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Eco-friendly Green Biosynthesized Metallic Nanoparticles and Biotechnological Applications in Pharmaceuticals Sciences

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Abstract: The next years will prove the importance of greensynthesis methods for MNPs and MONPs production because they are not only easy to execute, fast, and cheap but also less toxic and environmentally ecofriendly. Nanoparticle synthesis using microorganisms and plants by green synthesis technology is biologically safe, cost-effective, and environment-friendly. Plants and microorganisms have established the power to devour and accumulate inorganic metal ions from their neighboring niche. The biological entities are known to synthesize nanoparticles bothextra and intracellularly. The capability of a living system to utilize its intrinsic organic chemistry processes in remodeling inorganic metal ions into nanoparticles has opened up an undiscovered area of biochemical analysis. Metal nanoparticles (MNPs) and metal oxidenanoparticles (MONPs) are used in numerous fields. The new nano-based entities are being strongly generated and incorporated into everyday personal care products, cosmetics, medicines, drug delivery, and clothing toimpact industrial and manufacturing sectors, which means that nanomaterials commercialization and nanoassisted device will continuously grow. They can be prepared by many methods such as green synthesis and the conventional chemical synthesis methods. The green synthesis of nanoparticles (NPs) using living cells is a promising and novelty tool in bionanotechnology. Chemical and physical methods are used to synthesize NPs; however, biological methods are preferred due to its eco-friendly, clean, safe, cost effective, easy, and effective sources for high productivity and purity. Greensynthesis includes infinite accession to produce MNPs and MONPs with demanding properties. The structure–function relationships between nanomaterials and key information for life cycle evaluation lead to the production of high execution nanoscale materials that are gentle and environmentally friendly. Majority of plants have features as sustainable and renewable suppliers compared with microbes and enzymes, as they have the ability to pick up almost 75% of the light energy and transform it into chemical energy, contain chemicals like antioxidants and sugars, and play fundamental roles in the manufacture of nanoparticles. Plants considered the main factory for the green synthesis of MNPs and MONPs, and until now, different plant species have been used to study this, but the determined conditions should be taken into consideration to execute this preparation.

Key words: Nanotechnology, green synthesis, MNPs, MONPs, biotechnological application, plant leaf extracts.

1. Green Nanotechnology and Properties of Nonmaterials

Over the last decade, novel synthesis approaches/methods for nanomaterials (such as metal nanoparticles, quantum dots (QDs), carbon nanotubes (CNTs), graphene, and their composites) have been an interestingarea in nanoscience and technology [1-9] owing to their novel properties, as shown in Scheme 1.

Nanotechnology is cited as a key technology of the 21st century and has generated a great deal ofexcitement world-wide, but it has been slowed down because of the poor understanding of hazardsassociated with nanotechnology and fewer policies to manage new risks. Researchers, however, continue to move ahead, engaging themselves to conquer the challenges ranging from managing, producing, funding, regulatory, and

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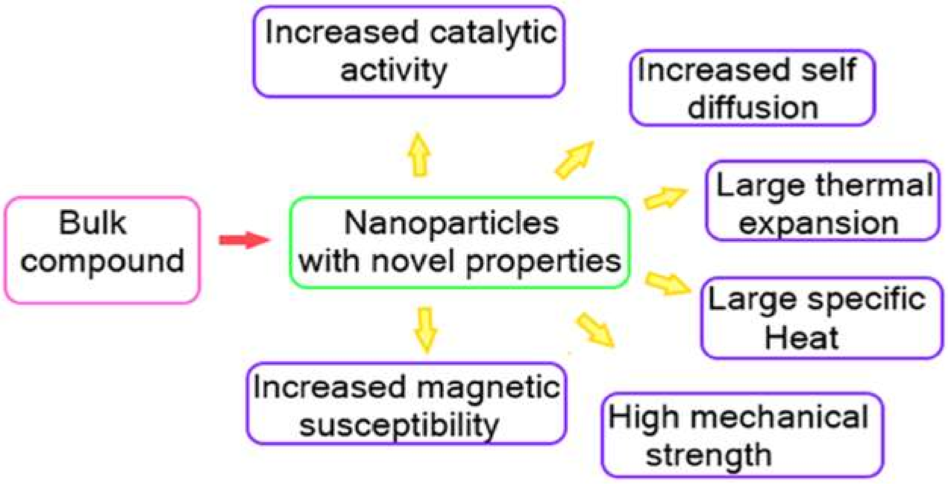
technical aspects. Green nanotechnology is a branch of greentechnology that utilizes the concepts of green chemistry and green engineering, where the word“green” refers to the use of plant products (Fig. 1). It reduces the use of energy and fuel by using lessmaterial and renewable inputs wherever possible. Furthermore, nanotechnological products, processes, and applications are expected to contribute significantly to environmental and climate protection bysaving raw materials, energy, and water, as well as by reducing greenhouse gases and hazardouswaste. There is some “truly” green nanotechnology, i.e., fully growingnanomaterials in plants—however, they will never reach the scale required for the industrial production of nanomaterials. In order to make a conclusive observation, green nanotechnologyneeds a full process assessment like other industrially manufactured products [10, 11].



Scheme 1 **Properties of nonmaterial.**

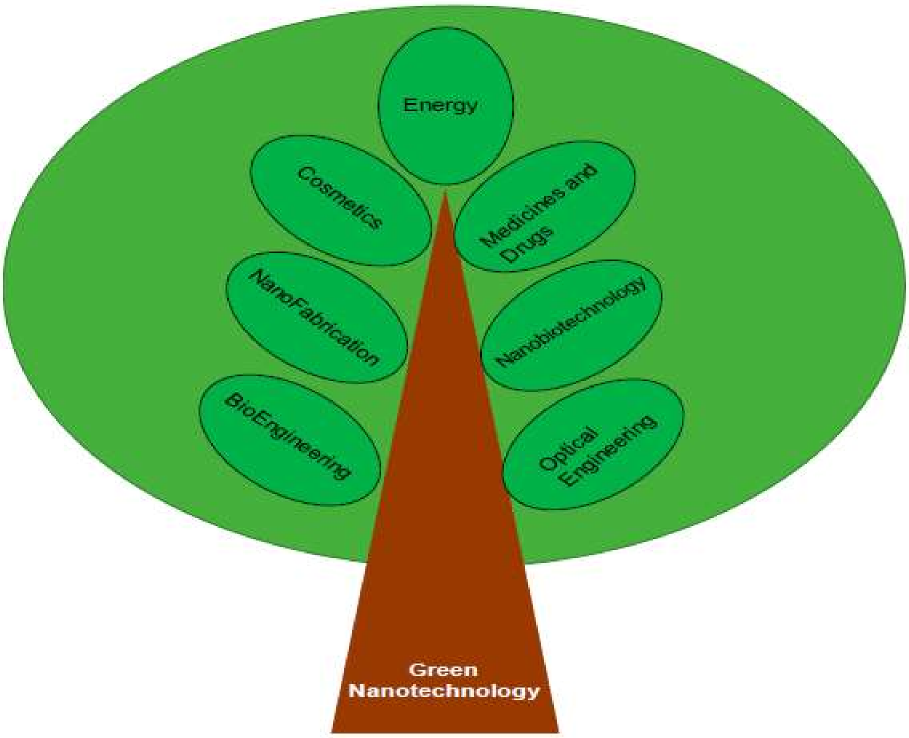


Fig. 1 **Branches of green nanotechnology.**

The term nanotechnology incorporates the production of novelmaterials at the nanoscale range between 1 and 100 nm. Nanotechnology in conjunction withbiology gives rise to an advanced area of nanobiotechnology that involves living entitiesof both prokaryotic and eukaryotic origin, such as algae, cyanobacteria, actinomycetes, bacteria, viruses, yeasts, fungi, and plants. Every biological system varies in itscapabilities to supply metallic nanoparticles. However, not all biological organisms canproduce nanoparticles due to their enzymatic activities and intrinsicmetabolic processes.Therefore, biological entities or their extracts are used for the green synthesis of metallicnanoparticles through bio-reduction of metallic particles leading to the synthesis ofnanoparticles. These biosynthesized metallic nanoparticles have a range of unlimitedpharmaceutical applications including delivery of drugs or genes, detection of pathogensor proteins, and tissue engineering. The effective delivery of drugs and tissue engineeringthrough the use of nanotechnology exhibited vital contributions in translational researchrelated to the pharmaceutical products and their applications. Collectively, this chapter covers the green synthesis of nanoparticles by using various biological systems as wellas their applications.

Nanotechnology is amongst the most widely used technologies in translational research. Thedevelopment of metallic nanoparticles employing biological materials by an eco-friendly approachhas attracted significant attention. Nanotechnology deals with particles of a size ranging from 1 to 100 nm, their synthesis strategy, and manipulation. This knowledge domain naturally comminglesall the fields of natural sciences together with chemistry, physics, biological sciences, engineering, materials science, and computational sciences for the formulation of nanostructures [12, 13]. The nanostructures have different applications attributable to theirnew or increased properties [14, 15] depending upon their size, distribution, and morphology. It has applications in various fields including biomedical, catalysis, chemical industries, cosmetics, drug delivery, electronics, environment, energy science, food and feed, health care, mechanics, optics, space industries, non-linear opticaldevices, single-electron transistors, and photo-electrochemicalapplications. The metallic nanoparticles are considered one ofthe most promising systems for all the aforementioned functions [16-18]. A nanoscale drug carrier acts as a single unit with respect toits properties and transport. These nanoclusters have narrow sizedistribution and a minimum of one dimension between 1 and 10nanometers. The agglomerates of ultrafine particles, nanoclustersor nanoparticles, are nanopowders whereas nanocrystals are thecrystals of nanoparticle size

Nanoparticles (NPs) with attractive shapes are synthesizedby numerous physical and chemical methods. Nowadays, biologicalsyntheses are preferred because they are safe, clean, cheap and easily scaled up for the well-built scale synthesis ofNPs. NPs have great applications in different fields as magneticdevices, photocatalysts, microelectronic devices, anticorrosivecoatings, biomedicals, and electrocatalysts and alsoin powder metallurgy. The biotechnological applications ofNPs have increased day by day due to its cutting-edge character, biocompatibility, anti-inflammatory and antimicrobialactivity, effective drug delivery, bioactivity, bioavailability, tumor targeting, and bio-absorption [19-29]. On the other hand, NPs can be used in industrial and electronic fields as catalystsand as conductors in transistors and in cancer detection apparatus [30, 31]. Recently, magnetic NPs have been used inmultidisciplinary fields such as in cancer treatment, drug delivery, tumor detection, resonance imaging, and separationprocesses [32]. Biological activities of magnetic NPs couldbe attributed to their smaller size, magnetic properties, highbiocompatibility, and easy surface modifications [33].

Green synthesis of NPs using different biological entities can overcomes many of the destructive effects of physical and chemical techniques. These include the biosynthesis of NPs atmild pH, pressure, and temperature and do not require toxic orhazardous substances as well as avoid the addition of externalreducing, capping, and stabilizing agents [34]. Recently, variouspublished reports enumerate different forms of metal, metal oxide, and dioxide NPs including core/shell (CS) NPs[35]; polymer-coated NPs [36]; Ag-NPs [37]; Cu-NPs [38];CuO-NPs [22]; ZnO-NPs [26]; Au-NPs [39]; Pt-, Pd-, Si-, and Ni-NPs [40-43]; FeO-NPs [44]; TiO_2-NPs [45]; and ZrO_2-NPs [46]. Each one of these NPs has its specific charactersand applications. NPs have different classifications according to their properties as shown in Fig. 2.

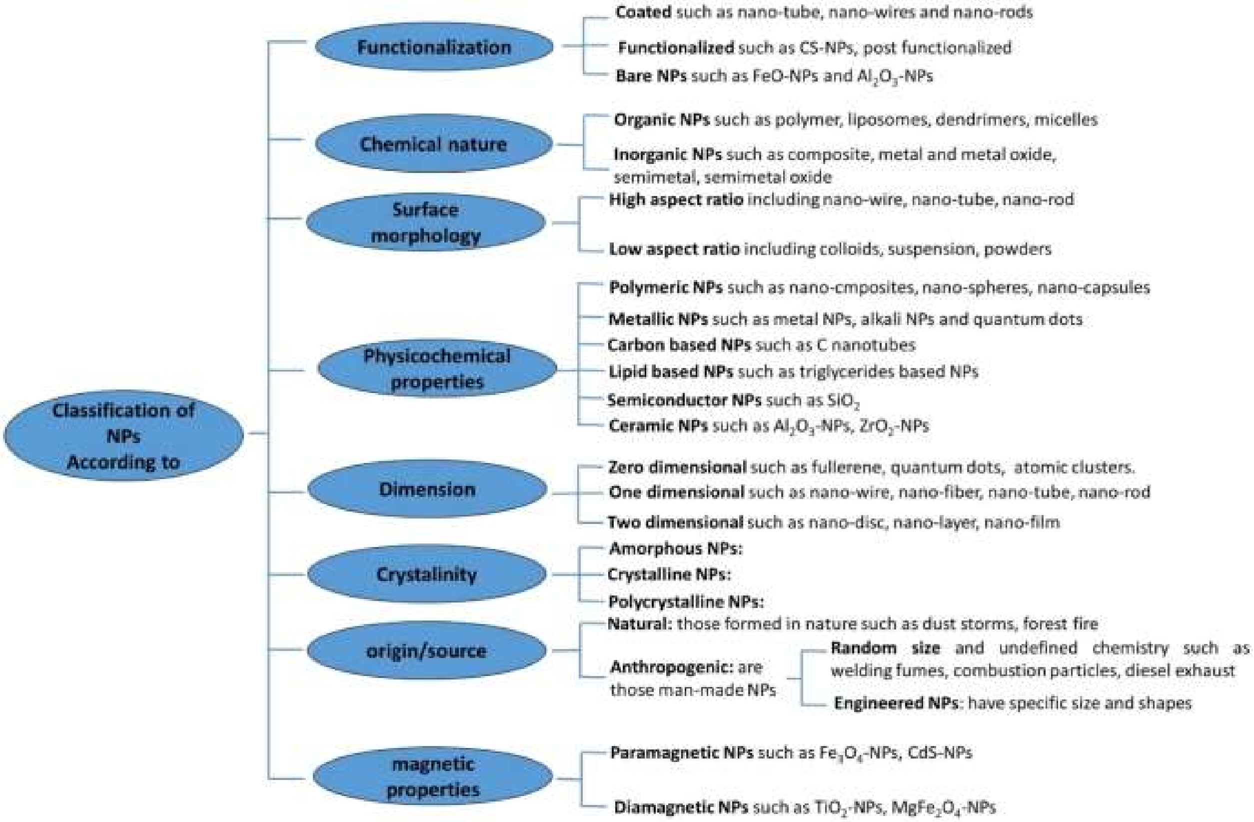


Fig. 2 Classification of NPs according to different approaches [47].

In this chapter, we focus on the biosynthesis procedures to synthesize MNPs and MONPs, including comparison between green synthesis and the classicalchemistry methods as well as the several new orientationof green synthesis of nanoparticles from different plantparts, especially plant leaf extracts. Plants with reducing compounds is the preferred choice for the synthesis ofnoble metals-metal ions can be reduced to thecorresponding metals in the absence of any otherchemicals under microwave irradiation conditions usingbenign solvent, water. Noble metals such as gold (Au), silver (Ag), platinum (Pt), and palladium (Pd) and othermetals such as copper (Cu) and nickel (Ni), which arecharacterized by their optical, electronic, mechanical, magnetic, and chemical properties, leading to different technological applications. Plants with numerous reducingagents are suitable candidates for the manufacture of noble MNPs. The main purpose of this research is to give abackground on green nanotechnology prospective evolution,pertinent concerns appeared related to the greensynthesis of metal and metal oxide from plant extracts,nanoparticle formation mechanism, and the importanceof flavonoids, vitamin B_2, ascorbic acid (vitamin C), andphenolic compounds in the MNP and MONP production.The traditional sorghum beers are produced in manycountries in Africa, but diversity in the production processmay depend on the geographic localization. These beersare very rich in calories; B-group vitamins includingthiamine, folic acid, riboflavin, and nicotinic acid; andessential amino acids such as lysine. However, the Westernbeers are more attractive than the traditional sorghumbeers. The traditional sorghum beers have poor hygienicquality, organoleptic variations, and shorter shelf lifecompared with the Western beers. Many research studieson traditional sorghum beers have been carried out anddocumented in several African countries, especially themicrobiological and biochemical properties, the technologiesused in the manufacture processes, and syntheticcharacteristics of African traditional sorghum beers (ikigage,merissa, doro, dolo, pito, amgba, and tchoukoutou).The excellent resources for the production of greenerbiomaterials are plants and considerable advances havebeen achieved in many fields such as biotechnology andgene transfer. The manufactured biological nanomaterials have a great application in the pharmaceutical industry such as novel pharmaceuticals preparation, drug delivery personification procedures, and production of functional nanodevices [20-31].

1.1 NPs Characterization

Physicochemical characterization of generated NPs is an importantstage that should be carefully considered before nanoparticle application. Studying the size, shape, surface area, homogeneity, stability, and other features will provide valuableinformation of nanoscale systems and insight into thesynthesis control of nanoparticles for commercial applications.Some common techniques of characterization such asthe color change test; UV–visible spectrometry; Fourier transformationinfrared spectroscopy (FT-IR); electron microscopyincluding transmission, high-resolution, scanning, and fieldemissionscanning (TEM, HR-TEM, SEM, and FE-SEM); energy-dispersive spectroscopy (EDX-map); dynamic lightscattering (DLS); powder X-ray diffraction (XRD); vibratingsample magnetometer (VAM); thermogravimetric analysis (TGA); and other instruments are shown with their functionsin [23, 48-55].

1.2 Factors Affecting Biological NPs Synthesis

Adjusting the sizes and shapes of metal nanomaterials appearseither to be compelled by their environmental development orshifted by functional molecules [23]. Improving the reactionconditions for the synthesis of nanoparticles, including temperature, pH, incubation period, aeration, salt concentration, redox conditions, mixing ratio, and irradiation, has been investigated [56, 57]. The size and shape of NPs depend onchemical and physical factors. The optimum metal ion concentration, temperature, and pH of the reaction mixture playkey roles in nanoparticle synthesis. The rate of intracellularnanoparticle creation and then the size of the NPs could, to anamount, be influenced by scheming parameters such as temperature, pH, substrate concentration, and exposure period tosubstrate [58].

Table 1 Factors affecting biological synthesis of metal nanoparticles.

S. No Factors	Influence on biological synthesis of metal nanoparticles	References
1. pH	Size and shape of the synthesized nanoparticle	[59, 60]
2. Reactant concentration	Shape of the synthesized nanoparticles	[61]
3. Reaction time	Size and shape of the synthesized nanoparticle	[62]
4. Reaction temperature	Size, shape, yield and stability of the synthesized nanoparticle	[60, 63]

The morphological characteristics of nanoparticles can bemanipulated by means of various parameters viz. reaction time, reactant concentrations, pH, and temperature (Table 1). Suchparameters are crucial to understand the effect of environmentalfactors for the synthesis of NP as they may play an importantrole during the optimization of metallic NPs synthesis bybiological means.

1.2.1 pH.

The reaction medium pH plays a critical role in the formationof nanoparticles [64]. Size andshape of nanoparticles vary with the pH of the medium, andlarge sized nanoparticles are produced in acidic pH [59, 60]. The rod-shaped goldnanoparticles were synthesized by using biomass of Avena sativa (Oat) resulting in the size range from 25 to 85 nm at pH 2 which was comparatively smaller (5-20 nm) at pH 3 and 4 [65]. Further, accessibility of functional groups for particle nucleation in the extract was better at pH 3 or 4 as compared to the pH 2 as fewer functional groups were available prompting particle aggregation to formlarger Au nanoparticles. An increased number of spherical Agnanoparticles were synthesized in Cinnamon zeylanicum barkextract at higher pH (pH > 5) [66]. Aslight increase was observed in particle size at higher pH whenCinnamon zeylanicum bark extract was used for the synthesisof palladium (Pd) nanoparticles, and particle size was estimatedfrom 15 to 20 nm at pH < 5, and 20-25 nm at the higher pH [66].

1.2.2 Reactant Concentration

The formation of metallic nanoparticles is affected by theconcentration of biomolecules present in the extract. The shapeof the biosynthesized Au and Ag nanoparticles by using the sundriedCinnamomum camphora (camphor) leaf extract affectedby the amount of biomass in the reaction medium [67]. Exposure of the precursor chloroauric acid togrowing concentrations of the extract resulted in the synthesisof spherical nanoparticles instead of triangular. A change inthe ratio of spherical nanoparticles to triangular plates in thereaction medium having chloroaurate ions due to the presence of carbonyl compounds in the extract was observed when treatedwith varying concentrations of Aloe vera leaf extract [61]. Nanoparticle size can be modulated between 50 and 350 nm by using different extract concentrations [61]. Spherical, triangular, hexagonal, and decahedralshapes of AgNPs were produced by varying the concentrationof Plectranthu samboinicus leaf extract in the reaction medium [68]. An increase in the variety of Ag nanoparticles was observed with increasing concentration of Cinnamon zeylanicum bark extract [66]. The extracellular [69] and intracellularsynthesis [70] of Au nanoparticles wasaffected by biomass and Au salt concentration using marineyeast, Yarrowia lipolytica. An increased Au salt concentrationproduced both nanoscale spheres and plates. In another study, a silver-tolerant yeast strain MKY3 synthesized spherical Agnanoparticles extra-cellularly with the size ranging from 2 to 5 nm [71].

1.2.3 Reaction Time

The reaction time plays an important role for synthesizingnanoparticles [72]. A rapid color change was observed within 2 min when Anana scomosus (Pine apple) extract was usedfor AgNPs synthesis, and aqueous $AgNO_3$ solution was rapidlydecreased, forming nanoparticles within 2min. The reactioncontinued for up to 5 min and then there was a slight colorchange. The shape of synthesized nanoparticles was sphericalwith a mean size of 12 nm [72]. Chenopodium albumleaf extract was used for the biogenic production of Ag and Aunanoparticles. The nanoparticles were formed within 15 min ofthe reaction and the reaction continued over a period of 2 h andvery few nanoparticles with larger size were synthesized [73]. Change in the particle size (ranging 10-35 nm) was observed when reaction time was increased from 30 min to 4 h using Azadirachta indica leaf extract and $AgNO_3$ [62].

1.2.4 Reaction Temperature

The reaction temperature is a critical component which plays akey role in determining the shape, size, and yield of synthesizednanoparticles using plants [60, 63]. The peel extract of Citrus sinensis (sweet orange) produced particles with an average size of around 35 nm at 25 °C. The average size of the nanoparticles decreased to 10 nm with the rise in the reaction temperature to 60 °C [74]. The stable Ag nanoparticles were synthesized by Diospyroskaki (persimmon) leaf extract at the reaction temperaturevarying from 25 to 95 °C [75]. The variationin the temperature of reaction conditions for the synthesis of Au nanoparticles using Avena sativa (oat) biomass ended inmodifications in the shape and size of the nanoparticles produced [65]. A higher temperature supports anincreased rate of formation of Au nanoparticles. The sphericalAu nanoparticles were predominantly formed at the lowertemperature whereas at higher temperatures rod-like and platelikenanoparticles were formed [76, 77]. The reaction rate and particle formation rate increased with theincrease in the reaction temperature. The particle conversion ratesteadily increased and average particle size saw a decrease withthe rise in the reaction temperature to 60 °C.

The extracellularly produced PtNPs amount was reported tobe 5.66 mg l-1 [78], with the variation in thetemperature that affects production rates of the PtNPs. The slightchange in pH from the standard inhibits the PtNPs formation [78].

2. Greener Nanomaterials and Sustainable Implementation

Global research studies give a great interest to green nanotechnology, as green nanotechnology is a resultant field and nascent branch of nanotechnology. Green nanotechnology is the perfect solution to decrease the negative effects of the production and application of nanomaterials, lowering the nanotechnology riskiness [79]. Fig. 3 shows the key merits of green synthesis. The generation of engineered nanomaterials represents an essential breakthrough in nanotechnology and materials science. The real world should be created by moving these products beyond thelaboratory. More than thousands of such products areavailable in the market, of which a large majority are integrated in everyday personal care products, cosmetics, and clothing. Developments of the modern products that consumers need are expected to affect positively almostevery industrial and production sectors, involving medicineand drug delivery. The continuous growth of thenanomaterials marketing and nano-assisted device is veryobvious [80]. The commercialization of successful disruptivetechnologies is fundamental for numerous implementationsto humans and global development, butcritical interest is necessary for potential, health

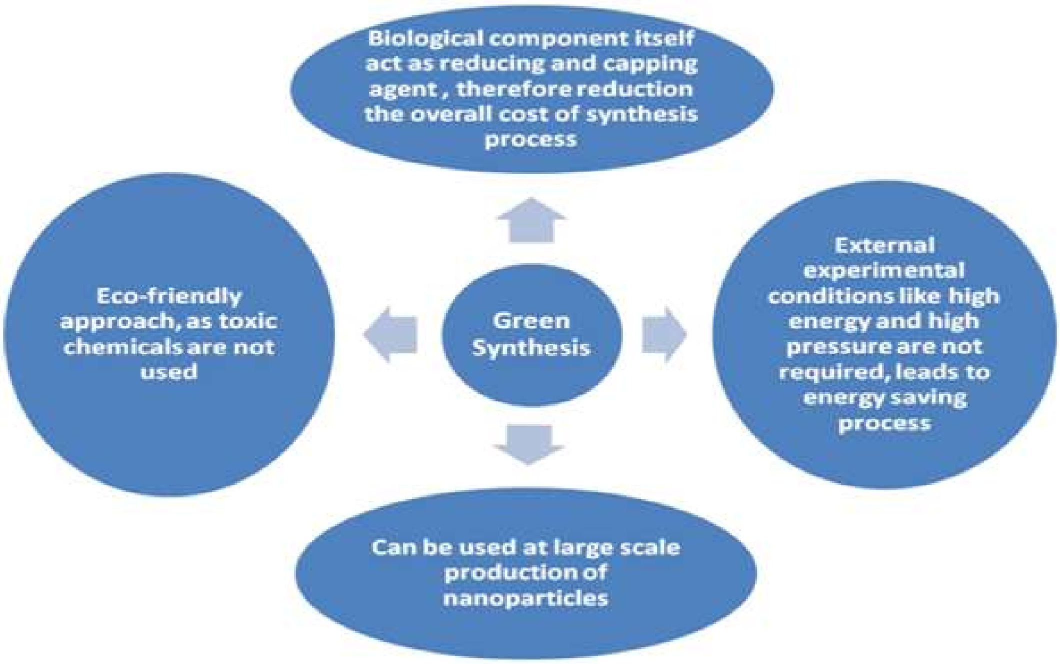


Fig. 3 Key merits of green synthesis [88].

assessmentand environmental effects of these materials [80-83]. Itis a clear reality that the health hazards due to nanoparticlesexposure are slowly comprehended and need to beaddressed rapidly [84] and their manufacture and utilizationare practically uncontrolled [85], particularly in the universedevelopment. This is predominately discouraging when thenew nano-based entities are being generated and incorporatedinto consumer products at an alarmingly quick rate, thus oversight mechanisms is an urgent need since the finalexistence of the majority of the nanotechnology innovations resulted from the research groups which considered simplestartup work must based on instructions and recommendationfrom regulatory bodies and should not be oppositelyaffected by the boosted cost loads connected with suchincreased oversight [86]. Health and safety regulations willhave to carefully negotiate regulatory testing cost load, which will in turn have an essential role in giving priority to hazards associated with nanomaterials [87]. The essentialaspect of the green chemistry emerging sector is theutilization of a group of basics lowers or removes thehazardous substances utilization or generation concerningdesign or production and chemical products' applicationwhile designing new chemical processes visualizes smallrisk as the execution criteria.

Green chemistry basics implementation in the newmaterials expansion and enforcements is all the moreconsiderable in opinion of the principle that the technologyis an early expansion phase and is foreseeable to be widelyutilized and doled out around the world. The strong relationbetween chemical structure and function groups thatconnects specifically to nanomaterials and boosting understanding"key" information for life cycle evaluation of suchmethods could lead to new "design principles" for theproduction of high rendering nanoscale materials that arebenign and environmentally friendly [89].

The molecules, cells, and organs of the aforementioned plants have been bioengineered to provide new nanomaterials with demanding sustainable advantages. Green nanotechnology gives us the chance to prevent the negative effects. Green nanotechnology has an enterprising effect on the nanomaterials or the products design by removing or lowering pollution, which means that it remediates the existingenvironmental problems, as indicated in Fig. 4. The environmental friendly methods such as catalytic potential [90], electrical conductivity [91], optical sensitivity [92], magnetic behavior [93], or biological reactivity [94] are usedto characterize the chemical, physical, and biological propertiesof nanomaterials in addition to many factors such as size,shape, surface charge, chemical structure, surface area, andcoagulation properties of nanoscale distinct materials [95]. The organic solvents and chemical reagents are not used inthe preparation of metal nanoparticles (MNPs). MNPs have unique properties with their nanostructures [96]. The atoms ordered to the nano-scale differ from the bulk metallicmaterials [97], and the unique properties of MNPs and metaloxide nanoparticles (MONPs) are engendered from them.MNPs and MONPs have many applications such as catalysts [98]; drug delivery systems [99]; boosting contrast agents [100]; active food packaging materials [101]; components pointing to nano-biosensor construction [102]; gene transfersystem [99]; antibiotics, antiseptics, and disinfectants tocontrol pathogens and pests [103]; and nano electronic components [104].

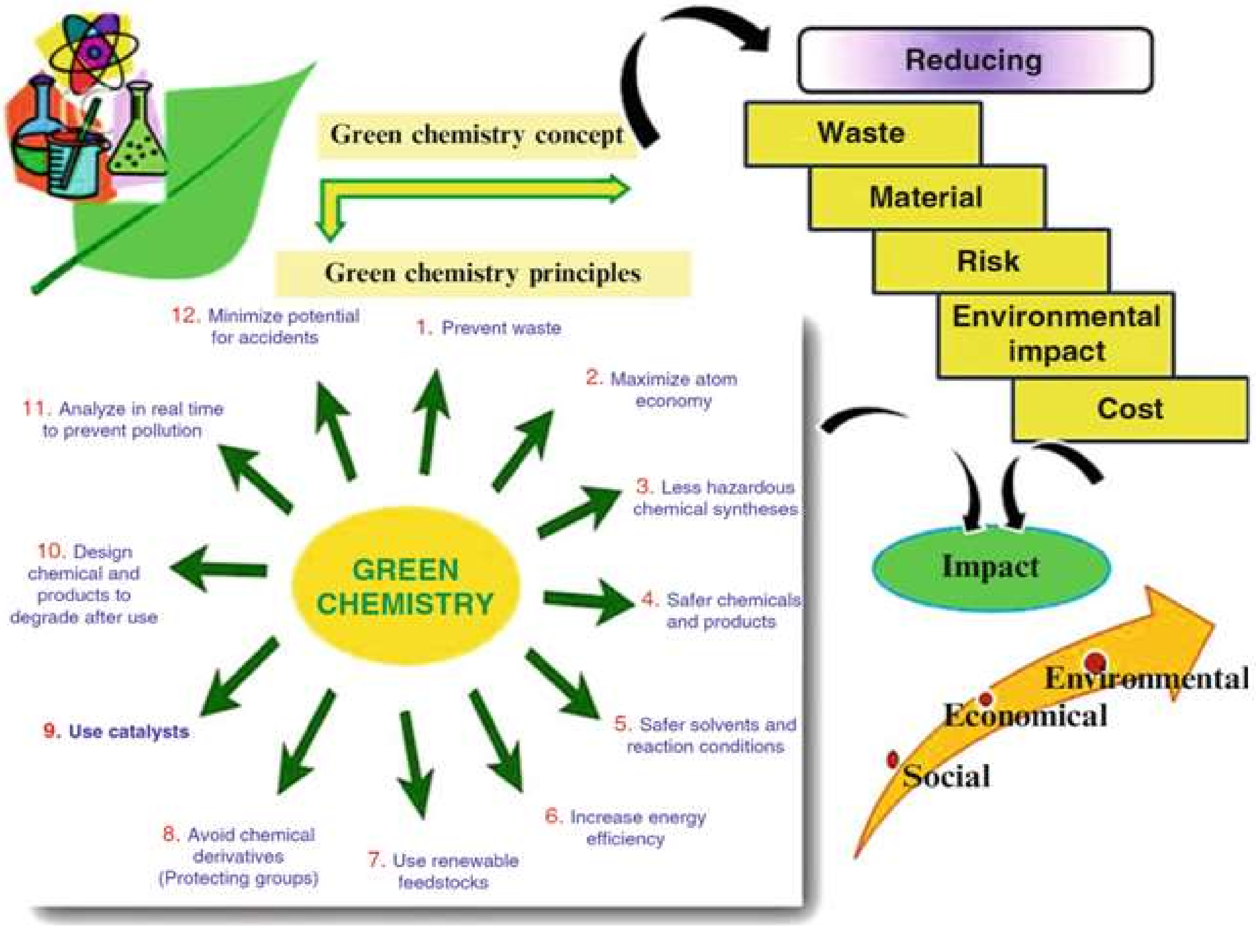
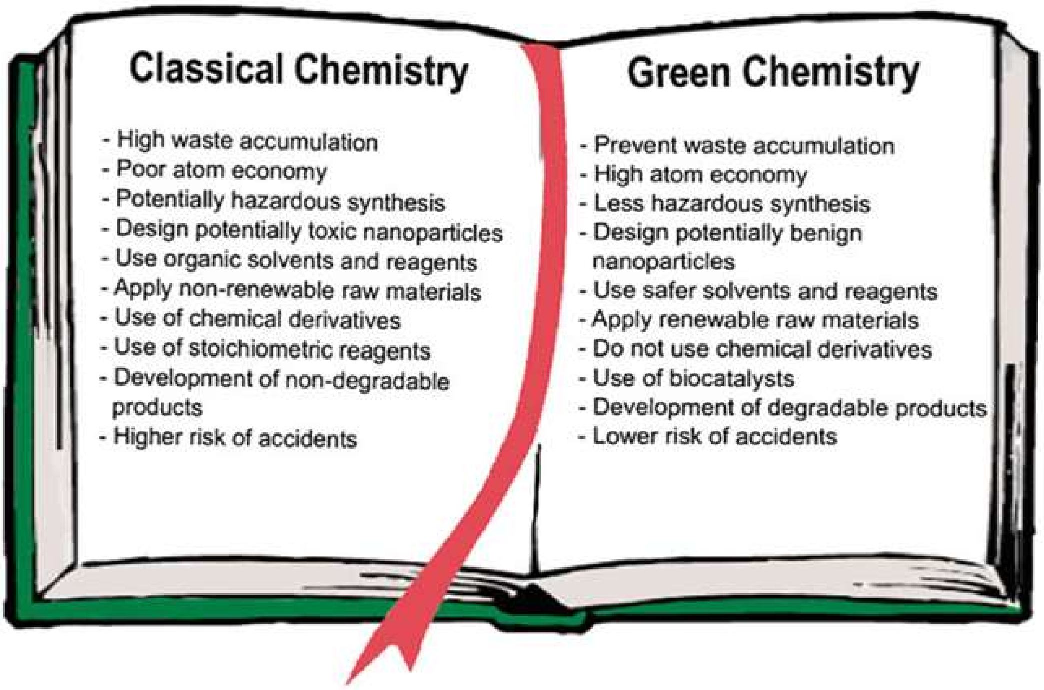


Fig. 4 Schematic exemplification of green chemistry combination in metal nanomaterials cloning [105].



Classical Chemistry	Green Chemistry
- High waste accumulation	- Prevent waste accumulation
- Poor atom economy	- High atom economy
- Potentially hazardous synthesis	- Less hazardous synthesis
- Design potentially toxic nanoparticles	- Design potentially benign nanoparticles
- Use organic solvents and reagents	- Use safer solvents and reagents
- Apply non-renewable raw materials	- Apply renewable raw materials
- Use of chemical derivatives	- Do not use chemical derivatives
- Use of stoichiometric reagents	- Use of biocatalysts
- Development of non-degradable products	- Development of degradable products
- Higher risk of accidents	- Lower risk of accidents

Fig. 5 Comparison of the concepts and repercussions of traditional chemistry and green chemistry [108].

2.1 Comparison between Classical Chemistry and Green Chemistry for MNPs and MONPs Synthesis

The next years will prove the importance of greensynthesis methods for MNPs and MONPs production because they are not only easy to execute, fast, and cheap but also less toxic and environmentally friendly [106, 107] as shown in Fig. 5 [108].

3. Strategies Methods for NPs Synthesis

The preparation of nanomaterials via several chemical methods using benign reagents in the matrix, in which they are to be utilized, need to develop "greener" synthetic strategies, thus reducing or eliminating the utilization of normally used hazardous substances, exposure to them, and generation risk.To obtainnanomaterials of desired sizes, shape, and functionalities,two different fundamental principles of synthesis (i.e., topdown and bottom up methods) have been investigated inthe existing literature (Fig. 6). In the former, nanomaterials/nanoparticles are prepared through diverse rangeof synthesis approaches like lithographic techniques, ball milling, etching, and sputtering [109]. The use of abottom up approach (in which nanoparticles are grownfrom simpler molecules) also includes many methodslike chemical vapor deposition, sol-gel processes, spray pyrolysis, laser pyrolysis, and atomic/molecularcondensation.

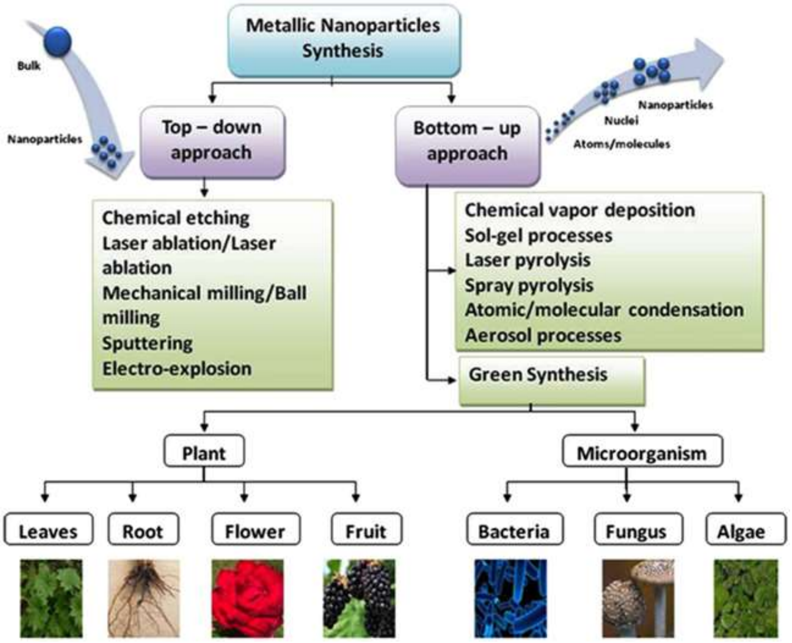


Fig. 6 Different synthesis approaches available for the preparation of metal nanoparticles.

There are two general strategies for the synthesis ofnanomaterials: the top-down approach, wherein a largerstructure is broken down into smaller pieces using chemical,physical, and biological energy; and the bottom-up approach, in which material is synthesized from the atomic levelusing various chemical, physical, or biological reactionsto make a large nanostructure [110]. Thechemical and biological methods are primarily accustomedto build nanostructured carriers (NC) employing this approach (Fig. 6).

The physical and chemical strategies are in-use for the synthesis of nanoparticles. The utilization of toxic chemicalscould exert potential hazards like carcinogenicity, toxicity, andenvironmental toxicity [111]. The toxicityproblems are quite prominent due to the use of hazardoussubstances such as reducing agents, organic solvents, and stabilizers. These chemicals prevent the agglomeration ofcolloids. The use of toxic solvents and chemical contaminationslimits the use of nanoparticles in various clinical and biomedicalapplications [112]. Therefore, a reliable, clean, biologically appropriate, and environmental-friendly techniqueis indeed required to synthesize nanoparticles [113-115]. The biological synthesis of nanoparticles may prove to be anattractive alternative. It includes adoption of multicellular andunicellular biological entities- bacteria [116-120], actinomycetes [121-123], fungi [124-128], plants [129, 130], viruses [131-133], and yeasts [71, 76, 77, 134]. The biologicallysynthesized nanoparticles have a broad area to study with respectto their shape, size, composition, and physicochemical properties [135]. Further, biological entitiesmay operateas a pattern for the assembly, synthesis, and organization ofthe nanometer scale. The present review covers the use ofbiological routes for the synthesis of metal oxide and metalnanoparticles, and various factors affecting their synthesis, andpossible mechanisms employed along with likely applications ofnanoparticles formed using biological factories.

Two approaches of nanoparticle synthesis are known as top-downand bottom-up methods. In the top-down method, therupture of bulk materials to fine particles is conducted byvarious techniques such as evaporation–condensation, laserablation, or other physical methods as seen in Fig. 6. In contrast, in the bottom-up method, the atoms are assembled tonuclei and then grown to NPs. Biological and chemicalmethods which are used for NPs synthesis are consideredbottom-up approach.

Arrays of chemical, physical, and biological techniques have been utilized to synthesize nanomaterials with specificshapes and sizes [136].

3.1 Polyphenols of Plants and Agricultural Residues

Nanometal/nanometal oxide/nanostructured polymersynthesis and following stabilization (using dispersants,biodegradable polymers, among others) in a “greener” fashion include the use of natural renewable resources such as plant extracts and polyphenol antioxidants fromtea and coffee [137], biodegradable polymers such ascarboxymethyl cellulose (CMC) [138], reducing sugars [139], and agricultural residual waste (red grape performancefrom winery waste) [140].

3.2 Vitamins

Nanoparticles preparation by using sustainable syntheticactivity involves benign alternatives, which reduce orremove the use and production of the risky substances. Vitamins B1, Vitamin B2 [141], vitamin C [142], tea [137], and wine phenols [140], which all act as both reducing andcapping agents. They offer extremely simple one-potgreensynthetic methods to synthesize bulk quantities of nanospheres, nanorods, nanowires, aligned nanobelts, nanoballs, and metals nanoplates in water without the need oflarge amounts of insoluble templates [89, 141].

4. General Consideration for MNPs and MONPs Synthesis

To synthesize MNPs and MONPs, researchers used a strongbase (reducing agent), e.g., sodium borohydride or sodiumhydroxide, in metal ion reduction from salt solutions, followed by the addition of a capping agent or a stabilizer (stabilizing agent) [143], as indicated in Figs. 7-8.

To dissolve the stabilizers, they used solvents and thereagents that act as reducing agents, which are toxicsubstances and have counteractive and harmful effects ifthe rest of these materials are left in the rear part of the nanosystem, as the bottom-up path to synthesize the nanoparticlesoften needs the offensive chemical reduction agents such assodium borohydride and hydrazine and a capping agent andmay also involve a volatile organic solvent such as toluene orchloroform. Although these procedures may effectivelyproduce pure products [147], the manufacturing cost is veryhigh, both materially and environmentally. This may providenew stand by accession achieving this synthesis and steerthem to consider safety applications of MNPs

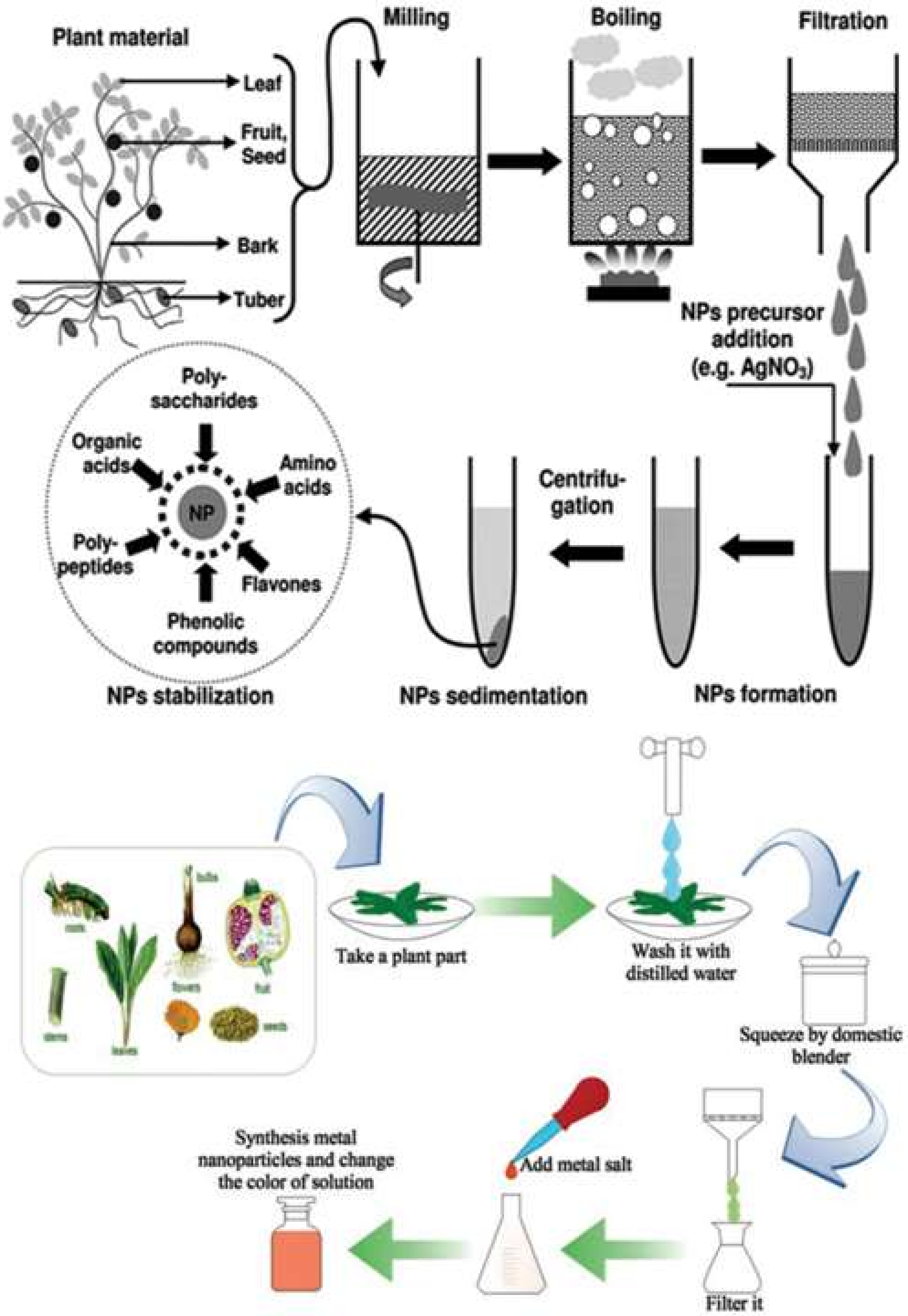


Fig. 7 Two schematic features of MNP synthesis using plant extracts [144, 145].

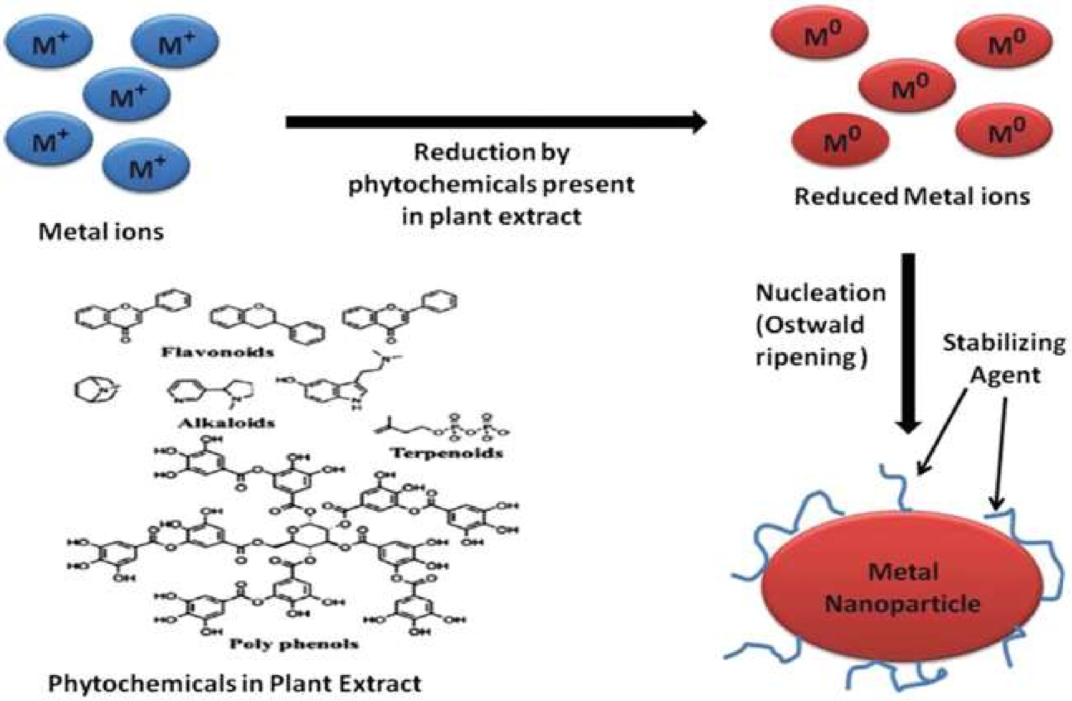


Fig. 8 Nanoparticle consistency mechanisms by plant leaf extract [146].

and MONPs [148]. The green synthesis of MNPs and MONPs is consideredone of the alternatives that depend on the green chemistry principles by using the biological systems [149-152]. The green synthesis of MNPs and MONPs is accomplished by usingprokaryotic [153] or eukaryotic [92] organisms (involving microorganisms, plants, and animals) or their parts, andcan take place intracellularly [154] or extracellularly [155]. Theprimary and secondary metabolites of plants are used toproduce MNPs and MONPs by executing a target metal ionreduction, as shown in Fig. 9.

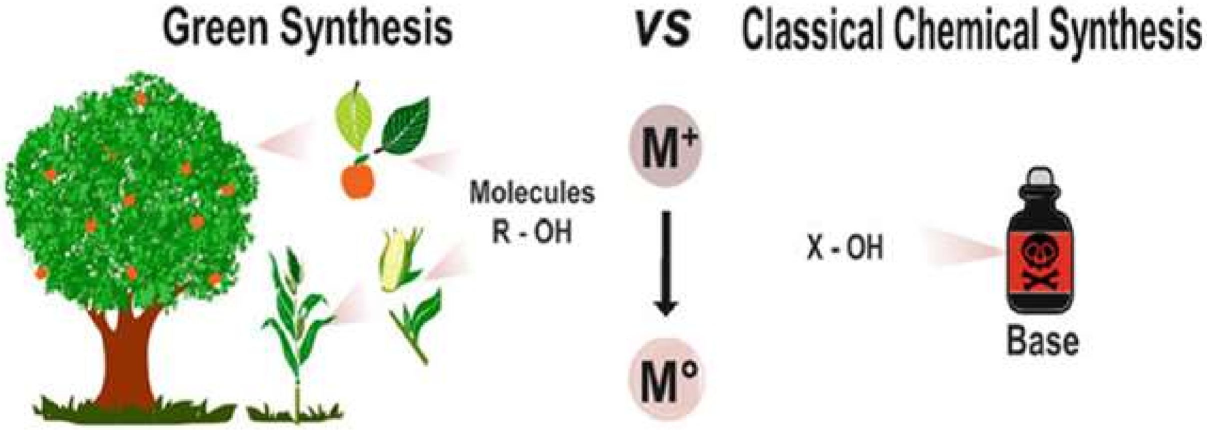


Fig. 9 Schematic explanation of the two main approaches used for the synthesis of MNPs and MONPs: green and chemical (classical) synthesis. Dicotyledons and monocotyledons are used as the reducing and stabilizing agents in the metal salt reduction for the greensynthesis of MNPs and MONPs [108].

Formation of coating layer (stabilizing layer) on thesurface of the MNPs and MONPs by reducing compounds orother besetment molecules lowering them to coagulate/aggregate otherwise ordered in an upset way within theirpreparation [156]. MNPs and MONPs preparation and theirproperties can be polished by setting different conditions suchas temperature, pH, and reagent concentration [91]. Thescientists have utilized the organ/tissue extracts or the whole organisms [66, 157] of plants to execute the green synthesis of MNPs and MONPs. Various plant parts such as leaves, seeds, barks, roots, and fruits, is the factory for the nano-object production with different properties [158, 159], but the researchers should consider the specific phytochemical profile of each plant part with different structures and concentrations according to the needs of each organ and the type of biotic orabiotic stress to which a plant may be exposed, as indicated in Fig. 10.

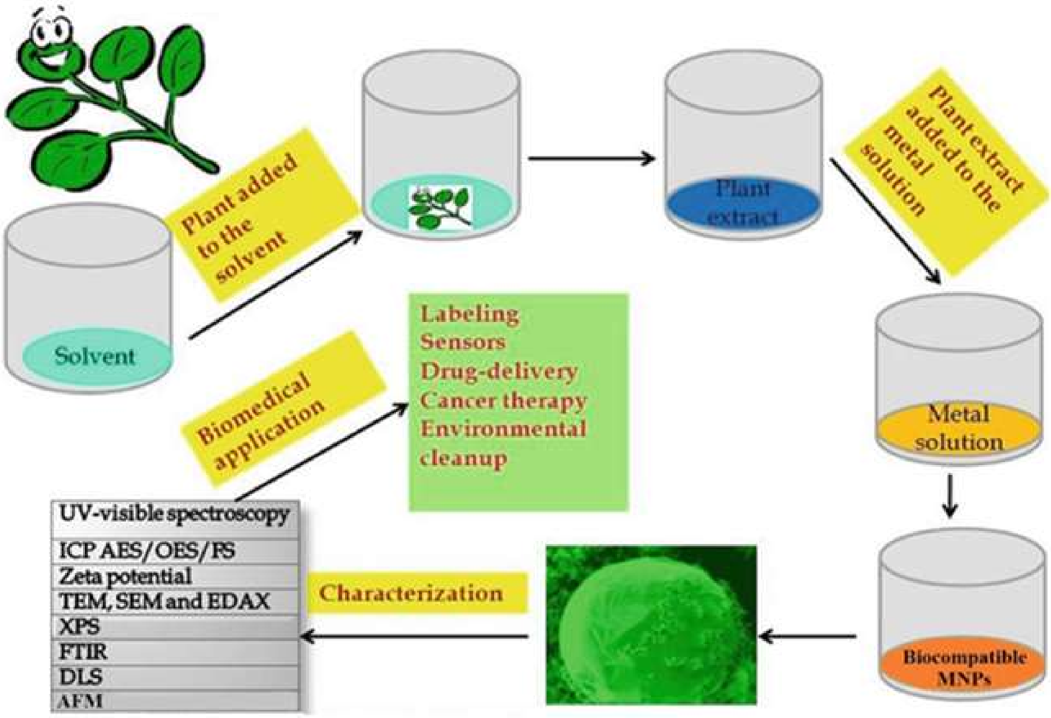


Fig. 10 **A schematic illustration of plants as a source for the green synthesis of nanoparticles and the properties and biomedicalimplementation of nanoparticles [160].**

5. Physical and Chemical Techniques for NPs Synthesis

A number of researchers have developed different chemicaland physical methods to accomplish the synthesis of NPs suchas geometries which can be utilized in varied applications. Photolithography, ball milling, ion beam lithography, microcontact printing, dip pen lithography, evaporation–condensation, electrochemical synthesis, and nanoimprint lithography are reflected as novel techniques for realizing such solegeometries in NPs [161]. The geometries can be also accomplished by physical methods [162]. On the other hand, the chemical procedures start with reducing the metal ions to metalatoms which is followed by controlled bulk of atoms [163]. Generally, chemical and physical methods have been expanded for the synthesis of numerous types of NPs owing to their specificity and creation of monodisperse NPs [164]. Various methods, such as metal ion reduction by any type of reducing agents as hydrazine hydrate, sodium citrate, and sodium borohydride [165]; solvothermal synthesis [166]; sol–gel technique and microwave-assisted synthesis [167]; laser ablation and microemulsion [168]; and ion sputtering, gamma-ray irradiation, electrochemical reduction, and autoclaving, have beenused for the synthesis of metal NPs [169]. The greatest commonly used techniques for NPs synthesis are related to one ormore disadvantages such as high operation cost, toxicity, and energy inefficiency, thus raising many environmental concerns.

These methods often need numerous treating steps, controlled pressure, pH, temperature, much expensive equipment, and toxic chemicals. In addition, these techniques also generate several by-products which are toxic to ecosystems. A variety of different chemical methods, so-called bottom-up constructiontechniques of NPs, are thus now settled in polar aswell as in nonpolar solvents. Therefore, today, metallic NPs can be synthesized in numerous shapes, sizes, solvents, and material compositions [170]. The various physical and chemicaltechniques which are used for NP synthesis are costly, and they produce highly toxic and dangerous chemicals whichcause different biological hazards. Therefore, the requirement of generating an eco-friendly method using biological andgreen synthesis approaches is urgently recommended [171].

6. Green Synthesis of NPs

Green or the biological synthesis of NPs avoids many of the harmful features by allowing the synthesis of NPs at mild pressure, temperature, and pH and at a significantly lower cost [172]. The green synthesis of NPs by biomass filtrate obtained from various biological systems such as yeast, bacteria, actinomycetes, fungi, algae, and plant extract has been reported.

Various microorganisms, especially bacteria and fungi, have been investigated to produce different metal NPs of silver, gold, zinc, titanium, copper, alginate, and magnesium [173]. Several reports have appeared that metal NPs, such assilver, gold, silver–gold alloy, tellurium, platinum, copper, zinc, selenium, palladium, silica, zirconium, quantum dots, titanium, and magnetite, can be biosynthesized by actinomycetes,bacteria, fungi, and viruses [23, 26, 38, 174, 175]. Recently, different organisms including unicellular and multicellular areused for the green synthesis of NPs as represented in Fig. 11.

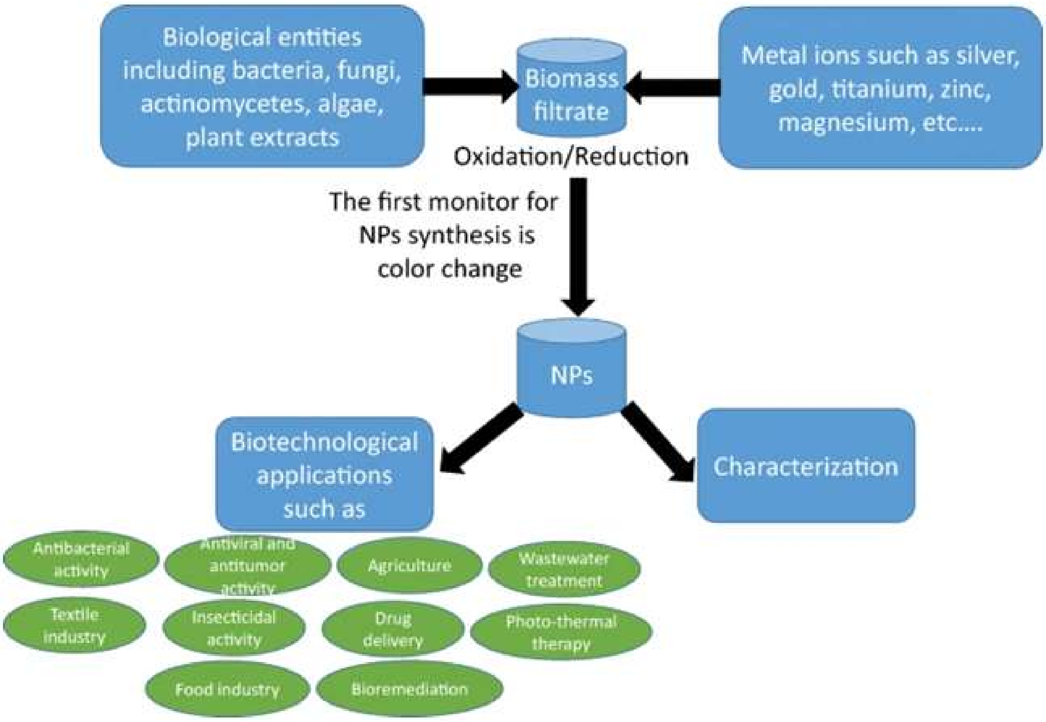


Fig. 11 **Flowchart represents thegreen synthesis of nanoparticles and their prospective biotechnological applications.**

The green synthesis of NPs reflects a bottom-up approach where NPs are formed due to the oxidation/reduction process of metallic ions by secreted biomolecules such as enzymes, proteins, sugars, carbohydrates, etc. [176]. However, a complete understanding of microbial NP synthesis mechanism isyet to be completely developed because each kind of microorganisms interrelates with metallic ions using several routes. The biochemical processing and the interaction activities of aspecific microorganism as well as the effect of environmental conditions such as temperature and pH eventually affect thesize, shape, and morphology of the synthesized NPs [177]. Therefore, the main challenges that can hinder the green synthesis processes can be briefly summarized in the following points: optimization processes that are required for the greensynthesis of NPs with specific sizes and shapes are reflected intheir biological activities. Also, determining the role of eachcompound in the biofabrication process requires complete chemical analysis for biological biomass filtrate. Scale-upNP production needs more studies for commercial uses. The mechanism of NP fabrication requires more explanations. On the other hand, the synthesis of nanomaterial by green approaches needs co-operation between basic science, chemical engineering, and industrial media to produce novel commercial materials. Nanoparticles are formed either by intracellular or extracellular depending on the type of microorganisms [23]. For thebiological synthesis of NPs, living cell extracts have beenexploited by researchers. The main biological routes usedfor the synthesis of NPs are briefly discussed in the follow ingsections.

Organisms have advanced to endure in environments of high concentrations of metals [178-180]. These organisms may alter the chemical nature of the toxic metals by lowering their toxicity or making them nontoxic [181-184]. The formation of nanoparticles is the “consequence” of the resistance mechanism of an organism in contrast to aspecific metal (Fig. 12).

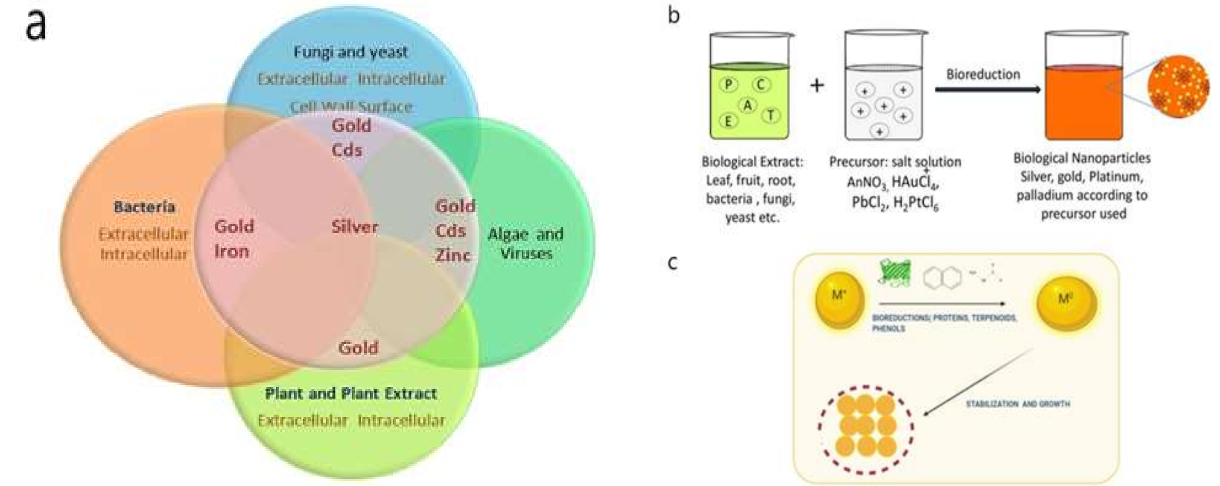


Fig. 12 (a, b) various biological syntheses of nanoparticles; (c) Mechanism of plant-mediated metallic nanoparticles synthesis.

The synthesis of “Natural” biogenicmetallic nanoparticle synthesis is split into two categories:

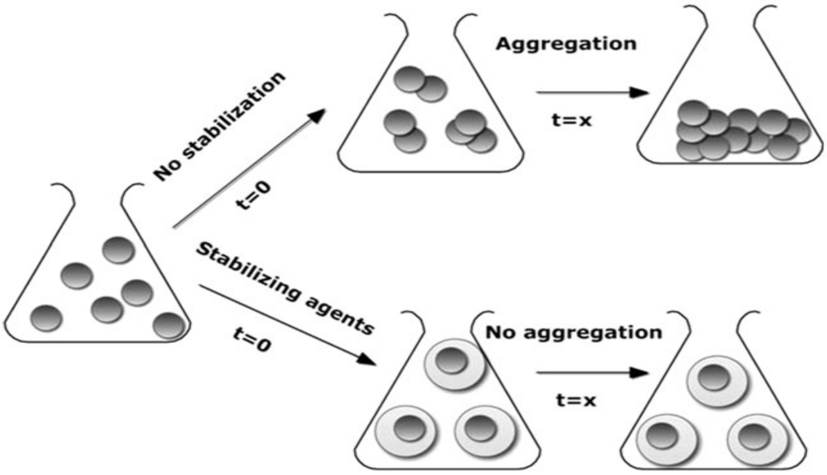
(a) **Bioreduction**: More stable forms of metal ions may beachieved by chemical reduction using biological means and isachieved by dissimilatory metal reduction. The metal ion isreduced and the enzyme is oxidized [185]. Thisconcludes in the production of impotent metallic nanoparticleswhichmay be harmlessly recovered froma contaminated sample.

(b) **Biosorption**: The metal ions bind to the organism itself from an aqueous sample or soil sample. Either the metal ions arebonded to the cell wall or peptides are synthesized by some plants, bacteria, and fungi, and these synthesized peptides assembles intostable nanoparticulate structures [186].

The selection of biological methods for synthesis andengineering of nanoparticles is dependent upon several variables.The form of the metal nanoparticle to be synthesized is themost important variable. Resistance developed against a small number ofmetals by the organisms limit the choice of organisms. Following are a number of the microbial resources (algae, fungi, bacteria, viruses, and yeast) used for most of the frequently studied metal and metal salts nanoparticles consisting of copper, silver, gold, cadmium, platinum, palladium, cadmium sulfide, titanium dioxide, and zinc oxide [187, 188].

6.1 Green Synthesis of NPs by Using Biodegradable Polymers and Enzymes

The high chemical activity with an improved surface of the engineered nanoparticles is mainly because of the unfavorable intense and predominantly irreversible operations like aggregation [189]. Reduction of the specific surface area and the interfacial free energy can be achieved by aggregation, there by minimizing the particle reactivity (Scheme 2) [190], so it is fundamental to boost the nanoparticle stability improvement during storage, transportation, and its overalllife cycle. The majority of the stabilization methods involve Dispersant molecules such as surfactants or polyelectrolytes, which not only modify the chemistry and nanoparticle surface physics but also fabricate an enormous waste stream because they take up a worthy (morethan 50%) of the nanoparticle mass fraction system [191]. Hence, there is a necessity to find environmentally benign stabilization and functionalization passages as well asbioconvenient to obviate pollution and the following counteractive effects on the environment, i.e., non-immunogenic, nontoxic, and hydrophilic stabilizing agents. Different stabilizing agents are used to prevent the aggregation of the nanoparticles and to functionalize theparticles for the desired implementation at the same time [192-194]. However, the usual acute reaction conditions andthe toxic chemicals may not be appropriate for thebiological and biochemical implementation [195]. Presently, there are numerous “green stabilizing agents” such aspolyphenols, enzymes, citric acid, vitamins (B, C, D, and K), biodegradable polymers, and silica, which has the ability tostabilize and functionalize MNPs without the unfavorable effects on the environment and biosynthesis.



Scheme 2 Schematic of nanoparticle aggregation in the presence and absence of the stabilizing agents [196].

6.1.1 MNPs recoverability and reusability

It is very substantial to functionalize and stabilize MNPsfor varied implementation; however, simple and relativelylow-cost recoverability and therefore nanoparticles'reuse is currently acquiring an increased attentionamong the scientific society. Nanoparticles havemagnetic properties have been inclusively used in themetal ion and dye coat, drug delivery, enzymeimmobilization, and protein and cell separation fieldsbecause the magnetic separation of these nanoparticlesoffers individual high competency and cost leverage andis fast in comparison with other nanoparticles, which areharmoniously emerging as heterogeneous supports (socalled magnetic nano-cores) in numerous catalytictransformations, providing easy recoverability witheasy magnet advantages, thereby eliminating solventswelling exigency before or catalyst filtration after thereaction [197-200].

6.1.2 Biodegradable Polymers

Biodegradable polymers perhaps produced from numerous renewable sources (corn, wood, cellulose, polylactides, thermoplastic starch, plant oils, gelatin, and chitosan), petroleum sources (aliphatic polyesters or aliphatic–aromaticcopolyesters), small molecules in bacteria, or biomass and petroleum mixtures [201]. Rozenberg and Tenne [202] debated the nanoparticles stabilized by surfaceactive polymers, which are adsorbed strongly on theparticle surface due to the van der Waals attractive forces between the surface of the particle and the monomer unitsin polymer chain, preventing the aggregation because of their large surface energyminimization in comparisonwiththe native particles. Block copolymers are even stronger nanoparticle separation and show individual properties such as surface reactivity, flexibility, selectivity, and impedance [203]. MNPs stabilization can be fulfilled bymetals in a polymer gel simple enclosure, free radical polymerization with a radical initiator [204], thiol-supported polymer adsorption [205], or in situ MNPs formation during polymerization [205].

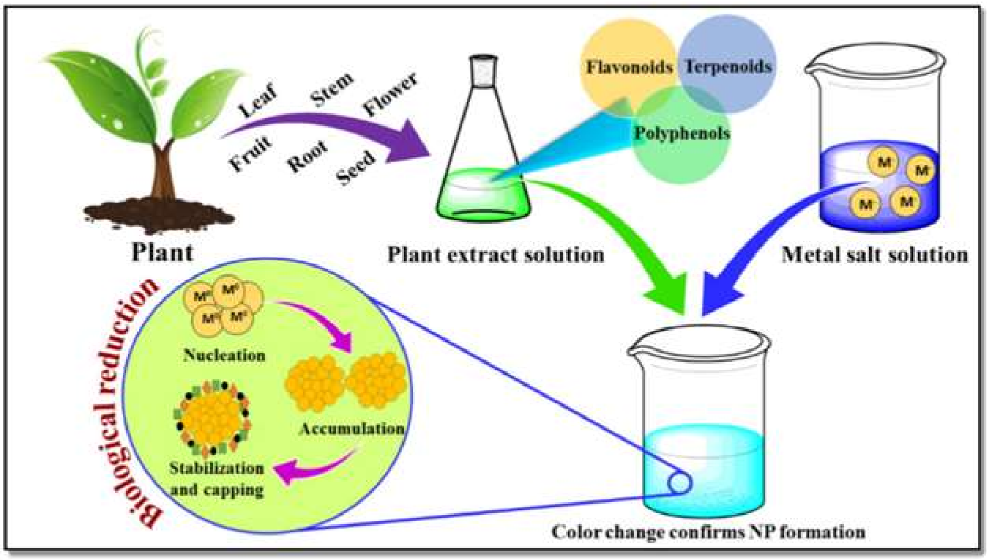
7. Plants are the Main Factory for the Green Synthesis of MNPs and MONPs

Plants contains wide range of bioactive compounds which includes alkaloids, flavonoids, terpenoids, steroids, etc which act as a reducing agent in the synthesis of nanoparticles. Plants including Acalypha indica, Ficus benghalensis, Zingiber officinale, Plumbago zeylanica, Centella asictica, Parthenium hysterophorus, Sapindus rarak, Passiflora foetida, etc [206-212] have recently been used to synthesise various types of nanoparticles (Table 2). Plant extracts have greater benefits than microorganisms for synthesis of green nanoparticles because it’s one-steps process, nonpathogenic and cost-effective process (Scheme 3) [212]. It aids in the elimination of hazardous by-products while also assisting in nanoparticle size fine-tuning. Extract from *Camellia sinensis* were utilised in making iron oxide NPs with spherical and irregular cluster configurations. Zinc oxide nanoparticles were made from leaf extracts of *Acalypha indica*, *Hibiscus rosa-sinensis*, *Coriandrum sativum*, *Calotropis gigantea*, and. Titanium oxide nanoparticles were made using extracts of *Jatropha curcas* or *Eclipta prostrata*. Oxides of copper were generated by leaf extracts of *Aloe barbadensis* and *Aloe sylvestris.*

Peralta-videa et al. (2016) [208] reported synthesis of plant based metallic nanoparticles and its applications. Metals from their constituents are reduced and stabilised by macromolecules and phytonutrients [phenolics, flavonoid, ethyl alcohol, terpenes, and phenolic acids] present in plant extracts. These macromolecules are split into two groups: [i] redoxed intermediaries for metals reductions, or [ii] capped agent for non-agglomeration and post-surface modification of nanoparticles. Furthermore, the produced nanoparticles are free of pollutants and suitable for physiologically mediated applications [212]. A number of experiments employing diverse plant components to synthesise ZnO with different characteristics have been reported. Herbal extract from plant like *V. trifolia, O. basilicum L. var. purpurascens Benth, S. chirayita, C. alata, C. roseus, S. multiflorus, A. indica, E. crassipes, and A. betulina* has been utilised to synthesise spherical shaped ZnO nanoparticles for antibacterial and biomedical purposes [212]. Ikram et al. (2021) [207] reported synthesis of selenium

Table 2 Plant synthesis of nanoparticles[212].

NPs	Plants	Size (nm)	Application
Ag	*Morus alba L.*	80–150	Antibacterial
	Panax ginseng	5–15	Anticancer and antiviral
	Dolichos lablab	4–16	Antimicrobial and anticancer
	Alternanthera bettzickiana	5–15	Antimicrobial and anticancer
	Thymus vulgaris	30	Anticancer and antioxidant
Au	*Camellia sinensis*	10	Antibacterial
	Nigella arvensis	3–37	Antibacterial, antioxidant, cytotoxicity and catalytic
Cu	*Morus alba L.*	50–200	Antibacterial
	Crotalaria candicans	30	Antibacterial
Se	*O. tenuiflorum*	15–20	Medical and pharmaceutical
	Zinziber officinale	100–150	Antimicrobial and antioxidant
Pt	*Taraxacum laevigatum*	2–7	Antibacterial
Pd	*Morus alba L*	50–100	Antibacterial
	Couroupita guianensis Aubl.	5–15	Antibacterial and cytotoxicity
ZnO	*Aloe socotrina*	15–50	Drug delivery
	Olive leaves	40.5–124	Antibacterial
	Tecoma castanifolia	70–75	Antioxidant, antibacterial, and anticancer
	Passiflora caerulea	30–50	Antibacterial
TiO_2	*Trigonella foenum graecum*	20–90	Antimicrobial
	Artemisia, haussknechtii	92.85	Antimicrobial and antioxidant
FeO	*Skimmia laureola*	56–350	Antibacterial



Scheme 3 Plant synthesis of nanoparticles (Dikshit et al., 2021)[213]..

nanoparticles from different plants and their potential applications.

The green synthesis of MNPs and MONPs may be done by using the living organisms, which symbolize the kingdom of the biology system. The living organisms are not only necessary for food and nutritional purposes but also used in green synthesis. Due to the biomass abundance of many plants, the scientists give priority to the plants toexecute the green synthesis of MNPs and MONPs because of their molecular ammunition and biomass profusion. The resulted response to the stress factors (pathogens, herbivores, and climate changes) and survival agents (seasonal changes and reproductive manner) concerning plants are affected by the primary and secondary metabolites of the plants, and these strategies will makethe plants the main bioreactors and molecule suppliers for green synthesis. Due to the presence of metallic counterparts and the stabilization of the surface of the MNPs and MONPs [108], the primary compounds of plantssuch as amino acids, citric acid [93], flavonoids, phenolic compounds, terpenoids [114], heterocyclic compounds [67], enzymes, peptides, polysaccharides [214], saponins [215], and tannis [216] are responsible for the metal ion reduction. The whole organs/tissues [66,157] or the extracts of the organs/tissues anddifferent parts (e.g., seeds, leaves, barks, roots, and fruits) of the plants are utilized for the green synthesis of MNPs and MONPs and may produce nano-objects with several properties [217, 218], so we deal with each part of the plants discretely for their different concentrations and their unique phytochemical characterization, and this depends on the biotic or abiotic stress type to which a plant perhaps subjected and the needs of each organ.

8. Advanced Orientations

The research studies on the green synthesis of MNPs and MONPs using plants can easily understanding the molecular mechanism, coordinating bioreduction, nucleation, growth, and stability. The first stage was utilization of theplant extracts selected from the endemic or globalbiological variation. The extract from different plant partsand species in the presence of metal salts results in theproduction nanoparticles of different sizes, shapes, compositions, and activities, as indicated in Fig. 13.

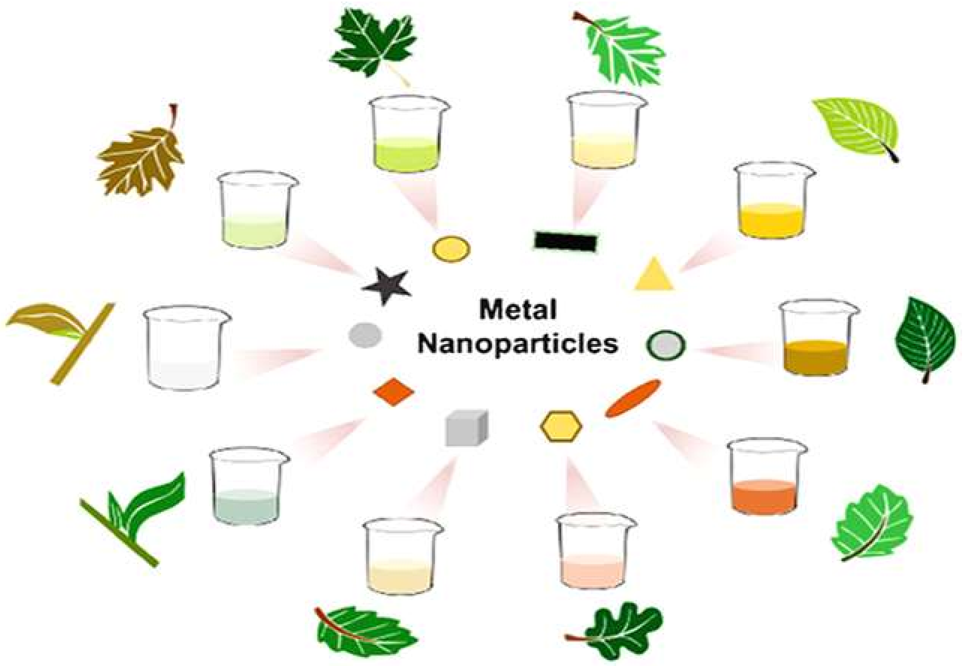


Fig. 13 Green synthesis of MNPs using the extracts obtained from the leaves of different plant species leading to the production ofstructures with different compositions, shapes, and sizes [108].

Reduction of noble metals [91, 172, 173, 219, 220] including gold (Au), silver (Ag), and platinum (Pt) and other metals suchas copper (Cu) was studied in many research studies on thegreen synthesis of MNPs and MONPs.

8.1 Noble Metal Synthesis

Noble metals are characterized by their optical, electronic, mechanical, magnetic, and chemical properties, which attract interest and lead to various applications in different technological applications [221-226]. MNPs are synthesized by using extremely reactive reducing agents, e.g., sodiumborohydride (NaBH4) and hydrazine, which are not ecofriendly. The use of toxic chemicals in these methods limits their use due to environmental precautions. The plants̓ability to synthesize MNPs has conquered a new axis andspectacular approach toward the development of naturalnanofactories. Majority of plants have features as sustainableand renewable resources compared with microbes andenzymes as they have the ability to pick up nearly 75% ofthe light energy from sun and convert it into chemicalenergy, which needs expensive production methods [137, 140, 196, 227]. Furthermore, plants contain chemicals like antioxidants and sugars and play essential roles in the manufacture of nanoparticles [228-232].

Consequently, a pressing need to promote more costeffective and environmentally friendly alternatives to theseexisting procedures, the environmentally compatible solventsystem choice, using an eco-friendly reducing agent forstabilizing the nanoparticles are three essential criteria for a “green” nanoparticle synthesis [196].

8.1.1 Plants and beet for green synthesis of MNPs

The preferred choice is plants with reducing compoundsfor synthesis of noble metals as the correspondingmetals, which are produced by the reduction of metal ions inthe absence of any other chemical materials [137, 140, 196, 233, 234]. The reducing agent is an essential factor in the synthesis of noble MNPs by the corresponding metal ion salt solutions; hence, plants with various reducing agents are favorablecandidates for the manufacture of noble MNPs. Beet is abountiful agriculture product and it belongs to the Chenopodiaceae family. Its purple root is fundamental in theproduction of table sugar and mangelwurzel. It has a great reductive capability because of sugar-rich content, which canbe used in the synthesis of nanomaterials, but it has not beeninvestigated in detail [235, 236]. Beet juice was utilized for thesynthesis of nanometals such as Ag, Au, Pt, and Pd undermicrowave (MW) irradiation condition using benign solvent, water. For example, the prepared Ag nano-particles exhibitperfect catalytic efficiency in converting 4-nitrophenol to 4-aminophenol with elevated reuse, which is higher than $NaBH_4$ [237].

The green synthesis of MNPs and MONPs usingplants [91, 238-240] helps researchers understand and determine the characteristics of MNPs and MONPs. The shapes of the MNPs and MONPs are usually spheres [81, 238-240] and triangles [239, 241]. Their size is in the range of 15-50 nm of hydrodynamic diameter [242].

MNPs and MONPs produced by green synthesis using plants have various activities such as antibacterial [243, 244], antifungal [91], anticancer [245], and larvicidal [246].

The MNPs and MONPs were also produced by greensynthesis using various plant organs such as seeds, bark, flowers, tubers, and root extracts [156] but leaf extract isthe most important for the production of MNPs and MONPs as it is the major resource for metabolites because they are rejuvenated and non-devastating compared with other plant tissues. MNPs and MONPs synthesis and characterization were affected by different factors such as the season or the plant organs collection place in addition to abiotic existence (cold, water, metal existence, or pesticides) or biotic (pest or pathogen existence) compression agents. Plant designs are essential for scaling-up of MNPs and MONPs production and reproducibility. By using various plant extracts, we can synthesize MNPs and MONPs with nanoscale features, and researchers canmoderate more condition for the synthesis. The qualification and velocity of the green synthesis of MNPs and MONPs sympathize the model lineaments of the traditional chemical synthesis. Controlling MNPs and MONPs synthesis factor variation is very important toproduce MNPs and MONPs with demanding properties and provide background on consistent mechanism [243, 244, 247]. The green synthesis of MNPs and MONPs happens in the plant in vivo [248, 249]. The binding and complexation process with phytochelatins and secondary metabolites [250-253] causes a stress, which affects the plants, and it is aslower and more expensive process than the green synthesis processes of MNPs and MONPs from the plant extract.

9. Bacteria Mediated Synthesis of Nanoparticles

Pure gold nanoparticles were synthesized by bacterium, Delftiaacidovorans [254]. Delftibactin is a small nonribosomalpeptide and is considered liable for the synthesisof gold nanoparticles as it is known to induce resistanceagainst toxic gold ions. The transition metal, gold, did notexert toxicity toward bacterium due to the formation of inertgold nanoparticles (AuNPs) bound to delftibactin [255]. A substitutive method for gold nanoparticlesynthesis by the bacterium Rhodopseudomonas capsulata wasshown to produce extracellular gold nanoparticles ranging in sizefrom 10 to 20 nm via NADH-Dependant Reductase [256]. Green productsmay act as a stabilizing and reducing agentfor AuNPs synthesis and these preparations exhibit medicinalapplications [257].

Palladium (Pd), one of the members of the Platinum GroupMetals (PGM) has a compilation of highly catalytically activemetals, and is being employed as a catalyst for hydrogenationand dehalogenation reactions. The heavy contamination ofthose bacteria that had been isolated from Alpine sites withthat of heavy metals led to the synthesis of zero-valent Palladium (Pd^0) nanoparticles [258]. Amongstvarious bacteria isolated from the site, only Pseudomonascells exhibited the potential to produce catalytically activePd nanoparticles. Furthermore, they were able to carry outthe reductive dehalogenation of congeners like tri and tetrachlorinateddioxin. Escherichia coli synthesized Pd^0 nanoparticlesusing hydrogenases present in the cells [259]. Pdnanoparticles were synthesized on the bacterial cell envelope andmay be separated easily.

The bacterium, Bacillus licheniform, reportedly producedsilver nanoparticles (AgNPs) intracellularly [260]. The production/synthesis of nanoparticles required 24 h and was demonstrated by the color modification ofculture into dark brown after the augmentation of silver ions.However, as the nanoparticles were synthesized intracellularlyan additional extraction step was required. Intracellular AgNPswere synthesized by themembers of the Bacillus spp. Subculturedin $AgNO_3$ containing media and the reaction was completed in 7 days [261]. The culture supernatantwas tested for its capability to form metallic nanoparticles [262] in 5 min. The extracellular productionof nanoparticles is recommended compared to the intracellularsynthesis due to the simple purification process with theincreased production rate [263].

Green synthesis of AgNPs using lactic acid bacteria wasdemonstrated by Sintubin et al. [264]. Lactobacillus spp., Pediococcus pentosaceus, Enterococcus faecium, and Lactococcusgarvieae was shown to synthesize the nanoparticles by manybacteria. The procedure of AgNP formation was proposed to bea two-step method. The biosorption of Ag ions on the cell wallwas followed by a reduction of these ions resulting in AgNPsformation [264]. Additionally, the cell wall couldbe thought to be a capping agent, maintaining their stability bystopping their aggregation.

The biosynthesis of Ag and AuNPs has been a focal point ofresearch because of their antimicrobial attributes. The extensive studies were conducted to synthesize the metallic nanoparticlesusing Bacillus species due to their metal accumulating abilities [260, 261, 265]. Bacillus sphaericus JG-A12 can collect excessiveconcentrations of Al, Cd, Cu, Pb, and U (Fig. 14).

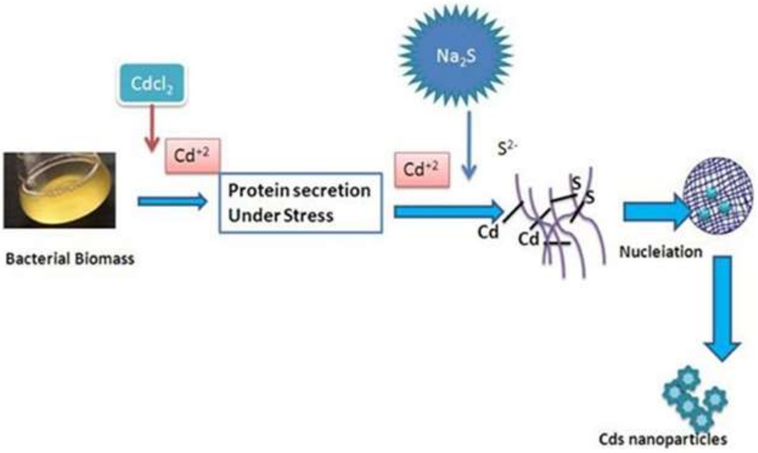


Fig. 14 Green synthesis of nanoparticles by plants.

The Uraniumbioremediation from the aqueous environment was attributedto the S-layer proteins of B. sphaericus. It is a porous layersurrounding the bacterial cell and is made up of identicalproteins, ~5-15 nm thick, with the pores ranging in size from2 to 6 nm. The S-layer contributes up to 15% of the total proteinsof the cell. The S-layer has been stated to be liable for the bindingof heavy metals from the aqueous environments [265] with a capability to bind up to 20mg U/g of protein, and theU binds to the phosphate and carboxyl and groups of the S-layerprotein [265].

Copper (Cu) is not reportedly stable and is oxidized rapidlyto copper oxide (CuO) [266]. Therefore, Cu nanoparticles need to be stabilized as soon as they areformulated. The synthesis of Cu nanoparticles using Morganellamorganii is proved with the help of intracellular uptake ofCu ions accompanied by the means of binding of ions to ametallic ion reductase or a comparable protein ensuring in thereduction of the ion to metallic Cu0 [266]. The metallic Cu nanoparticles then accumulate extracellularlysince they are effluxed out of the cell. Morganella sp. Additionallyextracellularly synthesized AgNPs [267]. The Cunanoparticles synthesis using M. morganii may be due to anAg resistance mechanism to provide elemental Cu nanoparticlesthrough silE homolog to copper-binding protein from differentmicroorganisms [268].

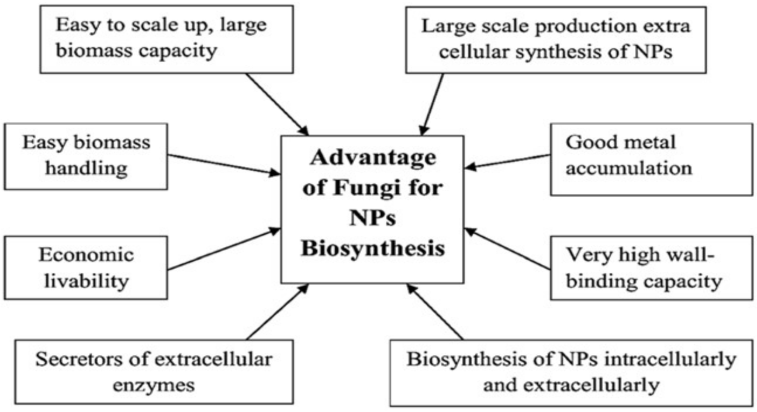
Bacteria are preferred to synthesize NPs due to its requiredslight conditions, easy purification, and high yield. Therefore, bacteria have become the widely studied microorganism, withthe title of “the factory of nanomaterials.” In recent years, Bacillus thuringiensis was used to synthesize Ag-NPs withsize ranging from 43.52 to 142.97 nm [269]. Also, bacterialspecies belonging to Bacillus licheniformis, Klebsiellapneumonia, and Morganella psychrotolerans were used for Ag-NPs synthesis [270]. On the other hand, titanium dioxidenanoparticle was synthesized by Bacillus subtilis andLactobacillus sp. [271]. Gold nanoparticles were synthesizedby Pseudomonas aeruginosa, Rhodopseudomonas capsulata, Escherichia coli DH5α, Bacillus subtilis, and Bacilluslicheniformis [272], while Escherichia coli, Clostridiumthermoaceticum, and Rhodopseudomonas palustris were usedpreviously for the synthesis of cadmium nanoparticles [273]. Bacteria can be used as biocatalyst for inorganic material synthesis; they can act as bioscaffold for mineralization or take anactive part in nanoparticle synthesis [274]. Bacteria can synthesizenanomaterials in broth media during an incubation periodeither as extracellular or intracellular. This phenomenonmakes the biosynthesis of NPs using bacteria a reasonable, flexible, and suitable technique for large-scale production.

10. Synthesis of NPs by Actinomycetes

Actinomycetes are good sources for the biosynthesis of NPs withappreciable surface and size characteristics due to a wide range ofsecreted secondary metabolites.Actinobacteria have the ability toproduce metallic NPs either through intra- or extracellular methodologies. Extracellular production has gotten additional commercialadvantages in contrast to the intracellular one since polydispersityplays an important role [275]. The literature reportswidely on the intra- or extracellular synthesis of metallicnanomaterials by actinomycetes [22, 38, 276]. Gold NPs are successfullysynthesized by Rhodococcus sp., Thermoactinomycete sp., Streptomyces viridogens, S. hygroscopicus, Nocardiafarcinica, and Thermomonospora [277]. On the other hand, silver, copper, zinc, and manganese nanoparticles [22, 38, 278, 279] weresuccessfully synthesized by using Streptomyces spp.

11. Nanoparticle Synthesis Using Fungi

Fungi have been extensively used for NPs biosynthesis due tothe high efficiencies of fungal metabolites to fabricate differentNPs [23, 26, 280]. Fungi are considered a good current addition tothe catalog ofmicroorganisms that are used for NPs fabrications.The widespread use of different fungal species can be attributedto their ability to secrete well-built amounts of proteins or enzymesand they are easier to trade in the laboratory [281]. Theuse of fungi in synthesizing metallic NPs has received greatinterest due to having certain advantages that overcome otherorganisms. The ease of scaling up and downstreamhandling, theeconomic feasibility, and the presence of mycelia presenting anincreased surface region are valuable advantages that should betaken into consideration [156]. Also, fungi have been given moreattention as they are involved in the study on biological synthesisof metallic nanomaterials due to their tolerance and metalbioaccumulation capability [282]. The broadness of fungiscale-up has resulted in a split favor of utilizing them in thesynthesis of NPs (e.g., utilizing a thin solid substrate fermentationsystem). Since fungi are very effectual secretors of extracellularenzymes or proteins, therefore achieving vast constructionof enzymes is viable [283]. The economic facility and livabilityof using biomass is another advantage for the application of thegreen approach facilitated by fungal cells or metabolites to synthesizemetallic nanomaterials (Scheme 4).



Scheme 4 Advantages of fungi asbiofactories for NPs production[284].

Moreover, severalspecies of fungi grow rapidly and formed huge amount of masscells and maintaining them in a specific laboratory is actual easy [26]. Fungi can form metal NPs in different structures as mesoandnanostructures via reducing enzyme extra- or intracellularlyand the process of biomimetic mineralization [284].

The syntheses of NPs using fungi and their biotechnological applications, especially in medicine, are considered under theterm of myco-nanotechnology. This scientific term is the boundarybetween “mycology” and “nanotechnology” and has significantpotential, due to the extensive range and variety of the fungi [23, 162, 175]. Different species of fungi can be used to produce goldand silver nanoparticles such as Phanerochaete chrysosporium, Pleurotus sajorcaju, Coriolus versicolor, and Schizophyllumcommune [285, 286]. Other species including Aspergillus niger, Aspergillus terreus, Fusarium keratoplasticum, Fusariumoxysporum, and Alternaria alternata have been reported tobiosynthesize zinc oxide and iron oxide nanoparticles [23, 287]. Fusarium spp., Fusarium keratoplasticum, Helminthosporiumtetramera, and Schizophyllum radiatum were used for the biosynthesisof Ag-NPs [288-291]. Interestingly, Penicilliumaurantiogriseum, P. waksmanii, P. citrinum, Fusariumoxysporum, and Aspergillus sydowii were used for Au biosynthesis [292-294], while Aspergillus sp. was used for the biosynthesisof iron nanoparticles [295]. Fusarium oxysporum can beused to produce zinc sulfide (ZnS), lead sulfide (PbS), cadmiumsulfide (CdS), and molybdenum sulfide (MoS) nanomaterials, when the appropriate salt is added to the growth medium [126].

A few studies reported the successful biosynthesis of Ag-NPs by yeasts, counting the yeast strain MKY3, Candidaalbicans, Saccharomyces boulardii, and Candida utilis [296]. Extremophilic yeasts that have been isolated from acidsource drainage are used as biocatalyst for gold and silver NPssynthesis [297]. The yeast strain Magnusiomyces ingens LHF1 has been explored for intracellular production of stableselenium nanoparticles [298].

The production of AgNPs using fungi has been the focalpoint of investigation because of their applications in numerousindustries such as antimicrobials and electronics [299, 300] (Rai et al., 2008; Ummartyotin et al., 2012). The capability of the fungus Fusariumoxysporum to synthesize AgNPs has been verified with sizesranging from 5 to 15 nm which had been capped through fungalproteins to lead them to becoming stable. Fusarium oxysporumcould also synthesize nanoparticles extracellularly [299, 300] as compared to earlier studiesin which intracellular production of Ag and AuNPs, lead sulfide(PbS), cadmium sulfide (Cds), molybdenum sulfide (MoS), andzinc sulfide (ZnS) nanoparticles intracellular production of Agand AuNPs, cadmium sulfide (Cds), lead sulfide (PbS), zincsulfide (ZnS), and molybdenum sulfide (MoS) had been reported [121,126].

Aspergillus fumigatus is used to synthesize extracellular silvernanoparticles of larger sizes ranging from5 to 25 nmas comparedto Fusarium oxysporum, with the disadvantage of difficulty inanticipating the catalytic activity with the size difference inevery batch [128]. However, the bioproductionof AgNPs using A. fumigatus is an attractive prospectas organism reduces Ag ions into nanoparticles within 10minof contact [128]. Fungus Trichodermareesei could also be used for extracellular production of AgNPswith a size range of 5-50 nm nanoparticles. It took 72 hto synthesize AgNPs which was appreciably slower than A.fumigatus and Fusarium oxysporum [126-128]. Furthermore, the use of T. reeseihas an advantage over the use of other fungi since it has beenan extensively-studied organism which may be manipulatedfor the production of an excessive quantity of enzymes [301, 302] and may help increase therate of production of nanoparticles. However, the nanoparticleswere not as homogenous as those which were produced by A. Fumigates [128] and F. oxysporum [126]. The fungal attribute to produce intracellularnanoparticles is helpful in getting rid of the fungus and itsgathered metallic contaminant. A white-rot fungus (Coriolusversicolor) is suggested to provide and accumulate AgNPs extraand intracellularly by manipulating reaction conditions [303]. Only a few fungi are considered to have thepotential to synthesize gold nanoparticles despite the increasingdemand in various fields. The small size of gold nanoparticlescauses them to become more reactive and appropriate ascompared to the bulk form to be used as precursors forelectronics applications and catalysts [124, 304]. The synthesis of AuNPs usingVerticillium sp. by the biological reduction of $AuCl_4$ localized onthe surface of the mycelia [124].

Biological synthesis of Platinum nanoparticles (PtNPs) wascarried out by the use of fungus Neurospora crassa. It producedsingle PtNPs (Platinum nanoparticles) intracellularly rangingin size from 4 to 35 nm in diameter. They may additionallysynthesize spherical nano-agglomerates in the range of 20-110 nm diameter [235]. Both biomass andextract of N. crassa were used to synthesize PtNPs. The PtNPs synthesized using the N. Crassa extract contains single-crystalnano agglomerates [235, 235]. PtNPs were alsoreportedly synthesized extra and intracellularly by F. oxysporumbut with sub-optimal quantity when synthesized intracellularly [78]. The phytopathogenic fungus F. oxysporumand the endophytic fungus Verticillium sp. had been reportedto synthesize magnetite (a common iron oxide) nanoparticles (MaNPs) intracellularly [305] (Bharde et al., 2006).

The use of fungi for nanoparticles synthesis has some benefitsover the use of bacteria namely; scaling up and easy downstreamprocessing, the economic status, and an increased surface areaprovided by the fungal mycelia [124]. Thehigher amount of proteins secreted by using fungi should likelyincrease the productivity of nanoparticle synthesis but safety iscompromised since a number of fungi are phytopathogenic andmay pose a safety risk [306]. Trichodermaasperellum and Trichoder mareesei are non-pathogenic makingthem ideal for commercial applications [301, 302, 307]. T. reesei is broadly used inanimal feed, food, paper, pharmaceuticals, and textile industries [307].

Production of nanoparticles using fungus has been a focus of study due to its application in a broad range of sectors, like antimicrobials and electronics. The ability of the Fusarium oxysporum fungus to synthesize Ag nanoparticles with diameters ranging from 5 to 15 nm has been confirmed, and they have been covered with mycological proteins to make them stable. Studies have reported internal synthesis of Ag and AuNPs, and sulphide of cadmium, molybdenum, and zinc nanoparticles and intra-cellular productions of Ag, Au, cadmium sulphide, molybdenum sulphide and zinc sulphide nanoparticles. They are superior abiotic factors for the production of metals and their oxide nanoparticles because they include a variety of intracellular enzymes. Competent fungus may create larger quantities of nanoparticles than bacteria. Due to the occurrence of enzymes, peptides, and reductive elements on the surface of cells, fungi have a significant advantage over other species. Enzymatic reductions (reductase) in cell walls or inside infectious cells are the most likely technique for the creation of metal nanoparticles. Furthermore, infectious enzymes increase the quantity of synthesized nanoparticles and speed up the reductive abilities for stable nanoparticle production. Extracellularly synthesized nanoparticles are often considered to be less or nontoxic. Pt nanoparticles of diameter ranges from 15 to 30 nm were generated extracellularly at room temperature using Fusarium oxysporum extract. Castro-Longoria et al. observed that using the Neurospora crassa fungus to make Ag nanoparticles needed a particular temperature and that resulting particles was quasi-round with a diameter of 20-110 nm. Overall, these investigations shown that fungal extracts may be used to stabilise and reduce Pt nanoparticles. Pt nanoparticles were produced biologically using the fungus Neurospora crassa and it was intracellularly produced with sizes from 4.5 to 35 nm. They may also produce spherical nanoagglomerates with dimensions ranging from 20 to 110 nm. Pt nanoparticles were synthesised using all feedstock and extracts from N. crassa. Single-crystal nanoagglomerates are found in the Pt nanoparticles synthesised from N. crassa extract. Pt nanoparticles were also shown to be synthesised by Fusarium oxysporum both extracellularly and intracellularly, but under ideal quantities when produced intracellularly. Magnetite [common ferrous oxide] nanoparticles were found to be synthesised intracellularly by the phytopathogenic fungus F. oxysporum and the endophytic fungus

Table 3 Fungal synthesis of nanoparticles[212].

NPs	Organism	Size(nm)	Applications
Ag	*Candida glabrata*	2-15	Antibacterial
	Trichoderma longibrachiatum	10	Antimicrobial
	Fusarium oxysporum	21.3-37	Antibacterial
	Aspergillus terreus	16–57	Antibacterial
	Ganoderma sessiliforme	45	Antibacterial, antioxidant, and anticancer
	Rhodotorula glutinis	15.45	Antifungal, cytotoxic, and dye degrading
	Aspergillus sp.	5-30	Antibacterial and cytotoxicity
	Arthroderma fulvum	15.5	Antifungal
	Penicillium aculeatum Su1	4-55	Drug distribution and antimicrobial
	Trichoderma harzianum	20-30	Antifungal
	Fusarium oxysporum	34-44	Antibacterial
Au	*Cladosporium cladosporioides*	60	Antibacterial and antioxidant
	Pleurotus ostreatus	10-30	Antimicrobial, anticancer
ZnO	*Fusarium keratoplasticum A1-3*	10-42	Antibacterial, cytotoxic, and textile-loading
	Aspergillus niger G3-1	8-38	Antibacterial and cytotoxic
	Aspergillus terreus	10-45	Antibacterial and cytotoxic
Al_2O_3	*Colletotrichum sp.*	30-50	Antimicrobial

Verticillium sp. Table 3 summarises different types of nanoparticles synthesised by several fungal species.

12. Nanoparticle Synthesis Using Yeast

Yeasts can absorb and accumulate a good quantity of lethalmetals from their adjacent areas due to their large surfaces [162, 308]. Yeast usesa range of detoxification mechanisms to adapt to toxic metalssuch as bio-precipitation, chelation, extracellular sequestrationand bio-sorption. These mechanisms adapted through yeast cellsare used during nanoparticle synthesis to form and increasethe durability of nanoparticles, giving rise to variation inparticle size, particle properties, and location [309]. The intracellular synthesis of CdS quantumdots turned into confirmed via Candida glabrata when exposedto cadmium salts [134]. The growth phaseof yeast Schizosaccharomyces pombe cells and the formation of CdS quantum dots are linked together [310].Torulopsis sp. synthesizes PbS quantum dots when exposedto Pb^2 ions and Pichia jadinii synthesizes Au nanoparticlesintracellularly. The size range of these nanoparticles is from a fewnanometers to around 100 nm. Themorphological characteristicsof these nanoparticles were easily conducted by monitoring thecellular activities and growth of P. jadinii during the synthesisof the nanoparticle [76, 77]. The use ofmetallic nanoparticles has become vital due to their safety andprospective applications.

13. Algae Synthesis of Nanoparticles

Algae are organisms which have been shown to assimilate heavy metals from the environment as well as synthesis metallic nanoparticles (Fig.15).

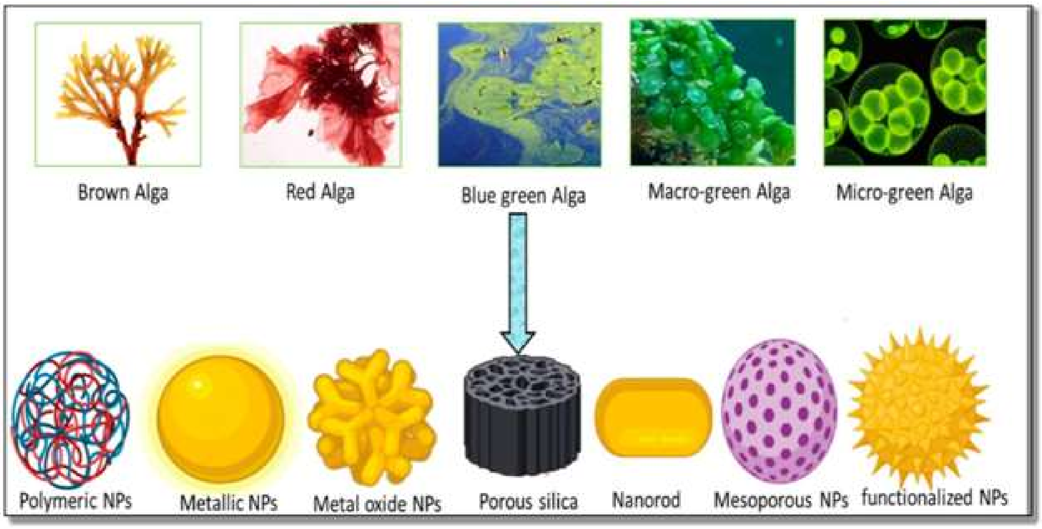


Fig. 15 Synthesis of nanoparticles from different algae (Chaudhary et al., 2020) [311].

Fucus vesiculosus, a brown alga, is now being researched for its potential to bioreduce and biosorb Au [III] ions. Reduced tetrachloroaurate ions were utilised to generate Au nanoparticles from dried algal cells of Chlorella vulgaris. Because algae absorb metals and reduce metal ions, they're termed “bio-nano factories” and they able to synthesise metallic nanoparticles from both live and dead dry biomass. Microalgae are photosynthetic microorganisms that form colonies and filamentous that belongs to various divisions such as Chlorophyta, Charophyta, and Bacillariophyta. They make up a significant portion of the planet's biodiversity. Bioreduction with Fucus vesiculosus could be used as a more ecologically acceptable alternative to recover Au from microelectronic scrap leachates and dilute hydrometallurgical mixtures. Phaeodactulum tricornatum is a phytoplanktonic alga with CdS nanocrystals with phytochelatin coatings were made in response to the findings. Proteins in the algal extract act as a stabiliser, reducer, and shape-control modifier, among other things. Sargassum wightii, an ocean alga, also generated extrinsic Au, Ag and Au/Ag bi-metallic nanoparticles. Using *S. wightii*, Singaravelu et al., (2007) found the fast formation of extrinsic Au nanoparticles ranging in sizes from 8 to 12 nm. Kappaphycu salvarezii, Fucus vesiculosus, Tetraselmisko chinensis, Chondrus crispus, and Spirogyra insignis are among the algae that were reported in the synthesis of Au and Ag nanoparticles. Because they were made from living Euglena gracilis microalgal cells that was already cultivated in either mixotropic [light-exposed and cultivated as in carbon-rich organic culture medium] as well as autotropic (non-light-exposed as well as grown in an organic carbon-rich culture mediums) environments (Dahoumane et al., 2016), Au nanoparticles synthesised possess dynamics, outputs, and solubility. Algae are easier to work with, less poisonous and less damaging to the air; manufacturing may be done at room pressure and temperature, and in simple watery conditions with a neutral acidity. Several algae species are used for the synthesis of nanoparticles (Table 4).

Table 4 Algal synthesis of nanoparticles[212].

NPs	Organism	Size (nm)	Application
Ag	*Pseudomonas sp.*	20-70	Antibacterial
	Bacillus thuringiensis	43.5-142.9	Larvicidal action
	Ochrobactrum anhtropi	38-85	Antibacterial
	Bacillus spp.	77-92	Antimicrobial and antiviral

	Pantoea ananatis	8.06-91.31	Antibacterial
	Bacillus brevis NCIM 2533	41-68	Antibacterial
	Bacillus mojavensis BTCB15	105	Antibacterial
	Actinobacter	13	Antibacterial
	Sinomonas mesophile	4-50	Antimicrobial
	Bacillus brevis	41-68	Antibacterial
	Bacillus methylotrophicus DC3	10-30	Antimicrobial
Cu	*Shewanella loihica*	10–16	Antibacterial
Au	*Micrococcus yunnanensis*	53	Antibacterial and anticancer
	Mycobacterium sp.	5-55	Anticancer
TiO_2	Aeromonas hydrophila	28-54	Antibacterial
ZnO	Halomonas elongata IBRC-M 10,214	18.11	Antimicrobial
	Sphingobacterium thalpophilum	40	Antimicrobial
	Staphylococcus aureus	10-50	Antimicrobial

Algae are seamicroorganisms that have been reported not only touptake heavy metals from the environment, but also to synthesizemetallic NPs. For example, the dried algal cells of Chlorellavulgaris were expanded to produce Au-NPs by reduced tetrachloroaurateions to form Au-NPs [312]. Studies are ongoingon the bioreduction and biosorption of Au (III) ions by Fucusvesiculosus which is defined as a brown alga [313]. Bioreductionwith Fucus vesiculosus might be expanded as a replacement ecofriendlytreatment for claiming Au from leachates of microelectronicscraps and dilute hydrometallurgical mixes. Diatoms canbe used as a resource for fabrication of siliceous materials [314].The phytoplanktonic alga, Phaeodactulum tricornatum, possessesphytochelatin-covered CdS nanocrystals fabricated in responseto Cd [315]. Rapid formation of Au-NPs through extracellularbiosynthesis has been created viable in a marine alga ofSargassum wightii Greville [316]. Konishi et al. [317] reportedthat Shewanella algaehas have the ability to reduce aqueous$PtCl_6$ to elemental Pt at neutral pH under room temperaturewithin 60 min using lactate as the electron donor. Biogenic Pt-NPs of 5 nm are observed in the periplasm, which is a preferableposition for simple and quick recovery [317]. Brayner and coauthorsdescribed the synthesis of platinum, gold, palladium, andsilver NPs using cyanobacteria [318]. Other alga like Turbinariaconoides was used for gold nanoparticle biosynthesis [319]. On the other hand, four marine macroalgae, viz., Pterocladiacapillacae, Jania rubins, Ulva faciata, and Colpmenia sinusa, were used for the biosynthesis of Ag-NPs [319-321]. There are some representative examples for NPs synthesized by different algae with their size and applications [48].

Algae are regarded to accumulate heavy metals and may be utilized for the biogenic synthesis of metallic nanoparticles.Dried unicellular alga Chlorella vulgaris could synthesizenanoparticles of diverse shapes—tetrahedral, decahedral, and icosahedral accumulated near the surface [312]. The extract of Chlorella vulgaris produced Agnanometer scale plates at room temperature. Biosynthesis of $CuFe_2O_4$@Ag nano composite from Chlorella vulgaris combinedwith ciprofloxacin confirmed promising bactericidal activitytoward multidrug resistant Staphylococcus aureus which is arising global risk [322]. The proteinspresent in the algal extract perform a primary function as astabilizing agent, reducing agent, and shape-control modifier [323]. Sargassum wightii, a marine alga, couldalso synthesize extracellular Ag, Au, and Au/Ag bimetallicnanoparticles [324]. Rapid synthesis ofextracellular Au nanoparticles with a size from 8 to 12 nm viaS. Wigh tii has been demonstrated by Singaravelu et al. [316]. Several other algae Kappaphycu salvarezii [325], Fucus vesiculosus [326], Tetraselmiskochinensis [327], Chondrus crispus, andSpirogyra insignis [328] have been reportedto synthesize Au and Ag nanoparticles [325]. By using the living cells of Euglena gracilis microalgawhich have been grown under either mixotropic (exposedto light and grown in an organic carbon-enriched culturemedium) or autotropic condition, the gold nanoparticlessynthesized were of true yield, kinetics and colloidal stability [329].

14. Nanoparticles Synthesis Using Cyanobacteria (Blue Green Algae)

Green and valuable synthetic techniques have attracted great interest in the synthesis of nanoparticles [330]. Cyanobacteria strains are an inexpensive eco-friendlytool for nanometal formation. Cyanobacterial technology offersthe merits of eco-friendly methods, such as timesaving forlarge-scale production at ambient temperatures. They growmuch faster compared to the plants and could easily bemanipulated as needed. Studies onmolecular biology and ecologyregarding synthesis of nanoparticles offer a great opportunity forefficient development of application-oriented nanoparticles. Thecommon cyanobacterial strains used in nanoparticle biosynthesisvary from unicellular and colonial species. Colonies mightform sheets, filamentous, or even hollow balls. They may fixatmospheric nitrogen besides fixing the atmospheric carbondioxide during photosynthesis. Some strains grow in dark under organotrophic/chemotrophic/lithotrophic conditions offering awide range of modes of nutrition with normal plants-likephotosynthesis. Few strains exhibit symbiotic conditions with lichen (Fungi), bryophytes (Liverworts), gymnosperms (Cycas), and with higher plants (Macrozamia). They require a lesserquantity of chemicals as they are all photoautotrophic and may also grow under the chemo-autotrophic condition in lightand dark.

Out of the 30 different strains of cyanobacteria (unicellular, colonial, undifferentiated and differentiated filamentous) studiedfor the silver nanoparticles biosynthesis, the filamentousheterocystous strain Cylindrospermum stagnale was the bestorganism synthesizing nanoparticles of 38-40 nm [331]. In general, the time frame varied from 30 to 360 h, andthe size varied from 38 to 88 nm [331]. Thetechniques of synthesis of AgNPs using cyanobacteria Spirulinaplatensis and Nostoclinckia have been studied [332]. There is a need to understand the optical conditions of theinteraction among the biomass and solution containing Ag ionsthat may allow nanoparticles without biomass degradation at thetime of Ag nanoparticle formation [332, 333]. The green synthesized silver nanoparticles via simplebiological protocol using Oscillatoria limnetica aqueous extractthat had provided both a decreasing and stabilizing agent forthe biosynthesis of nanoparticles by suspending the live andwashed biomass into the $AgNO_3$ solution and by adding $AgNO_3$into a cell-free culture liquid [334] assessed theselected strains of cyanobacteria for the ability to synthesize AgNPs. Around 14 out of 16 tested strains have been utilizedfor the AgNPs biosynthesis. Mostly, AgNPs have been formedin the presence of biomass in addition to the cell-free culturemedia indicating that the Ag-NPs formation technique engagesan extracellular compound inclusive of polysaccharide. TEMevaluation revealed that nanoparticles were set in an organicmatrix. AgNPs varied in shape and sizes that ranged between 13 and 31 nm, depending upon the organismused [334]. With the exception of one strain of Cyanobacterium Limnothrixsp., all strains confirmed the antibacterial activity of Ag-NPs [334]. For the gold nanoparticles green synthesis, Lyngbya majuscula and Spirulina subsalsa were investigated asbioreagents. The cyanobacterial biomass turned purple within 72 h of incubation at 15 mg L-1 Au^{3+} solution, indicating anintracellular reduction of Au^{3+} to Au^0 and subsequent formationof gold nanoparticles. Spirulina subsalsa showed the synthesisof spherical nanoparticles of ~5 to ~30 nm in diameter alongwith very few nanorods.

Lyngbya majuscule showed the presenceof spherical and hexagonal nanoparticles of ~2 to ~25 nm indiameter. The reduction of Au^{3+} to Au^0 was proved by the XRD study. FTIR analysis indicated the presence of proteinshells around the gold nanoparticles [335]. The biosynthesis of AgNPs and their antimicrobial propertyand photocatalytic activity for photodegradation of organic dyewere studied by San Keskin et al. [336]. The characterizationof synthesized Ag nanoparticles was carried out by UV–Visspectrophotometer (surface plasmon resonance band at 430-450 nm). The Attenuated Total Reflection Fourier TransformInfrared Spectroscopy (ATR-FTIR) study confirmed the reducingnature of proteins. The Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) were used todetermine the structure of AgNPs and was found to bespherical. The AgNPs showed photocatalytic activity that isphotodegradation of organic dye i.e., methylene blue. It wasshown that methylene blue was degraded by ~18% within 4 h with biosynthesized AgNPs [336]. The biosynthesis of AgNPs has been efficaciously performedwith the use of bloom-forming filamentous undifferentiatedcyanobacterium Plectonema boryanum which reacted withsolution of $AgNO_3$ (~560 mg/L Ag) for up to 28 days at 25-100 °C. The precipitation of spherical AgNPs and octahedralsilver platelets (of up to 200 nm) in solutions is promotedby interaction of cyanobacteria with $AgNO_3$ Solution. Themechanism of formation of AgNPs via cyanobacteria mayinvolve the metabolic processes in which nitrate is used at 25 °C, and organics are released from the lifeless cyanobacteriaat 25-100 °C [118, 337]. The cyanobacteriumGloeocapsa sp. was an effective strain for nanosilver production [338]. The extracellular synthesis of AgNPswas initially detected by visual inspection for color changing of the cultured flasks solutions from transparent to brown thenblack, as well as nanoparticles characterization through UV-Visspectrophotometer and Fourier TransformInfrared spectroscopy (FTIR) with characteristic surface Plasmon absorption peaksat range 400-450 nm. The FTIR spectrum data in additionconfirmed the presence of specific functional groups such asproteins and does have an important role as a capping andstabilizing agent in the biosynthesis of AgNPs [338]. Cyanobacteria could play an instrumental role as anexcellent candidate for nanoparticle biosynthesis.

15. Synthesis of NPs by Viruses

The usage of viruses in the biosynthesis of nanoparticles is anovel method that has been capable to produce inorganicnanomaterials such as cadmium sulfide (CdS), silicon dioxide (SiO_2), iron oxide (Fe_2O_3), and zinc sulfide (ZnS). Semiconductor nanomaterials such as ZnS and CdS are of interestto the green chemistry and electronics industry approachesfor their synthesis has been widely investigated. Theuse of whole viruses to synthesize quantum dots has beeninspected over the previous decade [339]. The bacteriophagehas an exact detection moiety for ZnS surfaces. In 2003, Chuanbin Mao’s group found a new synthesis route to a semiconductornanoscale heterostructure using M13 bacteriophage [340]. Also, Yoon Sung Nam and his group arrived at the biosynthesisof a high-performance, flexible nanogenerator usinganisotropic $BaTiO_3$ nanocrystals on an M13 viral template bythe genetically programmed nature assembly of metal ion precursors [341]. An attractive characteristic of viruses is theircomplicated surface protecting the capsid protein structure thatforms an extremely sensitive surface with the cooperation ofmetal ions [177]. In a similar study, low concentrations of TMVs (tobacco mosaic virus) were inserted to Au or Ag solutionsbefore the addition plant cell extracts of Hordeum vulgare orNicotiana benthamiana. The presence of the virus not onlydecreased the size of the biosynthesized NPs, but also radicallyincreased their numbers in contrast to the solutions without thevirus [342].

16. MNP and MONPs Synthesis by Using Flavonoids as a Fundamental Agent

Flavonoids are considered a fundamental agent for theMNP and MONPs synthesis. Flavonoids include anthocyanins, isoflavonoids, flavonols, chalcones, flavones, and flavanones [343], which are considered a group ofphenolic compounds. Aglycone is the major structure offlavonoid. The presence of benzene ring is the base onwhich flavonols, flavanones, or its hydro derivatives arecategorized. The position of the benzenoid substituentdivides the flavonoid into 2-position flavonoids and 3-position isoflavonoids. The C_2-C_3 double bond andthe hydroxyl group at the 3-position distinguish flavonolsfrom flavanones [344]. These compounds can reducemetal ions to produce nanoparticles and chelate metalions. Flavonoids have different functional groups, whichhave the ability to produce nanoparticles. Reactivehydrogen atoms are released during the tautomericconversion of flavonoids from the enol form to the ketoform, which is responsible for the metal ion reduction toproduce nanoparticles [343]. Ahmad et al. discussedthe silver nanoparticles production and found that theenol- to keto-form transformation is the main reason forsilver nanoparticles production from silver ions byusing Ocimumbasillicum extracts and transformation offlavonoids such as luteolin and rosmarinic acid [345]. Zheng et al. [346] indicated that flavonoids content of theplant extract facilitates the platinum ion bioreduction tosynthesize the platinum nanoparticles. The internalmechanism; ketone conversion to carboxylic acid inflavonoids; leads to metal ions formation such as Fe^{2+},Fe^{3+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}, Pb^{2+}, and Co^{2+} by theircarbonyl groups or π-electrons [343]. In brief, flavonoidsare responsible for chelation and reduction to producenanoparticles through growth, nucleation, and stabilization. Nanoparticles may be produced by combination of phytochemicals or flavonoids. Metal ion may be reducedby phenolic compounds, which are phytochemicals [347-350]. Holtz et al. [351] discussed that MONPs maybe synthesized by using terpenoids as a reducing agent. Laghari et al. [352] proposed that MONPs may be producedby using alkaloids from the plant extract. Phytochemicalsin the plant extract play an essential role in the MONPformation, so it should be taken into consideration [353-355]; however, the definite role of phytochemicalsin the nanoparticle synthesis has not been determined yet. The plant leaf extracts that contain flavonoids are moreeffective than other phytochemicals, as flavonoids reducenano-composition toxicity and they act as a stabilizingagent. ROS produced from metal oxides can be reduced byflavonoids due to their antioxidant activity [356, 357]. Flavonoids have hepatoprotective [358], anticancer [359, 360], and antiviral [361-364] properties. The MONPs formation by using plant extracts containing large amountof flavonoids make them gain more properties, which leadto many important applications.

17. Synthesis of MNPs and MONPs by Utilizing Plants

Biosynthesis of metallic nanoparticles using plant extracts is firstly reported by Gardea-Torresdey et al. [365], who reportedthe synthesis of Ag-NPs using Alfalfa sprouts. The major importantandspecial feature of nanoparticles is that they exhibitlarger surface region to volume ratio [366]. Plant extracts suchas soya, Aloe barbadensis Miller, and Tridax procumbens leafcell extract have been used for the synthesis of Cu and CuONPs [367, 368]. Recently, plant-mediated biosynthesis of ZnO-NPs has been accomplished in Partheniumhysterophorus, Sapindus rarak, Passiflora foetida, Acalyphaindica, Ficus benghalensis, and Zingiber officinale [369]. Several reports were made on the biosynthesis of nanoparticles (Au, Ag, ZnO, Fe, etc.) using aqueous extracts of numerousplant parts. An aqueous leaf cell extract of Couroupitaguianensis and Turnera ulmifolia for the biosynthesis of Ag-NPs [370, 371], Allium cepa cell extract for Au-NPs [372], Eucalyptus leaf extract for the construction of Fe-NPs andcomposites [373], and plant extracts of Punica granatum forthe biosynthesis of ZnO-NPs [374] were used.The green synthesis of NPs using plant extracts has more advantages than using microorganisms because it is a singlestepmethod, is nonpathogenic and economic, produces a hugeamount of metabolites, is cost-effective, and is an eco-friendlyapproach [375].

Plant extracts contain various bioactives, such asalkaloids, proteins, phenolic acids, sugars, terpenoids, and polyphenols, which have been found tohave an important role in first reducing and then stabilizing the metallic ions, as shown in Fig. 16. Plant-mediated biosynthesis of NPs with theirsize and applications is summarized in [48].

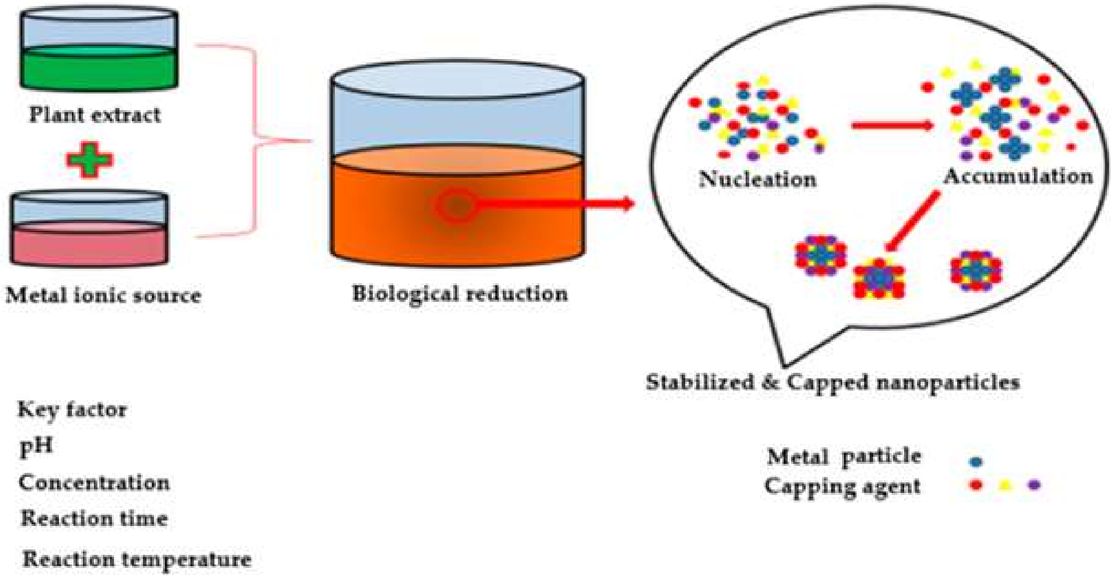


Fig. 16 Biological synthesis of nanoparticles by using plant extracts.

The biovariations of plants offers plentiful biochemical properties and introduces particular source to synthesizenanoparticles [376]. The extract from the plant leaf can be obtained very simply to use and has numerous metabolitesthat act as reducing agents to synthesize nanoparticles [377]. A solution containing metals such as nickel, cobalt, zinc, and copper is mixed with the extract of the plant leafat room temperature [378]. Different factors such as pH, temperature, contact time, metal salt concentration andphytochemical profile of the plant leaf particles affect thenanoparticles goodness, nanoparticle stabilization, quantityproduced, and yield rate. The metal ion reduction inplants is faster than that in fungi and bacteria, as theyneed a long time for incubation because of the presence ofwater-soluble phytochemicals [379].

The numerous phytochemicals present in the plantleaf extracts can be extracted facilely [380, 381] so theplant leaf extracts are considered as a wonderful tool for MNPs and MONPs synthesis.

The advantage of plant leaf extracts to act asstabilizing agents and reducing agents facilitates thenanoparticle synthesis [376]. Biomedical reducing agentsare present at different concentrations in different typesof leaf extracts, so the leaf extract composition has agreat effect on the nanoparticle synthesis [382, 383]. Terpenoids, flavones, ketones, amides, aldehydes, and carboxylic acids are the essential phytochemicals involvedin the nanoparticle synthesis [377].

The plants are considered to be more suitable compared tomicrobes for green synthesis of nanoparticles as they are nonpathogenicand various pathways are thoroughly researched (Fig. 17).

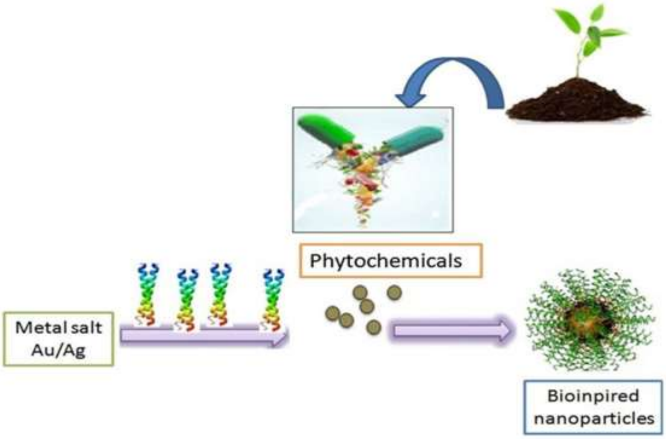


Fig. 17 Green syntheses of Cds nanoparticles by bacteria.

A wide spectrum of metal nanoparticles has beenproduced using different plants [110, 378, 384, 385]. These nanoparticles have unique optical, thermal, magnetic, physical, chemical, and electrical properties in comparison totheir counterpart bulk material with numerous applications innumerous fields of human interest [386, 387]. There are various biological entities whichare used for AgNPs synthesis [388]. Jatroa curcasextract results in the production of homogenous (10-20 nm) AgNPs from $AgNO_3$ salt in 4 h [238]. The leaf extractsof Acalypha indica have exhibited the capability to synthesizeAgNPs. The size of the AgNPs obtained became extensivelyhomogeneous and ranged from 20 to 30 nm [389]. In another study, Medicago sativa seed exudates were usedfor the synthesis of AgNPs. The reduction of Ag^+ happenedalmost immediately as nanoparticles had been reported withina minute of metal salt exposure and 90% of Ag^+ was reducedat 30 °C in < 50 min. The resulting nanoparticles were flowerlikeand/or triangular and spherical with a size range of 5-108 nm and had a heterogeneous size distribution [390]. The leaf extract of Ocimum sanctum can alsoreduce Ag^+ resulting in the AgNPs of 3-20 nm in sizeproduction The particles were spherical and stabilized by theway of a component of the leaf broth [391].Terminalia chebula fruit extract has been used to promptlyproduce Ag nanoparticles [392]. Eucalyptus macrocarpa leaf extract producedAg nanoparticles of cubic shape ranging in size from 50 to 200 nm [393]; spherical gold nanoparticles ofaround 20 nm by Nyctanthes arbor tristis (night jasmine) flowerextract [394]; leaf extract from Coriandrum sativum(coriander) leaf extract produce Ag and Au nanoparticles of 7-58 nm [378]. Phyllanthin extracted from theplant Phyllanthus amarus may be used to produce both gold andsilver nanoparticles. This study is unique for the use of singleconstituent of a plant extract to synthesize metallic nanoparticlesin comparison to different investigations wherein the wholeplant was used [395]. The shape and size ofnanoparticles produced had been affected by the concentration ofphyllanthin used. Low concentrations of phyllanthin resulted inthe triangular and hexagonal AuNPs formation, whereas higherconcentrations produced increased spherical NPs [395]. Plant derived polysaccharides and phytochemicalsnanoparticle [214], soluble starch [96], cellulose [396], dextran [397], chitosan [398], alginic acid [399], and hyaluronic acid [400] maybe harnessed and studied for the synthesis of silver and goldnanoparticles successfully. These compounds offer benefits ofusing less toxic chemical compounds and render capability tocreate nanocomposites with different metals. The incubationof the extract from lemon-grass plant, Cymbopogon flexuosus, with gold tetrachloride solution resulted in the formation ofa unique type of liquid-like nanotriangles by the aggregation of spherical AuNPs, the surface of which forms a complex with the aldehydes and/or ketones present in the plant extract, contributing to the fluidity [401]. The leaf broth of Azadirachta indica, forms a complex when dealing with thesalts of silver, gold, and then both metallic ions concurrentlyproduced silver, gold, and bimetallic silver-gold NPs. The rate of formation of nanoparticles became faster having attainedthe plateau in 2 h. The stability of NPs was attributed to theterpenoid and flavanone components of the leaf [401]. Phytochemically reduced NiO NPs with garlic and gingeradd on to the increased bactericidal activity toward multiple drug resistant Staphylococcus aureus which may address drugresistance issues to an extent [402].

Alloying Ag and Au has brought about the formationof bimetallic nanoparticles. Their production entails thecompetitive reduction between two aqueous solutions havingone of a kind of metallic ion precursor used together with aplant extract. The Ag-Au nanoparticle, the core-shell structureis manufactured from Au due to its larger reduction potential, and Ag ions are reduced and form a shell with Ag coalescingon the core. Few plants have been efficiently used to synthesizeAg-Au bimetallic nanoparticles like Azadirachta indica [401], Anacardiumoccidentale [403], Swieteniamahagony [404], and cruciferous vegetableextracts [405].

Extracts from various plants have been used to synthesizenanoparticles of copper (Cu) and copper oxide (CuO). Cunanoparticles varying from 40 to 100 nm in size were synthesizedfrom Magnolia kobus leaf extract [406] and fromSyzygium aromaticum (Clove) [407] showing spherical to granular shape with 40 nm of an averageparticle size. The Latex from the stem of Euphorbia nivulia (Common milk hedge) was used to synthesize an important classof Cu nanoparticles stabilized and coated through terpenoids andpeptides of the latex [408] and synthesis ofa notably stable spherical nanoparticles of CuO was confirmedfrom Sterculia urens (Karaya gum) with a particle size of 4.8 nm[409].

The synthesis of the first platinum nanoparticles wasdemonstrated with the help of Song et al. [75] Diospyroskaki (Persimmon) leaf extract and carboxylic acids, amines, alcohols. Ketones present in the leaf extract act as a functionalgroup for the reduction of Pt ions. There was 90% reductionof Pt ions into nanoparticles in ~2.5 h. The possibility of anenzyme mediated process was ruled out due to the temperatureof execution of the experiment (95 °C) which is high enoughto denature proteins. Palladium nanoparticles were synthesizedusing the extract of Cinnamon zeylanicum bark [410,411] and Annona squamosa (custard apple) peelextract for the synthesis of Pd nanoparticles of size 75-85 nm [412]. Nanoparticles with a mean size of 15 nmhad been synthesized from the leaf extract of soybean (Glycinemax) [413]. The extracts from commonly availableCamellia sinensis (Tea) and Coffe aarabica (Coffee) have beenutilized to produce nanoparticles of palladium of sizes rangingfrom 20 to 60 nm with faced centered cubic crystal symmetry [413]. Furthermore, when an extract of Gardeniajasminoides (Cape jasmine) is used to synthesize nanoparticlesof palladium the antioxidants (geniposide, chlorogenic acid, crocins, and crocetin) present in the extracts acts as stabilizingand reducing agents [414]. Other plants likeOcimum sanctum leaf extract (Holy basil) [415], plant wood nanomaterials [416] and ligninfrom red pine (Pinus resinosa) were used for the synthesisof nanoparticles of platinum and palladium [417].

Nanoparticles of spherical size and ranging in size from 100 to 150 nm from metal oxide which includes titanium dioxide(TiO_2) were synthesized efficaciously using numerous plantextracts viz. Annona squamosa peel [412], Cocos nucifera coir [418], Nyctanthes arbor-tristisleaf extracts [330], Psidium guajava [419], Eclipta prostrata [325, 420], and Catharanthus roseus [421]. Spherical shaped zinc oxide (ZnO) nanoparticles were obtained using the latex of Calotropis procera [422], Aloe vera [387], Physalis alkekengi [423], and Sedum alfredii [424, 425]. Biogenic Indium oxide

(In_2O_3) spherical nanoparticleswere synthesized with a variable size range from 5 to 50 nm byusing leaf extracts from Aloe vera (Aloe barbadensis) [426].

Iron (Fe) nanoparticles were synthesized by the use of greenchemistry methods including the aqueous Sorghum bicolor branextracts [427] and leaf extracts of Azadirachtaindica [428], Euphorbia milii, Tridaxprocumbens, Tinospora cordifolia, Datura innoxia, Calotropisprocera, and Cymbopogon citratus [429]. The latexfrom Jatropha curcas has been used to synthesize spherical Pbnanoparticles of sizes from 10 to 12.5 nm [120]. Synthesis ofmetallic nanoparticles includes the use of the extracts of plant parts or whole plant extracts. Also, metallic nanoparticlesmay be synthesized inside living plants and a novel approach forthe synthesis of PdNPs by the use of Arabidopsis thaliana wasreportedly developed [430] by growing the plantin the usual growth medium, and medium was then replacedwith potassium tetrachloropalladate (K_2PdCl_4) followed by theincubation for 24 h in the salt solution. PdNPs of 2-4 nm wereproduced as visualized by transmission electron microscope.These biologically synthesized PdNPs had been utilized inSuzuki-Miyaura coupling reactions with better catalytic activityas compared to the commercially available PdNPs [430]. The Alfalfa plant seeds were grown with variousconcentrations of $K(AuCl_4)$ for 2 weeks for the formation of AuNP nanoparticles [431]. The timetaken for the synthesis of nanoparticles via this method exceeds 2 weeks, limiting its commercial feasibility. However, if productiontime is reduced, it might be a great strategy for creating a cheapgreen method for synthesizing nanoparticles.

18. Nanoparticles Synthesis from Plant Leaf Extracts Mechanism

Proteins and carbohydrates are important constituents of the plant extracts, which act as reducing agents and areresponsible for the formation of MNPs and metal ionreduction [432].

Functional amino groups and proteins in the plant extracts play an essential role in the metal ion reduction [433]. Huang et al. [67] discussed that the functionalgroups of alkaloids, flavones, and anthracenes, such as –C–O–C–, –C–O–, –C═C–, and –C═O–, assist the MNPsynthesis.

Kesharwani et al. [434] proposed that the metal ionreduction may be carried out with the help of quinines and plastohydroquinone molecules present in the plantleaf extract, which indicate that the extracellular MNPsynthesis can be done by biomolecules and heterocycliccompounds in plants. Despite the complete vision of MONP synthesis by using plants is not well understooduntil now, the phytochemicals of the plants led to theproduction of MONP, like MNP.

First, the phytochemicals of the plant extract areresponsible for the metal reduction. Oxygen producedfrom either atmosphere or degrading phytochemicals links the reduced metal ions. Electrostatic attraction will link metal oxide ions to each other and lead to the formation of nanoparticles. They are stabilized by phytochemicalsthat prevent agglomeration between them.

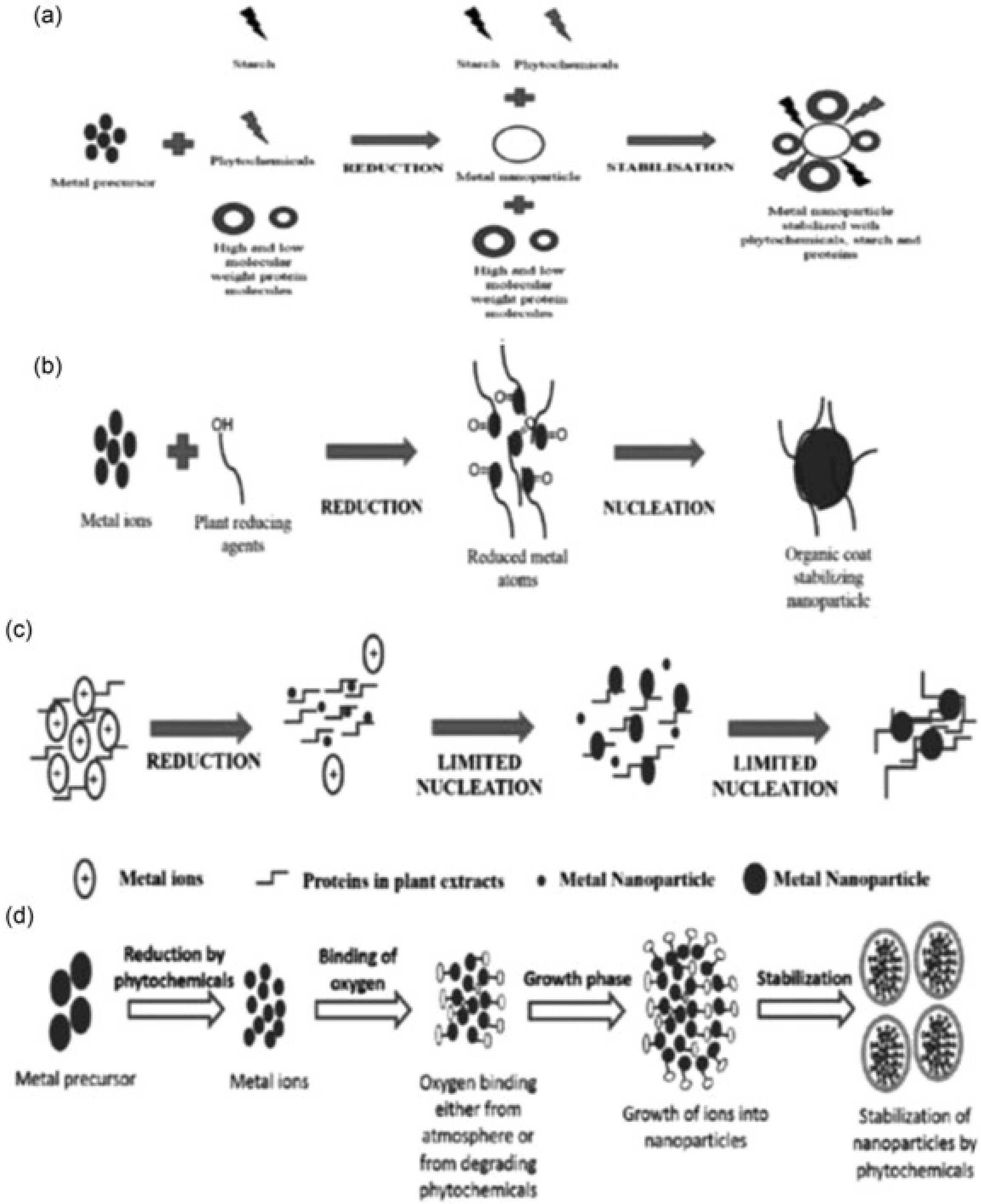


Fig. 18 Metal and metal oxide nanoparticles formation mechanism by phytochemicals: Metal and metal oxide nanoparticle formation by phytochemicals: (a) the use of high- and low-weight phytochemicals, proteins, and starch mixtures present in the plant extracts with metal precursor. (b) proteins of plant extracts act as a reducing and stabilizing agents and the metal atom will be encapsulated as organic covering in three steps. (c) metal ion reduction and reduced metal ion nucleation will be in the activated phase to have the final shape of the nanoparticles formed during the termination step. (d) the MONPs production mechanism which may also be executed by different methods [67, 88,377,382,383, 434-438].

The superoxide-driven Fenton reaction is the mainprovenance for reactive oxygen species (ROS) [156] and isrepressed by the phenolic compounds with carboxylgroups and hydroxyl groups of plants.

Mukherjee et al. [435] suggested the use of high- and low-weightphytochemicals, proteins, and starch mixtures presentin the plant extracts, as indicated in Fig. 18a. Newmanet al. [436] also explained the possibility of theproduction of MNPs and MONPs by proteins of plantextracts, which act as reducing and stabilizing agents, asmentioned in Fig. 18b.

Markarov et al. [343] proposed that metal atoms willbe encapsulated as organic covering in three steps fortheir magnitude stabilization after reduction by plantextracts, as shown in Figure 8b. Metal ion reduction andnucleation of reduced metal atom will be in theactivation phase, the nanoparticle stability increasedthrough the growth phase, and the shape of thenanoparticles formed during the termination phase, asindicated in Fig. 18c [437]. They could summarize theprocess by the following steps:

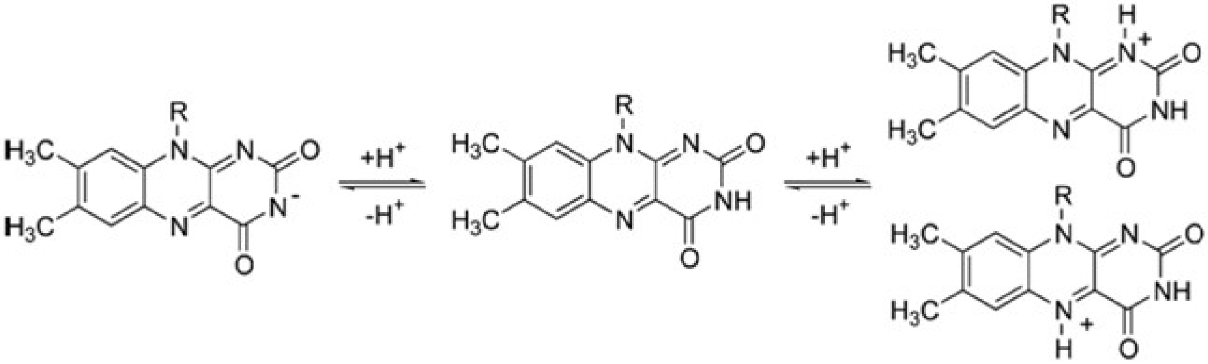
(1) The metals such as copper, silver, gold, zinc, titanium, iron, and nickel result in the formation oftheir metal oxides by phytochemicals.

(2) Using phytochemicals, metal ions will go throughgrowth and stabilization phases.

(3) Oxygen is produced either by degradation of phytochemicalsor by atmosphere, and before growth andstabilization phases, it will be linked to metal ionas mentioned in Fig. 18d which explains the MONPs production mechanism may also be executedby different methods described in the literature[88, 377, 382, 383, 438].

19. Vitamin B$_2$ as a Double Agent (Reducing Agent and Capping Agent)

Vitamin B$_2$ functions as both a reducing and a cappingagent as it manifests to be a quixotic multifunctionalagent in the manufacture of nanomaterials and it has high water solubility, biodegradability, and low toxicity compared with other reducing agents such as sodiumborohydride ($NaBH_4$) and hydroxylamine hydrochloride. Vitamin B$_2$ is the most abundant organic cofactor foundin nature, and it exists in three different redox states:fully oxidized, one-electron reduced, and fully reduced [439] (Scheme 5), as each of these redox states canpresent in a cationic, a neutral, or an anionic formdepending on the pH of the solution, and all can transfer electrons [141].



Scheme 5 Structure of the anionic (left), neutral (center), and cationic (right) vitamin B2 species in the fully oxidized redox state (R =-$CH_2(CHOH)_3CH_2OH$) [141, [439].

20. MNP and MONPs Synthesis from Ascorbic Acid (vitamin C) and its Derivatives as Fundamental Factors

Vitamin C (Fig. 19) is abundantly present in manynatural sources, including fresh fruits and vegetables.The richest sources of ascorbic acid include Indiangooseberry; citrus fruits such as limes, oranges, andlemons; tomatoes; potatoes; papaya; green and red peppers; kiwifruit; strawberries; cantaloupes; greenleafy vegetables such as broccoli; and fortified cereals, and their juices are also worthy sources of vitamin C.Another source of vitamin C is animals. They usually produce their own vitamin C, which is

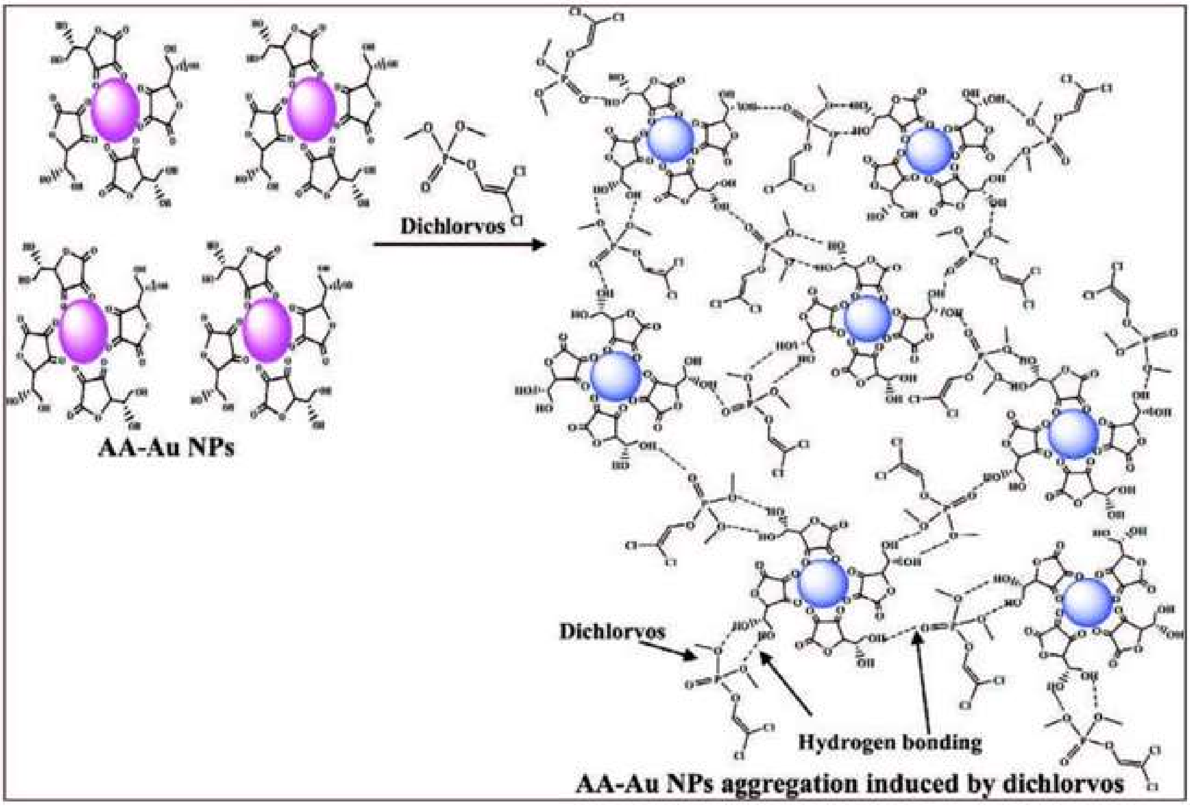
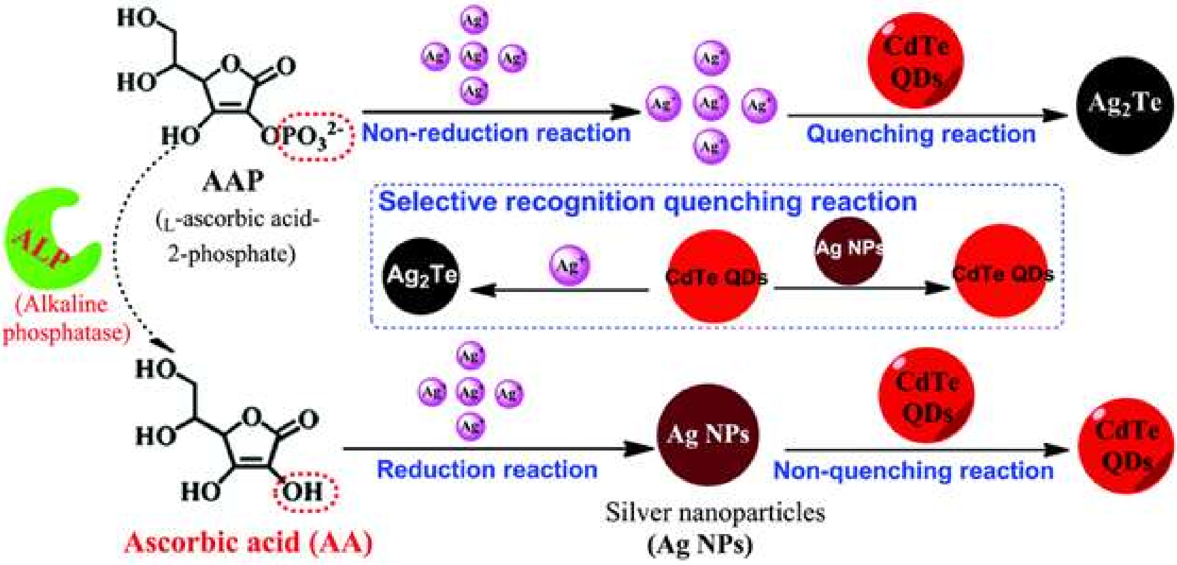


Fig. 19 Detection of dichlorvos by utilizing AA–Au NPs as a colorimetric probe: an analytical process [445].



Scheme 6 Schematic illustration of the fluorescence Ascorbic acid (AA) and alkaline phosphatase (ALP) assay based on the controlled generation of silver nanoparticles and selective quenching reaction.

highly concentratedin the liver part [440, 441]. The structure of vitaminC and its derivatives are given in Scheme 6.

Vitamin C (vit C) or ascorbic acid (AA) is ahydrophilic molecule, which consists of six carbons, similar to glucose [67]. In the organisms, vit C can befound in the reduced form (ascorbic acid or ascorbate) orin the oxidized form called dehydroascorbic acid, whichis generated from two-electron oxidation of ascorbicacid [441].

Some alterations have been done to vit C molecule toimprove its stability. One option is to connect ionic saltsto the molecule. In this sense, one of the most well-knowncomplexes is ascorbyl 2-phosphate, which is formulatedwith sodium (SAP) or magnesium (MAP) salts and hashydrophilic characterization. These structures are given in Scheme 5. The introduction of phosphate group at thesecond position of the cyclic ring of the molecule is effective against oxidation. Despite being more stable, these derivatives appear to be less permeable through theskin in comparison with ascorbic acid [442].

The nanoparticles that are generated from thenatural polymers have been comprehensively used in the pharmaceutical and food industries. These systemshave low toxicity and are bioconvenient and biodegradable. Ascorbic acid functions as a reducing and cappingagent for the synthesis of MNPs such as silver, gold, andcopper. Ascorbic acid molecules can cap or surround theparticles and prevent the uncontrolled growth of theparticles to micron-sized dimensions. A study by Khan etal. in 2016 reported the copper nanoparticles synthesisusing ascorbic acid as the reducing agent [443]. Sunet al. reported in the Journal of Materials Science in 2009 that gold nanoparticles can be produced in inversemicelles without the addition or introduction of anyreducing or capping reagent [444]. In Analytical Methodsin 2014, D'souza et al. explained the use of AA–Au nanoparticlesas a colorimetric probe for the detection ofdichlorvos in water and wheat samples. The concentrationof ascorbic acid has an influence on the aggregationinduced by dichlorvos in AA–Au nanoparticles (Fig. 19), and the optical property of the AA–Au nanoparticles wasinvestigated by UV-vis spectroscopy [445].

21. Phenolic Compounds as Substantial Agent for MNP and MONPs Synthesis

The phenolic compounds also offer protection for plantsagainst ROS generated during photosynthesis andexposure to anthropogenic contaminants [446]. Phenolicacids have been widely used in medicine due to their powerful antioxidant activities, as they are consideredphenolic derivatives with at least one functional carboxylicgroup. The majority of phenolic acids includelarger polyphenols and other organic and structuralcompounds [447, 448]. The two major categories of thenatural phenolic acids are benzoic acid derivatives and cinnamic acid derivatives. The categorization is based on the number of hydroxylation sites in the aromatic ring (Fig. 20) [449]. ROS and free radicals can be scavenged bythe hydroxyl groups of these structures [450]. The chemical structures of both groups of phenolic acids are represented in Fig. 20.

Medicinal plants have large quantities of phenolic compounds as secondary metabolites. A widerange of plant-based foods and syrups contain phytochemical phenolic acid, which are well known for the antioxidant, anti-cancer, and anti-inflammatory properties [451]. Phenolic acids can be used as a reducing agent for the preparation of MNPs by a thermodynamic equilibrium approach, and nucleation is commenced by injecting the reducing agent (phenolic acids) at themetal ion supersaturation concentration, followed bythe MNPs ulterior growth through progressive ion reduction [452]. The inception can be expedited bythe high oxidation inclination of phenolic acids [453]. The oxidation of hydroxyl functional group of caffeicacid would present electron (e^-) required for neutralizinggold ions (Au^{3+}), which was inspected by Hyun-soeket al. [454]. The reducing capacities of propyl gallate, ferulic acid, caffeic acid, vanillic acid, and protocatechuic acid in the presence of hydrogen tetrachloroaurate were

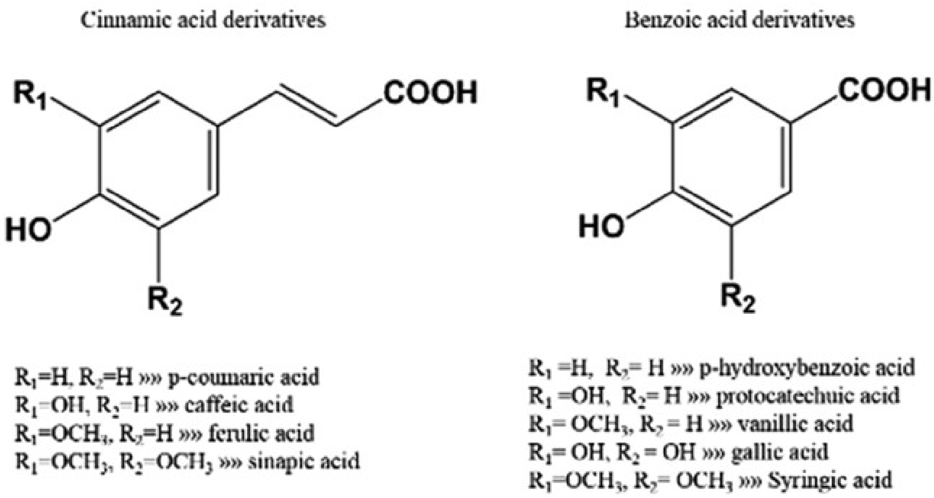


Fig. 20 The phenolic acids used for the preparation of MNPs and their main chemical structures [449].

inspected by Scampicchio et al. [455] using the UV vis spectroscopy and colorimetry methods. The phenolicacid bioreduction potential was directly linked to the number of functional hydroxyl groups, which wasdeclared by other authors. The absorbance of phenolicacid attached to the MNPs surface is generated from the formation of an absorbent bond between carboxyl group and the metal atom [456, 457].

The metal ion chelation capability of phenolic acids such as caffeic acid and coumaric acid also participates in the nanoparticle formation process [458]. The MNPs prepared by phenolic compounds have higher stability than those prepared by other organic or inorganic reducing agents such as citrate or sodium borohydride [459], and the synthesized MNPs can be coated on the surface with protonated reducing agents such as citrate through various mechanisms based on the inter molecular inter actions between the absorbed molecules andthe metal surface [343]. Natural phenols with functional hydroxyl [460] and carboxyl [461] groups have protonating and absorbing capabilities and catechol group ofsome phenolic compounds is a perfect metal absorbing moiety. This functional group can be absorbed on the surfaces of MNPs through three different configurations including bidentate bridging bonding, bidentate chelating bonding, and monodentate ester-like bonding (Fig. 21) [462, 463]. Different spectroscopic techniqueshave been applied for studying the phenolic acidabsorption on the MNPs surfaces. Although the UV-visabsorption spectroscopy technique has confirmed the phenolic acids capability of reducing metal ions, this method could not confirm the phenolic acids attachmentto the surface of the prepared nanoparticles [464].

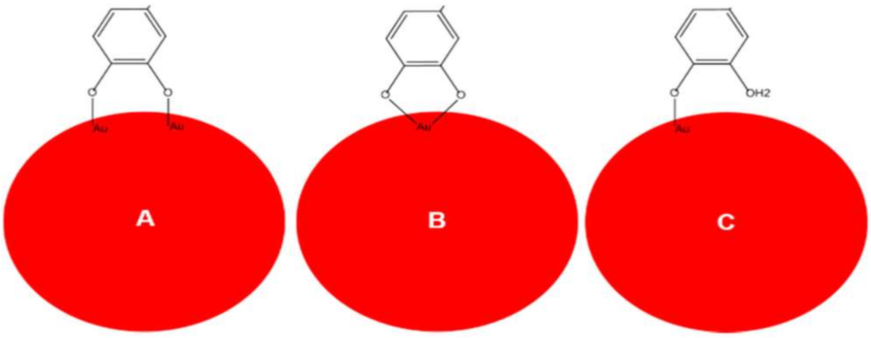


Fig. 21 Schematic explanation of catechol group binding; three different configurations on the surface of the MNPs. (a) Bidentate bridging bonding, (b) bidentate chelating bonding, and (c) monodentate ester-like bonding [462,463].

Furthermore, it is conceivable to reveal the distinctive absorbance peaks of capsaicin, cinnamic acid, gallicacid, salicylic acid, and other phenolic acids attached to the surfaces of the MNPs using the Fourier transform infrared spectroscopy technique [465-468]. Last, it is contingent to acquire the micrographs of the phenolicacids coated on the MNPs and MONPs by transmission electron microscopy (TEM) (Fig. 22) [469-472]. Greenchemistry through plant biomass or extract is anapproach for the production of biocompatible MNPs. Specific plant or algae may be worthy due to its contentof some phenolic acids compound; however, still, there is a multitude of other materials, that makes theinvestigation of the function of the phenolic acids compound in the spotted toxicity generated from synthesized MNPs very complicated. In general, thereported toxicity effect of the MNPs prepared using plantextract is dialectical in pieces of the literature. However, the MNPs that have been synthesized from plant extracthave higher biocidal activity compared with the chemically synthesized nanoparticles, which was reported previously [473].

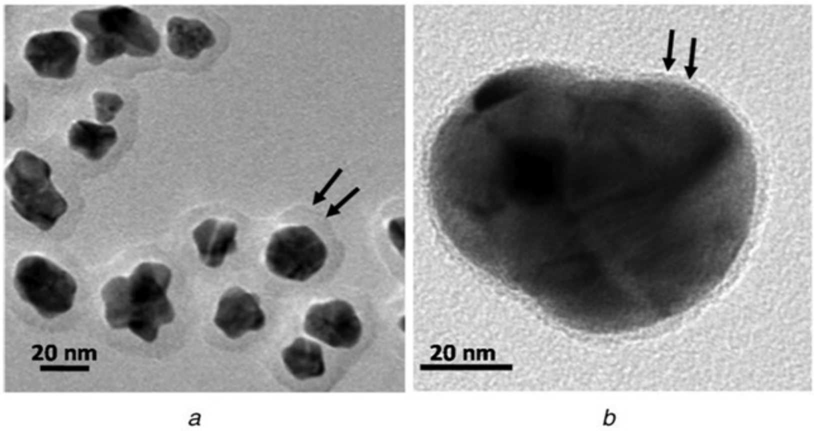


Fig. 22 TEM micrographs of (a) phenolic acid-coated gold nanoparticles [469] and (b) silver/lenium alloy nanoparticles [470].

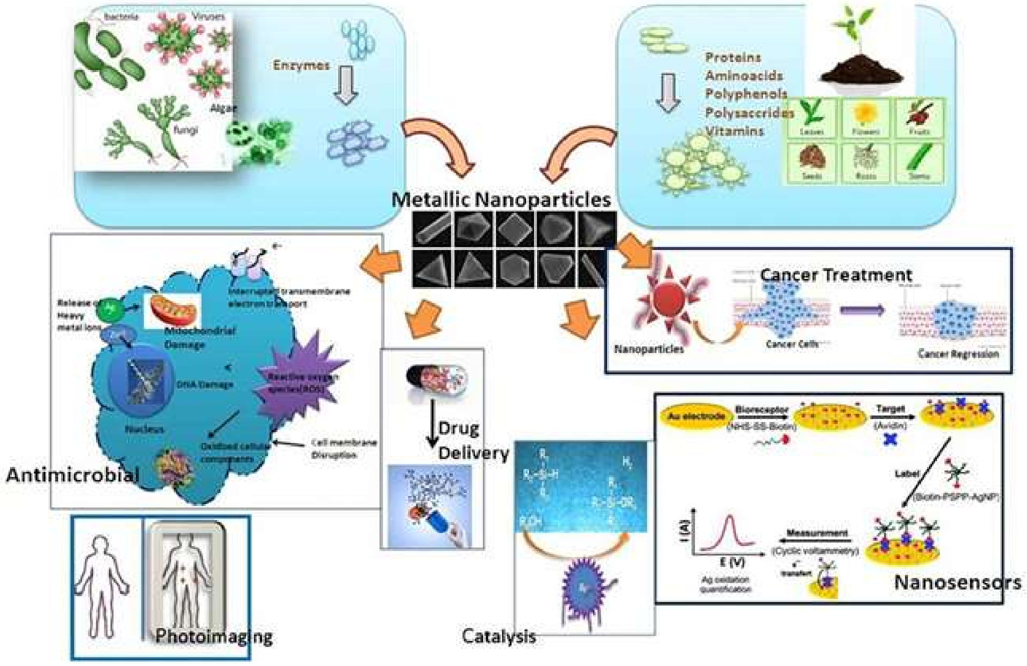


Fig. 23 Application of Green synthesis of metallic nanoparticles..

22. Biotechnological Applications of NPs

Nanoparticles have wide applications in both biomedical and physicochemical fields. They may be used for pharmaceutical, drug delivery, biosensing, bio-imaging, and biomolecular recognition (Fig. 23) in bio-medical research. Such nanoparticles are integrated in various materials of every day use which includes cosmetics, toothpaste, deodorants, water purification systems, and humidifiers due to their anti-microbial properties [474]. They have an important role to play in agriculture technology such as detection and abatement of plant diseases andminimizing nutrient leaching to increase the crop yield. The major biotechnological applicationsof NPs will be addressed below.

22.1 Microwave Heating

Microwave (MW) technology is emanating as a substitutional energy source potent enough to fulfill chemical transformations in minutes, instead of hours or even days. In the nanomaterial preparation context, it is more pertinent when the material properties investigation depends solely on the size and shape, and the control over the synthetic methodologies is crucial. This refers to the materials' growth in nanoscale is largely subordinate on the thermodynamic and kinetic barriers in the reaction as known by the reaction trajectory and is influenced by vacancies, defects, and surface reconstructions. Traditional thermal techniques are instituted on blackbody radiation conduction to boost the reaction, where the reaction vessel performs as intermediary for conveying energy from the heating mantle to the solvent and last to the reactant molecules, which can give rise to severe thermal gradients throughout the bulk solution and incomplete, nonregular reaction conditions. In the nanomaterials preparation, this has been a problematic issue where uniform nucleation and growth rates are stringent to the material quality. MW heating method can classify the heating problems in homogeneity in the classic thermal techniques as its use provides boosted reaction kinetics, and fast primary heating, and, hence, improved reaction rates culminating in clean reaction products with fast consumption of starting materials and higher yields [31].

The methodology is viable under a set of conditions even for enzymatic and biological systems. A bulk and shape-controlled noble nanostructures with different shapes such as prisms, cubes, and hexagons were synthesized via the MW-assisted spontaneous reduction of noble metal salts using an aqueous solution containing α-d-glucose, sucrose, and maltose. The ensuring nanoparticles size can be simply controlled by changing the concentration of sugars; a higher concentration offers regularly smaller size particles, which increases with minimization in the concentration of the sugars. A general method has been improved for the crosslinking reaction of poly(vinyl alcohol) (PVA) with metallic systems, such as Pt and Cu, and bimetallic systems, such as Pt–In, Ag–Pt, Pt–Fe, Cu–Pd, Pt–Pd, and Pd–Fe, single wall carbon nanotubes and multiwall carbon nanotubes (MWNT) and buck minster fullerene (C-60). The formation of biodegradable CMC composite films with noble nanometals is the extension of the strategy, such as metal decoration and carbon nanotubes alignment in CMC by using a MW-assisted approach, which enables the shape-controlled bulk synthesis of Ag and Fe nanorods in poly(ethylene glycol) solutions. A cleaner approach to the formation of tantalum oxide nanoparticles is optimized using the ethyl glycol–mediated pathway [31]. A newer form of the carbon-doped porous Titania, which can be useful for the visible light-induced photodegradation of contaminants, has been synthesized using dextrose, a benign natural polymer [473]. The fluffy nature of the TiO_2 is due to the spontaneous heating of the solvent, water, and its ulterior evaporation and combustible sugar dextrose. This general and eco-friendly protocol utilizes dextrose to create a spongy porous structure and can be extended to other transition metal oxides such as ZrO_2, Al_2O_3, and SiO_2. The noble nanocrystals undergo catalytic oxidation with monomers such as pyrrole to generate noble nanocomposites, which have potential functions in catalysis, biosensors, energy storage systems, and nanodevices. The wet chemical synthesis of Ag cables wrapped with polypyrrole has been carried out at room temperature without using any surfactant/capping agent and/or template. The MW hydrothermal process delivers magnetic nanoferrites, micro-pine structured catalysts, and metal oxides with 3D nanostructures, which are obtained from facilely available metal salts. These materials were synthesized from low-cost materials in water without using any reducing or capping reagent. This principle could ultimately enable the fine-tuning of the material responses to magnetic, electrical, optical, and mechanical stimuli. The particles with various well-defined morphologies, including octahedron, sphere, triangular rod, pine, and hexagonal snowflake were obtained, and the size range of 100-500 nm were acquired, as shown in Fig. 24 [31].

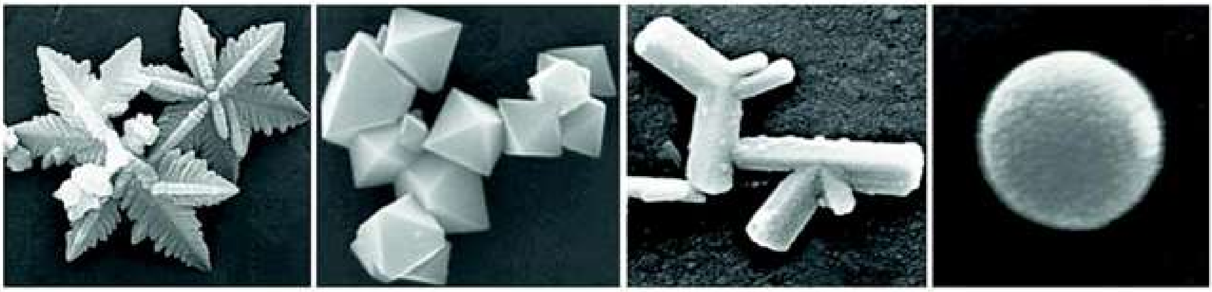


Fig. 24 Well-known morphologies of metal oxides [31].

22.2 Antimicrobial Activities and Cytotoxicity Agents

The major challenges for medicinal practitioners aresummarized in the appearance of new drug-resistant microbes.Therefore, the development of novel drugs is necessary tocope with various diseases. The applications of NPs in medicinehave different advantages such as in early detection systems, diagnosis using NP-based imaging, and treatment ofdifferent diseases caused by drug-resistant microbes [475, 476]. The development of nanotechnology and methods usedfor the synthesis of nanocomposites/NPs has likewise revolutionized the field of biomedicine because of theirantimicrobial and immunoassay activities [477, 478]. Varioustypes of NPs, including metals and metal oxides such as Ag, Au, Ag_2O, ZnO, TiO_2, CaO, CuO, MgO, and SiO_2, are developedby different researchers to use in medical applications [22, 26, 38, 479-483]. Plant- and different microbe-mediated biosyntheses of NPs are suitable candidates for a novel productionof antimicrobial nanomaterials [37, 484]. Fig. 25 represents the cytotoxic mechanism of biological nanoparticles.

Recently, the green-synthesized ZnO-NPs showed antimicrobial activities against different pathogenic Gram-negative and Gram-positive bacteria such as E. coli, Pseudomonasaeruginosa, Salmonella typhimurium, Listeria monocytogenes, Staphylococcus aureus, and Bacillus subtilis [37, 485]. On theother hand, Au-NPs and Ag-NPs exhibit highly antibacterial activity toward pathogenic Gram-negative bacteria such as E. coli, Klebsiella pneumonia, Salmonella typhimurium, Pseudomonas aeruginosa, Proteus mirabilis, Shigelladysenteriae, Enterobacter aerogenes, and Citrobacter sp. Also, the biosynthesized Au-NPs and Ag-NPs have activities againstpathogenic Gram-positive bacteria such as Staphylococcus epidermidis, Staphylococcus aureus including MRSA, Streptococcus pyogenes, Enterococcus faecalis, and Bacillussubtilis [281, 478, 486, 487]. The activities of NPs as antifungal agents for different pathogenic fungi have been widely evaluated [488,489]. Several studies have reported the activities ofbiosynthesized Ag-NPs as antifungal agents against multicellular and unicellular fungi such as Trichophyton mentagrophytes, Aspergillus flavus, Candida glabrata, Aspergillus fumigatus, Candida parapsilosis, Cryptococcus neoformans, Candidakrusei, Fusarium solani, Trichophyton rubrum, Cryptococcusgattii, Candida tropicalis, Sporothrix schenckii, Epidermophyton floccosum, Candida albicans, and Mucorhiemalis. In the same regard, Ag-NPs showed activities against plant pathogenic fungi such as Aspergillus niger, Colletotrichumsp., Fusarium sp., Culvularia lunata, and Rhizoctonia solani [37, 490-493]. Recently, cancer diagnosis and treatment have received more attention. Alarge multiplicity in nanomaterials has been evaluated to improve its efficacy in cancer therapy as well as to reduce negative impacts compared with conventional therapies [494]. The toxicity impact of NPs synthesized by green methods is evaluated mainly by changes in viability and cellmorphology, as well as metabolic activities [26, 495]. NPs have been localized in the mitochondria, inducing functional damageand structural as well as oxidative emphasis [496]. The physicochemical properties of NPs have a critical important role in cytotoxicity effect. The nature and size of NPs, its surface area, and its surface functionalization (capping agents) are important factors that affect their toxicity [23]. The small-sized NPs are moretoxic compared with the bigger ones [492].

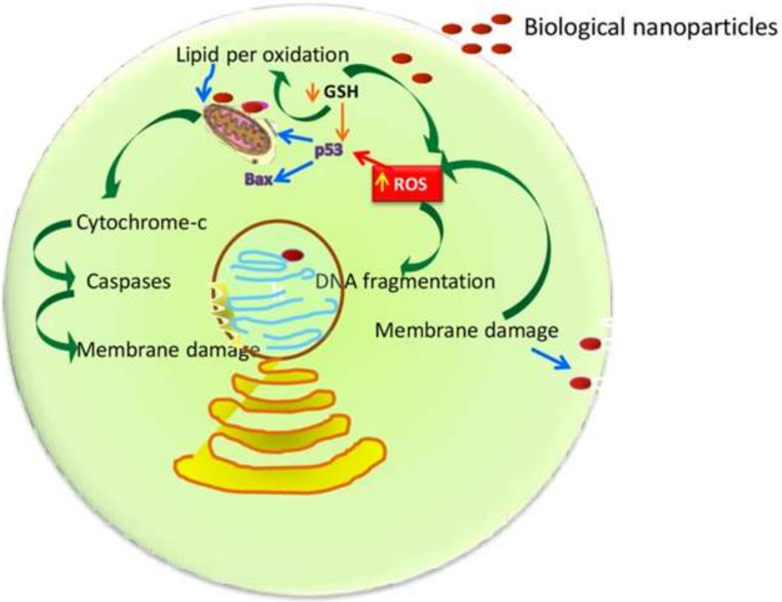


Fig. 25 Cytotoxic mechanism of biological nanoparticles.

There are three defined prospective mechanisms that explainthe antimicrobial activity of metal NPs: firstly, damageof the cell wall and cell membrane; secondly, damage of intracellular microbial components after penetration of the cell wall; and finally, oxidative stress mechanism (Fig. 26).

The cell wall and cell membrane protect microbes agains texternal harmful condition and remain a transport mechanism of nutrients in/out of the cell. According to cell wall components, Gram-positive bacteria possess a thick layer of peptidoglycan, while Gram-negative contain thin layer of peptidoglycan [497, 498]. The metallic NPs exhibit higher antibacterial activity against Gram-negative bacteria more than those recordedfor Gram-positive bacteria [499]. This activity maybe attributed to the negative charge of lipopolysac charides (LPS) in Gram-negative bacteria that permit adhesion of NPs to bacterial cell wall. The metallic NPs interact with bacterialcell wall through attraction between the microbial cellwall's negative charge and NPs' positive charge [500]. Due tothis interaction, the permeability function of the cell membrane changes and, hence, the bacterial integrity disrupts and causes cell death [501]. Interestingly, the cellular components such as protein, nucleic acid, ions, and enzymes escape out ofthe cell membrane and adversely influence cellular activity [502]. Therefore, the degradation of bacterial cell wall and cellmembrane due to NPs adhesions is considered the first monitor for antimicrobial activity. On the other hand, Ghosh andco-authors [503] reported that the ability of NPs to interact with proteins in bacterial outer membrane causes harmful change in the bacterial cell wall.

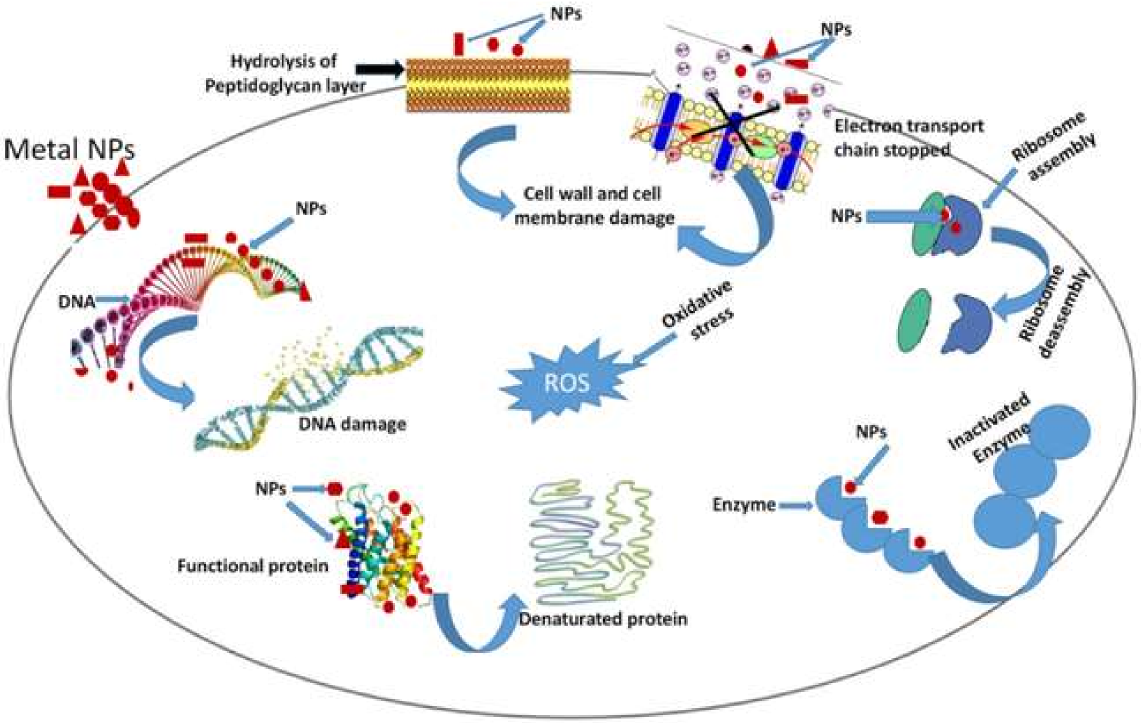


Fig. 26 **Prospective mechanismsfor antimicrobial activity formetallic NPs.**

According to the degree of damage in the cell wall, metallic NPs permeate the cell and cause irreversible effect in DNAand protein. Once NPs enter the bacterial cell, it interacts with DNA and converts it from normal state to condensed state, and hence, DNA loses replication ability [504]. Moreover, NPs cause enzyme inactivation due to reaction with a thiol group which is found in cysteine amino acid.

Recently the Rutin-SBA-16 drug delivery system has been prepared [505]. The techniques of characterization provided proof that the array of mesoporoussilica (SBA-16) was prepared successfully. Impregnation of Rutin on silica was confirmed from the FTIR techniques and the adsorption/desorption of nitrogen. The kinetic tests showed high linearity, with a correlation coefficient (R^2) of 0.999 for the Higuchi model. This was due to the diffusion of Rutin by the poresof the array through the monolithic system, where the interactions that occurbetween silica and Rutin are of the hydrogen bond type. The Rutin-SBA-16 system released 284 μg of Rutin by mg of silica in a period of 24 h. Moreover, it wasable to provide a controlled release of the drug and included an array for futuretests of toxicities and in vivo applications [505].

22.3 Antitumor Activities

Despite the availability of medications, millions of people die due to cancer every year. Additionally, the survival of patientsis subjected to negative side effects due to consumption ofavailable antineoplastic medicines. Therefore, the developmentof new NP-based drugs has received more attention due to its being more effective, providing little negative impacts and targeting cancer cells. These activities may be attributed to the large surface area of NPs that facilitate the combination of high drug doses [506]. Several types of NP-sized 0 drug carriers such as polymeric micelles, liposomes, dendrimers, and inorganic NPs have been checked in cancertherapy to reduce the negative impacts of conventional anticancerdrugs and improve the antitumor drug efficacy of targettherapies [507, 508]. Inorganic nanomaterials, including metaloxides and metal (zinc oxide, iron oxide, titanium dioxide, gold, silver, and nickel particles), are promising materials applicablein medicine, such as in cell imaging, biosensing, geneor drug delivery, and cancer therapy [509-511].

22.4 Gold and Silver Nanoparticles

The variation in shape, size, and surface properties of Aunanoparticles [16, 512-515] makes themvery beneficial for their potential applications within the area ofbiosensors [516, 517], hyperthermia therapy [2], delivery systemsfor therapeutic drugs and genetic materials [518], as well as anti-bacterial drugs [519, 520]. Gold nanoparticles from Sesbaniadrummondii (rattlebush) have shown the catalytic activity that maybe beneficial in the reduction of aromatic nitro compounds inwaste decontamination.

The rise in antibiotic resistance among pathogenic bacteriahas highlighted the antibacterial properties of nanoparticles andtheir ability to be used as new medical tools. The antimicrobialactivity of Ag is widely known and is used in multiple medicalpreparations against pathogens [66, 519, 521]. The antibacterial properties of AbNPs have allowed for their extensive usein food storage, the health industry, textile coatings and severalenvironmental applications. Silver nanoparticles synthesizedby the use of Tridax procumbens (tridax daisy) extract haverobust antibacterial activity toward Escherichia coli, Shigelladysenteriae, and Vibrio cholera [522]. Silver nanoparticles obtained by using Pinusthun bergii (Japaneseblack pine) cone extracts exhibit antibacterial activity against diverse Gram-negative and Gram-positive agricultural pathogens [523], and the antifungal effect of Ag nanoparticles has been confirmed [524]. Theirutility as antifungal agents is found to be safer as compared tothe conventional fungicides [214]. Ag nanoparticles interact closely with the bacterial cell membrane due to their high surface area to volume ratio as well as size [525]. Recent antimicrobial studies of Ag nanoparticles have shown that they can cause significant membrane damage and DNA toxicity via bio-sorption and cellular uptake [526, 527]. AgNPs are alreadyin-use as antimicrobial agents in many commercially availablemedical and consumer goods. Despite decades of its use, it isimportant to note that the evidence of the silver toxicity is notyet fully explored. Their applications have been discovered bothin the field of medicine and home remedies. Silver sulfadiazine creams are often used to prevent burn site infection and some companies have also built silver into their washing machines. Presently, silver seems be a part of many consumer products suchas computer keyboards, acne creams, and clothing (e.g., socks and athletic wear) that protects the wearer from emitting bodyodor further to deodorizing sprays. A range of organizations that offer accreditation like US-FDA, US-EPA, Korea’s Testing, SIAA of Japan and Research Institute for Chemical Industry and FITI Testing and Research Institute have approved productscontaining silver nanoparticles [242]. The silver nanoparticles also display an anti-tumorigenic ability due to their cytotoxic activity against various tumor cells. The growth and survival of HeLa cells were inhibited by the silver nanoparticles synthesized from Iresine herbstii (Herbst’s bloodleaf). AgNPs produced by latex extracts of Euphorbia nivulia (leafymilk hedge) exhibited toxicity toward the human lung cancer cells (A549) [528]. Nerium oleander (oleander) extractedsilver nanoparticle displayed robust larvicidal activity against malaria vector larvae [529], as optical sensors that form small molecule adsorbates [530], as selective and sensitive nanoscale affinity biosensors to investigatethe transport across the membrane of living microbial cells (P. aeruginosa) in real time [531]. Silver nanoparticles and their composites demonstrate better catalytic activities in dyereduction and their elimination [532, 533].

22.5 Copper and Copper Oxide Nanoparticles

The nanoparticles of CuO display anti-oxidant, anti-bacterial, and antimicrobial activity against common pathogenic strains such as *Escherichia coli* and Staphylococcus aureus and are shown to have tremendous application potential [409, 534, 535]. Cu nanoparticles have antibacterial potential against common pathogenic bacteria *Escherichia coli* [536]. They have functional decontaminating properties against several infectious microorganisms with the potential to be used as bactericidal material [407, 537, 538]. The Cu nanoparticles synthesized by stemlatex of Euphorbia nivulia were seen toxic to human lung cancercells (A549) [539] surfacing their potential application in the field of cancer therapy.

22.6 Palladium and Platinum Nanoparticles

The catalytic activity of platinum nanoparticles extracted from Ocimum sanctum (Holy basil) for the electrolysis of water toproduce hydrogen fuel elements has been studied [415]. A few Pt nanoparticle based catalysts show elevatedactivity for the electro-oxidation of formic acid used for the cleaning of surroundings [540].

22.7 Titanium Dioxide and Zinc Oxide Nanoparticles

TiO_2 suspensions have been explored successfully for bothadulticidal and larvicidal properties against Hippobosca maculate (hematophagous fly) and Bovicolaovis (sheep louse) [421]. TiO_2 nanoparticles synthesized from the extractof Psidium guajava confirmed the effective antibacterial activityagainst Aeromona shydrophila, Escherichia coli, Proteus mirabilis, Pseudomonas aeruginosa, and Staphylococcus aureus, pathogens with strong antioxidant behaviors [419, 534]. TiO_2 oxide nanoparticles have shown applications in the biomedical industry, disinfection of waste water, and beauty products. ZnO nanoparticles additionally possess antibacterial activity that was used in waste water treatments and food packaging [541]. Biogenic ZnO nanoparticles can be used as a drug delivery vehicle for doxorubicin [542]. The nanoparticles of magnetite were used in biomedical applications such as magnetic resonance imaging [17, 543] and oscillation damping and position sensing [544]. Furthermore, a fore-mentioned NPs have many non-medical applications that include magnetic recording devices.

23. Future Research and Outlook of Metallic Nanoparticles

With the inception of NPs over a half-century, the perception of NPs is still now not clearly understood by the researchers. Green chemistry philosophy warrants the synthesis of NPs as an eco-friendly alternative for conventional methods of NPs synthesis. Moreover, the green chemistry approach of NPs synthesis stands on the viewpoint that NPs synthesis should be a benign process, utilization of natural resources, avoiding usage of hazardous materials, free from toxicity and cost inexpensive.

Hitherto, numerous reports have documented the synthesis of metal/metal oxide NPs using the resources plants, bacteria, fungi, yeast, and actinomycetes. Among the natural resources, plants are widely employed for NPs synthesis owing to the ethnobotanical value, active ingredients, easily available, simplified process, and cost inexpensive. Despite the facts, there are a lot of key issues and technical challenges to be addressed by the researchers to develop green NPs as a successful one.

Physical and chemical-based methods of NPs synthesis produce uniformity, homogeneity, and mono NPs but in biological-based, it is questionable.

The following are the key issues about green NPs synthesis and development:

➢Lack of holistic knowledge to develop green NPs using plants entity.

➢The logical strategy should be adopted to develop green NPs with discrete size and shape.

➢Uniformity of NPs should be ensured. Plant-mediated NPs produce more variant size, shape, and structure.

➢Conversion of salt to ion is the main challenge to be addressed. In plant-mediated synthesis, the maximum conversion of salt to ion should be accomplished.

➢The precise role of plant molecules in NPs should be elucidated. These molecules act as a reducing and stabilizing agent.

➢Whether the NPs fabricated are homogenous since there is a difference in substance [biological resources] utilized for synthesis.

➢The transfer of technology processes should be implemented to fabricate NPs from the lab to the industrial level.

➢ Industrial production of NPs should have come with a benign method focusing on ease of synthesis, utilization of resources, particle generation [monodispersity, uniformity, reproducibility], waste management, and toxicity perspective.

➢It is a distant dream to produce NPs completely free from toxicity. In our review also, we explain the potential threat of toxicity of plant-mediated metallic nanoparticles to humans and the environment. Henceforth, at least researchers should be directed to fabricate NPs with minimal toxicity.

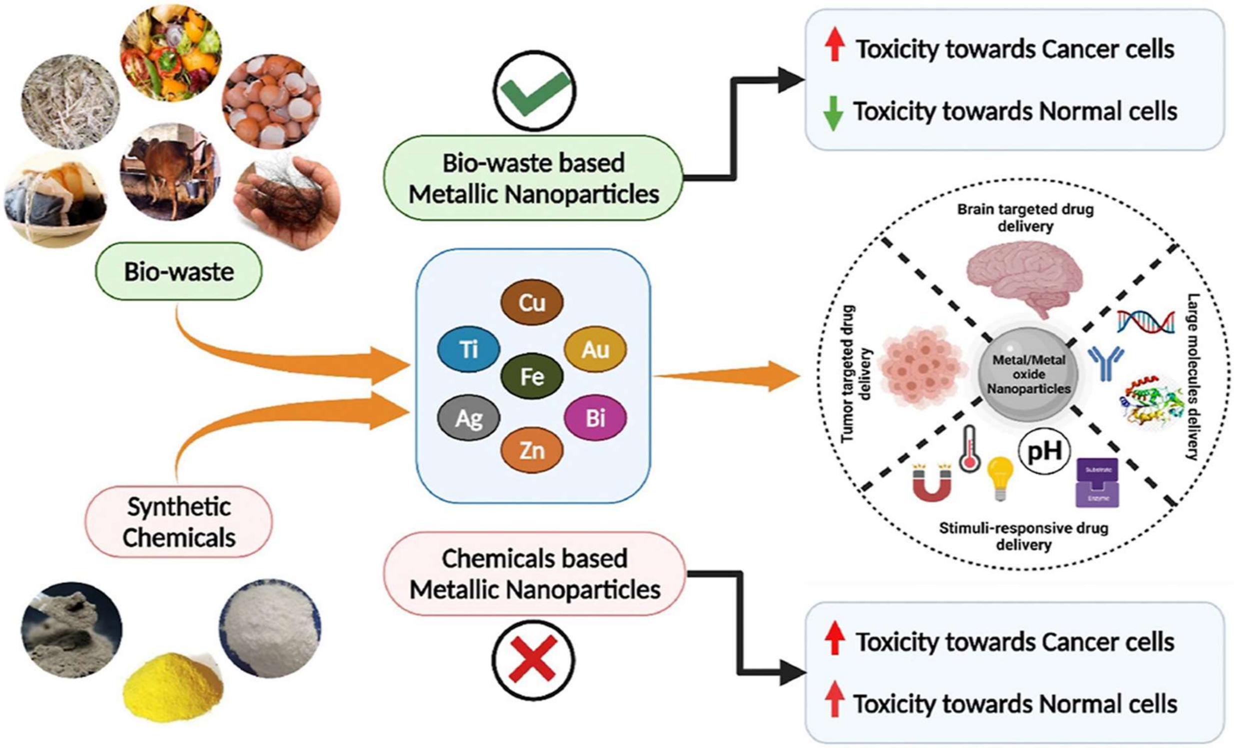
➢ It is also imperative to understand the ecotoxicological perspective of metallic NPs for environmental applications. Studies on the aquatic ecosystem, various habitats on niche areas, nontarget organisms should also be carried out.

Another important and most serious concern to be addressed is the utilization of NPs in biomedical applications. Infectious diseases are caused by bacteria, viruses, fungi, and parasites. In practice, routine usage of antibiotics led to the development of resistance mechanisms by microbes. In some cases, these antibiotics also create toxicity to humans and they are non-selective too.

We are living in an exciting age where these size dependencies offer both challenges and opportunities, and that, if we take the appropriate approach, this will give us more room for discoveries and applications.

24. Conclusions

Nanoparticles have received much attention in biomedical applications due to their unique physicochemical properties. The metal/metal oxide nanoparticles are involved in various applications, including drug delivery, therapy, and diagnosis. Subsequently, many hazardous chemicals and organic solvents were utilized to synthesize the metallic nanoparticles. Therefore, the green synthesis came into the limelight to overcome the economic and environmental burden [545]. The green synthesis represents the production of nanoparticles that reduce or terminate the use of hazardous materials and solvents that encourages environmental safety. The frequently utilized green materials in numerous metallic nanoparticle syntheses include microbes, plants, fruits, and other food sources. However, the burden on global food security and limited natural resources creates distress over environmental sustainability. Thus, adopting bio-waste materials to produce highly efficient, biocompatible, economic, and eco-friendly metallic nanoparticles could support waste valorization and lead to environmental sustainability. Therefore, the present review focuses on the various bio-waste materials adopted to synthesize metal/metal oxide nanoparticles. We have thoroughly discussed the potential of chemicals-mediated metal/metal oxide nanoparticles in different drug delivery applications such as tumor targeting, brain targeting, and stimuli-responsive drug release followed by large molecules delivery. Consequently, this can open a new road for researchers to explore drug delivery applications using bio-waste mediated green synthesized metallic nanoparticles. Finally, the cytotoxicity aspects of such nanoparticles are meticulously discussed compared to chemically synthesized counterparts Scheme 7 [545].



Scheme 7 Bio-waste mediated metal/metal oxide nanoparticles for drug delivery [545].

Recently, metals and metal oxide NPs are widely synthesized fordifferent biotechnological applications such as in biomedical. The green synthesis of NPs using biological entities such as bacteria, actinomycetes, fungi, algae, and plants has been developed as a significant part of biotechnology. The synthesis of NPs using the green approach has different advantages such asease of synthesis and being cost-effective, eco-friendly, and easy to scale-up, hence overcoming the disadvantages of conventional methods. Therefore, increasing knowledge about greenchemistry as greener routes for NPs synthesis opens the wayfor numerous biotechnological applications. Fundamentally, thegreen production of metal/metal oxide NPs using green methodshas different uses, such as for antimicrobial and antitumor activity, controlling of different phytopathogens, the bioremediation process, the food industry, the textile industry, and wastewater treatment.

The major challenges that were observed during the greensynthesis of NPs can be summarized as follows:

●MNPs and MONPs synthesis from plant extracts is dependable, efficacious, foreseeable, scalable, reproducible, and safe to be applied through many fields, so they must find ingenious solutions to all the affronts they will meet to open new horizons.

●The synthesis of a specific size and shape by the greenmethod requires more optimization studies. Also, the productionof NPs with specific physicochemical characteristics requires more studies especially for biomedical applications.

●The mechanistic aspect used for the fabrication of NPs bygreen methods requires more investigation.

●The metabolites involved in biological biomass filtrate should be completely analyzed to detect the role of each compound in NPs biofabrication.

●Scaling-up production of NPs by green methods is considered another challenge encountered in its commercialization.

●The stability of NPs with high yields correlated with optimizing factors such as pH, salt concentration, contacttime, and temperature. These factors differ according tobiological entities used.

●The bioreduction mechanism, nucleation, growth, and stabilization of MNPs and MONPs by using plant extracts should be comprehend by them and their task to execute this implementation in a satisfying way, all the development concerning differences and alterations should be taken into consideration in depth, not just performing the process as a whole.

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