioxidant activities	[121]
Green and black tea	Leaf	Flavonoids and phenols	Spherical; 26–40 nm	Aflatoxins adsorbent; antibacterial and antifungal activities	[122]
<i>Eichhornia crassipes</i>	Flower	Lawsone and phenols	Spherical; 12–15 nm	Detection of hazardous hydrogen peroxide	[123]
<i>Falcaria vulgaris</i>	Leaf	–	Spherical; 20 nm	Cutaneous wound healing potentials without any cytotoxicity; antioxidant, antifungal and antibacterial activities	[124]
<i>Millettia pinnata</i> ,	Flower	Proteins, acids, favonoids, polyphenols, carboxylic acid and alkaloids	Spherical; 23 ± 1.10 nm	Antioxidant, antibacterial, antidiabetic and anti-inflammatory agents	[21]
<i>Persea americana</i>	Seed	Carboxylic acid acid alkanes	Spherical; 42–90 nm	Antibacterial, antifungal and antioxidant activities	[125]
<i>Quisqualis indica</i>	Floral parts	Alcohols and phenols	Spherical; 39.3 ± 5.45 nm	Suppression of B16F10 melanoma cell proliferation and inhibition of tumor growth	[95]
<i>Ziziphus spina-christi</i>	Fruit	Alcohols and phenols	Cubic type; FESEM:8–15 nm, XRD:8–15 nm	Nanoadsorbent and antibacterial activity	[96]

frequency. It is difficult to distinguish between Cu-O of cupric oxide and those of cuprous oxide as the NPs may be a mixture of both the CuO and Cu₂O. Since the gum used in this work is a naturally occurring bio-polymer it contains sugars and amino acids which act as reducing as well as capping agent for CuO-NPs. Also they remain adhered to the surface of the gum matrix through electrostatic force. Abboud et al. [56] have reported the fabrication of CuO-NPs from *Bifurcaria bifurcata* (brown alga) purely in aqueous medium. Formation of NPs was ascertained from a change in colour from dark blue → colourless → deep red → black. It was a slow process but on heating at 100 °C the reduction of Cu²⁺ to CuO-NPs was facilitated [57]. UV-Vis spectrum of CuO-NPs exhibited peaks at 260 and 650 nm. The former was assigned to cuprous oxide NPs and the latter has been attributed to cupric oxide NPs [58, 59]. Terpenoids present in the algal extract are responsible for the reduction of Cu²⁺ to CuO-NPs. However, the peak observed at 260 nm in the UV-region cannot be assigned to the presence of cuprous oxide NPs because metal oxides (owing to their colour) can absorb only in the visible region of the spectrum. The colour of the colloidal mixture is neither purely black nor reddish. It is reddish black owing to the presence of both the cuprous and cupric oxide NPs which is also supported by uneven distribution and two crystalline phases corresponding to mono-clinic cupric oxide (CuO) and cubic cuprous oxide Cu₂O NPs [45, 59, 60]. There were two types of NPs identified from TEM images. Spherical ones were in abundance along with some elongated CuO-NPs ranging between 5 and 45 nm diameters. Diterpenoids are the major components in alga which work as reductant and stabilizer for CuO-NPs [61].

Fabrication of CuO-NPs from leaf extract (*Aloe vera*) by Vijay Kumar et al. [62] were shown to be monoclinic with an average particle size of 20 nm. Vishveshvar et al. [63] have shown CuO-NPs (obtained from *Ixoro coccinea* leaf extract) of an average size of 300 nm because of the formation of NP clusters. CuO-NPs obtained from *Ruellia tuberosa* aqueous extract were characterized by UV-Vis, FTIR, TEM, FE-SEM, EDAX and DLS [64]. In this experiment, the aqueous copper sulphate solution was added to the leaf extract showing a pale yellow to brownish black colour which had indicated the formation of CuO-NPs Fig. 3a). The absorption peak at 327 nm was confirmed by SPR (Fig. 3b) and also the formation of CuO nanorods of ~ 83.23 nm. Further, the FTIR studies have shown the characteristic peaks at 452 cm⁻¹, 612 cm⁻¹, 794 cm⁻¹, 893 cm⁻¹, 1120 cm⁻¹, 1652 cm⁻¹ and 3184 cm⁻¹ in 500–4000 cm⁻¹ range (Fig. 3c). Bands at 3184 cm⁻¹ exhibited O–H stretch due to carboxylic acids, those at 1652 cm⁻¹ established C=C– bending due to alkenes. Strong bands at 1120 cm⁻¹ exhibited the

presence of C–O stretch due to alcohols and esters. The peak at 893.62 cm⁻¹ has been assigned to C–H bending due to aromatic groups. Strong peaks at 452 cm⁻¹, 612 cm⁻¹ and 794 cm⁻¹ revealed the presence of Cu–O vibrations in the fabricated CuO-NPs. Vasantharaj et al. [64] have suggested that the FTIR investigation had confirmed the availability of carboxylic acids, alkenes, esters, alcohols and aromatic compounds in the bio-fabricated CuO-NPs. Fabrication of CuO-NPs from leaf extract of *Psidium guajava* has been reported by Singh et al. [65]. In this investigation, CuO-NPs of different shapes and size ranging from nanorods to nano spheres were found.

CuO-NPs from *Eichhornia crassipes* weed has been successfully synthesized in aqueous medium under laboratory conditions [66]. The colloidal solution containing CuO-NPs and weed extract showed absorption at 310 nm in UV-Vis spectrum. SEM and TEM images showed spherical shaped CuO-NPs of approximately 28 nm. It is interesting to note that CuO-NPs were free from impurity which is confirmed from EDX pattern which showed peaks only for copper and oxygen.

Ghidan et al. [67] have also investigated the biosynthesis of CuO-NPs from aqueous peel extract of *Punica granatum* at room temperature. It has been observed that peel extract contains amines amino acids and phenols which reduce copper ions to CuO-NPs. Crystalline and spherical NPs of nearly 40 nm size were found to be agglomerated. SEM images showed particles of 10–100 nm. Toxicity of CuO-NPs was investigated against the mortality of green peach Aphids at different concentrations. Maximum mortality was observed at 8000 µg/ml which is quite significant.

Sivaraj et al. [68] have synthesized CuO-NPs from *Tabernaemontana divaricate* leaf extract in water. They were obtained in good yield as brownish black powder and identified from a peak between 220 and 225 nm in UV-Vis spectrum. Presence of phenol, amine and proteins has been suggested on the basis of IR spectral peaks. Spherical CuO-NPs of 48 ± 4 nm appear to be in pure state as the EDX showed sharp signals only for copper and oxygen [69]. These NPs inhibit the growth of *E. coli* at a very low dose of 25 µgml⁻¹. It is more than twice as effective as tetracycline.

CuO-NPs from dried aqueous fruit extract (*Tribulus terrestris*) has been shown to contain carbonyl and hydroxyl groups in the fruit extract [70]. Although many other compounds are suspected to be present in the extract the IR spectrum exhibited the presence of a single component. CuO-NPs of 5–22 nm size were dispersed nicely and biological molecules in the extract appear to be deposited on them.

Aqueous leaf extract of *Pterospermum acerifolium* has been used to synthesize CuO-NPs from hydrated copper

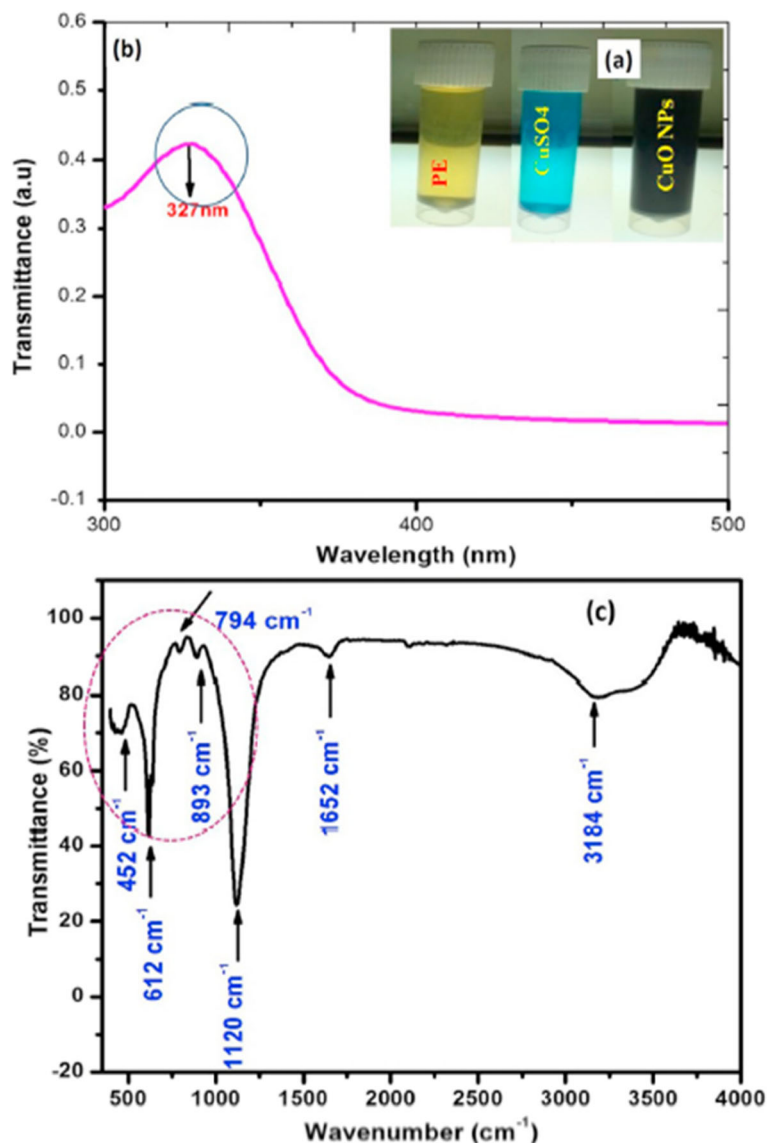


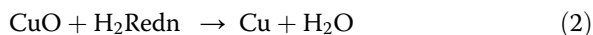
Fig. 3 a Colouration of bio-fabricated CuO-NPs, b surface plasmon resonance UV-vis spectrum, c FTIR spectrum of CuO-NPs as fabricated from *Ruellia tuberosa* aqueous extract [64]

nitrate [71]. NPs were oval shaped and pure as evidenced from EDX. They were more stable than the engineered NPs. However, hydrodynamic diameter of plant mediated CuO-NPs increased from 212 ± 47 to 634 ± 40 nm, whereas the particle size of engineered NPs increased up to 1037 ± 171 nm after 72 h. This property of increasing the hydrodynamic diameter may be used to control the size of CuO-NPs in aqueous medium. Perhaps the green synthesized NPs are capped by the phytochemicals present in the leaf extract and are therefore less aggregated. It has been noted that the rate of release of copper ions from engineered CuO-NP is much faster than plant synthesized NPs for identical concentration. It has been ascribed to stability and capping of plant

synthesized CuO-NPs. It can be more effective and lasting if used in crop protection against pest and microbes as it is antibacterial in nature. Copper ion release is dependent on time, concentration and temperature to some extent [72, 73].

CuO-NPs and dissolved copper generally accumulate over the organisms exposed to them. Effect of NPs and free copper ions on *Elodea nuttallii* has been studied by Regier et al. [74]. CuO-NPs with large hydrodynamic size (1059 ± 88 nm) very quickly agglomerate and did not change even when irradiated with UV light. Uptake of CuO-NPs in suspension by *E. nuttallii* is less than the dissolved copper [75]. However, it is contradictory because large quantity of accumulated copper has been

found in *Landoltia punctata* when exposed to CuO-NPs than when they were exposed to similar concentration of dissolved copper [76]. It has been argued that copper is solubilized from CuO-NPs due to acid exuded from growing shoots. However, copper ions would be available only if reduction of CuO-NPs occurs followed by its oxidation.



It is obvious that more copper ions will be available from copper salts because it is highly ionized in water and can be transported to different parts of plants through osmosis. CuO-NPs get accumulated due to large size.



CuO-NPs from *Gloriosa superb* leaf extract in water have been synthesized [77]. Spherical CuO-NPs of 8–17 nm were obtained in pure state as the XRD pattern shows single phase monoclinic structure although SEM images show particles of smaller size (5–10 nm).

Formation of CuO-NPs from *Carica papaya* leaf extract has been reported [78]. A sharp peak in the FTIR spectrum of colloidal cupric oxide NPs at 473 cm^{-1} has been taken as an evidence for its formation. Presence of cuprous oxide NPs has been eliminated due to absence of any characteristic peak around $605\text{--}660 \text{ cm}^{-1}$. Rod shaped CuO-NPs of 140 nm are crystalline and have FCC structure [79]. Larger particles (614 nm) are not monodispersed perhaps due to capping by the phytochemicals in the papaya leaf extract.

Leaf extract of *Calotropis gigantea* has also been used for the fabrication of CuO-NPs. Steroids and polyphenols in the extract reduce Cu^{2+} ions to CuO-NPs and also act as stabilizer for them. It has been stated [26] that oxygen of ester and phenols form metal chelate with copper ion. On heating the chelate complex, CuO-NPs are obtained. It is surprising that the authors have said that CuO-NPs are formed by the phytochemicals and pure NPs are obtained after heating at 400°C . A metal complex can be formed by a metal ion only. Free metal in atomic state cannot form a complex. A chelate with phenol cannot be formed as it is a monodentate ligand and cannot form a ring. By heating copper nitrate at 400°C , CuO-NPs cannot be obtained because oxidation of copper to CuO can occur only at 900°C . CuO-NPs were already formed by the leaf extract, and there were no complex whatsoever. Such hypothesis is baseless. Heating at 400°C will cause burning of any organic matter left in excess and shall leave soot or carbon as impurity. Spherical CuO-NPs of 20–30 nm were formed as the

EDX showed peaks only for copper and oxygen separately. The NPs were not well scattered.

Natural phytochemicals are frequently used for the fabrication of metal and or metal oxide NPs. A facile synthesis of CuO-NPs from *Gundelia tournefortii* aqueous extract of has been reported [80]. It has been shown that Cu^{2+} to CuO-NPs conversion occurs after heating the mixture of plant extract and CuCl_2 at 60°C for 2 h. IR spectra of extract and NPs exhibited the presence of phenolic compounds absorbed on the surface of CuO-NPs [81, 82]. NPs are highly crystalline [80] and spherical. Authors have concluded from EDX pattern that the presence of oxygen refers to the oxidation of Cu-NPs when exposed to air. It is not true because the Cu and oxygen peaks are due to CuO-NPs.

CuO-NPs fabricated from the aqueous flower extract of *Anthemis nobilis* had FCC, crystalline structure [83]. These NPs were found to be useful for the synthesis of propargylamines in moderate yield. Vegetable peels have also been used for the synthesis of CuO-NPs [84]. Cauliflower (*Brassica oleracea*), potato (*Solanum tuberosum*) and pea (*Pisum sativum*) peel extracts yield CuO-NPs from $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. This reaction was very slow as it took 24 h at 60°C to yield NPs. All NPs obtained from the above sources were monoclinic ranging from 22.2 to 31.60 nm. Since IR spectra did not show any peak at 610 cm^{-1} the presence of Cu_2O was ruled out [85]. As the Cu_2O is deep red it could have been easily noticed. Distinction between Cu_2O and CuO can hardly be made on the basis of Cu-O stretching frequencies as they are very closely spaced. Morphology of CuO-NPs prepared from different vegetable wastes vary in size. Their catalytic activity is also different from each other due to their shape, size and concentration.

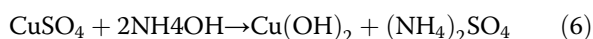
Mixed metal nanomaterials have also gained popularity due to their multidisciplinary application. Biofabrication of Pd/CuO-NPs from *Theobroma cacao* seed extract and their application as catalyst has been reported [86]. The Pd/CuO-NPs were highly stable because no change was observed even when it was left for 30 days. Antioxidants like epicatechin, catechin and their derivatives in cocoa seed extract act as strong reducing as well as capping agent. Pd has face centered cubic structure mixed with CuO-NPs of about 40 nm. Agglomeration is prevented due to capping of Pd/CuO-NPs. Presence of oxygen in EDS spectrum has been ascribed to oxidation of Cu NPs to CuO-NPs. When Pd/CuO does not contain free copper ions what is the need of oxygen for oxidation of CuO-NPs. However, oxidation of metallic copper in presence of water can take several hours nevertheless it would give CuSO_4 with a characteristic blue colour. However, authors assumption needs verification. The mechanism proposed for the formation of metal NPs and their nucleation is not convincing. All

the phenolic –OH groups cannot be oxidized even in multiple steps as the drainage of electron from it will make the ring unstable. If such nucleation occurs a metal cluster would be formed.

Seeds of many leguminous plants also contain fairly reasonable amount of proteins, phenols, flavonoids, alkaloids and amino acids [87–89] and hence they are used as reducing agent to synthesize metal NPs. Crystalline monoclinic CuO-NPs of 26.6 nm have been synthesized from black bean extract and their anti-cancer activity against HeLa cells has been reported [90]. They were effective in a very low concentration range (0.5–1 mg ml⁻¹) and short duration of time (12–48 h). It has been ascribed to intracellular ROS generation in a dose dependent manner.

The mechanism suggested for the formation of CuO-NPs is beyond imagination and conceptually non convincing. Authors have argued that the precursor CuSO₄ reacts with hydroxyl anion OH⁻, generated by the ionization of water molecules and eventually reduced by phytochemicals present in the seed extract. It must be clarified at this stage that:

(a) It is universally known that water is not ionized until acidified water is electrolysed and (b) Cu (OH)₂ can be formed only if NaOH or requisite amount of NH₄OH is added to a copper salt as shown below.



However, CuSO₄ remains ionized in aqueous medium or it may form hexaaquo copper complex, [Cu(H₂O)₆].



Free Cu²⁺ ion is then reduced by protein or polyphenol available in the black bean extract. Phenol is

oxidized to phenolate ion which provides electron to Cu²⁺ ions to form CuO-NPs.

Bawadi [91] and Bobe et al. [92] have reported that black bean extract inhibits the proliferation of breast, colon liver and prostate cancer cell. Also, it does not interfere with the functioning of healthy cells [93, 94]. It is still not understood as to why some peel/plant extract yield Cu-NPs and some of them produce CuO-NPs from the same precursor. As such CuSO₄ will produce Cu²⁺ ions in aqueous medium and reduced to Cu-NP by phytochemicals. For CuO-NPs, Cu²⁺ is to be reduced to Cu-NPs and subsequently oxidized to CuO-NPs. However, its whole chemistry is yet to be investigated. Further details of various plant species and their parts used in Cu-NPs synthesis and other associated activities are presented in Table 2.

Application of Cu-NPs/CuO-NPs

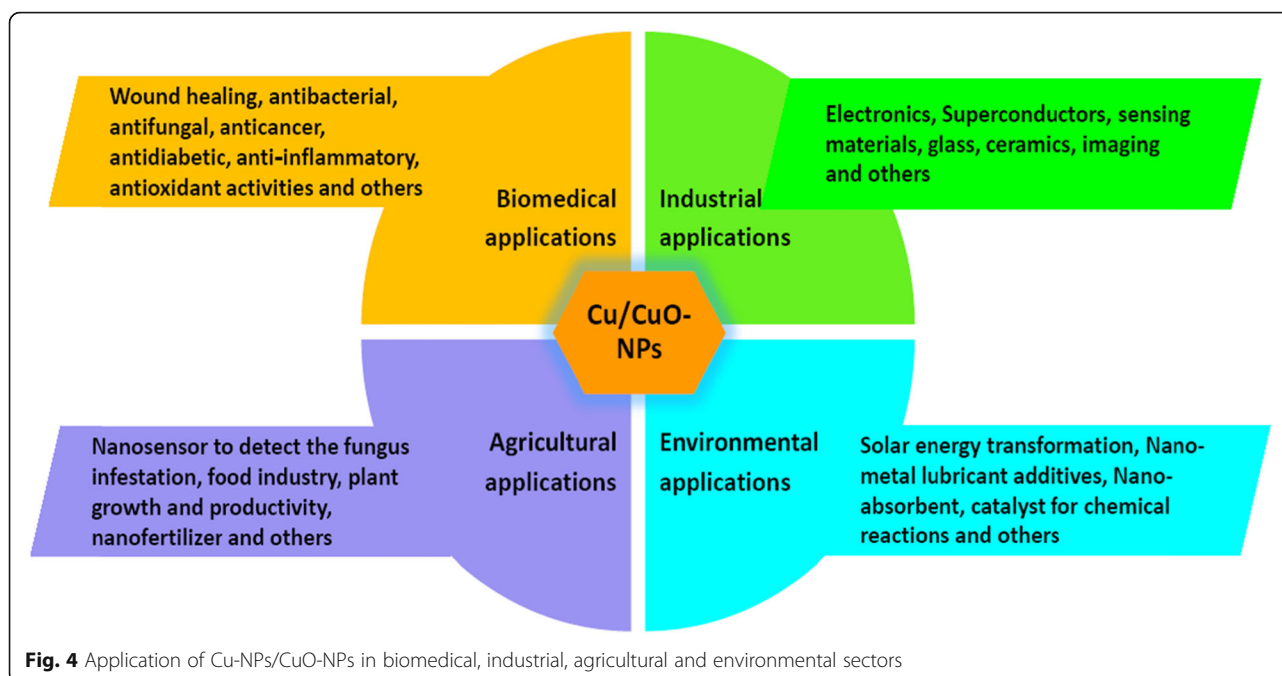
Application of Cu-NPs/CuO-NPs has been consolidated in Tables 1, 2 and Fig. 4.

Antibacterial activity

Antibacterial activity of foam coated and uncoated Cu-NPs was screened. Biosynthesized Cu-NPs from *Magnolia kobus* aqueous leaf extract exhibited greater activity against *Escherichia coli* than those shown by chemically fabricated NPs [29]. Antibacterial activity of Cu-NPs synthesized from Citron juice (*Citrus medica*) was examined [49]. In vitro antimicrobial activity screened against *Escherichia coli*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *Propionibacterium acnes* and *Salmonella typhi* showed that Cu-NPs were significantly effective against them. However, among the examined plant pathogenic fungi, *Fusarium culmorum* was observed to be most sensitive followed by *F. oxysporum* and *F. graminearum*. Cu NPs synthesized from *Punica granatum*

Table 2 Recent studies (during 2018–19) on plant-mediated synthesis of CuO-NPs, their morphology and various applications

Plant	Part of plant used	Active compounds	Shape and size	Various applications	Key references
<i>Aloe vera</i>	Leaf	–	Octahedral; 24–61 nm	Photocatalytic activity	[126]
<i>Ferulago angulata</i>	Aerial part	–	Shell like sheet structure; 44 nm	Photocatalytic activity	[127]
<i>Galeopsis herba</i>	Plant extract	Flavonoids and phenolic acids	Spherical; 10 nm	Antioxidant and catalytic activity	[128]
<i>Ixoro coccinea</i>	Leaf	Carboxylic acids, alkenes, esters, alcohols and aromatic compounds	Spherical; SEM: 300 nm; TEM: 80–110 nm	–	[63]
<i>Malus domestica</i>	Leaf	Carbonyl, methyl, saturated aliphatic and alkane/alkyl groups	Spherical and crystalline; 18–20 nm	DNA cleavage, antibacterial and antioxidant activities	[129]
<i>Psidium guajava</i>	Leaf	–	Spherical; 2–6 nm	Photocatalytic activity	[65]
<i>Stachys lavandulifolia</i>	Leaf	–	Less than 80 nm	Antifungal activity	[130]
<i>Terminalia bellerica</i>	Fruits	–	Spherical; 9–14 nm	Antibacterial activity	[131]
<i>Ruellia tuberosa</i>	Leaf	Carboxylic acids, alkenes, esters, alcohols and aromatic compounds	Nanorods; 83.23 nm	Antibacterial and photocatalytic activities	[64]



peel extract have been found to be highly bactericidal against *Micrococcus luteus*, *Pseudomonas aeruginosa*, *Salmonella enterica* and *Enterobacter aerogenes* [51]. Their antibacterial efficacy was higher than that exhibited by standard antibiotic, streptomycin [97–99]. Bio-synthesized Cu-NPs from *Millettiapinnata* flower extract of was examined against some pathogenic bacteria [21]. These particles were found to be more effective against *Staphylococcus aureus* and *Bacillus subtilis* (gram-positive) than *Pseudomonas aeruginosa* and *E. coli* (gram-negative).

CuO-NPs obtained from gum karaya showed very high antibacterial activity against *E. coli* and *S. aureus* [96]. Efficacy was found to be dependent on the size of NPs [100], the thickness of bacterial cell wall and incubation time. Smaller particles were more toxic than larger ones even if they do not penetrate the bacterial cell wall. Fabrication of CuO-NPs from *Bifurcaria bifurcate* have also been found to be significantly antibacterial against *Enterobacter aerogenes* and *Staphylococcus aureus* [56]. Bactericidal property has been attributed to the release of copper ions and their interaction with microbial cells. CuO-NPs obtained from an aquatic noxious weed, *Eichhornia crassipes* have been found to act as growth inhibitor of *Fusarium culmorum* and *Aspergillus niger* [66]. CuO-NPs obtained from the aqueous dried fruit extract of *Tribulus terrestris* were examined for their in vitro cytotoxicity and antibacterial activity [70]. CuO-NPs also inhibit the growth of bacterial strains but they were found to be most effective against *Escherichia coli* [68]. SEM images of bacterial cells exposed to CuO-NP showed complete rupture of cell wall in 60 min which

suggested that efficiency is time dependent. However, when bacteria were exposed to different concentrations of 2.5–100 µg/ml for about 1 h maximum decrease was found for lowest concentration. CuO-NPs obtained from *Gloriosa superba* leaf extract and examined for their antibacterial activity against *Klebsiella aerogenes*, *Pseudomonas desmolyticum*, *E. coli* and *Staphylococcus aureus* has been investigated [74]. CuO-NPs indicated significant activity against all bacterial strains but there is no conclusive study to propose a mechanism of action.

Catalytic activity

Synthesis of Cu/RGO-Fe₃O₄ (Cu/Reduced graphene oxide-Fe₃O₄) nanocomposite from barberry fruit juice (*Berberis vulgaris*) and its application as a heterogeneous catalyst for the ortho arylation of phenols in presence of aryl halide has been reported [101]. It is interesting to note that nano composite was easily recovered and used several times without loss of catalytic activity. Since, barberry fruit juice contains mainly vitamin C and polyphenols, they act as reducing and capping agent for Cu-NPs. Although, CuO-NPs have been used in the hydration of phenylcyanamide to urea the yield was very small, it improved by increasing the temperature of reaction mixture. Reduction of 4-nitrophenol to 4-aminophenol by NaBH₄ in presence of CuO-NPs has also been done. It takes only 70s for complete reduction but in absence of CuO-NPs the same reaction is not initiated even after 3 h. Fabrication and catalytic activity of Pd/CuO-NPs using *Theobroma cacao* was investigated through Heck coupling reaction and through reduction of nitrophenol

to aminophenol [86]. The catalyst was reused up to 6 cycles. Mechanistic pathway is yet to be established. Cu-NPs from aqueous leaf extract of *Euphorbia esula* has also been used for catalytic reduction of 4-nitrophenol and ligand free Ullmann-coupling reaction [50].

The CuO-NPs fabricated from the leaf extract of *Psidium guajava* has exhibited a remarkable degradation efficiency against the industrial dyes. It degraded Nile blue by 93%, and reactive yellow 160 by 81% in just 120 min with apparent rate constants of 0.023 and 0.014 min⁻¹, respectively [65]. CuO-NPs obtained from *Carica papaya* leaf extract has been exploited in the photocatalytic degradation of Coomassive brilliant blue dye in sunlight [78].

Plant growth response

Plants are very susceptible to minor changes in the environment (abiotic stress) and supply of any trace element/NPs either as a nutrient or as a foreign matter [28, 102–108]. Cu-NPs enhanced the root and shoot growth of mung bean [109], but reduced shoot growth in wheat [110]. Yasmeen et al. [111] synthesized Cu and Fe-NPs and demonstrated their role on the growth as well as yield of wheat varieties. The metal NPs synthesized from onion extract of 15–30 nm diameters had irregular shape. Wheat varieties were treated with 20, 25, 30, 35 and 40 ppm Cu-NPs at different stages of growth until production of seeds. Spike length was invariably increased or remained unchanged when treated with 25 ppm Cu-NPs but significantly increased the number of grains. However, higher Cu concentration reduced the number of grains/spike and overall 1000 grain weight. Copper and iron NPs together at 25 ppm concentration have better effect on production and yield of wheat than copper or iron alone. Cu-NPs increased the grain yield and stress tolerance in wheat plant through starch degradation. Sugar content and SOD activity was enhanced in seeds treated with copper and iron NPs. Quantity of copper was increased while iron remained unchanged in seeds treated with Cu and Fe NPs [111].

ACF coated with copper and stabilized with sodium dodecyl sulphate have been used as carrier for copper transport [53]. It was calcined at 350 to CuO-ACF and finally reduced in a current of hydrogen to generate Cu-ACF carbon nanofibers. They were then grown on Cu-ACF to produce Cu-CNF/ACF [112]. The *Cicer arietinum* plant treated with Cu-CNF grew well in comparison to control plants.

Impact of engineered CuO-NPs on growth and development of *Arabidopsis thaliana* at molecular level has been explored [113]. Their seedlings were treated with different doses of CuO-NPs for 3 weeks. Plant biomass, total chlorophyll content and root elongation invariably decreased while an increase in anthocyanin, lipid peroxidation and proline were observed. Lignin was also found

to be deposited in root. CuO-NPs treated seedlings also showed an increase in superoxide and hydrogen peroxide in leaves and roots which is directly proportional to its concentration. As a consequence of oxidative stress, the main root growth was inhibited but lateral root formation was initiated. This is mainly due to metabolic imbalance and as a response to resistance caused by CuO-NPs [114]. However, the plant system in response to such stress produces antioxidants to prevent the damage by ROS [104, 105, 115] which subsequently causes some changes in metabolic functions. Very recently, Chung et al. [116] have examined the effect of CuO-NPs on *Brassica rapa* seedlings. CuO-NPs treated seedlings have shown reduced root and shoot length, chlorophyll, carotenoid and sugar content, while proline and anthocyanins were increased. Additionally, production of malondialdehyde and hydrogen peroxide were increased in CuO-NPs treated seedlings which has been associated with DNA damage.

Miscellaneous response

Recently, the biosynthesized Cu-NPs from flower extract of *Millettia pinnata* have also been shown to exhibit anti-diabetic and anti-inflammatory activities [21]. Human mesenchymal stem cells exposed to CuO-NPs at a concentration of 25 µg ml⁻¹ reduced their viability. CuO-NPs at a dose of or below 10 µg/ml were non toxic to normal cells and therefore, a safe concentration may be used to prevent the interaction of CuO-NPs with normal mesenchymal cells. It has been suggested that CuO-NPs release Cu ions which are antibacterial and anticancerous [117, 118]. It also means that reduction of Cu-NPs to copper ions occur which are toxic to normal bacterial cells and cancer cells in mammals. Toxicity of CuO-NPs obtained from aqueous leaf extract of *Pterospermum acerifolium* was determined against *Daphnia magna* at several concentrations [71]. The engineered NPs were several times more toxic to *Daphnia* than green synthesized NPs [119, 120]. Release of copper ions from CuO-NPs is the main cause of toxicity to *Daphnia*. Dissolved copper ions from CuO-NPs get accumulated around *Daphnia* which cause toxicity.

Conclusion

Plenty of nano particles are synthesized every year but only some of them are put to beneficial use. Green synthesized NPs of desired shape, size and stability can enhance their overall qualities for future applications. It appears that all plant species contain some type of phytochemicals which reduce the metal salts and metal oxides into their NPs. Cu and CuO-NPs have shown great promise as biocide and mild antibacterial agent. Even though, biofabrication of metal NPs from plants and microbes do not leave toxic residues in environment, their

safe disposal is necessary. Further, it is also essential to utilize the fabricated Cu and CuO-NPs as biomedicine, environmental remediation and agricultural practices. Attention must be focused on their biocompatibility.

Abbreviations

NPs: Nanoparticles; Cu-NPs: Copper nanoparticles; CuO-NPs: Cupric-oxide nanoparticles; UV-Vis: Ultraviolet-visible spectroscopy; SEM: Scanning electron microscopy; TEM: Transmission electron microscopy; XRD: X-ray diffraction; FTIR: Fourier transform infrared spectroscopy; SAED: Selected area (electron) diffraction; EDAX: Energy-dispersive x-ray spectroscopy; ACF: Activated carbon microfibers.

Acknowledgements

Authors are thankful to publishers for permission to adopt figures in this review.

Authors' contributions

AH gathered the research data. KSS and AH analyzed these data and wrote this review paper. Both authors read and approved the final manuscript.

Funding

Not applicable.

Availability of data and materials

Not applicable.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

Author details

¹Department of Chemistry, Aligarh Muslim University, Aligarh, Uttar Pradesh 202002, India. ²Wolaita Sodo University, P.O. Box: 138, Wolaita, Ethiopia.

Received: 11 March 2020 Accepted: 5 May 2020

Published online: 03 June 2020

References

- Husen A, Siddiqi KS. Phytosynthesis of nanoparticles: concept, controversy and application. *Nano Res Lett*. 2014;9:229.
- Siddiqi KS, Husen A, Rao RAK. A review on biosynthesis of silver nanoparticles and their biocidal properties. *J Nanobiotechnol*. 2018;16:14.
- Husen A. Introduction and techniques in nanomaterials formulation: An overview. In: Husen A, Jawaid M, editors. *Nanomaterials for Agriculture and Forestry Applications*. Cambridge: Elsevier Inc; 2020. p. 1–14.
- Siddiqi KS, Husen A. Fabrication of metal and metal oxide nanoparticles by algae and their toxic effects. *Nano Res Lett*. 2016;11:363.
- Siddiqi KS, Husen A. Fabrication of metal nanoparticles from fungi and metal salts: scope and application. *Nano Res Lett*. 2016;11:98.
- Phillip D, Unni C, Aromal SA, Vidhu VK. *Murraya koenigii* leaf-assisted rapid green synthesis of silver and gold nanoparticles. *Spectrochim Acta A Mol Biomol Spectrosc*. 2011;78:899–904.
- Banerjee P, Satapathy M, Mukhopadhyay A, Das P. Leaf extract mediated green synthesis of silver nanoparticles from widely available Indian plants: synthesis, characterization, antimicrobial property and toxicity analysis. *Bioresour Bioprocess*. 2014;1:3.
- Nagar N, Jain S, Kachhawah P, Devra V. Synthesis and characterization of silver nanoparticles via green route. *Korean J Chem Eng*. 2016;33:2990–7.
- Husen A. Gold nanoparticles from plant system: synthesis, characterization and their application. In: Ghorbanpour M, Manika K, Varma A, editors. *Nanoscience and Plant-Soil Systems*. Soil Biology. Cham: Springer; 2017;48: 455–479.
- Siddiqi KS, Husen A. Recent advances in plant-mediated engineered gold nanoparticles and their application in biological system. *J Trace Elements Med Biol*. 2017;40:10–23.
- Siddiqi KS, Rashid M, Rahman A, Tajuddin HA, Rehman S. Biogenic fabrication and characterization of silver nanoparticles using aqueous-ethanolic extract of lichen (*Usnea longissima*) and their antimicrobial activity. *Biomater Res*. 2018;22:23.
- Siddiqi KS, Rashid M, Tajuddin RS, Husen A. Synthesis of silver nanoparticles using aqueous leaf extract of *Diospyros montana* Roxb. And their antimicrobial activity against some clinical isolates. *BioNanoSci*. 2019;9:302–12.
- Umer A, Naveed S, Ramzan N, Rafiqi MS. Selection of a suitable method for the synthesis of copper nanoparticles. *Nano*. 2012;7:1230005.
- Jain S, Jain A, Kachhawah P, Devra V. Synthesis and size control of copper nanoparticles and their catalytic application. *Trans Nonferrous Met Soc China*. 2015;25:3995–4000.
- Tiwari M, Jain P, Hariharapura RC, Narayanan K, Udaya BK, Udupa N, Rao JV. Biosynthesis of copper nanoparticles using copper-resistant *Bacillus cereus*, a soil isolate. *Process Biochem*. 2016;51:1348–56.
- Borkow G, Gabbay J. Copper, an ancient remedy returning to fight microbial, fungal and viral infections. *Cur Chem Biol*. 2009;3:272–8.
- Zheng XG, Xu CN, Tomokiyo Y, Tanaka E, Yamada H, Soejima Y. Observation of charge stripes in cupric oxide. *Phys Rev Lett*. 2000;85:5170–3.
- Ren G, Hu D, Cheng EW, Vargas-Reus MA, Reip P, Allaker RP. Characterisation of copper oxide nanoparticles for antimicrobial applications. *Int J Antimicrob Agent*. 2009;33:587–90.
- Din MI, Arshad F, Hussain Z, Mukhtar M. Green adeptness in the synthesis and stabilization of copper nanoparticles: catalytic, antibacterial, cytotoxicity, and antioxidant activities. *Nano Res Lett*. 2017;12:638.
- Apostolov AT, Apostolova IN, Wesselinowa JM. Dielectric constant of multiferroic pure and doped CuO nanoparticles. *Solid State Commun*. 2014; 192:71–4.
- Thiruvengadam M, Chung IM, Gomathi T, Ansari MA, Khanna VG, Babu V, Rajakumar G. Synthesis, characterization and pharmacological potential of green synthesized copper nanoparticles. *Bioprocess Biosyst Eng*. 2019;42: 1769–77.
- Pariona N, Mtz-Enriquez AI, Sanchez-Rangel D, Carrion G, Paraguay-Delgado F, Rosas-Saito G. Green-synthesized copper nanoparticles as a potential antifungal against plant pathogens. *RSC Adv*. 2019;9:18835–43.
- Lee Y, Choi JR, Lee KJ, Stott NE, Kim D. Large-scale synthesis of copper nanoparticles by chemically controlled reduction for applications of inkjet-printed electronics. *Nanotechnology*. 2008;19:598–604.
- Rubilar O, Rai M, Tortella G, Diez MC, Seabra AB, Durán N. Biogenic nanoparticles: copper, copper oxides, copper sulphides, complex copper nanostructures and their applications. *Biotechnol Lett*. 2013;35:1365–75.
- Waser O, Hess M, Güntner A, Novák P, Pratsinis SE. Size controlled CuO nanoparticles for Li-ion batteries. *J Power Sour*. 2013;241:415–22.
- Sharma JK, Akhtar MS, Ameen S, Srivastava P, Singh G. Green synthesis of CuO nanoparticles with leaf extract of *Calotropis gigantea* and its dye-sensitized solar cells applications. *J All Comp*. 2015;632:321–5.
- Wang F, Li H, Yuan H, Sun Y, Chang F, Deng H, Xie L, Li H. A highly sensitive gas sensor based on CuO nanoparticles synthesized via a sol-gel method. *RSC Adv*. 2016;6:79343–9.
- Joshi A, Sharma A, Bachheti RK, Husen A, Mishra VK. Plant-mediated synthesis of copper oxide nanoparticles and their biological applications. In: Husen A, Iqbal M, editors. *Nanomaterials and Plant Potential*. Cham: Springer International Publishing AG; 2019. p. 221–37.
- Lee HJ, Song JY, Kim BS. Biological synthesis of copper nanoparticles using *Magnolia kobus* leaf extract and their antibacterial activity. *J Chem Technol Biotechnol*. 2013;88:1971–7.
- Song JY, Jang HK, Kim BS. Biological synthesis of gold nanoparticles using *Magnolia kobus* and *Diopyros kaki* leaf extracts. *Process Biochem*. 2009;44: 1133–8.
- Kulkarni V, Suryawanshi S, Kulkarni P. Biosynthesis of copper nanoparticles using aqueous extract of *Eucalyptus* sp. plant leaves. *Curr Sci*. 2015;109:255–27.
- Nagar N, Devra V. Green synthesis and characterization of copper nanoparticles using *Azadirachta indica* leaves. *Mat Chem Phys*. 2018;213: 44–51.
- Brumbaugh AD, Cohen KA, Angelo SKS. Ultrasmall copper nanoparticles synthesized with a plant tea reducing agent. *ACS Sustain Chem Eng*. 2014;2: 1933–9.

34. Pileni MP, Lisiacki I. Nanometer metallic copper particle synthesis in reverse micelles. *Colloids Surf A Physicochem Eng Asp.* 1993;80:63–8.
35. Singh M, Sinha I, Premkumar M, Singh AK, Mandal RK. Structural and surface plasmon behavior of Cu nanoparticles using different stabilizers. *Colloid Surf A.* 2010;359:88–94.
36. Vazquez-Vazquez C, Banobre-Lopez M, Mitra A, Arturo Lopez-Quintela M, Rivas J. Synthesis of small atomic copper clusters in microemulsions. *Langmuir.* 2009;25:8208–16.
37. Narayanan KB, Sakthivel N. Coriander leaf mediated biosynthesis of gold nanoparticles. *Mater Lett.* 2008;62:4588–90.
38. Sheny DS, Mathew J, Philip D. Phytosynthesis of Au, Ag and Au–Ag bimetallic nanoparticles using aqueous extract and dried leaf of *Anacardium occidentale*. *Spectrochim Acta Part A.* 2011;79:254–62.
39. Yu W, Xie H, Chen L, Li Y, Zhang C. Synthesis and characterization of monodispersed copper colloids in polar solvents. *Nano Res Lett.* 2009;4:465–70.
40. Engels V, Benaskar F, Jefferson DA, Johnson BFG, Wheatley AEH. Nanoparticulate copper - routes towards oxidative stability. *Dalton Trans.* 2010;39:6496–502.
41. Zhang Y, Zhu P, Li G, Zhao T, Fu X, Sun R, Zhou F, Wong C. Facile preparation of monodisperse, impurity-free, and antioxidation copper nanoparticles on a large scale for application in conductive ink. *ACS Appl Mater Interf.* 2014;6:560–7.
42. Cheirumadurai K, Biswas S, Murali R, Thanikaivelan P. Green synthesis of copper nanoparticles and conducting nanobiocomposites using plant and animal sources. *RSC Adv.* 2016;4:19507–11.
43. Wang Y, Biradar AV, Wang G, Sharma KK, Duncan CT, Rangan S, Asefa T. Controlled synthesis of water-dispersible faceted crystalline copper nanoparticles and their catalytic properties. *Chemistry.* 2010;16:10735–43.
44. Demirskiy D, Agrawal D, Ragulya A. Neck formation between copper spherical particles under single-mode and multimode microwave sintering. *Mat Sci Eng: A.* 2010;A527:2142–5.
45. Swarnkar RK, Singh SC, Gopal R. Effect of aging on copper nanoparticles synthesized by pulsed laser ablation in water: structural and optical characterizations. *Bull Mater Sci.* 2011;34:1363–9.
46. Shende S, Ingle AP, Gade A, Rai M. Green synthesis of copper nanoparticles by *Citrus medica* Linn. (Idilimbu) juice and its antimicrobial activity. *World J Microbiol Biotechnol.* 2015;31:865–73.
47. Sastry ABS, Aamanchi RBK, Rama Linga Prasad CS, Murty BS. Large-scale green synthesis of Cu nanoparticles. *Environ Chem Lett.* 2013;11:183–7.
48. Hirai H, Wakabayashi H, Komiyama M. Preparation of polymer-protected colloidal dispersions of copper. *Bull Chem Soc Japan.* 1986;59:367–72.
49. Zhu YJ, Qian YT, Zhang MW, Chen ZY, Xu DF. Preparation and characterization of nanocrystalline powders of cuprous oxide by using C-radiation. *Mater Res Bull.* 1994;29:377–83.
50. Nasrollahzadeh M, Sajadi SM, Khalaj SM. Green synthesis of copper nanoparticles using aqueous extract of the leaves of *Euphorbia esula* L and their catalytic activity for ligand-free Ullmann coupling reaction and reduction of 4-nitrophenol. *RSC Adv.* 2014;4:47313–8.
51. 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.* 2016;9:33–8.
52. Hashemipour H, Zadeh ME, Pourakbari R, Rahimi P. Investigation on synthesis and size control of copper nanoparticle via electrochemical and chemical reduction method. *Int J Phys Sci.* 2011;6:4331–6.
53. Ashfaq M, Verma N, Khan S. Carbon nanofibers as a micronutrient carrier in plants: efficient translocation and controlled release of Cu nanoparticles. *Environ Sci: Nano.* 2017;4:138–48.
54. Padil VWT, Černík M. Green synthesis of copper oxide nanoparticles using gum karaya as a biotemplate and their antibacterial application. *Int J Nanomedicine.* 2013;8:889–98.
55. Das D, Nath BC, Phukon P, Dolui SK. Synthesis and evaluation of antioxidant and antibacterial behavior of CuO nanoparticles. *Coll Surf B Biointerf.* 2013;101:430–3.
56. Abboud Y, Saffaj T, Chagraoui A, El Bouari A, Brouzi K, Tanane O, Ihssane B. Biosynthesis, characterization and antimicrobial activity of copper oxide nanoparticles (CONPs) produced using brown alga extract (*Bifurcaria bifurcata*). *Appl Nanosci.* 2014;4:571–6.
57. Krithiga N, Jayachitra A, Rajalakshmi A. Synthesis, characterization and analysis of the effect of copper oxide nanoparticles in biological systems. *Ind J Nano Sci.* 2013;1:6–15.
58. Borgohain K, Murase N, Mahamuni S. Synthesis and properties of Cu₂O quantum particles. *J Appl Phys.* 2002;92:1292–7.
59. Yin M, Wu CK, Lou Y, Burda C, Koberstein JT, Zhu Y, O'Brien S. Copper oxide nanocrystals. *J Am Chem Soc.* 2005;127:9506–11.
60. Rahman A, Ismail A, Jumbiant D, Magdalena S, Sudrajat H. Synthesis of copper oxide nanoparticles by using *Phormidium cyanobacterium*. *Indo J Chem.* 2009;9:355–60.
61. Kiruba Daniel SCG, Nehru K, Sivakumar M. Rapid biosynthesis of silver nanoparticles using *Eichhornia crassipes* and its antibacterial activity. *Curr Nanosci.* 2012;8:1–5.
62. Vijay Kumar PPN, Shameem U, Kollu P, Kalyani RL, Pammi SVN. Green synthesis of copper oxide nanoparticles using *Aloe vera* leaf extract and its antibacterial activity against fish bacterial pathogens. *BioNanoSci.* 2015;5:135–9.
63. Vishveshvar K, Aravind Krishnan MV, Haribabu K, Vishnu Prasad S. Green synthesis of copper oxide nanoparticles using *Xirol coccinea* plant leaves and its characterization. *BioNanoSci.* 2018;8:554–8.
64. Vasantharaj S, Sathiyavimal S, Saravanan M, Senthilkumar P, Kavitha G, Shanmugavel M, Manikandan E, Pugazhendhi A. Synthesis of ecofriendly copper oxide nanoparticles for fabrication over textile fabrics: characterization of antibacterial activity and dye degradation potential. *J Photochem Photobiol B Biol.* 2018;191:149.
65. Singh J, Kumar V, Kim KH, Rawat M. Biogenic synthesis of copper oxide nanoparticles using plant extract and its prodigious potential for photocatalytic degradation of dyes. *Environ Res.* 2019;177:108569.
66. Vanathi P, Rajiv P, Sivaraj R. Synthesis and characterization of *Eichhornia*-mediated copper oxide nanoparticles and assessing their antifungal activity against plant pathogens. *Bull Mater Sci.* 2016;39:1165–70.
67. Ghidan AY, Al-Antary TM, Awwad AM. Green synthesis of copper oxide nanoparticles using *Punica granatum* peels extract: effect on green peach aphid. *Environ Nanotechnol Monit Manag.* 2016;6:95–8.
68. Sivaraj R, Rahman PK, Rajiv P, Salam HA, Venckatesh R. Biogenic copper oxide nanoparticles synthesis using *Tabernaemontana divaricate* leaf extract and its antibacterial activity against urinary tract pathogen. *Spectrochim Acta A Mol Biomol Spectrosc.* 2014;133:178–81.
69. Huang J, Li Q, Sun D, Lu Y, Su Y, Yang X, Wang H, Wang Y, Shao W, He N, Hong J, Chen C. Biosynthesis of silver and gold nanoparticles by novel sun dried *Cinnamomum camphora* leaf. *Nanotechnology.* 2007;18:105104–15.
70. Gopinath V, Priyadarshini S, Al-Maleki AR, Alagiri M, Yahya R, Saravanan S, Vadivelu J. In vitro toxicity, apoptosis and antimicrobial effects of phyto-mediated copper oxide nanoparticles. *RSC Adv.* 2016;6:110986–95.
71. Saif S, Tahir A, Asim T, Chen Y. Plant mediated green synthesis of CuO nanoparticles: comparison of toxicity of engineered and plant mediated CuO nanoparticles towards *Daphnia magna*. *Nanomaterials.* 2016;6:205.
72. Odzak N, Kistler D, Behra R, Sigg L. Dissolution of metal and metal oxide nanoparticles in aqueous media. *Environ Pollut.* 2014;191:132–8.
73. Adam N, Leroux F, Knäpen D, Bals S, Blust R. The uptake of ZnO and CuO nanoparticles in the water-flea *Daphnia magna* under acute exposure scenarios. *Environ Pollut.* 2014;194:130–7.
74. Regier N, Cosio C, von Moos N, Slaveyko VI. Effects of copper-oxide nanoparticles, dissolved copper and ultraviolet radiation on copper bioaccumulation, photosynthesis and oxidative stress in the aquatic macrophyte *Elodea nuttallii*. *Chemosphere.* 2015;128:56–61.
75. Perreault F, Oukarroum A, Melegari SP, Matias WG, Popovic R. Polymer coating of copper oxide nanoparticles increases nanoparticles uptake and toxicity in the green alga *Chlamydomonas reinhardtii*. *Chemosphere.* 2012;87:1388–94.
76. Shi J, Abid AD, Kennedy IM, Hristova KR, Silk WK. To duckweeds (*Landoltia punctata*), nanoparticulate copper oxide is more inhibitory than the soluble copper in the bulk solution. *Environ Pollut.* 2011;159:1277–82.
77. Raja Naika H, Lingaraju K, Manjunath K, Kumar D, Nagaraju G, Suresh D, Nagabhushana H. Green synthesis of CuO nanoparticles using *Gloriosa superba* L. extract and their antibacterial activity. *J Taibah Univ Sci.* 2015;9:7–12.
78. Sankar R, Manikandan P, Malarvizhi V, Fathima T, Shivashangari KS, Ravikumar V. Green synthesis of colloidal copper oxide nanoparticles using *Carica papaya* and its application in photocatalytic dye degradation. *Spectrochim Acta A Mol Biomol Spectrosc.* 2014;121:746–50.
79. Ethiraj AS, Kang DJ. Synthesis and characterization of CuO nanowires by a simple wet chemical method. *Nano Res Lett.* 2012;7:70.
80. Nasrollahzadeh M, Maham M, Sajadi SM. Green synthesis of CuO nanoparticles by aqueous extract of *Gundelia tournefortii* and evaluation of

- their catalytic activity for the synthesis of N-monosubstituted ureas and reduction of 4-nitrophenol. *J Colloid Interface Sci.* 2015;455:245–53.
81. Adzet T, Puigmacia M. High-performance liquid chromatography of caffeoylquinic acid derivatives of *Cynara scolymus* L. leaves. *J Chromatograph A.* 1985;348:447–53.
 82. Haghi G, Hatami A, Arshi R. Distribution of caffeic acid derivatives in *Gundelia tournefortii* L. *Food Chem.* 2011;124:1029–35.
 83. Nasrollahzadeh M, Mohammad Sajadi S, Rostami-Vartooni A. Green synthesis of CuO nanoparticles by aqueous extract of *Anthemis nobilis* flowers and their catalytic activity for the A³ coupling reaction. *J Colloid Interface Sci.* 2015;459:183–8.
 84. Ullah H, Ullah Z, Fazal A, Irfan M. Use of vegetable waste extracts for controlling microstructure of CuO nanoparticles: green synthesis, characterization, and photocatalytic applications. *J Chem.* 2017;2721798:5.
 85. Ranjbar-Karimi R, Bazmandegan-Shamili A, Aslani A, Kaviani K. Sonochemical synthesis, characterization and thermal and optical analysis of CuO nanoparticles. *Phys B Condens Matter.* 2010;405:3096–100.
 86. Nasrollahzadeh M, Sajadi SM, Rostami-Vartooni A, Bagherzadeh M. Green synthesis of Pd/CuO nanoparticles by *Theobroma cacao* L. seeds extract and their catalytic performance for the reduction of 4-nitrophenol and phosphine-free heck coupling reaction under aerobic conditions. *J Colloid Interface Sci.* 2015;448:106–13.
 87. Geil P, Anderson J. Nutrition and health implications of dry beans: a review. *J Am Coll Nutr.* 1994;13:549–58.
 88. Mishra SB, Rao CV, Ojha SK, Vijayakumar M, Verma A. An analytical review of plants for anti diabetic activity with their phytoconstituent and mechanism of action: a review. *Int J Pharmacol Sci Res.* 2010;1:29–44.
 89. Bachheti A, Sharma A, Bachheti RK, Husen A, Pandey DP. Plant allelochemicals and their various application. In: Mérillon JM, Ramawat KG, editors. *Co-Evolution of Secondary Metabolites, Reference Series in Phytochemistry.* Cham: Springer International Publishing AG. https://doi.org/10.1007/978-3-319-76887-8_14-1 (2019).
 90. Nagajyothi PC, Muthuraman P, Sreekanth TVM, Kim DH, Shim J. Green synthesis: in-vitro anticancer activity of copper oxide nanoparticles against human cervical carcinoma cells. *Arab J Chem.* 2017;10:215–25.
 91. Bawadi HA. Inhibition of Caco-2 colon, MCF-7, and Hs578T breast, and DU 145 prostatic cancer cell proliferation by water soluble black bean condensed tannins. *Can Lett.* 2005;218:153–62.
 92. Bobe G, Barret KG, Mentor-Marcel RA, Saffiotti U, Young MR, Colburn NH, Albert PS, Bennink MR, Lanza E. Dietary cooked navy beans and their fractions attenuate colon carcinogenesis in azoxymethane-induced Ob/Ob mice. *Nutri Cancer.* 2008;60:373–81.
 93. Hangen L, Bennik MR. Consumption of black beans and navy beans (*Phaseolus vulgaris*) reduced azoxymethane-induced colon cancer in rats. *Nutr Cancer.* 2002;44:60–5.
 94. Thompson MD, Mensack MM, Jiang W, Zhu Z, Lewis MR, McGinley JN, Brick MA, Thompson HJ. Cell signaling pathways associated with a reduction in mammary cancer burden by dietary common bean (*Phaseolus vulgaris* L.). *Carcinogenesis.* 2012;33:226–32.
 95. Mukhopadhyay R, Kazi J, Debnath MC. Synthesis and characterization of copper nanoparticles stabilized with *Quisqualis indica* extract: evaluation of its cytotoxicity and apoptosis in B16F10 melanoma cells. *Biomed Pharmacother.* 2018;97:1373–85.
 96. 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.* 2018;255:541–9.
 97. Machado TDB, Leal ICR, Amaral ACF, Dos Santos KRN, Da Silva MG, Kuster RM. Antimicrobial Ellagitannin of *Punica granatum* Fruits. *J Braz Chem Soc.* 2002;13:606–10.
 98. Voravuthikunchai SP, Sririrak T, Limsuwan S, Supawita T, Iida T, Honda T. Inhibitory effects of active compounds from *Punica granatum* pericarp on Verocytotoxin production by Enterohemorrhagic *Escherichia coli* O157: H7. *J Health Sci.* 2005;51:590–6.
 99. Naz S, Siddiqi R, Ahmad S, Rasool SA, Sayeed SAJ. Antibacterial activity directed isolation of compounds from *Punica granatum*. *J Food Sci.* 2007;72:341–5.
 100. Azam A, Ahmed AS, Oves M, Khan MS, Memic A. Size-dependent antimicrobial properties of CuO nanoparticles against gram-positive and -negative bacterial strains. *Int J Nanomedicine.* 2012;7:3527–35.
 101. Nasrollahzadeh M, Maham M, Rostami-Vartooni A, Bagherzadeh M, Sajadi SM. Barberry fruit extract assisted in situ green synthesis of CuO nanoparticles supported on a reduced graphene oxide-Fe₃O₄ nanocomposite as a magnetically separable and reusable catalyst for the O-arylation of phenols with aryl halides under ligand-free conditions. *RSC Adv.* 2015;5:64769–80.
 102. Getnet Z, Husen A, Fetene M, Yemata G. Growth, water status, physiological, biochemical and yield response of stay green sorghum (*Sorghum bicolor* (L.) Moench) varieties-a field trial under drought-prone area in Amhara regional state, Ethiopia. *J Agron.* 2015;14:188–202.
 103. Embiale A, Hussein M, Husen A, Sahle S, Mohammed K. Differential sensitivity of *Pisum sativum* L. cultivars to water-deficit stress: changes in growth, water status, chlorophyll fluorescence and gas exchange attributes. *J Agron.* 2016;15:45–57.
 104. Siddiqi KS, Husen A. Engineered gold nanoparticles and plant adaptation potential. *Nano Res Lett.* 2016;11:400.
 105. Siddiqi KS, Husen A. Plant response to engineered metal oxide nanoparticles. *Nano Res Lett.* 2017;12:92.
 106. Husen A, Iqbal M, Aref IM. Plant growth and foliar characteristics of faba bean (*Vicia faba* L.) as affected by indole-acetic acid under water-sufficient and water-deficient conditions. *J Environ Biol.* 2017;38:179–86.
 107. Husen A, Iqbal M, Sohrab SS, Ansari MKA. Salicylic acid alleviates salinity-caused damage to foliar functions, plant growth and antioxidant system in Ethiopian mustard (*Brassica carinata* A. Br.). *Agri Food Sec.* 2018;7:44.
 108. Husen A, Iqbal M, Khanum N, Aref IM, Sohrab SS, Meshresha G. Modulation of salt-stress tolerance of Niger (*Guizotia abyssinica*), an oilseed plant, by application of salicylic acid. *J Environ Biol.* 2019;40:94–104.
 109. Dimkpa CO, McLean JE, Latta DE, Manangon E, Britt DW, Johnson WP, Boyanov MI, Anderson AJ. CuO and ZnO nanoparticles: phytotoxicity, metal speciation, and induction of oxidative stress in sand-grown wheat. *J Nanopart Res.* 2012;14:1125–9.
 110. Pradhan SP, Patra S, Das S, Chandra S, Mitra KK, Dey S, Akbar P, Palit A, Goswami A. Photochemical modulation of biosafe manganese nanoparticles on *Vigna radiata*: a detailed molecular, biochemical, and biophysical study. *Environ Sci Technol.* 2013;47:13122–31.
 111. Yasmeen F, Raja NI, Razzaq A, Komatsu S. Proteomic and physiological analyses of wheat seeds exposed to copper and iron nanoparticles. *Biochim Biophys Acta.* 2017;2017:28–42.
 112. Ashfaq M, Singh S, Sharma A, Verma N. Cytotoxic evaluation of the hierarchical web of carbon microrofibers. *Ind Eng Chem Res.* 2013;52:4672–82.
 113. Nair PMG, Chung IM. Impact of copper oxide nanoparticles exposure on *Arabidopsis thaliana* growth, root system development, root lignification and molecular level changes. *Environ Sci Pollut Res.* 2014;21:12709–22.
 114. Lequeux H, Hermans C, Lutts S, Nathalie V. Response to copper excess in *Arabidopsis thaliana*: impact on the root system architecture, hormone distribution, lignin accumulation and mineral profile. *Plant Physiol Biochem.* 2010;48:673–82.
 115. Husen A. Growth characteristics, physiological and metabolic responses of teak (*Tectona grandis* Linn. F.) clones differing in rejuvenation capacity subjected to drought stress. *Silvae Gene.* 2010;59:124–36.
 116. Chung IM, Rekha K, Venkidasamy B, Thiruvengadam M. Effect of copper oxide nanoparticles on the physiology, bioactive molecules, and transcriptional changes in *Brassica rapa* ssp. *rapa* seedlings. *Water Air Soil Pollut.* 2019;230:48.
 117. Karlsson HL, Cronholm P, Gustafsson J, Moller L. Copper oxide nanoparticles are highly toxic: a comparison between metal oxide nanoparticles and carbon nanotubes. *Chem Res Toxicol.* 2008;21:1726–32.
 118. Heinlaan M, Ivask A, Blinova I, Dubourguier HC, Kahru A. Toxicity of nanosized and bulk ZnO, CuO and TiO₂ to bacteria *Vibrio fischeri* and crustaceans *Daphnia magna* and *Thamnocephalus platyurus*. *Chemosphere.* 2008;71:1308–16.
 119. Tavares KP, Caloto-Oliveira Á, Vicentini DS, Melegari SP, Matias WG, Barbosa S, Kummrow F. Acute toxicity of copper and chromium oxide nanoparticles to *Daphnia similis*. *Ecotoxicol Environ Contam.* 2014;9:43–50.
 120. Adam N, Vakurov A, Knapen D, Blust R. The chronic toxicity of CuO nanoparticles and copper salt to *Daphnia magna*. *J Hazard Mater.* 2015; 283:416–22.
 121. Rajeshkumar S, Menon S, Venkat Kumar S, Tambuwala MM, Bakshi HA, Mehta M, Satija S, Gupta G, Chellappan DK, Thangavelu L, Dua K. Antibacterial and antioxidant potential of biosynthesized copper nanoparticles mediated through *Cissus amotiana* plant extract. *J Photochem Photobiol B.* 2019;197:111531.

122. Asghar MA, Zahir E, Shahid SM, Khan MN, Asghar MA, Iqbal J, Walker G. Iron, copper and silver nanoparticles: green synthesis using green and black tea leaves extracts and evaluation of antibacterial, antifungal and aflatoxin B1 adsorption activity. *LWT*. 2018;90:98–107.
123. Roy K, Ghosh CK, Sarkar CK. Rapid detection of hazardous H₂O₂ by biogenic copper nanoparticles synthesized using *Eichhornia crassipes* extract. *Microsyst Technol*. 2019;25:1699–703.
124. Zangeneh MM, Ghaneialvar H, Akbaribazm H, Ghanimatdan M, Abbasi N, Goorani S, Pirabbasi E, Zangeneh A. Novel synthesis of *Falcaria vulgaris* leaf extract conjugated copper nanoparticles with potent cytotoxicity, antioxidant, antifungal, antibacterial, and cutaneous wound healing activities under in vitro and in vivo condition. *J Photochem Photobiol B Biol*. 2019;197:111556.
125. Rajeshkumar S, Rinith G. Nanostructural characterization of antimicrobial and antioxidant copper nanoparticles synthesized using novel *Persea americana* seeds. *OpenNano*. 2018;3:18–27.
126. Kerour A, Boudjadar S, Bourzami R, Allouche B. Eco-friendly synthesis of cuprous oxide (Cu₂O) nanoparticles and improvement of their solar photocatalytic activities. *J Solid State Chem*. 2018;263:79–83.
127. Mehr ES, Sorbiun M, Ramazani A, Fardood ST. 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*. 2018;29:1333–40.
128. Dobrucka R. Antioxidant and catalytic activity of biosynthesized CuO nanoparticles using extract of *Galeopsisida herba*. *J Inorg Organomet Polym Mat*. 2018;28:812–9.
129. Jadhav MS, Kulkarni S, Raikar P, Barretto DA, Vootla SK, Raikar US. Green biosynthesis of CuO & Ag–CuO nanoparticles from *Malus domestica* leaf extract and evaluation of antibacterial, antioxidant and DNA cleavage activities. *New J Chem*. 2018;42:204–13.
130. Khatami M, Varma RS, Heydari M, Peydayesh M, Sedighi A, Askari HA, Rohani M, Baniasadi M, Arkia S, Seyed F, Khatami S. Copper oxide nanoparticles greener synthesis using tea and its antifungal efficiency on *Fusarium solani*. *Geomicrobiol J*. 2019;36:777–81.
131. Akhter SMH, Mohammad F, Ahmad S. *Terminalia bellerica* mediated green synthesis of nanoparticles of copper, iron and zinc metal oxides as the alternate antibacterial agents against some common pathogens. *BioNanoSci*. 2019;9:365–72.

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Ready to submit your research? Choose BMC and benefit from:

- fast, convenient online submission
- thorough peer review by experienced researchers in your field
- rapid publication on acceptance
- support for research data, including large and complex data types
- gold Open Access which fosters wider collaboration and increased citations
- maximum visibility for your research: over 100M website views per year

At BMC, research is always in progress.

Learn more biomedcentral.com/submissions

