

## Review

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# Green synthesis of metal and metal oxide nanoparticles from plant leaf extracts and their applications: A review

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**Abstract:** Metal nanoparticles (MNPs) and metal oxide nanoparticles (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 to impact industrial and manufacturing sectors, which means that nanomaterials commercialization and nano-assisted device will continuously grow. They can be prepared by many methods such as green synthesis and the conventional chemical synthesis methods. Green synthesis 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. In this study, we focus on the biosynthesis procedures to synthesize MNPs and MONPs, including comparison between green synthesis and the classical chemistry methods as well as the several new orientation of green synthesis of nanoparticles from different plant parts, especially plant leaf extracts. Plants with reducing

compounds is the preferred choice for the synthesis of noble metals – metal ions can be reduced to the corresponding metals in the absence of any other chemicals under microwave irradiation conditions using benign solvent, water. Noble metals such as gold (Au), silver (Ag), platinum (Pt), and palladium (Pd) and other metals such as copper (Cu) and nickel (Ni), which are characterized by their optical, electronic, mechanical, magnetic, and chemical properties, leading to different technological applications. Plants with numerous reducing agents are suitable candidates for the manufacture of noble MNPs. The main purpose of this research is to give a background on green nanotechnology prospective evolution, pertinent concerns appeared related to the green synthesis of metal and metal oxide from plant extracts, nanoparticle formation mechanism, and the importance of flavonoids, vitamin B<sub>2</sub>, ascorbic acid (vitamin C), and phenolic compounds in the MNP and MONP production. The traditional sorghum beers are produced in many countries in Africa, but diversity in the production process may depend on the geographic localization. These beers are very rich in calories; B-group vitamins including thiamine, folic acid, riboflavin, and nicotinic acid; and essential amino acids such as lysine. However, the Western beers are more attractive than the traditional sorghum beers. The traditional sorghum beers have poor hygienic quality, organoleptic variations, and shorter shelf life compared with the Western beers. Many research studies on traditional sorghum beers have been carried out and documented in several African countries, especially the microbiological and biochemical properties, the technologies used in the manufacture processes, and synthetic characteristics of African traditional sorghum beers (iki-gage, merissa, doro, dolo, pito, amgba, and tchoukoutou). The excellent resources for the production of greener biomaterials are plants and considerable advances have been achieved in many fields such as biotechnology and gene transfer. The manufactured biological nanomaterials have a great application in the pharmaceutical industry such as novel pharmaceuticals preparation, drug delivery

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personalification procedures, and production of functional nanodevices.

**Keywords:** nanotechnology, MNPs, MONPs, plant leaf extracts, applications

## 1 Introduction – prospective evolution of green nanotechnology: greener approach to nanomaterials and their numerous 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 [1]. Figure 1 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 the laboratory. More than thousands of such products are available in the market, of which a large majority are integrated in everyday personal care products, cosmetics, and clothing. Development of the modern products that consumers need are expected to affect positively almost

every industrial and production sectors, involving medicine and drug delivery. The continuous growth of the nanomaterials marketing and nano-assisted device is very obvious [2]. The commercialization of successful disruptive technologies is fundamental for numerous implementations to humans and global development, but critical interest is necessary for potential, health assessment and environmental effects of these materials [2–5]. It is a clear reality that the health hazards due to nanoparticles exposure are slowly comprehended and need to be addressed rapidly [6] and their manufacture and utilization are practically uncontrolled [7], particularly in the universe development. This is predominately discouraging when the new nano-based entities are being generated and incorporated into consumer products at an alarmingly quick rate, thus oversight mechanisms is an urgent need since the final existence of the majority of the nanotechnology innovations resulted from the research groups which considered simple startup work must based on instructions and recommendation from regulatory bodies and should not be oppositely affected by the boosted cost loads connected with such increased oversight [8]. Health and safety regulations will have to carefully negotiate regulatory testing cost load, which will in turn have an essential role in giving priority to hazards associated with nanomaterials [9]. The essential aspect of the green chemistry emerging sector is the utilization of a group of basics lowers or removes the hazardous substances utilization or generation concerning design or production and chemical products' application while designing new chemical processes visualizes small risk as the execution criteria.

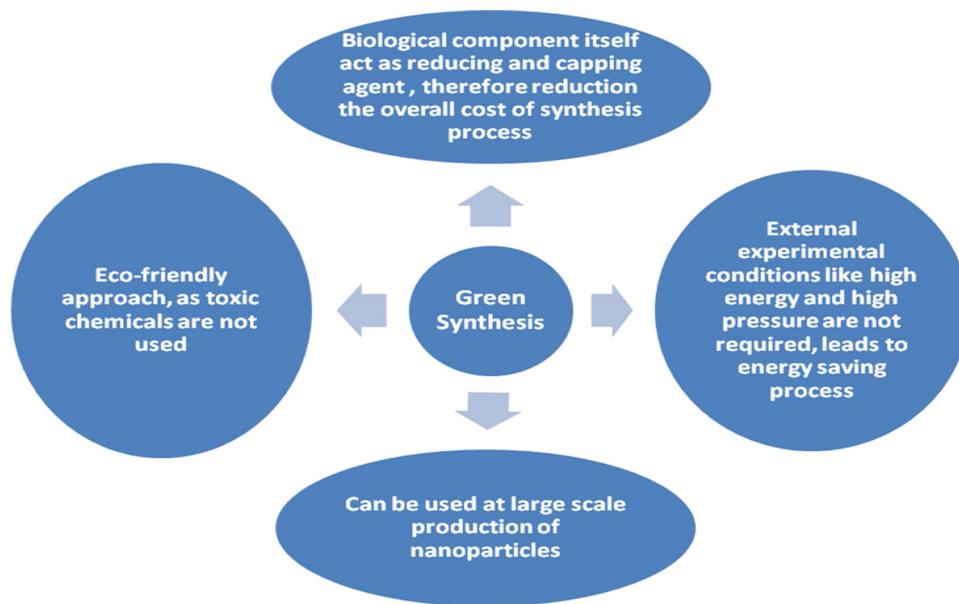


Figure 1: Key merits of green synthesis [26].

Green chemistry basics implementation in the new materials expansion and enforcements is all the more considerable in opinion of the principle that the technology is an early expansion phase and is foreseeable to be widely utilized and doled out around the world. The strong relation between chemical structure and function groups that connects specifically to nanomaterials and boosting understanding “key” information for life cycle evaluation of such methods could lead to new “design principles” for the production of high rendering nanoscale materials that are benign and environmentally friendly [10].

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 existing

environmental problems, as indicated in Figure 2. The environmental friendly methods such as catalytic potential [11], electrical conductivity [12], optical sensitivity [13], magnetic behavior [14], or biological reactivity [15] are used to characterize the chemical, physical, and biological properties of nanomaterials in addition to many factors such as size, shape, surface charge, chemical structure, surface area, and coagulation properties of nanoscale distinct materials [16]. The organic solvents and chemical reagents are not used in the preparation of metal nanoparticles (MNPs). MNPs have unique properties with their nanostructures [17]. The atoms ordered to the nano-scale differ from the bulk metallic materials [18], and the unique properties of MNPs and metal oxide nanoparticles (MONPs) are engendered from them. MNPs and MONPs have many applications such as catalysts [19]; drug delivery systems [20]; boosting contrast agents [21]; active food packaging materials [22]; components pointing to nano-biosensor construction [23]; gene transfer

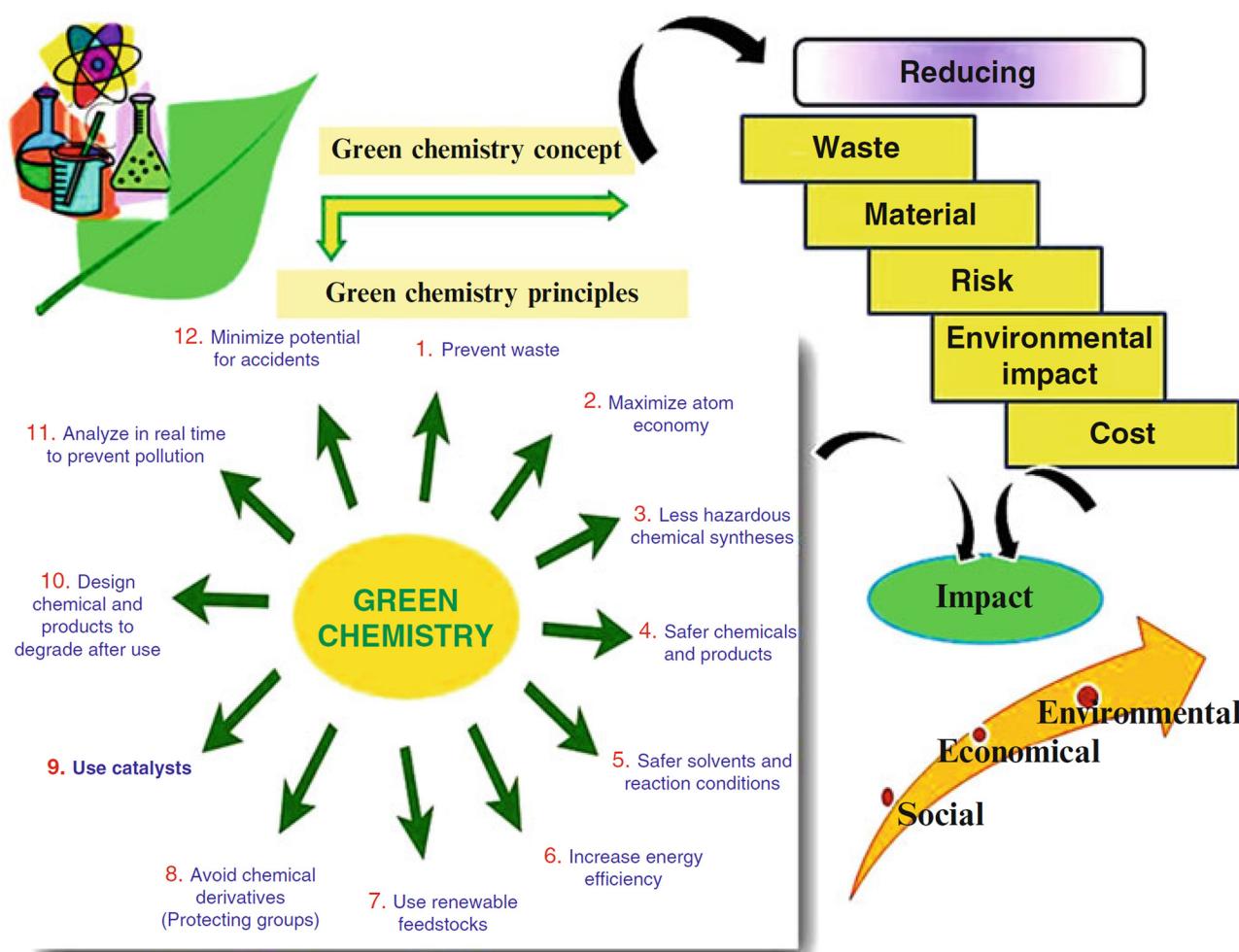


Figure 2: Schematic exemplification of green chemistry combination in metal nanomaterials cloning [27].

system [20]; antibiotics, antiseptics, and disinfectants to control pathogens and pests [24]; and nanoelectronic components [25].

## 2 General consideration taken into account for MNPs and MONPs synthesis

To synthesize MNPs and MONPs, researchers used a strong base (reducing agent), e.g., sodium borohydride or sodium hydroxide, in metal ion reduction from salt solutions, followed by the addition of a capping agent or a stabilizer (stabilizing agent) [28], as indicated in Figures 3 and 4.

To dissolve the stabilizers, they used solvents and the reagents that act as reducing agents, which are toxic substances and have counteractive and harmful effects if the rest of these materials are left in the rear part of the nano-system, as the bottom-up path to synthesize the nanoparticles often needs the offensive chemical reduction agents such as sodium borohydride and hydrazine and a capping agent and may also involve a volatile organic solvent such as toluene or chloroform. Although these procedures may effectively produce pure products [32], the manufacturing cost is very high, both materially and environmentally. This may provide new stand by accession achieving this synthesis and steer them to consider safety applications of MNPs and MONPs [33]. The green synthesis of MNPs and MONPs is considered one of the alternatives that depends on the green chemistry principles by using the biological systems [34–37]. The green synthesis of MNPs and MONPs is accomplished by using prokaryotic [38] or eukaryotic [13] organisms (involving microorganisms, plants, and animals) or their parts, and can take place intracellularly [39] or extracellularly [40]. The primary and secondary metabolites of plants are used to produce MNPs and MONPs by executing a target metal ion reduction, as shown in Figure 5.

Formation of coating layer (stabilizing layer) on the surface of the MNPs and MONPs by reducing compounds or other besetment molecules lowering them to coagulate/aggregate otherwise ordered in an upset way within their preparation [42]. MNPs and MONPs preparation and their properties can be polished by setting different conditions such as temperature, pH, and reagent concentration [12]. The scientists have utilized the organ/tissue extracts or the whole organisms [43,44] 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 [45,46], 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 or abiotic stress to which a plant may be exposed, as indicated in Figure 6.

## 3 Plants are the main factory for the green synthesis of MNPs and MONPs

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 to execute 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 make the plants the main bioreactors and molecule suppliers for green synthesis [48]. Due to the presence of metallic counterparts and the stabilization of the surface of the MNPs and MONPs [41], the primary compounds of plants such as amino acids [49], citric acid [14], flavonoids [50], phenolic compounds [51], terpenoids [52], heterocyclic compounds [53], enzymes [54], peptides [55], polysaccharides [56], saponins [57], and tannins [58] are responsible for the metal ion reduction. The whole organs/tissues [43,44] or the extracts of the organs/tissues and different 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 [59,60], 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.

## 4 Modern orientations

The research studies on the green synthesis of MNPs and MONPs using plants can easily understanding the molecular mechanism, coordinating bioreduction, nucleation,

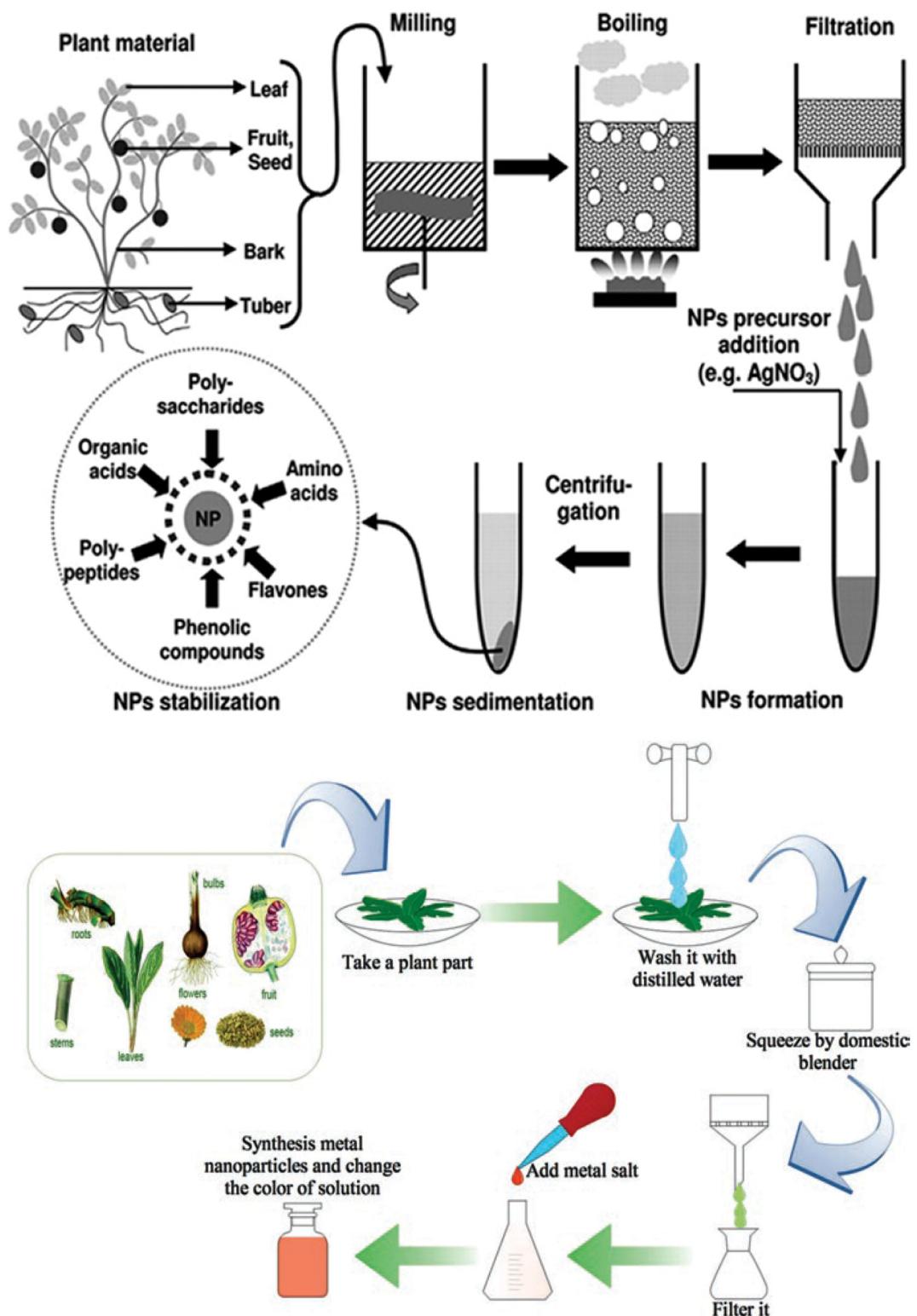


Figure 3: Two schematic features of MNP synthesis using plant extracts [29,30].

growth, and stability. The first stage was utilization of the plant extracts selected from the endemic or global biological variation. The extract from different plant parts

and species in the presence of metal salts results in the production nanoparticles of different sizes, shapes, compositions, and activities, as indicated in Figure 7.

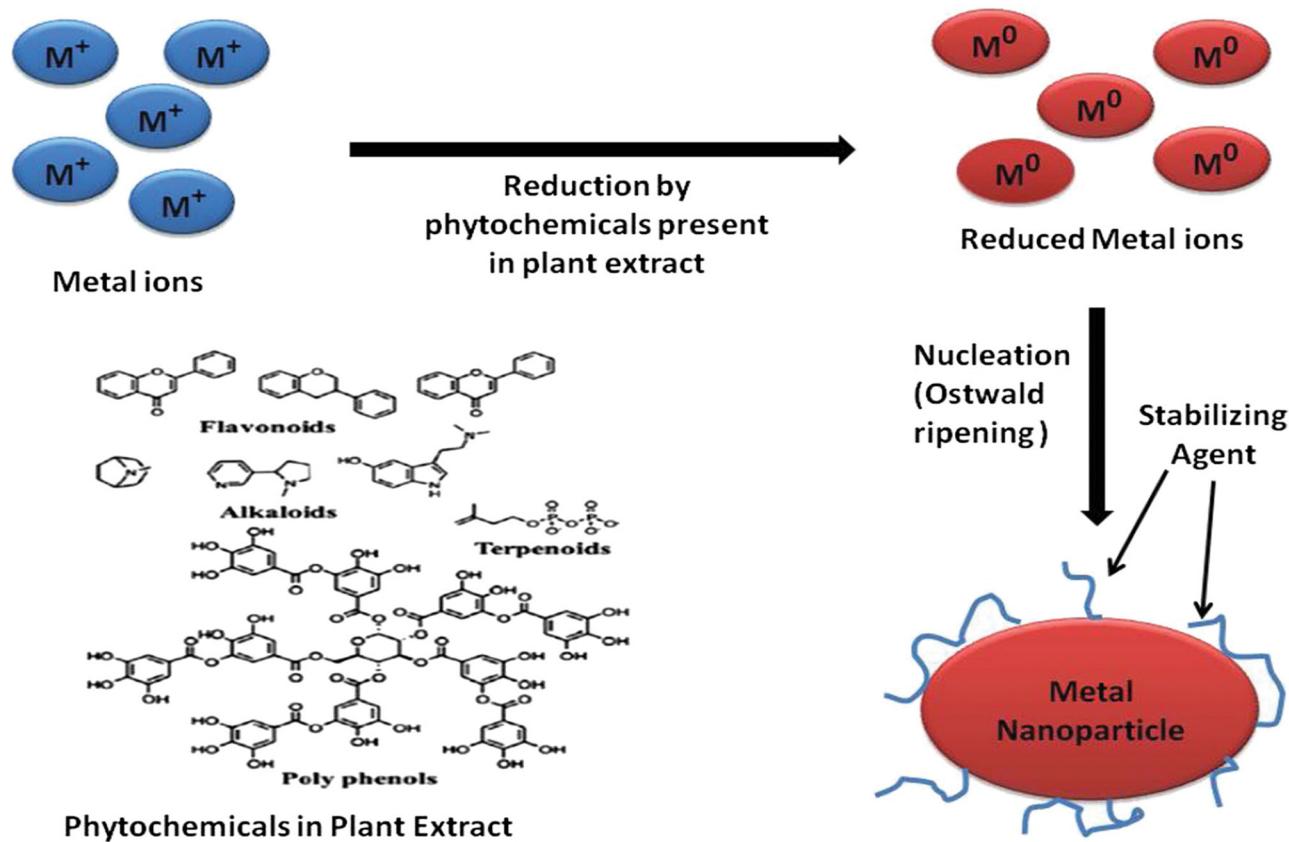


Figure 4: Nanoparticle consistency mechanism by plant leaf extract [31].

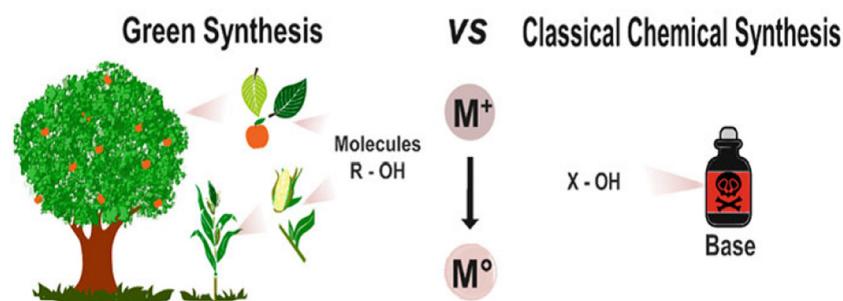


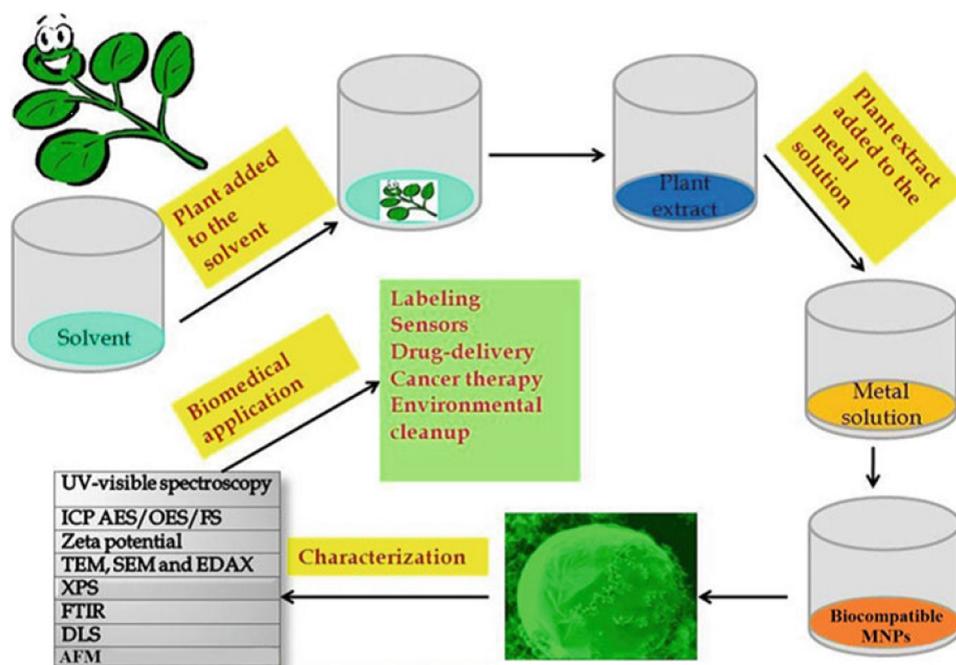
Figure 5: Schematic explanation of the two main approaches used for the synthesis of MNPs and MONPs: green and chemical (classical) synthesis. Dicotyledons and monocotyledons are used as the reducing and stabilizing agents in the metal salt reduction for the green synthesis of MNPs and MONPs [41].

Reduction of noble metals [12,42,43,61,62] including gold (Au), silver (Ag), and platinum (Pt) and other metals such as copper (Cu) was studied in many research studies on the green synthesis of MNPs and MONPs.

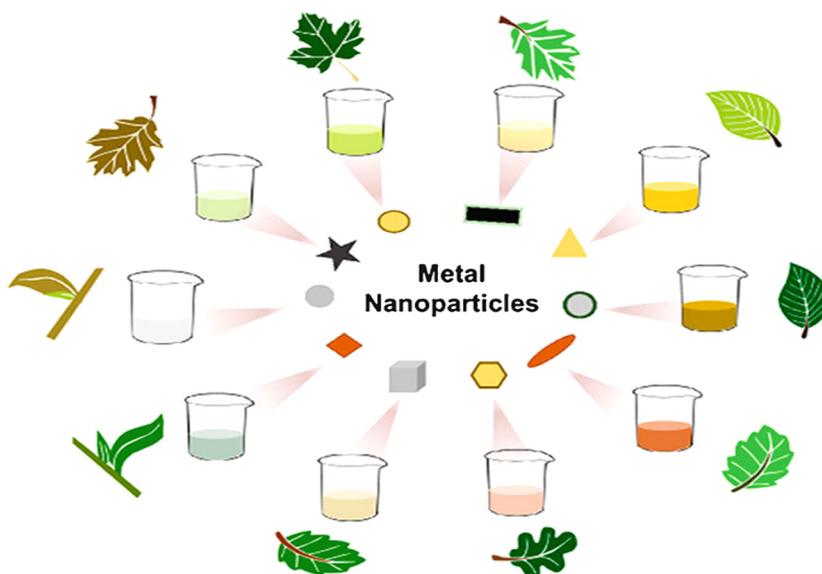
attract interest and lead to various applications in different technological applications [63–68]. MNPs are synthesized by using extremely reactive reducing agents, e.g., sodium borohydride (NaBH<sub>4</sub>) and hydrazine, which are not eco-friendly. The use of toxic chemicals in these methods limits their use due to environmental precautions. The plants' ability to synthesize MNPs has conquered a new axis and spectacular approach toward the development of natural nano-factories. Majority of plants have features as sustainable and renewable resources compared with microbes and enzymes as they have the ability to pick up nearly 75% of

#### 4.1 Noble metal synthesis

Noble metals are characterized by their optical, electronic, mechanical, magnetic, and chemical properties, which



**Figure 6:** A schematic illustration of plants as a source for the green synthesis of nanoparticles and the properties and biomedical implementation of nanoparticles [47].



**Figure 7:** Green synthesis of MNPs using the extracts obtained from the leaves of different plant species leading to the production of structures with different compositions, shapes, and sizes [41].

the light energy from sun and convert it into chemical energy, which needs expensive production methods [69–72]. Furthermore, plants contain chemicals like anti-oxidants and sugars and play essential roles in the manufacture of nanoparticles [73–77].

Consequently, a pressing need to promote more cost-effective and environmentally friendly alternatives to these existing procedures, the environmentally compatible solvent

system choice, using an eco-friendly reducing agent for stabilizing the nanoparticles are three essential criteria for a “green” nanoparticle synthesis [70].

#### 4.1.1 Beet for green synthesis of MNPs

The preferred choice is plants with reducing compounds for synthesis of noble metals as the corresponding

metals, which are produced by the reduction of metal ions in the absence of any other chemical materials [70–72,78,79]. 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 favorable candidates for the manufacture of noble MNPs. Beet is a bountiful agriculture product and it belongs to the Chenopodiaceae family. Its purple root is fundamental in the production of table sugar and mangelwurzel. It has a great reductive capability because of sugar-rich content, which can be used in the synthesis of nanomaterials, but it has not been investigated in detail [80,81]. Beet juice was utilized for the synthesis of nanometals such as Ag, Au, Pt, and Pd under microwave (MW) irradiation condition using benign solvent, water. For example, the prepared Ag nano-particles exhibit perfect catalytic efficiency in converting 4-nitrophenol to 4-aminophenol with elevated reuse, which is higher than  $\text{NaBH}_4$  [82].

The green synthesis of MNPs and MONPs using plants [12,83–85] helps researchers understand and determine the characteristics of MNPs and MONPs. The shapes of the MNPs and MONPs are usually spheres [3,83–85] and triangles [84,86]. Their size is in the range of 15–50 nm of hydrodynamic diameter [87].

MNPs and MONPs produced by green synthesis using plants have various activities such as antibacterial [88,89], antifungal [12], anticancer [90], and larvicidal [91].

The MNPs and MONPs were also produced by green synthesis using various plant organs such as seeds, bark, flowers, tubers, and root extracts [42] but leaf extract is the 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 can moderate 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 to produce MNPs and MONPs with demanding properties and provide background on consistent mechanism [88,89,92]. The green synthesis of MNPs and MONPs happens in the plant *in vivo* [93,94]. The binding and complexation

process with phytochelatins and secondary metabolites [95–98] causes a stress, which affects the plants, and it is a slower and more expensive process than the green synthesis processes of MNPs and MONPs from the plant extract.

## 5 Synthesis of MNPs and MONPs by utilizing plant leaf extract

The biovariations of plants offers a plentiful biochemical properties and introduces particular source to synthesize nanoparticles [99]. The extract from the plant leaf can be obtained very simply to use and has numerous metabolites that act as reducing agents to synthesize nanoparticles [100]. A solution containing metals such as nickel, cobalt, zinc, and copper is mixed with the extract of the plant leaf at room temperature [101]. Different factors such as pH, temperature, contact time, metal salt concentration and phytochemical profile of the plant leaf particles affect the nanoparticles goodness, nanoparticle stabilization, quantity produced, and yield rate. The metal ion reduction in plants is faster than that in fungi and bacteria, as they need a long time for incubation because of the presence of water-soluble phytochemicals [102].

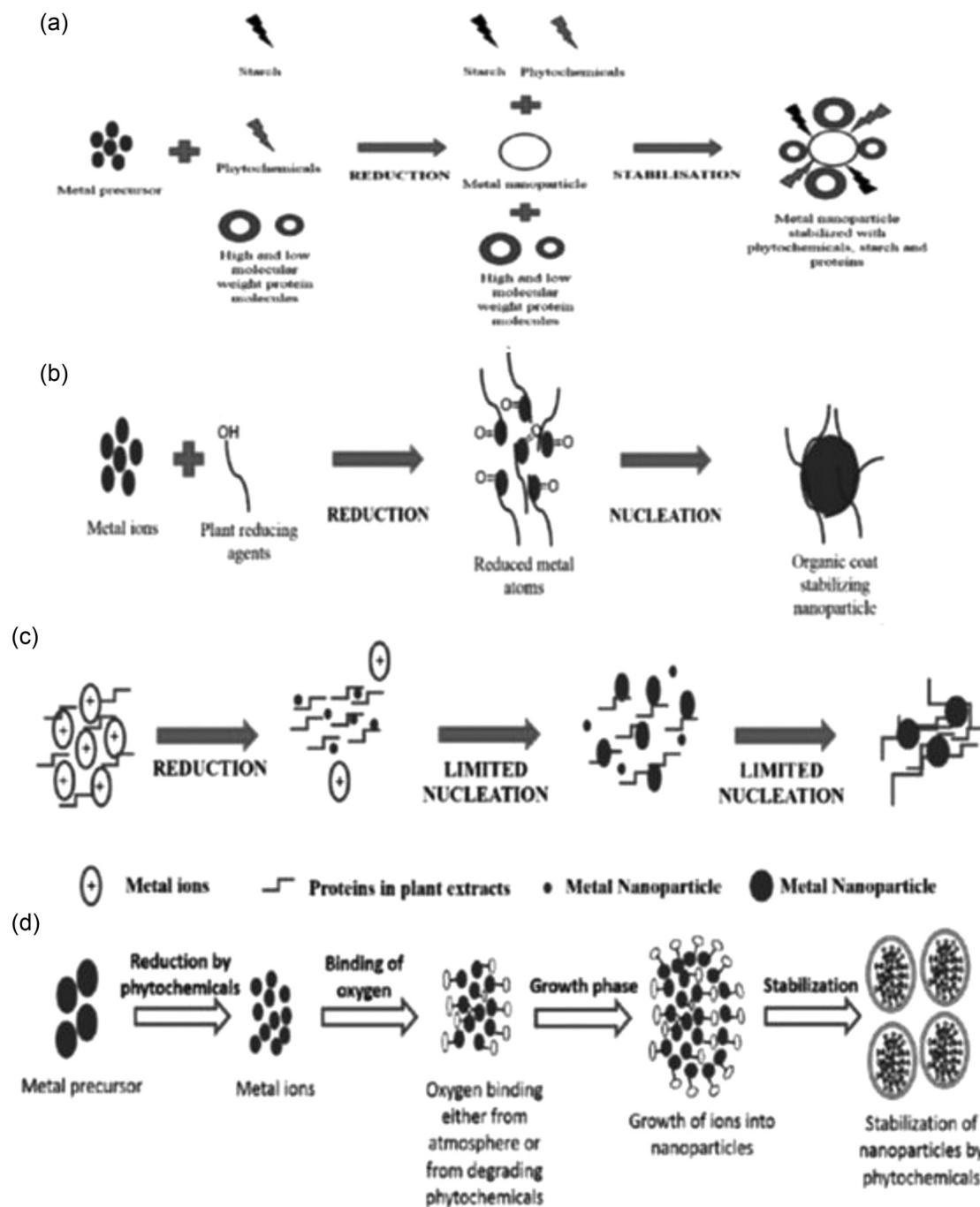
The numerous phytochemicals present in the plant leaf extracts can be extracted facilely [103,104], so the plant leaf extracts are considered as a wonderful tool for MNPs and MONPs synthesis.

The advantage of plant leaf extracts to act as stabilizing agents and reducing agents facilitates the nanoparticle synthesis [99]. Biomedical reducing agents are present at different concentrations in different types of leaf extracts, so the leaf extract composition has a great effect on the nanoparticle synthesis [105,106]. Terpenoids, flavones, ketones, amides, aldehydes, and carboxylic acids are the essential phytochemicals involved in the nanoparticle synthesis [100].

## 6 Nanoparticles synthesis from plant leaf extracts mechanism

Proteins and carbohydrates are important constituents of the plant extracts, which act as reducing agents and are responsible for the formation of MNPs and metal ion reduction [107].

Functional amino groups and proteins in the plant extracts play an essential role in the metal ion reduction



**Figure 8: 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 [26,100,105,106,109–116].

[108]. Huang et al. [109] discussed that the functional groups of alkaloids, flavones, and anthracenes, such as  $-C-O-C-$ ,  $-C-O-$ ,  $-C=C-$ , and  $-C=O-$ , assist the MNP synthesis.

Kesharwani et al. [110] proposed that the metal ion reduction may be carried out with the help of quinones and plastohydroquinone molecules present in the plant leaf extract, which indicate that the extracellular MNP synthesis can be done by biomolecules and heterocyclic compounds in plants. Despite the complete vision of MONP synthesis by using plants is not well understood until now, the phytochemicals of the plants led to the production of MONP, like MNP.

First, the phytochemicals of the plant extract are responsible for the metal reduction. Oxygen produced from 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 phytochemicals that prevent agglomeration between them.

The superoxide-driven Fenton reaction is the main provenance for reactive oxygen species (ROS) [111] and is repressed by the phenolic compounds with carboxyl groups and hydroxyl groups of plants. Mukherjee et al. [112] suggested the use of high- and low-weight phytochemicals, proteins, and starch mixtures present in the plant extracts, as indicated in Figure 8a. Newman et al. [113] also explained the possibility of the production of MNPs and MONPs by proteins of plant extracts, which act as reducing and stabilizing agents, as mentioned in Figure 8b.

Markarov et al. [114] proposed that metal atoms will be encapsulated as organic covering in three steps for their magnitude stabilization after reduction by plant extracts, as shown in Figure 8b. Metal ion reduction and nucleation of reduced metal atom will be in the activation phase, the nanoparticle stability increased through the growth phase, and the shape of the nanoparticles formed during the termination phase, as indicated in Figure 8c [115]. They could summarize the process by the following steps:

- (1) The metals such as copper, silver, gold, zinc, titanium, iron, and nickel result in the formation of their metal oxides by phytochemicals.
- (2) Using phytochemicals, metal ions will go through growth and stabilization phases.
- (3) Oxygen is produced either by degradation of phytochemicals or by atmosphere, and before growth and stabilization phases, it will be linked to metal ion as mentioned in Figure 8d which explains the MONPs production mechanism may also be executed

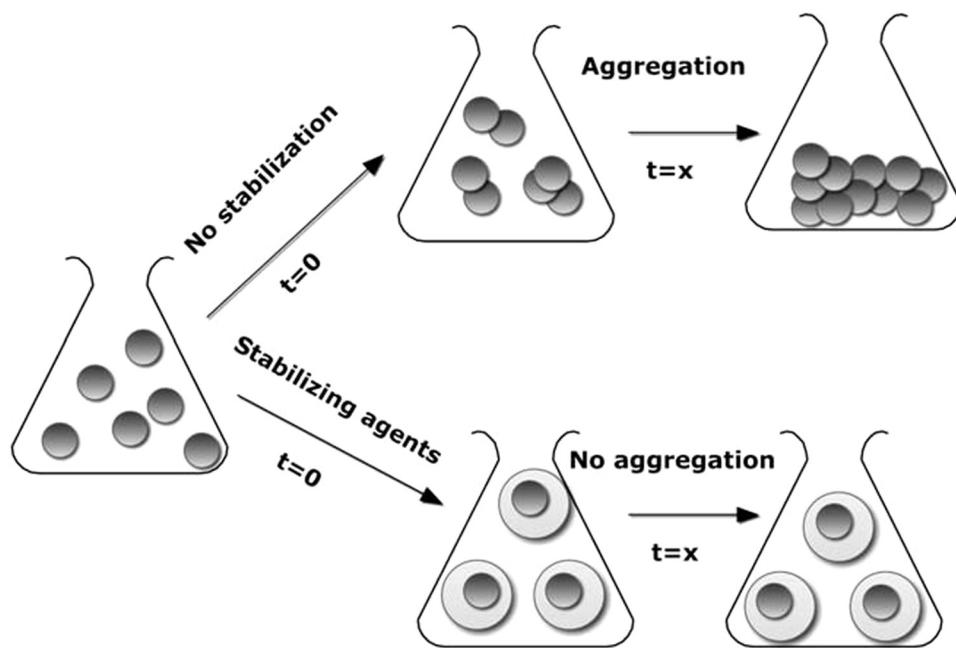
by different methods described in the literature [26,100,105,106,116].

## 7 MNPs green synthesis: stabilization and functionalization 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 [117]. Reduction of the specific surface area and the interfacial free energy can be achieved by aggregation, thereby minimizing the particle reactivity (Scheme 1) [118], so it is fundamental to boost the nanoparticle stability improvement during storage, transportation, and its overall life 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 (more than 50%) of the nanoparticle mass fraction system [119]. Hence, there is a necessity to find environmentally benign stabilization and functionalization passages as well as bioconvenient 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 the particles for the desired implementation at the same time [120–122]. However, the usual acute reaction conditions and the toxic chemicals may not be appropriate for the biological and biochemical implementation [123]. Presently, there are numerous “green stabilizing agents” such as polyphenols, enzymes, citric acid, vitamins (B, C, D, and K), biodegradable polymers, and silica, which has the ability to stabilize and functionalize MNPs without the unfavorable effects on the environment and biosynthesis.

### 7.1 MNPs recoverability and reusability

It is very substantial to functionalize and stabilize MNPs for varied implementation; however, simple and relatively low-cost recoverability and therefore nanoparticle’s reuse is currently acquiring an increased attention among the scientific society. Nanoparticles have magnetic properties have been inclusively used in the metal ion and dye coat, drug delivery, enzyme



**Scheme 1:** Schematic of nanoparticle aggregation in the presence and absence of the stabilizing agents [70].

immobilization, and protein and cell separation fields because the magnetic separation of these nanoparticles offers individual high competency and cost leverage and is fast in comparison with other nanoparticles, which are harmoniously emerging as heterogeneous supports (so called magnetic nano-cores) in numerous catalytic transformations, providing easy recoverability with easy magnet advantages, thereby eliminating solvent swelling exigency before or catalyst filtration after the reaction [124–127].

## 7.2 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–aromatic copolymers), small molecules in bacteria, or biomass and petroleum mixtures [128]. Rozenberg and Tenne [129] debated the nanoparticles stabilized by surface active polymers, which are adsorbed strongly on the particle surface due to the van der Waals attractive forces between the surface of the particle and the monomer units in polymer chain, preventing the aggregation because of their large surface energy minimization in comparison with the native particles. Block copolymers are even stronger

nanoparticle separation and show individual properties such as surface reactivity, flexibility, selectivity, and impedance [130]. MNPs stabilization can be fulfilled by metals in a polymer gel simple enclosure, free radical polymerization with a radical initiator [131], thiol-supported polymer adsorption [132], or *in situ* MNPs formation during polymerization [132–134].

## 8 Greener synthetic strategies

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.

### 8.1 Polyphenols of plants and agricultural residues

Nanometal/nanometal oxide/nanostructured polymer synthesis 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 from

tea and coffee [71], biodegradable polymers such as carboxymethyl cellulose (CMC) [135], reducing sugars [136], and agricultural residual waste (red grape performance from winery waste) [72].

## 8.2 Vitamins

Nanoparticles preparation by using sustainable synthetic activity involves benign alternatives, which reduce or remove the use and production of the risky substances. Vitamins B<sub>1</sub>, Vitamin B<sub>2</sub> [137], vitamin C [138], tea [71], and wine phenols [72], which all act as both reducing and capping agents. They offer extremely simple one-pot green synthetic methods to synthesize bulk quantities of nanospheres, nanorods, nanowires, aligned nanobelts, nanoballs, and metals nanoplates in water without the need of large amounts of insoluble templates [10,137].

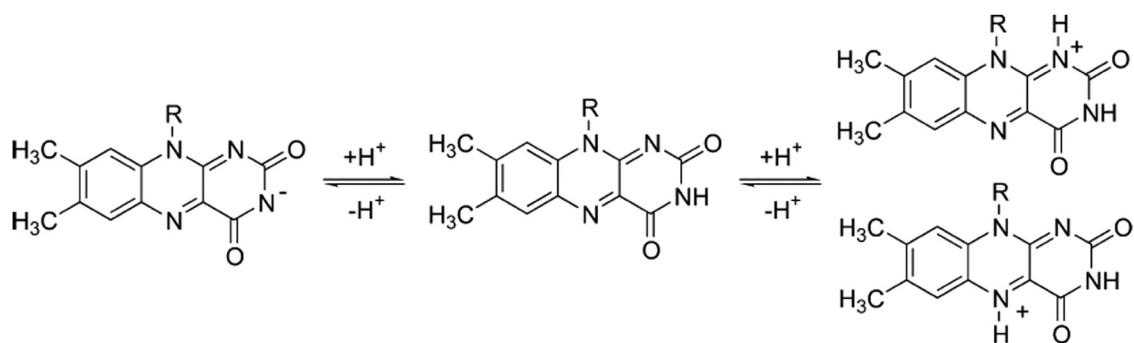
## 9 MNP and MONPs synthesis by using flavonoids as a fundamental agent

Flavonoids are considered a fundamental agent for the MNP and MONPs synthesis. Flavonoids include anthocyanins, isoflavonoids, flavonols, chalcones, flavones, and flavanones [114], which are considered a group of phenolic compounds. Aglycone is the major structure of flavonoid. The presence of benzene ring is the base on which flavonols, flavanones, or its hydro derivatives are categorized. The position of the benzenoid substituent divides the flavonoid into 2-position flavonoids and 3-position isoflavonoids. The C<sub>2</sub>-C<sub>3</sub> double bond and the hydroxyl group at the 3-position distinguish flavonols from flavanones [139]. These compounds can reduce metal ions to produce nanoparticles and chelate metal ions. Flavonoids have different functional groups, which have the ability to produce nanoparticles. Reactive hydrogen atoms are released during the tautomeric conversion of flavonoids from the enol form to the keto form, which is responsible for the metal ion reduction to produce nanoparticles [114]. Ahmad et al. discussed the silver nanoparticles production and found that the enol- to keto-form transformation is the main reason for silver nanoparticles production from silver ions by using *Ocimum basilicum* extracts and transformation of flavonoids such as luteolin and rosmarinic acid [140].

Zheng et al. [141] indicated that flavonoids content of the plant extract facilitates the platinum ion bioreduction to synthesize the platinum nanoparticles. The internal mechanism; ketone conversion to carboxylic acid in flavonoids; leads to metal ions formation such as Fe<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>, Pb<sup>2+</sup>, and Co<sup>2+</sup> by their carbonyl groups or  $\pi$ -electrons [114]. In brief, flavonoids are responsible for chelation and reduction to produce nanoparticles through growth, nucleation, and stabilization. Nanoparticles may be produced by combination of phytochemicals or flavonoids. Metal ion may be reduced by phenolic compounds, which are phytochemicals [142–145]. Holtz et al. [146] discussed that MONPs may be synthesized by using terpenoids as a reducing agent. Laghari et al. [147] proposed that MONPs may be produced by using alkaloids from the plant extract. Phytochemicals in the plant extract play an essential role in the MONP formation, so it should be taken into consideration [148–150]; however, the definite role of phytochemicals in the nanoparticle synthesis has not been determined yet. The plant leaf extracts that contain flavonoids are more effective than other phytochemicals, as flavonoids reduce nano-composition toxicity and they act as a stabilizing agent. ROS produced from metal oxides can be reduced by flavonoids due to their antioxidant activity [151,152]. Flavonoids have hepatoprotective [153], anticancer [154,155], and antiviral [156–159] properties. The MONPs formation by using plant extracts containing large amount of flavonoids make them gain more properties, which lead to many important applications.

## 10 Vitamin B<sub>2</sub> as a double agent (reducing agent and capping agent)

Vitamin B<sub>2</sub> functions as both a reducing and a capping agent as it manifests to be a quixotic multifunctional agent in the manufacture of nanomaterials and it has high water solubility, biodegradability, and low toxicity compared with other reducing agents such as sodium borohydride (NaBH<sub>4</sub>) and hydroxylamine hydrochloride. Vitamin B<sub>2</sub> is the most abundant organic cofactor found in nature, and it exists in three different redox states: fully oxidized, one-electron reduced, and fully reduced [160] (Scheme 2), as each of these redox states can present in a cationic, a neutral, or an anionic form depending on the pH of the solution, and all can transfer electrons [137].



**Scheme 2:** Structure of the anionic (left), neutral (center), and cationic (right) vitamin B<sub>2</sub> species in the fully oxidized redox state (R = -CH<sub>2</sub>(CHOH)<sub>3</sub>CH<sub>2</sub>OH) [137,160].

## 11 Ascorbic acid (vitamin C) and its derivatives as fundamental factors for MNP and MONPs preparation

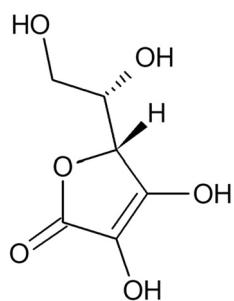
Vitamin C (Figure 9) is abundantly present in many natural sources, including fresh fruits and vegetables. The richest sources of ascorbic acid include Indian gooseberry; citrus fruits such as limes, oranges, and lemons; tomatoes; potatoes; papaya; green and red peppers; kiwifruit; strawberries; cantaloupes; green leafy 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 highly concentrated in the liver part [161,162]. The structure of vitamin C and its derivatives are given in Figure 10.

Vitamin C (vit C) or ascorbic acid (AA) is a hydrophilic molecule, which consists of six carbons, similar to glucose [109]. In the organisms, vit C can be found in the reduced form (ascorbic acid or ascorbate) or in the oxidized form called dehydroascorbic acid, which

is generated from two-electron oxidation of ascorbic acid [162].

Some alterations have been done to vit C molecule to improve its stability. One option is to connect ionic salts to the molecule. In this sense, one of the most well-known complexes is ascorbyl 2-phosphate, which is formulated with sodium (SAP) or magnesium (MAP) salts and has hydrophilic characterization. These structures are given in Figure 10. The introduction of phosphate group at the second position of the cyclic ring of the molecule is effective against oxidation. Despite being more stable, these derivatives appear to be less permeable through the skin in comparison with ascorbic acid [163].

The nanoparticles that are generated from the natural polymers have been comprehensively used in the pharmaceutical and food industries. These systems have low toxicity and are bioconvenient and biodegradable. Ascorbic acid functions as a reducing and capping agent for the synthesis of MNPs such as silver, gold, and copper. Ascorbic acid molecules can cap or surround the particles and prevent the uncontrolled growth of the particles to micron-sized dimensions. A study by Khan et al. in 2016 reported the copper nanoparticles synthesis using ascorbic acid as the reducing agent [164]. Sun et al. reported in the *Journal of Materials Science* in 2009 that gold nanoparticles can be produced in inverse micelles without the addition or introduction of any reducing or capping reagent [165]. In *Analytical Methods* in 2014, D'souza et al. explained the use of AA-Au nanoparticles as a colorimetric probe for the detection of dichlorvos in water and wheat samples. The concentration of ascorbic acid has an influence on the aggregation induced by dichlorvos in AA-Au nanoparticles (Figure 11), and the optical property of the AA-Au nanoparticles was investigated by UV-vis spectroscopy [166].



**Figure 9:** L-Ascorbic acid molecular structure [161].

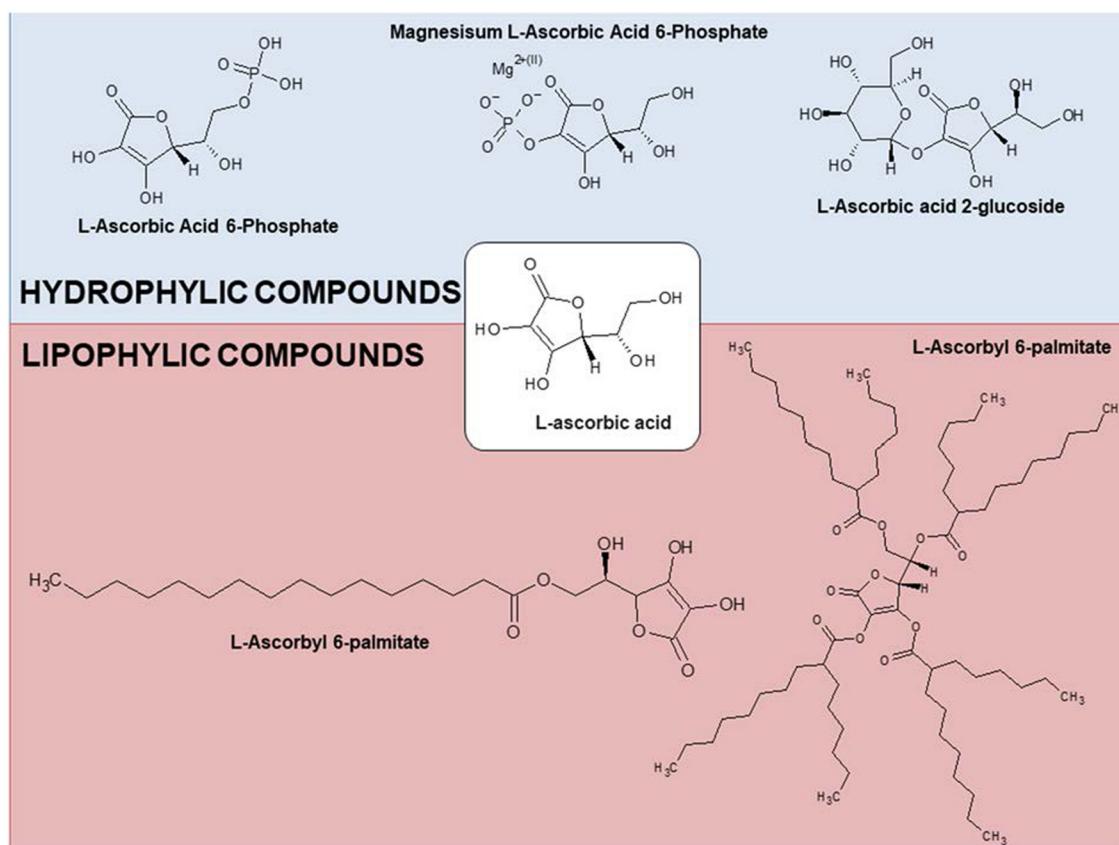


Figure 10: The structure of L-ascorbic acid and its derivatives [161,162].

## 12 Phenolic compounds as substantial agent for MNP and MONPs production

The phenolic compounds also offer protection for plants against ROS generated during photosynthesis and exposure to anthropogenic contaminants [167]. Phenolic acids have been widely used in medicine due to their powerful antioxidant activities, as they are considered phenolic derivatives with at least one functional carboxylic group. The majority of phenolic acids include larger polyphenols and other organic and structural compounds [168,169]. The two major categories of the natural phenolic acids are benzoic acid derivatives and cinnamic acid derivatives. The categorization is based on the number of hydroxylation sites in the aromatic ring (Figure 12) [170]. ROS and free radicals can be scavenged by the hydroxyl groups of these structures [171]. The chemical structures of both groups of phenolic acids are represented in Figure 12. Medicinal plants have large quantities of phenolic compounds as secondary metabolites. A wide

range of plant-based foods and syrups contain phytochemical phenolic acid, which are well known for the antioxidant, anti-cancer, and anti-inflammatory properties [172]. 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 the metal ion supersaturation concentration, followed by the MNPs ulterior growth through progressive ion reduction [173]. The inception can be expedited by the high oxidation inclination of phenolic acids [174]. The oxidation of hydroxyl functional group of caffeic acid would present electron ( $e^-$ ) required for neutralizing gold ions ( $Au^{3+}$ ), which was inspected by Hyun-soek et al. [175]. The reducing capacities of propyl gallate, ferulic acid, caffeic acid, vanillic acid, and protocatechuic acid in the presence of hydrogen tetrachloroaurate were inspected by Scampicchio et al. [176] using the UV-vis spectroscopy and colorimetry methods. The phenolic acid bioreduction potential was directly linked to the number of functional hydroxyl groups, which was declared by other authors. The absorbance of phenolic

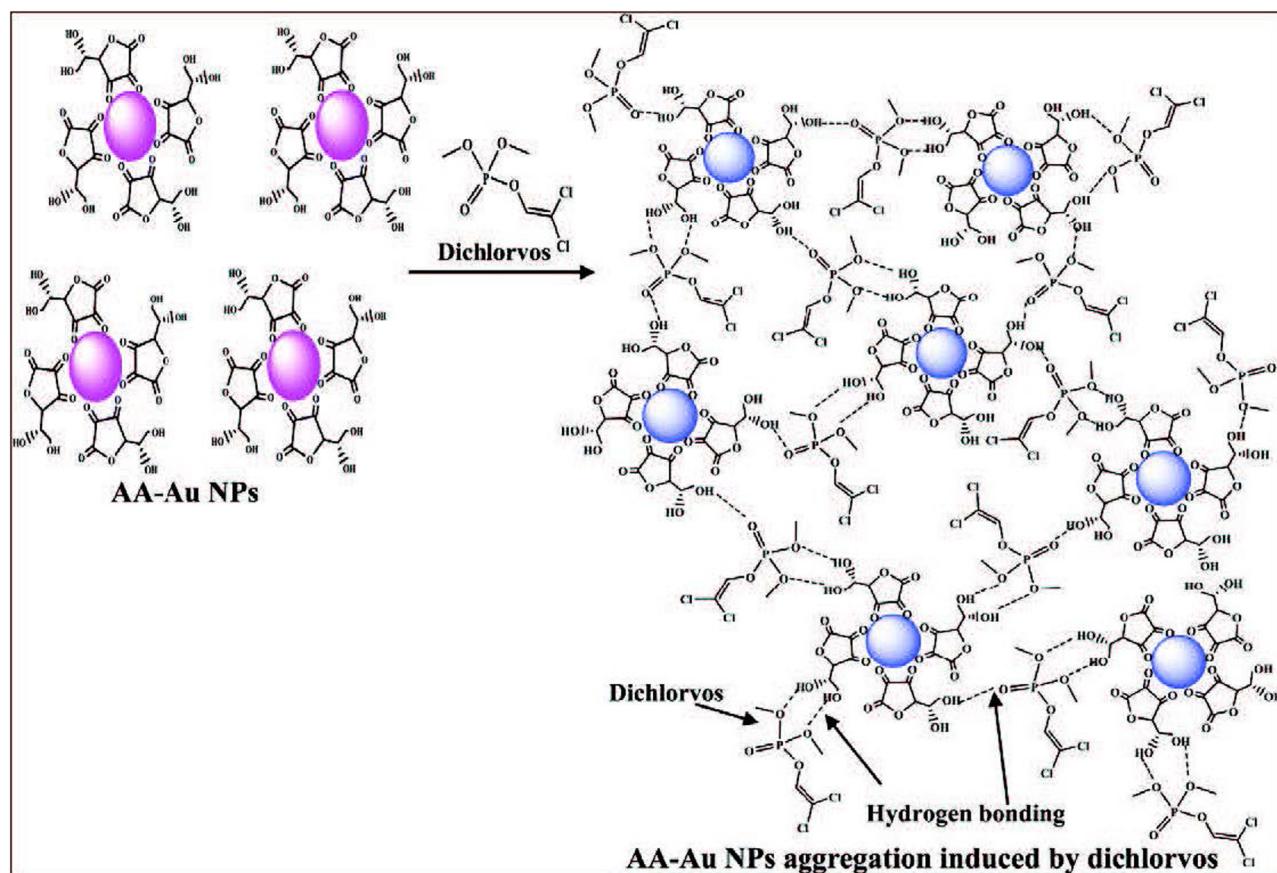


Figure 11: Detection of dichlorvos by utilizing AA–Au NPs as a colorimetric probe: an analytical process [166].

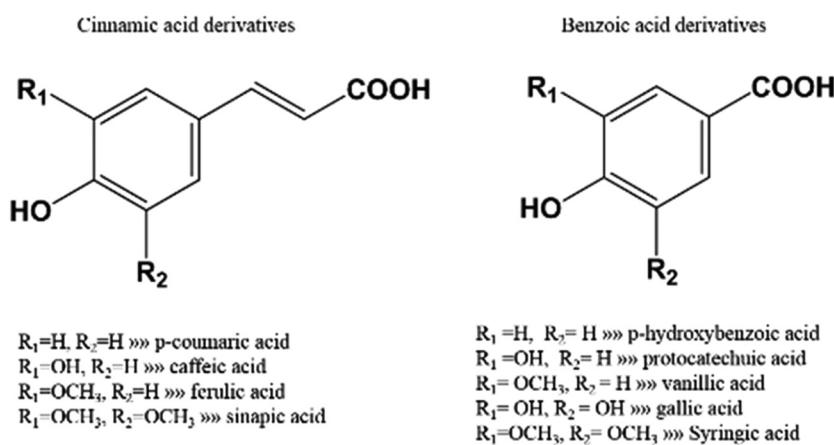
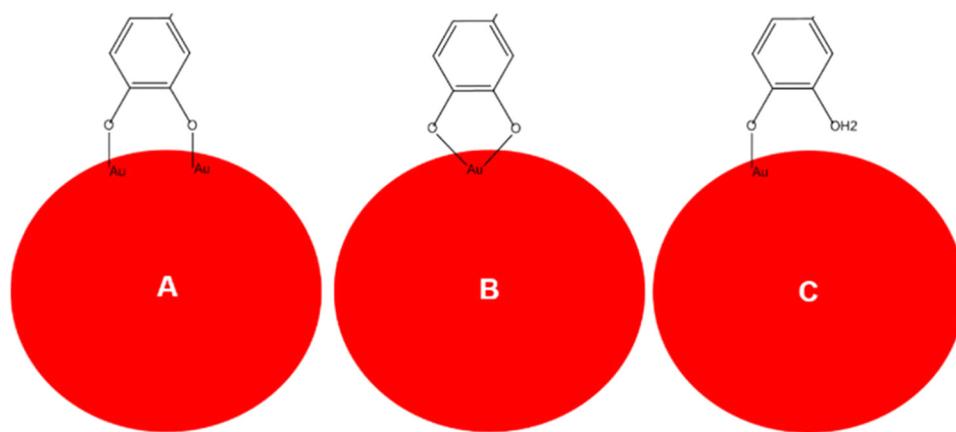


Figure 12: The phenolic acids used for the preparation of MNPs and their main chemical structures [170].

acid attached to the MNPs surface is generated from the formation of an absorbent bond between carboxyl group and the metal atom [177,178].

The metal ion chelation capability of phenolic acids such as caffeic acid and coumaric acid also participates in the nanoparticle formation process [179]. 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 [180], and the synthesized MNPs can be coated on the surface with protonated reducing agents such as citrate through various mechanisms based on the intermolecular interactions between the absorbed molecules and the metal surface [114]. Natural phenols with functional

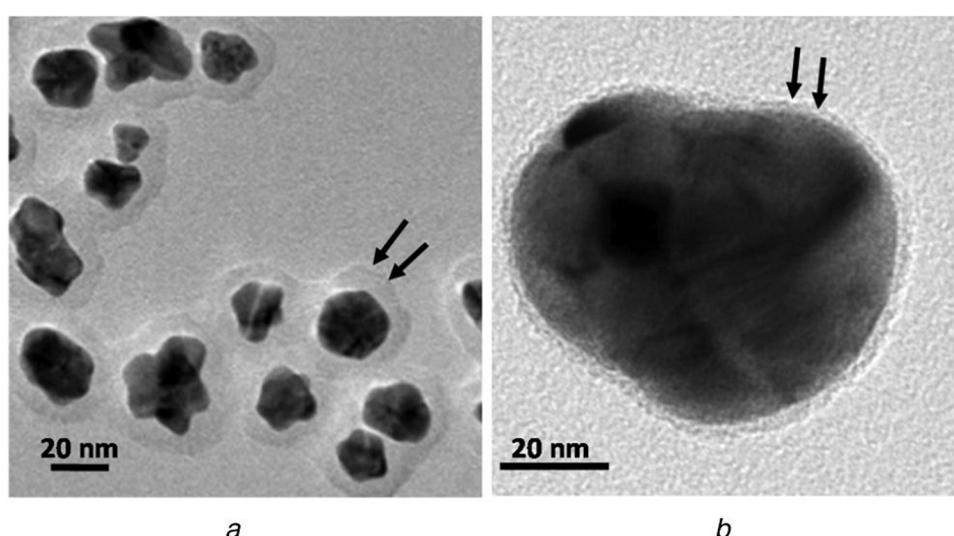


**Figure 13:** Schematic explanation of catechol group binding; three different configurations on the surface of the MNPs. (a) Bidentate bridging bonding, (b) bidentate chelating bonding, and (c) monodentate ester-like bonding [183,184].

hydroxyl [181] and carboxyl [182] groups have protonating and absorbing capabilities and catechol group of some 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 (Figure 13) [183,184]. Different spectroscopic techniques have been applied for studying the phenolic acid absorption on the MNPs surfaces. Although the UV-vis absorption spectroscopy technique has confirmed the phenolic acids capability of reducing metal ions, this method could not confirm the phenolic acids attachment to the surface of the prepared nanoparticles [185].

Furthermore, it is conceivable to reveal the distinctive absorbance peaks of capsaicin, cinnamic acid, gallic

acid, salicylic acid, and other phenolic acids attached to the surfaces of the MNPs using the Fourier transform infrared spectroscopy technique [186–189]. Last, it is contingent to acquire the micrographs of the phenolic acids coated on the MNPs and MONPs by transmission electron microscopy (TEM) (Figure 14) [190–193]. Green chemistry through plant biomass or extract is an approach for the production of biocompatible MNPs. Specific plant or algae may be worthy due to its content of some phenolic acids compound; however, still, there is a multitude of other materials, that makes the investigation of the function of the phenolic acids compound in the spotted toxicity generated from synthesized MNPs very complicated. In general, the reported toxicity effect of the MNPs prepared using plant extract is dialectical in pieces of the literature. However,



**Figure 14:** TEM micrographs of (a) phenolic acid-coated gold nanoparticles [190] and (b) silver/selenium alloy nanoparticles [191].

the MNPs that have been synthesized from plant extract have higher biocidal activity compared with the chemically synthesized nanoparticles, which was reported previously [194].

## 13 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 material's 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 [195].

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  $\alpha$ -D-glucose, sucrose, and maltose [136]. 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 [196], single wall carbon nanotubes and

multiwall carbon nanotubes (MWNT) and buckminsterfullerene (C-60) [197]. The formation of biodegradable CMC composite films with noble nanometals is the extension of the strategy [135], such as metal decoration and carbon nanotubes alignment in CMC by using a MW-assisted approach [198], which enables the shape-controlled bulk synthesis of Ag and Fe nanorods in poly(ethylene glycol) solutions [199]. A cleaner approach to the formation of tantalum oxide nanoparticles is optimized using the ethyl glycol-mediated pathway [200]. 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 [201]. The fluffy nature of the  $\text{TiO}_2$  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  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$ . 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 [202]. The MW hydrothermal process delivers magnetic nanoferrites [203], micro-pine structured catalysts, and metal oxides with 3D nanostructures, which are obtained from facilely available metal salts [204]. 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 Figure 15.

## 14 MNPs and therapeutic proteins

Plants has many features compared with mammalian and insect cells, as the system is completely scalable and cheap and avoids potential contamination with mammalian pathogens. Manipulated plants can be used with some chemical compounds for the biomaterials production, but they do not have the ability to generate variety of prepared polymers by utilizing current chemical polymerization techniques. Though, by prevailing the gene transfer technology, it is

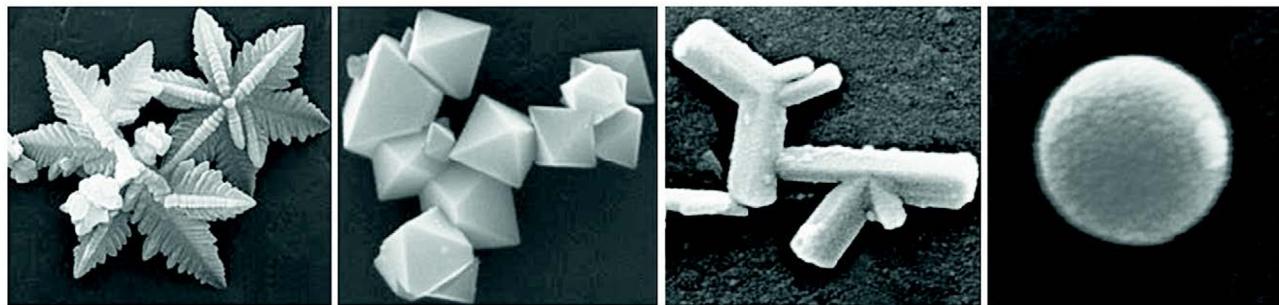


Figure 15: Well-known morphologies of metal oxides [10].

practical to recognize the compound compositions of interest and have a control over physicochemical properties and implementation which is difficult to attain, using chemical techniques [205]. A considerable advance has been achieved in many fields such as biotechnology and gene transfer. Worthy pharmaceutical compounds and antibodies were produced using transgenic plants, but because of negative public realization and the gene escape prospect danger, the full implementation of this technology was constrained. Hence, prevailed new systems have used heterogeneous proteins that depend on viral vectors, which are not produced by transgenic plants. The excellent resources for production of greener biomaterials are plants and many biomaterials like collagen, gelatin, polyhydroxyalkanoates, silk, and elastin have been highlighted [206–209]. The use of phytomedicines has been increased because of their therapeutic value when compared with allopathic medicines, as these biocompounds have fewer side effects. A better understanding of functions and kinetics of phytopharmaceuticals should aid in laying out novel drug molecules and dynamic treatments [210]. Plant extracts comprise important secondary metabolites, including alkaloids, terpenoids, phenolic acids, and flavonoids, which are the key compounds involved in the preparation of bulk metallic nanomaterials and MNPs [211]. Such metabolites are routinely used in the redox reactions to synthesize eco-friendly nanoparticles. It is well recognized that different plants, herbs, and species are the key sources of powerful antioxidants, such as phytochemical subunits present in leaves, stems, seeds, and fruits [212,213]. The plant-based nanoparticles and other nanoparticles by-products utilization is very essential for a decisive solidarity connection between plant science and nanotechnology [214,215]. The nanotechnology plays a major role in drug delivery, in which a small particle size is allowed to the arrival to the all drugs surface area and on the other hand cements fast dissolution in the blood. In addition, drug delivery is targeted in a specific characterization to a site-specific action of the drug. Microspheres and liposomes can easily thread via sinusoidal spaces in the bone marrow and

spleen compared with other systems due to their very small size. Nanoparticles increase the proteins uniformity against enzymatic decay and displayed distinction over classical methods in terms of competence and effectiveness. Drugs or other active compounds can be loaded on the engineered nanoparticles for effective targeted transfer to particular sites in an organism. Prominent efforts have been made to inspect the broad applications of the engineered nanoparticles in human systems, mainly for targeted drug delivery, cancer therapy, and treatment of different genetic disorders, which can be well classified by their functional uses [209]. Recently, Aminianfar et al. [216] realized that the toxicity of botulinum toxin type A was minimized when it was coupled with nano-silver (Ag) and intraperitoneally injected into rats. *Cuscuta chinensis* can be used to produce nano-sized drugs by a nanosuspension method for their antioxidant and hepatoprotective effects. Similarly, *Radix salviae* nanoparticles synthesized by the spray drying method have been used in the treatment of coronary heart disease and myocardial infarction [217,218]. The potential use of nanotechnology techniques leads to an increased bioactivity and bioavailability of phytomedicine by lowering the particle size, surface alteration, and trapping the phytomedicine with different nanomaterial polymers. In the future, it is indispensable to converge the new multifunctional nanomaterial designs and development and *in vivo* studies of their formulations for dynamic implementation in the pharmacological domain [217,218].

## 14.1 Phyto-nanotechnology and plant-made nanostructures

Plant-based eco-friendly and greener nano-accesses for the assembly of nanoparticles have major features compared with the classical methods of nanoparticle preparation using toxic and hazardous materials. Plant extracts are renewable in nature and often treated in an eco-friendly aqueous

medium. Furthermore, the reaction conditions used in the manufacture processes are mild [217–220]. Since the plant extracts and phyto-nanoproducts are cheap, non-risky, and energy efficient, they are receiving attention. Phyto-nanotechnology has a large prospect in the manufacture of different nanoparticles by using the extracts of various plant parts such as leaves, seeds, flowers, and roots [205,221]. The prepared biological nanomaterials have noble applications in the pharmaceutical industry such as novel pharmaceuticals preparation, imaging, drug delivery, diagnosis processes, and making operative nano-devices [222]. Hence, the greener production of nanoparticle is the key factor for improving new therapies to monitor different epidemic diseases [223]. The fast growth in the commercial applications of the nanomaterials is directed to an intense search for the greener pathways for the preparation of nanoparticles, particles of nanometer size, i.e.,  $10^{-9}$  m [224]. Improving alternative eco-friendly processes for producing nanoparticles is mandatory [225]. Researchers have prioritized their inspections to the nanomaterials biopreparation as a “bottom-up” track; various organisms could prepare nanoparticles in an ambient environment (pressure and temperature), avoiding the production of harmful agents and risky by-products [226]. Historically, nanoparticles bioproduction using plants was adduced in the early 1900s – the colloidal Ag aggregation in the organs of living organisms [227] and ion bioreduction by plant roots [228]. Also, the MNPs preparation using plant seed extracts has been presented [229], via the Ag nitrate reduction, including formation inside the plant cells [230]. Although a change in the color of Ag nitrate to yellow [229] or yellowish-brown [228] was considered as a signal for nano-Ag consistency [231], the ensuring reduction products were not peculiarly analyzed [228,229]. Notably, alfalfa plant, *Medicago sativa* [232], with the experimental evidence of various living plants preparation [233] were used for the demonstration of well known nanoparticle preparation with ground plant biomass. Several reports have shown the potential applications of various plant parts, including leaves [234,235], seeds [236], flowers [237], fruits [238], latex [239], tuber [240], bark [241], and cultured tissues [242], to produce nanoparticles.

## 15 Silver nanoparticles green synthesis by using glutathione in water using microwaves

To remove or at least lower waste generation, there is an increased affirmation on improving green and sustainable

chemical methods, as implementing sustainable methodologies in almost all sectors of chemistry, including nanomaterial preparation, requires removal of toxic reagents and solvents. The use of a multipurpose agent that acts a reducing, capping, and dispersing agent may be achieved by the choice of an environmentally benign solvent, which is one of the key issues in the green preparation of nanomaterials [243]. Silver nanoparticles have a wide range of applications in catalysis [244], electronics [245], photonics [246], optoelectronics [247], sensing [248], and pharmaceuticals [249]. The attention of the scientific society to improve more modern green preparation processes for producing these nanoparticles leads to the preparation of these particles that are powerful candidates for the surface-enhanced Raman spectroscopic studies [250]. Silver nanoparticles have been synthesized with various morphologies as well as size allocations by several pathways including  $\text{NaBH}_4$  reduction [251], polyol method [252,253], use of plant extracts [254,255], and photoreduction [256]. Majority of these processes use strongly interacting reducing agent such as sodium borohydride and hydrazine, which means they proceed via the wet chemistry methods and some of them use noxious and highly volatile organic solvents. The use of amino acids [257], vitamins [138], and other environmentally friendly biological agents in the preparation of MNPs prevents the use of toxic reducing agents. Microwave irradiation (MW) is emerging as a fast and eco-friendly procedure of heating for nanomaterials generation in conjunction with the use of these environmentally friendly reducing agents and solvents. It offers steady nucleation and growth conditions for nanomaterial preparation [199,203,258,259] through a rapid and volumetric approach and provides a fast and volumetric heating of solvents, reagents, and intermediates. The silver nanoparticles can be synthesized rapidly and easily using glutathione (GSH) as a reducing and capping agent under MW irradiation conditions in pure aqueous medium; GSH (Figure 16) was selected as a reducing agent due to its benign nature and strongly interacting thiol group, which can be utilized to reduce the metal salts. GSH is a tripeptide consisting of glutamic acid,

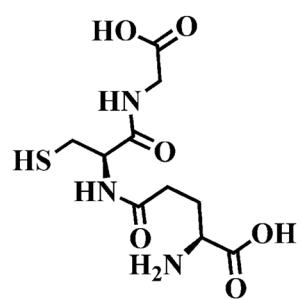


Figure 16: Molecular structure of GSH (reduced) [250].

cysteine, and glycine units and is an omnipresent antioxidant present in the human and plant cells. In addition to the thiol group, each GSH molecule contains amine and carboxylate groups, which offer coupling prospects for further cross-linking to other molecules of biological or sensing interest.

## 16 Coffee and tea extracts to prepare silver and palladium nanoparticles at room temperature

There are many technological applications for noble MNPs due to their widespread use and different wet chemical preparation methods have been described previously [137,260–270]. Due to the extraordinary properties of the synthesized metal and semiconductor nanoparticles, they attract a great interest, as they vary when they are in bulk, which is considered a modern attention in using green chemistry concepts to prepare MNPs [135,137,196,271,272]. For example, silver and gold nanoparticles manufactured from vegetable oil can be used in antibacterial paints [273]. Strategies to address mounting need to eco-friendly benign solvents, biodegradable polymers, and nontoxic chemicals were built. In the synthesis of MNPs by the reduction of corresponding metal ion salt solutions, there are three areas of opportunity to engage in green chemistry:

- (i) Solvent selection.
- (ii) The reducing agent used.
- (iii) The capping agent (or the dispersing agent) used.

Increased interest has been given to distinguish eco-friendly materials that are multifunctional. The caffeine/polyphenols used as both a reducing and capping agent for the synthesis of Ag and Pd nanospheres; due to its large water solubility, low toxicity, and biodegradability, caffeine is the most widespread and effective robust drug in the universe. In North America, 80–90% of adults use caffeine. However, there are no reports on the synthesis of noble metals using caffeine, which acts a critical part in many medical applications. For the first time, the noble metals such as Ag and Pd were prepared using tea/coffee extract, as caffeine/polyphenols can form complexes with metal ions in solution and reduce them to the corresponding metals. Different brands of tea and coffee such as Sanka coffee, Bigelow tea, Luzianne tea, Starbucks coffee, Folgers coffee, and Lipton tea were used to prepare nanoparticles by the single-pot method, which uses no surfactant, capping agent, and/or template, and the resulted nano-

particles were in the size range of 20–60 nm and crystallized in face centered cubic symmetry [71].

## 17 Green and controlled synthesis of gold and platinum nanomaterials using vitamin B<sub>2</sub>: nanospheres, wires, and rods density-assisted self-assembly

The highly structured nanoparticles assembly preparation such as wires, rings, and superlattices is being inspected thoroughly [274–286]. The major challenge is how to control the particle size and shape during preparation, and some physical and solid state chemical methods have been improved to manufacture semiconductors, metal nanowires, nanobelts, and nanodots [287]. Nowadays, there are various method for making rods with some approaches [288], pH-dependent assembly of gold nanorods [289]. The improvement of bulk solution preparation processes that provide shape control is of fundamental importance if the full labor of these materials is to be observed, as these solution-based processes are usually proceeded at elevated temperatures and often confer poor yields of the desired materials with adequate shape. The reaction medium density that cements the noble MNPs self-assembly into spheres, nanowires, and nanorods in the presence of vitamin B<sub>2</sub> (a crucial reaction parameter). There is an increased assertion on the preparation of nanoparticles using greener processes [290]. This environmentally benign approach offers an easy access to produce multiple shaped noble nanostructures, which could have prevalent technological and medicinal applications. The preparation and self-assembly was executed by reacting the competent metal salts with vitamin B<sub>2</sub> dissolved in solvents of varying densities, such as ethylene glycol ( $\rho = 1.113$ ), acetic acid ( $\rho = 1.049$ ), *N*-methyl pyrrolidine ( $\rho = 1.03$ ), water ( $\rho = 0.998$ ), isopropanol (i-PrOH,  $\rho = 0.790$ ), acetone ( $\rho = 0.790$ ), and acetonitrile (MeCN,  $\rho = 0.782$ ) at room temperature [137].

Vitamin B<sub>2</sub> reduction potential is  $-0.3$  V vs standard calomel electrode (SEC<sup>10</sup>), which is adequate to reduce  $\text{Au}^{3+}$  to  $\text{Au}^0$ , whose reduction potential is  $1.50$  V vs SCE, which is similar to that of Pt (reduction potential is  $1.20$  V) and other noble metals such as Pd (reduction potential  $0.915$  V) and Ag (reduction potential  $0.80$  V). Au and Pt nanoparticles were prepared with vitamin B<sub>2</sub> [291] by the following steps:

1. Complexation with Au and Pt metal salts.
2. Simultaneous reduction of Au and Pt metal salts and capping formation with oxidized vitamin B<sub>2</sub>.
3. Self-assembly of nanoparticles to form spheres, nanowires, and nanorods.

## 18 Green preparation of Ag, ZnO, and Ag/ZnO nanoparticles for manufacturing clinical antimicrobial wound-healing bandages

Open wounds are due to the loss of skin integrity and subcutaneous layers, giving rise to visible external bleeding, which are prone to infection, and germs can enter fastly to the deeper layers of the skin, access the lymph nodes, and squander throughout the body. Thus, all scars should be cleaned and covered completely and the coating should be uniform. Appropriate wound coating helps manage bleeding, inhibits contamination via blood absorption and secretion from the wound, and recuperate the wound rapidly [292]. A bandage impregnated with alcohol or Betadine is usually used to inhibit the prosperity and proliferation of pathogens in the wound. Betadine (povidone-iodine) and alcohol are robust microbicidal solutions, which can destroy all types of bacteria, viruses, fungi, and other microorganisms [293]. Lavelle et al. [294] presented that the absorption of iodine led to an unclarified anomaly and renal failure in some patients. This solution has no harmful effect if used on the dry skin, but if it is applied on the wound, it will lead to allergic reaction in some people [295] and absolutely retard the healing of the wound, and the scars will stay, and the solution should not be used on wounds such as burns or surgical areas. Using Betadine to treat the wounds of skin of pregnant mother hurt the baby and sanitization of umbilical cord with iodine as well as other agents leads to hypothyroidism in infants [296]. The use of alcohol also brings about intense agitation and can destroy the healthy cells. The problem with antibiotics is that the resistance of renitent strains and microbial strains is restricted to one or few types of antibiotics. Renitent wounds grow faster if the feeding tissue get infected and can even lead to patient death. Managing renitent strains and preventing epidemics has become particularly

complicated when intense unexpected crises such as earthquakes, floods, or large fires occur, that lead to a large numbers of patients injured with supercritical and profound wounds in the hospitals. Because of the obvious misuse of betadine, alcohol, and the multidrug resistant to microbes, global interest of research studies is now focused on the alternative newer antimicrobials to use it periodically to inhibit the epidemic of the microbial strains.

We visualized to manage microbial strains and wounds remediation, particularly surgical, fungal, or diabetic wounds, by using nanoparticle-based bandages; nanoparticles are one-dimensional particles with size ranging from 1 to 100 nm [297]. The antimicrobial activity of silver (Ag) and zinc oxide (ZnO) has been boosted on a nanoscale, and they can be utilized to manage different human and animal pathogens with nanotechnology [298–307]. The material dimensions and nanoparticles capping are also key factors influencing the materials characteristics, as polyphenolic compounds, sugars, and epicatechin present in plant extracts [10] and tea or coffee are fundamentally responsible for the reduction of salts and capping of ensuring nanoparticles. Microbes act as an adequate substitute for nanoparticles generation; greener preparation of nanoparticles by bacteria and fungi has been considered [308–311]. The bacterial strains *Acinetobacter baumannii* and *Pseudomonas aeruginosa* mainly cause the infection in burn wounds. Due to these pathogenic strains resistance to popular antibiotics and the biofilms generation, finding new antimicrobials is now mandatory, so the trial to manufacture clinical antibacterial bandage is growing faster. Over the past years, significant efforts have been made to manufacture antibacterial coatings on different surfaces of the objects, such as clothing and medical accommodation merging Ag nanoparticles. Ag and ZnO nanoparticles were prepared by an ecofriendly procedure because of the exigency of coping with drug-resistant pathogens and offering modern antimicrobial coatings for operative ulcers remediations, as Ag and ZnO nanoparticles produced via greener preparation were used for the manufacture of clinical nanoparticle-based antimicrobial wound remediations. Besides their composition and structure [312,313], Ag and ZnO nanoparticles are widely used in different fields such as medicine, pharmacy, physics, and chemistry [314,315], and they are highly esteemed by the researchers for their perfect conductivity, chemical stability, and catalytic, photonic, optoelectronic, and antioxidant characteristics. In biological research, Ag and ZnO nanoparticles have been used as antibacterial factors and in biosensors

[316–321], and silver has been used in wound care for hundreds of years [322], with the nanotechnology improvement, the generation of Ag and ZnO nanoparticles and their use as a potent antibacterial material has been suggested. Different physical, biological, and chemical procedures, including laser abrasion, chemical reduction, and electrochemical recovery, have been proposed for nanoparticle preparation. The disadvantages of these processes are use of toxic reducing agents and higher energy consumption, which increases effective hazards to human health and the environment, and the manufacture on an industrial scale is overall forbidden as well. The biological preparation of nanoparticles with low energy exhaustion and cost is an attractive approach because of the higher costs of their chemical preparation and the increased bacterial resistance to antibiotics. Thus, phytochemical processes using the natural antioxidants have been improved to manufacture environmentally friendly and high-cost nanoparticles.

## 19 African traditional beers brewed with sorghum malt

Sorghum is a drought-tolerant crop with a pivotal role in the livelihoods of millions of people in marginal areas. The genetic structure of this varied crop in Africa has been investigated. On the continent broad scale, there are three main sorghum inhabitants (central, southern, northern). Sorghum, not similar hardly, is very well modernized to the semi-arid and sub-tropical conditions predominant over majority of the African countries [323]. Such hardly, sorghum belongs to the grass family Gramineae. In Africa, sorghum grain is the main cereal crop used to produce the classical “opaque” beers [324,325]. However, only particular sorghum varieties (e.g., red grain) are principally used to generate sorghum beers. These beers are known ikigage in Rwanda [326], tchoukoutou in Benin and Togo [327], dolo in Burkina Faso [328], pito or burkutu in Nigeria and Ghana [329,330], amgba in Cameroon [331,332], doro or chibuku in Zimbabwe [333], merissa in Sudan [334], mtamain Tanzania [335], bili bili in Chad [336], and Kaffir in South Africa. Classical sorghum beer producing processes basically include malting, drying, milling, souring, boiling, mashing, and alcoholic fermentation; but differences may happen based on the geographic localization [337]. These beer types vary from European lager types in the fact that lactic fermentation also

occurs during sorghum beer processing. Besides, African traditional sorghum beer is used while it is still fermenting, and the drink contains large amounts of fragments of insoluble materials [338].

These fractions are fundamentally starch residues and dextrans that are not digested during mashing and fermentation [339]. Sorghum beers have very little resemblance in appearance to Western beer made with barley. However, some research studies have proposed that the use of sorghum malt (instead of barley malt) in lager-beer brewing is out of the way to manage due to some inseparable problems (enzymes, starch characteristics, polyphenols) associated with sorghum [340–342]. Numerous studies on the microbiological and biochemical properties of the classical sorghum beers and their engineering have been carried out and reported in various African countries. A diverse yeast and lactic acid bacterial flora were found in African sorghum beers, although *Saccharomyces cerevisiae* and heterofermentative *Lactobacillus* usually predominate [343–345]. The traditional African sorghum beers are very rich in calories, B-group vitamins including thiamine, folic acid, riboflavin, and nicotinic acid, and essential amino acids. The beers are wasted at different celebrations and African ceremonies (e.g., marriage, birth, baptism, and designate a fountain of economic return for the female). However, in most of the African countries, the traditional sorghum beers are less appealing than Western beers brewed with barley malt due to their poor hygienic quality, low ethanol content, organoleptic variation, and dissatisfying preservation [346].

## 20 Comparison between classical chemistry and green chemistry for MNPs and MONPs synthesis

The next years will prove the importance of green synthesis methods for MNPs and MONPs production because they are not only easy to execute, fast, and cheap but also less toxic and environmentally friendly [347,348], as shown in Figure 17 [41].

## 21 Conclusions

The development of nanoformulations and their numerous applications make the green preparation of

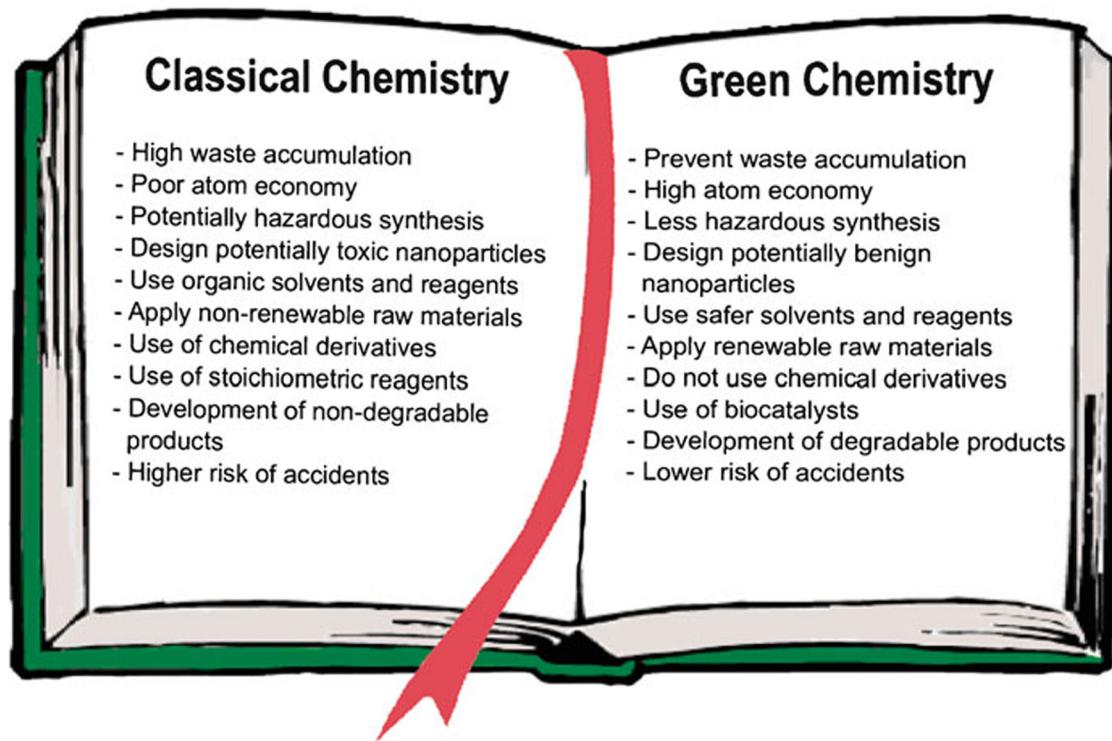


Figure 17: Comparison of the concepts and repercussions of traditional chemistry and green chemistry [41].

MNPs and MONPs hopeful and favorable area for different studies. The factors that affect the green synthesis of MNPs and MONPs from plant extracts, especially plant leaf extracts, distinctive kinetics, and nanoparticles production mechanism are still not well comprehensively understood, despite their several advantages like toxicity reduction ability, and the ease of the process execution, which make it an extensively utilized source for nanoparticle synthesis with effective, extremely eclectic, comparatively cheap, conventional and “historically secure” reducing agent, that was used for many years to prepare different organic molecules and compounds successfully. The whole green synthesis of nanoparticles requires incorporation of other more secure, sustainable, and credible reducing and capping agents, and finally avoiding the use of hazardous chemicals such as  $\text{NaBH}_4$  and hydrazine. The engineered green nanoparticles are used in many applications such as biomedicine; biology; materials science; electronics; biosensors; pharmaceutical, food, and cosmetic industries; and environmental remediation scope. For example, beet juice is used as a reducing and capping agent for the preparation MNPs such as Ag, Au, Pt, and Pd nanoparticles, which are capped with organics by the fast microwave-supported green procedure. The Ag nanoparticles prepared by beet juice display higher catalytic

activity and toughness than those synthesized by  $\text{NaBH}_4$  by the reduction of 4-nitrophenol to 4-aminophenol due to organic capping and better stampede. There is a fast and green treaty for silver nanoparticles preparation as well as other noble metals using glutathione, a benign antioxidant, which renders as both a reducing and capping agent, which means the full process was carried out in pure water without utilizing any toxic reagents or organic solvents. The silver nanoparticles ranging in size from 5 to 10 nm were prepared under MW irradiation conditions. It has been produced within 30–60 s at a power level as low as 50 W. The MW power influence on the morphology of ensuring silver nanoparticles is examined for the green and sustainable process, which is adjusted for the palladium, platinum, and gold nanoparticles synthesis. The Ag and Pd nanoparticles was synthesized using coffee and tea extracts by an eco-friendly, one-step procedure by the reduction of corresponding metal ions in tea and coffee extracts without adding any special capping agents at room temperature, which is considered a greener approach to different medicinal as well as technological applications. The green and controlled synthesis of Au and Pt nanoparticles using vitamin B<sub>2</sub> was carried out as follows:

1. A high yield, room temperature, density-assisted self-assembly of Au and Pt nanospheres, nanowires, and

nanorods using vitamin B<sub>2</sub> in various solvent media, thus providing new chances in many applications, like catalysis, antibacterial coatings, and fuel cell membranes.

2. A procedure that functions without any special capping or dispersing agent, nor any polymer as a coating agent.
3. The formation of multiple Au and Pt shapes and reliance of their self-assembly on the density of the solvent used. The particles will form particular spheres as the density increases, and the particles will self-assemble to produce nanorods and nanowires with a decrease in density.
4. The environmentally benign and general approach may manage different medicinal and technological implementation and is extended to other noble metals such as Ag and Pd. The main advantages of the greener preparation methods are their cheapness and the antimicrobial nanoparticles synthesis easiness using local plant extracts without the need for a toxic chemical reducing agent, and additional capping agents, as it offered bandages with high antibacterial activity, that were impregnated with Ag and ZnO nanoparticles. The bandages covered with Ag nanoparticles liquid solution have more antimicrobial effect than that of ZnO and mixed Ag/ZnO nanoparticles; however, this variation is not important. After continuous clinical attempts and examination of the possible side effects of the Ag and ZnO nanoparticles, these antibacterial bandages can be probably used for remediating and coating contagion-critical wounds such as diabetic wounds or burns, so the local resources can be mobilized dynamically in improving countries, thus classified local troubles using new nanotechnology. The traditional sorghum beers have a sociocultural and nutritional value in Africa. Compared with the brewing of European beer with barely, the brewing of classical sorghum beer is characterized by the complexity of the malting operation, the speed and short time of alcoholic fermentation, and the presence of lactic fermentation. In Africa, the association of sorghum with other cereals (e.g., *Eleusine coracana*, *Pennisetum glaucum*, and sweet potato) available in Africa could solve the problem of the lack of  $\beta$ -amylase in sorghum malt and offer tools to avoid the use of the commercial enzymes and barely malt. The presence of unidentified microorganisms from the classical leaven makes the fermentation operation difficult to manage and produces the products of variable quality. The use of starter cultures appears to be a good method to

reduce the organoleptic differences and to reduce the risk of contamination with pathogenic organisms. The current differences in the manufacturing operations of African classical sorghum beer could be incorporated into the development of a larger variety of sorghum beers in Africa.

Managing the gap between different studies will boost the green synthesis of nanoparticles from plant leaf extracts, especially flavonoids, vitamin B<sub>2</sub>, ascorbic acid (vitamin C), and phenolic compounds, which are all the main tools for MNP and MONPs preparation; as an auspicious process for non-toxic nanoparticles production, so the researchers must keep in their mind that:

1. 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.
2. 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.

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